

VOLUME II

VADOSE ZONE

SCIENCE AND
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SOLUTIONS

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Flow and Transport Modeling of the Vadose Zone

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INTRODUCTION

Over the last two decades, tremendous advances have been made in flow and transport modeling of subsurface systems. During the late 1970s and early 1980s, simple analytical solutions or numerical analyses, involving at most a few hundred gridblocks, were the only available tools to address flow and transport problems. Today it is common to use hundreds of thousands of gridblocks to solve flow and transport problems involving multiple processes and components. These important advances in flow and transport modeling came about because of increased concern about environmental problems, the need for efficient utilization of natural resources (such as fossil energy and geothermal resources), and the need for evaluation of geological disposal sites for radioactive waste products (Figure 5-1). However, there are still significant uncertainties in flow and transport predictions for subsurface systems.

This chapter deals primarily with flow and transport modeling of the vadose zone using finite difference, finite element, and other conventional numerical methods. These commonly used modeling approaches are based on macroscale continuum concepts that may not be applicable

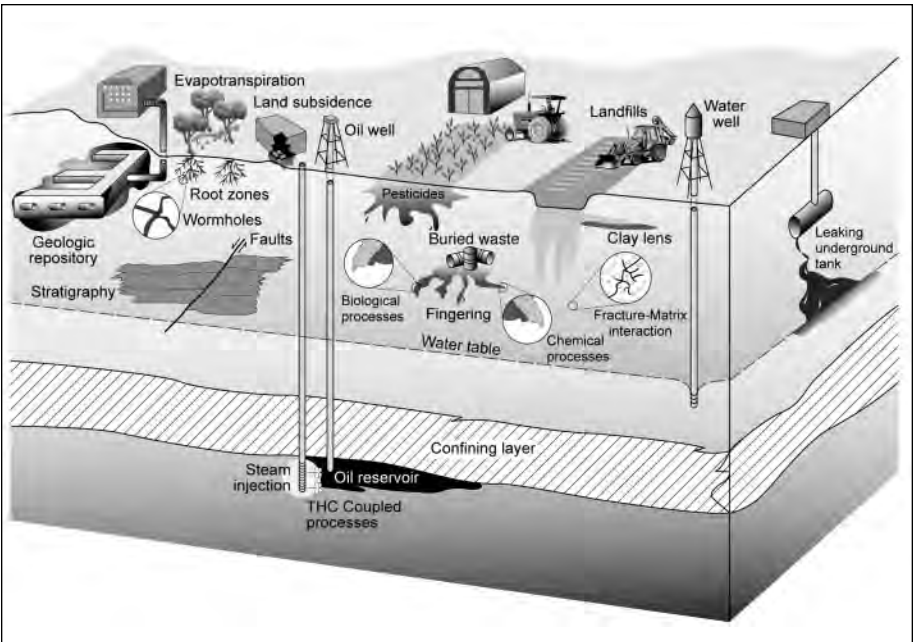


Figure 5-1. Various problems that are commonly addressed by flow and transport models. Some of the complex geological features at multi-scale processes are shown.

to certain problems and processes in the vadose zone (Pruess *et al.* 1999). Alternative approaches such as transfer functions (Chestnut *et al.* 1979, Jury 1982), weeps models (Gauthier *et al.* 1992), fracture network models (see, for example, National Research Council 1996) and chaos models (see, for example, Weeks and Sposito 1997) are not described here; these are summarized in a recent article by Pruess *et al.* (1999). In addition, we discuss physical aspects of flow and transport modeling in the context of conventional hydrogeology, which generally neglects complexities such as non-ideal waters and complex geochemical and biological reactions (Nielsen *et al.* 1986).

In the hydrogeology and reservoir engineering literature, the term “model” has different meanings. This can be confusing, because the specific meaning may become clear only from the context. A “conceptual model” of a field site denotes a qualitative representation of major hydrogeologic features, active constituents of the system (fluid phases

and components), flow and transport processes, and initial and boundary conditions. The term “mathematical model” refers to a set of governing equations, usually partial differential equations (PDEs), that represent the flow and transport processes of interest. The term “numerical model” is used in two different, but related, meanings. It can be synonymous with “numerical simulator,” computer software for simulating flow and transport processes. Alternatively, “numerical model of site X” denotes a specific quantitative model of hydrogeologic conditions and processes at field site X.

A site-specific numerical model consists of two components: (a) a more-or-less general numerical simulator for flow and transport processes, and (b) one or several data files (with geometric and hydrogeologic parameters of the flow system; constitutive relations and pressure-volume-temperature [PVT] properties; initial, boundary, and sink/source conditions; and computational parameters) that can serve as input files for the simulator.

Today, there are many numerical simulators available to address subsurface flow and transport problems. These codes vary greatly in complexity, from rather simple one-dimensional, single-process codes, to fully three-dimensional general simulators that are able to address and solve non-isothermal, multiphase, and multicomponent problems. The selection of an appropriate code depends primarily on the problem being addressed and the objective of the modeling exercise. If there are many simulators that can address the problem being considered, the analyst should select the simulator that he/she is most familiar and comfortable with. It is often advantageous to avoid the use of a complex, general simulator if it is not needed. Such simulators generally require more complex data input, and this can lead to modeling errors.

Currently, flow and transport simulators are being used for design and analysis of laboratory and field tests, for gaining understanding of single or multiple processes in geologic media, or for performing a full evaluation of an entire site. The application of these simulation tools to the design and analysis of laboratory and field tests has often been very successful. Their application to actual field sites involving multiple scales and processes has been less successful, primarily because of the difficulties in collecting field data of sufficient quality and quantity. Because of the heterogeneity of subsurface systems and the limited field data available for most sites, the results of subsurface flow and transport

simulations should be used with caution. This is especially true for contaminant transport results, because they are much more sensitive to system heterogeneities than are fluid flow results.

The site characterization should be guided by flow and transport models. This ensures that the most important data are collected in an appropriate quantity and at an appropriate scale, and results in a more reliable flow and transport model. In current practice, the key data needed for the conceptual and numerical models are often not collected; instead, a large volume of less useful data is collected. When possible, field data should be collected at the scale appropriate to the modeling activities. However, it may not always be possible to collect all the data required to fully resolve multiscale heterogeneities.

Flow and transport modeling can be approached in many different ways. We believe that it is most important to start with a simple model that only considers the essential features of the problem. The analyst can then gradually add more complexity as insights are gained into the behavior of the system. The development of a reliable conceptual model of the problem under consideration is probably the most important requirement for successful modeling. One must very carefully and thoroughly evaluate all of the available data, so that a reliable conceptual model can be developed. Care must be exercised not to get lost in details, since the modeling results are often dominated by only a few essential features of the conceptual model. Moreover, it is important to evaluate alternative conceptual models so that one can fully appreciate the variability of the simulation results.

In general, the reliability of a site flow and transport model depends on the quantity, quality, and diversity of data sets used in the calibration of the model. A calibration activity using simultaneous inversions of multiple data sets is very important for the “confidence building” of the model. Useful data sets for such calibrations include saturation and moisture tension data, pneumatic test data, monitoring data, and temperature data, as well as concentration data for contaminants and for various geochemical isotopes such as Cl, Cl-36, Sr, and C-14 (Bodvarsson and Tsang 1999). In addition to the calibration activities, blind predictions of individual tests, or large-scale, field-wide response to a remediation activity, will help quantify the uncertainties of the model and generally make it more reliable. Of the utmost importance is the contin-

uous evaluation and verification of the numerical model, which is developed by blind predictions and subsequent comparisons to field data.

Although the tools for modeling flow and transport processes of subsurface rocks are getting more and more sophisticated, the analyst remains the most important component of the modeling exercise. Complex numerical codes can be misused or inappropriately applied by inexperienced analysts. It is essential that the analyst has a good understanding of the capabilities of the simulator being used, and more importantly, of the limitations and approximations of that simulation code. Even an experienced analyst must continually review the simulation results obtained and validate them by whatever means possible.

In this chapter, we present many aspects of flow and transport modeling. Our purpose is to provide background theory, specific methods and approaches, and a modeling philosophy that will help analysts and managers with vadose zone flow and transport problems. While not exhaustive, the chapter reflects our collective experiences and preferences, with a focus on the main issues relevant to successful flow and transport modeling in the vadose zone.

In the section “Physical Processes and Setting for Contaminant Flow and Transport in the Vadose Zone,” we discuss the basic processes that occur in subsurface systems and illustrate the various geological complexities that control flow and transport.

In the section “Mathematical Models and Numerical Formulations,” we present the mathematical equations and numerical formulations that are the basis of flow and transport modeling in the vadose zone. We start by giving very generalized equations, and then focus on the most useful subformulations for various applications.

In the section “Data Needs and Prioritization,” we discuss the available data frequently collected to characterize subsurface systems, and attempt to prioritize the data collection activities. Data will always be scarce, so it is important to collect the data that will most affect the subsurface processes and conditions being modeled.

In the section “Development of Site-specific Models,” we discuss the process of developing a numerical model for site applications, including the appropriate and necessary steps that must be undertaken and the various pitfalls that should be avoided.

In the section “Model Calibration,” we discuss inverse modeling approaches and applications. Because of the importance of inverse mod-

eling, we provide a rather detailed discussion of the methodology, uncertainty analysis, and model predictions, with examples from various sites.

Finally, in the section “Future Research Directions,” we discuss and prioritize important future research topics. These include research elements for data collection, process descriptions, code development, and model utilization.

PHYSICAL PROCESSES AND SETTING FOR CONTAMINANT FLOW AND TRANSPORT IN THE VADOSE ZONE

INTRODUCTION

Insofar as varied and diverse geological processes are responsible for the formation of soils, sediments, and rocks comprising the vadose zone, the resulting formations are heterogeneous over a wide range of length scales. Superimposed on this geological complexity are the macropores formed by various intrusions into the vadose zone by plants and animals, including root casts, burrows, and wormholes. Man-made vadose zone constructs such as furrows, trenches, roadbase, underground utilities and their backfill, filled land and its contents, and tunnels, add even more complexity in the areas where contamination is most likely, for example, at industrial and disposal facilities, near buried tanks and pipes, and along roadways and railroads. Additional variations in the vadose zone are caused by weather and climate through, for example, changes in water table elevation, moisture content, barometric pressure, and clay swelling. The physical processes associated with infiltration and recharge of aquifers—and more generally, flow and transport of water, soil gas, and contaminants—occur within this temporally and spatially heterogeneous setting of the vadose zone. Contaminants that can be hazardous to human health, such as hydrocarbons, volatile organic chemicals (VOCs), pesticides, fertilizers, radionuclides, and metals, are often introduced into the vadose zone, where they are subject to flow and transport processes. Despite its inherent complexity a great deal has been learned about the vadose zone because of its importance to agriculture, for water resources, and in civil engineering. Nevertheless, the needs of these various fields have not always overlapped, and thus a detailed understanding of the vadose zone, including its many non-ideal

and non-equilibrium behaviors, has remained an elusive goal (Nielsen *et al.* 1986).

In this section, we discuss the general processes and setting for contaminant flow and transport in the vadose zone. The emphasis is on modeling and simulating vadose zone flow and transport associated with subsurface contamination common to industrial and government facilities; modeling and simulation are used as tools for analysis and remediation design. We discuss the processes and settings associated with actual contamination problems, while, at the same time, focusing on concepts. Mathematical formulations of processes are presented in the section “Mathematical Models and Numerical Formulations,” below. We purposely limit the scope of the discussion, omitting near-surface flow phenomena, such as precipitation runoff, and focusing, instead, on processes relevant to problems faced by industry and government where deep regions of the vadose zone are contaminated. This distinction between near-surface and deep levels of the vadose zone arises because contaminants in near-surface soils can be readily remediated by excavation, and therefore do not pose a difficult remediation problem. When present in deeper levels of the vadose zone, however, contaminants are difficult to remove and continued migration generally occurs.

Consistent with the coupled nature of vadose zone flow and transport processes and their settings, we present figures that illustrate both processes and settings. Our discussion sets the stage for a discussion, in subsequent sections, of the development of practical modeling and simulation analysis methods. While we make frequent reference to the literature on flow and transport processes, our purpose here is not to present an exhaustive or historically complete review of the literature on every aspect of vadose zone flow and transport. The references are presented as resources where interested readers can find more information.

PHYSICAL PROCESSES

Flow

The term “flow” refers to the movement of liquid and gaseous phases, while “transport” refers to the migration of chemical constituents. Chemical constituents can either move with the phases by advection (as dissolved components) or move independently of the phase velocity (for example, by molecular diffusion). In this section, we discuss the flow of

liquid and gas phases (most commonly water and air) filling the voids between soil, sediments, and rock (the solid fraction) in the porous and permeable vadose zone. The main source of water and air in the vadose zone is the atmosphere, from which precipitation falls on the ground surface and enters the vadose zone through the process of “infiltration” (see, for example, Philip 1969). The subsequent downward flow of water aided by gravitational forces is called “percolation.” Water passing from the vadose zone to the saturated zone at the water table is referred to as “recharge.” These processes and a schematic soil profile are shown in Figure 5-2. Figure 5-3 shows some man-made constructs relevant to vadose zone processes.

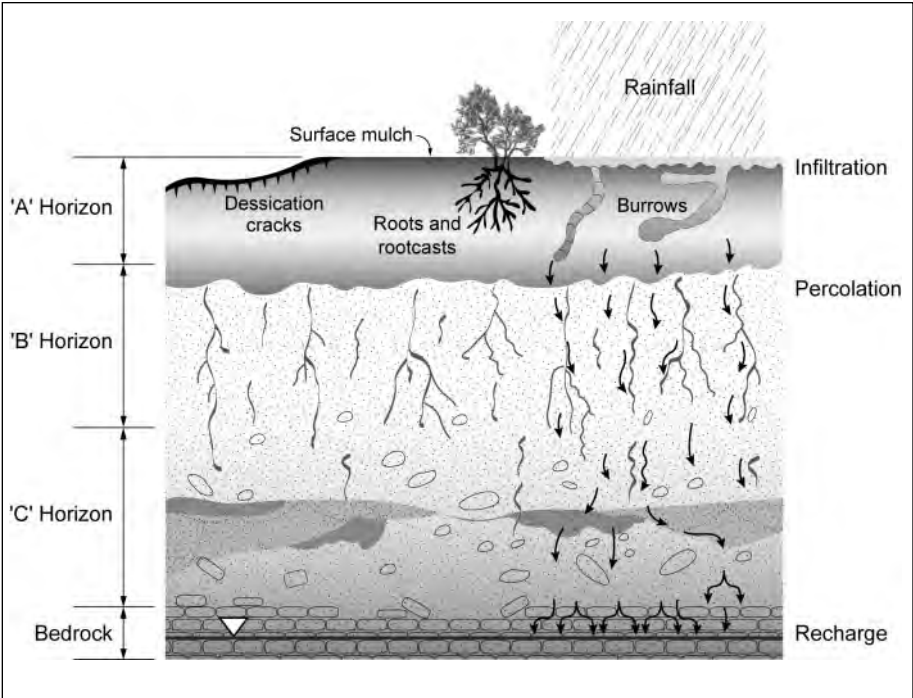


Figure 5-2. Near-surface soils with macropores comprised of desiccation cracks, root casts, worm holes, and burrows. The ‘A,’ ‘B,’ and ‘C’ horizons generally represent zones of organic matter and leaching, accumulation of clay and carbonate, and transition to weathered parent rock, respectively. Macropores create preferential flow paths for infiltration into the vadose zone. Percolation is also affected by heterogeneity, which can lead to preferential flow as water moves downward to the water table, where recharge occurs.

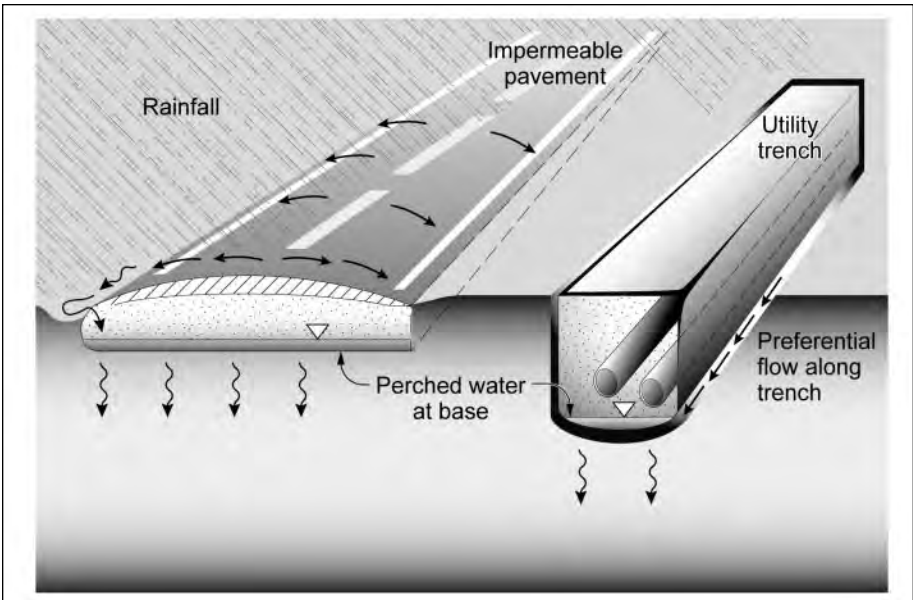


Figure 5-3. Impermeable roads, roadbase, utilities and backfill. These man-made constructs create surface runoff and concentrated infiltration and provide conduits for preferential flow.

The downward flow of water through the vadose zone is impeded by the solid grains, where interactions between water, air, and the surfaces of the solid grains of the matrix lead to capillary effects as well as flow resistance. Thus, gravity and capillarity are the primary driving forces for the flow of water in the vadose zone. The gas phase, which consists primarily of water vapor and air, flows by displacement (as water migration occurs), as well as in response to forces generated by atmospheric pressure, temperature, and composition changes. Water and other condensable gases in the gas phase are referred to as vapors, whereas air is a noncondensable gas. Other liquid and gas phases, such as nonaqueous phase liquid (NAPL) contaminants and their vapors, are acted upon like water and air. Although the forces driving the flow of water and air in the vadose zone are understood, the resulting flows at contaminated sites can be complex, as suggested by Figures 5-2 and 5-3. Below, we discuss particular kinds of flow in the vadose zone and the various physical properties that control them.

Darcy-Buckingham Flow

The flow of liquid through a porous medium at scales much larger than the pore scale, under the forces generated by pressure gradients and gravity, is governed by a version of Darcy's law that was proposed by Buckingham (1907). Buckingham described the movement of liquid and gas phases, on large scales, by pressure gradient, capillary, and gravitational forces. In Darcy-Buckingham flow, viscous drag on the fluid, due to the presence of the stationary solid fraction, is assumed to dominate, and inertia is assumed to be negligible. Under these assumptions, flow is always laminar, and there is no shear stress transmitted from the fluid to stationary bodies like there is in Poiseuille flow. Fluid movement is resisted by the permeability of the formation and by the viscosity of the fluid. In the vadose zone, where both liquid and gaseous phases occupy the pore space, the relative permeability of the phases becomes important. Relative permeability is a reduced permeability and is a function of the fraction of the pore space occupied by the phase (that is, the phase saturation). In addition, capillary forces are present that can either induce or inhibit liquid phase flows.

The wetting of a porous medium is referred to as "sorption" (or "imbibition"), while drainage is referred to as "desorption." Note that this use of sorption and desorption needs to be carefully distinguished from the geochemical definition presented in Chapter 6. One of the fundamental complications of the flow of water in a porous medium is that the capillary pressures and relative permeabilities are different depending on whether the medium is undergoing sorption or desorption. Hysteresis is the deviation in the capillary pressure and relative permeability, depending on whether sorption or desorption is occurring. Hysteresis occurs because of the variability in pore geometry and differences in contact angles (which depend on whether water is advancing or draining), on trapped air, and on swelling of clay minerals (Hillel 1998).

Vadose zone gas flow is often driven by gravity acting on gases of variable density, due to compositional and thermal effects on soil gas density (Falta *et al.* 1989; Mendoza and Frind 1990a, b). For example, humid soil gas is less dense than dry soil gas, while volatile organic chemical vapors greatly increase ambient soil gas density. In addition to barometric pressure changes, displacement of gas due to liquid flow and

pressure buildup due to volatilization and microbial action can also drive gas-phase flow in unsaturated landfills (Farquhar and Rovers 1973).

Preferential Flow

A preferential flow occurs whenever the percolation flux in a fracture or porous medium is not uniformly distributed. The most basic cause of preferential flow is heterogeneity of the medium. In Figure 5-4, a schematic is presented of heterogeneous alluvial and fluvial sediments, including a low permeability caliche layer in the shallow subsurface. Such heterogeneity in permeability and grain-size distributions causes preferential flow. Figure 5-5 shows sloping clay lenses in a sandy sedimentary sequence that cause flow diversion due to the low permeability of the clay. At the downslope edge of the clay lens, preferential flow will occur as the accumulated moisture flows downward through the sand. When the clay layers are horizontal or concave upwards, perched water may form. Figure 5-5 also shows capillary barriers created when fine-grained layers with strong capillary suction are overlying coarser layers with weaker capillary suction. Percolation in this case tends to remain in the fine layer. If the

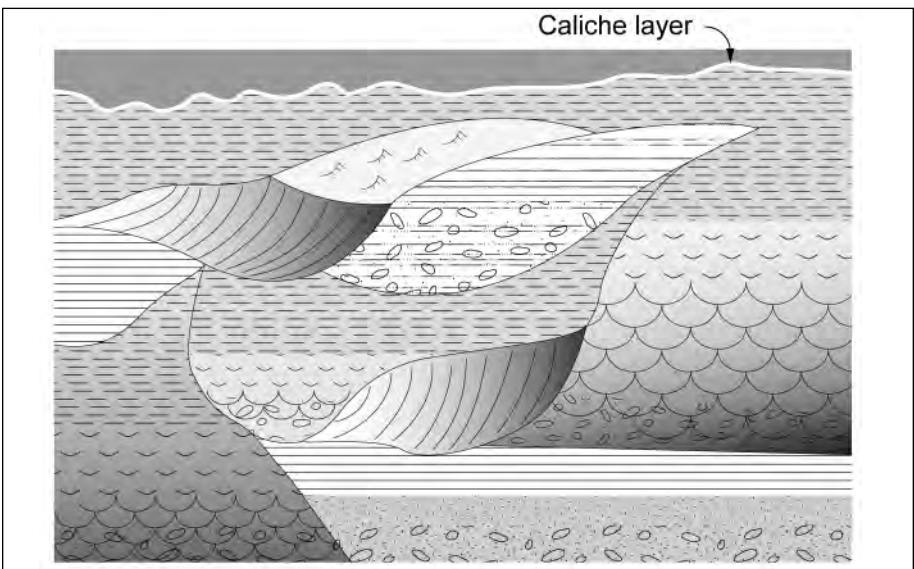


Figure 5-4. Alluvial and fluvial sediments with caliche layer. Caliche layers can limit infiltration. Fluvial deposits are normally sequences of fining-upward sediments that are truncated, irregular, and anisotropic.

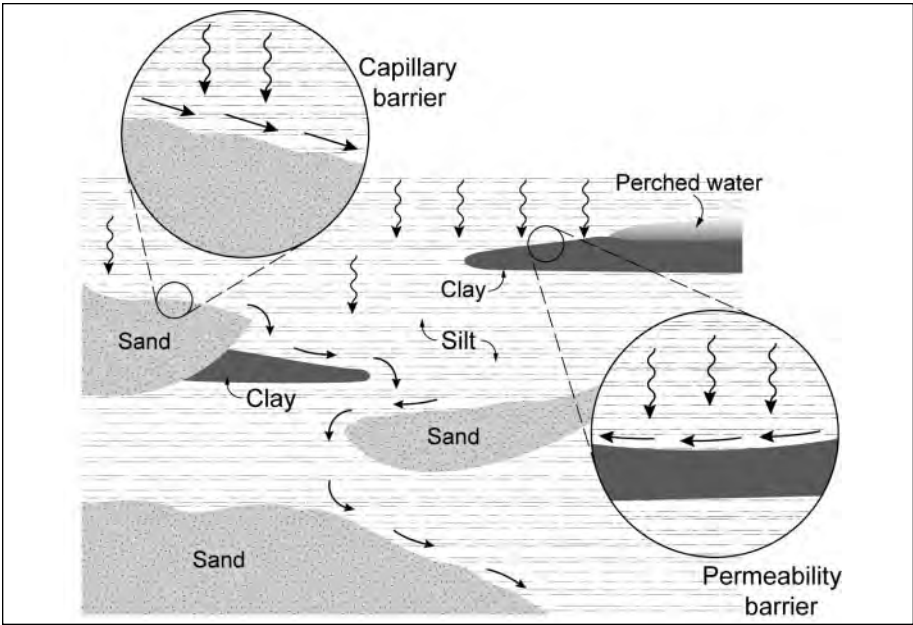


Figure 5-5. Fluvial and estuarine sediments of silt, sand, and clay. Layered sediments create permeability and capillary barriers that cause lateral diversion and preferential flow in the vadose zone. Low-permeability rocks and sediments in the vadose zone can lead to locally saturated regions of perched water.

interface between fine and coarse layers is horizontal, moisture builds up in the fine layer until it breaks through into the coarse layer. When the interface is tilted, capillary diversion occurs with effects similar to a permeability barrier (Zaslavski and Sinai 1981, Ross 1990, Oldenburg and Pruess 1993, Ho and Webb 1998b). While important exceptions exist (see, for example, Wierenga *et al.* 1991 and Hills *et al.* 1991), many examples of preferential flow have been documented (Kung 1990a, b; Ghodrati and Jury 1990, 1992; Flury *et al.* 1994; Li and Ghodrati 1994). Preferential flow is the dominant downward liquid flow process in fractures (Pruess 1998, 1999). Fast flow paths can also be provided by utility backfills and roadbase (Figure 5-3), greatly complicating the spread of contaminants.

Fingering

Irrespective of heterogeneity, the flow of liquid phase fronts through unsaturated, porous media is subject to hydrodynamic instabilities that

lead to fingering, a special form of preferential flow Hill and Parlange 1972, Raats 1973). Fingers are lobe-shaped regions of higher liquid saturation where liquid moves downward under gravity faster than in adjacent, drier regions. The mechanism of fingering is intuitively simple and involves convergent flow lines leading to higher relative permeability and positive feedback to cause more convergence of flow lines (Hillel and Baker 1988). Fingering has also been shown to occur in fracture flow (Glass *et al.* 1988, Glass *et al.* 1989). While hydrodynamic instabilities leading to fingering can occur in uniform porous media, in actual field systems it is the heterogeneity of the site that tends to determine fingering and preferential flow behavior (Kueper and Frind 1988).

Fracture Flow

Fracture flow occurs in the vadose zone when gravity overcomes capillarity in a fracture and pulls liquid phases downward. Because fractures provide little resistance to flow, they can act as fast flow paths for both liquid and gas phases. In Figure 5-6, a schematic example of

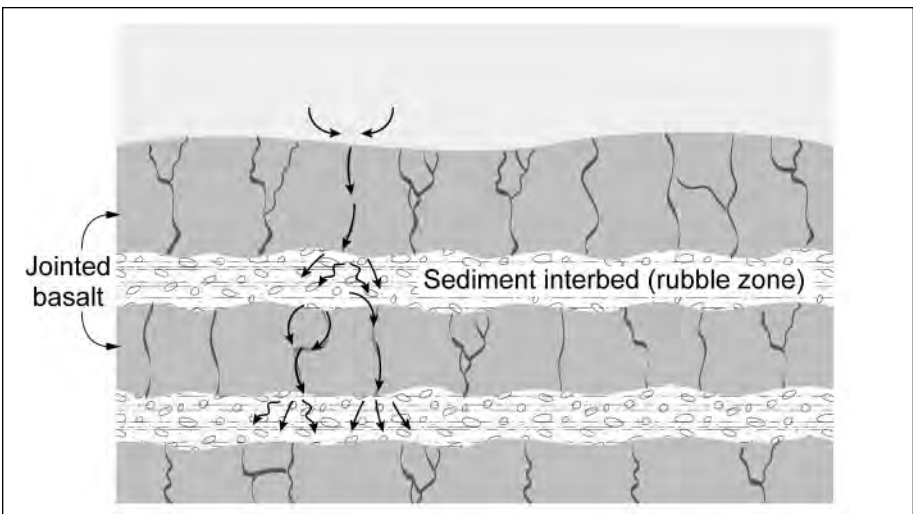


Figure 5-6. Fractured rock with interbeds. Fractured crystalline rock overlies nonfractured porous materials where, for example, columnar jointed basalt flows overlie sedimentary interbeds, or where welded tuff overlies nonwelded tuff.

fracture flow in columnar jointed basalt is shown, along with transitions to Darcy-Buckingham flow in sedimentary interbeds. Water in the fractures interacts with permeable matrix rock by a process generally referred to as fracture-matrix interaction. Deep infiltration through soils and fast flow in the vadose zone can occur by viscous flow of water down the sidewalls of macropores or fractures (Bouma and Dekker 1978; Bevan and Germann 1982; Tokunaga and Wan 1996). Such flows are mostly driven by gravity and resisted by viscosity. Relative permeability and capillary pressure functions must account for the fact that the film wets only the sidewalls of the macropore or fracture rather than spanning the entire gap. Flow in fractures, like flow in porous media, tends to be channelized. These processes and features of fracture flow are illustrated in Figure 5-7.

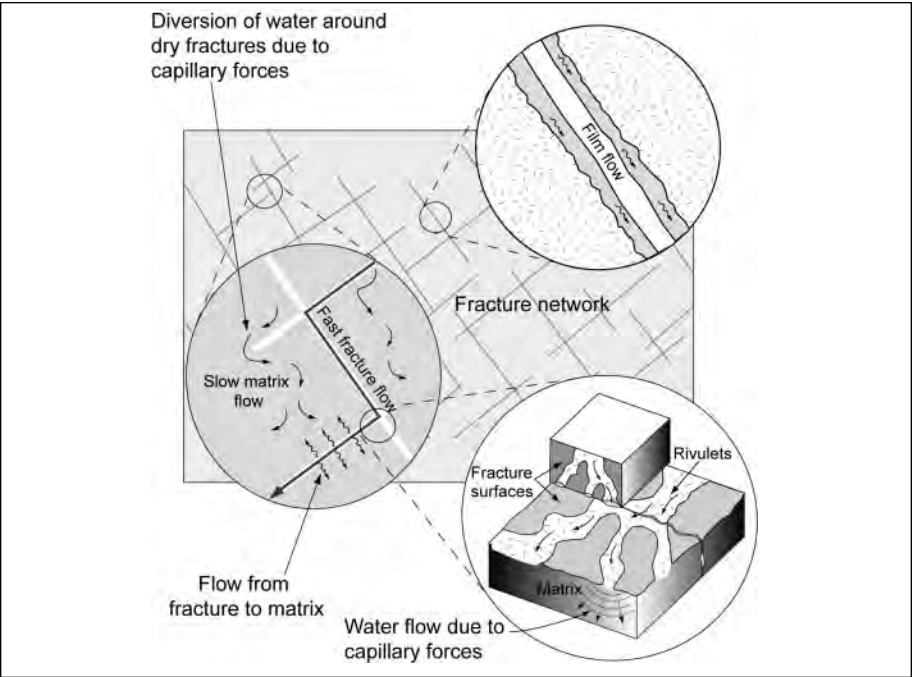


Figure 5-7. Fractured rock. Fractures are pervasive in crystalline and competent sedimentary rocks. Fractures provide permeability for liquid and gas phases through what is otherwise nearly impermeable rock. Despite the low permeability of the matrix, interaction between fluids in the matrix and in fractures affects flow and transport.

Summary of Flow Processes

The flow processes of Darcy-Buckingham flow, preferential flow, fingering, and fracture flow are generally relevant in one way or another at the scale of vadose zone site contamination problems. Preferential flow, in particular, is a common flow pattern in vadose zone systems. The flow processes discussed above are inherently scale-dependent. For example, Darcy-Buckingham flow is assumed to occur on scales much larger than the pore scale. At smaller scales, pore-level processes must be considered. Film flow occurs at a small scale, but such flow is fast and its effects are important over much larger scales. Fingering as discussed above is assumed to occur over scales that are considered large relative to the pores and small relative to the system under investigation. In some cases, it may suffice to assume an average flow and disregard the finger-flow component. In other cases, such an averaging approach is not acceptable, since it may not capture a regulatory criterion such as the time of first arrival. In summary, there are several mechanisms by which fast flow can occur, and there is strong field evidence for fast flow in the vadose zone.

TRANSPORT

Introduction

The flow of the mobile aqueous and gas phases, and any free phase contaminant present, gives rise to advective transport of contaminants when they are dissolved in the aqueous, gas, and NAPL phases. However, transport of the chemical constituents is controlled by many other processes as well. In this section, we focus on the main processes, relevant to vadose zone transport of contaminants, commonly found at industrial and government sites. Table 5-2 summarizes the main processes affecting vadose zone contaminant transport.

Molecular Diffusion

Liquid Phase

Diffusion is the process by which chemical components migrate from regions of high concentration to regions of lower concentration (Bird *et al.* 1960, Cussler 1997). The process of diffusion in simple binary

systems is adequately described by Fick's laws. In the multicomponent systems present in the vadose zone, diffusion is greatly complicated, and an extended Fick's law is required to account for the diffusive flux of each component and its dependence on the concentration gradients of the other components (see, for example, Rard and Miller 1988). The effective diffusivity of chemical components through a liquid in a porous medium is reduced, relative to the pure phase values, due to the presence of the porous medium, the fraction of the pore space occupied by the phase, and the tortuous geometry of the pore space. Because of the relatively high density of liquids, and the reductions in diffusivity to account for the porous medium, diffusion in liquids in subsurface systems is generally much slower than advection. In a liquid phase, a typical time scale for diffusion over length scales larger than 1 meter is on the order of several decades. Nevertheless, aqueous phase diffusion is an important process over small length scales, as it controls the spreading of contaminants at the pore scale. For example, diffusion of contaminants into rocks and sediments with low permeability can effectively isolate the contaminant from the flow system. Following active remediation (such as by soil vapor extraction), diffusion outward from these zones can result in a rebound effect, where contaminant concentrations increase with time following remediation.

Gas Phase

Because of the lower density of gases relative to liquids, molecular diffusion in the gas phase is three or more orders of magnitude faster than diffusion in liquid. Molecular diffusion in the gas phase is an important process at all scales relevant to vadose zone flow and transport. Because diffusion is sensitive to phase density, the pressure in subsurface systems affects diffusion in the gas phase. Depending on the dimensions of the pore space and the gas pressure, special consideration must be given to gas-phase diffusion to account for the mean free path of molecular motion in the pore space. In particular, at low pressures, effective slip of molecules along the pore walls can occur. This is called Knudsen diffusion and results in effectively higher diffusivities (Klinkenberg 1941, Thorstenson and Pollock 1989). Knudsen diffusion is parameterized by the Klinkenberg parameter, which modifies permeability to account for this process. Here, as in many other places in vadose zone flow and transport, the strong coupling between flow and

transport is apparent by the parameterization of a diffusive process (such as Knudsen diffusion) in terms of a flow property (for example, permeability modified by the Klinkenberg parameter).

An alternative model for gas-phase diffusion relevant to the vadose zone is the dusty-gas model (Cunningham and Williams 1980, Mason and Malinauskas 1983). In the dusty-gas model, kinetic theory governs the gas-phase components, while the solid grains are considered analogous to a dust contained by the gas. The dusty-gas model includes full coupling between advective flow and diffusion. Detailed studies have shown the dusty-gas model to be in excellent agreement with experimental data, while the standard advective-diffusive model has fundamental limitations (Webb 1998).

Enhanced Vapor Diffusion

Molecular diffusion of water vapor, and some condensible chemical vapors, may be enhanced by the presence of liquid (water or a nonaqueous phase liquid) in the pore space and the associated evaporation and condensation that occur locally. The process by which the apparent diffusivity of vapor is larger than its pure phase value is referred to as *enhanced vapor diffusion* (Philip and de Vries 1957, Jury and Letey 1979, Cass *et al.* 1984). While enhanced vapor diffusion may be a fundamental process affecting drying and moisture redistribution in the vadose zone, the only direct evidence of the process comes from laboratory experiments (Ho and Webb 1998a). Upon drying, the effective vapor diffusivity can diminish, resulting in a minimum overall diffusivity that may promote the development of drying fronts (van Keulen and Hillel 1974, Hillel 1998). Dry fractures can also limit flow and transport by creating barriers to flow and molecular diffusion, as illustrated in Figure 5-8. On the other hand, faulting can lead to intense fracturing and fault gouges that create regions of preferential liquid flow and enhanced vapor diffusion (Figure 5-9). Drying effects are particularly important for the problem of water entry into tunnels and underground workings (see, for example, Philip *et al.* 1989), as shown schematically in Figure 5-10. For some tunnels and workings, evaporation due to ventilation limits dripping, and water enters the tunnel in the vapor phase (see, for example, Finsterle and Pruess 1995).

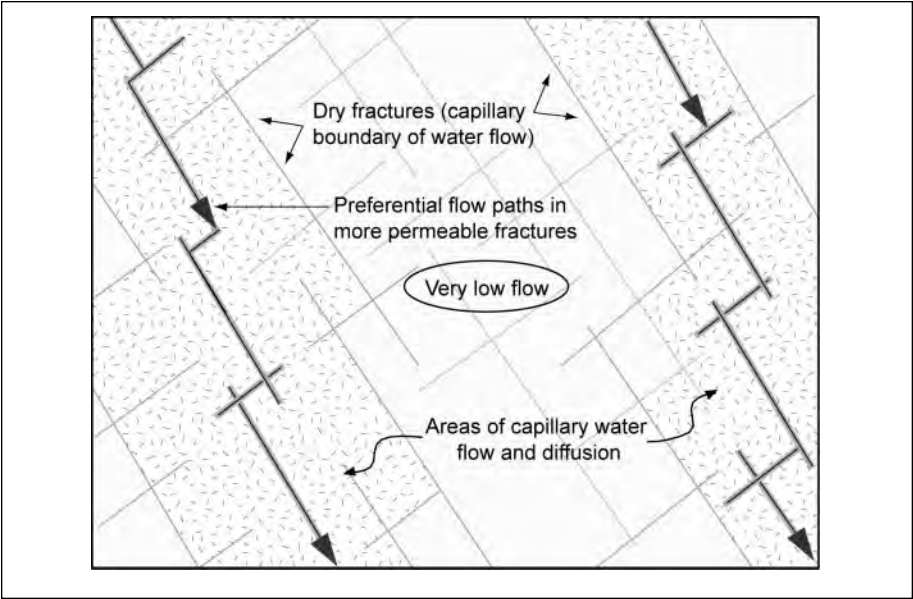


Figure 5-8. *Dry fractures.* Dry fractures reduce effective liquid permeability and gas-phase diffusivity to create barriers to flow and transport.

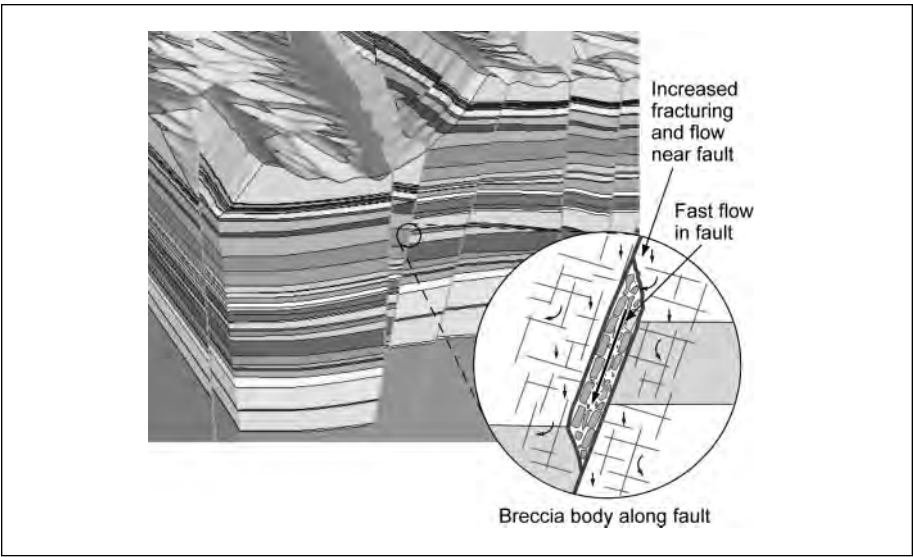


Figure 5-9. *Fault zone.* Dense fracturing, breccia, and fault gouge in fault zones provide permeability for percolation and gas-phase flow and transport in otherwise low-permeability rock.

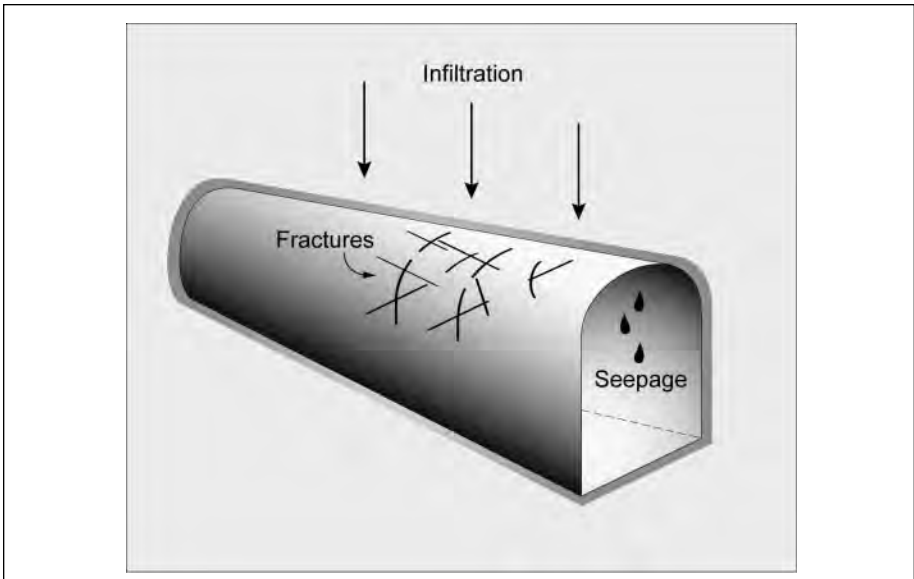


Figure 5-10. *Tunnels and underground workings.* Seepage and vapor flow are important processes in underground workings and waste isolation.

Adsorption

The process by which chemical components attach themselves to solid grains in the matrix is called *adsorption* (see, for example, Rao *et al.* 1979, Schweich and Sardin 1981). With a solid matrix comprising the majority of volume in the vadose zone, adsorption onto the surfaces of the matrix is an important process by which chemical components are partitioned from groundwater, both in the subsurface, by natural materials, and in treatment systems above ground where activated carbon is used to adsorb contaminants (Nyer 1992). The macroscopic effect of adsorption on the chemical concentration of a solution flowing through porous media is that of retardation of the transport of the chemical components undergoing adsorption relative to those that are not sorbing. Figure 5-11 shows the adsorption of chlorinated solvents onto organic carbon in landfills, which receive a wide variety of household and industrial wastes.

There are two important limitations to the process of adsorption relevant to contaminant flow and transport: (1) access and delivery to

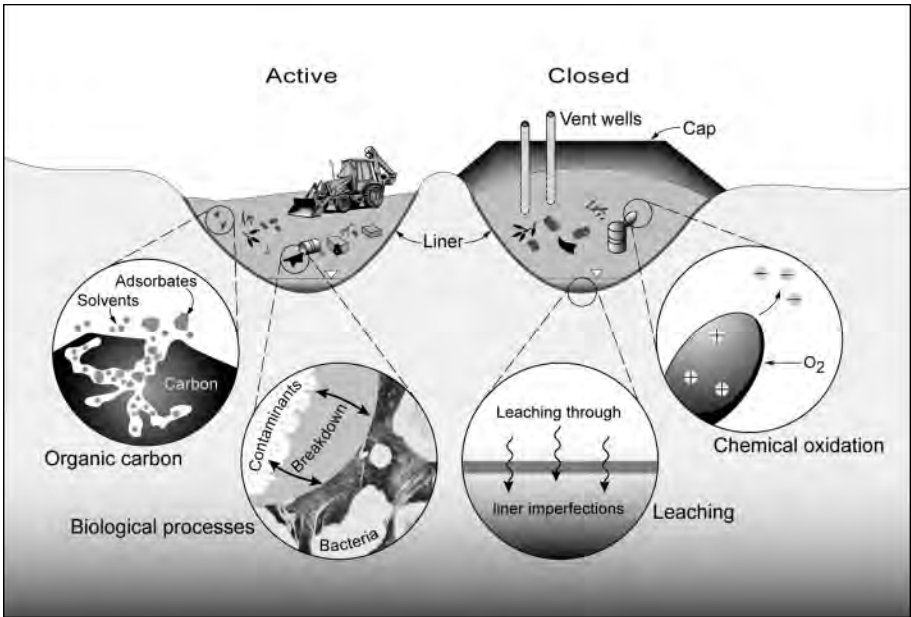


Figure 5-11. Landfills. Landfills and their contents are another unsaturated region of the subsurface where contaminant flow and transport processes occur. The landfill processes of adsorption, aerobic and anaerobic biodegradation, advection, and chemical reaction are illustrated.

adsorption sites depends on flow, which as discussed previously often occurs in preferential flow paths in the vadose zone; and (2) adsorption is an intrinsically unsteady process that only occurs until all adsorption sites to which the contaminants are delivered become filled. The first limitation means that even if the bulk formation contains large amounts of clay minerals or organic carbon capable of sorbing contaminants, the flow or diffusion must bring the contaminants to these sites, or else the actual adsorption capacity will be a small fraction of the potential capacity. The second limitation means that, eventually, all available adsorption sites will become filled, and contaminants will simply exchange with sorbed species or not interact at all (hence the need to replace the activated carbon in treatment systems).

Radioactive Decay

In many instances, radioactive components have been introduced into the vadose zone, where they undergo radioactive decay (Rogers 1978). Radioactive decay occurs by the spontaneous emission of alpha or beta particles, and results in transformation of the radionuclides into lighter elements. The rate at which radioactive decay occurs varies widely with the radionuclide of interest. For example, radon has a half-life of approximately 4 days, while some uranium isotopes have half-lives on the order of the age of the earth. Clearly, the relevance of radioactive decay on flow and transport modeling depends on the time scale of the system under consideration and the specific radionuclide being modeled.

Chemical and Biological Transformation

Separate from, but closely coupled to the processes of diffusion, adsorption, and radioactive decay, are chemical and biological processes that act on liquid solutions and gases in the vadose zone. Examples of biological and chemical processes that can occur in the artificial environment of a vadose zone landfill are shown schematically in Figure 5-11. Apart from biologically mediated reactions, there are numerous, and often coupled, inorganic chemical reactions in the vadose zone involving minerals, aqueous solutions, and gaseous phase species (see, for example, Phillips 1991). Mineral precipitation and dissolution place strong controls on water chemistry, and on the relationships between advective and diffusive transport of aqueous species and diffusion of gaseous species, particularly CO_2 and O_2 , which buffer pH-dependent and oxidation-reduction reactions (see, for example, Krauskopf 1967). Details of geochemical processes in the vadose zone are presented in Chapter 6. The dynamics of transport of aqueous and gaseous species often control the extent of reactions and their spatial distribution. For example, in a medium that is fractured or contains structures of high permeability and low liquid saturation, gaseous species transported rapidly by diffusion and/or advection in these zones will interact with the surrounding lower permeability media at a rate governed by local diffusive and advective processes. These processes can have substantial effects on the large-scale transport of chemical components in the vadose zone, as well as causing heterogeneity in mineral alteration and precipitation patterns at all spatial scales.

Colloid-facilitated Transport

Just as chemical components can adsorb onto immobile solid particles of the matrix, they also can adsorb onto colloidal particles that can be carried along with the flowing liquid phase. In this way, the transport of contaminants that might otherwise undergo dilution by diffusion if they remain in solution is actually facilitated by colloidal transport. While colloids have been proposed to account for rapid transport of radionuclides in the saturated zone (Kersting *et al.* 1999), the air-water interface in the vadose zone may also trap colloids and retard colloidal transport (Wan and Tokunaga 1997).

General Processes

In addition to the potentially important vadose zone processes discussed above, there is a myriad of general physical processes relevant to vadose zone flow and transport, depending on the system of interest. For example, in-soil vapor extraction, volatilization, and vaporization are key processes (see, for example, Baehr *et al.* 1989). Natural vapor extraction effects also occur because of barometric pumping (Auer *et al.* 1996). In systems with heavy metal contamination, dissolution and precipitation, as well as reduction-oxidation reactions, are important (see, for example, Wunderly *et al.* 1996). Surface barriers and phytoremediation involve processes of osmosis and evapotranspiration (Hillel 1998). Clay swelling can alter percolation (Miller 1975), while ionic solutes percolating downward can be subject to anion exclusion (Gvirtzman and Gorelick 1991). Isotopic fractionation due to gravitational effects during gaseous diffusion in the vadose zone has been documented in sandy formations (Severinghaus *et al.* 1996). These and other processes deemed important for given sites can be accounted for in vadose zone modeling studies.

Transport of Heat

Heat transfer in the vadose zone on a macroscopic scale appropriate to vadose zone remediation problems is relatively straightforward. Heat is transported by advection of the flowing phases (convection) and by conduction through the matrix and the fluid phases. Because of conduction into the matrix, heat transport is effectively retarded relative to a

purely convective transport. Thermal retardation can be very large for low-porosity formations, but like adsorption of chemical components, thermal retardation is a transient effect (Grant *et al.* 1982). While there are extreme situations such as steam injection for NAPL remediation, vapor-dominated geothermal reservoirs, and high-level nuclear waste repositories, vadose zone temperatures are generally in the range of 10–20°C. The temperature gradients that drive conductive heat transfer are mostly due to the seasonal and diurnal variations in temperature at the ground surface. However, the relatively low thermal conductivity of vadose zone rocks and sediments, coupled with the large retardation, limits the depth to which even low-frequency seasonal ground surface temperature fluctuations penetrate the vadose zone to a few meters (Hillel 1998). On the other hand, the process of thermal conduction is fast relative to diffusive transport processes, and may play an important role in heat transfer applications involving large temperature gradients. Sources of significant temperature gradients that will drive heat flow include microbial activity, such as in landfills, and radiogenic heating from highly concentrated sources, such as high-level nuclear waste canisters.

Heuristic Processes

Mechanical dispersion is a heuristic process that accounts for the spreading of dissolved chemical components due to the tortuous flow paths taken by the fluid phases through the medium (Scheidegger 1974, de Marsily 1986). This heuristic process is needed because Darcy-Buckingham flow, as described by the extended Darcy's law, does not travel in a tortuous path and will not lead to mechanical mixing of dissolved components, as observed in laboratory and field tests. To make up for this deficiency, the process of mechanical dispersion was introduced to augment diffusive mixing. In essence, mechanical dispersion accounts for small-scale advective mixing not accounted for in Darcy-Buckingham flow. This concept has been extended to include phase dispersion as well as solute dispersion (Pruess 1996b). However, there are serious limitations to the heuristic process of mechanical dispersion. In particular, spurious upstream migration can occur (de Marsily 1986). In addition, the mixing that occurs by the mechanical dispersion model should not be equated with dilution, as actual *in situ* concentrations of contaminants may be high in some regions and low in others, making the aver-

age concentration low on the scale of pumping or sampling. Finally, dispersivities of subsurface formations are dependent on the scale of the flow system.

Another dispersive mechanism that arises solely from flow processes is Taylor dispersion. At the pore scale, Taylor dispersion arises from the local velocity gradient present in flow with a zero-velocity boundary condition (Taylor 1953). Such small-scale velocity gradients tend to smooth advecting solute fronts. The process of Taylor dispersion has also been proposed to occur over large scales where different permeability formations effectively give rise to macroscopic velocity gradients in groundwater flow (Lake and Hirasaki 1981). The need for invoking Taylor dispersion in large-scale systems for vadose zone transport will only arise when flow is not modeled in sufficient detail, and it is our opinion that better resolution in the flow modeling should be used to eliminate the need to include this heuristic process.

Summary of Transport Processes

Whether in the vadose zone or saturated zone, the above transport processes should not be considered independent of flow, nor should they be considered independent of one another. All of these processes are coupled, and the interactions between processes can be important. For example, advection and molecular diffusion are responsible for delivering chemical components to adsorption sites, making these two processes closely linked. When preferential flow occurs, adsorption sites may be bypassed, and the effective retardation of the formation is diminished. Similarly, transport properties are typically temperature dependent, and therefore heat transfer is coupled to the transport of chemical components.

Summary of Vadose Zone Processes and Settings

In summary, the vadose zone is a complex environment in which a variety of flow and transport processes occur. Heterogeneity in the vadose zone occurs over all length scales relevant to subsurface contamination problems. “Flow” generally refers to the movement of mobile liquid and gas phases such as water, free phase contaminant, and soil gas, whereas “transport” refers to the movement of chemical com-

ponents. Flow in the vadose zone is very often preferential, with small channels carrying most of the percolation flux. Transport processes in the vadose zone have common underlying driving forces, but the local environment of each vadose zone problem controls local behavior. The processes of flow and transport in the vadose zone are strongly coupled, and coupled modeling is needed to capture fundamental vadose zone processes. Table 5-1 presents a summary of vadose zone flow processes, while Table 5-2 summarizes the main transport processes.

The settings for real-life vadose zone flow and transport problems, of vital interest to government and industry, are complex but can be analyzed through modeling and simulation. With this introduction to vadose zone flow and transport processes and setting, we are now in a position to discuss practical modeling approaches.

TABLE 5-1		Summary of main vadose-zone flow processes.		
Flow Process	Description	Key Properties	References	Notes
Darcy-Buckingham flow	Movement of liquid and gas phases by pressure gradient, capillary, and gravitational forces.	Permeability, relative permeability, capillary pressure, viscosity, and density.	Buckingham 1907, Bear 1972, de Marsily 1986.	Occurs on length scales much larger than the pore scale.
Preferential flow	Percolation that is concentrated in particular zones, such as regions of strong capillarity and large effective permeability.	Permeability and grain-size distribution of the vadose zone.	Starr <i>et al.</i> 1978, Ghodrati and Jury 1990.	Occurs for both liquid and gas phases.
Fingering	Unstable flow of phase fronts downward in finger-shaped lobes.	Rate of wetting, capillary pressure, relative permeability, density, viscosity, and permeability.	Hillel and Baker 1988, Glass <i>et al.</i> 1988.	Occurs for both liquid and gas phases.

(continued)

TABLE 5-1		Summary of main vadose-zone flow processes. (continued)		
Flow Process	Description	Key Properties	References	Notes
Fracture flow	Movement of liquid primarily by gravitational forces down fractures and macropores.	Wettability, roughness, connectivity, viscosity, and density.	Tokunaga and Wan 1996, Pruess 1999.	Film flow occurs only for liquid phases.
Density-driven gas flow	Flow driven by buoyancy effects in the gas phase.	Partial pressures and molecular weights of gas components, permeability.	Falta <i>et al.</i> 1989.	Especially important for VOC-contaminated sites.

TABLE 5-2		Summary of main vadose zone transport processes.		
Process	Description	Key Properties	References	Notes
Advection	Movement of chemical components with a flowing phase.	Phase velocity, concentration.	Bear 1972.	Important transport mechanism in both liquid and gas phases.
Molecular diffusion	Movement of chemical components down concentration gradient.	Molecular diffusivity, tortuosity, porosity, phase saturation, pressure (for gas phase), and strength of interaction between multiple regions or continua.	Cussler 1997, Thorstenson and Pollock 1989.	More rapid in gas phase than in liquid phase. Gas phase diffusion includes non-Fickian effects such as Knudsen diffusion.

(continued)

TABLE 5-2**Summary of main vadose-zone transport processes.** *(continued)*

Process	Description	Key Properties	References	Notes
Adsorption	Chemical or physical attraction and holding of molecules on a solid surface.	Surface area of the solid and partition coefficient.	Rao 1979.	Transient effect only. Flow can bypass sorption sites.
Radioactive decay	Transformation of radioactive elements by emission of alpha particles (alpha decay) or electrons (beta decay).	Half-life and molecular weight.	Rogers 1978.	Heating may occur in extreme cases.
Enhanced vapor diffusion	Enhanced effective gas-phase diffusion due to local condensation and evaporation within the pore space.	Vapor pressure, temperature, temperature gradient, and aqueous phase saturation.	Phillip and de Vries 1957, Ho and Webb 1998a.	Contributes to formation of drying fronts.
Chemical and biological transformation	Contaminants in liquid and gas phases are affected by a wide range of chemical and biological processes.	Reaction equilibrium constants, energetics, availability of reactants, pH, etc.	Phillips O.M. 1991.	Chemical reactions such as oxidation and reduction may be biologically mediated.
Colloid-facilitated transport	Transport of colloids and adsorbed contaminants by suspended colloidal particles.	Colloidal concentration and surface characteristics, pore geometry, phase saturations.	Wan and Tokunaga 1997.	Entrapment of colloids at air-water interface causes retardation for transient flow and transport.

MATHEMATICAL MODELS AND NUMERICAL FORMULATIONS

INTRODUCTION

In order to model the flow and transport processes occurring in the vadose zone, one needs mathematical models or governing equations to describe the physical processes quantitatively. In this section we discuss development and solution techniques of such mathematical models. After reviewing mechanisms that govern flow and transport phenomena in porous and fractured media, we describe them using a general formulation for multiphase fluid flow, multicomponent transport, and heat transfer in porous and fractured media. We show that the various governing equations in vadose zone studies can be derived by simplifying the general formulation to a particular application, such as Richards' equation (Richards 1931), multiphase immiscible flow and displacement, or tracer and radionuclide transport. In an effort to demonstrate how to solve these flow and transport equations, we present a general numerical approach of a control volume discretization, which can be applied to the different situations typically encountered in studies of flow and transport in the vadose zone.

The physical processes associated with flow and transport in porous media are governed by the same fundamental conservation laws as those used in any branch of science or engineering. Conservation of mass, momentum, and energy govern the behavior of fluid flow, chemical transport, and heat transfer through porous and fractured media. These physical laws at the pore level in porous media are well known. In practice for a particular study, however, one may be interested only in global behavior or volume-averaging of the system. Due to the complexity of pore geometries, macroscopic behavior is not easily deduced from pore level behavior. For example, any attempts to directly apply the Navier-Stokes equation to flow problems through a lot of pores in a porous medium system will face tremendous difficulties. These include poorly-defined pore geometries, complex phenomena of physical and chemical interactions between pore fluids or between fluids and solids, and too many unknowns or equations that cannot be solved at present. The macroscopic continuum approach is most commonly used in practical applications. Almost all theories on flow phenomena occurring in porous media lead to macroscopic laws applicable to a finite volume or a subdomain of the system under investigation, with dimensions that are

large compared with those of the pores. Consequently, these laws lead to equations in which the porous medium is treated as if it were continuous and characterized by the local values of a number of variables and parameters defined for all points with appropriate averaging.

The physical laws governing flow of several fluids, transport of multicomponents, and heat transfer in porous media are often represented mathematically on the macroscopic level by a set of partial differential or integral equations. The equations are generally non-linear. In addition to the conservation or continuity equations of mass and thermal energy, we also need specific relationships or mechanisms that describe fluid flow, solute transport, and heat transfer occurring in porous and fractured media. The following specific laws act as such mechanisms by governing local fluid flow, component transport, and heat transfer processes in porous media. Many of the concepts and definitions given in the following subsections were introduced in Chapter 1. The reader may wish to review or refer to that chapter before proceeding.

Darcy's Law for Multiphase Flow

Darcy's law has been the foundation for studies of flow and transport phenomena through porous media. Even though originally derived only for the flow of a single-phase fluid, Darcy's law has been extended to describe the flow of multiple, immiscible fluids (Scheidegger 1974). The generalized Darcy's law for the simultaneous flow of immiscible fluids in a multiphase system is given as

$$\mathbf{v}_\beta = -\frac{\underline{k} k_{r\beta}}{\mu_\beta} (\nabla P_\beta + \rho_\beta g \nabla z) \quad (5.1)$$

where $\mathbf{v}_\beta$ is a vector of the Darcy's velocity, or volumetric flow rate of phase β , with β being fluid phase index ($\beta = g$ for gas, w for water, and n for NAPL or oil); $P_\beta, \mu_\beta, \rho_\beta$, and g are pressure, viscosity and density of fluid phase β , and gravitational constant, respectively; z is the elevation; $\underline{k}$ is absolute or intrinsic permeability, a tensor in general; and $k_{r\beta}$ is the relative permeability to fluid phase β . It should be mentioned that the SI units are used throughout this section for all the variables and parameters (see Table 5-3 for nomenclature used herein).

TABLE 5-3	Nomenclature

General Nomenclature

A_{ij}	area between connected grid blocks or nodes i and j (m^2).
A^k	accumulation terms for mass component ($k = 1, 2, 3, \dots, N_c$) (kg/m^3) or energy ($k = N_c + 1$) (J/m^3) .
$A_i^{k,n+1}$	accumulation terms for mass component ($k = 1, 2, 3, \dots, N_c$) (kg/m^3) or energy ($k = N_c + 1$) (J/m^3) of grid block or node i and time level $n+1$.
C_r	rock compressibility ($1/Pa$).
C_T	rock thermal expansion coefficient ($1/^\circ C$).
C_β^k	concentration of component k in phase β (kg/m^3).
$C_{\beta 0}^k$	initial concentration of component k in phase β (kg/m^3).
D_i	depth from a reference datum to the center of node i (m).
d_i, d_j	distance from the centers of first (i) and second (j) nodes, respectively, to their common interface (m).
D_β^k	molecular diffusion coefficient (m^2/s) of component k in a fluid phase β .
$\underline{D}_\beta^k$	diffusion-dispersion tensor accounting for both molecular diffusion and mechanical dispersion for component k in a fluid phase β (m^2/s).
f_{oc}	fraction of organic carbon in soils (dimensionless).
F^h	heat flux vector of convection and conduction (W/m^2).
$F_{A,ij}^k$	components of advective mass flow of component k along connection ij ($kg/s\ m^2$).
$F_{D,ij}^k$	components of diffusive mass flow component k along connection ij ($kg/s\ m^2$).
F_{ij}^k	flow components of mass ($k = 1, 2, 3, \dots, N_c$) ($kg/s\ m^2$) or energy ($k = N_c + 1$) (W/m^2) flow along connection ij .
$F_{\beta,ij}$	flow components of mass of phase β along connection ij ($kg/s\ m^2$).
F_β^k	mass flux vector of advection and dispersion of component k in phase ($kg/s\ m^2$).
g	gravitational constant (m/s^2).
h_g	specific enthalpy of gas (J/kg).
h_β	specific enthalpy of phase β (J/kg).
h_β^k	specific enthalpy of component k in phase β (J/kg).
$\underline{k}$	absolute permeability tensor of fractures or matrix (m^2).
k_{rg}	relative permeability of gas phase (dimensionless)
k_{rn}	relative permeability to NAPL (dimensionless).

continued

TABLE 5-3 Nomenclature (*continued*)**General Nomenclature**

k_{rw}	relative permeability to water phase (dimensionless).
$k_{r\beta}$	relative permeability to fluid phase β (dimensionless).
K_T	overall rock thermal conductivity (W/m °C).
k_{rn}^{ng}	relative permeability to NAPL in the NAPL-gas, two-phase system (dimensionless).
k_{rn}^{nw}	relative permeability to NAPL in the water-NAPL, two-phase system (dimensionless).
k_{rn}^{*nw}	relative permeability value to NAPL at residual water saturation in the water-NAPL, two-phase system (dimensionless).
K_d^k	distribution coefficient of component k between the water (liquid) phase and rock solids (m ³ /kg).
K_H^k	Henry's constant of component k (Pa).
K_{oc}^k	chemical-organic carbon partitioning coefficient (m ³ /kg).
$K_{\alpha;\beta}^k$	Equilibrium partitioning coefficient of component k between α and β phases (dimensionless).
n_{ij}	unit vector at the connection between two grid blocks i and j .
N	total number of grid blocks or nodes of the grid.
N_c	total number of mass components in the porous medium.
ij	two connected elements; or connection of i and j .
P	pressure (Pa).
P_g	pressure of the gas phase (Pa).
P_n	pressure of NAPL or the oil phase (Pa).
P_w	pressure of the water phase (Pa).
P_{cgn}	gas-NAPL capillary pressure (Pa).
P_{cgw}	gas-water capillary pressure (Pa).
P_{cnw}	NAPL-water capillary pressure (Pa)
P_β	pressure of a fluid phase β (Pa).
P^o	reference pressure (Pa).
P_{cgn}^{gn}	gas-NAPL capillary pressure in a gas-NAPL, two-phase system (Pa).
P_{cgw}^{gw}	gas-water capillary pressure in a gas-water, two-phase system (Pa).
P_{cnw}^{nw}	NAPL-water capillary pressure in a NAPL-water, two-phase system (Pa).

continued

TABLE 5-3	Nomenclature <i>(continued)</i>

General Nomenclature *(continued)*

P_g^k	saturated partial pressure of component k in the gas phase (Pa).
q_β	source/sink, fracture-matrix mass exchange terms for phase β (Kg/s m ³).
q^g	source/sink, fracture-matrix mass exchange terms for gas (Kg/s m ³).
q^k	source/sink, fracture-matrix mass exchange terms for component k (kg/s m ³).
q^h	source/sink, fracture-matrix energy exchange terms (W/m ³).
q^w	source/sink, fracture-matrix mass exchange terms for water (kg/s m ³).
$Q_i^{k,n+1}$	source/sink, or generation terms for mass component ($k = 1, 2, 3, \dots, N_c$) (kg/s) or energy ($k = N_c + 1$) (J/s) at grid block or node i of time level $n+1$.
R^k	mass generation terms due to chemical reactions (kg/s m ³).
R^h	energy generation terms due to chemical reactions (W/m ³).
$R_i^{k,n+1}$	residual term of balance equations for mass component ($k = 1, 2, 3, \dots, N_c$) (kg/s) or energy ($k = N_c + 1$) (J/s) at grid block or mode i of time level $n+1$.
S_g	saturation of the gas phase in the porous medium (dimensionless).
S_n	residual saturation of NAPL (dimensionless).
S_w	saturation of the water phase in the porous medium (dimensionless).
S_{wr}	residual saturation of the water phase (dimensionless).
S_β	saturation of phase β in the porous medium (dimensionless).
S_n^*	threshold NAPL above which air-water interfaces cease to exist (dimensionless).
$\bar{S}_g$	normalized saturation of gas in the porous medium (dimensionless).
$\bar{S}_w$	normalized saturation of water in the porous medium (dimensionless).
$\bar{S}_\beta$	normalized saturation of phase β in the porous medium (dimensionless).
t	time (s).
T	formation temperature (°C).
$T_{1/2}$	half-life of the tracer/radionuclide component (s).
T^0	reference formation temperature (°C).
Δt	time step (s).
u_g	internal energy of gas (J/kg).
u_s	internal energy of rock solids (J/kg).
u_β	internal energy of fluid phase β (J/kg).
u_g^k	internal energy of component k in the gas phase (J/kg).
v_g	Darcy's velocity of the gas phase (m/s).

continued

TABLE 5-3 Nomenclature (*continued*)**General Nomenclature** (*continued*)

v_w	Darcy's velocity of the water phase (m/s).
v_β	Darcy's velocity of phase β (m/s).
V_i	volume of control-volume grid block or node i (m^3).
x_i	generic notation for the i th primary variable ($i=1, 2, 3, \dots, N_c + 1$).
X_β^k	mass fraction of component k in phase β (dimensionless).
X_s^k	mass of component k sorbed per mass of solids (kg/m^3).
z	vertical coordinate(m).

Greek Symbols

α	parameter of NAPL phase transition (dimensionless).
α_{vG}	parameter α of van Genuchten function (m^{-1}).
β	parameter n of van Genuchten function (dimensionless).
α_L^β	longitudinal dispersivity in phase β (m).
α_T^β	transverse dispersivity in phase β (m).
δ_{ij}	Kronecker delta function. ($\delta_{ij} = 1$ for $i = j$, and $\delta_{ij} = 0$ for $i \neq j$).
ϕ	effective porosity of porous media (dimensionless).
ϕ^o	effective porosity at reference conditions (dimensionless).
γ	parameter m of van Genuchten function ($\gamma = 1 - 1/\beta$) (dimensionless).
γ_{ij}	transmissivity (m^3).
η_i	set of direct neighboring nodes of node i .
φ	parameter of Brook and Corey function ($\varphi = 1 + 2/\lambda$) (dimensionless).
λ	index of Brook and Corey pore-size distribution (dimensionless).
λ_k	radioactive decay constant of component k (s^{-1}).
μ_β	dynamical viscosity of phase β ($\text{Pa} \cdot \text{s}$).
ρ_g	density of the gas phase (kg/m^3).
ρ_n	density of NAPL or the oil phase (kg/m^3).
ρ_s	density of rock grains (kg/m^3).
ρ_w	density of the water phase (kg/m^3).

continued

TABLE 5-3	Nomenclature <i>(continued)</i>

Greek Symbols *(continued)*

ρ_β	density of phase β (kg/m ³).
τ_β	tortuosity of phase β in the porous media (dimensionless).
χ_β^k	mole fraction of component k in phase β (mol/m ³).
ψ_β^i	flow potential term for phase β at grid block or node i (Pa).

Subscript

β	index for a fluid phase ($\beta = g$ for gas, w for water, and n for NAPL or oil).
c	capillary pressure.
g	gas phase.
i	index for grid block or node, primary variables, or Cartesian coordinates.
j	index for grid block or node of direct neighbors to node i , or Cartesian coordinates.
ij	connection between two connected grid blocks or nodes i and j .
$ij+1/2$	proper averaging of the parameters between grid blocks or nodes i and j along their connection.
m	primary variables.
n	NAPL.
p	Newton iteration level.
r	relative or rock.
s	solids of rock.
T	thermal energy, temperature or heat.
vG	van Genuchten.
w	water.
wr	residual water.

Superscript

0	reference conditions.
g	gas.
k	index for mass component or equation for mass component ($k = 1, 2, 3, \dots, N_c$); for energy ($k = N_c + 1$).
n	previous time step level.
$n+1$	current time step level.
T	thermal energy.
w	water.
β	index for a fluid phase ($\beta = g$ for gas, w for water, and n for NAPL or oil).

The generalized Darcy's law (5.1) correlates flow rates of a fluid and flow properties, as well as flow potential gradients in a multiphase, porous-medium system. This relationship depends only on the instantaneous, local state of the system, and the flow is driven by pressure, gravity, and viscous forces, with effects of phase interference included in relative permeability and capillary forces.

Advective and Dispersive Transport

The movement of dissolved mass components or chemical species within a fluid in a multiphase, porous-medium system is governed by advective, diffusive, and dispersive processes. It is also subject to other processes such as radioactive decay, adsorption, dissolution and precipitation, mass exchange or partition between phases, and other chemical reactions. The advective transport of a component or solute is carried by flow of a fluid, and the diffusive and dispersive flux is contributed by molecular diffusion and mechanical dispersion. The combined effects of molecular diffusion and mechanical dispersion are often called hydrodynamic dispersion and are described using a modified Fick's law for transport through a single-phase, porous medium (Scheidegger 1961, Bear 1972).

Analogous to the extension of the Darcy's law from single-phase flow to multiphase flow, Fick's law of diffusion has been generalized to describe the transport of components in multiphase, miscible, or immiscible fluid systems (Corapcioglu and Baehr 1987; Sleep and Sykes 1989). The generalized Fick's law, including hydrodynamic dispersion effects in a multiphase system, is used in this section to evaluate dispersive flux of transport. The total mass flux of advection and dispersion in a fluid is written as

$$F_{\beta}^k = \rho_{\beta} X_{\beta}^k v_{\beta} - \underline{D}_{\beta}^k \nabla (\rho_{\beta} X_{\beta}^k) \quad (5.2)$$

where superscript k is an index for mass components (for air, water, NAPL constituents, tracer, radionuclides, and so on); F_{β}^k is the dispersive flux vector of component k within fluid β ; X_{β}^k is the mass fraction of component k in fluid β ; and $\underline{D}_{\beta}^k$ is the hydrodynamic dispersion tensor accounting for both molecular diffusion and mechanical dispersion for

component k in phase β . We extend the general dispersion model (Scheidegger 1961) to include multiphase fluid effects as

$$\underline{D}_{\beta}^k = \alpha_T^{\beta} |\mathbf{v}_{\beta}| \delta_{ij} + (\alpha_L^{\beta} - \alpha_T^{\beta}) \frac{v_{\beta} v_{\beta}}{|\mathbf{v}_{\beta}|} + \phi S_{\beta} \tau_{\beta} D_{\beta}^k \delta_{ij} \quad (5.3)$$

where α_T^{β} and α_L^{β} are transverse and longitudinal dispersivities, respectively, in fluid β of porous media; ϕ is the effective porosity of the porous medium; S_{β} is saturation of fluid β ; τ_{β} is tortuosity of phase β in the porous medium; D_{β}^k is the molecular diffusion coefficient of component k within fluid β ; and δ_{ij} is the Kronecker delta function ($\delta_{ij} = 1$ for $i = j$, and $\delta_{ij} = 0$ for $i \neq j$), with i and j being coordinate indices.

The hydrodynamic dispersion tensor (5.3) describes that the combined effects of hydrodynamic dispersion consist of mechanical dispersion (the first two terms on the right-hand side of equation [5.3]) and molecular diffusion (the last term on the right-hand side of equation [5.3]). The mechanical dispersion within a fluid phase is proportional to the magnitude of the velocity of the fluid, and consists of longitudinal dispersion along the direction of the flow and transverse dispersion perpendicular to the flow direction.

There are many critics regarding the approach of handling hydrodynamic dispersion using the modified Fick's law, as discussed above. Hydrodynamic dispersion arises from an interplay between non-uniform advection and molecular diffusion in "real" porous media that have heterogeneities on multiple scales, from pore-to-basin scale. This process is commonly modeled using the Fickian diffusion (Brownian motion) analog proposed by Scheidegger (1954). The Fickian model is well-supported by laboratory experiments, but numerous studies in the hydrogeology literature of the last twenty years have demonstrated that it has serious limitations when applied to field-scale problems. Field tracer tests can generally be matched with the advection-dispersion equation, but such matching and associated parameters have little predictive power. There is much evidence that when the Fickian dispersion model is calibrated to field tracer data, the calibration "success" does not indicate that a realistic description of dispersion in the flow system has been obtained. Dispersivities are generally found to increase with space

and time scales of observation (Gelhar *et al.* 1992). Observed “dispersivities” tend to reflect the mixing that occurs when subsurface flow systems are observed (perturbed) and sampled, such as when fluids are extracted from wells. They do not imply that such mixed fluid compositions exist *in situ*. It has also been established that the amount of mixing and dilution implied by the Fickian model is unrealistically large. “Fickian plumes” represent a probability distribution, not a distribution of solute; they strongly overestimate the dilution to be expected in any particular representation of a heterogeneous medium. This can lead to serious errors for transport predictions, but may have even more unrealistic consequences for reactions that depend on concentrations in a non-linear manner. Another fundamental flaw of Fickian dispersion is that it may give a spurious “upstream” dispersion in the direction opposite advective flow. Given these serious problems and implications with the modified Fickian model, one wonders why it continues to be used at all. The answer is that there is a lack of better, generally acceptable and applicable alternatives. The Fickian analog does capture certain aspects of dispersion processes; it can provide useful insight as long as the analyst is keenly aware of its limitations.

Convective and Conductive Heat Transfer

Heat transfer in porous media is, in general, a result of both convective and conductive processes. These processes are complicated by interactions between multiphase fluids and multicomponents, and associated changes in phases, internal energy, and enthalpy. Heat convection is contributed by thermal energy carried mainly by bulk flow of all fluids, as well as by dispersive mass fluxes. On the other hand, heat conduction is driven by temperature gradients and may follow Fourier’s law. The overall heat flux vector may be described as

$$F^h = \sum_{\beta} (h_{\beta} \rho_{\beta} \mathbf{v}_{\beta}) - \sum_{\beta} \sum_k \left(h_{\beta}^k \underline{D}_{\beta}^k \cdot \nabla (\rho_{\beta} X_{\beta}^k) \right) - (K_T \nabla T) \quad (5.4)$$

where F^h is the combined heat flux vector, including both advective and conductive heat flow in a multiphase, multicomponent system; h_{β} and h_{β}^k are specific enthalpies of fluid phase β and of component k in fluid β ,

respectively; K_T is the overall thermal conductivity, which is a function of fluid saturations; and T is temperature.

As shown in equation (5.4), the total heat flow in a multiphase, multicomponent system is determined by heat convection of flow and mass dispersion, the first two terms on the right-hand side of the equation, as well as heat conduction, the last term on the right-hand side.

FLOW AND TRANSPORT EQUATIONS

In this section, we present a set of generalized governing equations for multiphase fluid flow, multicomponent transport, and heat transfer in porous and fractured media. The objective is to include physical processes of the vadose zone as completely as possible. This will provide a framework for discussions and simplifications in the following subsections in an effort to cover the majority of possible scenarios of flow and transport in the vadose zone. All other types of flow and transport equations—including unsaturated flow and transport in a gas-water, two-phase system; immiscible multiphase displacement; black-oil models; and decoupled solute transport—can be directly derived from the general governing equations.

Governing Equations

A multiphase system consists of several fluid phases (such as gas, water, and NAPLs), each of which consists of a number of mass components. To derive a set of generalized governing equations for multiphase fluid flow, multicomponent transport, and heat transfer, we assume that these processes can be described using a continuum approach within a representative elementary volume (REV) in a porous or fractured medium (Bear 1972). In addition, we assume a condition of local thermodynamic equilibrium, so that temperatures, phase pressures, densities, viscosities, enthalpies, internal energies, and component concentrations or mass fractions are the same locally within each phase of fluids in REV of the porous medium at any instant. However, the assumption of local chemical equilibrium is not required. These chemical reactions can be described using either equilibrium or kinetic reaction processes, including adsorption.

A combination of mass and energy conservation principles with the flow and transport constitutive laws cited above give rise to a set of governing equations described below. The mass conservation equations of each component k in the porous continuum can be written as

$$\frac{\partial}{\partial t} \left\{ \phi \sum_{\beta} (\rho_{\beta} S_{\beta} X_{\beta}^k) + \rho_s (1-\phi) X_s^k \right\} + \lambda_k \left\{ \phi \sum_{\beta} (\rho_{\beta} S_{\beta} X_{\beta}^k) + \rho_s (1-\phi) X_s^k \right\} - q^k - R^k = - \sum_{\beta} \nabla \cdot (\rho_{\beta} X_{\beta}^k \mathbf{v}_{\beta}) + \sum_{\beta} \nabla \cdot (\underline{D}_{\beta}^k \cdot \nabla (\rho_{\beta} X_{\beta}^k)) \quad (5.5)$$

and the energy conservation equation is

$$\frac{\partial}{\partial t} \left\{ \sum_{\beta} (\phi \rho_{\beta} S_{\beta} u_{\beta}) + (1-\phi) \rho_s u_s \right\} - q^h - R^h = - \sum_{\beta} \nabla \cdot (h_{\beta} \rho_{\beta} \mathbf{v}_{\beta}) + \sum_{\beta} \sum_k \nabla \cdot (h_{\beta}^k \underline{D}_{\beta}^k \cdot \nabla (\rho_{\beta} X_{\beta}^k)) + \nabla \cdot (K_T \nabla T) \quad (5.6)$$

where k is the index for the components, $k = 1, 2, 3, \dots, N_c$, with N_c being the total number of mass components; ρ_s is the density of rock solids; X_s^k is the absorbed mass fraction of component k on rock solids to account for adsorption effects; λ_k is the first-order decay constant of component k ; q^k and q^h are external source/sink terms, or fracture-matrix exchange terms, for component k and energy; R^k and R^h are the internal generation terms for component k and for energy, respectively, from equilibrium or non-equilibrium chemical reactions; and u_{β} and u_s are the internal energies of fluid β and rock solids, respectively.

Equations (5.5) and (5.6) describe that the flow of each fluid phase is determined by Darcy's law, the transport of mass components is by advection and dispersion processes, and heat transfer by convection and conduction mechanisms. In addition, first-order decay is taken into account for the mass components that are subject to radioactive decay, and adsorption of a component on rock solids is described to correlate with the component concentration in the water phase. Many different processes, such as other types of chemical reactions (Xu *et al.* 1997), biodegradations (de Blanc *et al.* 1996), and colloid-facilitated contaminant transport (Corapcioglu and Jian 1993) can be included in the internal generation term for component k , R^k .

Constitutive Relations

To complete the mathematical description of multiphase flow and multicomponent transport in the vadose zone, the governing equations (5.5) and (5.6), which are the generalized mass and energy balance equations, need to be supplemented with a number of constitutive equations. These constitutive correlations express interrelations and constraints of physical processes, variables, and parameters, and allow the evaluation of secondary variables and parameters as functions of a set of primary unknowns or variables selected to make the governing equations solvable. Many of these relationships were presented in Chapter 1. They are reintroduced here for completeness.

Saturation and Mass Fraction Constraints

The equation for fluid saturations is

$$\sum_{\beta} S_{\beta} = 1 \quad (5.7)$$

The mass fractions of component k within phase β are subject to

$$\sum_k X_{\beta}^k = 1 \quad (5.8)$$

Capillary Pressure and Relative Permeability

In a multiphase system, the capillary pressure relates pressures between the phases. When dealing with a three-phase system of gas, water, and NAPL, water- and gas-phase pressures are related by

$$P_w = P_g - P_{cgw}(S_w, S_g) \quad (5.9)$$

where P_{cgw} is the gas-water capillary pressure. The NAPL phase pressure is related to the gas phase pressure through

$$P_n = P_g - P_{cgn}(S_w, S_n) \quad (5.10)$$

where P_{cgn} is the gas-NAPL capillary pressure in a three-phase system.

For most subsurface geologic materials, the wettability order is (1) aqueous phase, (2) NAPL phase, and (3) gas phase. The gas-water capillary pressure is usually stronger than the gas-NAPL capillary pressure. In a three-phase system, the NAPL-water capillary pressure, P_{cnw} , can be derived from

$$P_{cnw} = P_{cgw} - P_{cgn} = P_n - P_w \quad (5.11)$$

The relative permeabilities of a fluid phase in a three-phase system are normally assumed to be functions of fluid saturations only as

$$k_{r\beta} = k_{r\beta}(S_w, S_g) \quad (5.12)$$

The functions of capillary pressure and relative permeability are generally determined from laboratory and field studies for a given site in a tabulated form (see Chapter 3). There are certain limitations for the capillary and relative permeability functions, discussed above, which should be noted. For example, effects of hysteresis of the medium are not explicitly included, and thermal effects are ignored.

Under isothermal, two- or three-phase flow conditions, there are many parametric models, closed-form functions, and commonly used approximations in the literature to determine capillary pressure and relative permeability functions (see Chapter 3). We present several of the most frequently used relations in the following sections.

Two-Phase Flow Relations

A most widely used capillary pressure function is the van Genuchten model (van Genuchten 1980), which defines gas-water capillary pressure as a function of water saturation

$$P_{cgw}(S_w) = \frac{\rho_w g}{\alpha_{vG}} \left\{ \left(\bar{S}_w \right)^{-1/\gamma} - 1 \right\}^{1/\beta} \quad (5.13)$$

with the effective or normalized water saturation defined as

$$\bar{S}_w = \frac{S_w - S_{wr}}{1 - S_{wr}} \quad (5.14)$$

where γ , β , and α_{vG} are parameters of the van Genuchten functions, with $\gamma = 1 - 1/\beta$; and S_{wr} is the residual (irreducible) water saturation in the porous medium.

Relative permeabilities in a two-phase gas-water flow system are generally assumed to be only functions of water saturation. One of the two commonly used forms of two-phase relative permeability is the Brooks-Corey function (Brooks-Corey 1964, Honarpour *et al.* 1986), given by

$$k_{rw}(S_w) = (\bar{S}_w)^{2+\varphi} \quad (5.15)$$

and

$$k_{rg}(S_w) = [1 - \bar{S}_w]^2 [1 - (\bar{S}_w)^\varphi] \quad (5.16)$$

where $\varphi = 1 + 2/\lambda$, and λ is referred to as the Brook-Corey pore-size distribution index.

Another popular relative permeability model is that of Mualem (1976) and van Genuchten (1980), given by

$$k_{rw} = (\bar{S}_w)^{1/2} \left\{ 1 - \left(1 - (\bar{S}_w)^{1/\gamma} \right)^\gamma \right\}^2 \quad (5.17)$$

for estimating the relative permeability to the wetting, water phase. Note that the model parameter, γ , used here is the same as in the capillary pressure function of Equation (5.13).

The relative permeability to the non-wetting, gas phase, may be described (Parker *et al.* 1987) by

$$k_{rg} = (\bar{S}_g)^{1/2} \left(1 - (\bar{S}_w)^{1/\gamma} \right)^{2/\gamma} \quad (5.18)$$

where the effective gas saturation is defined as

$$\bar{S}_g = \frac{S_g}{1 - S_{wr}} \quad (5.19)$$

normalized to a maximum mobile water saturation.

Three-Phase Flow Relations

There are few experimental studies and data available in the literature on the constitutive relations needed for modeling three-phase flow and transport in porous media. As pointed out by Gee *et al.* (1991), “the lack of information on constitutive relations may be the foremost element impeding the development of modeling tools to accurately predict and assess environmental consequences of subsurface organic liquid contamination.” In particular, we have very limited knowledge of characteristics of capillary pressure and relative permeability functions in a three-phase system. This is despite significant efforts in this area over the past half century, mainly by those in petroleum reservoir engineering. The highly heterogeneous and anisotropic soils in the vadose zone, combined with the unstable flow regime, make it more difficult to handle inferences of three-phase flow than the corresponding modeling of a relatively homogeneous oil reservoir.

A commonly used approach for handling three-phase flow is to estimate capillary pressures and relative permeability using sets of relations measured from separated two-phase systems. This is because two-phase flow measurements can be much easier to obtain in the laboratory than three-phase measurements. Following the pioneering investigation of Leverett and Lewis (1941), capillary pressures between oil and water or between gas and oil in a three-phase system are often represented by

$$P_{cnw} = P_{cnw}^{nw}(S_w) \quad (5.20)$$

and

$$P_{cnw} = P_{cnw}^{nw}(S_w) \quad (5.21)$$

respectively, where P_{cnw}^{nw} is capillary pressure between NAPL (or oil) and water in the NAPL-water two-phase system; and P_{cgn}^{gn} denotes capillary pressure between gas and NAPL in the gas-NAPL two-phase system.

For many applications, however, the only capillary pressure curves available may be those obtained from a two-phase experiment, such as capillary pressure curves measured for a gas-water, two-phase system. However, since certain parts of the model domain may be at gas-water, two-phase conditions (or even at single-phase condition) for most of the

simulation time, we need to handle one-, two-, or three-phase conditions as well as transitions in the model. In these cases the following two relations (Forsyth 1991) are provided:

$$P_{cnw}(S_w)\phi = \alpha P_{cnw}^{nw}(S_w) \quad (5.22)$$

$$P_{cgn}(S_w, S_n) = \alpha P_{cgn}^{gn}(S_g) + (1 - \alpha) P_{cgw}^{gw}(S_w) \quad (5.23)$$

where P_{cgw}^{gw} is capillary pressure between gas and water in a gas-water, two-phase system. In equations (5.22) and (5.23), we introduce a fluid interface transitional parameter, α , defined as

$$\alpha = \min \left\{ 1, \frac{S_n}{S_n^*} \right\} \quad (5.24)$$

where S_n^* is a NAPL threshold saturation above which air-water interfaces cease to exist within all pores of an REV and its value may be approximated by a residual NAPL saturation. These modifications provide both physically and numerically smooth transitions of capillary forces between single-phase, two-phase, and three-phase conditions.

Relative permeabilities are assumed to be simplified, as follows, for three-phase flow (Stone 1970). The relative permeability is described as

$$k_{rw} = k_{rw}(S_w) \quad (5.25)$$

for the water phase

$$k_{rn} = k_{rn}(S_w, S_g) \quad (5.26)$$

for the NAPL phase, and

$$k_{rg} = k_{rg}(S_g) \quad (5.27)$$

for the gas phase.

When no three-phase relative permeability data are available (which is almost always the case), the NAPL relative permeability is often estimated using the Stone method II (Aziz and Settari 1979):

$$k_{rn} = k_{rn}^{*wn} \left[\left(\frac{k_{rn}^{wn}}{k_{rn}^{*wn}} + k_{rw} \right) \left(\frac{k_{rn}^{ng}}{k_{rn}^{*wn}} + k_{rg} \right) - (k_{rw} + k_{rg}) \right] \quad (5.28)$$

where k_{rn}^{*wn} is the relative permeability value to NAPL at residual water saturation in the water-NAPL (nw), two-phase system; k_{rn}^{nw} is the relative permeability to NAPL in the water-NAPL, two-phase system; and k_{rn}^{ng} is the relative permeability to NAPL in the NAPL-gas (ng), two-phase system. With equation (5.28), the Stone II function, we can evaluate three-phase relative permeability using two sets of two-phase flow relative permeabilities determined from water-NAPL and NAPL-gas systems, respectively.

In addition, several functional forms of three-phase capillary pressure and relative permeability functions are discussed in the literature. For example, the extended three-phase capillary pressure and relative permeability of the van Genuchten model by Parker *et al.* (1987) may be used as an alternative for describing three-phase flow in the vadose zone when no laboratory experimental data are available for site-specific studies. These functions are much simpler to use, and they need only parameters of van Genuchten, which are determined from two-phase flow analyses.

When using these models to estimate capillary pressure and relative permeabilities for describing two- or three-phase flow, it should be kept in mind that these empirical functions have limitations and may or may not be applicable to a particular type of rock or soil under study. Model parameters determined from curve fitting of laboratory or field data may not cover the entire range of moisture conditions for modeling studies. For ranges outside observation data, the models can provide only approximations or extrapolations on the soil retention curves. For example, at the dry end near the residual saturation, the van Genuchten model will predict infinitely high capillary pressures, which may not be physically meaningful. In addition, a potential problem may occur because of a direct correlation between capillary pressure and relative permeability functions with the van Genuchten model, and this correlation needs to be verified for a particular application. Site-specific studies are recommended so that experimental data can be used directly in determining capillary pressure and relative permeability relations, even in table

lookup. The closed-form relations discussed in this section should be used only as alternatives.

Fluid Density and Viscosity

Density of a fluid phase is treated as a function of pressure and temperature as well as mass composition, described by

$$\rho_{\beta} = \rho_{\beta}(P, T, X_{\beta}^k) \quad (k = 1, 2, 3, \dots, N_c) \quad (5.29)$$

for the gas phase. Unless very high pressures are involved, the ideal gas law is often used for studies in the vadose zone. Under the conditions of most environmental investigation, this is a valid assumption.

The viscosities of liquid and gas phases are described by

$$\mu_{\beta} = \mu_{\beta}(P, T, X_{\beta}^k) \quad (k = 1, 2, 3, \dots, N_c) \quad (5.30)$$

The functional dependence or empirical expressions of viscosities of water and air versus pressure and/or temperature can be found in standard thermodynamics textbooks and tables.

Phase Partitioning and Volatilization

Phase partitioning, or interphase mass transfer, refers to the phenomena of local exchange in mass components that occurs between fluid phases in a multiphase environment. Under local chemical equilibrium conditions, the concentration of a component in a phase is related to its concentration in another phase through a partitioning coefficient. This equilibrium-partitioning coefficient is, in general, a function of pressure, temperature, and concentration under given soil characteristics and moisture conditions. As a special case of phase partitioning, volatilization means the transfer of mass components from liquid and solid phases (soils) to the vapor or the gaseous phase. It is often determined by vapor pressure, water solubility of the component, and other factors, such as the organic carbon content in soil for NAPL constituents.

Henry's law is commonly used to determine partitioning of air or chemicals between the gas phase in liquid water, while partitioning of a component between NAPL and air phases is described using Raoult's law (Corapcioglu and Baehr 1987; Mercer and Cohen 1990). Local equilibrium is often assumed between air and liquids. Henry's law

relates the concentration of a dissolved chemical in water to the partial pressure of the chemical in gas in a gas-water system (Falta *et al.* 1992a) as

$$P_g^k = K_H^k \chi_w^k \quad (5.31)$$

where P_g^k is the partial pressure of component k in the gas phase, K_H^k is Henry's constant for component k , and χ_w^k is the mole fraction of component k in the water phase.

How to represent and correlate the equilibrium concentrations of multiple components in a multiphase system is a key to solving the transport equations. We use the following general relation for a phase partitioning (Panday *et al.* 1995; Adenekan *et al.* 1993):

$$\chi_\alpha^k = K_{\alpha:\beta}^k \chi_\beta^k \quad (5.32)$$

where χ_α^k and χ_β^k are the mole fractions of component k in phases α and β , respectively. $K_{\alpha:\beta}^k$ is the equilibrium partitioning coefficient of component k between phases α and β . $K_{\alpha:\beta}^k$ depends on the chemical properties of the component and is a function of temperature, pressure, and composition as follows:

$$K_{\alpha:\beta}^k = K_{\alpha:\beta}^k(P_\beta, T, \chi_\beta^k) \quad (5.33)$$

Experimentally determined partitioning coefficients, or K -values, should be used whenever possible.

Adsorption

Adsorption is a process of partitioning a chemical component from its solution so that it adheres onto the surface of soils or rock solids. The energy acting on the surfaces of soils or rock pores causes chemicals to be adsorbed onto particles. Adsorption of NAPL components onto soils can be modeled as an equilibrium or as a kinetic process (de Blanc *et al.* 1996). If the rate of adsorption and desorption is fast relative to other processes occurring in the aquifers, the solute(s) can be assumed to be at equilibrium between the fluid and solid phases. The equilibrium partitioning of solutes between the solid and fluid phases can then be described using an isotherm in which the solid phase concentration is a function of the concentration of the solute in the fluid. The most

common isotherms are the linear isotherm, or K_D approach, and the non-linear Freundlich or Langmuir isotherms.

In general, the equilibrium adsorption may be related to the concentration of component k in phase β as

$$X_s^k = K_D^k \rho_\beta X_\beta^k \quad (5.34)$$

where X_s^k is the mass of component k sorbed per mass of solid, and the distribution coefficient, K_D^k , is treated as a constant or as a function of the concentration or mass fraction in a fluid phase under the local chemical equilibrium condition. When the local equilibrium assumption is not applicable, kinetic expressions should be used for adsorption processes. For organic chemicals, the distribution coefficient between soil and water depends largely on the amount of organic carbon present in the soil and may be determined by

$$K_D^k = K_{oc}^k f_{oc} \quad (5.35)$$

where K_{oc}^k is the organic carbon partitioning coefficient and f_{oc} is the organic carbon fraction in the soil (Hunt *et al.* 1988; Brusseau 1995).

Other types of reactions can also be described in the transport equations using mass generation terms R^k . These reactions may include dissolution and precipitation reactions of multi-species minerals or metals in the aqueous species, kinetic interphase mass transfer biodegradation for organic compounds and others, and colloid-facilitated contaminant transport.

Decay

Certain components, such as radionuclides or radioactive tracers, may undergo radioactive decay. Radioactive decay is commonly described using a first-order expression

$$C_\beta^k = C_{\beta 0}^k e^{-\lambda_k t} \quad (5.36)$$

where C_β^k is the concentration of component k in phase β and is equal to $C_{\beta 0}^k$ at $t = 0$; and λ_k is the radioactive decay constant, defined as

$$\lambda_k = \frac{\ln(2)}{t_{1/2}} \quad (5.37)$$

where $t_{1/2}$ is the half-life of the radioactive component. This formulation may be used for any first order decay reaction.

Thermal Properties

In many cases, specific enthalpy for the liquid phase may be assumed to be independent of its composition and is determined as a function only of temperature and pressure. Then the specific enthalpy of liquid water and NAPL can be defined as

$$h_{\beta} = u_{\beta} + \frac{P_{\beta}}{\rho_{\beta}} \quad (\beta = w \text{ and } n) \quad (5.38)$$

where the internal energy, u_{β} , of phase β is also a function of pressure and temperature. For the liquid water, it can be determined from a steam table.

In the gas phase, the specific enthalpies of air, water, and NAPL vapors are needed to evaluate diffusive heat fluxes. The specific enthalpies of component k in the gas phase are determined by

$$h_g^k = u_g^k + \frac{P_g^k}{C_g^k} \quad (5.39)$$

where u_g^k is the specific internal energy of component k in the gas phase.

The overall gas-phase specific enthalpy is calculated as

$$h_g = \sum_k X_g^k h_g^k \quad (5.40)$$

The gas-phase internal energy is estimated from

$$u_g = \sum_k X_g^k u_g^k \quad (5.41)$$

The overall thermal conductivity of the porous medium is treated as a function of fluid saturations by

$$K_T = K_T(S_g, S_w, S_n) \quad (5.42)$$

to include effects of both fluids and rock solids.

Rock Properties

The effective porosity of porous materials is generally treated as a function of pressure and temperature as

$$\phi = \phi^{\circ} (1 + C_r (P - P^{\circ}) - C_T (T - T^{\circ})) \quad (5.43)$$

where ϕ° is the effective porosity at a reference pressure, P° , and a reference temperature, T° ; and C_r and C_T are the compressibility and thermal expansion coefficient of the medium, respectively.

Initial and Boundary Conditions

The initial and boundary conditions of a model must be specified before the governing equations can be solved. The initial status or initial condition of a multiphase system is specified by assigning a complete set of primary thermodynamic variables within the model domain. Initial conditions are commonly estimated according to capillary-gravity equilibrium conditions in a multiphase system of the vadose zone.

First-type, or Dirichlet, boundary conditions denote constant or time-dependent phase pressure, as well as saturation, temperature, and concentration conditions. Flux-type, or Neuman, boundary conditions refer to recharge/injection or discharge/pumping rates specified at wells or along the boundary. For modeling multiphase fluid flow, multicomponent transport, and heat transfer in the vadose zone, specification of boundary conditions is by no means an easy task. In most cases, boundary conditions are a combination of different types and physical constraints for different phases, components, or heat. Ground surfaces and water tables are commonly used as boundaries in vadose zone studies. On the ground surface, atmospheric or gaseous pressures, temperature, and humidity may be approximated as constants. Water recharges from precipitation, connections to surface water bodies, interactions with seepage faces, and NAPL contaminants need to be described at the same boundaries. In addition, the land surface boundary is often subject to other processes, such as ET and atmospheric-subsurface interactions. The problem becomes more complicated when considering a situation of multi-layered pumping or injection wells. In general, boundary conditions for multiphase flow and transport models consist more of phys-

ical constraints rather than conforming to their traditional concepts in the solution of partial differential equations.

Solution Approaches

As discussed above, the physical laws governing flow and transport in the vadose zone are represented mathematically on the macroscopic level by a set of partial differential equations. These governing equations (for example, equations [5.5] and [5.6]) are intrinsically non-linear as long as multiphase flow or heat transfer is involved. Solving these equations with complex boundary and initial conditions has been a scientific challenge over the past half century in many disciplinary areas of science and engineering. Significant progress has been made due to research efforts in petroleum and geothermal reservoir engineering, groundwater hydrology, and soil sciences. In general, solution methodologies developed so far consist of three major approaches: (1) analytical solutions; (2) numerical methods; (3) alternative approaches. The applicability, advantages, and limitations of these approaches are discussed in this section.

Analytical Solutions

The analytical approach is the traditional method for solving governing equations of flow and transport through porous media. In this method, exact mathematical solutions are obtained and used to describe physical problems of interest. Historically, analytical solutions have made important contributions to understanding flow and transport behavior of fluids through porous media (Muskat 1946; Carslaw and Jaeger 1959). Even though significant progress has been made in numerical simulation techniques of fluid flow in porous media since the late 1950s, analytical approaches have proven to be irreplaceable by numerical techniques. Analytical solutions, if available, provide direct insights into the physics of flow and transport phenomena occurring in porous media, especially when dealing with the effects of multiple parameters on a given problem. In addition, the analytical solutions of transient fluid flow and solute transport provide the theoretical basis for well and laboratory testing analyses, which are widely used to determine fluid and porous medium properties in reservoir engineering, groundwater hydrogeology, and soil sciences (Earlougher 1977, Driscoll 1986, Javan-

del *et al.* 1984). Even in numerical studies of subsurface fluid flow and solute transport problems, analytical solutions are always needed to examine and verify numerical schemes and results.

A considerable amount of work has been devoted to the development of both exact and approximate analytical solutions for transient flow of fluids and solute transport through porous media (see, for example, Streltsova 1988, van Genuchten and Alves 1982). Traditionally, many of those solutions were borrowed from the heat transfer literature (Carslaw and Jaeger 1959, Ozisik 1980), because the governing equations are the same in form in many cases for heat conduction in solids and for slightly compressible, single-phase fluid flow and transport in porous media. The most commonly used analytical methods for porous medium transient fluid flow and solute transport problems are (1) separation of variables; (2) the integral transformation, including Laplace and Fourier transformations, and finite transformation; (3) Green's function; and (4) similarity transformation.

Analytical solutions, however, have limited applicability to analyzing flow and transport in the vadose zone. This is primarily because of the non-linearity in the governing equations and/or in the boundary conditions for flow and transport problems. Moreover, they are generally unable to account for the heterogeneity of the vadose zone. Under very special circumstances with many idealizations and simplifications, analytical solutions may become possible for a two- and three-phase flow problem. Such an example is the Buckley-Leverett solution of non-capillary, two-phase displacement in a one-dimensional, homogeneous system (Buckley and Leverett 1942), which can also be extended to flow in a composite, one-dimensional heterogeneous system (Wu *et al.* 1993). In addition, several forms of analytical solutions with capillary effects have been presented (McWhorter and Sunada 1990, Chen 1988).

In general, problems involving coupled flow, solute transport, and heat transfer processes in a multi-dimensional domain of the vadose zone are analytically intractable. Numerical solutions have to be used if (1) the flow domain has a complicated geometry; (2) the problem is non-linear or coupled either in the governing equation and/or in the boundary conditions; and (3) the porous medium is heterogeneous and anisotropic. In recent years, the semi-analytical and semi-numerical techniques of combining the Laplace transformation with the finite difference (Moridis and Reddell 1991) and finite element (Sudicky 1989)

numerical approaches have provided a promising technique to solve flow and transport problems in porous media.

Numerical Methods

Numerical simulation of multiphase subsurface flow and transport phenomena may be one of the most important developments in earth sciences during the second half of the 20th century. Due to its generality and effectiveness in handling subsurface multiphase flow and transport problems, the numerical simulation technique has become the major tool used by scientists and engineers in studies of flow and transport processes in a porous medium. The development of numerical approaches has been motivated by a variety of needs in many industries, from developing subsurface natural resources to addressing environmental concerns. Since the late 1950s, significant progress has been made in developing and applying numerical simulation techniques in petroleum engineering (Coats 1987, Aziz and Settari 1979, Peaceman 1977, Thomas 1982) and in groundwater literature (Huyakorn and Pinder 1983, Istok 1989). It should be mentioned that the technical advances in numerical simulations have benefited significantly from rapidly developing modern computer technology and the associated computational algorithms.

Numerical modeling approaches currently used for simulating coupled multiphase flow and transport processes are generally based on methodologies developed for petroleum and geothermal reservoir simulations. They involve solving fully coupled formulations describing these processes using finite-difference or finite-element schemes with a volume averaging approach. Earlier studies on modeling multiphase flow in porous media were primarily performed during the development of petroleum reservoirs (Douglas *et al.* 1959, Peaceman and Rachford 1962, Coats *et al.* 1967) and geothermal reservoirs (Mercer *et al.* 1974, Thomas 1978, Pruess 1987). During the same time, problems involving unsaturated and two-phase flow and transport in aquifers and subsurface soils were increasingly recognized and investigated in groundwater hydrology and soil science. Many numerical approaches were developed and applied to modeling flow and transport phenomena in the vadose zone (see, for example, Narasimhan and Witherspoon 1976, Cooley 1983, Huyakorn *et al.* 1984, Morel-Seytoux and Billica 1985, Celia *et al.* 1990).

Soil and groundwater contamination by NAPL, such as contamination from oil and gasoline leakage or other organic chemicals, has received increasing attention in recent years. The NAPL-related environmental concern has motivated significant research activities in developing and applying multiphase flow and transport models for assessing NAPL contamination and associated cleanup operations. As a result, many numerical models and computational algorithms have been developed and improved upon for solving multiphase fluid flow and organic chemical transport problems through porous and fractured media in the vadose zone (Abriola and Pinder 1985; Faust 1985; Forsyth 1988, 1991, and 1994; Forsyth and Shao 1991; Kaluarachchi and Parker 1989; Falta *et al.* 1992a, b; Huyakorn *et al.* 1994; Panday *et al.* 1994, 1995; Wu *et al.* 1994; Helmig *et al.* 1994; Nitao, 1996; White and Oostrom, 1996). Numerical modeling approaches have currently become standard techniques used in investigating subsurface NAPL contamination and in implementing remediation measures.

There are many kinds of numerical approaches developed and used in the literature for solving flow and transport equations in porous media. Perhaps the most commonly used numerical techniques for multiphase flow are the finite or integral finite difference and the finite element approaches. In addition, other numerical methods, such as the characteristics and boundary element method, have also found certain applications.

Alternative Modeling Methods

In addition to the analytical and numerical solutions discussed above, many alternative modeling approaches have been developed and used to study multiphase flow and transport problems. Among these alternatives, stochastic methods (Gelhar 1993), transfer function models (Jury 1982), and particle tracking (Thompson and Gelhar 1990) have received attention in recent years because of their capability and promise in characterizing flow and transport behavior in the unsaturated zone. Recent investigations of water seepage in thick unsaturated zones of fractured rocks of Yucca Mountain have indicated that flow and transport processes in such an environment may occur in non-volume-averaged fashion and proceed, in part, by means of localized preferential pathways (Pruess *et al.* 1999). Conventional continuum concepts and modeling approaches may not adequately capture the physics of partially saturated flow in fractured rocks if the spatial variability is not properly

represented by the constraints of the computational requirements. Several mechanistic models have been proposed to deal with those preferential flows through unsaturated fractured rocks (Pruess, 1999; Pruess et al. 1999).

However, when compared with the traditional finite difference and finite element numerical methods, increasing difficulties and complexities make these alternative methods less attractive in handling fully coupled, multiphase flow, multicomponent transport and heat transfer problems in heterogeneous porous or fractured media. One major problem with these alternative modeling approaches is that there have been few studies to address the issue of how to perform verification or validation studies of model results, which is extremely important to practical applications.

Approximations and Simplifications

In presenting the governing and constitutive equations, we have implicitly or explicitly introduced many simplifying assumptions during the discussions. For example, one of the implicit approximations is to ignore the effects of general mechanical deformations on permeability and movement of rocks or soils. Even with these assumptions, equations (5.5) and (5.6) are still difficult to use in numerical modeling of flow and transport processes in the vadose zone. These two general conservation equations may still be unnecessarily complex for many applications because they contain too many unknowns, too many undetermined parameters, and too many correlations, which may make them not feasible to be solved in a given field study. In practice, many restrictions in deriving these two governing equations can be relaxed, and further approximations and simplifications can be made for different situations and focuses of field-specific investigations.

The first commonly used simplifying assumption is to assume a model system at isothermal conditions. Then no heat transfer calculation is needed, the energy equation is removed, and the model formulation is significantly simplified. Isothermal simulations provide good approximations to many vadose zone flow and transport studies, such as in soil sciences, in which the main concern is water flow and solute transport under average, ambient, isothermal conditions. However, the isothermal assumption will break down when dealing with thermal remediation of

subsurface contamination, such as in the case of a steam flooding cleanup operation, thermally driven vapor diffusion near land surface, and high-level radioactive waste disposal.

The second simplification of the flow and transport problem is to decouple the flow and transport processes, so that multiphase flow is not affected by transport of solutes or chemical composition of fluids. This approach of decoupling flow from transport is widely used when modeling the transport of slightly soluble or dilute solute components in a multiphase system, as long as the existence of components or their concentration has little effect on the flow properties, densities, viscosities, and other properties of the fluids.

One of the often-used approximations in unsaturated flow modeling for a given problem is the reduction of the number of active flowing phases. For example, unsaturated flow in an isothermal, gas and water system may be modeled using the classical Richards' equation (Richards 1931). This approximation can be made if one is concerned only with the flow of the aqueous phase. The Richards' equation has provided the theoretical basis for analyzing water flow and solute transport processes in the unsaturated zone in many areas (Nielsen *et al.* 1986). Using Richard's equation, gas pressure is treated as a constant and the dynamics of gas flow is ignored. A physically more accurate explanation of Richards' flow condition is that gas flow is so fast that when compared with water flow, on the time scale of interest, it is instantaneously completed. Then gas flow dynamics can be assumed to be already known, or at steady state.

Similar to Richards's flow, simplified, single-phase gas flow can be described using only a gas conservation equation in a gas-water, two-phase system, in which water flow and moisture distribution are regarded to be at steady state. This flow simplification may be useful for field gas-flow analyses in the variably saturated media (Wu *et al.* 1996a).

The most important approximation, however, may be the local thermodynamic and chemical equilibrium assumption, which has been extensively applied in all kinds of modeling studies of flow and transport in the porous medium. The local thermodynamic equilibrium assumption is a necessary condition for deriving governing equations of flow and transport in defining the basic thermodynamic variables, such as pressures, temperatures, and concentrations within an REV. This

assumption makes it possible to quantitatively describe physical processes of phase partitioning, adsorption and dissolution, decay, other chemical reactions, phase changes, and heat exchanges using well-established thermodynamic principles.

UNSATURATED FLOW AND TRANSPORT EQUATIONS

In this section, we discuss simplified flow and transport equations under the Richards' flow condition from the general governing equations (5.5) and (5.6). We are concerned with flow and transport in a two-phase system of two fluids (water and gas) and one or several slightly soluble (dilute) solutes under isothermal conditions. The additional assumptions are: (1) there are no mass exchanges of air and water components between phases; (2) flow and transport processes can be separated; (3a) gas-flow dynamic can be ignored—that is, Richards' equation applies for active aqueous phase flow; or (3b) moisture distributions are at steady state and water flow dynamic can be ignored for one active gaseous phase flow. This leads to two simple, but useful, governing equations for flow and transport in the unsaturated zone, which are presented below.

Governing Equations of Richards' Flow and Solute Transport

Under the Richards' flow condition, the mass conservation of water may be simplified as

$$\frac{\partial}{\partial t}(\phi \rho_w S_w) - q^w = -\nabla \cdot (\rho_w v_w) \quad (5.44)$$

Note that here Richards' equation is expressed in a mass-balance form of the aqueous phase in terms of water saturation and Darcy's velocity. Equation (5.44) is called a mixed, pressure-based formulation, and it can be easily converted to a form in terms of moisture content and heads, commonly used in groundwater and soil sciences.

One or several components are assumed to be dissolved only in the aqueous phase and are transported according to equation (5.5), with the aqueous phase as an active phase. The flow properties, such as water viscosity and density, and Darcy's velocity, are assumed to be independent of the concentration of solutes in the aqueous phase.

Governing Equations of Active Gas Phase Flow and Solute Transport

In parallel to the Richards' equation for one active water phase, if water-flow dynamics can be ignored, the mass conservation of the gas in the gaseous phase is simplified as

$$\frac{\partial}{\partial t}(\phi \rho_g S_g) - q^g = -\nabla \cdot (\rho_g v_g) \quad (5.45)$$

The transport of one or several gaseous components is also described by Equation (5.5). In this case, however, we need to know that distributions of the moisture, which are treated as known. The gas-flow properties, such as gas viscosity and density and Darcy's velocity, are assumed to be independent of the concentration of solutes in the gaseous phase. The adsorption term should be handled using a relation to the concentration in the aqueous phase. This is because, in general, water as the wetting phase separates the gaseous phase from rock solids.

ISOTHERMAL MULTIPHASE FLOW AND TRANSPORT EQUATIONS

In this section we discuss governing equations of three-phase flow and associated solute transport under isothermal conditions. This is another demonstration of how to derive a set of simplified flow and transport equations from the general governing equations, (5.5) and (5.6). In this case, we are concerned with flow and transport in a three-phase, isothermal system of gas, water, and NAPL, with each phase consisting of a number of components. Radioactive decay is not accounted for. This is a typical situation encountered in modeling LNAPL or DNAPL vadose zone contamination under ambient conditions.

Two common scenarios of LNAPL and DNAPL subsurface contamination of an unconfined aquifer are shown in Figures 5-12(a) and 5-12(b) (Mercer and Cohen 1990), respectively. Figure 5-12(a) depicts the distribution of organic chemicals in multiphase fluids resulting from a release of LNAPL, and Figure 5-12(b) shows the case for DNAPL mobilization. Once introduced into the subsurface, gravity becomes the driving force for NAPL to migrate downward through the vadose zone as a distinct liquid. This vertical migration is also accompanied, to some extent, by the lateral spreading due to the effects of capillary forces and medium spatial variability (for example, layering). As the NAPL progresses downward through the vadose zone, it leaves residual liquid

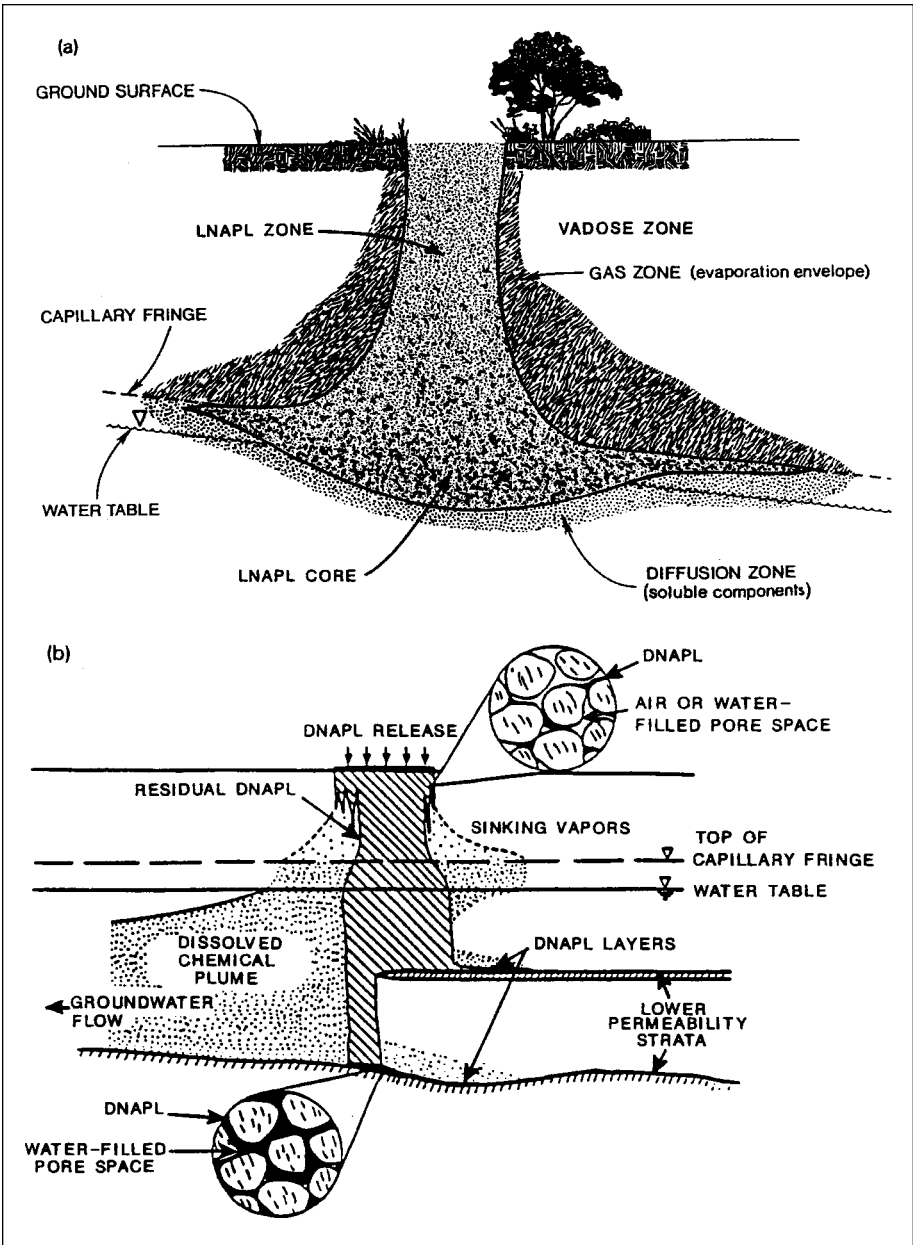


Figure 5-12. (a) Scenario of LNAPL contamination; (b) Scenario of DNAPL contamination (Mercer and Cohen, 1990).

(residual saturation) trapped in the pore spaces because of the effects of surface tension and soil heterogeneity. If the NAPL release is sufficiently large, some of the NAPL will eventually reach the water table. LNAPL will spread laterally along the capillary fringe, floating on the water table and moving with the ambient water. On the other hand, once DNAPL reaches the water table, it will displace the water and continue its downward migration until it encounters a low-permeability barrier or layer, forming a pool. During the migration in both the vadose and saturated zones, the NAPL components are also subject to phase partitioning, dispersion, and adsorption effects. A volatilized NAPL vapor zone or dissolved chemical plume may form surrounding the NAPL plume. Both scenarios can be effectively modeled using the isothermal multiphase flow and transport formulation of this section. If one is concerned with migration of the free product of NAPL, the formulation can be further simplified for multiphase flow only.

Governing Equations of Multiphase Flow and Transport

Under isothermal conditions, the processes of flow and transport of each component k in the multiphase system under consideration are governed only by the mass conservation equations as

$$\begin{aligned} \frac{\partial}{\partial t} \left\{ \phi \sum_{\beta} (\rho_{\beta} S_{\beta} X_{\beta}^k) + (1 - \phi) \rho_s \rho_w X_w^k K_d^k \right\} - q^k = \\ - \sum_{\beta} \nabla \cdot (\rho_{\beta} X_{\beta}^k \mathbf{v}_{\beta}) + \sum_{\beta} \nabla \cdot (\underline{D}_{\beta}^k \cdot \nabla (\rho_{\beta} X_{\beta}^k \mathbf{v}_{\beta})) \end{aligned}$$

($\beta = g, w$ and n) and ($k = 1, 2, 3, \dots, N_c$) (5.46)

Assuming local equilibrium, this represents a set of N_c equations for describing flow of three-phase fluids and transport of N_c components.

In general, these flow and transport equations for assessing a subsurface contamination scenario or a remediation scheme should be solved fully-coupled as long as volatile organic chemicals or NAPL are involved. In these situations, flow properties such as density and viscosity are strong functions of phase compositions, and the flow and transport processes are fully-coupled. In practice, however, coupled flow and transport equations may still present serious problems because of the

computational intensity necessary for solving the large number of governing equations and the difficulties in determining flow and transport properties. For many applications, the simplifications presented below may be needed.

Governing Equations of Multiphase Flow Only

The processes of flow and transport can be further simplified if interfacial mass transfer between the phases is ignored. Although each of the three phases contains a number of components, each is treated here as a single “pseudo-component” with averaged properties of the fluids. In addition, the three fluid components—gas, water, and NAPL—are assumed to be present only in their associated phases. This leads to a unification of flow and transport processes, and the problem becomes multiphase flow only; that is immiscible displacement in porous media. This assumption and resultant models are widely used for assessing contamination by free NAPL products and remediation by direct pumping or water flooding (Faust *et al.* 1989; Huyakorn *et al.* 1994).

In an isothermal system containing three mass components of gas, water, and NAPL, only three mass balance equations are needed to fully describe the flow problem, as

$$\frac{\partial}{\partial t}(\phi S_{\beta} \rho_{\beta}) - q_{\beta} = -\nabla \cdot (\rho_{\beta} \mathbf{v}_{\beta}) \quad (5.47)$$

$(\beta = g, w \text{ and } n)$

where q_{β} is the sink/source term of phase β per unit volume of formation.

One additional simplification to equation (5.47), commonly used in modeling NAPL flow in the vadose zone, is to ignore gas flow dynamics (Faust 1985; Forsyth 1988; Kaluarachchi and Parker 1989). This approach is similar to Richards’ equation in describing unsaturated flow, where the air phase is treated as a passive phase. Therefore the gas balance equation is eliminated from the model; only water and NAPL equations need to be solved.

NUMERICAL FORMULATIONS

The methodology of using numerical approaches to simulate multiphase subsurface flow and transport consists of the following three

steps: (1) spatial discretization of mass and energy conservation equations, (2) time discretization (using, for example, a fully implicit scheme), and (3) iterative approaches to solve the resultant non-linear, discrete algebraic equations. Among various numerical techniques for simulation studies is the mass- and energy-conserving discretization scheme that is based on the finite or integral finite difference or the finite element methods. This approach is the most commonly used, and is discussed here.

First, we present a generalized, generic numerical formulation that can be universally used for simulating different types of fluid flow, solute transport, and heat transfer processes in the subsurface. Then, we discuss solution techniques for solving linearized algebraic equations, treatment of initial and boundary conditions, and averaging flow and transport properties. In particular, we discuss a dual-continua approach for handling flow and transport through fractured media. Finally, we demonstrate how to derive different numerical formulations from the general numerical formulation for the different modeling needs in the vadose zone studies.

Discrete Equations

The component mass- and energy-balance equations (equations [5.5] and [5.6]) are discretized in space using a control-volume concept. The control-volume approach described in this section is a general spatial discretization. This is a scheme that can typically represent one-, two-, or three-dimensional domains using a set of discrete meshes. Each mesh has a certain (control) volume for a proper averaging or interpolation of flow and transport properties or thermodynamic variables. The control volume concept includes the conventional finite difference scheme (Peaceman 1977; Faust 1985), an integral finite difference method (Narasimhan and Witherspoon 1976; Pruess 1991), a control-volume finite element (Forsyth 1991), and Galerkin finite element methods (Huyakorn *et al.* 1994). These are the most widely used discretization schemes for multiphase flow simulation. The time discretization is usually carried out using a backward, first-order, fully implicit finite-difference scheme. The discrete nonlinear equations for components of water, air, NAPL, and heat at grid block or node i can be written in a general form:

$$\left\{ A_i^{k,n+1} (1 + \lambda_k \Delta t) - A_i^{k,n} \right\} \frac{V_i}{\Delta t} = \sum_{j \in \eta_i} F_{ij}^{k,n+1} + Q_i^{k,n+1} \quad (5.48)$$

$$(k = 1, 2, 3, \dots, N_c, N_c+1) \text{ and } (i = 1, 2, 3, \dots, N)$$

where superscript k is here the equation index for all mass components, with $k = 1, 2, 3, \dots, N_c$ and $k = N_c+1$ denoting the heat equation; superscript n denotes the previous time level; $n+1$ is the current time level to be solved; subscript i refers to the index of grid block or node i with N being the total number of nodes in the grid; Δt is time step size; V_i is the volume of node i for a finite difference discretization; η_i contains the set of direct neighboring nodes (j) of node i ; A_i^k , F_{ij}^k , and Q_i^k are the accumulation term at node i ; the “flow” term between nodes i and j , and sink/source term at node i for component k or thermal energy, respectively, and they are defined below.

Equation (5.48) has the same form regardless of the dimensionality of the system; that is, it applies to one-, two-, or three-dimensional flow and transport analyses. The accumulation terms for mass components (5.49) and thermal energy is (5.50) are defined below. We drop the nodal index i and time-level index n or $n+1$ below for simplicity.

$$A^k = \sum_{\beta} (\phi S_{\beta} \rho_{\beta} X_{\beta}^k) + (1 - \phi) \rho_s \rho_w X_w^k K_D^k \quad (5.49)$$

$$(k = 1, 2, 3, \dots, N_c)$$

is for mass components, and

$$A^{N_c+1} = \sum_{\beta} (\phi \rho_{\beta} S_{\beta} U_{\beta}) + (1 - \phi) \rho_s u_s \quad (5.50)$$

is for the thermal energy.

The flow term in (5.48) is generic, and it includes mass fluxes by advective and dispersive processes, as described by equation (5.2), as well as heat transfer, described by equation (5.4). For a mass component, the flow term, or the net mass flux by advection and hydrodynamic dispersion of a component along the connection of nodes i and j , is determined by

$$F_{ij}^k = F_{A,ij}^k + F_{D,ij}^k \quad (k = 1, 2, 3, \dots, N_c) \quad (5.51)$$

where $F_{A,ij}^k$ and $F_{D,ij}^k$ are the net mass fluxes by advection and hydrodynamic dispersion along the connection, respectively, with

$$F_{A,ij}^k = A_{ij} \sum_{\beta} (X_{\beta}^k)_{ij+1/2} F_{\beta,ij} \quad (5.52)$$

and

$$F_{D,ij}^k = -n_{ij} \cdot A_{ij} \sum_{\beta} \underline{D}_{\beta}^k \cdot \nabla (\rho_{\beta} X_{\beta}^k) \quad (5.53)$$

where A_{ij} is the common interface area between connected blocks or nodes i and j , and n_{ij} is the unit vector along connection of the two blocks i and j . The mass flux of fluid β along the connection is given by a discrete version of Darcy's law as

$$F_{\beta,ij} = \left(\frac{\rho_{\beta} k_{r\beta}}{\mu_{\beta}} \right)_{ij+1/2} \gamma_{ij} [\psi_{\beta j} - \psi_{\beta i}] \quad (5.54)$$

(for $\beta = g, w$ and n)

where γ_{ij} is conductance and is defined differently for finite difference or finite element discretization. If the integral finite-difference scheme is used (Pruess 1991), the conductance is calculated as

$$\gamma_{ij} = \frac{A_{ij} k_{ij+1/2}}{d_i + d_j} \quad (5.55)$$

where d_i is the distance from the center of block i to the interface between blocks i and j . The flow potential term in (5.54) is defined as

$$\psi_{\beta i} = P_{\beta i} + \rho_{\beta, ij+1/2} g D_i \quad (5.56)$$

where D_i is the elevation to the center of block i from a reference datum.

The total heat flux along the connection of nodes i and j includes convective, dispersive, and conductive terms, and may be evaluated, when using a finite difference scheme, by

$$F_{ij}^{N_c+1} = A_{ij} \sum_{\beta} \left[(h_{\beta})_{ij+1/2} F_{\beta,ij} \right] + \sum_{\beta} \sum_k \{ (h_{\beta}^k)_{ij+1/2} F_{D,ij}^k \} + \quad (5.57)$$

$$(K_T)_{ij+1/2} \left[\frac{T_j - T_i}{d_i + d_j} \right]$$

In evaluating the flow terms in the above equations, subscript $ij+1/2$ is used to denote a proper averaging or weighting of fluid flow, component transport, or heat transfer properties at the interface, or along the connection between two blocks or nodes i and j (see the subsection “Parameter Weighting Scheme,” below, for more discussion). The convention on the signs of the flow terms is that flow from node j into node i is defined as “+” (positive).

The mass or energy sink/source in equation (5.48) at node i , Q_i^k is defined as mass or energy exchange rate per unit volume of rocks or soils. It is normally used to treat boundary conditions, such as surface infiltration, pumping, and injection through wells. More generally, it can include the generation rates from various types of chemical reactions, biodegradation, or fracture-matrix interactions for fractured media, and the like.

Note that we present explicit, discrete expressions for estimating all the flow terms above, except for dispersive fluxes in equation (5.53). This is because of the numerical difficulties introduced in handling the hydrodynamic tensor of dispersion, which is treated very differently, using numerical approaches such as finite difference or finite element. In most formulations for solute transport, the off-diagonal terms and contributions of the dispersion tensor are ignored and the dispersive transport is considered only along the principal directions. A general procedure for using the integral finite difference to incorporate a full dispersion tensor is presented by Wu and Pruess (1998).

It is interesting to note that equation (5.48) presents an exact form of the balance equation for heat and each mass component in a discrete form. It states that the rate of changes in mass or energy accumulation at a node over a time step is exactly balanced by inflow/outflow of mass and energy and also by sink/source terms, when existing, for the node. As long as all the flow terms have such a property that flow from node i to node j is equal to and opposite to that from node j to node i for fluids, components, and heat, no mass or energy will be lost or created in the formulation during the solution. Therefore, the discretization in (5.48) is conservative.

A mass or energy conservative form of discretized equations, such as equation (5.48), will guarantee a mass and energy conservative solution, as long as a converged solution is obtained. In general, a mass conservative scheme of a numerical formulation may be defined as a

discretization that guarantees mass and energy conservation, and for which the conservative results are independent of how refined a grid is, the size of the time steps, how the non-linear equations are solved, or which primary variables are selected. Once a solution converges, mass and energy balance errors will become sufficiently small, which are related directly to the convergence tolerance specified for the problem.

Numerical Solution Scheme

There are a number of numerical solution techniques that have been developed in the literature over the past few decades to solve the non-linear, discrete equations of reservoir simulations. When handling multicomponent transport and heat transfer in a multiphase flow system, the predominant approach is to use a fully implicit scheme. This is due to the extremely high non-linearity inherent in those discrete equations and the many numerical schemes with different level of explicitness that fail to converge in practice. Even with active research and development for over half a century in the effort to look for better numerical solution techniques, no methods have proven themselves to be more efficient or more robust than a simple Newton iteration (normally called a Newton Raphson iteration) scheme for simulating multiphase flow and transport problems. In this section, we discuss a general procedure to fully solve the discrete non-linear equation (5.48) using a Newton iteration method.

Let us write the discrete non-linear equation (5.48) in a residual form as

$$R_i^{k,n+1} = \left\{ A_i^{k,n+1} (1 + \lambda_k \Delta t) - A_i^{k,n} \right\} \frac{V_i}{\Delta t} - \sum_{j \in \eta_i} F_{ij}^{k,n+1} - Q_i^{k,n+1} = 0 \quad (5.58)$$

$$(\beta = g, w \text{ and } n; k = 1, 2, 3, \dots, N_c + 1; i = 1, 2, 3, \dots, N)$$

Equation (5.58) defines a set of $(N_c + 1) \times N$ coupled non-linear equations, which need to be solved for the balance equations of the mass components and heat, respectively. Here, the superscript $n+1$ indicates the new time-level while n indicates the old time-level. In general, $(N_c + 1)$ primary variables per node are needed for using the Newton iteration for the associated $(N_c + 1)$ equations per node. The primary variables are usually selected from among fluid pressures, fluid saturations,

mass (mole) fractions of components in fluids, and temperatures. In many applications, however, primary variables cannot be fixed and must be allowed to vary dynamically in order to deal with phase appearance and disappearance (Forsyth 1993 and 1994). The rest of the dependent variables—such as relative permeability, capillary pressures, viscosity and densities, partitioning coefficients, specific enthalpies, thermal conductivities, dispersion tensor, and other factors, as well as nonselected pressures, saturations, and mass (mole) fractions—are treated as secondary variables.

In terms of the primary variables, the residual equation (5.58) at a node i is regarded as a function of the primary variables at not only node i but also at all its direct neighboring nodes. The Newton iteration scheme gives rise to

$$\sum_m \frac{\partial R_i^{k,n+1}(x_{m,p})}{\partial x_m} (\delta x_{m,p+1}) = -R_i^{k,n+1}(x_{m,p}) \quad (5.59)$$

where x_m is primary variable m with $m = 1, 2, 3, \dots, N_c+1$, respectively, at node i and all its direct neighbors; p is the iteration level; and $i = 1, 2, 3, \dots, N$. The primary variables in (5.59) are updated after each iteration as

$$x_{m,p+1} = x_{m,p} + \delta x_{m,p+1} \quad (5.60)$$

The iteration process continues until the residuals $R_i^{k,n+1}$ or changes in the primary variables $\delta x_{m,p+1}$ over an iteration are reduced below pre-set convergence tolerances.

Numerical methods are generally used to construct the Jacobian matrix for equation (5.59), as outlined by Pruess (1991) and Forsyth *et al.* (1995). At each Newton iteration, equation (5.59) represents a system of $(N_c+1) \times N$ linearized algebraic equations with sparse matrices, which are solved by a linear equation matrix solver.

Treatment of Initial and Boundary Conditions

The initial conditions are required to start a transient simulation; that is, a complete set of primary variables need to be specified for every grid block or node. Using a restart option is a common procedure for speci-

ifying a capillary-gravity equilibrium, NAPL-free initial condition. In this procedure, a complete set of initial conditions or primary unknowns is generated in a previous simulation with proper boundary conditions described. For modeling remediation of a NAPL contamination site, however, the initial condition may correspond to the final stage of a site-characterization study, in which the contamination sources are identified under the ambient flow condition.

Due to more physical and chemical constraints, boundary conditions for a multiphase flow and transport problem are generally much more difficult, to handle than, for a single-phase situation. When using a block-centered grid, first-type, or Dirichlet, boundary conditions can be effectively treated using either an “inactive cell” or “large-volume” method, as normally used in the TOUGH2 code (Pruess 1991). In this method, a constant pressure/saturation/concentration/temperature node is specified as an inactive cell or with a large volume, while keeping all the other geometric properties of the mesh unchanged. However, caution should be taken in (1) identifying phase conditions when specifying the “initial condition” for the inactive or large-volume boundary node, and (2) distinguishing upstream/injection from downstream/production nodes. For a downstream node, diffusion and dispersion coefficients can be set to zero to turn off unphysical diffusive fluxes, which may occur as a result of large concentration gradients. Once specified, primary variables will be fixed at the boundary nodes.

With finite-element or edge-centered (that is, with nodal centers on mesh boundaries) finite-difference grids, first-type boundary conditions and Neuman boundary conditions with any type of grids can be treated using a generalized, sink/source term approach (Thomas 1982, Wu *et al.* 1996b). Certain flux-type boundary conditions are easy to handle for a situation where flux distribution along the boundary is known, such as in dealing with surface infiltration. However, a description of more general types of flux- or mixed-boundaries, such as seepage faces and multilayered wells, is part of the solution. The general procedures of handling such boundary conditions are discussed in Wu *et al.* (1996b) and Wu (1999a).

Parameter Weighting Scheme

How to select a proper spatial weighting scheme for averaging flow and transport properties in a highly heterogeneous formation is much debated among the modelers. Traditionally in petroleum literature,

upstream weighting is used for relative permeabilities, and harmonic weighting is used for absolute permeabilities in handling multiphase flow in heterogeneous porous media (Aziz and Settari 1979). The rationale for this is that under single-phase, steady-state flow conditions, flow terms calculated using harmonically weighted permeabilities are physically correct and satisfy the mass balance requirement at an interface of two adjacent grid blocks. This technique works reasonably well for cases of multiphase flow, as long as the contrasts in flow properties of adjacent formation layers are not very large (for example, in single-porosity oil reservoirs). For simulating multiphase flow in fractured porous media, Tsang and Pruess (1990) found that this traditional weighting scheme led to artificial flow resistance and may lead to physically incorrect solutions for highly heterogeneous composite formations with alternate layers of nonwelded and welded tuffs, such as at Yucca Mountain. Indeed, in general heterogeneous media, the factorization of effective phase permeability into absolute and relative permeabilities is ambiguous; no consistent manner exists in which different weighting could be justified for absolute and relative permeabilities. Accordingly, Tsang and Pruess proposed using a full upstream weighting scheme for both relative and absolute permeabilities in order to obtain physically plausible solutions.

Selection of a consistent weighting scheme becomes more critical when dealing with multiphase flow, multicomponent transport, and heat transfer in a porous or fractured medium. This is because flow, transport, and heat transfer processes differ greatly in characteristics in time and spatial scales of a typical simulation and are fully coupled. In recent years, more attention has been paid to weighting methods of flow and transport properties in the community of groundwater and unsaturated zone modeling. It has been found that upstream-weighted relative permeability will result not only in physically consistent solutions, but also mathematically unconditional or stable (Forsyth *et al.* 1995) for modeling unsaturated flow using a finite volume discretization. Other weighting schemes, such as central weightings, may converge to an incorrect, unphysical solution (Forsyth and Kropinski 1997).

In addition to the weighting scheme for evaluating multiphase flow, we also need to select proper weighting techniques for calculating dispersive and advective transport, as well as for heat flow. Recent work has shown that using total variation diminishing (TVD) or flux limiter schemes can be very promising and efficient in reducing numerical dis-

person effects (Unger *et al.* 1996, Oldenburg and Pruess 1997, Forsyth *et al.* 1998) in predicting a dissolved solute plume in a multiphase system. For dispersive flux, certain averaging of diffusion-dispersion coefficients is also needed to resolve diffusive flux across grid blocks with step-change phase saturations. For example, a harmonic-weighted phase saturation is proposed as a weighting function for diffusion coefficients (Forsyth 1994).

In general, however, there are no universally applicable weighting schemes that can be used for all problems of flow and transport encountered in the vadose zone, and selection of proper weighting schemes is problem-dependent. Our recommendations are as follows:

- (a) Upstream weighting should always be used for evaluating relative permeability for flow between fracture or matrix blocks and between fracture and matrix.
- (b) Harmonic or upstream weighting should be used for evaluating absolute permeabilities for global fracture or matrix flow and for evaluating matrix-absolute permeability for fracture-to-matrix flow.
- (c) TVD or flux limiter schemes should be used for evaluating tracer concentrations for advective transport fluxes.
- (d) Phase saturation-based weighting functions should be used to determine diffusion coefficients.
- (e) Upstream weighted enthalpies should be used for advective heat flow.
- (f) Central weighted schemes should be used for thermal conductivities.

Fractured Media

Flow and transport through fractured vadose zones have received considerable attention in recent years because of increased environmental concern. A key issue for simulating fluid and heat flow and chemical transport in fractured porous rocks is how to handle fracture and matrix interactions under multiphase, multicomponent, and nonisothermal conditions. The available methods for treatment of fracture and porous

matrix interactions using a numerical approach include: (1) an explicit, discrete-fracture and matrix representation; (2) the dual-continua method (Barenblatt *et al.* 1960, Warren and Root 1963, Kazemi 1969), including double- and multiporosity (Wu and Pruess 1988), dual-permeability, or the more general “multiple interacting continua” (MINC) method (Pruess and Narasimhan 1985); and (3) the generalized effective continuum method (ECM) (Wu 1999b). The different idealizations of the dual-continuum models are shown in Figure 5-15.

The discrete-fracture-modeling approach is, in general, computationally intensive and requires detailed knowledge of fracture and matrix geometric properties and their spatial distributions, which are rarely known at a given site. For these reasons, it has found limited field applications in modeling multiphase, nonisothermal flow and transport in fractured rocks. The dual-continua method is conceptually appealing and computationally much less demanding than the discrete-fracture-modeling approach, and, therefore, has become the most common approach. However, it also requires detailed fracture and matrix geometric properties and their spatial distributions. The ECM method has been widely used in simulating steady-state multiphase flow and heat transfer (Wu *et al.* 1999b) because of its simplicity in terms of data requirements and computational efficiency. However, the ECM approach cannot handle rapid transient flow and transport processes through fractured media (Doughty 1999).

The dual-continua methodology for handling flow, transport, and heat transfer through fractured rocks treats fracture, matrix flow, and matrix interactions using a multi-continua numerical approach. The classical double-porosity concept of the dual-continua methodology for modeling flow in fractured porous media was developed by Warren and Root (1963). In this method, a flow domain is composed of matrix blocks of low permeability, which are embedded in a network of interconnected fractures. Global flow in the reservoir occurs only through the fracture system, which is described as an effective porous continuum. The matrix behaves as spatially distributed sinks or sources to the fracture system without accounting for global matrix-matrix flow. The double-porosity model accounts for fracture-matrix interflow, based on a quasi-steady-state assumption.

The more rigorous method of MINC describes gradients of pressures, temperatures, and concentrations between fractures and matrix by

appropriate subgridding of the matrix blocks (Pruess 1991). This approach provides a better approximation for transient fracture-matrix interactions than using the quasi-steady-state flow assumption of the Warren and Root model. The MINC method is based on the assumption that changes in fluid pressures and concentrations will propagate rapidly through the fracture system, while only slowly invading the tight matrix blocks. Therefore, changes in conditions at a location inside the matrix will be controlled locally by the distance from the location to the fractures. Fluid flow and transport from the fractures into the matrix blocks can then be modeled by means of one- or multidimensional strings of nested grid blocks. In general, matrix-matrix connections can also be described by the MINC methodology.

As a special case of the MINC concept, the dual permeability model considers global flow occurring not only between fractures, but also between matrix grid blocks. In this approach, fracture and matrix are each represented by one grid block, each connected to the other. Because of the one-block representation of fractures or matrix, the interflow between fractures and matrix has to be handled using some type quasi-steady-state flow assumption, such as that used with the Warren and Root model.

The mathematical and numerical formulations discussed above are applicable to both single-continuum and multi-continua media, as long as the physical processes concerned can be described in a continuum sense within either continuum. When handling flow and transport through a fractured rock using the numerical formation of this section, a large portion of the work consists of generating a mesh that represents both the fracture system and the matrix system. Several fracture and matrix subgridding schemes exist for designing different meshes for different fracture-matrix conceptual models (Pruess 1983).

The Case Study "Modeling Fast Flow Paths in Unsaturated Fractured Rock," by Clifford K. Ho, provides an example for modeling water flow through unsaturated fractured rocks. The case study compares two different modeling approaches, dual-permeability and ECM, used to simulate transient flow and rapid transport through fractured tuffs. *See page 785.*



Once a proper grid of a fracture-matrix system is generated, fracture and matrix blocks are identified to represent fracture or matrix domains, separately. Formally, they are treated identically for the solution in the model. However, physically consistent fracture and matrix properties, parameter weighting schemes, and modeling conditions must be appropriately specified for fracture and matrix systems, respectively.

Simplified Numerical Models

Various simplified numerical models for flow and transport in the vadose zone can be readily derived from equation (5.48), a generalized, discrete governing equation for component mass and energy balance. Examples given here for such simplifications include the numerical formulations for Richards' equation and one active phase-gas flow in unsaturated zones, an immiscible three-phase fluid flow, and decoupled solute transport.

Discrete Models for One Active Phase and Multiphase Flow

The isothermal, flow-governing equations for one active aqueous or gaseous phase, as well as for multiphase fluid flow in the vadose zone, were discussed above. The numerical discrete equations for these special types of flow in unsaturated zones can be derived directly from equation (5.48) as

$$\left\{ (\phi S_{\beta} \rho_{\beta})_i^{n+1} - (\phi S_{\beta} \rho_{\beta})_i^n \right\} \frac{V_i}{\Delta t} = \sum_{j \in \eta_i} \left(\frac{\rho_{\beta} k_{r\beta}}{\mu_{\beta}} \right)_{ij+1/2}^{n+1} \gamma_{ij} [\psi_{\beta j}^{n+1} - \psi_{\beta i}^{n+1}] + Q_i^{\beta, n+1} \quad (5.61)$$

for fluid β ($\beta = g, w$ and/or n)

for solving an active water or gas flow, or general three-phase flow problem. If $\beta = w$ only, equation (5.61) becomes the discrete form of Richards' equation for one active water-phase flow. For $\beta = g$ only, it becomes the gas-flow-only equation. For the case of three-phase, gas, water and NAPL flow, ($\beta = g, w$, and n), equation (5.61) represents three discrete mass-balance equations for the three fluids for each node or grid block i , which should be solved simultaneously.

Discrete Models for Decoupled Solute Transport

A decoupled formulation of solute transport from single-phase or multiphase flow is a simplified, but useful, conceptual model for analyzing flow and transport processes in the vadose zone. This model is commonly used for simulating transport of dilute solutes when fluid fields are at steady-state conditions, and they can also be decoupled from a transient flow simulation using a sequential numerical approach. The decoupled transport governing equations under one active aqueous or gaseous phase and multiphase fluid flow were presented earlier. The numerical equations for decoupled transport of multicomponents in unsaturated zones can also be derived directly from (5.48) as

$$\{A_i^{k,n+1}(1 + \lambda_k \Delta t) - A_i^{k,n}\} \frac{V_i}{\Delta t} = \sum_{j \in \eta_i} (F_{A,ij}^k + F_{D,ij}^k) + Q_i^{k,n+1} \quad (5.62)$$

with $(k = 1, 2, 3, \dots, N_c)$

Equation (5.62) can be used to solve transport solutions of one or multi-species in one active aqueous ($\beta = w$) or gaseous phase flow ($\beta = g$) conditions, or general three-phase flow ($\beta = g, w$, and n) conditions. The flow properties, such as fluid velocities saturations and densities and mass-flow rates, are treated as constants for transport calculations, which may be predetermined in a previous flow simulation.

Many other types of multiphase flow and transport processes in the vadose zone can be directly derived using Equation (5.48). A model for non-isothermal multiphase multi-species reactive chemicals transport is discussed by Xu *et al.* (1997). A modeling approach for tracers or radionuclides in a multiphase, non-isothermal system of porous and fractured media is presented by Wu and Pruess (1998). A numerical model for transport of an arbitrary number of solutes and/or colloids in the vadose zone is provided by Moridis *et al.* (1999). For more general cases of multiphase flow and multicomponent transport in a non-isothermal medium, several numerical formulations are developed (Falta *et al.* 1992a and 1992b; Adenekan *et al.* 1993; Forsyth 1994; Panday *et al.* 1995). All of the numerical formulations of these models can be shown to be in the form of equation (5.48).

LIMITATIONS AND RESEARCH DIRECTIONS

The continual development and enhancement of the methodology in mathematical modeling of flow and transport processes in porous media over the past half century have provided geoscientists, engineers, and hydrologists with powerful modeling tools for their work. During the same time, our understanding of porous medium phenomena and our ability to apply this knowledge to practical problems have been significantly improved by using the quantitative modeling approach. Numerical modeling approaches have matured and become standard practices in subsurface contamination investigations and remediation scheme evaluations. Numerical studies or experiments are routinely conducted to investigate physical phenomena and to evaluate alternative cleanup proposals. In many cases, the critical insights obtained would not be possible without a numerical tool.

Despite this progress, however, there are still considerable uncertainties in our understanding of the inherently heterogeneous vadose zone system. Serious limitations also exist in our ability to make accurate assessments and long-term model predictions for a given contamination site. This is especially true with respect to several critical areas, which are discussed below.

Description of Constitutive Relations

Comprehensive investigations and subsequent progress have been very limited in a number of areas, including fully coupled effects of multiple physical processes in multiphase flow and transport, chemical reactions, and heat transfer in the vadose zone. In particular, there is a lack of constitutive relations to describe the coupling and interrelations between fluid flow, chemical transport, and heat transfer processes. The available data and correlations become extremely scarce with regard to the key multiphase flow and transport properties, including three-phase flow characteristics (such as relative permeability and capillary pressure functions), phase partitioning and adsorption coefficients, and kinetic relations. For example, thermal effects on these properties and relations are often ignored, even in thermal modeling studies, because no experimental data is available for a given site. This lack of both existing data and descriptive models for constitutive relations is now posing a serious

problem for further development and successful application of simulation technologies.

Handling of Heterogeneity

Heterogeneity is intrinsic to vadose zone soils, both porous and fractured media. Effects of heterogeneity in different scales in a porous or fractured medium on flow and transport processes currently are poorly understood in a multiphase, isothermal system. Until better understanding and more efficient modeling approaches to handling the heterogeneity problem are developed, reliable predictions using mathematical models will be questionable for real-world applications. In addition, there are many related issues, such as spatial and temporal scales of parameters, anisotropy, and hysteresis, which need to be better understood. It is apparent that a substantial amount of work remains to be done before the field scale physical processes of flow and transport in the vadose zone can be modeled with a high degree of accuracy and reliability.

Qualifications of Uncertainties of Study Systems

To begin a simulation study using a numerical simulator for a given site, we need to know initial and boundary conditions. In many cases, however, these basic modeling conditions are poorly defined or unknown. Even with a substantial amount of work completed and investment spent during the site-characterization phase, there are still usually significant uncertainties regarding the current status of a contamination site, including contaminant sources, moisture and geochemical data, and possible past and future conditions which may impact the site. These are the crucial data for any successful modeling investigation. Therefore, we need to use more efficient scientific means for better quantifying the uncertainties associated with the current and past status of a system under a site-characterization study.

Computational Scheme

Current numerical modeling capabilities used in vadose zone studies and in reservoir simulation, in general, are quite powerful, but there are some serious shortcomings and limitations. These relate primarily to

solving increasingly complicated problems arising from (1) coupled processes with strong and usually non-linear interactions among fluid flow, heat transfer, mass transport, chemical and biological activity, and rock mechanical deformation; and (2) processes encountered in the vadose zone that involve multiple spatial and/or time scales.

New modeling capabilities and more efficient computational algorithms are needed in several key areas to develop (1) robust general-purpose approaches that consider most important processes and their coupling, and (2) improved algorithms and software that take advantage of state-of-the-art computer technology and new hardware architectures, such as advanced parallel processing capabilities.

In summary, directed and focused research efforts are needed to solve these problems so that the national interests in subsurface resources and environmental concerns can be addressed.

DATA NEEDS AND PRIORITIZATION

INTRODUCTION

A model is an approximation of a natural system, largely represented by a variety of data collected from a site. For a given vadose zone flow and transport problem, data are always limited for many practical reasons. How to appropriately make use of data in building a model is critically important for making the model represent a natural system as accurately as possible on the scale of interest.

The main objective of this section is to briefly review data that are needed for vadose zone modeling studies and discuss the use of data in developing models. We also discuss how a model can be used to guide data collection and present our perspectives on upscaling issues related to vadose zone flow and transport modeling.

DIFFERENT TYPES OF DATA

Data determined on both laboratory and field scales can be classified in different ways. In this chapter, we classify data based on their use in developing models. Understanding that their roles can be case-dependent, we only provide a general picture about how different types of data can be used in modeling vadose zone flow and transport processes. A summary of the data to be discussed in this section is given in Table 5-4.

TABLE 5-4 Summary of Different Types of Data		
Use	Data	Comments
Determination of hydrogeologic structure	1. Hydraulic properties (permeability and porosity) 2. Geologic formation (well logs, surface mapping, and geophysical measurements)	1. The primary geologic formation data are well logs and surface mapping. Geophysical measurements provide additional information on distribution of geologic formations. 2. Within a hydrogeologic unit, hydraulic properties should be similar.
Characterization of site contamination	1. Loading history of source 2. Contaminant data from soil core, soil pore water, and gas sampling 3. ER data, gamma spectral data, GPR data, and other indirect measurements 4. Partitioning tracer test data	1. Source history data generally have large degrees of uncertainty. 2. Primary data for site contamination are from direct sampling. Indirect measurements may be used as support data.
Estimation of flow parameters and thermal property	1. Absolute permeability 2. Constitutive relations 3. Porosity 4. Fracture spacing 5. Heat conductivity and capacity	In some cases, absolute permeability and constitutive relations can be roughly estimated from other properties, such as porosity and grain size distributions.
Estimation of transport parameters	1. Diffusion coefficient 2. Dispersivity 3. K_d, partition coefficients, and kinetic reaction parameters	1. A good understanding of published dispersivity values is needed before using them for modeling. 2. Several other commonly used parameters for vadose zone transport modeling are given in Table 5-5.

continued

TABLE 5-4 Summary of Different Types of Data (*continued*)

Use	Data	Comments
Determination of infiltration rates	1. Precipitation and ET 2. Environmental tracer 3. Temperature	Infiltration rates are generally determined based on the water balance method using precipitation, ET and other relevant data. In some cases, temperature and environmental tracer can also be used to determine infiltration rates.
Model calibration	1. Water saturation/potential 2. Pneumatic data 3. Perched water data 4. Temperature data 5. Geochemical data 6. Contamination data	Detailed discussions on the use of these data for model calibration can be found in the section "Model Calibration."

Data for Determining Hydrogeologic Structures

It is well known that subsurface heterogeneity is a key feature governing flow and transport processes in the subsurface. Heterogeneity is particularly important for the vadose zone because the combination of heterogeneity with non-linearity and instability of unsaturated flow can result in complex flow and transport patterns, including fingering and preferential flow. Carefully determining the hydrogeologic structure for a site is thus an important task for modeling vadose zone flow and transport processes, as described in the following section of this chapter, "Development of Site-specific Models."

Ideally, the structural distribution of hydrogeologic properties for a site is directly determined from *in situ* hydraulic properties, such as the spatial permeability distribution of subsurface materials. However, in most cases, such data is very limited and is insufficient for providing a reliable estimation of a vadose zone site's hydrogeologic structure. Because the hydraulic property distribution is generally correlated to the distribution of geologic formations (geologic framework) a combination

of hydraulic property data (including permeability and porosity) and geologic information is frequently used to characterize subsurface heterogeneity (see, for example, Bandurraga and Bodvarsson 1999, Anderson 1989, Sun *et al.* 1995).

Geologic formation data are commonly obtained from well logs and site-specific surface geologic mapping (Kramer and Keller 1994). Some geophysical data, such as cross-borehole seismic topography and ground-penetrating radar data, can be used to generate additional geologic information of a site. Interpolation techniques, which are either deterministic or based on geostatistics, need to be used to combine these geologic data into a multidimensional geologic framework. The resulting product is a distribution of geologic formations. Within each geologic formation, hydraulic property distributions are often assumed to be uniform (see, for example, Bandurraga and Bodvarsson 1999; McKenna and Poeter 1995). However, it is important to note that a distribution of geologic formations only corresponds to relatively large-scale heterogeneities. Even within a geologic formation, significant heterogeneities can still exist. A fractal-based approach seems to be more accurate for dealing with this multiscale heterogeneity (Molz and Boman, 1993). More discussions on geological complexity for a variety of vadose-zone problems are given in the section “Physical Processes and Setting for Contaminant Flow and Transport in the Vadose Zone,” above.

Within a geologic formation, spatial variations of the hydraulic properties are smaller than those between different geologic formations. Available hydraulic property data are generally few for a given site, but they are important for developing the hydrogeologic structure for modeling purposes because these data are directly related to flow and transport processes. The geologic framework developed with geologic information needs to be modified based on available hydraulic property data, such as permeability and porosity, to better represent the hydrogeologic structure of the site. This modification is important because the correlation between a geologic formation distribution and the corresponding hydraulic property distribution is not perfect. In addition to geologic formations, some other features within a site, such as clastic dikes, unsealed monitor wells, subsurface tunnels, and buried pipe lines also need to be considered in developing the hydrogeologic structure of the site. These features can be important for vadose zone flow and transport processes.

Finally, it should be noted that the development of a hydrogeologic structure for a given site is generally an iterative procedure. The structure needs to be updated during modeling studies when more data become available or when the conceptual model is refined. Further discussions on this topic can be found later in this chapter in the sections “Site-specific Models” and “Model Calibration.”

Data for Characterizing Site Contamination

Models are generally used to predict contaminant transport and evaluate the usefulness of remediation schemes for a site. In this case, site contamination information must be obtained or estimated as input into models.

The loading history of the contamination source is important for estimating the potential extent of site contamination. The loading history describes how the concentration of a contaminant or its rate of production varies as a function of time at the source (Domenico and Schwartz 1990). Even relatively rough estimates of the history are valuable for modeling studies. Unfortunately, a large degree of uncertainty generally exists in loading-history data. Consequently, detection of the extent of site contamination is generally needed. This detection activity generates data for describing contaminant distribution in the vadose zone.

Depending on the physical and chemical properties of contaminants involved, different techniques can be used for detecting vadose zone contamination (Domenico and Schwartz 1990; Mercer and Cohen 1990; Durant and Myers 1995). Generally speaking, the contaminant-related data is obtained from direct samplings, including soil-core, soil pore water and gas samplings, and indirect measurements from geophysical methods. Partitioning tracer tests can also be used to detect residual NAPL in the vadose zone (see, for example, Whitley *et al.* 1999). The direct sampling data are considered to be more reliable and should be used as primary data to characterize the site contamination, while the indirect measurements should be used as support data. These indirect measurements include electrical resistivity (ER) data, gamma spectral analysis data (for radioactive contaminants), and ground-penetrating radar (GPR) data. For example, ER and borehole spectral gamma logging data have been used for characterizing the extent of vadose zone contamination at the DOE Hanford site (GJPO 1996). The

Environmental Protection Agency has found that GPR is capable of detecting hydrocarbon contamination in both the vadose zone and saturated zone under some conditions (Durant and Myers 1995).

Once the contamination information is available from measurements, an interpolation scheme (which can be either deterministic or stochastic) is needed to generate a spatial distribution of contaminants. This spatial distribution will be used as input for modeling studies to predict the contaminant transport. However, it is of interest to note that if the source loading history is well defined for some contamination problems, the contamination data can be used to calibrate the model. In this case, the corresponding model is adjusted such that the simulated contaminant concentrations are consistent with measured ones for the given source loading history. More detailed discussions on model calibration will be presented later in this chapter, in the section “Model Calibration.”

Flow Parameter and Thermal Property Data

As discussed previously in the section on mathematical modeling, flow and transport processes are represented by a group of differential equations with a number of flow and transport parameters. To solve these equations, we need parameter values as inputs into numerical models. However, modelers must understand how these parameter values are measured or estimated before using them for modeling studies. This is particularly true for a vadose zone characterized by complex flow and transport processes and heterogeneity.

Special attention needs to be given to two issues when using the flow-parameter data. The first is the scale issue. Because of the complexity of vadose zone flow processes, a large portion of flow-parameter values, such as those characterizing the retention curve and relative permeability (constitutive relations), may be obtained from laboratory measurements on core samples. Since flow parameters are generally scale-dependent, upscaling is needed in most cases to make use of these measurements for field-scale modeling studies. (A further discussion of upscaling issues is given later on in this section.) The second issue concerns assumptions made in deriving flow parameter values in both field and laboratory measurements. In some cases, flow-parameter values are not directly “measured” data, but data derived from relevant observations based on a number of assumptions. For example, a common field

method to determine saturated and unsaturated hydraulic conductivities is to use tension infiltrometers (Hussen and Warrick 1995). These parameter data are estimated from flow-rate measurements within the infiltrometer using a number of analytical solutions that are valid for homogenous soils. When using a numerical model, use of parameter data outside of the valid range of relevant assumptions is inappropriate and can make the modeling results meaningless.

Flow parameters and thermal properties of importance for modeling studies include:

- Absolute permeability
- Constitutive relations
- Porosity
- Fracture spacing (for fractured rocks)
- Thermal conductivity and heat capacity

Absolute permeability is probably the most important flow parameter for control of fluid flow in both saturated and vadose zones. A number of field and laboratory methods are available for determining saturated hydraulic conductivity in the vadose zone. For unsaturated fractured rocks, air-permeability data are often collected to estimate fracture permeabilities (Wang *et al.* 1999, LeCain 1998). These data are the primary data to determine permeability values for different geologic formations in modeling studies. When these data are not available, alternative approaches exist to estimate permeability based on porosity and representative grain sizes of porous media. For example, several approaches of this kind are listed in Domenico and Schwartz (1990). However, these approaches only provide rough order of magnitude estimates of permeability. In modeling studies, they should be used with caution.

Capillary pressure and relative permeability, as functions of liquid saturation (constitutive relations), are important inputs into models for vadose-zone flow and transport. They are generally represented using empirical relations with a number of parameters (see, for example, van Genuchten 1980 and Brooks and Corey 1964). As discussed in Chapter 3, measuring these relations is very time-consuming. While considerable progress has been made in developing field methods, laboratory-scale measurements are still heavily relied on for determining these

relations, especially for a thick vadose zone. The presence of nonaqueous-phase liquid in the vadose zone leads to a three-phase fluid system, which makes the constitutive relations more complicated. While few techniques exist to measure these relations in the laboratory, the relations for three-phase fluid systems can be estimated from those for two-phase fluid (such as water-air) systems (see, for example, Lenhard and Parker 1987). For soils, an alternative scheme, the pedotransfer function, is available for making rough estimates of constitutive relations based on soil porosity, texture, permeability, and other commonly measured properties (see, for example, Vereecken *et al.* 1992).

For fractured rocks, in general, the constitutive relations cannot be measured directly. A systematic method to estimate van Genuchten (1980) relations for the fracture continuum of unsaturated fractured rocks has been developed and documented by scientists working on the Yucca Mountain Project using fracture air permeability and spacing data (see, for example, Sonnenthal *et al.* 1997). Fracture spacing is calculated using fracture mapping from a number of sources. Fracture spacing is also important for modeling flow and transport between fractures and matrix. In unsaturated fractured rocks, gravity-driven fingering and preferential flow is a common flow mechanism in fractures. As indicated in Liu *et al.* (1998), an additional constitutive relation used to characterize the liquid filled interface area between fractures and matrix is needed for unsaturated fractured rocks to account for fingering when dual-continua approaches are used. In this case, capillarity and relative permeability relations also need to be modified to include effects of fingering and preferential flow. An additional parameter to characterize the new constitutive relation can be inferred from the related measurements, such as matrix saturation and water potential data (Liu *et al.* 1998).

Compared with permeability, porosity generally exhibits a relatively small degree of spatial variation and is easily measured from core samples of porous media. For fractured rocks in the vadose zone, fracture porosity can be estimated from gas-tracer tests (see, for example, LeCain 1998).

In addition to liquid flow and contaminant transport, heat transfer is another important process in the vadose zone, as discussed previously in the sections “Physical Processes and Setting for Contaminant Flow and Transport in the Vadose Zone” and “Mathematical Models and Numerical Formulations.” The main parameters relevant to heat transfer are

thermal conductivity and heat capacity. Generally, thermal conductivity and heat capacity are functions of fluid saturations, and these parameters tend to vary over a much smaller range compared to the hydraulic parameters.

Transport Parameter Data

Contaminant transport in the vadose zone involves both physical processes, such as advection, diffusion and dispersion, interphase mass transfer, and geochemical and biological reactions within and between different phases in the vadose zone. The reactions of interest for a given site are determined by properties of geological materials and contaminants, as well as by the transport of limiting reagents. Rather than discussing data to characterize detailed reactions, we will focus on those data that describe transport associated with relatively simple and commonly used reaction models.

Transport parameters of importance for modeling include, at a minimum:

- Diffusion coefficient
- Dispersivity
- Distribution coefficient K_D , partition coefficients, and kinetic reaction parameters.

Advection is generally more important than diffusion for subsurface contaminant transport. However, aqueous diffusion of dissolved species is important in specific situations in the vadose zone. For example, Bodvarsson *et al.* (1999b) indicated that mass transport as a result of diffusion between fracture and matrix might be a dominant mechanism for transport in unsaturated fractured rocks. Therefore, accurate determination of effective liquid-diffusion coefficients becomes important for modeling some vadose zone contaminant-transport problems.

The case study “Aqueous Diffusion in the Vadose Zone,” by James L. Conca and Judith Wright, discusses additional situations where aqueous diffusion is the dominant transport mechanism. See page 796.



The effective diffusion coefficient used in modeling is determined from the molecular diffusion coefficient with modification to account for effects of the solid phase and the unsaturated condition. The ratio of the effective diffusion coefficient to the latter is a function of porosity and saturation. A number of empirical relations exist for estimating this ratio (Millington 1959; Millington and Quirk 1961). The case study “Aqueous Diffusion in the Vadose Zone,” by James L. Conca and Judith Wright, also gives a plot of measured effective diffusion coefficients as a function of water content for a number of geologic materials. If site-specific data are not available, empirical relations and/or plots can be used to estimate the effective diffusion coefficient. Similar empirical relations may be used to estimate diffusion coefficients for modeling transport of gas-phase contaminants (Jin and Jury 1996). Unlike transport in the liquid phase, the gas-phase diffusion dominates advection when the pressure difference is small (Falta *et al.* 1989). And, because the diffusion coefficient in air is much greater than in water, the gas-phase diffusion also dominates dispersion.

Dispersivity values are needed for modeling vadose zone transport processes. These values can be relatively easily estimated from the laboratory column experiments. However, it is well known that field-scale dispersivity is significantly larger than laboratory-scale values, because of subsurface heterogeneity (see, for example, Gelhar 1993; Dagan 1984; Liu and Molz 1997). In many cases, field-scale tracer test data may not be available to estimate site-specific dispersivity values. Experimental studies to determine field-scale dispersivity values based on well-controlled tracer tests are limited for the vadose zone. Modelers may need to use their own judgment, using published dispersivity values estimated from other field-scale tests. Some of these published values are summarized in Gelhar (1993).

Dispersion for field-scale problems is discussed in other sections of this chapter. Here we provide some principles for determining dispersivity values for vadose zone transport problems:

- First, dispersivity is dependent on resolution of the heterogeneous distribution of hydraulic properties in the model. The higher the resolution, the lower the dispersivity (Güven *et al.* 1986, Liu and Molz 1997). If the resolution is high enough, laboratory-scale dispersivity values could be used for modeling studies. Most

published values (Gelhar 1993) were obtained by treating geologic materials as macroscopically homogeneous media. As a consequence, these values may be used as upper limits of dispersivity for modeling studies when subsurface heterogeneity is explicitly represented.

- Second, large-scale dispersion behavior in the vadose zone is different from that in the saturated zone (Liu and Dane 1996). The main transport direction is vertical in the vadose zone and horizontal in the saturated zone, while geological formations are roughly considered to be horizontal layers. Therefore, it is not appropriate to determine dispersivity values based on data from saturated zone tests.
- Third, it is important for a modeler to carefully evaluate the role of dispersion in a given problem before spending much time on determining reasonable dispersivity values. In some cases, accuracy of a dispersivity value may not be important for the overall behavior of contaminant transport. For example, a recent study by Bodvarsson *et al.* (1999b) indicates that for unsaturated fractured rocks, overall contaminant transport behavior is sensitive to parameters that control mass transfer between fractures and matrix, but not to dispersivity values for the fracture continuum. This is because large-scale transport behavior is mainly controlled by the largest heterogeneity, corresponding to differences of flow and transport parameters between fracture and matrix continua. In this case, effects of fracture heterogeneity become secondary.

In modeling contaminant transport, we need to relate the mass fraction of a given species within all phases, as discussed in the previous section of this chapter. (Generally, it is assumed that there is local equilibrium and that the mass fraction of a species in one phase is proportional to that of the same species in other phases.) The proportionality is called the partition coefficient. Some values of the distribution coefficient K_D , which may be considered as a partition coefficient for sorption into the solid phase, are given by Domenico and Schwartz (1990) for selected radionuclides for a variety of rock types. Since K_D has an important effect on contaminant transport, site-specific values for the given geochemical environment should be measured. Other partition coefficients for different contaminants can be directly obtained from relevant databases (see,

for example, Sims *et al.* 1991). Note that some of these partition coefficients can also be determined from Henry’s law constants and solubility relations (Mercer and Cohen 1990). In cases where local equilibrium is not valid, kinetic interphase mass transfer models need to be used. Parameter values describing kinetic reactions can be measured or obtained from literature. However, these kinetic processes are scale-grid-block-size dependent, and there is very little published research on the upscaling of this phenomenon to the field scale.

In addition to the transport parameters discussed above, Kramer and Cullen (1995) provide several commonly used parameters for vadose transport models. These parameters are listed in Table 5-5, which includes measurement methodology or reference for obtaining parameter values (Kramer and Cullen 1995).

Data for Determining Infiltration Rates

The bottom boundary condition generally corresponds to the water table for vadose zone modeling studies. The top boundary condition is generally determined by infiltration from the ground surface. Since contaminant transport from the vadose zone to the saturated zone is largely controlled by water flow originating from infiltration at the ground surface, infiltration data are often important inputs into a vadose zone model. Infiltration rates are commonly estimated on the basis of the

TABLE 5-5	Some additional transport parameters for vadose zone modeling (Adapted from Kramer and Cullen, 1995)
Parameters	Measurement Methodology or Reference
Specific surface area	MOSA, 1986 Chap. 16, pp. 413–423
Cation exchange capacity	USEPA SW-846-9081
Solubilities	Sims <i>et al.</i> 1991
Biodegradation rates	Sims <i>et al.</i> 1991
Radioactive decay rates	Sims <i>et al.</i> 1991
Organic matter content	ASTM1995

water balance at the ground surface. Important data needed for the estimation include precipitation, evapotranspiration (ET), overland flow, topography, and other relevant climatological data.

Alternative approaches to estimating infiltration into the deep vadose zone are also available (Sonnenthal and Bodvarsson 1998; Gee and Hillel 1988; Phillips 1994). One approach is called the chloride mass balance method (CMB). Environmental chloride (resulting from inputs from precipitation and dry deposition) has been widely used as an indicator of water movement in arid regions. For example, a review of the use of environmental tracers for estimating water movement in desert soils was given in Phillips (1994). Under the assumption of steady state, the ratio of net infiltration to precipitation must be equivalent to the ratio of precipitation chloride concentration to soil-water chloride concentration near the ground surface.

The case study “Measurement of Unsaturated-Zone Water Fluxes Adjacent to A Radioactive-Waste-Management Unit,” by S.W. Tyler *et al.*, discusses the estimation of the measurement of vadose zone water flux using environmental chloride as a tracer to estimate soil-water ages from the soil water chloride concentration profile along a deep borehole. See page 797.



Temperature data from deep boreholes can also be used to estimate and constrain infiltration rates. Assuming that heat transfer in the vadose zone is one-dimensional and at steady state in the deep zone, vertical temperature distributions along boreholes can be related to infiltration rates. A more detailed discussion of this approach can be found in Sonnenthal and Bodvarsson (1998).

Data for Model Calibration

Model calibration, the combination of forward and inverse modeling studies, is an important step for model-building for several reasons. First, important flow and transport parameters may not be available or measurable at a given site and need to be inferred from other available or easily measured data. Even when the relevant parameter data are available, large degrees of uncertainty generally exist in estimated parameter values because of the scarcity of data and the limitations of

estimation procedures. All these necessitate model calibration for determining reliable estimates of model parameters for a given conceptual model. Second, vadose zone flow and transport processes are generally complicated. Building a good conceptual model for a given flow and transport problem is not always straightforward. Model calibration is important for evaluating and refining conceptual models based on different kinds of data representing different physical and chemical processes at a given site. A good conceptual model, combined with calibrated model parameters, should be consistent with all the data related to flow and transport at the site. In summary, model calibration will enable the model to better represent site conditions and, therefore, increase the reliability of model predictions. Further discussions on model calibration can be found in the sections “Development of Site-specific Models” and “Model Calibration.”

Data that can be used for model calibration include the following:

- Water saturation/potential data
- Pneumatic data
- Perched-water data
- Temperature data
- Geochemical data
- Contamination data from site monitoring

Water saturation and potential data are primary data for model calibration because *in situ* measurements of water saturation and potential are closely related to flow processes and can be relatively easily obtained. These data are particularly useful for determining permeability and constitutive relations during model calibration. Pneumatic data are gas pressure signals, as functions of time, resulting from air-pressure fluctuations at the ground surface. Pneumatic data should mainly be used to calibrate permeabilities. Perched water is a result of the existence of local low-permeability zones in the vadose zone, and thus perched-water data, such as location, volume and age of perched water, are useful for identifying the major low-permeability zones and lateral flow and transport paths. As discussed above, temperature data can be used to constrain infiltration rates. They can also be used to calibrate

thermal properties of geological materials, which are functions of water saturation. Geochemical and isotopic (environmental tracer) data generally correspond to signatures of transport paths and times. These data are useful for confirming major flow structures determined from other data and for calibrating transport parameters. Geochemical data should also be considered in conceptual model development, because it can provide a long-term record of transport. Some useful geochemical systems are listed in Table 5-6. In some cases, if a monitoring network already exists at the site of interest, contaminant data (as a function of time) may be available from the monitoring network. These data are especially impor-

TABLE 5-6

Geochemical species and isotopes (natural and anthropogenic) for vadose zone model calibration and validation^a

Species/ Isotope	Behavior	Application	Reference
Cl	Conservative	Infiltration rate, transport processes, relative ages	1, 2, 5, 6, 7, 10
Sr	Reactive	Infiltration rate, flow pathways	6
⁸⁷ Sr/ ⁸⁶ Sr	Conservative - reactive	Infiltration rate, water sources	8, 11
²³⁴ U/ ²³⁸ U	Reactive	Water sources	8
¹³ C/ ¹² C	Biological fractionation, climate effects	Climatic changes, soil zone biological processes	
¹⁸ O/ ¹⁶ O	Vapor - liquid fractionation, climate effects	Infiltration processes/ water sources	12
D/H	Vapor - liquid fractionation, climate effects	Infiltration processes/ water sources	12
¹⁴ C	Naturally occurring and bomb-pulse radionuclide	Age dating	2, 9
³ H	Bomb-pulse radionuclide	Infiltration rate / fast flow paths	1, 3, 4, 10
³⁶ Cl	Naturally occurring and bomb-pulse radionuclide	Age dating infiltration rate / fast flow paths	1, 3, 7, 9, 10

^aThis list is by no means exhaustive, and the applicability of geochemical data depends on the geology, hydrology, and time-scale of interest for a particular site. It should be noted that geochemical data can include mineral chemistry in addition to aqueous and gaseous-phase compositions.

1. Phillips 1994	7. Scanlon 1991 1992
2. Tyler <i>et al.</i> 1996	8. Stuckless <i>et al.</i> 1991
3. Phillips <i>et al.</i> 1988	9. Plummer <i>et al.</i> 1997
4. Gvirtzman and Margaritz 1986	10. Tyler and Walker 1994
5. Ginn and Murphy 1997	11. Johnson and DePaolo 1994
6. Sonnenthal and Bodvarsson 1999	12. Aggarwal and Dillion, 1998

tant for evaluating model performance for predicting flow and transport at the site.

A calibrated model should be consistent with all these site data. For example, Figure 5-13 shows major field data being collected from the unsaturated zone of Yucca Mountain, Nevada (Bodvarsson *et al.* 1999a), including a variety of hydrological and geochemical data. Based on model calibration, all of these data have been incorporated into the three-dimensional, unsaturated-zone site-scale flow model in order to quantify the flow of gas, moisture, solutes, and heat through Yucca Mountain.

PRIORITIZATION OF DATA COLLECTION

Since data collection is generally expensive and time-consuming, prioritization of data collection is an important issue. This issue is discussed in this section because data obviously provide one of the most important foundations for modeling studies, as discussed in the introductory section of this chapter. However, prioritization relies on the model objectives, the availability of existing data, the project budget, and many other practical factors. Here, we do not attempt to provide comprehensive prioritization lists for data collection for different cases, but rather focus on a general prioritization of commonly used data for vadose zone modeling studies. Sensitivity studies with models are useful for determining site-specific prioritization of data collection, as discussed in the next subsection.

Table 5-7 lists data that need to be collected according to their priority for vadose zone modeling studies. Contamination data are considered to be the most important data, because the presence of contaminants most often drives vadose zone modeling studies. If historic contamination data are available, they can be used to calibrate and refine models, provided that the contamination source history can be reasonably estimated. The second most important data are geologic formation data, considering that subsurface heterogeneity, which can be characterized by geologic formation data, is a key factor controlling flow and transport in the subsurface.

Permeability and fracture mapping (for fractured rocks), water retention curve, and water content/potential data are ranked third through fifth, respectively, in priority. Permeability is a basic input into flow and

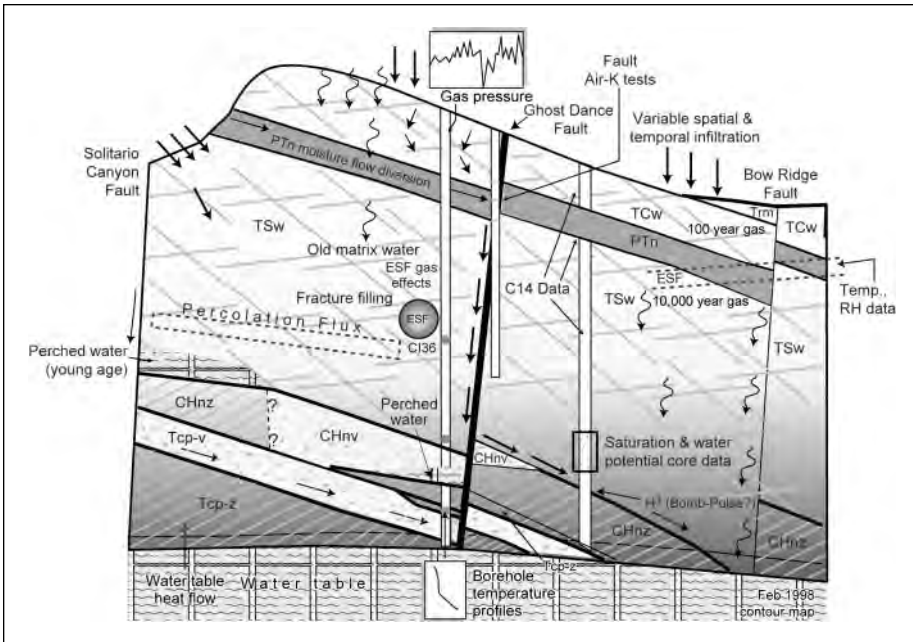


Figure 5-13. A schematic cross-section through Yucca Mountain showing some of the field data being collected. (adapted from Bodvarsson *et al.*, 1999a).

TABLE 5-7 Data listed according to priority for modeling studies^a

1. Site contamination data	9. Geochemical data
2. Geologic formation data	10. K_D and other relevant parameters to characterize mass transfer between different phases
3. Permeability and fracture mapping	11. Diffusion coefficient and dispersivity
4. Water retention curve	12. Porosity and grain density
5. Water content and potential data	13. Thermal conductivity and heat capacity
6. Infiltration data (environmental tracer and temperature data)	14. Other data
7. Perched water data	
8. Pneumatic data	

^aThis table only provides a general prioritization of commonly used data for vadose zone modeling studies. The priority orders may not be appropriate in some cases.

transport models, and its distribution is crucial to determining the subsurface heterogeneity, as discussed above. The water retention curve is the basis for determining all other constitutive relations. For example, relative permeability and three-phase constitutive relations can be estimated from the water retention curve (van Genuchten 1980; Lenhard and Parker 1987). *In situ* water saturation and potential data are generally available for most sites and are the primary data used to calibrate a model. The sixth ranking in priority is given to infiltration data, an important driving force for vadose zone contaminants to the saturated zone. As discussed above, in some cases environmental tracer and temperature data can also be used to estimate infiltration rates. Environmental tracer data are also useful for estimating water travel paths and time and temperature data within the vadose zone for modeling heat-transfer processes.

In Table 5-7, perched-water data, pneumatic data, and geochemical data are listed as important data for model calibration. Discussions about the use of these data for model calibrations can be found in the section “Model Calibration.” Following are K_D and other parameters that characterize chemical mass transfer between different phases, porosity and grain density, and diffusion coefficient/dispersivity, respectively. These data are closely related to contaminant transport, the importance of which was discussed previously. We give higher priorities to data describing flow than to these data because advection resulting from flow is the basic mechanism for transport. Thermal conductivity and heat capacity data are basic model inputs for heat transfer. Additional useful data may be assumed as included in the “other data” category in the table.

METHODOLOGY OF MODEL GUIDANCE IN DATA COLLECTION

Numerical models should play an important role in guiding data collection. In this subsection, we briefly discuss how numerical models can be used in data-collection procedures.

Two important questions facing hydrogeologists collecting data from a site are (1) what additional data should be collected to provide the most useful information for understanding and predicting flow and transport processes and (2) from where should that data be collected. With the complexity of vadose zone flow and transport processes,

answers to these questions may not always be straightforward. Sensitivity studies, using a model built with the currently available data, can be employed to help identify key parameters and locations (or geologic formations) for the flow and transport processes under investigation.

Field tests, such as infiltration and tracer tests, are often used for determining field-scale flow and transport parameter values in the vadose zone. Pre-test model predictions should be made to optimize test design. One should assess the feasibility of the test configuration to be used, the potential unfavorable impact of tests on contaminant transport at the site, and the sensitivity of data to be collected to flow and transport parameter values of interest. As discussed before, in many cases, flow and transport parameters are not directly measured, but inferred from relevant observations based on simple analytical solutions under idealized conditions. Pre-test model studies are thus also useful for evaluating the validity of these analytical solutions at the test site. Doing these studies will avoid potential misinterpretation of the test data to be collected. More importantly, a comparison between pre-test model prediction and actual test data provides an unbiased evaluation of model performance. Post-test model interpretations of test data are generally needed. It is not uncommon that large discrepancies may exist in the comparison at initial stages of model development. As a matter of fact, this interpretation is often very helpful for refining models by enabling the modeler to get a better understanding of the data.

In summary, data collection and model-building are not separate procedures, though the close relation between them may not be fully realized by many modelers and experimentalists. Models can be used for guiding many aspects of data collection, including identifying important data that need to be collected and locations for data collection, optimizing test design, and making the best use of test data based on the pre-test prediction and post-test interpretation approach. Further discussions on these issues can be found in the section “Model Calibration.”

UPSCALING ISSUES

When numerical models are used for modeling field scale flow and transport processes in the subsurface, the problem of “upscaling” arises. Typical scales, corresponding to spatial resolutions of subsurface het-

erogeneity in models, are generally much larger than measurement scales of the parameters and physical processes involved. The upscaling problem is, then, one of assigning parameters to gridblock scale based on parameter values measured on small-scales. For vadose zone flow and transport problems, these parameters include permeability or saturated hydraulic conductivity, parameters characterizing constitutive relations, and dispersivity. Upscaling issues remain topics of active research in subsurface hydrology (see, for example, Gelhar 1993, Liu and Molz 1997, Desbarats 1998), although studies on the vadose zone are relatively limited.

While relevant issues regarding large-scale dispersivity have been discussed in other sections of this chapter, we focus here on upscaling permeability and constitutive relations. It also should be noted that describing large-scale processes with volume averaging might involve more than simply “upscaling” of parameters, as indicated in the following section of this chapter. In fact, volume averaging may give rise to “effective” processes that may not have a small-scale counterpart (Pruess 1996a, b). In this subsection, our discussion is based on an assumption that small-scale counterparts still exist for large-scale “effective” processes.

It is well known that large-scale effective permeabilities have much larger values than small-scale permeabilities (Neuman 1994; Clauser 1992). For example, Bodvarsson *et al.* (1999b) show that measured air-permeability values for fracture network in the vadose zone of Yucca Mountain, Nevada, are consistently increased with measurement scale (Figure 5-14). They also found that estimated fracture permeability values using pneumatic data are about one or two orders of magnitude higher than averaged values estimated from small-scale air injection tests. An intuitive explanation for the scale-dependent behavior of permeability for subsurface materials is that a large measurement scale, in an average sense, corresponds to a larger opportunity to encounter more permeable zones or paths when measurements are made, which considerably increases the values of measured permeability.

Based on the Landau-Lifshitz conjecture (Landau and Lifshitz 1960), Paleologos *et al.* (1996) proposed an upscaling approach to estimate effective hydraulic conductivity of strongly heterogeneous porous media. The large-scale effective hydraulic conductivity is a function of mean, spatial correlation structures, and variance of log hydraulic con-

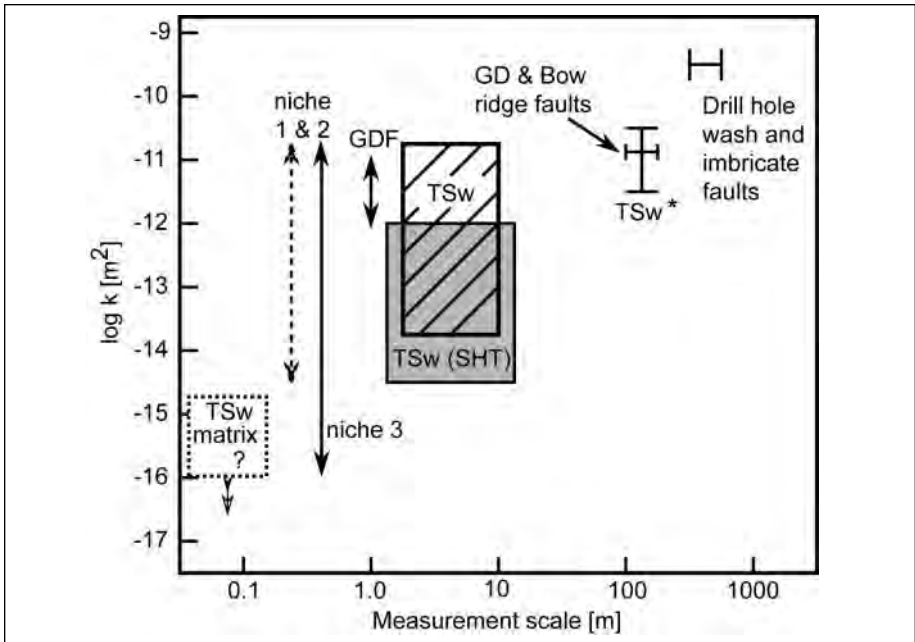


Figure 5-14. Measured air-permeability value for fracture network in the vadose zone of Yucca Mountain, Nevada, as a function of measurement scale (adapted from Bodvarsson *et al.*, 1999b).

ductivity at a small scale. Effects of small-scale correlation structures can be ignored if characteristic lengths of the domain of interest (such as a geologic formation) are much larger than the correlation scales. Another practical approach for upscaling permeability or saturated hydraulic conductivity is the spatial averaging approach (Desbarats 1992, Sanchez-Vila *et al.* 1995). In this approach, the upscaled permeability is a power-law average of small-scale measurements. The value of the exponent is generally case-dependent. For the particular case of a statistically isotropic field and a cubic domain, a power value of $1/3$ has been established (Desbarats 1992, Sanchez-Vila *et al.* 1995). A number of other upscaling approaches are also available in the literature (see, for example, McKenna and Rautman 1996).

Compared with upscaling permeability, the upscaling of constitutive relations is a more challenging task because of the high nonlinearity of vadose zone flow processes. Among a number of reasons for the scale-

dependence of the constitutive relations, one important reason is that liquid water distribution is determined by different mechanisms at different scales. At a core scale, water distribution is mainly determined by capillarity. Therefore, for a given capillary pressure, liquid-water distribution at a small core scale in laboratory is determined by the pore-size distribution. A number of researchers have used this as the basis for developing mathematical expressions for a water retention curve and for developing relations between water-retention curve and relative permeability (van Genuchten 1980, Brooks and Corey 1964). However, at a large scale, gravity becomes important, and subgrid fingering may occur, making constitutive relations that are measured at a small scale invalid at a scale of interest for practical modeling studies. However, in some special cases, large-scale relations may be relatively easily estimated from small-scale measurements.

Recently, Green *et al.* (1996) found that for steady gravity drainage in a perfectly layered medium, upscaled water-retention curves could be approximated by arithmetic averaging from individual layers, assuming a uniform matric potential. Bodvarsson *et al.* (1999b) indicate that arithmetic averaging can also be used to determine upscaled water-retention curves from core measurements for matrix in the vadose zone of Yucca Mountain. The tuff matrix has much smaller pore size, corresponding to stronger capillarity, than most subsurface materials. Under steady-state flow conditions, liquid water distribution in the matrix at large gridblock scales similar to that at core scale is still mainly controlled by capillarity.

A more general study on both water retention and relative permeability relations was published by Desbarats (1998). His results show that under steady-state flow conditions, an upscaled pore-size distribution parameter is very well approximated by a power law average of its measurement-scale values. Furthermore, the averaging exponent is found to be the same as that associated with the upscaling of saturated hydraulic conductivities over the same domain. These interesting results may need to be confirmed by more studies. A brief review of several other approaches is also given in Desbarats (1998).

At this point, it is fair to say that a rigorous and easily used approach has not yet been developed for upscaling constitutive relations in a general case. On the other hand, for many practical modeling problems, only a very limited number of measurements are available for constitutive relations because these relations are difficult to measure. Even if a

rigorous approach were available, the limited measurements would still cause upscaled relations to have large degrees of uncertainty. Hence, in many modeling studies, simple averaging remains a practical choice for upscaling constitutive relations.

It is obvious from the above discussion that directly estimating large-scale effective parameters from small-scale measurements involves a large degree of uncertainty because of the limitations of the currently available upscaling approaches and data availability. To overcome this problem, Bodvarsson *et al.* (1999b) proposed a two-step approach to deal with upscaling issues for the vadose zone. In the first step, large-scale parameters are estimated from small-scale measurements with the currently available upscaling approaches. In the second step, large-scale or coarse grid inverse modeling studies are performed to refine large-scale parameter values by calibrating against relevant data, such as water saturation and potential. These data are gridlock-scale data calculated from small-scale measurements based on simple averaging schemes. In an inverse modeling study, the estimates from the first step are used as prior information to constrain property values. In other words, the refined parameter values from this step will not be very different from those estimated from the first step, but are consistent with other kinds of data. This approach has been used for estimating site-scale vadose zone flow parameters at Yucca Mountain. Further discussions on model parameter identification and associated uncertainty are given in the section “Model Calibration.”

CONCLUDING REMARKS

In this section, we have discussed the available data that are frequently collected to characterize the vadose zone and the prioritization of data collection activities. While tremendous advances have been made in developing a variety of numerical models (as discussed in the section “Mathematical Models and Numerical Formulations”) how to appropriately make use of data becomes increasingly important for improving the reliability of modeling results. Among many issues regarding the use of data for modeling purpose, we believe that the following ones are especially important for vadose zone flow and transport modeling, and deserve considerable attention in future researches.

It is obvious that upscaling remains a challenging issue for vadose zone hydrogeologists. Although some approaches have been developed, a rigorous and easily-used approach has not yet been established for upscaling constitutive relations in a general case. Most of the relevant researches have focused on porous media, and studies on upscaling for dual-continua corresponding to unsaturated fractured rocks are very limited because of the complexity of the problem.

Fingering and preferential flow have been recognized as common flow mechanisms in the vadose zone, and have important implications for contaminant transport. While the physical mechanisms behind it have been well understood, how to model the flow on a scale of interest is largely unknown. For practical modeling practices, subgrid fingering generally occurs because it is practically impossible to use a fine enough grid system to resolve all individual fingers. Developing approaches that account for subgrid fingering (in an average sense) is crucial for vadose zone modeling. The relevant studies are limited at this stage.

Field data are always scarce. How to combine data generally obtained at “points” into spatial distributions is another important issue for vadose zone modeling. These determined distributions are basic inputs into a model and significantly affect the modeling results, which are further complicated by the existence of multiscale heterogeneity. While different approaches have been developed, fractal-based interpolation approaches seem to be promising in resolving the problem regarding multiscale heterogeneity (Molz and Boman 1993). Further studies are needed in this area to enhance the reliability of model inputs.

DEVELOPMENT OF SITE-SPECIFIC MODELS

INTRODUCTION

Let us suppose we have some knowledge of hydrogeologic conditions, distribution of contaminants, and relevant physical and chemical processes at a field site. Let us also suppose that we have access to mathematical models—either in the form of (semi) analytical solutions, or in the form of numerical simulators—that can represent these processes. How do we then go about using these various pieces of information and mathematical and computational tools to develop a “model” of the site? The term “model” is here used to denote a specific, quantitative representation of conditions and processes at a given field site. The present

section attempts to outline the process of “model building” in general terms; more specific information will be given in the following section on model calibration and in the various field examples and case studies presented elsewhere in this chapter. Our discussion is limited to “mechanistic” modeling approaches that are based on the sound principles and well-established continuum field theories of classical theoretical physics, usually expressed in the form of PDEs (Morse and Feshbach 1953; Narasimhan 1982a, 1982b). Alternative approaches such as lattice gas (Chen *et al.* 1991), cellular automata (Lee and Chung 1993), and invasion percolation (Lenormand and Zarcone 1985; Glass and Yarrington 1996) have proven useful for analysis of laboratory experiments and for improving basic process understanding (Pruess *et al.* 1999), but do not seem to lend themselves to field applications. Non mechanistic phenomenological approaches such as transit time distributions and transfer functions are of considerable interest in vadose zone hydrology (Jury 1982; Jury and Roth 1990; Chesnut 1992, 1994a, b), but are outside the scope of this article.

OBJECTIVES

Flow and transport processes in the vadose zone occur on a huge range of space and time scales. Chemical reactions and sorption processes at interfaces may be dominated by pore-scale effects (Nielsen *et al.* 1986), while mobilization of contaminants in the capillary fringe region may depend on seasonal water-table fluctuations on a regional scale. Episodic infiltration events and advection in the gas phase may cause significant redistribution of contaminants over short time scales (hours or days), while diffusive processes tend to be slow and may require years or decades for migration to occur over significant distances.

It is obvious that characterization and modeling of vadose zone processes is only possible over limited ranges of space and time. Modeling can never achieve a “true” representation of a reality. That remains, in part, elusive. Instead, modeling must focus on specific issues that are to be addressed. The approach taken and approximations made must be commensurate with the objectives of the modeling effort. A set of specific, well-defined objectives is perhaps the single most important prerequisite for a successful modeling effort. In the simplest case, the objectives of a modeling study may include an assessment of certain

hydrogeologic conditions (for example, the importance of embedded clay lenses), or an evaluation of specific process mechanisms (such as the relative importance of contaminant migration in aqueous and gas phases or the effects of dissolved electrolytes on water migration). Numerical simulation may be able to distinguish between alternative hypotheses or between alternative conceptual models (see below). At its most ambitious, numerical simulation may incorporate detailed site-specific conditions and comprehensive process descriptions (for example, of flow, transport, thermal effects, and chemical reactions), on a range of space and time scale, to achieve site-specific predictive power by calibration against diverse field data. A frequent goal of modeling efforts is to obtain guidance for site characterization and monitoring, and for the design of remediation schemes.

CONCEPTUAL MODEL

The conceptual model of a site represents a synthesis of all pertinent information, integrated on the basis of generally accepted physical and chemical principles. As a comprehensive, qualitative model of conditions and processes at a given site, it is an essential stepping stone in the modeling process. The conceptual model will usually take the form of a series of diagrams and sketches that emphasize the most relevant hydrogeologic features (for example, distribution of hydrogeologic units, location of zones with high or low permeability, capillary barriers, clay lenses, fractured horizons, and faults). It will include a judgment, often tentative, on process aspects that are “essential,” as opposed to being of minor importance. A typical example involves the decision as to whether a Richards’ equation approach with a passive gas phase is adequate, or whether a full multi phase treatment will be required, possibly coupled with non isothermal effects. Another important aspect is the identification of heterogeneity structures that may require multi- continua or multi-region approaches, such as fractures, root and wormholes, paleo stream channels, embedded clay lenses, and others (Pruess and Narasimhan 1985; Gwo *et al.* 1996; Mohanty *et al.* 1997). The conceptual model also needs to describe initial and boundary conditions (for example, water saturation, perched-water bodies, distribution of contaminants, location of the water table, surface topography, drains,

and trenches), and sinks/sources (for example, injection and extraction wells, if present).

After a conceptual model has been developed, the next step in the modeling process involves the use of numerical simulators to assemble a specific, quantitative model of flow and transport processes at a field site. The modeling tools (numerical simulators) must be chosen to provide adequate capabilities for representing the important features, processes, and data identified in the conceptual model.

Depending on the objectives of the modeling study, the intrinsic variability and complexity of a site, and the quantity and quality of data that are available, a conceptual model may be simple or complex. Conceptual models may have considerable uncertainty. They should be considered preliminary, to be revised as the consequences of the model are elaborated in quantitative detail and compared with observations. In some cases, the ambiguities at the start of a modeling effort may be such that several alternative conceptual models are possible and should be pursued simultaneously.

The case study “TCE Contamination at the Savannah River Site,”
by K. Pruess, presents a very simple conceptual model. *See page 792.*



GEOMETRIC DESCRIPTION

For numerical simulation of flow and transport processes, the continuous space coordinates must be discretized. Modeling studies aiming at testing and improving understanding of process mechanisms and controls may often be made with considerably simplified geometric descriptions, and may conveniently use regular grid systems, referred to a global system of coordinates. Site-specific studies attempting to represent actual hydrogeologic features will more often than not have to deal with complex, irregular geometric shapes and their partitioning into computational grids. The process of translating a conceptual model into a computational grid suitable for numerical simulation can be very tedious and is fraught with potential for serious errors that may not be apparent during the simulation.

The process of partitioning space into discrete, finite-size subdomains, or gridblocks, requires volume averaging over the scale of the gridblock, because no intrinsic variability on a scale smaller than

the gridblock can be resolved. This discretization raises troublesome issues for modeling phenomena such as preferential flow along localized pathways. Localized preferential flow of aqueous and non-aqueous fluids is becoming recognized as an important and often dominant feature for solute and contaminant transport at many sites (Pruess 1999). There is also much field evidence for preferential flow in the gas phase. For example, in after soil vapor extraction (SVE) for removal of volatile organic chemicals (VOCs) from the vadose zone, contaminant concentrations often show tailing and tend to rebound when the system is turned off. This behavior suggests that some regions are bypassed by the air stream, so that contaminants are removed from them only slowly (for example, by diffusion). It is frequently observed that estimations of contaminant inventory from soil gas concentrations tend to be low, which also suggests that contaminants may lodge in inaccessible regions that are subject to bypass flow. Mechanistic modeling of such processes may require spatial resolution on a scale of decimeters to centimeters or better, which may be difficult if not impractical for field-scale problems.

An important issue is whether processes are subject to internal volume averaging because of physical mechanisms in the flow system itself or whether, in cases where internal averaging mechanisms are weak, the averaging is performed by the analyst rather than the system. From a formal point of view, processes subject to internal averaging mechanisms are described by parabolic or elliptic PDEs (for example, transient propagation of gas pressures in the vadose zone or liquid pressures in the saturated zone, gas diffusion, or heat conduction), while non-averaging processes are described by (nearly) hyperbolic PDEs (for example, solute transport dominated by advection and gravity-driven downflow of liquids in unsaturated zones with weak capillary effects). It has been recognized that the process of volume averaging may involve more than simply “upscaling” of parameters; in fact, volume averaging may give rise to “effective” processes that may not have a small-scale counterpart (Pruess 1996a, b).

Special discretization concepts have been developed for flow systems with hierarchical permeability structures, such as fractured media, sedimentary formations with embedded clay lenses, and structured soils with systems of cracks or roots and wormholes. In such media, pressure propagation and mass transport may occur rapidly through the network of high-permeability features, while the regions of low permeability are

invaded only slowly. This leads to persistent non-equilibrium conditions and long-term exchange of fluid, solutes, heat, and the like between high- and low-permeability features on a local scale. The general approach for dealing with such processes involves augmenting “global” discretization by adding partitioning of the flow domain into several interacting continua locally. As an example, Figure 5-15 shows geometric models for interporosity flow that are applicable to unsaturated fractured media. In the classical double-porosity approach (Warren and Root 1963), global flow occurs exclusively through the high-permeability continuum, while matrix blocks of low permeability may exchange fluid (or solutes or heat) with the fractures locally. This local exchange is approximated as being quasi-steady; that is, spatial variability within the blocks is not modeled. The extension of this concept to “multiple interacting continua” (Pruess and Narasimhan 1982, 1985) allows resolution of the spatial gradients (of fluid pressure, solute concentration, temperature) within the matrix blocks for a fully transient description of interporosity flow. The most general flow topology is represented by the dual-permeability concept shown in Figure 5-15c, in which global flow can occur in both fracture and matrix continua, while fractures and matrix can also exchange fluids locally. This kind of approach can account for multiphase flow conditions where global flow of one phase may occur predominantly through the fractures and flow of another phase predominantly through the matrix. For example, in fractured vadose zones, the wetting (aqueous) phase may flow primarily through the matrix, while the non-wetting (gas) phase may flow primarily through the fractures (Wang and Narasimhan 1993). “Multi region” approaches similar to those shown in Figure 5-15 have also been used for structured soils (Gwo *et al.* 1996)

Apart from the issues related to volume averaging, by discretizing the continuous space coordinates, we replace the governing differential (or integral) equations for flow and transport by difference equations, which can only provide approximate solutions to the underlying differential equations. Artifacts from space discretization are often called “space truncation errors” (Peaceman 1977; Aziz and Settari 1979); they may cause sharp fronts (of water saturation or solute concentration) to become more diffuse as they propagate; they may also cause “grid orientation errors,” where the results of a simulation become sensitive to the spatial orientation of the grid. These spurious effects can be reduced

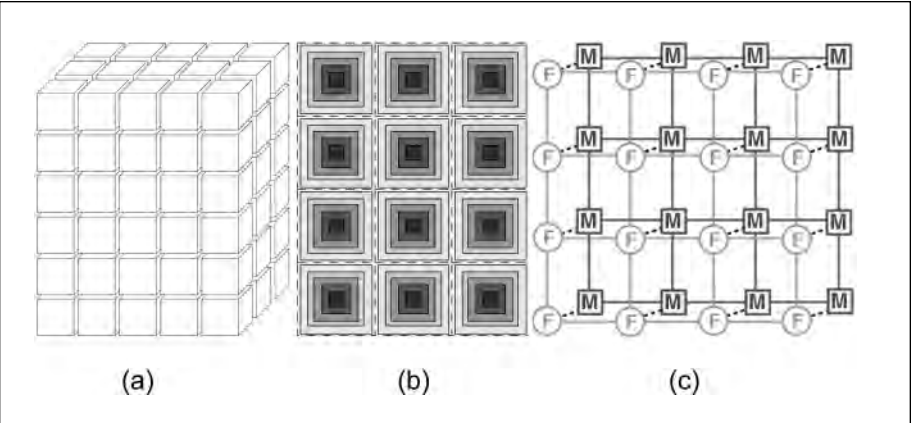


Figure 5-15. Geometric models for flow in fractured media, (a) double-porosity (Warren and Root, 1963), (b) multiple interacting continua (MINC; Pruess and Narasimhan, 1982, 1985), and (c) dual permeability.

by means of finer grid spacing or higher-order differencing methods (Yanosik and McCracken 1979,; Pruess 1991b,; Oldenburg and Pruess 1998).

It is desirable to try and represent geologic features such as layering, faults, inch-outs etc. as accurately as possible. Depending on geologic complexity, this can be a formidable task. It will in general require irregular grids for which the issues of space discretization errors tend to be more serious and less amenable to analysis and control.

The case study “Integrated Geological Interpretation for Computational Modeling,” by Carl W. Gable, discusses computer representation of geologic geometry in computational modeling. *See page 799.*



NUMERICAL SIMULATION

A considerable number of numerical simulation codes have been developed and are available for modeling flow and transport processes in the vadose zone. Table 5-8 provides information on some simulators currently in use for vadose zone flow and transport applications. This list is not intended to be complete, and many other excellent simulation programs are available. Much useful information on numerical simulation software is available on the Internet, for example, through the

TABLE 5-8**Selected numerical simulation programs for vadose zone flow and transport modeling**

Program	Process Capabilities	Methods	Features, Limitations	References
CHAIN_2D	2-D unsaturated [§] flow; solute transport	finite elements; Picard iteration		Simunek and van Genuchten, 1994
FEHM, FEHMN	3-D multi-phase flow; aqueous and gas phase transport; chain decay	control volume finite elements	non-isothermal; flexible gridding of irregular geometries	Zyvoloski <i>et al.</i> 1995; Dash <i>et al.</i> 1997
MAGNAS	3-D multi-phase flow; aqueous and gas phase transport; first-order degradation; dissolution and precipitation	finite elements	optional simplified formulations, including pseudo-three-phase, and pseudo-3-D	Huyakorn <i>et al.</i> 1994; Panda <i>et al.</i> 1994
MODFLOW-SURFACT99	3-D variably saturated flow and contaminant transport; chain decay; non-linear sorption	finite difference	optionally can treat either water or air as inactive phase; dual-porosity and TVD schemes	Panday and Huyakorn, 1996
MUFTE	3-D multi-phase flow and transport	finite element, finite volume	non-isothermal	Helmig <i>et al.</i> 1994
MURF, MURT	2-D unsaturated [§] flow; solute transport	finite elements	multi-region	Gwo <i>et al.</i> 1994, 1995
NUFT	3-D multi-phase flow; aqueous and gas phase transport	integral finite differences		Nitao 1996
STOMP	3-D multi-phase flow and transport			White <i>et al.</i> 1995; Lenhard <i>et al.</i> 1995
SUTRA	2-D variably saturated flow; dispersion; diffusion; adsorption	finite elements	non-isothermal	Voss, 1984
TOUGH2, T2VOC, iTOUGH2	3-D multi-phase flow; aqueous and gas phase transport; chain decay	integral finite differences	non-isothermal; MINC; automatic model calibration	Pruess 1991a; Pruess <i>et al.</i> 1999; Falta <i>et al.</i> 1995; Finsterle 1999
TRUST	3-D unsaturated [§] flow	integral finite differences	1-D consolidation	Narasimhan <i>et al.</i> 1978
VAM3D	3-D unsaturated [§] flow; solute transport; linear sorption; first-order degradation	finite elements; Picard or Newton-Raphson iteration	optional "pseudo-unsaturated" mode	Huyakorn <i>et al.</i> 1986
VLEACH	1-D unsaturated [§] flow; gas diffusion; sorption; volatilization	finite difference		Turin 1990

[§]The term "unsaturated flow" as used here denotes a Richards' equation approximation (passive gas phase; Richards 1931)

listings of the International Groundwater Modeling Center in Golden, Colorado (<http://www.mines.edu/igwmc/>).

Selection of an appropriate numerical simulator is an important, if somewhat subjective, step in the modeling process. Numerical simulators are tools, and, as such, should obviously be selected to be suitable for the task at hand., but However, they are only one component of the modeling process. Familiarity of the analyst with the numerical simulator and the methods used in it is essential for obtaining meaningful results in demanding applications. No finite process exists by which it could can be demonstrated that a simulator is free of errors. The working assumption in simulator applications has to be, therefore, that errors may be present. It is the responsibility of the analyst to perform whatever tests and checks are necessary to build confidence in the accuracy and realism of a numerical modeling effort. This can be done in a number of ways, such as comparing with (semi-) analytical solutions of simplified versions of the modeling problem, by comparing with results obtained with other simulation codes, by checking on symmetries or invariances that should be present, and others.

In order to translate a conceptual model of a flow system into a numerical simulation problem, we must assign specific numerical values to numerous parameters and constitutive properties. For flow modeling, the main hydrogeologic parameters that need to be specified are permeability, porosity, relative permeability, and capillary pressure. For transport modeling, we also require diffusivities and dispersivities, tortuosity coefficients, and constitutive models for sorption. A description of the thermodynamic and thermophysical properties of the fluids includes fluid viscosity, density, enthalpy, and partitioning of components among fluid phases. For chemically reactive species, many additional parameters are needed to characterize the reactive fluids and their interactions with solid phases.

Corresponding to the sequence of events and processes in the flow system under study, numerical modeling usually will proceed through several phases. The first phase will involve modeling of a “natural” state that represents system conditions prior to the release of contaminants or other man-made perturbations. In vadose zone modeling, the natural state is often taken to be represented by gravity-capillary equilibrium for space-and-time averaged infiltration conditions. A steady-state approximation may be an oversimplification, however, as vadose zone

systems can be quite dynamic even in the absence of man-made perturbations. After a suitable “natural” state has been achieved, the next modeling phase will address the release and migration of known or suspected contaminants, as is thought or known to have occurred at a site. Such modeling may provide useful guidance for site characterization and will set the stage for the subsequent modeling phase that will address predictive simulations for future contaminant behavior. Predictive simulations may entail a baseline “no action” scenario, as well as simulations, and comparative evaluation of various remediation schemes. In all phases of a simulation study, parametric sensitivities and uncertainties are important and need to be addressed.

When beginning a simulation study, it is generally a good idea to “start simple” and limit the complexity and detail in the numerical model. This will facilitate preparation of input data and analysis of results. Detailed 3-D site models with reasonably fine gridding (necessary to resolve hydrogeologic features, and to limit numerical dispersion effects) require and generate large amounts of data, and require considerable processing time. This makes them unwieldy and may seriously impair the ability of the analyst to develop a sound understanding of the interplay between different processes and features. Such an understanding is vital for a meaningful, iterative refinement of a model. A fruitful paradigm for numerical simulations is to view them as “numerical experiments,” analogous to laboratory experiments. Before aiming for great precision and detail, it is important that the main processes in the system and their controls be identified. Results of simulations should be examined and explained in terms of the physical processes and conditions being modeled.

Simulator inputs may typically include a number of parameters that may be rather well known, as well as others for which only rough estimates are available. For example, formation porosities may often be rather well-constrained from laboratory measurements on samples, while permeabilities, being subject to strong scale effects, may be poorly constrained. The process of adjusting parameters to better represent conditions and observed flow and transport behavior at a field site is known as “model calibration” or “history matching.” Model calibration is accomplished in an iterative process, by making estimates for parameters that are uncertain or unknown, carrying out a flow (or transport) simulation, comparing model predictions with field observations, and then revising parameters as needed to reduce the discrepancy

between predicted and observed behavior. Depending on the objectives of a simulation study and the availability of field and laboratory data, model calibration can be performed manually as a trial-and-error process, or it can be formalized and automated through “inverse modeling” techniques (see the following section, “Model Calibration”). The calibration process may fail, (for example, no satisfactory agreement between model predictions and observations may be obtained), in which case it may be necessary to revise the conceptual model and start over.

MODEL VALIDATION/CALIBRATION USING GEOCHEMICAL AND ISOTOPIC DATA

Model calibration and validation using hydrological data, such as water saturation, moisture tension, ambient pneumatic signals, air-permeability testing, and temperature, were treated in the sidebar discussing studies performed at Yucca Mountain. In addition to these data, validation and calibration of numerical models of flow and transport in the vadose zone are greatly aided by the consideration of various geochemical and isotopic systems. Many geochemical systems are greatly sensitive to transport processes in the vadose zone because diffusive equilibration of aqueous species is usually slow, compared with water flow, and differences in the chemistry of waters can be quite large as a result of different water sources, processes such as evapotranspiration, climate changes, and water-rock interaction. A listing of some more commonly used geochemical species and isotopic systems, along with some referenced applications, was presented in Table 5-6.

It is useful to separate geochemical systems into a few categories. One category would be tracers that are generally conservative in nature (in that they are little affected by mineral-water reactions), such as including chloride, bromide, and sulfate. Naturally occurring species, such as Cl, as well as those produced by atmospheric nuclear weapons testing in the 1950s and 1960s, such as ^3H (tritium) and ^{36}Cl , have been employed for age dating and analyzing water flow and transport processes in the vadose zone (Phillips *et al.* 1988; Phillips 1994). These species can be used to infer rates of infiltration, transport velocities, and subsurface mixing/dispersion/diffusion in the vadose zone. It should be recognized that such tracers are not conservative in all geologic media and fluid compositions, especially not in clay-rich soils where anion

exclusion effects may increase transport velocities for chloride relative to water (Gvirtzman and Margaritz 1986).

Because the half-life of tritium is only 12.42 years (Phillips *et al.* 1988), and the dominant source was from weapons testing, it can only be used for transport processes that have spanned the past few decades. The half-life of ^{36}Cl is 301,000 years and, in addition to nuclear fallout from weapons testing, it is produced in the atmosphere through cosmic ray interactions with argon (Phillips *et al.* 1988). Ratios of $^{36}\text{Cl}/\text{Cl}$ have varied similarly to ^{14}C abundances over the past several tens of thousands of years (Plummer *et al.* 1997), and therefore it can be used to estimate the water age in addition to being an indicator of relatively recent infiltration.

Another broad category of geochemical/isotopic systems are those that undergo changes as a results of water-rock interaction (for example, major cations, $^{87}\text{Sr}/^{86}\text{Sr}$, $^{234}\text{U}/^{238}\text{U}$). A third category would be those systems that undergo isotopic fractionation, such as $^{13}\text{C}/^{12}\text{C}$, $^{18}\text{O}/^{16}\text{O}$, and D/H (deuterium/hydrogen). For the most part, systems such as $^{87}\text{Sr}/^{86}\text{Sr}$, $^{234}\text{U}/^{238}\text{U}$, and the stable isotopic systems $^{13}\text{C}/^{12}\text{C}$, $^{18}\text{O}/^{16}\text{O}$, and D/H, have been used for analysis of vadose zone processes and for general validation of process models (Stuckless *et al.* 1991). Whereas there have been some numerical studies of Sr isotopes in the vadose zone (Johnson and DePaolo 1994), few modeling studies have coupled stable and radiogenic isotopic systems to vadose zone flow, reaction, and transport for vadose zone problems. In many cases, vadose zone processes are inferred from analyses of groundwater compositions (see, for example, Davisson *et al.* 1999). However, the ability to make meaningful direct validation of flow and transport models using geochemical data is much greater today as a result of improvements in the extraction of water from unsaturated media, in the techniques for measurement of isotopic ratios, and in computational speed and the processes treated in reactive transport codes.

MODEL ASSESSMENT: PREDICTIONS, UNCERTAINTIES, AND LIMITATIONS

There are many potential benefits of a successful modeling effort. The modeling process itself, by creating a common focus for field characterization, laboratory measurements, remediation design, and regulatory compliance, can serve as an integration tool for the many specialties that must come together for a successful field project. A calibrated

model of a field site offers a convenient, cost-effective way of assessing future releases of contaminants to the accessible environment, examining alternative remediation designs, and demonstrating compliance with environmental regulations.

The application of models for predicting future flow and transport behavior, under undisturbed conditions or subject to human intervention, requires a great deal of caution. Experience has shown that over time, model predictions may increasingly deviate from real system behavior, even when careful calibration was made against comprehensive data sets. Model development does not end when calibration against a given data set has been achieved. Rather, site-specific modeling should be viewed as an iterative process, to be updated and refined as new data become available. Much experience with numerical simulation of multiphase systems exists in petroleum engineering, where a general rule of thumb holds that useful predictive modeling may be made for a length of time comparable to the calibration (or history match) period. Calibrated site models tend to be more reliable when used to compare the relative impacts of alternative human interventions and engineering designs, rather than as “absolute” predictors of future system behavior.

In some cases, available data may be too limited for calibrating a deterministic model. Modeling can still be used to explore the sensitivity of system behavior to uncertainties and can help optimize site characterization efforts by focusing field observation and monitoring on those aspects that most reduce existing ambiguities. If uncertainties in model parameters cannot be reduced to acceptable levels, the methods of stochastic hydrology can be used to explore the behavior of alternative models that make different assumptions about unknown system features (Gelhar 1993; Dagan and Neuman 1997). Exploring the consequences of model uncertainties can provide useful insights for designing monitoring and remediation systems.

CURRENT RESEARCH DIRECTIONS

The vadose zone is an environment with a high degree of internal variability. Exceedingly complex physical, chemical, and biological processes are being played out in the vadose zone, on many space and time scales. Current modeling capabilities are limited in their ability to treat coupled processes and multi scale phenomena (Nielsen *et al.*

1986). Modeling applications are hampered by the generally rather sparse spatial and temporal coverage of field observations and by the paucity of field data on “appropriate” scales. Modeling is most useful when it is fully integrated into all phases of field tests and field data collection, from design to implementation to post-test analysis.

The case study “A Vadose Zone Injection Experiment for Testing Flow and Transport Models,” by M.J. Fayer, describes injection experiments at the Hanford nuclear waste disposal site. *See page 804.*



MODEL CALIBRATION

INTRODUCTION

Motivation and Scope

Subsurface flow and transport simulators are continually improved in terms of physical process description as well as speed, accuracy, and robustness of the numerical solution. Vadose zone problems of increasing complexity can be studied by means of numerical modeling. Such model predictions are theoretically very accurate, as the simulator correctly calculates the time-dependent solution of the governing equations for the given set of initial and boundary conditions and provides the state of the hydrologic system at any calculation point in space and time.

Despite advances in numerical simulation techniques, model calculations frequently fail to predict actual system behavior. Calculated travel times of contaminants, the predicted spreading of a NAPL plume, or the projected efficiency of a proposed cleanup operation are often inconsistent with data collected in the field. (Whether such inconsistencies can be considered acceptable or not depends on the overall purpose of the study, as will be discussed below.) The reliability of model predictions—if not used to improve our general understanding of flow and transport in the vadose zone—must be questioned.

There are four main reasons for the inconsistency between model predictions and field observations:

- (a) The conceptual model is inappropriate.
- (b) The process model is inappropriate.

- (c) The input parameters are inappropriate.
- (d) The data are erroneous or incompatible with the model output.

Errors in (a) the conceptual model and (b) its implementation into a numerical process model are the primary reason why model applications are unsuccessful. If key geological features such as faults or underground, man-made structures are overlooked, the model prediction is likely to be wrong. If a relevant process, such as diffusion into stagnant water bodies or fast transport in thin water films, is not considered in the model, the travel time of a contaminant will be grossly underestimated or overestimated, respectively. Finally, if contaminant source location, infiltration rate, or water-table elevation are unknown or uncertain, the prediction will be highly uncertain as well.

In general, the model must be capable of reproducing salient features of the system to be studied. A salient feature is an aspect of the system that has a significant impact on the behavior of interest; it is the objective of the study that determines which features of the system are important and to which degree they can be simplified. Bear in mind, however, that a model is always a result of an abstraction process. No exact solution is sought, but the approximations must be valid so that they do not lead to unacceptable errors in the prediction.

The second source of prediction errors is inappropriate input parameters, such as wrong values for permeability, porosity, unsaturated hydraulic properties, and adsorption coefficients. While some of the input parameters can be determined in the laboratory or inferred from the analysis of field tests, most of the many parameter values required for a simulation of multiphase flow processes are difficult to measure or estimate. Moreover, these measured parameters may represent a local property in a heterogeneous system and are thus conceptually different from the parameters required by a numerical model, which often requires effective, large-scale values. An error or uncertainty in an input parameter is directly translated into prediction errors or uncertainties, proportional to the sensitivity of the model result to the parameter.

Finally, the data used to check a model prediction are uncertain. Besides systematic errors or noise in the measurements, they may also be conceptually different from the model output to which they are compared. For example, contaminant concentrations measured on a

small sample taken from a heterogeneous soil cannot be directly compared to the average, large-scale concentration value calculated by a numerical model. Both the representativeness of measured point values as well as the averages calculated by the model should be critically assessed. These discrepancies are a major source of apparent inconsistency between models and field data.

Inverse modeling—the topic of this section—deals with all four aspects discussed above. The main purpose of inverse modeling is to estimate input parameters by calibrating the model output against observed data, thus addressing the issue of inappropriate input parameters cited above. During the calibration process, however, questions about the appropriateness of a certain conceptual model and its implementation become very important, as will be discussed in detail. Since inverse modeling consists of matching observed data, measurement uncertainties and the consistency between data and the model must be carefully addressed.

The development of a conceptual model and the determination of input parameters based on laboratory or field data are major tasks of any site-characterization effort. Inverse modeling is an attempt to formalize model calibration, which is an essential and often tedious step in the model-development process. However, inverse modeling goes beyond automatic history matching. The basic concepts behind inverse modeling can be adapted and used to evaluate alternative models, to better design experiments, and to optimize field operations.

The scope of this section is limited to describing the key concepts and steps of inverse modeling. Much has already been said in the previous sections about the development of a conceptual model. Setting up the so-called “forward model”—the model that calculates the system response for a given set of input parameters—is the most difficult, and also most important, task because it provides the basis for all subsequent inverse modeling steps. A short overview of the methodology will be given before we discuss a number of applications, which highlight certain aspects of inverse modeling.

General Remark About Model Parameters

Parameter estimation, history matching, model calibration, and inverse modeling are terms describing essentially the same technique with a slightly different objective in mind. The ultimate goal is to assess

the best model and its parameters for predicting the behavior of a dynamic subsurface flow system. The reliability of these predictions depends on the appropriateness of the conceptual model and the correctness of the model's parameters.

Note that it is the intended use of the model that determines the required degree of model sophistication and the level of accuracy with which the parameters are to be estimated. For example, consider the case in which peak contaminant concentrations at a drinking water well must be calculated with a prediction uncertainty that does not exceed a specified level. The latter constraint allows us to approximately estimate the required accuracy with which the input parameters must be determined. In general, sensitive parameters must be accurately determined, whereas it is sufficient to obtain a rough estimate of input parameters that do not strongly affect the calculated peak concentration at the well of interest. The ranking of these parameter sensitivities changes with the objectives of the study. For example, the properties of fast-flow pathways may not strongly affect peak concentration values, but they certainly have a large influence on the contaminant breakthrough time. If the objective of the study is to predict early breakthrough times rather than peak concentrations, a different set of parameters must be determined with high accuracy. Consequently, a different set of laboratory and field tests must be designed to make sure that the key parameters can be determined with sufficient accuracy (see also the subsection "Inverse Modeling and Test Design," below). Even a standard sensitivity analysis requires that the objective is well defined. Model predictions, test design, and data analyses are therefore interrelated and should be performed in an iterative manner, with the overall objective as the criterion driving the analysis.

In this overall scheme, parameter estimation by inverse modeling is only one (albeit important) step in the process of model development. Inverse modeling consists of estimating model parameters (such as permeability, porosity, and initial NAPL saturation) from measurements of the system response (such as pressure, saturation, and concentration) made at discrete points in space and time. Automatic model calibration can be formulated as an optimization problem, which has to be solved in the presence of uncertainty because the available observations are incomplete and exhibit random (and potentially systematic) measurement errors. The parameters to be estimated are selected coefficients in

the governing flow equations. They may include hydrogeologic and thermophysical properties, initial and boundary conditions, as well as parameterized aspects of the conceptual model. Unfortunately, the interpretation of these parameters depends—to a certain extent—on the conceptual model and the details of its implementation into a numerical model. In this sense, the parameters are strictly to be seen as *model* parameters (or *model-related* parameters) rather than parameters of the geologic formation. In other words, estimating parameter values from measurements relates the real multiphase flow system to its idealized representation. This is both an advantage and disadvantage of inverse modeling. The important advantage is that the parameters determined by inverse modeling can be considered optimal for the given conceptual model. When estimated by inverse modeling, the parameters are automatically related to the model structure, scale, and relevant physical processes. This direct reference of the parameters to the model is advantageous because it minimizes the negative impact of using independent parameters that are likely to be conceptually different. Estimating scale-adjusted, model-related, and process-specific parameters that lead to the best possible reproduction of observed data generally increases the reliability of subsequent model predictions. The disadvantage is that they cannot be transferred to another model without carefully considering whether the nature—and thus optimal value—of the parameter may change. Note that this disadvantage is not specific to parameters estimated by inverse modeling, but applies also to more-or-less “directly” measured parameter values. This important point will be emphasized throughout our discussion of inverse modeling results.

We mention in passing that using so-called transfer functions to predict unsaturated flow and transport can be considered an extreme example of the parameters being strictly model-related. In this approach (Jury 1982, Jury and Roth 1990), little or no knowledge about the actual flow and transport processes is used to develop the functional model, and the fitting parameters are often devoid of any physical meaning.

Inverse modeling involves several iterative steps. Starting from a conceptual model of the physical system, the results of parameter estimation may indicate that the underlying model structure has to be modified, for example, by inserting an additional hydrologic layer into the model. This process of iteratively updating the conceptual model and its parameters is sometimes referred to as “model identification.” This section

focuses on the more narrow aspect of inverse modeling, namely parameter estimation by automatic model calibration. Optimality and model identification criteria, which can be used to evaluate alternative conceptual models, will be briefly discussed below in the subsection “Model Identification Criteria.”

Inverse Modeling Procedure

Parameter estimation by inverse modeling is an iterative procedure, in which a model is run with various trial parameter sets and the model output is compared to the observed data. The parameters are then updated following one of many available strategies. An overview of the inverse modeling procedure is given in this section, followed by a detailed discussion of each element. The major steps are visualized in the flowchart in Figure 5-16. They can be described as follows:

1. Inverse modeling starts with the formulation of the so-called “forward problem.” A model must be developed that is capable of simulating the general features of the system behavior under measurement conditions. This step involves, among other considerations, the mathematical and numerical description of the relevant physical processes, the definition of model geometry, the assignment of initial and boundary conditions, the discretization in space and time, and the selection of zones over which the model parameters are believed to be constant.
2. The next step is to select the parameters to be estimated by inverse modeling. The parameters must be model *input* parameters. They may include hydrogeologic characteristics, thermal properties, and initial and boundary conditions, as well as all aspects of the model that can be parameterized (see the subsection “Parameterization,” below). They are summarized in the parameter vector p of length n .
3. An initial guess or estimate is assigned to each element of p .
4. Information about the model parameters is drawn from measurements of the system state (see the subsection “Observations and Residuals,” below). The availability of sufficient, sensitive data of high quality is the key requirement for reliable parameter estimation. The measured and calculated system response must

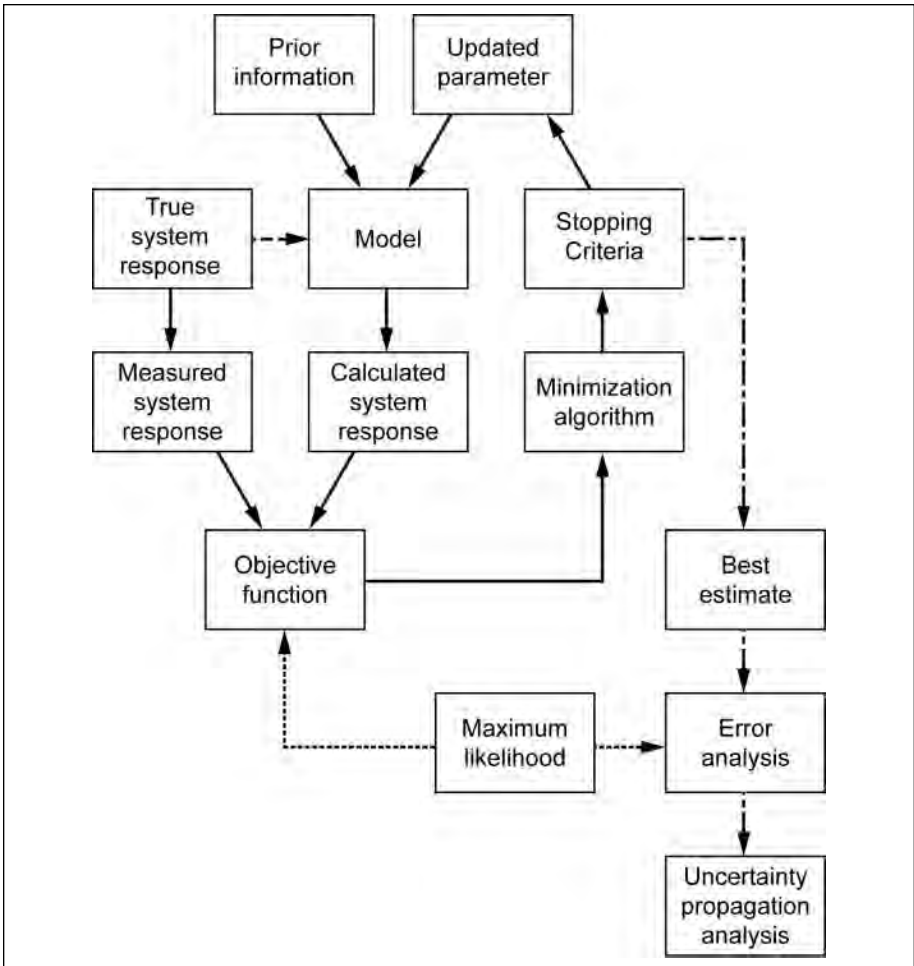


Figure 5-16. Overview of iterative inverse modeling procedure

correspond in terms of character, location, time, and scale. Model output and measured data are compared only at discrete points in space and time, at the “calibration points.” The vector holding the data measured at or interpolated to the calibration points is denoted by z^* . The corresponding model output, which is a function of space, time, and the model parameters p , are summarized in vector $z(p)$: Differences between the measured and calculated

system response at the calibration points are summarized in the residual vector $r = z^* - z(p)$.

5. The observation vector includes data that are of different type, magnitude, and accuracy. This requires that each residual be appropriately weighted before an aggregate measure of misfit can be calculated. The inverse of the measurement covariance matrix C_{zz} is often used as the weighting matrix (see the subsection “The Stochastic Model,” below).
6. A simulation is performed with the current parameter vector p to obtain the elements of vector $z(p)$. The simulation will be repeated with updated parameters as proposed by the minimization algorithm (see Steps 8 and 9).
7. The calculated and measured system responses are compared based on an aggregate measure of misfit, which is termed *objective function*, S . The weighted least-squares objective function is the most widely used misfit criterion (see the subsection “Objective Function,” below).
8. The purpose of the minimization algorithm is to find the minimum of the objective function by iteratively updating the model parameters. Since the model output $z(p)$ depends on the parameters to be estimated, the fit can be improved by changing the elements of parameter vector p . Minimization algorithms are discussed in the subsection “Minimization Algorithm,” below.
9. Once no further decrease in the objective function can be achieved, the iterative minimization procedure is terminated.

One of the key advantages of a formalized approach to parameter estimation is that it is possible to assess the sensitivity and importance of individual parameters, the goodness-of-fit, the estimation error, and the uncertainty of the model predictions. Note that if the data are not properly reproduced by the model, the resulting parameter set is likely to be inadequate. On the other hand, a good match does not imply that the estimates are reasonable. They may be highly uncertain as a result of low sensitivity or high parameter correlation. The residual, error, and uncertainty propagation analyses are discussed in the section “Error and Uncertainty Analysis,” below.

Introductory Example

The process of parameter estimation by automatic model calibration is illustrated in the following example, which is described in detail in Finsterle and Persoff (1997). A laboratory experiment was designed to estimate hydrogeologic parameters of very tight rock samples. (A schematic of the experimental apparatus is shown in Figure 5-17.) A rock sample is dried and placed in a sample holder, which is attached to two relatively small gas reservoirs. To conduct a test, the upstream reservoir is rapidly pressurized using nitrogen gas to a value about 300 kPa above the initial pressure of the system. Gas starts to flow through the sample, and the change of pressure with time is monitored in both reservoirs.

The steps listed in Table 5-9 and discussed in general terms in the previous section are followed here for the specific example.

1. As part of the model conceptualization, the relevant physical processes have to be identified, mathematically described, and implemented into the numerical simulator. In this example, it is

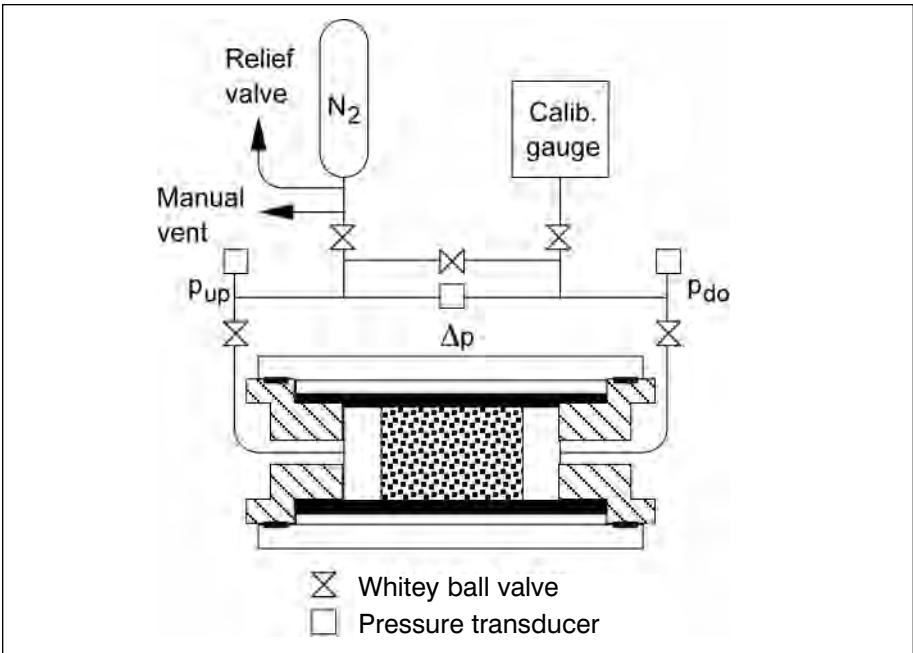


Figure 5-17. Schematic of gas-pressure-pulse-decay apparatus.

sufficient to consider single-phase gas flow. In porous media with very low permeability and porosity, the mass flux F [$\text{kg s}^{-1} \text{m}^{-2}$] of gas may be enhanced as a result of slip flow known as the Klinkenberg effect:

$$F = -k \left(1 + \frac{b}{p} \right) \frac{\rho}{\mu} \nabla p \quad (5.63)$$

Here, k is the absolute permeability (m^2), ρ is the density (kg m^{-3}), μ is the dynamic viscosity (Pa s), and p is the gas pressure (Pa). The term in parentheses accounts for enhanced gas slip flow, which becomes relevant at low pressures and in small pores, when a significant fraction of molecular collisions is with the pore wall rather than with other gas molecules. In equation (5.63), b (Pa) is the Klinkenberg slip factor, which is a characteristic of both the geometry of the pore space and the thermophysical properties of the gas. It is directly proportional to the mean free path of the molecules (Klinkenberg 1941). This flow equation and the appropriate equations-of-state enter the mass- and energy-balance equations solved by an appropriate numerical simulator. Furthermore, the gas reservoirs and the core are discretized as a one-dimensional flow problem, and the initial pressure in the model is set to the first measured pressure value.

2. The parameters to be estimated are the porosity ϕ , the absolute permeability k (m^2), and the Klinkenberg slip factor b (Pa). Since both k and b are expected to vary over many orders of magnitude, we will estimate the logarithm of these two parameters. The parameter vector is therefore given by $p^T = [\phi, \log(k), \log(b)]$.
3. Based on estimates from similar models, the initial parameter values are chosen to be $\phi=0.015$, $\log(k)=-19.0$, and $\log(b)=7.0$.
4. Observations available for model calibration are the pressure data in the upstream and downstream gas reservoir. It is obvious from equation (5.63) that the absolute permeability and the Klinkenberg slip factor are strongly correlated if the average pressure in the sample remains constant. Therefore, three experiments performed on the same core but at three different pressure levels are inverted jointly to allow for an independent estimation of k and b .

We select 30 calibration points in time, logarithmically spaced between 100 and 68,600 seconds.

5. We assume that the measurement errors of the pressure data are uncorrelated and on the order of $\sigma_{zi} = \sigma_{zi} = 1000 \text{ Pa}$, $i = 1, \dots, m$.
6. The experiment is simulated using the numerical model TOUGH2 (Pruess 1987 1991a). The initial pressures in the upstream reservoirs of the three experiments are set to about 300 kPa above the respective initial pressures in the core. The dash-dotted lines in Figure 5-18 show the pressure in the upstream and downstream reservoirs through time as calculated with the initial parameter set.
7. The difference between the model calculation and the data at the calibration points is measured by the objective function. The standard least-squares objective function is chosen here; that is,

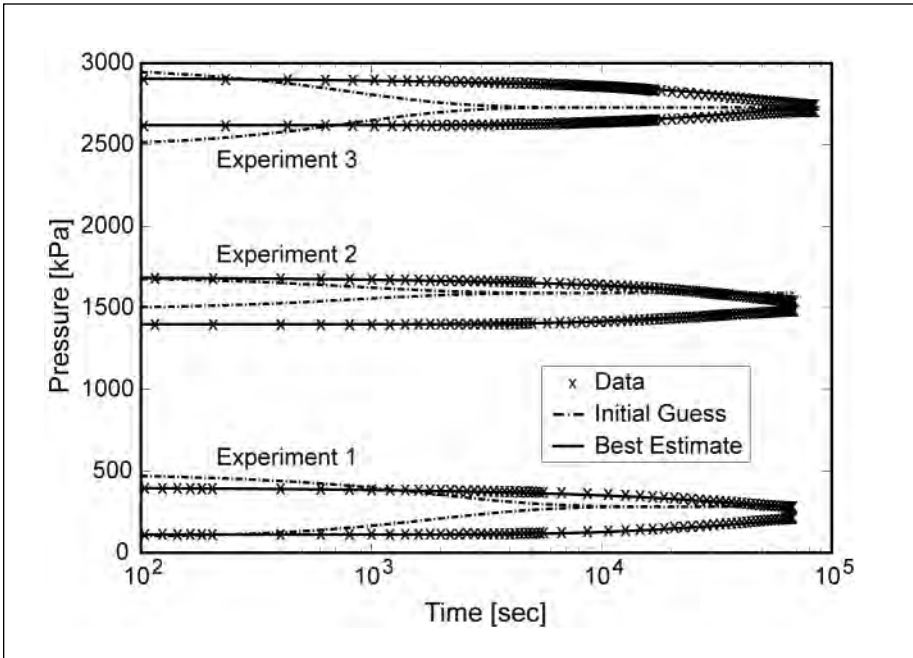


Figure 5-18. Comparison between measured and calculated pressure transients with the initial and final parameter sets.

the measure-of-misfit is the sum of the squared residuals, weighted by the inverse of the assumed measurement error.

8. The Levenberg-Marquardt minimization algorithm (see the subsection “Minimization Algorithm”) is used to propose new parameter sets that iteratively reduce the value of the objective function. The Levenberg-Marquardt algorithm requires evaluating the sensitivity of the calculated pressures z_j with respect to the parameters p_i , providing the search direction in the n -dimensional parameter space.
9. If a certain convergence criterion is met (here, the maximum number of unsuccessful uphill steps was reached), go to Step 10, otherwise repeat Steps 6 through 8 with the updated parameter vector. The fit obtained after 7 iterations is shown in Figure 5-18 (solid lines), matching the observed data (symbols) reasonably well.
10. The error analysis reveals, however, that the standard mean error is larger than the expected mean residual of 1000 Pa. The reason for the unsatisfactory match is a systematic error (a leak in the measuring apparatus and inappropriate initial conditions), which could be interpreted as either a data error (the data are corrupted as a result of leakage) or an error in the conceptual model (leakage was not simulated). The inconsistency between data and model becomes apparent when examining the residual plot shown in Figure 5-19. Given this result, the estimated parameters are likely to be biased despite a relatively small estimation uncertainty. These difficulties are resolved by parameterization of the systematic errors as discussed in Finsterle and Persoff (1997).

The example illustrates the process and main elements of inverse modeling, which will be discussed in detail in the following sections. The example also demonstrates the importance of a formalized approach and of the error analysis, which identified weaknesses in the data and the conceptual model.

METHODOLOGY

References

The basic concept of estimating parameters by matching the model to observations dates back to Carl Friedrich Gauss, who introduced the

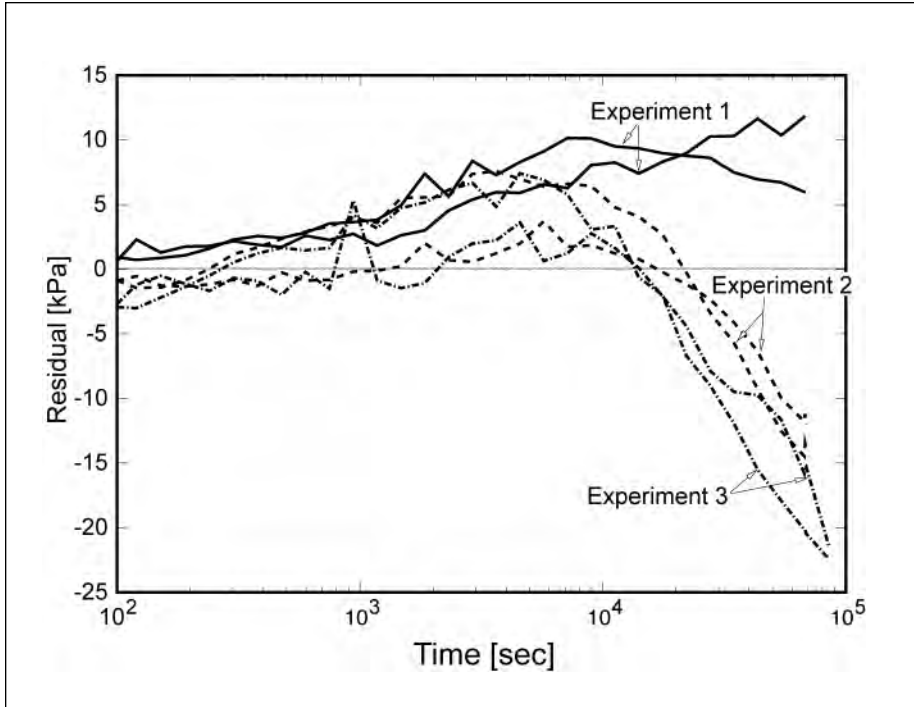


Figure 5-19. Residuals as a function of time, showing systematic overprediction of pressures at late times for Experiments 2 and 3.

method of least squares for the analysis of astronomical and geodetic data during the last decade of the eighteenth century (Gauss 1821). Gauss made contributions to all aspects of parameter estimation, providing a detailed discussion of measurement errors, a probabilistic justification of the least-squares objective function, advances in computational methods (Gaussian elimination), and an analysis of estimation uncertainty. While the algorithms for identifying the minimum of the objective function have been continually refined, the basic idea, as well as the difficulties associated with solving the inverse problem, remain essentially the same.

The theory of inverse modeling is described in a variety of textbooks for applied mathematics and mathematical statistics (see, for example, Beck and Arnold 1977; Bickel and Doksum 1977; Gill *et al.* 1981; Scales 1985; Larsen and Marx 1986; Van Huffel and Vandewalle 1991;

Stengel 1994; and Björck 1996). Many of these textbooks focus on a discussion of optimality conditions for specific types of functions and constraints. In groundwater and multiphase flow modeling, the model output is usually a highly nonlinear, complex function of the parameters, which are constrained by simple physical bounds. A theoretical analysis of the objective function's convexity is not feasible for numerically calculated model output. Practical aspects of how to formulate the inverse problem, and how to identify the minimum of the objective function, are of primary interest to the hydrogeologist. Good introductions from a general, practical perspective are given by Beck and Arnold 1977, Gill *et al.* (1981), and Scales (1985). A concise description of certain aspects of inverse modeling can also be found in Press *et al.* (1992).

A large number of research papers and books discuss the concept of inverse modeling in the context of hydrogeology. They are summarized and reviewed by Neuman (1973), Yeh (1986), Kool *et al.* (1987), Carrera (1988), Ewing and Lin (1991), Sun (1994), and McLaughlin and Townley (1996). The reader is also referred to special issues of *Advances in Water Resources* (Volume 14, Numbers 2 and 5, 1991), in which different inverse modeling approaches have been presented. The approach discussed here follows that described in the classic series of papers by Carrera and Neuman (1986a, b, c).

A large number of computer codes solving inverse and optimization problems have been developed in the mathematical sciences (see, for example, Moré and Wright 1993 and <http://wwwfp.mcs.anl.gov/otc/Guide/SoftwareGuide>). Specialized codes for applications in hydrogeology mainly deal with automatic well-test analysis and the inversion of pressure head and tracer data. All of these codes are based on flow and transport simulations in the saturated zone. To our knowledge, only a few inverse modeling codes have been developed that are capable of dealing with complex, nonisothermal multiphase flow problems. The program ONE-STEP (Kool *et al.* 1985) and its modifications by van Dam *et al.* (1990) and Eching and Hopmans (1993) specifically address the estimation of soil hydraulic parameters from one- and multi-step outflow experiments.

The HYDRUS software (Simunek *et al.* 1998; <http://www.mines.edu/igwmc/software/igwmcsoft/hydrus1d.htm>;) can be used to estimate parameters of hysteretic retention and hydraulic conductivity functions, as well as solute transport parameters, from unsaturated flow and con-

centration data. The iTOUGH2 code (Finsterle 1999a, b, c; <http://www.esd.lbl.gov/iTOUGH2>) allows estimation of any input parameter to the multiphase flow simulator TOUGH2 (Pruess 1987; 1991a). Note that any forward model can be linked to a general, model-independent, nonlinear, parameter-estimation package such as PEST (Watermark Computing 1994; <http://www.ozemail.com.au/~wcomp>) or UCODE (Poeter and Hill 1998, <http://www.mines.edu/igwmc/software/igwmcsoft/ucode.htm>) or to any commercially available optimization package, thus providing inverse modeling capabilities with various degrees of flexibility.

The case study “Inverse Estimation of Unsaturated Soil Hydraulic and Solute Transport Parameters Using the Hydrus-1D Code,” by Jirka Simunek and Martinus van Genuchten, describes experiments using a parameter estimation procedure for measuring unsaturated hydraulic conductivity. *See page 815.*



Parameterization

As the term “parameter estimation” implies, inverse modeling deals with a *parameterized* form of the natural system; certain aspects of the system are lumped together and represented by averaged properties. A number of questions arise, including how the continuous, heterogeneous formation can be characterized using a finite number of parameters, what the attainable spatial resolution would be, and which parameters should be subjected to inversion given a certain set of calibration data. These questions must be addressed during the development of the conceptual model (see “Development of Site-specific Models,” above).

The parameter vector p of length n contains those input parameters of a numerical flow and transport model that are to be estimated by inverse modeling. These parameters may represent hydrogeologic characteristics (such as permeabilities, porosities, any parameter of the capillary pressure or relative permeability function, adsorption coefficients, or dispersivities), thermal properties (for example, thermal conductivity or specific heat), initial or boundary conditions (such as initial NAPL saturation or infiltration rate), and all aspects of the model that can be parameterized (for example, fracture spacing or unmodeled data trend). Note that for a heterogeneous aquifer with properties continuously varying in

space, the dimension of the parameter vector is theoretically infinite. In practice, however, the spatial variables, as well as the continuous partial differential equations, are discretized with constant properties for each gridblock. Furthermore, multiple gridblocks can be assigned to specific subregions of the model domain, which are characterized by constant parameter values, further reducing the number of parameters to be estimated. This process is referred to as “zonation.” Finally, heterogeneity can be described by geostatistical methods, in which the spatial variability is characterized by a relatively small number of geostatistical parameters (for example, parameters of a variogram, values at pilot points, attractor parameters). For a review of geostatistically based inverse methods, see Zimmerman *et al.* (1998).

The reduction of the number of parameters from infinity to a finite value n is called “parameterization” (Yeh 1986). Physical processes, such as leaks in an experimental apparatus or time-varying boundary conditions, can also be subjected to parameterization by describing them with a coefficient or a function, making these processes accessible to estimation. Parameters are sometimes transformed to reduce the nonlinearity of the inverse problem, to eliminate constraints, or to reflect certain distributional assumptions. The most frequently applied transformation is taking the logarithm of a parameter. This can make the inverse problem more linear (see, for example, Carrera and Neuman 1986c), prevents the parameter from becoming negative, and produces a lognormal distribution of the parameter’s uncertainty.

There is often some independent, prior information available about the parameters to be estimated. Prior information, such as “directly” measured parameter values, can be included in the analysis to regularize the inverse problem and to constrain the estimates (Carrera and Neuman 1986a, Chavent 1991, Vasco *et al.* 1997, Neumaier 1998). Differences between measured parameter values and the corresponding estimates are treated in the same manner as the differences between the observed and calculated system states.

The use of prior information as a means to regularize the inverse problem is convenient. However, it may also be misleading, because it suggests that the inverse problem is well posed despite the fact that the data available for calibration contain a finite amount of information about the parameters to be estimated. If data are insufficient and lead to an ill-posed inverse problem, it can be almost always turned into a well-

posed problem by regularization. This means, however, that new information must be added, such as a smoothing criterion (Vasco *et al.* 1997), an arbitrary conditioning matrix (Kuczera and Mroczkowski 1998), or prior parameter information (Carrera and Neuman 1986a). In geophysical tomographic inversions, it is common practice to supplement the observed data with additional information, usually a smoothing criterion. These inversions are further stabilized by artificially reducing the dimension of the parameter space based on measures that evaluate the relative independence of each parameter. Such rank reduction methods are described, for example, in Parker (1994). While these regularization techniques eventually produce high-resolution images of the subsurface, it is important to know how much information is drawn from the actual data and to what degree the results are influenced by external information and mathematically imposed constraints. In other words, regularization sometimes masks the fact that the original data do not contain enough information for parameter estimation. Moreover, the prior information value must be conceptually consistent with the value determined from the observations of the system response to avoid biased estimation. For example, if the permeability measured on a laboratory core is used as prior information in an inversion of a regional flow model, the difference in scale may compromise the solution. The use of prior information is only reasonable if it is an integral, well-understood part of the overall calibration strategy. In the following sections, we consider the classical, overdetermined, well-posed inverse problem, in which relatively many data points are available to estimate a relatively small number of parameters.

A common pitfall of inverse modeling is overparameterization—that is, the attempt to estimate a large number of parameters based on limited data of insufficient sensitivity. Overparameterization is enticing, because adding more parameters to the vector of unknowns always leads to an improvement of the fit. However, overparameterization and the apparently better reproduction of data comes at the expense of increased estimation uncertainty, and thus reduced accuracy of subsequent model predictions. The error analysis described in the subsection “Uncertainty of Estimated Parameters,” below, and some of the model identification criteria mentioned in the subsection “Objective Function,” below, detail warning signs of overparameterization.

Obtaining meaningful estimates is only possible if enough data of good quality are available, and if the model output at the calibration points is sufficiently sensitive to changes in the parameters. Furthermore, the parameters must not be strongly correlated. Finally, it is important to realize that vector p contains only those parameters that will be subjected to the estimation process. All the other parameters specified in a numerical model are fixed and thus become part of the model structure. Because of inherent correlations between the fixed and the variable parameters, the best-estimate parameter set depends on the chosen values of the fixed parameters as well as the general features of the conceptual model. Once again, the parameters are strictly model-related and may have to be changed for applications that are based on a different model structure.

Observations and Residuals

Parameters are estimated by matching the model output to data measured in the laboratory or field. The observation vector $\mathbf{z}$ of length m contains the calibration points. Calibration points consist of observable variables at discrete points in space and time at which data are available, such as steady-state or time-dependent measurements of pressure, temperature, saturation, flow rate, or concentration. While the true system response is continuous in space and time, and described by an infinite number of variables, measurements are sparse, limiting the amount of information available for inverse modeling.

The spatial and temporal distribution of calibration points has an impact on the inverse modeling results. For example, selecting logarithmically spaced calibration times to match data from a transient test puts more weight on the early-time data relative to the late-time data, possibly affecting the support scale, and thus the nature of the parameter to be estimated. Similarly, a high data density in one area of the model emphasizes the corresponding subsystem, potentially compromising the match to data from an adjacent, less-densely sampled region.

Complementary to the observed values at the calibration points are the simulation results, which depend on the input parameters to be estimated. An observable variable qualifies as a calibration point only if it is sufficiently sensitive to changes in the parameters to be estimated. High sensitivity is a necessary, albeit not sufficient, requirement for

accurate parameter estimation, as is discussed in detail by Finsterle and Persoff (1997).

The residual vector r of length m contains the differences between the measured and calculated system response; its elements are given by

$$r_i = z_i^* - z_i \quad i = 1, \dots, m \quad (5.64)$$

In inverse modeling, parameters are estimated by minimizing some measure of misfit, the objective function (see the subsection “Objective Function,” below). Since the residuals determine the misfit criterion, it is crucial that the measurements z^* and the corresponding model output z represent the same physical entity. Any conceptual difference between the measured value and its representation in the numerical model necessarily leads to a bias in the estimated parameters.

Many reasons exist for a potential inconsistency between the measured and calculated values. For example, the support scale or averaging volume of a certain measurement may be significantly smaller than the size of the gridblock used in the numerical model. Drawdown measurements in a pumping well can only be directly compared with gridblock pressures if the well is fully discretized in the model. Downhole pressures or fractional flows at the head of a geothermal well may be different from the vertically averaged values calculated in a two-dimensional model of the reservoir. Relative pressure measurements may be influenced by atmospheric pressure fluctuations. If these effects are not properly accounted for, the parameters are moved away from their most likely estimates in an attempt to partly compensate for these systematic errors.

Maintaining conceptual consistency between the measured and simulated quantities is a difficult task and a major source of errors. If the two variables are conceptually different, appropriate compensation or correction must be made either in the numerical model (for example, by discretizing the well, or even the measuring device, or by accurate simulation of all factors that affect the measurements) or by preprocessing the data (by such means as appropriate averaging, interpolation, compensation for temperature effects; or removal of shifts and trends in the data). Examining the relative convenience or difficulty of each task, the analyst has the choice to either refine the model or reprocess the data. For instance, in the example discussed in the subsection “Introductory Example,” above, it was much easier to incorporate leakage into the

model than to seal the apparatus and rerun the experiment. The unwanted trend in the residuals (see Figure 5-19) was successfully removed by reanalyzing the data using a refined model (for more details, see Finsterle and Persoff 1997). In many cases, however, both the model and the measurements must be adjusted to ensure consistency between the two.

The Stochastic Model

The stochastic model deals with the statistical assumptions about the measurement errors and residuals. We start with a discussion of the fundamental difference between random and systematic errors. The residuals can be represented by a statistical model of the form

$$r_i = z_i^* - z_i(\hat{\mathbf{p}}) = e_{mi} + e_{di} = (b_m + \varepsilon_m)_i + (b_d + \varepsilon_d)_i \quad (5.65)$$

According to this equation, residual i is the sum of the error in the model, $e_{mi} = \tilde{z}_i - z_i(\hat{\mathbf{p}})$, and the error in the data, $e_{di} = z_i^* - \tilde{z}_i$, where $\tilde{z}_i$ is the true value. Both modeling error and data error have a systematic component b_i and a random component ε_i .

Consider a data set that is drawn from a true, but unknown system response (see Figure 5-20). The individual measurement error is defined as the difference between the measured and the true value. The modeling error is defined as the difference between the true and the calculated value. Since the true system response is unknown, neither the measurement error nor the modeling error is known—only the residual

$$r = e_d + e_m = (z^* - \tilde{z}) - (\tilde{z} - z(\hat{\mathbf{p}})) = z^* - z(\hat{\mathbf{p}}) \quad (5.66)$$

can be calculated. However, the errors may be described in statistical terms, implying that they are random following a certain distribution. Recall that estimating parameters by history matching is based on the assumption that the calculated system response is as close to the true system response as possible, the latter being represented by a set of noisy data points. If the true values are identified, the residuals are, by definition, equal to the measurement errors. In other words, the statistical characteristics of the residuals should be identical or at least similar to those of the measurement errors. Inverse modeling makes the implicit assumption that the final residuals are error terms; that is, they are random variables following a certain distribution, devoid of systematic

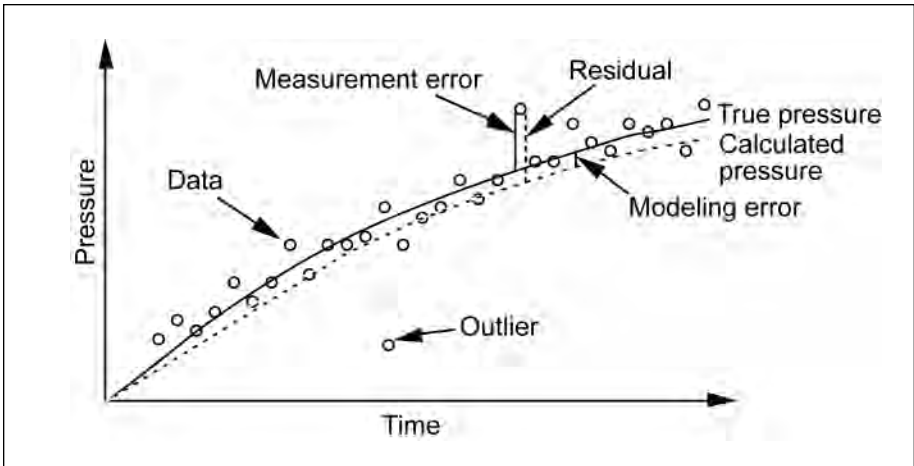


Figure 5-20. True, measured, and calculated system response, and definition of residual, measurement, and modeling error.

trends. The stochastic model can be considered the *a priori* assumption about the randomness of the final residuals.

If systematic errors are present—either as a result of a flaw in the conceptual model or data errors—the estimated parameter set will be biased, because the parameters are corrupted during the inversion to compensate for the systematic errors. Trends in the final residuals are a clear indication that the conceptual model must be further refined. In general, systematic errors must be removed from both the data and the model, so that the final residuals contain only random components that can be described by the stochastic model. A careful residual analysis must be conducted to identify potential trends in the final residuals as well as outliers.

In the absence of systematic errors, the distribution of the final residuals is supposed to be consistent with the distribution of the measurement errors. A reasonable assumption about the measurement errors is that they are uncorrelated, normally distributed random variables with zero mean. The *a posteriori* residual analysis will have to show that this assumption is justified. The *a priori* distributional assumption about the residuals can therefore be summarized in a covariance matrix C_{zz} , which is an $m \times m$ diagonal matrix. The j -th diagonal element is the variance

that represents the measurement error of observation z_i^* . The purpose of the elements of C_{zz} are manifold:

- They scale data of different quality; that is, an accurate measurement obtains a higher weight in the inversion than a poor or highly uncertain measurement.
- They scale observations of different types. For example, flow rates and pressures have different units and their values differ by many orders of magnitude. They need to be scaled appropriately to be comparable in a formalized parameter estimation procedure.
- They weigh the fitting error.
- C_{zz} is the stochastic model for maximum-likelihood estimation for normally distributed residuals.

One should realize that only the ratios $\sigma_{zi}^2/\sigma_{zj}^2$ are important for parameter estimation; the estimated parameter set is not affected by a linear scaling of the covariance matrix.

Objective Function

The purpose of the objective function—also termed the performance measure, penalty function, energy function, cost function, or misfit criterion—is to provide an integral measure of misfit between the model and the data; that is, a parameter set that reduces the value of the objective function is considered superior to those with higher values. The best-estimate parameter set minimizes the objective function.

There are many ways to measure the difference between the observed and calculated system response. In the standard procedure of trial-and-error calibration, the simulation results and data are plotted, and a rather subjective judgment is made as to how well the model output matches the data. A more objective way is to calculate a norm of the residual vector. The most commonly used norm is the Euclidean norm, equivalent to the least-squares estimator.

The choice of an appropriate objective function should be based on the properties of the residuals themselves. The maximum likelihood approach takes the distribution of the measurement errors as a basis for choosing the objective function. The central limit theorem leads to the

assumption that the residuals are normally distributed, making least squares a reasonable choice. It is straightforward to show (see, for example, Carrera and Neuman 1986a) that minimizing the least-squares objective function

$$S = (z^* - z(p))^T C_{zz}^{-1} (z^* - z(p)) = \sum_{i=1}^m \frac{r_i^2}{\sigma_{z_i}^2} \quad (5.67)$$

yields maximum-likelihood estimates for normally distributed residuals. The normality assumption is also made to facilitate statistical analysis of results.

Groundwater inverse modeling relies almost exclusively on least-squares methods (McLaughlin and Townley 1996). However, the distribution of the residuals often deviates from being Gaussian. For example, the presence of outliers in the data or systematic modeling errors lead to nonsymmetrical distributions, which often exhibit stronger tails than those predicted by the normal distribution. For these cases, alternative objective functions may be more appropriate to avoid biased estimates. These so-called robust estimators are discussed, for example, by Andrews *et al.* (1972), Huber (1981), Press *et al.* (1992), and Finsterle and Najita (1998).

The objective function is a hypersurface in the n -dimensional parameter space. It may be convex or exhibit multiple local minima. It may be close to quadratic or highly nonlinear, and it may be continuous or discontinuous, differentiable or not differentiable, smooth or rough. All these properties affect the efficiency of the minimization algorithm, and—more importantly—the quality of the solution, its stability, and the well-posedness of the inverse problem. Figure 5-21 is a visualization of the objective function S for $n = 2$. While generally of complex shape, the objective function near the global minimum is usually close to parabolic (leading to elliptical contour lines), because the standard function is a sum of squares. The second-order methods for identifying the minimum (see the subsection “Minimization Algorithm,” below) take advantage of this specific property of the objective function.

An ill-posed inverse problem exhibits level plains, long narrow valleys, or ridge lines where the minimum is poorly defined, if at all. The topology of the objective function indicates whether an inverse problem is wellposed or illposed. For example, multiple parameter combinations with S values close to that obtained at the global minimum indicate

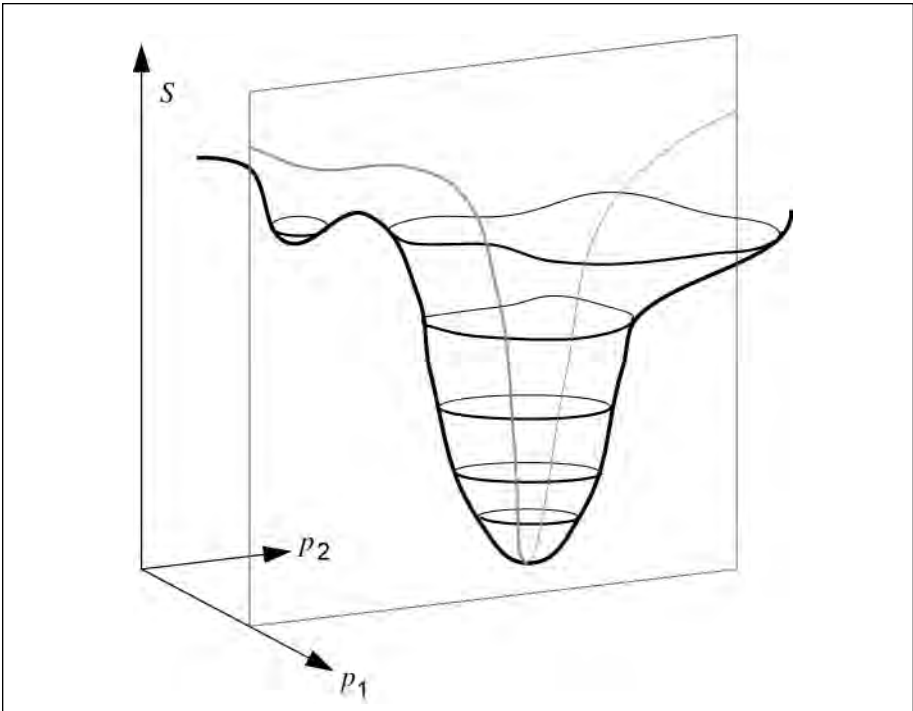


Figure 5-21. Objective function in two-dimensional parameter space.

nonuniqueness (the presence of local minima does *not* constitute nonuniqueness). Furthermore, the estimation uncertainty is related to the convexity of the objective function near the minimum, as will be discussed in detail in the section “Error and Uncertainty Analysis,” below.

Minimization Algorithm

The purpose of the minimization algorithm is to find the minimum of the objective function by iteratively updating the parameters of the model. The objective function is a global measure of misfit between the data and the corresponding model output. Since the model output $z(p)$ depends on the parameters, the fit can be improved by changing the elements of the parameter vector p . The search for the minimum occurs in the n -dimensional parameter space. A number of strategies were developed to find parameter combinations that reduce the value of the

objective function. We classify the methods according to whether they are based on a sequence of forward simulations only or whether they require calculation of the gradient or second-order derivatives. With the exception of simulated annealing, all methods described below identify only a local minimum in the vicinity of the starting point.

Non-Derivative Method

In these methods, the model is evaluated for different parameter combinations, mapping out the objective function in the n -dimensional parameter space. They are also referred to as “Function Comparison Methods.” Because no derivatives of the objective function, with respect to the parameters, need to be calculated, these methods are not restricted to smooth models. However, they usually require many trial simulations and are therefore inefficient. Examples of such direct search methods include:

- Trial and error
- Grid search
- Downhill simplex
- Simulated annealing
- Genetic algorithms

Gradient-Based Methods

These methods require calculating the gradient of the objective function with respect to the parameter vector. Updating the parameter vector in small steps along the search direction determined by the gradient is a robust, albeit inefficient, procedure. Various modifications of this basic scheme have been proposed. They differ in the choice of an appropriate step length. Efficient ways of calculating the gradient have been described in the literature (Carrera and Neuman 1986b, Sun and Yeh 1990, Vasco and Datta-Gupta 1999). Examples of gradient-based methods include:

- Steepest descent
- Quasi-Newton methods
- Conjugate gradient methods

Second Derivative Methods

These methods are based on the Hessian matrix or various approximations thereof (quasi-linearization). They perform well for nearly linear least-squares problems. The computational cost for calculating the second derivatives is usually compensated by an efficient stepping in the parameter space. Examples of second-order methods include:

- Newton method
- Gauss-Newton method
- Levenberg-Marquardt method

All methods presented here are iterative; that is, they start with an initial parameter set, and an update vector is calculated at each iteration. A step is successful if the new parameter set at iteration $(k+1)$

$$p_{k+1} = p_k + \Delta p_k \quad (5.68)$$

leads to a reduction in the objective function as

$$S(p_{k+1}) < S(p_k) \quad (5.69)$$

The algorithms described in the literature—each having its advantages and disadvantages—differ in the way they calculate Δp_k . Many gradient-based or second-order methods are modifications of the Gauss-Newton algorithm for nonlinear least-squares optimization, which is briefly discussed here. For details about the other minimization algorithms, the reader is referred to the literature.

In the Gauss-Newton method, the objective function is approximated by a quadratic function as illustrated for two parameters in Figure 5-22. By setting the derivatives to zero, the Gauss-Newton step at iteration k can be derived to yield

$$\Delta p_k = \left(J_k^T C_{zz}^{-1} J_k \right)^{-1} J_k^T C_{zz}^{-1} r_k \quad (5.70)$$

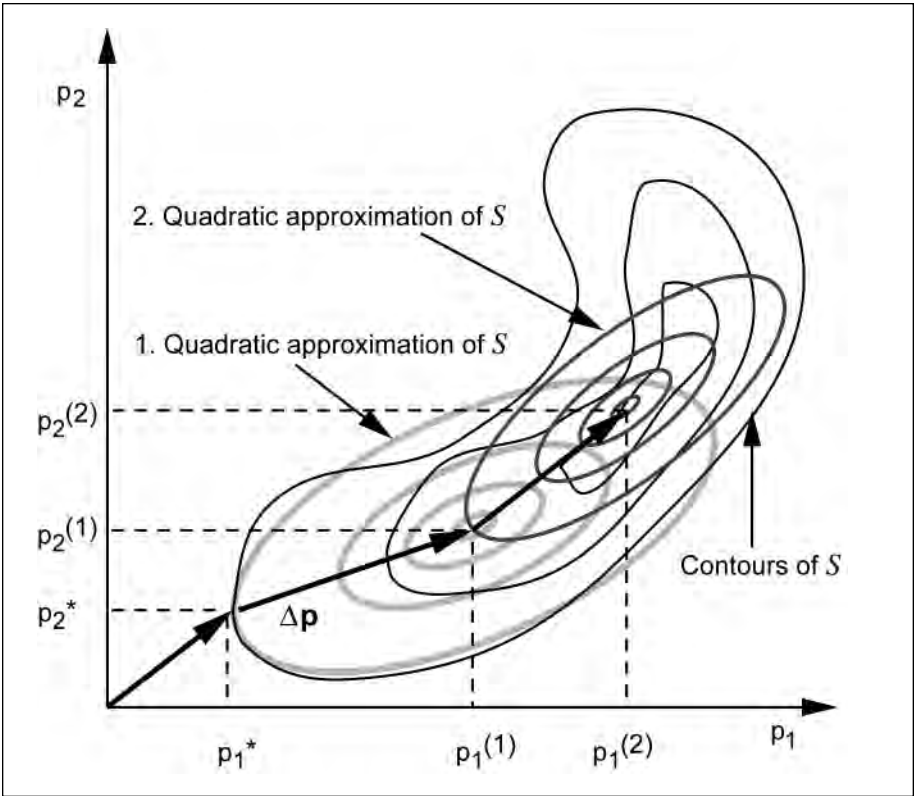


Figure 5-22. Objective function of a linearized least-squares problem as a function of two parameters. Two Gauss-Newton steps are also shown.

with the Jacobian or sensitivity matrix defined as

$$J = -\frac{\partial \mathbf{r}}{\partial \mathbf{p}} = \frac{\partial \mathbf{z}}{\partial \mathbf{p}} = \begin{bmatrix} \frac{\partial z_1}{\partial p_1} & \cdots & \frac{\partial z_1}{\partial p_n} \\ \vdots & & \vdots \\ \frac{\partial z_m}{\partial p_1} & \cdots & \frac{\partial z_m}{\partial p_n} \end{bmatrix} \quad (5.71)$$

Note that there are several methods for calculating the elements of the sensitivity coefficients, including (1) the Influence Coefficient or Perturbation Method, (2) the Sensitivity Equation or Direct Derivative Method, and (3) the Variational Method (Yeh 1986, Carrera 1988).

The Gauss-Newton step (see equation [5.70]) is the solution of the linear least-squares problem. For nonlinear models, the parameter vector is iteratively updated, and a new Gauss-Newton direction is calculated.

The performance of four different minimization algorithms is compared in Figure 5-23, which shows the contours of the objective

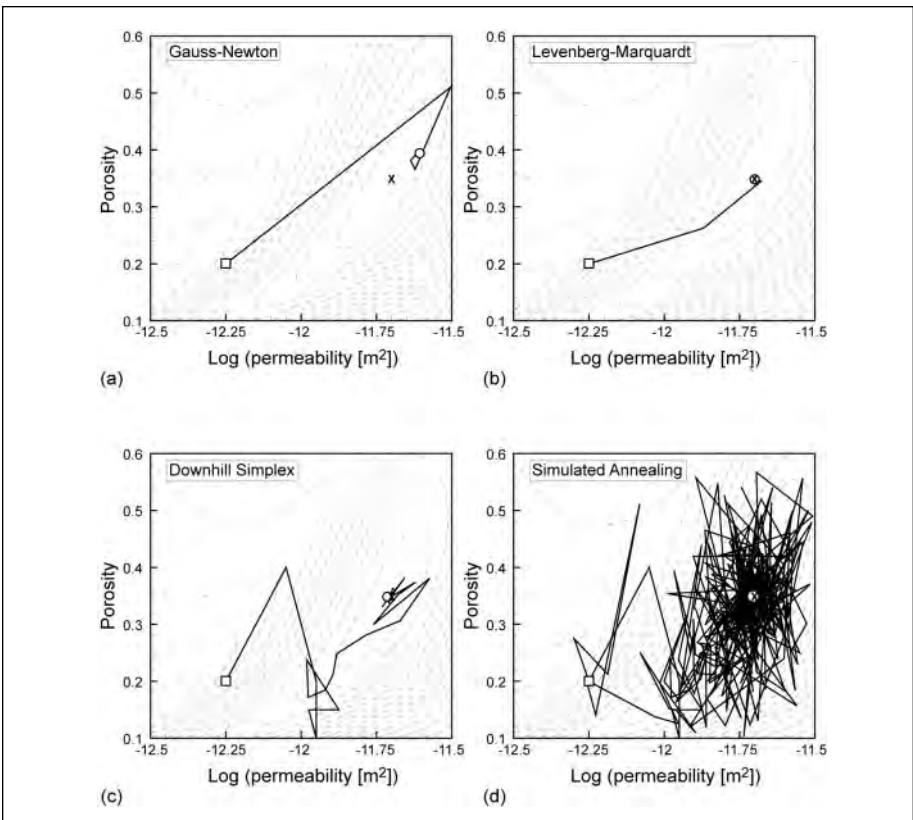


Figure 5-23. Solution paths of (a) Gauss-Newton, (b) Levenberg-Marquardt, (c) Downhill Simplex, and (d) Simulated Annealing minimization algorithms in the two-dimensional parameter space porosity-log(permeability). The square, circle, and cross indicate, respectively, the starting point, endpoint, and global minimum.

function—the byproduct of a grid search—and the respective solution paths taken in the two-dimensional parameter space. The inverse problem solved in the example is described in Finsterle (1999c), with the search area confined to the region shown in the figure. With the exception of the Gauss-Newton algorithm, which is misguided by its linearity assumption, the global minimum is accurately identified by all algorithms. The Levenberg-Marquardt algorithm is the most efficient method for this problem. Notice that the strategy underlying each method is clearly revealed by the solution path taken.

ERROR AND UNCERTAINTY ANALYSIS

Why Error Analysis

One of the key advantages of a formalized approach to parameter estimation is the possibility of performing an *a posteriori* error analysis. The sensitivity matrix (5.71) contains useful information regarding the impact of the parameters on the system behavior and how valuable certain data were for the solution of the inverse problem at hand. The residual analysis provides some measure of the overall goodness-of-fit and identifies systematic errors, trends in the model, or outliers in the data. Next, we can determine the estimation error or uncertainty of the parameters. Note that a good match does not necessarily mean that the estimates are reasonable. They may be highly uncertain as a result of high parameter correlation, which is usually an indication of overparameterization. The covariance matrix of the estimated parameters can be further analyzed to obtain correlation coefficients and parameter combinations that lead to similar matches. Model identification criteria provide a measure that can be used to compare the performance of alternative models with a different model structure. Finally, the uncertainty of model predictions can be calculated using either linear error propagation analysis or Monte Carlo simulations.

Sensitivity Analysis

The sensitivity coefficients of the sensitivity matrix (5.71) show the impact of a small parameter change on the calculated system behavior at the calibration points. They can also be interpreted as a measure of the relative contribution of the corresponding data point to the solution of

the inverse problem. As equation (5.74) below reveals, the higher the absolute value of the sensitivity coefficient, the lower the estimation uncertainty of the corresponding parameter. High sensitivity is a necessary but not sufficient condition for meaningful parameter estimation.

In order to make sensitivity coefficients comparable with one another, it is advantageous to scale them by the *a priori* standard deviation of the observation, σ_z , and the expected parameter variation, σ_p :

$$\tilde{J}_{ij} = J_{ij} \frac{\sigma_{p_j}}{\sigma_{z_i}} = \frac{\partial z_i}{\partial p_j} \cdot \frac{\sigma_{p_j}}{\sigma_{z_i}} \quad (5.72)$$

where J_{ij} is an element of the Jacobian matrix, equation (5.71). The scaling is necessary because the parameters concurrently estimated by inverse modeling usually have different units and may vary by orders of magnitude. The same is true for the different observation types used for calibration. Unlike J_{ij} , the scaled sensitivity coefficients $\tilde{J}_{ij}$ are dimensionless, which allows one to directly compare the contribution of each data point to the estimation of each parameter and to evaluate a number of composite sensitivity measures. The use of such sensitivity measures to design a laboratory experiment is described in Finsterle and Faybishenko (1999).

Residual Analysis

Minimizing the objective function leads to the best-estimate parameter set for a given functional and stochastic model. Unfortunately, this does not imply that the real system is properly represented by the model. If the conceptual model fails to reproduce the salient features of the system, the calibrated model may not be able to match the observed data as expected, where the expectation regarding the attainable fit is reflected in the *a priori* covariance matrix C_{zz} . A first and rather crude assessment of the match is the *a posteriori* or estimated error variance, which represents the variance of the mean weighted residual and is thus a measure of goodness-of-fit (Larsen and Marx 1986):

$$s_0^2 = \frac{r^T C_{zz}^{-1} r}{m - n} \quad (5.73)$$

If the model does not match the data sufficiently well—that is, s_0^2 is significantly larger than one—then the estimated parameters are meaningless, because the underlying model is erroneous. An inspection or statistical analysis of the residuals may point towards aspects of the model that need to be modified. Specifically, one should look for non-random patterns in the residuals, which indicate a systematic error or oversimplified model structure. For example, the residual plot shown in Figure 5-19 clearly indicates a systematic error that is time dependent; it is easily identified as a gas leak in the experimental apparatus and corrected by appropriate parameterization as discussed in Finsterle and Persoff (1997). In addition, large residuals (outliers) may be detected, which have a potentially negative impact on the estimates.

Uncertainty of Estimated Parameters

Under the assumption of normality and linearity, the covariance matrix of the estimated parameters is asymptotically given by the inverse of the curvature matrix $J^T C_{zz}^{-1} J$ multiplied by the estimated error variance s_0^2 :

$$C_{pp} = s_0^2 (J^T C_{zz}^{-1} J)^{-1} \quad (5.74)$$

Figure 5-24 shows how the ellipsoidal confidence region of the covariance matrix approximates the contours of the objective function at level $S(\hat{p}) + s_0^2 n F_{n, m-n, 1-\alpha}$. This means that the estimation uncertainty can be related to the convexity of the objective function at the minimum (Donaldson and Schnabel 1987).

The diagonal elements of C_{pp} contain the variances of the estimated parameters, σ_p^2 . They are a measure of parameter uncertainty, given the uncertainty of all the other concurrently estimated parameters. Note that they are directly proportional to the overall goodness-of-fit expressed by s_0^2 and uncertainty is inversely proportional to the absolute size of the sensitivity coefficients. Since the sensitivity coefficients can be evaluated without actually collecting data, the design of an experiment can be optimized *a priori* by looking for observation types and measurement points that yield large sensitivity coefficients.

The off-diagonal elements of C_{pp} can easily be transformed into statistical correlation coefficients. If correlations exist, the uncertainty of one parameter does affect the uncertainty of the other parameter. If two

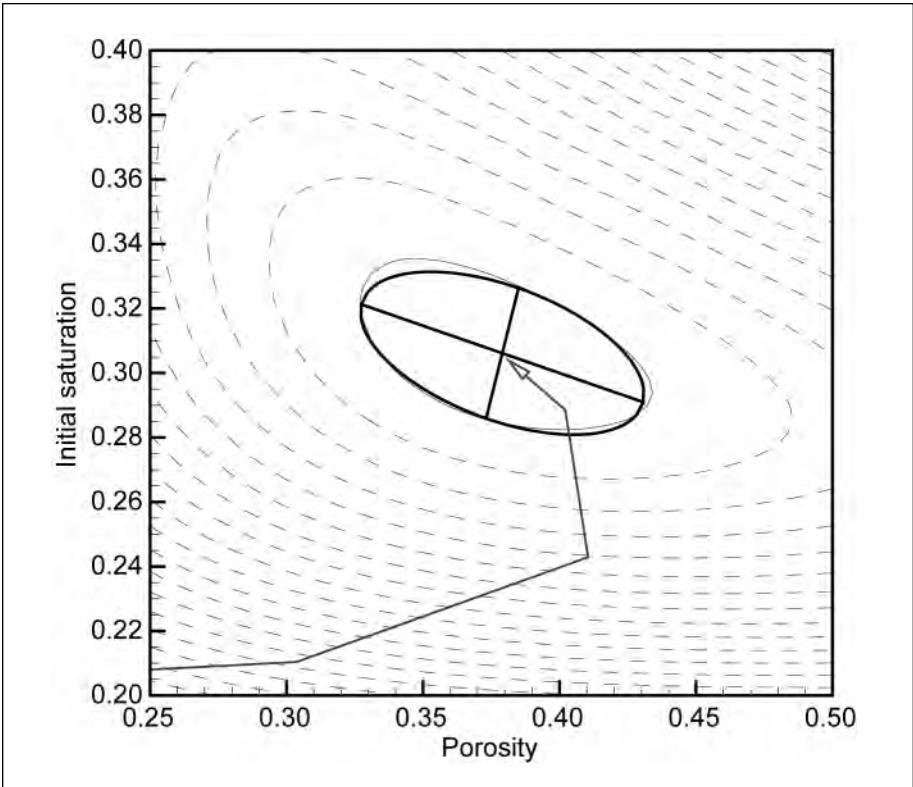


Figure 5-24. The ellipse approximates the contours of the objective function (dashed) at the minimum. The solid contour represents the actual confidence region. The arrow indicates the solution path taken by the minimization algorithm.

parameters are positively (negatively) correlated, a similar system response is obtained by increasing one and concurrently decreasing the other parameter. For example, a similar tracer breakthrough is obtained by decreasing both permeability and porosity, making the two parameters positively correlated when estimated from tracer data. However, if estimated from pressure data collected during a slug test, the two parameters are negatively correlated since the pressure declines faster if permeability is enhanced, which must be compensated by a reduction in porosity. This example demonstrates that correlations are not intrinsic features of parameter combinations, even though certain pairs of parameters may exhibit a preferential correlation structure.

We would like to emphasize that (1) reporting the estimation uncertainty should be an integral part of any discussion of inverse modeling results, (2) overparameterization leads to strong parameter correlations and thus high estimation uncertainties, and (3) providing upper limits for the estimation uncertainty is a useful criterion for the design of laboratory and field experiments, which can be evaluated prior to data collection (see the section “Examples” and subsection “Inverse Modeling and Text Design,” below, for specific examples and further discussion).

Model Identification Criteria

So far, we have discussed statistical measures that assess the results of a single inversion. If competing models have been developed and matched to the data, a criterion is needed to decide which of the alternatives is preferable. One of the most widely used criteria is the estimated error variance as a measure of goodness-of-fit (see the subsection “Residual Analysis,” above). The model that best matches the data is considered to be the best. However, since the match can always be improved by adding more fitting parameters, the goodness-of-fit is an inappropriate basis for model selection because it almost always leads to overparameterization, where an improvement of the fit comes at the expense of a reduction in model reliability. Consequently, model identification and optimality criteria should include some aggregate measure of overall estimation uncertainty to guard against overparameterization. For more details about this important topic, the reader is referred to the literature, where a number of tests for model discrimination have been described (see, for example, Steinberg and Hunter 1984, Carrera and Neuman 1986a, Russo 1988, Russo *et al.* 1991, Finsterle 1999a).

MODEL PREDICTIONS AND THEIR UNCERTAINTIES

Introduction

Model predictions and their uncertainties are briefly discussed here, even though they are not directly related to inverse modeling. Recall that the overall purpose of inverse modeling is not to reproduce data measured in the past, but to help develop a model that is used to predict future system behavior. We would like to make this prediction as accurate as possible, and inverse modeling makes a significant contribution to that aim.

We briefly present two methods used to assess prediction uncertainties as a result of uncertainties in the input parameters. These methods are based on deterministic, forward models. As an alternative approach not discussed here, methods of stochastic hydrology (Gelhar 1993, Dagan and Neuman 1997) can be employed to estimate the mean and covariance of model predictions.

Linear Uncertainty Propagation Analysis

Linear or “First-Order-Second-Moment” (FOSM) uncertainty propagation analysis translates the covariance of the input parameters into the covariance of the system response. The prediction covariance matrix $C_{\hat{z}\hat{z}}$ can easily be derived from a first-order Taylor series expansion of the model output about the mean parameter set $\hat{p}$, yielding

$$C_{\hat{z}\hat{z}} = J C_{pp} J^T \quad (5.75)$$

Here, J is the Jacobian, or sensitivity, matrix holding sensitivity coefficients of the model predictions at discrete points in space and time with respect to the parameters considered uncertain, $J_{ij} = \partial \hat{z}_i / \partial \hat{p}_j$, and C_{pp} represents the covariance matrix of the parameters determined (for example) by inverse modeling (see the subsection “Uncertainty of Estimated Parameters,” above).

Linear uncertainty propagation analysis has the following advantages and disadvantages:

Advantages:

- The uncertainties in the model predictions can be described in a compact way by means of the covariance matrix $C_{\hat{z}\hat{z}}$; as a result, they are easy to understand and convenient to report.
- Correlations among the parameters are automatically taken into account.
- The output covariance matrix $C_{\hat{z}\hat{z}}$ contains correlations among model predictions.
- Linear uncertainty propagation analysis is computationally inexpensive.

Disadvantages:

- The uncertainty in the input parameters is expected to be accurately described by a covariance matrix C_{pp} .
- If parameters are highly uncertain, the linearity assumption may be violated.
- Probabilities may be assigned to physically unreasonable system responses (for example, negative concentrations or saturations greater than one may exhibit a nonzero probability); this method should not be used to analyze extreme events in the tail of the distribution. A large number of Monte Carlo simulations is required when one is interested in the tail of the distribution.

Monte Carlo Simulations

An alternative to linear uncertainty propagation analysis is to perform Monte Carlo simulations. Monte Carlo (MC) requires repetitive solution of the simulation model, with the parameters randomly sampled from their suspected probability distributions. The output from MC runs is then used to analyze the statistical properties of the resulting distribution, which represents the uncertainty of the model predictions. The procedure is summarized in Table 5-9.

To consider correlations among the parameters, the random combination of parameter values in Step 3 must be modified such that the covariance function is correctly reproduced (see, for example, Kitterød and

TABLE 5-9	Monte Carlo Simulations
Step 1:	Define probability distribution for all uncertain input parameters.
Step 2:	Randomly sample parameter values from the defined distributions.
Step 3:	Combine sampled parameter values randomly to obtain a parameter vector.
Step 4:	Run simulation and store the results.
Step 5:	Repeat Steps (2) through (4) n_{MC} times.
Step 6:	Perform statistical analyses (histogram, moments) of ensemble of model output.

Gottschalk 1997). How many Monte Carlo runs should be performed? The number of Monte Carlo simulations n_{MC} can be considered sufficient if the following conditions are met:

- The selected probability density function of the input parameters is reasonably well approximated by the histogram of the randomly generated parameter values.
- The histogram of the model predictions allows for a statistical analysis. That implies that a sufficient number of realizations (simulation results) should fall within each interval used to calculate probabilities.

The minimum number of Monte Carlo simulations must be increased if the number of uncertain parameters increases because more parameter combinations are possible. From experience, the number of Monte Carlo simulations can be as low as 50 and as high as 2000 or greater.

Uncertainty propagation analysis by means of Monte Carlo simulations has the following advantages and disadvantages:

Advantages:

- Any distribution (uniform, normal, log-normal, exponential, or any arbitrary histogram) can be chosen to describe parameter uncertainty;
- No assumption is made about the distributional form of the model output, (that is, a full distribution of the predictions is obtained). Monte Carlo is thus termed a *full distribution analysis* method.
- Nonlinearities are inherently taken into account.
- Results from Monte Carlo simulations are always in the physically feasible range.

Disadvantages:

- Results from Monte Carlo simulations are difficult to report because they usually do not follow a normal distribution.
- Monte Carlo simulations are computationally expensive.

EXAMPLES

Overview

There are many examples of synthetic inversions and case studies for flow and transport in the saturated zone. However, only a few studies have been reported that deal with complex multiphase systems or flow and transport in the vadose zone. Moreover, most calibrations of these models are performed by trial-and-error history-matching rather than using a formalized approach, as discussed in this section. Finally, most studies make use of synthetic data or data from laboratory experiments, where conceptual uncertainties are minimal.

An incomplete list of formalized unsaturated zone or multiphase inverse modeling studies is given in Table 5-10. Three short examples are discussed below, addressing specific aspects of multiphase inverse modeling on various scales.

Design of Multistep Outflow Experiment

Single- and multistep outflow experiments are commonly used to determine unsaturated hydraulic properties (Kool and Parker 1988, van Dam *et al.* 1992, Eching *et al.* 1993). In this section, we discuss the design of a multistep, radial outflow experiment and assess its suitability for parameter estimation. The pressure at the center of a cylindrical core is reduced in discrete steps, while the cumulative outflow and the capillary pressure are recorded. The performance of the experiment is analyzed assuming that three parameters—the logarithm of the absolute permeability, $\log(k_{abs})$, the pore-size distribution index, λ , and the logarithm of the air entry pressure, $\log(p_e)$ —are to be estimated based on capillary pressure and cumulative outflow data. The pore-size distribution index and the logarithm of the air entry pressure are parameters of the characteristic functions by Brooks and Corey (1964). Details about the experiment can be found in Finsterle and Faybishenko (1999). While a standard sensitivity analysis may be useful to identify the optimal location of the tensiometer within the core, synthetic data must be inverted, and the estimation covariance matrix evaluated, to reveal potential correlations that may make it impossible to accurately estimate the parameters of interest (Steinberg and Hunter 1984).

TABLE 5-10 Overview of multiphase inverse modeling studies

Description	Observations	Parameters	Reference
one-step and multistep outflow experiments	cumulative outflow, pressure, water content	permeability, unsaturated hydraulic properties	Zachmann <i>et al.</i> (1981); Kool <i>et al.</i> (1985); Parker <i>et al.</i> (1985); Russo (1988); van Dam <i>et al.</i> (1992); Toorman <i>et al.</i> (1992); Eching and Hopmans (1993); Finsterle <i>et al.</i> (1998); Finsterle and Faybishenko (1999)
infiltration, drainage, evaporation	flow rate, water content, prior information	permeability, unsaturated hydraulic properties	Hornung (1983); Dane and Hruska (1983); Kool <i>et al.</i> (1985); Kool and Parker (1988); Russo <i>et al.</i> (1991); Zijlstra and Dane (1996)
gas pressure pulse decay experiment	pressure	permeability, Klinkenberg parameter, porosity	Finsterle and Persoff (1997); Finsterle and Najita (1998)
boiling experiment	steam saturation, heat flow rate	relative permeability	Guerrero <i>et al.</i> (1998)
disc infiltrometer	cumulative infiltration, water content, pressure head	permeability, unsaturated hydraulic properties	Simunek and van Genuchten (1996)
ventilation experiment	water potential, gas pressure, evaporation rate	permeability, two-phase flow parameters	Finsterle and Pruess (1995)
geothermal field	pressure, temperature, enthalpy	permeability, porosity, recharge	White (1995); Finsterle <i>et al.</i> (1997); Bullivant and O'Sullivan (1998); Finsterle <i>et al.</i> (1999)
oil reservoir concentration	water-cut, tracer	permeability	Vasco <i>et al.</i> (1998); Datta-Gupta <i>et al.</i> (1998)
pneumatic pressure fluctuations	pressure	gas diffusivity	Ahlers <i>et al.</i> (1999)

For problems with few unknown parameters, contouring the objective function (5.67) is a means to visualize the well- or ill-posedness of the inverse problem. Points of equal objective function lie on continuous surfaces in the parameter space. Figure 5-25 shows contour plots in the three parameter planes (a) $\log(k_{abs})$ - $\log(p_e)$, (b) $\log(k_{abs})$ - λ , and (c) λ - $\log(p_e)$. The top and middle row of panels show the objective function obtained when only flow rate or pressure measurements are available. The bottom row shows results from combining the two types of observations. The shape, size, orientation, and convexity of the minimum provides information about the uniqueness and stability of the inversion and represents the uncertainty and correlation structure of the estimated parameter set. Furthermore, the presence of local minima can readily be detected.

While devoid of local minima, the central panel of Figure 5-25 reveals that the joint estimation of $\log(k_{abs})$ and λ is likely to be unstable if only pressure measurements were available. However, the combination of pressure and flow rate data yields a well-defined global minimum, as shown by the central panel of the bottom row. Note that the orientation of the minima from the flow rate data tend to be orthogonal to the ones from the pressure data. When combined, a well-constrained minimum results. The study by Simunek and van Genuchten (1996) shows a similar behavior.

Synthetic inversions demonstrate that the global minimum is accurately identified by a number of different minimization algorithms. Recall that the value of the objective function is usually evaluated only at a few points in the parameter space along the path taken by the minimization algorithm. However, information about the structure of the objective function can be obtained from an analysis of the covariance matrix, which relies on a local examination of the objective function curvature at the minimum. In this case, the covariance matrix calculated at the minimum indicates that it should be feasible to obtain accurate parameter estimates using the multistep desaturation experiment.

Ventilation Experiment

Figure 5-26 shows a schematic of a ventilation experiment performed at the Grimsel Rock Laboratory, Switzerland. In order to determine the macroporosity of crystalline rocks, the total inflow of moisture into an isolated, ventilated drift section is measured in a cooling trap.

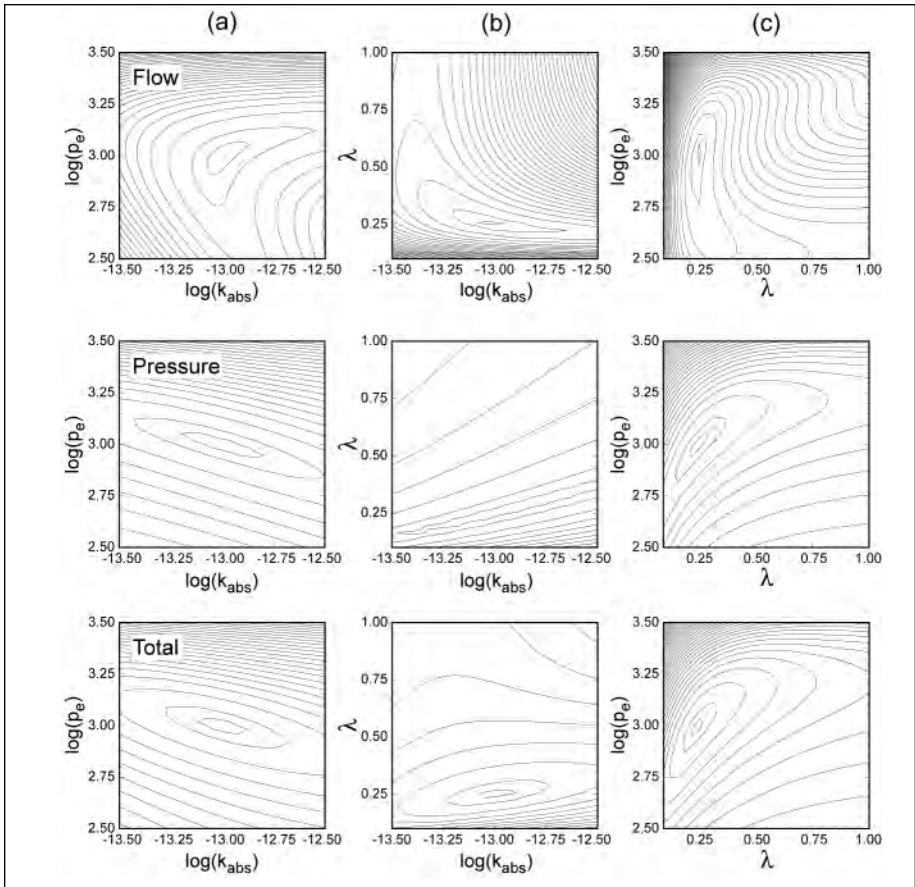


Figure 5-25. Contours of the objective function in the three parameter planes (a) $\log(k_{abs})$ - $\log(p_e)$, (b) $\log(k_{abs})$ - λ , and (c) λ - $\log(p_e)$. The first row shows the objective function when only cumulative outflow data are used, the second row includes only pressure data, and the third row comprises both observation types. The planes intersect the parameter space at the global minimum, that is, they contain the best estimate parameter set.

Because of ventilation, the initially saturated granodiorite formation starts to dry out radially from the drift despite a strong water pressure gradient. By measuring the water potential using thermocouple psychrometers (TP) (Gimmi *et al.* 1992), the gas pressure in two boreholes, and the average evaporation rate, it was possible to determine the absolute permeability as well as the two-phase flow parameters of the van Genuchten model (Luckner *et al.* 1947).

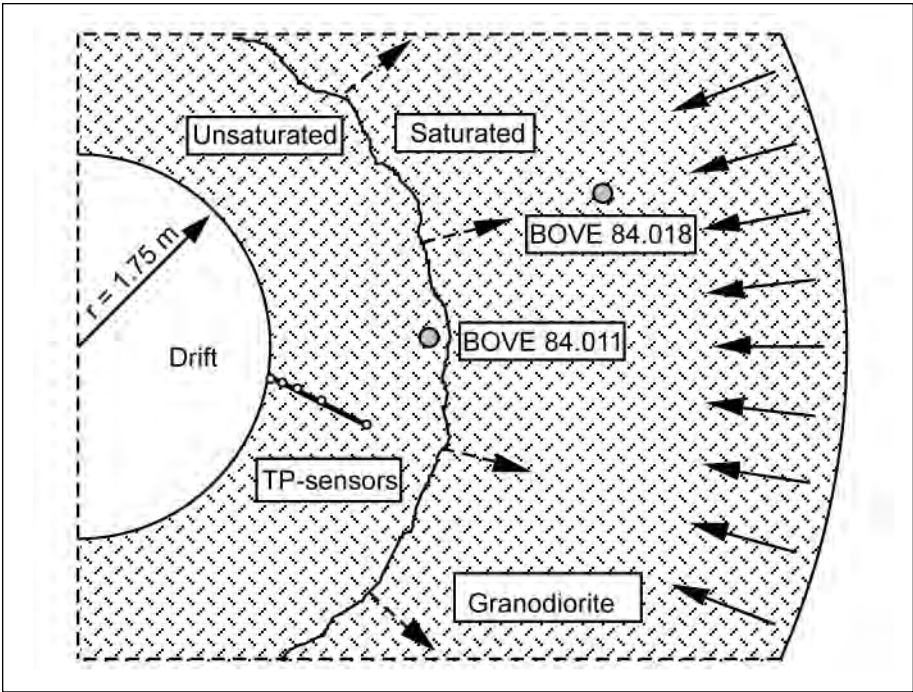


Figure 5-26. Schematic of model domain and instrumentation of ventilation experiment at the Grimsel Test Site.

After starting ventilation, water evaporates at the surface as a result of the reduced relative humidity, providing the main driving force for the desaturation of the formation. The reduced relative humidity is imposed as a boundary condition at the drift wall by specifying an equivalent capillary suction according to Kelvin's equation (Edlefsen and Anderson 1943). The simulated dry-out zone after 80 days of ventilation is shown in Figure 5-27. The calculated low-pressure region matches the two gas-pressure measurements indicated by symbols. The calculated flow of moisture into the drift of $0.31 \text{ mg m}^{-2} \text{ s}^{-1}$ compares well with the evaporation rate estimated by Kull *et al.* (1992). Matching these data greatly helped to constrain the solution of the inversion. However, the bulk of the information about the parameters is contained in the transient water potential data, which are shown in Figure 5-28.

In order to check whether the solution is likely to be at a global minimum, minimization is started from different initial parameter sets. Five

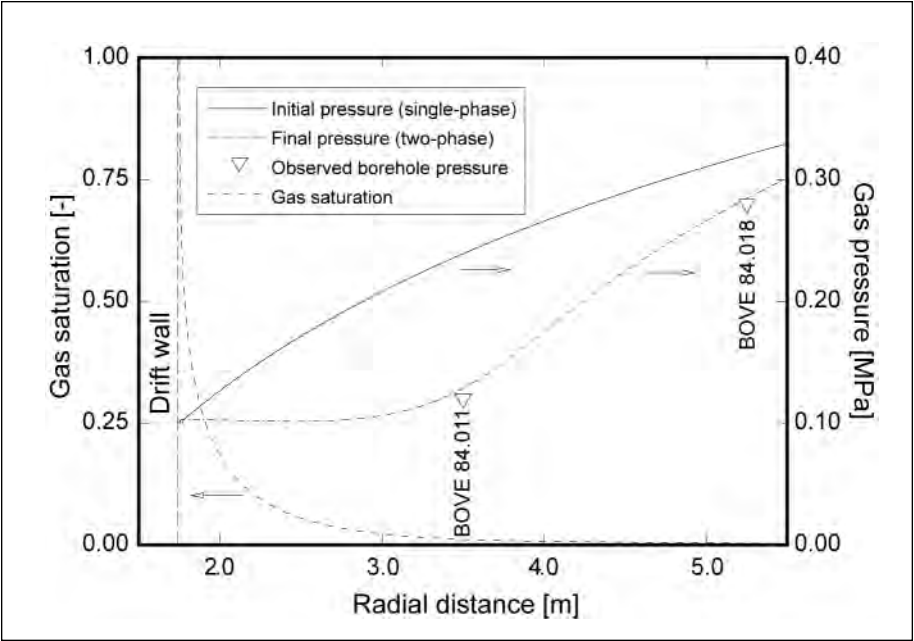


Figure 5-27. Calculated gas saturation and pressure profiles after 80 days of ventilation. The measured borehole pressures are shown as triangles. The calculation is based on parameters estimated by inverse modeling.

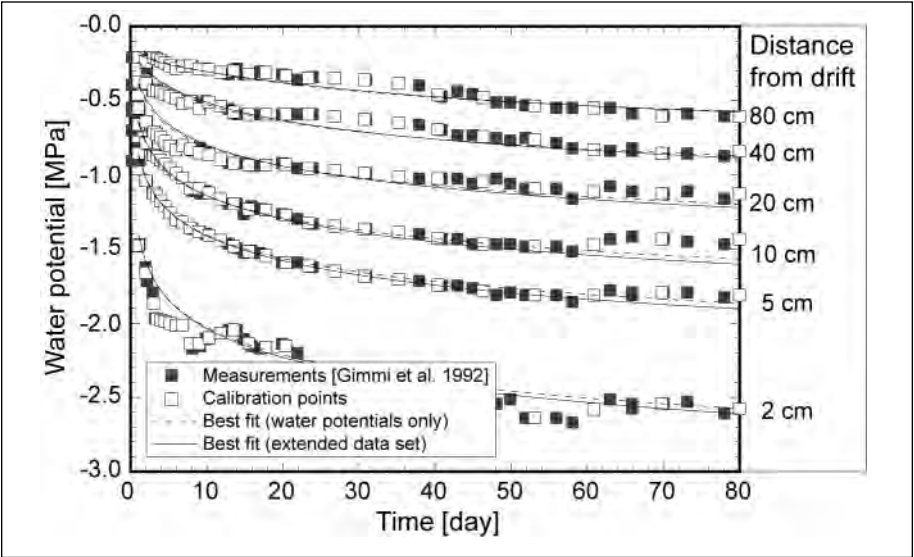


Figure 5-28. Comparison between calculated and measured water potentials.

initial parameter sets, the best estimates, and the initial and final values of the objective function, are summarized in Table 5-11. The five inverse runs result in parameter sets that are almost identical. From this, we conclude that the solution is likely to be unique within a rather large domain of the parameter space. The estimation uncertainty and correlation coefficients are shown in Table 5-12. Since decreasing the value for n reduces the liquid relative permeability, the absolute permeability has to be increased in order to maintain a certain water flow rate. This explains why n and $\log(k)$ are negatively correlated. Similarly, the water potentials decrease with higher air-entry pressure and higher permeability, leading to a negative correlation between these two parameters. Note, however, that the correlation coefficients shown in the upper triangle of Table 5-12 may include contributions from indirect correlations, as discussed in Finsterle and Pruess (1995).

TABLE 5-11**Estimates obtained starting from five different initial parameter sets**

Set No.	Parameter	Initial Guess	Initial Objective Function	Final Objective Function	Best Estimate
1	$\log(k \text{ (m}^2\text{)})$	-17.00	67670	123.3	-18.55
	$n \text{ (-)}$	3.00			2.46
	$\log(1/\alpha \text{ (Pa)})$	6.00			6.23
2	$\log(k \text{ (m}^2\text{)})$	-18.00	9127	124.3	-18.54
	$n \text{ (-)}$	2.00			2.47
	$\log(1/\alpha \text{ (Pa)})$	5.70			6.23
3	$\log(k \text{ (m}^2\text{)})$	-19.00	333	125.1	-18.56
	$n \text{ (-)}$	2.50			2.48
	$\log(1/\alpha \text{ (Pa)})$	6.30			6.23
4	$\log(k \text{ (m}^2\text{)})$	-20.00	3302	123.3	-18.54
	$n \text{ (-)}$	5.00			2.46
	$\log(1/\alpha \text{ (Pa)})$	6.20			6.23
5	$\log(k \text{ (m}^2\text{)})$	-21.00	4578	123.8	-18.54
	$n \text{ (-)}$	4.00			2.47
	$\log(1/\alpha \text{ (Pa)})$	6.40			6.23

TABLE 5-12

Covariance (diagonal and lower triangle) and correlation (upper triangle) matrices from linear error analysis

	$\log(k \text{ (m}^2\text{)})$	$n \text{ (-)}$	$\log(1/\alpha \text{ (Pa)})$
$\log(k \text{ (m}^2\text{)})$	6.74×10^{-4}	-0.42	-0.80
$n \text{ (-)}$	-3.17×10^{-4}	8.47×10^{-4}	0.02
$\log(1/\alpha \text{ (Pa)})$	-9.97×10^{-5}	3.73×10^{-6}	2.30×10^{-5}

The example demonstrates that virtually any type of sensitive data can be used in a joint inversion to estimate parameters that affect the observed system behavior. This flexibility of inverse modeling can be exploited to conceive new experimental designs and to analyze a larger variety of observations obtained under natural and testing conditions. The ventilation experiment, the problem of nonuniqueness, and a non-linear error analysis are further discussed in Finsterle and Pruess (1995).

Joint Inversion of Steady-State and Transient Pressure Data

Many simulations of transient events assume that the system is initially at equilibrium, from which it evolves after applying a perturbation. Equilibrium conditions are usually obtained by running the model to steady state in a calculation separate from the transient simulation. Steady-state conditions, however, may depend on one or more of the parameters that are to be estimated using the transient data. Furthermore, one might want to concurrently calibrate against steady-state data, representing the natural state, and transient data from the test response.

In this example, steady-state water percolation is calculated in two one-dimensional columns representing boreholes drilled into the thick unsaturated zone of Yucca Mountain, Nevada. The steady-state run is followed by a transient simulation of atmospheric pressure fluctuations that propagate from the land surface through several hydrogeologic layers to the water table. Profiles of saturation and water potentials believed to represent steady-state conditions are matched. Furthermore, pneumatic pressures are recorded at five locations within the two boreholes.

Calibration occurs at time zero (for steady-state data) and at time intervals of 6 hours (for the transient pneumatic data). We are primarily interested in estimating absolute permeability for each hydrogeologic layer. It is important to note that the observed saturations and water potentials are also strongly affected by the parameters of the capillary pressure and relative permeability functions, and the pneumatic pressure response is governed by gas diffusivity, which includes porosity.

Information about the absolute permeability is contained in the time lag and attenuation of the pneumatic pressure data, rather than in the absolute value of the observed gas pressure. If the mean pressure at a given elevation is not accurately reproduced by the model, a systematic error is introduced. Since an error in the mean pressure affects all data, the parameters will be adjusted to minimize the differences in the mean pressure rather than to match the time lag and attenuation of the pressure fluctuation. In order to avoid biased estimates, we consider the mean pressure as an additional parameter to be estimated; that is, we allow the pressure data to be shifted by an unknown constant value. The initial guess for the data shift is taken from a visual inspection of the match obtained with the initial parameter set. The initial permeability estimates are based on core data, and are thus included, as prior information, in the inversion.

Figure 5-29 shows the match of the pneumatic pressure data at three sensors in one of the two boreholes. Note that the estimated parameter set also honors the pneumatics in the second borehole, the steady-state saturation and water potential profiles, and prior information about the permeabilities. A better match could be obtained if only pneumatic data in the first borehole were considered. Nevertheless, attenuation and time lag are well reproduced by the model.

As shown by Ahlers *et al.* (1999), the calibrated model is able to accurately predict future pneumatic pressure fluctuations, providing useful information about the large-scale connectivity and permeability of the fracture network at Yucca Mountain.

CONCLUDING REMARKS

Inverse Modeling and Test Design

The purpose of almost any laboratory experiment (or field test) is to stress the sample (or aquifer) to reveal specific characteristics

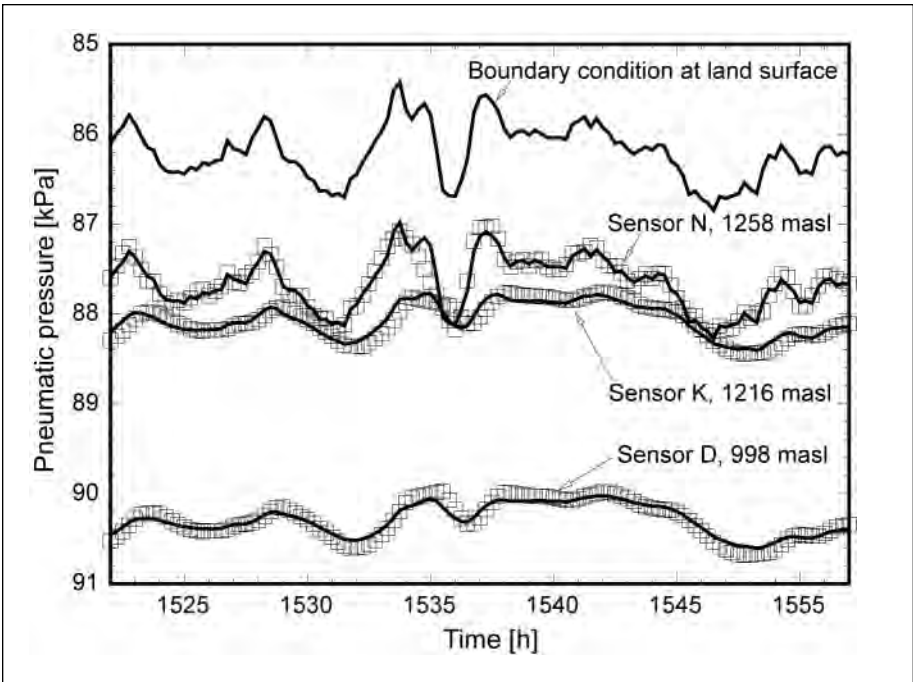


Figure 5-29. Match of pneumatic pressures at three elevations in one borehole.
(Data from Rousseau *et al.* 1996)

considered important for a better understanding of the natural system. These characteristics are then expressed through hydrologic parameter values. In the past, experiments had to be designed in a way that the data could be analyzed using graphical techniques or analytical solutions. Advances in computer simulation technology now enable joint analyses of multiple data sets collected under non-ideal conditions. However, in order to take advantage of this increased flexibility, an experiment must be carefully designed to make sure that the data to be collected actually contain the information needed for successful inversion, and that unique and accurate parameter values can be extracted. In this section, we briefly outline how inverse modeling can be used for experimental design.

Two elements of experimental design can be supported by inverse modeling. First, we can study different perturbations to determine which kind of experiment would be most suitable to identify the parameters of interest. Secondly, the type, amount, location, and accuracy of the

observations can be varied to improve parameter identifiability. The information content of an individual data point can be evaluated by a standard sensitivity analysis. However, potential nonuniqueness and parameter uncertainty can only be addressed by taking an inverse perspective. With this in mind, we need criteria to judge the performance of competing test designs. The main criterion will be the uncertainty of the estimated parameters, but we can also look at the ability of an experiment to discriminate between alternative conceptual models. Both criteria require performing inverse modeling runs rather than doing a standard sensitivity analysis. This approach to designing calculations mirrors the procedure that will be applied for the subsequent data analysis. It involves the following steps (see Figure 5-30):

1. Define a conceptual model that most likely represents the system to be studied.
2. Conceive a test design (that is, choose the sequence of test events, the type of data to be collected, the location and accuracy of sensors, etc).
3. Generate synthetic data for all potential observation points through forward modeling of the test sequence; random noise may be added to the synthetic data.
4. Solve the inverse problem for all unknown or uncertain parameters.
5. Analyze the Jacobian matrix, which provides information regarding the sensitivity of each observation with respect to each parameter. Revise the test design to increase sensitivity.
6. Analyze the covariance matrix of the estimated parameters. Optimize the test design to reduce estimation uncertainty and parameter correlation.
7. Change the model structure, and again try to fit the synthetic data. If they can be matched equally well, regardless of the model being used, then the test design does not produce selective data (that is, an erroneous conceptual model is not rejected, and the resulting parameter estimates will be biased). Revise the test design to produce selective data.

Reviews of experimental design procedures are given by Steinberg and Hunter (1984) and Sun and Yeh (1990).

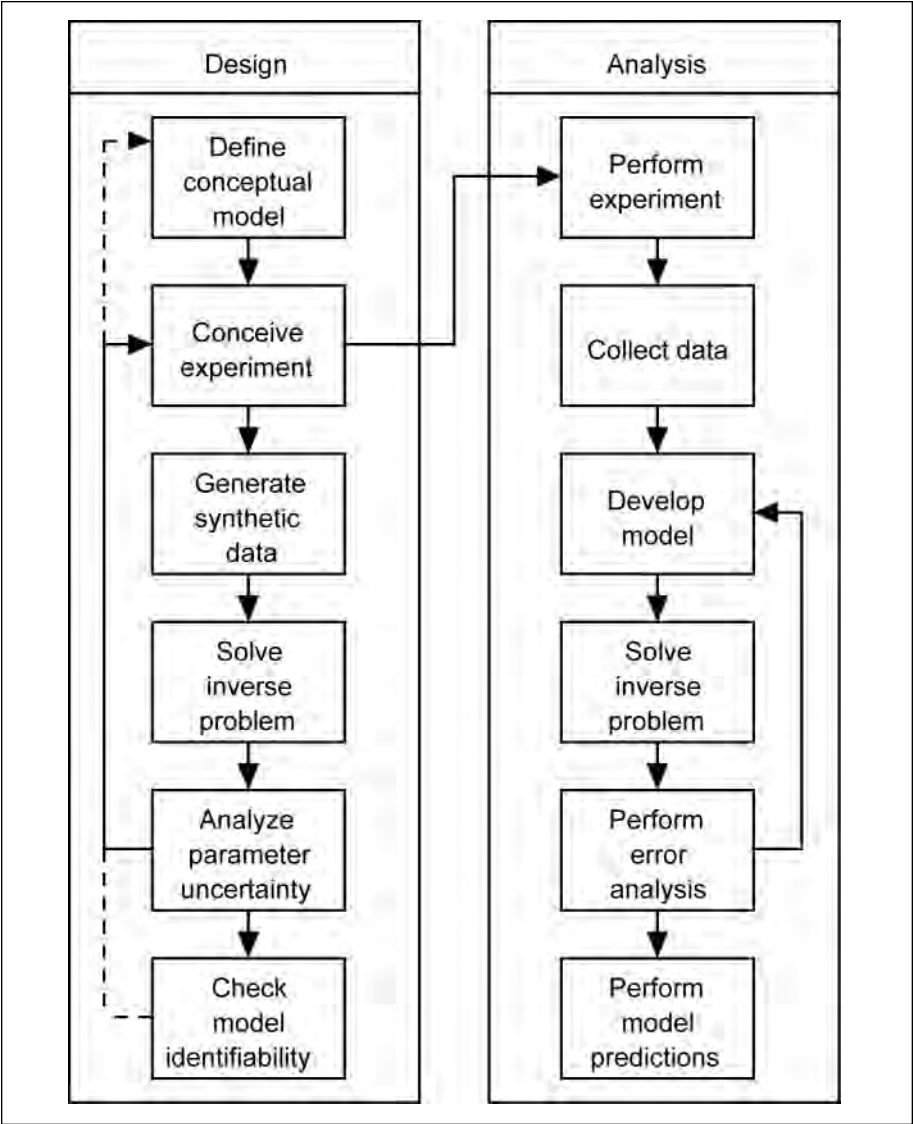


Figure 5-30. Flow chart showing experimental design based on inverse modeling; it mirrors the data analysis procedure.

Inverse Modeling and Scaling

The scaling of processes and properties is recognized as a key issue in groundwater and unsaturated zone hydrology. Parameters measured on laboratory cores must be appropriately transformed before they can be used in large-scale simulation studies. One of the key advantages of inverse modeling is the possibility to directly determine parameters on the scale of interest, avoiding the need for upscaling. For example, data collected during production from a geothermal field can be used to calibrate a large-scale reservoir model. These parameters automatically reflect the field-scale behavior (that is, they are effective parameters on the scale of interest). The estimated permeabilities, for example, may be significantly different from those determined on core plugs because they include the effects of flow through individual fractures and recognize the large-scale connectivity of the fracture network. Moreover, the parameters determined by inverse modeling reflect the key processes governing the system behavior, and are thus well suited for model predictions of future geothermal reservoir performance. It is obvious that model predictions are most reliable if the model is calibrated against data obtained on a similar support scale, involving similar flow and transport processes.

Inverse modeling could also be used to determine upscaling relationships. Data collected from experiments on different scales can be inverted and the estimated effective parameter values plotted as a function of support scale. A trend in such a plot would indicate a scale dependence of the parameter, and an approximate scaling law may be derived from the slope and shape of the curve. Nevertheless, upscaling and the description of multiscale processes remain challenging problems.

Inverse Modeling and Heterogeneity

Heterogeneity on many scales has a profound effect on saturated flow, and even more on flow and transport in the vadose zone (Pruess 1999). While seismic methods have the capability to provide high-resolution tomographs of the subsurface, the relation of these images to hydraulic properties governing flow and transport is difficult to assess. Estimating heterogeneous formation properties from inversions of hydrologic data faces the problem of non-uniqueness and instability as

a result of overparameterization. Zimmerman *et al.* (1998) have reviewed several geostatistically-based inverse methods to characterize spatial variability and uncertainty in hydrogeologic properties. They concluded that proper parameterization is the key factor affecting both calibration and subsequent stochastic prediction.

As mentioned before, inverse modeling provides effective parameters; that is, they reflect averaged properties and processes. If averaging is appropriate, the parameters can be considered reasonable to describe flow and transport in heterogeneous formations. In the cases where averaging is inappropriate, the attempt to match observed data will fail, thus indicating that an explicit representation of heterogeneity is required. The general structure of the heterogeneity must then be inferred from geological or geophysical information. Subsequently, inverse modeling can be used to estimate the small number of geostatistical parameters that describe the heterogeneity. Note that in this approach the geostatistical parameters are not determined by matching data of an empirical variogram. Instead, they are determined by matching pressure, saturation, or flow rate data. This requires that the generation of a heterogeneous property field—which is usually considered a preprocessing step—must be an integral part of the forward model. During the inversion, the geostatistical parameters are treated like any of the concurrently-estimated hydrological parameters. After each parameter update, a new heterogeneous property field is generated, and a flow and transport calculation is performed to match the data. Such an approach was described for saturated flow by Doughty (1995) using iterated function systems to characterize heterogeneity.

In summary, we have to consider two cases when dealing with heterogeneous formations. First, if the system behavior of interest is not strongly affected by the details of the heterogeneous property field, inverse modeling provides suitable estimates of average or effective parameters. If the discrete nature of the system becomes important and affects the quantities to be matched or predicted, heterogeneity must be explicitly modeled, and inverse modeling can help in the determination of parameters such as correlation lengths, fractal dimensions, covariances, and conditioning points. In the second case, information about the structure of the heterogeneity are combined and related to data reflecting flow and transport processes.

Future Research Directions

Multiphase inverse problems are challenging to solve from both a fundamental and computational point of view. Extensive research in a variety of areas is needed. Moreover, adequate education and training are required to make inverse modeling a standard practice in environmental and reservoir engineering.

Research and development of multiphase inverse modeling techniques can benefit from efforts and advances made in many fields of science. For example, increases in computational efficiency resulting from parallelization, fast linear equation solvers, and the use of advanced numerical algorithms, will permit inversions of complex multiphase flow and transport models in three dimensions. The main benefit will not be the reduction in computer time, but the possibility to use a more sophisticated and more accurate forward model in an inversion, reducing the negative impact of systematic modeling errors on the estimated parameters. Attention must be given to the specific requirements of the minimization algorithms employed in inverse modeling, so that special solutions can be developed. The efficient calculation of sensitivity coefficients either by parallelization, automatic differencing, or by developing novel algorithms should be at the center of attention in this area. Alternative strategies such as genetic algorithms, fuzzy logic, and stochastic inversion techniques are being developed to find the global minimum of the objective function and to handle uncertainty in a more consistent manner.

A second research area addresses some of the shortcomings discussed previously. The inherent ambiguity of individual inversions of either hydrological, geochemical, or geophysical data severely limits site characterization and the success of predictive modeling. A joint inversion of all types of data has the potential to characterize both the hydrogeologic properties and their spatial distribution with higher accuracy. This approach combines the strength of geophysical imaging methods (which provide the structure of the subsurface) with multiphase inverse modeling techniques (which provide process-relevant parameter values).

As a third area of research, a comprehensive modeling framework could be developed that allows one to evaluate the sufficiency of an experimental design, analyze field data, compare alternative conceptual models, make predictions, and estimate the impact of uncertainty. This

requires application and extension of the inverse modeling concepts to a variety of optimization and evaluation tasks.

In summary, future research should be directed towards the development of alternative models based on efficient joint-inversion techniques. This will eventually reduce prediction uncertainty of contaminant migration, help design monitoring systems, and optimize reservoir management and cleanup operations.

Summary

The purpose of this section was to demonstrate the power, usefulness, conceptual soundness, and advantage of a formalized inverse-modeling approach to characterizing unsaturated and multiphase flow systems. At the same time, we discussed many caveats, limitations, simplifying assumptions, and disadvantages that must be considered when applying inverse modeling techniques. The convenience of automatic model calibration is the most obvious strength of inverse modeling. It is important that the estimates are not applied for predictive runs without making sure that both the match to the data is satisfactory and the estimation uncertainty is reasonable. On the other hand, apparent limitations (for example, the model-dependency of parameters) may turn into an advantage (for example, that the parameters reflect relevant processes on the scale of interest) that is invaluable for practical model predictions. Inverse modeling can make a contribution to most phases of a typical engineering project, from test design, field experimentation, data acquisition, statistical data analysis, history matching, conceptual model testing, and uncertainty estimation, to decision making. It is this integration of information and knowledge that makes inverse modeling, a useful and powerful analysis tool.

Some considerations discussed in this section are summarized below:

1. Inverse modeling studies must be guided by clearly defined objectives. Test design, data collection, parameter estimation, model prediction, and monitoring are strongly interrelated and critically dependent on the overall purpose of the project.
2. Inverse modeling provides effective parameters that are related to scale, physical process, and parameterization of the numerical model. That the parameters are model-related is an important

advantage of inverse modeling over other parameter estimation techniques, because the parameters are, by definition, optimal for the given conceptual model. On the other hand, this strong connection to a specific model is sometimes regarded as a disadvantage, because parameters cannot be simply transferred to other models. It is often overlooked, however, that “directly” measured parameter values suffer from the same limitation, since they also refer to a specific scale and process, but lack the opportunity to adapt themselves to the specific assumptions and peculiarities of the analytical or numerical prediction model.

3. In both forward and inverse modeling, most attention should be given to the development of the conceptual model. A good general understanding of the system must be translated into a valid abstraction that includes a comprehensive process description and accurate numerical implementation. While the model-related estimates partly compensate for minor discrepancies between the natural system and its simplified representation in the model, any systematic error in the conceptual model leads to a bias in the estimated parameters, and thus reduces the significance and usefulness of the parameter in prediction studies.

Inverse modeling relates the numerical model to the real hydrogeologic system. It is thus an undertaking of immense practical relevance.

FUTURE RESEARCH DIRECTIONS

In this chapter, we have discussed many issues concerned with flow and transport modeling, including physical processes, data needs, numerical formulations, model building, and inverse modeling. All of these topics, as well as the numerous case studies presented, have pointed to the significant degree of uncertainty in predictions from numerical models on *in situ* flow and transport. We believe that the main sources of uncertainty generally arise from the limited field data available, followed by uncertainties in the data themselves, the conceptual model, the process descriptions, the modeling approach, the calibration activities, and the code limitations. Many of these issues have been discussed in previous sections of this chapter. Here we will briefly summarize our views regarding future research directions (see also Table 5-13).

TABLE 5-13 Issues for future research directions

ISSUE	Priority*	Importance	Proposed Research
Data Collection			
Preferential flow issues	1	Fast flow and transport issues	Evaluate role of heterogeneity on multiple scales. In addition, evaluate potential fast flow processes such as film flow.
Scale issues	1	Models need measurements at appropriate scales	Develop testing strategies for different spatial scales. Carry out verification studies at different sites.
Multi-phase property determination	2	Models need multi-phase properties	Perform field measurements of both gas and liquid properties in same medium. Perform laboratory experiments to determine multi-phase constitutive relations.
Colloid transport issues	2	Known to be important in saturated zone	Perform appropriate laboratory and field experiments for evaluation. Develop theory based on results.
Coupled processes	2	Data needed to verify models and for basic understanding	Perform laboratory experiments involving coupled processes such as non-isothermal reactive transport. Apply models to actual sites and evaluate field data.
Source term/Boundary Conditions/Initial Conditions	2	Conceptualizations of boundary and initial conditions are needed for models	Develop testing methodology to evaluate infiltration patterns. Perform field measurements of contaminant concentration plumes, etc.
Modeling Issues			
Modeling multiscale processes	1	Processes occur at different scales	Investigate multiscale modeling approach such as wavelets, subgridding, etc.
Joint inversions of multiple data sets	1	More reliable model calibration and parameter estimation	Apply automatic inversion codes such as ITOUGH to various data sets at different scales.
Modeling of preferential flow	1	Fast flow and transport is important to performance	Apply models to design and analyze experiments at Field Research Centers (FRCs). Develop models for various existing data sets on fast flow.
Modeling of coupled processes	2	Coupled processes occur frequently in nature and impact performance	Apply models to controlled laboratory experiments and field tests at the FRCs. Develop models for existing data sets involving coupled processes.

continued

TABLE 5-13 Issues for future research directions (*continued*)

ISSUE	Priority*	Importance	Proposed Research
Modeling Issues (<i>cont.</i>)			
Model validation	3	Models must be reliable	Design, perform blind prediction and recalibrate models against data sets from the FRCs and other locations.
Code Development			
Develop code architecture optimal for parallel processing	2	Faster, more efficient codes are needed for multi-process, multiscale problems	Choose a few major codes for application of parallel processing.
Code development for additional coupled processes	3	Fully coupled codes solving THMCB problems would be useful	Choose one or more major code for incorporation of all major coupled processes.

*Priorities of 1, 2, and 3 are given with 1 representing the highest priority

The quality and quantity of field data is, and will always be, a major source of uncertainty in model predictions of flow and transport at any site. The heterogeneous nature of geological formations does not readily lend itself to detailed characterization. As a result, the modeling activities at most sites are based on non-unique calibrations using multiple conceptual models. This, of course, leads to highly variable and diverse predictions for flow and transport in particular. These difficulties must be recognized, and remediation activities must be continually modified as new field monitoring data are collected and the model is updated.

Another problem is that often the most important data are not collected, while large amounts of less useful “easy-to-collect” data are collected (including core data and well log data). For most situations, however, the more useful and reliable data for flow and transport modeling relevant to remediation design and contaminant migration include

pressure transient gas or liquid data, infiltration experiments, and gas or liquid tracer tests. These data should be collected at different scales, obviating the need for upscaling to model grids. This is only possible with some data, such as pneumatic determination of permeability, while for other parameters such as dispersivity, scale effects must be considered.

To the extent possible, flow and transport modeling should guide both site characterization activities and remediation. The model should be continually exercised in “what if” scenarios to prioritize the data collection in terms of the data needed, the tests that should be undertaken, and the appropriate (desirable) scale of these tests. Feasibility and available budget will, of course, limit what can be done.

Some of the above data issues, as well as process description issues, can be addressed by establishing dedicated Field Research Centers (FRCs) in different geological settings, and, perhaps, at actual contaminated sites. These FRCs can address various key issues such as characterization of heterogeneities, multi scale issues and testing, preferential flow paths, multi phase property issues, colloidal transport, and coupled processes. The testing programs at the FRCs should be designed, and all tests predicted *a priori*, by numerical flow and transport models. The predictions should be periodically updated during the testing, and improvements should be documented. Similarly, the conceptual model of flow and transport for each site should be periodically updated as new data become available. It is expected that an FRC program will (1) provide a giant leap in the understanding and theoretical formulation of the above key issues, (2) help prioritize data collection at actual contamination sites, and (3) help mitigate shortcomings of limited data.

Important flow- and transport-modeling research topics that could be addressed at FRCs—as well as in other well-controlled laboratory and field-testing programs—include model calibration, simultaneous inversion of multiple data sets, improved process description, coupled process modeling, multi scale modeling issues, quantification of uncertainty, and model verification/validation issues. Table 5-13 gives a brief summary of what we consider to be some of the more important research areas. This table is not intended to be all-inclusive; rather, it gives examples of important issues related to data collection, modeling, and code development, and possible means of addressing them, including FRCs. The priorities assigned to these issues are again just our views, and as such, are certainly subject to scrutiny and revision.

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CASE STUDIES



MODELING FAST FLOW PATHS IN UNSATURATED FRACTURED ROCK

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INTRODUCTION

Modeling unsaturated flow through fractured rock has received a great deal of attention recently due, in part, to the characterization of Yucca Mountain, Nevada, as a potential high-level radioactive waste repository. As a result, several models of flow in unsaturated fractured rock have been used in recent years to predict the hydrology in the vadose zone at Yucca Mountain (see, for example, Bodvarsson *et al.* 1997, Ch. 5 and CRWMS M&O 1998, Section 2.2.3). Other related studies have also compared different conceptual models of flow through fractured rock to determine the applicability and limitations of the models (see, for example, Ho *et al.* 1995, Section 1.3, and Eaton *et al.* 1996).

Two of the most prominent models of flow through fractured rock at Yucca Mountain include the effective-continuum model (ECM) and the dual-permeability model (DKM). The ECM assumes thermodynamic equilibrium between the fractures and matrix. As a result, the equations of flow can be applied to a composite material consisting of properties and constitutive relations described by both the fractures and matrix. The ECM has been used in past simulations of Yucca Mountain (see CRWMS M&O 1995, Section 7.2) because of its computational efficiency. However, recent studies at Yucca Mountain have provided evidence of fast flow paths through fractures (Fabryka-Martin *et al.* 1998) that are not readily captured by the ECM. In contrast, the DKM allows disequilibrium between the fractures and matrix and, therefore, the ability for fast flow paths to occur in the fractures. Two separate and discrete continua represent the fractures and matrix, and each fracture element is connected to a corresponding matrix element to allow interaction between the fracture and matrix continua, as well as global flow through each continuum.

The purpose of the case studies presented here is to provide modeling comparisons between the ECM and DKM of flow through fractured rock. The first case study describes the modeling of a tracer test performed at Fran Ridge, near Yucca Mountain (Eaton *et al.* 1996). Transient models using both the ECM and DKM revealed that the DKM was required to adequately predict the significant amount of flow through fractures that was observed. The second case study investigates the modeling of steady-state unsaturated flow and tracer transport at Yucca Mountain for the Viability Assessment (see CRWMS M&O 1998, Section 2.5.1) using the DKM.

Partitioning of flow between matrix and fractures is illustrated along east-west cross sections of Yucca Mountain.

FRAN RIDGE TRACER TEST

The purpose of this case study is to summarize the study of Eaton *et al.* (1996), which investigated ECM and DKM simulations of an infiltration tracer test at Fran Ridge, near Yucca Mountain.

DESCRIPTION OF TRACER TEST

A major outcrop of densely welded, nonlithophysal Topopah Spring Tuff on the eastern side of Fran Ridge was selected as the site of a large block experiment as part of the Yucca Mountain Project (see Figure 1). Part of the preparation of the ridge for the large block experiment called for the removal of the surrounding country rock such that a 4.6 m high and 3 m x 3 m test block remained. Prior to the excavation of the region surrounding the large block, an infiltration tracer test was conducted by Nicholl and Glass (1995) over a region that was eventually excavated. During the test, water was ponded in a 1.5 m diameter region on a leveled surface of the surrounding country rock. In 36 minutes, 205 gallons of blue-dyed water infiltrated into the fractured rock. The removal of the country rock, in approximately 0.5 m lifts, provided an opportunity to map the *in situ* fracture frequencies (see Figure 2) and infiltration paths of the dyed water in a 2.4 m x 2.4 m x 4.6 m (8 ft x 8 ft x 15 ft) region. The location of the blue dye indicated significant flow through the fractures to the 4.6 m depth of the excavation.

NUMERICAL SIMULATIONS

The fracture frequency maps that were developed by Nicholl and Glass (1995) were used to calculate continuum fracture frequencies on 0.3 x 0.3 m horizontal grid blocks by dividing the total length of the fracture traces within each grid block by the area of the block (see Figure 2 and Eaton *et al.* 1996, Ch. 3). Ten continuum fracture frequency maps were created along 0.46 m (1.5 ft) intervals along the 4.6 m excavation depth. The continuum maps were used to create 10 heterogeneous layers in ECM and DKM representations of the system, as described in Eaton *et al.* (1996, Ch. 4). A total of 640 heterogeneous "core" elements were buffered by additional homogeneous elements in the horizontal and vertical directions to extend the boundaries away from the infiltration region. The ECM consisted of 2016 total elements, while the DKM consisted of 2016 matrix elements plus 2016 fracture elements. Fracture hydrologic parameters were derived from the continuum fracture frequency maps, and matrix hydrologic properties were taken from the literature. No-flux boundaries were applied to all perimeter elements of the model except for

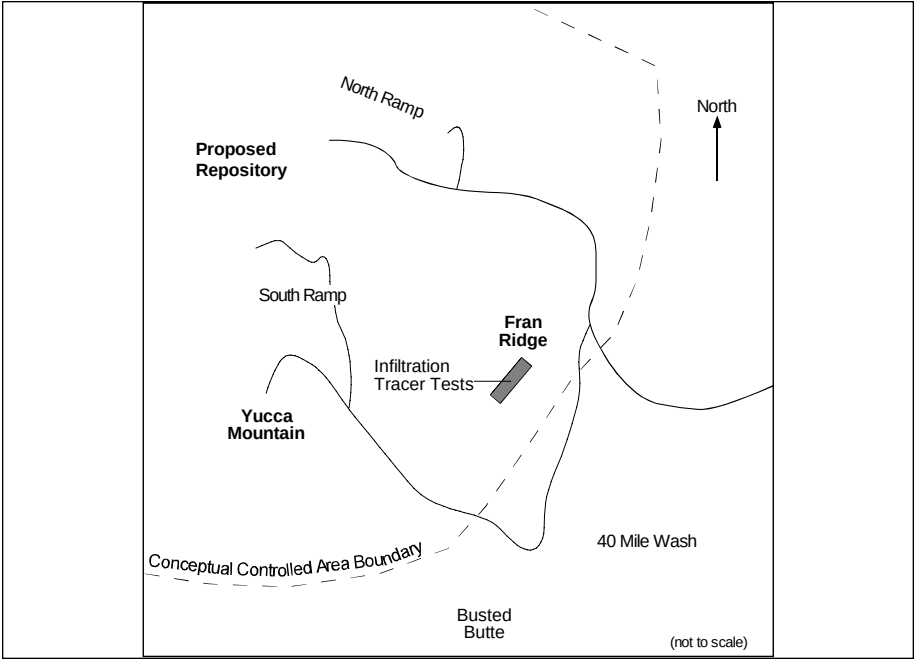


Figure 1. Location map of Fran Ridge and surrounding areas (not to scale; adapted from Eaton *et al.* 1996, Figure 2-1).

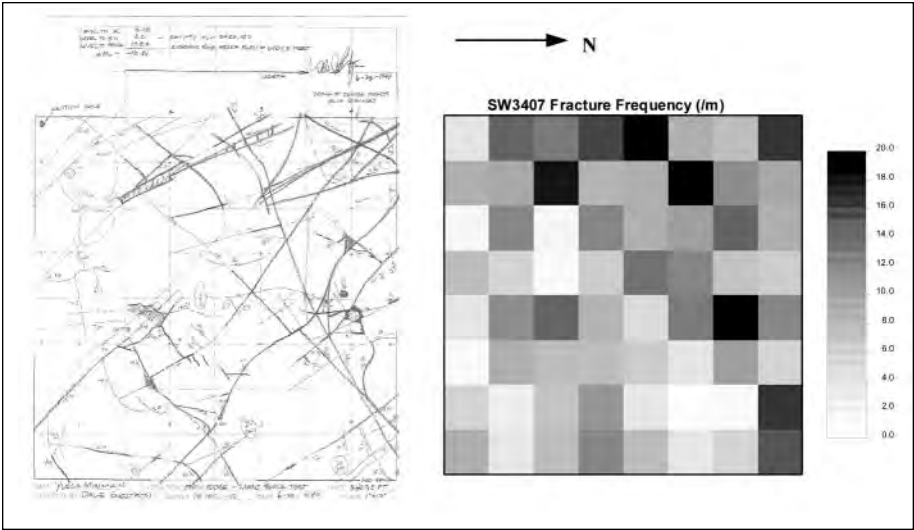


Figure 2. Fracture map from Fran Ridge site and corresponding fracture frequency continuum representation used in the numerical models. Mapped region is 2.4 m x 2.4 m (Eaton *et al.* 1996, Figure 3-1).

elements at the top surface that represented the water pond. These elements remained saturated for the duration of the simulations.

Results of the simulations showed that the DKM predicted a significant amount of infiltration through the fracture continuum within minimal matrix imbibition, while the ECM predicted a majority of the infiltration through the matrix (Figure 3). As a result, the infiltration penetration depth predicted in the DKM was much greater than in the ECM and more consistent with the observed results of the infiltration tracer test. In addition, the DKM predicted an amount of infiltration that was within ten percent of the observed infiltration during the 36 minute test, but the ECM predicted nearly twice the infiltration that was actually observed. The large discrepancy in the ECM predictions was due to the high conductivity of the fracture properties of the composite domain near the saturated boundary. Despite the large influx of water, deep penetration was restricted because of the high capillary suction and storage properties of the matrix of the composite material. Ho *et al.* (1995, Section 5.4) observed similar behavior in comparisons between ECM and DKM simulations of transient infiltration.

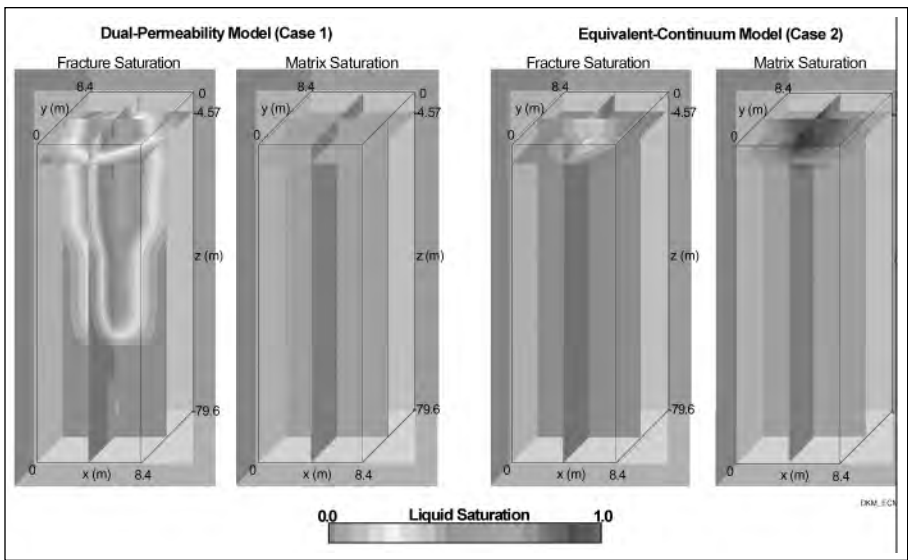


Figure 3. Planes of simulated fracture and matrix saturations at 36 minutes resulting from the dual-permeability model and the equivalent-continuum model. The horizontal planes at $z = -4.57$ m correspond to the bottom of the heterogeneous core region (not to scale; Eaton *et al.* 1996, Figure 4-6).

DKM SIMULATIONS OF YUCCA MOUNTAIN

Simulations of unsaturated flow at Yucca Mountain, the location for a potential high-level nuclear waste repository, have evolved from ECM representations to more rigorous DKM conceptualizations (see CRWMS M&O 1998, Section 2.2.3). The conversion has been due, in part, to recent evidence that fast flow paths exist at Yucca Mountain (Fabryka-Martin 1998). As described in the previous case study, the DKM can more accurately depict the fast flow paths via flow through the fracture continuum.

The development of the DKM for Yucca Mountain has progressed through sensitivity studies (Ho *et al.* 1995), calibration to observed data (see Bodvarsson *et al.* 1997, Ch. 6), and improved conceptual models of fracture/matrix interactions (Ho 1997, Liu *et al.* 1998). The most recent application of DKM simulations of flow through the fractured, unsaturated tuffs at Yucca Mountain have been described in CRWMS M&O (1998, Section 2.5.1). Figure 4 shows results of that study illustrating the flow along two cross-sections of Yucca Mountain. Conservative tracers were simulated and tracked from the surface to below the proposed repository. The paths are indicated by symbols, which denote whether flow was prevalent in the fractures or the matrix. Results show that matrix flow was prevalent in the non-welded tuffs, while fracture flow was dominant in the highly fractured, welded tuffs. In addition, lateral flow below the repository was simulated in the northern cross-section as a result of perched water (see Bodvarsson *et al.* 1997, Ch. 13). The results of these simulations are consistent with current characterizations of Yucca Mountain, but as new data and characterization of the site continues, models of unsaturated flow at Yucca Mountain will also evolve.

CONCLUSIONS

Numerical studies of an infiltration tracer test at Fran Ridge have demonstrated that DKM representations of flow through fractured tuff can more accurately depict transient flow and rapid transport through a fractured system than ECM representations. The use of separate fracture and matrix continua in the DKM numerical simulations allows rapid flow through the fractures that is in disequilibrium with the matrix. In contrast, the ECM requires that equilibrium exist between the fractures and matrix, causing a significant amount of the infiltration to be imbibed by the “matrix” material, prohibiting fast flow paths.

Simulations of unsaturated flow at Yucca Mountain have evolved from ECM simulations to more rigorous DKM simulations. Improved conceptual models of fracture/matrix interactions and calibrations have produced simulations of the system that are consistent with observed data and characterizations of the site. Results indicate non-uniform partitioning of the flow between the fractures and matrix in the welded and non-welded tuffs.

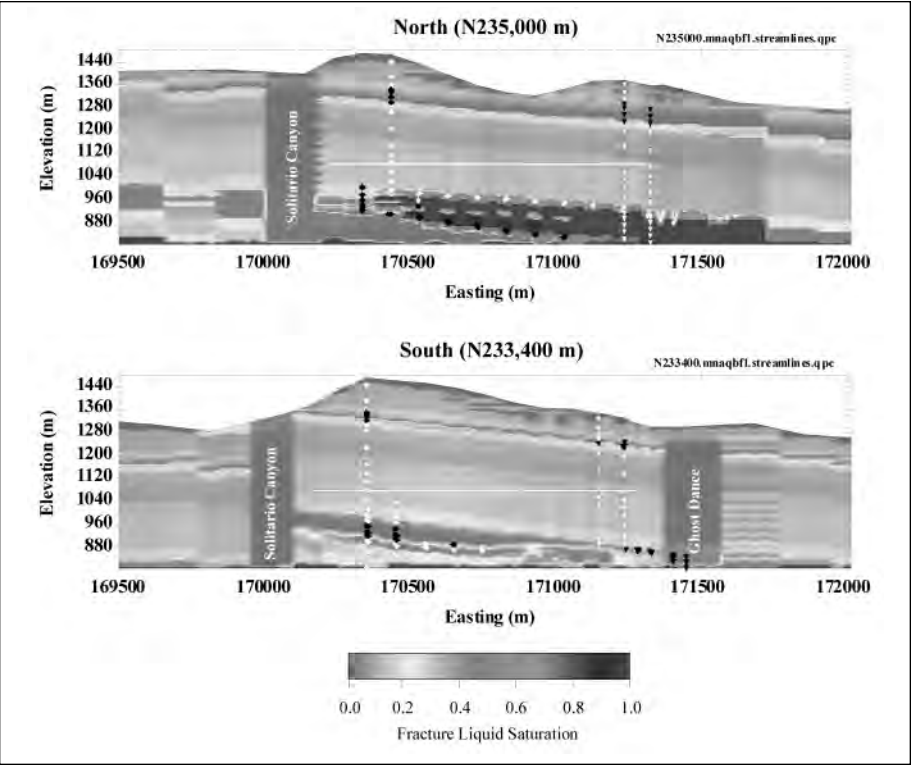


Figure 4. Simulated fracture saturation profiles and paths of conservative tracers (non-sorbing, no matrix diffusion) along two east-west vertical cross-sections of Yucca Mountain. The white symbols denote a higher concentration in the fractures, and the black symbols denote a higher concentration in the matrix. Significant lateral diversion exists in the north beneath the repository (denoted by the white line) where perched water is present (CRWMS M&O 1998, Figure 2-92).

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TCE CONTAMINATION AT THE SAVANNAH RIVER SITE

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In the M-area of the Savannah River Site, Aiken, South Carolina, the vadose zone was contaminated with TCE from a leaking process sewer line. Field observations indicated that contaminant concentrations were spatially highly variable, and tended to be highest near the top of clay rich zones (Eddy *et al.* 1991). A numerical simulation study was undertaken to explore the mechanisms leading to the observed contaminant distribution (Pruess 1992). The emphasis in the study was on understanding the interaction of a descending TCE plume with clay lenses and clay layers. For these limited objectives, a detailed three-dimensional representation of subsurface heterogeneity was considered unnecessary; instead, an idealized 2-D model was used to capture important hydrogeologic features at the site in a very simple, schematic way (Figures 1 through 3).

The vadose zone in the M-area is characterized by a sequence of sands separated by clay-rich layers with different thicknesses, ranging from clay lenses interspersed with sands to continuous areally-extensive layers. The water table is at an approxi-

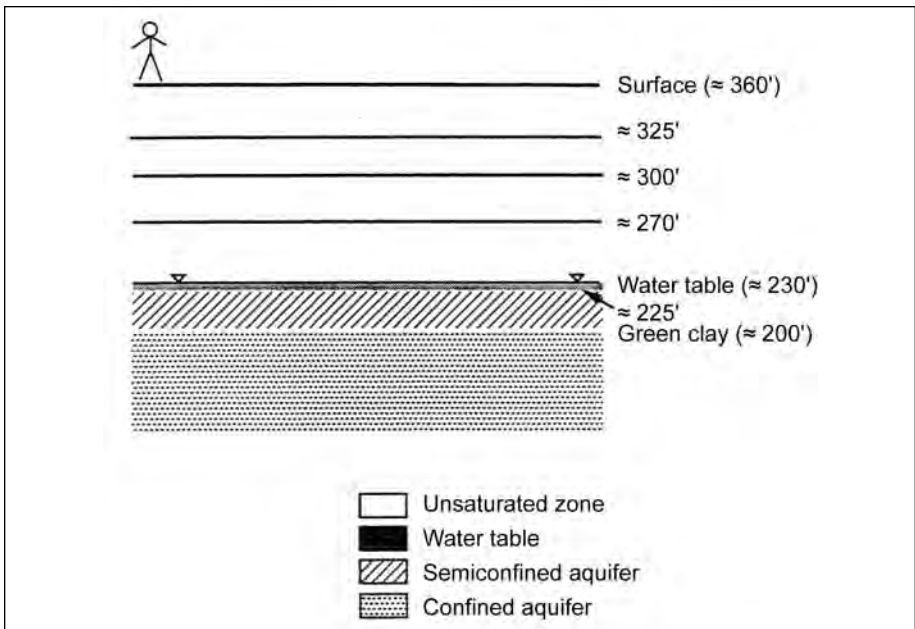


Figure 1. Schematic diagram of hydrogeologic features at the M-area. The horizons labeled 270, 300, and 325 ft, respectively, correspond to tops of clay layers.

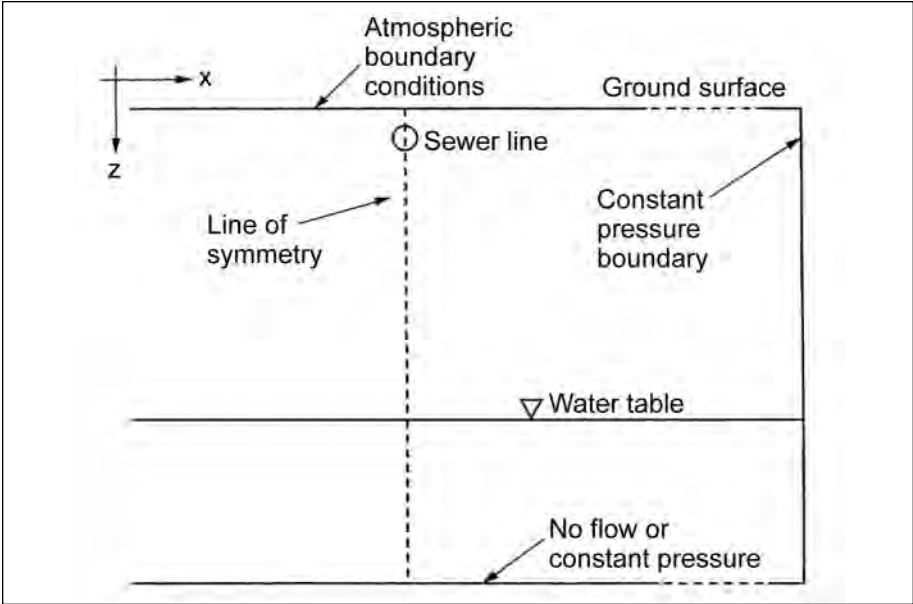


Figure 2. Vertical 2-D section used in the numerical model

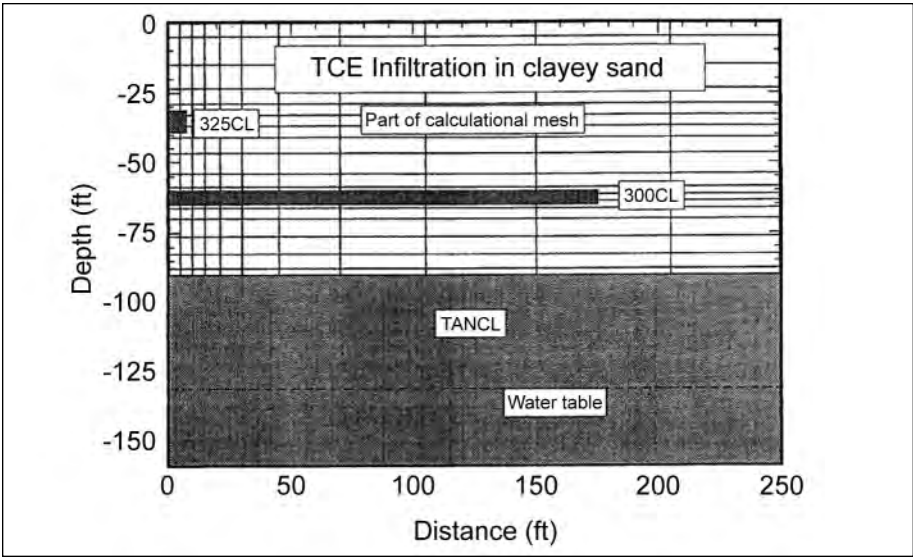


Figure 3. Portion of the 2-D numerical grid, showing clay zones of low permeability. The full grid extends to a distance of 1,000 ft.

mate depth of 130 ft (39 m). The vertical section in Figure 1 shows the main clay horizons that have been identified, and Figure 2 gives a schematic of the model system, which represents a vertical section of 1 m thickness perpendicular to the process sewer line. The lateral extent of the model domain is 1,000 ft, which is essentially infinite-acting for the time period of interest, of the order of 10 years. For numerical simulation, the model domain is discretized into 24 rows and 15 columns of variable spacing, for a total of 360 grid blocks; a portion of the calculational mesh is shown in Figure 101-3. The domains labeled "325CL" and "300CL" correspond to the clays encountered at the site at elevations of 325 ft and 300 ft, respectively. The domain "TANCL" corresponds to the 70 ft thick "tan clay" formation that is encountered at a depth of 90 ft (elevation 270 ft). Constant gas pressure conditions were prescribed at the top (atmospheric) boundary, and constant pressure conditions for both gas and aqueous phases were specified at the lateral boundaries. The bottom boundary of the model, 30 ft below the water table, was held at constant pressure conditions in some simulations and at no flow boundary conditions in others. Simulations were run with different levels of water infiltration specified at the ground surface.

The simulations were performed with the STMVOC code (Falta and Pruess 1991), a member of the TOUGH2 family and precursor of the T2VOC code (Pruess 1991, Falta *et al.* 1995). STMVOC represents three-phase flow of water, air, and NAPL (non-aqueous phase liquid), including partitioning of the volatile organic chemicals between gas and liquid phases, and diffusion in the gas phase. Before simulating the release of TCE, the model system was run to gravity-capillary equilibrium. Subsequently TCE was injected into the uppermost grid block at the left (symmetry) boundary of the domain, at a rate of approximately 9.0×10^{-6} kg/s, which corresponds to a spill rate of 2 barrels of TCE per month per meter of sewer line. Results for NAPL saturations and TCE concentrations in the gas phase after 10 years are shown in Figures 4 and 5, respectively.

TCE flows downward under gravity force, ponds atop the "325CL" clay lens, and then mostly flows around this low-permeability obstacle. A small fraction of the contaminant invades the clay lens and ultimately passes right through it. Ponding again occurs at the "300CL" clay, at a rate that slows with time because an increasing proportion of the TCE penetrates the clay as the ponded zone becomes areally more extensive. During downflow the TCE partially vaporizes, and partially dissolves in the ambient aqueous phase. TCE vapors spread over a volume that is considerably larger than the extent of the NAPL plume (note the expanded spatial scale on Figure 5 as compared to Figure 4). Vapors spread primarily by means of gas phase convection driven by negative buoyancy of the denser TCE. For the conditions simulated here, diffusive spreading of TCE is slower than advection and extends for less than 100 ft after 10 years. Vapor migration is shown to be a major process for contaminant transport, which leads to water contamination in the vadose zone as TCE vapors partially dissolve. Under the local equilibrium conditions assumed in the simulations, the amount of TCE dissolved per unit volume of aqueous phase is almost three times larger than what is present per unit volume of gas phase. A more detailed discussion and evaluation is available in the original report (Pruess 1992).

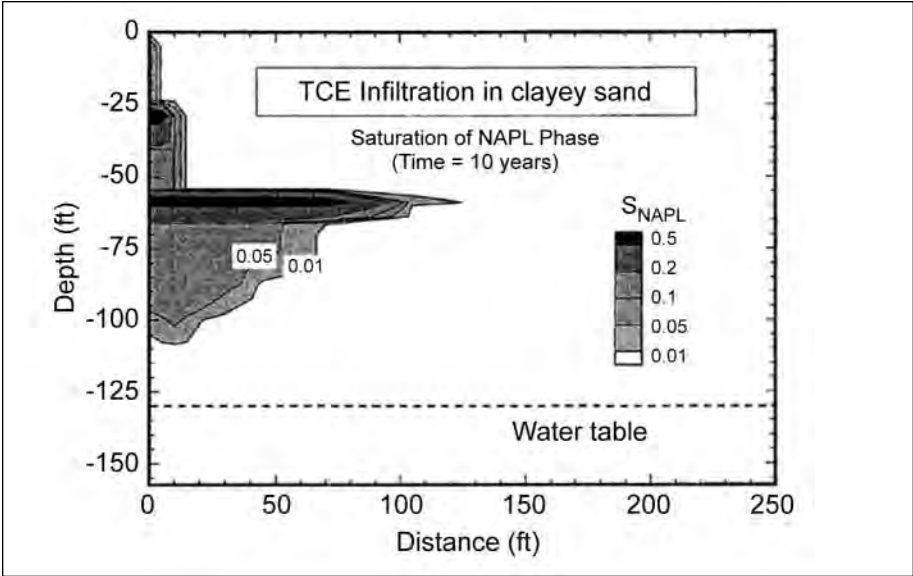


Figure 4. NAPL saturations after 10 years of infiltration.

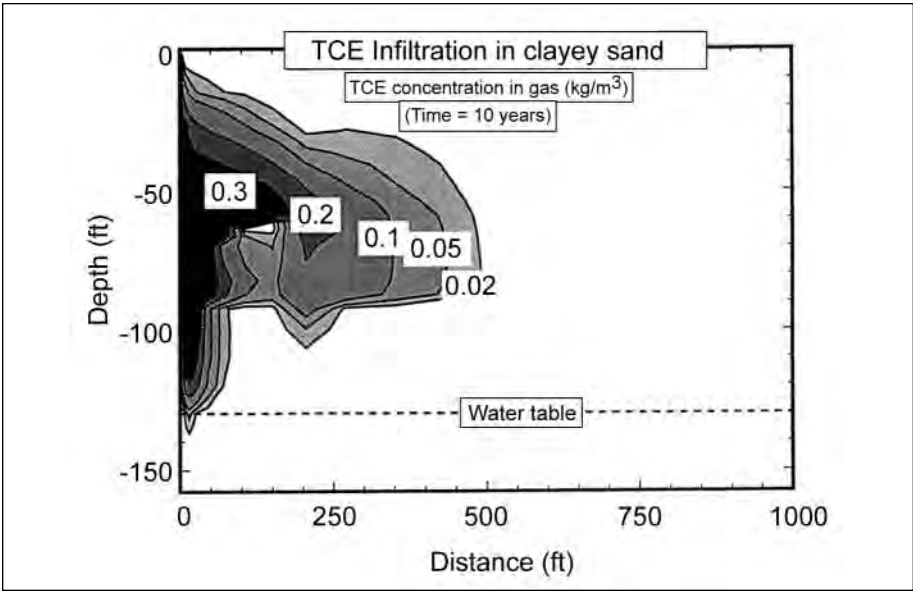


Figure 5. Concentrations of TCE in the gas phase after 10 years of infiltration.

AQUEOUS DIFFUSION IN THE VADOSE ZONE

Contributors: **James L. Conca** and **Judith Wright**

As a transport mechanism, aqueous diffusion of dissolved species is important in specific situations in the vadose zone when advective flow is negligible relative to diffusion. These situations include (1) relatively impermeable barriers or containers, such as compacted bentonite or concrete under all degrees of saturation, (2) diffusion through capillary breaks, such as a Richards Barrier, (3) highly unsaturated conditions in the vadose zone under negligible infiltration rates, and (4) solubility-controlled release from a waste form. In these cases, the effective diffusion coefficient is an important input parameter for modeling studies.

The effective aqueous diffusion coefficients were experimentally measured in a variety of porous/fractured geologic and engineered media, using the Nernst-Einstern method and the half-cell method (Conca and Wright 1990, 1992; Albinsson and Engkvist 1989; Relyea *et al.* 1986), and are shown in Figure 1. The coefficients are dependent primarily on the volumetric water content, and for all materials fall into a

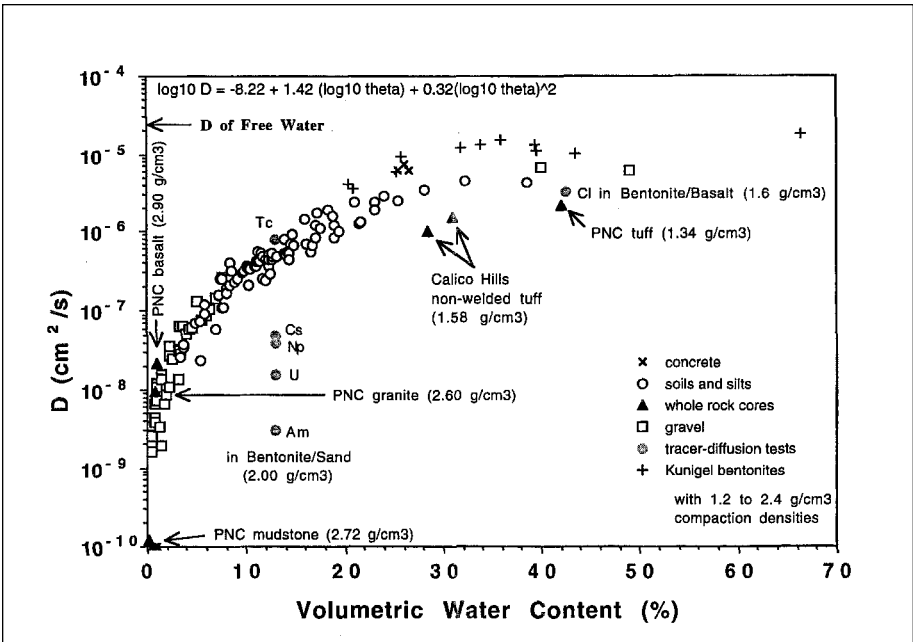


Figure 1. Effective diffusion coefficient versus volumetric water content for geologic materials using the Nernst-Einstern method and the half-cell method (closed circles).

narrow range of distribution fit by the mathematical relationship shown in the figure. The volumetric water content refers to the free volumetric water content and does not include interlayer water in clays or other structural water, such as hydration waters in gypsum or zeolite, in which species diffusion is orders of magnitude lower than in free water.



MEASUREMENT OF UNSATURATED-ZONE WATER FLUXES ADJACENT TO A RADIOACTIVE-WASTE-MANAGEMENT UNIT

Contributors: **S.W. Tyler, J. Chapman, S.H. Conrad, D.P. Hammermeister, D.O. Blout, J.J. Miller, M.J. Sully and J.M. Ginanni**

Measurement of water fluxes in arid vadose zones is a critical component in the performance assessment of waste disposal facilities. Yet in arid regions, measurement of the rates of water flux is difficult because of the low fluxes and dry soil conditions. While there are many methods to estimate deep infiltration and recharge in the vadose zone (Gee and Hillel 1988), most of these methods are plagued by large uncertainties and difficulties in field applications. Therefore, in vadose zone studies, it is important that multiple, independent methods are used to both reduce uncertainty and to provide greater confidence in water flux estimates.

In this brief case study, we illustrate one methodology for estimation of water flux using environmental chloride. Figure 1(a) shows the chloride concentration from one of the deep boreholes drilled in the Area 5 Radioactive Waste Management Site located on the Nevada Test Site. To estimate the soil water fluxes and ages in this deep vadose zone, we used chloride as an environmental tracer. Assuming the chloride ion to be conservative, the soil water age at any depth, z , can be estimated by calculating the time required to accumulate the mass of chloride stored above z provided the surface chloride flux is well constrained. Modern chloride accumulation rates at the site are approximately $75 \text{ mg/m}^2/\text{yr}$ (Tyler *et al.* 1996); however, paleo-deposition rates are likely to have been higher on account of increased precipitation.

Figure 1(b) shows the estimated soil water age versus depth assuming a paleo-chloride flux of $105 \text{ mg/m}^2/\text{yr}$, accounting for an estimated 50% increase in precipitation during the late Pleistocene. Soil water ages rapidly increase with depth, reaching an age of approximately 120,000 years near the modern water table. While this number represents the oldest waters recovered from vadose zone profiles, the timing is consistent with the Termination II, a period documented (by paleoclimate

proxies in the region) to be an extreme pluvial period. The chloride data are therefore consistent with recharge periods coinciding with full glacial conditions.

Analysis suggests that deep infiltration and recharge have been limited to pluvial periods corresponding to full glacial conditions. Chloride data, when combined with other isotopes, soil-hydraulic, and thermal data, are consistent with a state of negligible deep infiltration and recharge under today's climate conditions (Tyler *et al.* 1996).

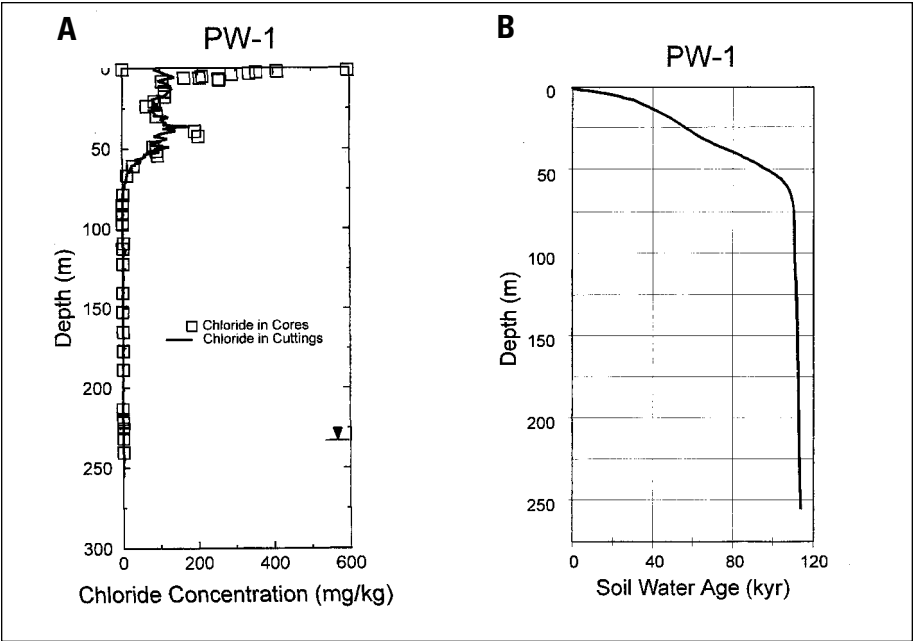


Figure 1. Chloride concentraion and soil water age-distibution along a vertical borehole.



INTEGRATED GEOLOGICAL INTERPRETATION FOR COMPUTATIONAL MODELING

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INTRODUCTION

Accurate representation of geologic geometries, such as fault structures and stratigraphy, within computational models is often critical when attempting to understand fluid flow and chemical transport within porous geological materials. However, the abstraction of geology to a computer representation of geometry is often overlooked and considered synonymous with computational mesh generation. If, however, geometry is defined independent of mesh generation, more flexibility is gained. This permits critical decisions about the type of mesh to create, the property distribution within stratigraphic layers, the compatibility between the study goals and numerical methods (finite difference, finite element, finite volume) used to represent physics and the compatibility between the computational method and computational mesh, to be made. One approach to this step of computational modeling is to separate geometry representation from mesh generation. This geometric modeling approach is of particular interest to the geosciences because complex geology, which incorporates structure, stratigraphy, tunnels, bore holes, faults and features with high aspect ratios, can be effectively modeled.

In addition, this approach offers advantages when increased resolution in a particular part of a model is required. A refined mesh will not only increase computational resolution in that domain, it will more accurately represent geometry. This approach, illustrated in hydrogeologic flow and transport studies, more accurately models complex geologic systems.

GEOLOGICAL COMPUTER AIDED DESIGN (CAD)

Geological interpretation and representation in three dimensions can be accomplished by utilizing commercially available software packages. The more sophisticated products target oil and gas applications, hydrology and environmental restoration. Other, software products tend to target smaller scale applications and are generally easier to use, and less expensive, but are generally more limited in functionality. Most Geographical Information System (GIS) packages are not well-suited to three dimensional geometric modeling since they tend to be two-dimensional with elevation treated as an attribute of the two-dimensional surface. Essential features of a geological CAD program are a) provide tools which allow geological data to be integrated into a geological interpretation with the full complexity of geology, and b) provide output data which allows the geological CAD model to be

transferred to other applications such as mesh generation and flow and transport modeling tools.

An important distinction is that geological models be independent of any mesh used for computation. A computational mesh should be able to be derived from the geological model, but the mesh should not be the model. This allows one to separate issues of geological model resolution from mesh resolution or quality. This separation is necessary in a computational mesh to resolve or accurately represent physical phenomenon.

MESH GENERATION FOR GEOLOGICAL APPLICATIONS

While geological applications have special problems (high aspect ratio, multiple internal interfaces), the general problem of creating a computational mesh has broad applications in all areas of science and engineering. Thompson et al. 1998, state:

“... grid generation is, unfortunately from a technology standpoint, still something of an art, as well as a science. Mathematics provides the essential foundation for moving the grid generation process from a user-intensive craft to an automated system. But there is both art and science in the design of the mathematics for—not of—grid generation systems, since there are no inherent laws (equations) of grid generation to be discovered. The grid generation process is not unique; rather it must be designed.”

This description points out the distinction between automatic and automated. The algorithms and software enable complex operations to be performed, but the process remains a series of expert judgment calls by the mesh generation specialist. There are automatic mesh generation strategies, such as superimposing a regular orthogonal grid onto the geologic model and assigning mesh node or cell attributes according to the geologic strata the node or cell resides in. However, even this very simple approach requires the modeler make initial judgments as to the resolution necessary to capture small features in the geological model and the resolution required to resolve physical phenomena.

EXAMPLES FROM UNSATURATED ZONE FLOW AND TRANSPORT MODELING

The points outlined above are illustrated by the following examples. They show small portions of grids developed for modeling unsaturated flow and contaminant transport. Details of the geologic characterization, geometric modeling and mesh generation are explained more fully in Gable et al. (1995) and Robinson et al. (1997). Figure 1 illustrates a situation where different sets of calculations required different resolution meshes. Each mesh uses the outlines of the stratigraphic layers as input, so that, regardless of the final resolution of the mesh, the layering is captured at a resolution determined by the point density of the mesh generation process rather

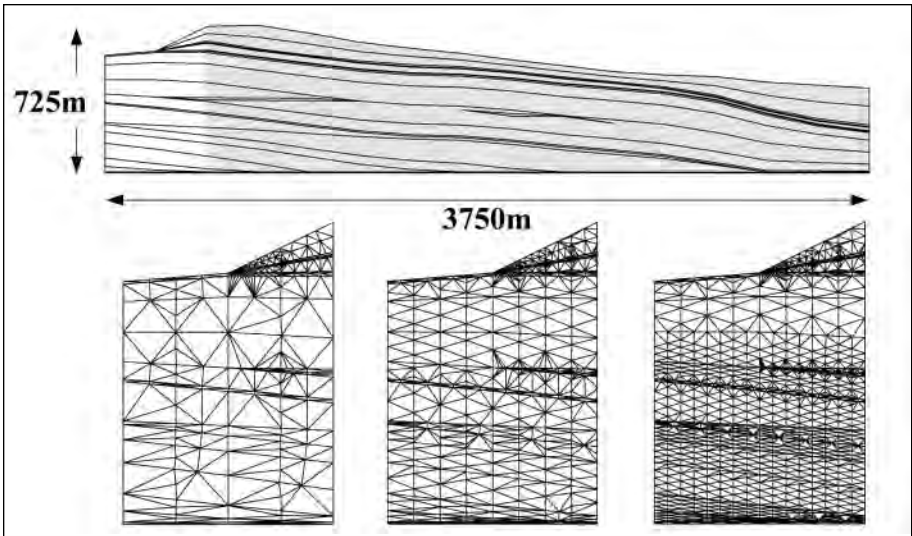


Figure 1. The outline of 21 stratigraphic horizons defines the geometry of the materials in a geologic cross section (Gable *et al.* 1995). The three triangular meshes, which show only the left 500m of the cross section, are used for different calculations. The first low-resolution mesh is used in initial calculations. Final calculations used the highest resolution grid which has increased resolution in the lower half to resolve contaminant transport from a release point at mid-depth.

than the resolution of the geometric definition of stratigraphy. By having a mesh generation process which maintains stratigraphic interfaces, the increased resolution mesh does a better job of capturing geometry.

In the example shown in Figure 2 the stratigraphic layering is similar to Figure 1, however there is the added complication of faulting which offsets stratigraphic layers. The outlines of structural blocks and stratigraphic layers are used to define the geometric inter-faces. Figure 3 shows the same example in three dimensions.

In Figure 3, material and structural interfaces are defined by triangulated surfaces rather than outlines. Each surface triangulation has elevations associated with the nodes. The triangulated surfaces are stacked together to define structure and stratigraphy. The final mesh in Figure 3 maintains the stratigraphic and structural interfaces by filling in the volume between surfaces with tetrahedra.

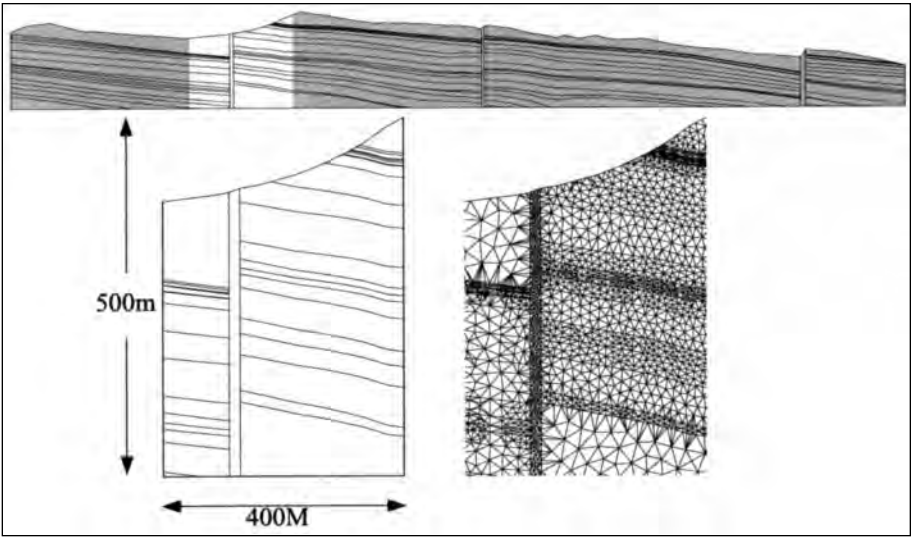


Figure 2. A small portion of a much larger mesh which includes faults that offset the stratigraphic layers (Robinson *et al.* 1997). The geometry defined by the stratigraphic and structural boundaries is used to control the mesh generation process insuring that all interfaces are maintained.

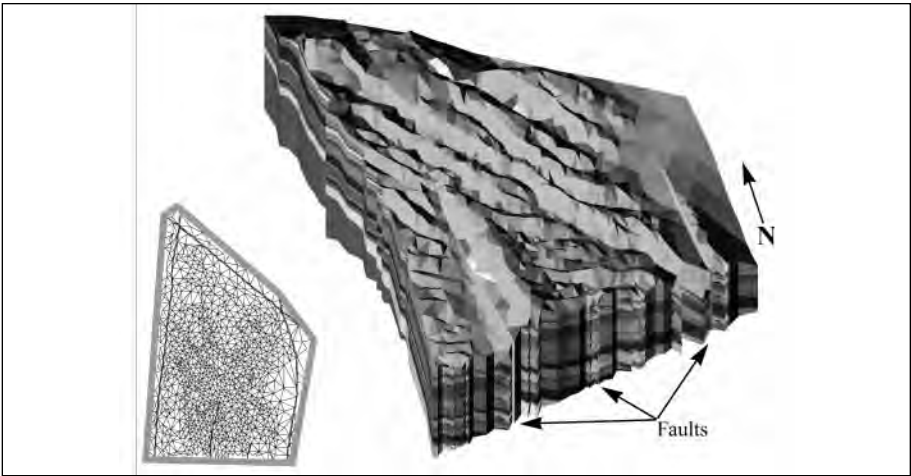


Figure 3. A three-dimensional tetrahedral mesh representing the vadose zone (Robinson *et al.* 1997) with 3X vertical exaggeration. The geometry is defined by triangulated surfaces, where each node of the triangulation is assigned an elevation. The total model depth is 725m. The NS extent is 5km, with the southern 2km removed. EW extent is 3km. The two-dimensional cross sections shown in Figures 1 and 2 are EW cross-sections from the region shown in the southern cut-away face of the three-dimensional model. Faults, which offset the stratigraphic layers, are part of the 3D computational mesh.

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A VADOSE ZONE INJECTION EXPERIMENT FOR TESTING FLOW AND TRANSPORT MODELS

M.J. Fayer

INTRODUCTION

From the mid-1940s to the mid-1980s, the U.S. government constructed and operated facilities at the Hanford Site in southeastern Washington to produce nuclear materials for defense purposes. During that 40-year period, large quantities of radioactive and chemical wastes were produced. Some wastes entered and contaminated the environment; the remainder is stored in various containers across the Hanford Site. The U.S. Department of Energy (DOE) Order 5820.2A (DOE 1988) mandates that site-specific radiological performance assessments be conducted before placing waste in disposal facilities. These performance assessments must provide a reasonable assurance that the disposal activities will protect long-term human health and safety before DOE approves the facilities. This case study describes a 1980 vadose zone injection experiment and subsequent modeling study intended to demonstrate that model results can provide a reasonable assurance of protection.

STATEMENT OF THE PROBLEM AND OBJECTIVES

Vadose zone flow and transport models are recognized as appropriate and necessary tools for baseline risk assessments. The most convincing way to demonstrate model appropriateness is to show that the model can reproduce reality (for example, the movement of water and contaminants in the field). This is generally called "validation." Bredehoeft and Konikow (1993) suggested calling the usual model validation process "history matching" because it is based largely on comparisons to existing data.

A vadose zone injection experiment was conducted at the Hanford Site in 1980 to test flow and transport models (Sisson and Lu 1980). The significant quantity of information that was collected during the test was subsequently supplemented with sediment analyses and borehole geophysical logging to provide better estimates of water contents, contaminants, and stratigraphy (Fayer *et al.* 1993, 1995). Multiple numerical modeling studies were conducted to demonstrate how well the model results matched the field observations (for example, see Sisson and Lu 1980, Lu and Khaleel 1993, Smoot and Lu 1994, Smoot 1995, Rockhold *et al.* 1997). The overall objective throughout these activities was to demonstrate the appropriateness of the conceptual model for the performance assessment, and, ultimately, to provide a data set that is sufficiently complete, detailed, and accurate to test models effectively.

SETTING

The 1,450 km² Hanford Site resides within the semi-arid Pasco Basin of the Columbia Plateau in southeastern Washington State. The injection site lies at the approximate center of the Hanford Site, midway between the two main processing areas, the 200 East and 200 West Areas.

GEOLOGY

The Columbia Plateau is formed from a thick sequence of basalt flows that have been folded and faulted over the past 17 million years, creating broad structural and topographic basins separated by asymmetrical anticlinal ridges. The basalt flows are exposed along the anticlinal ridges, where they have been uplifted as much as 1,097 m above the surrounding area. Filling the synclinal basins in the basalt flows are sediments (sometimes up to 518 m thick) of the late Miocene, Pliocene, and Pleistocene Age. The stratigraphy of the injection site consists of the basalt flows overlain by the sediments of the Ringold Formation, the Hanford formation and Holocene eolian deposits. The injection experiment and all subsequent measurements occurred entirely within the Hanford formation and eolian deposits.

The Hanford formation is an informal name that represents all the deposits of the cataclysmic floods of the Pleistocene (2 million to 13,000 years ago). Glacial Lake Missoula formed in the Clark Fork River valley in Montana behind continental glaciers that spread south as far as the present Columbia Plateau. The lake may have given way as many as 40 times, allowing the impounded water to spread across eastern Washington and form the Channeled Scablands. These flood waters collected in the Pasco Basin and formed Lake Lewis, which slowly drained through the small water gap in the Horse Heaven Hills called Wallula Gap.

Two types of Hanford formation deposits were left behind by the Missoula Floods at the injection site: (1) high-energy deposits consisting of gravel, and (2) coarse to fine sand deposits representing an energy transition environment. The sandy sequence occupies the upper 75 m. All testing occurred within this sequence.

Holocene deposits consisting of silt, sand, and gravel form a thin (<1.5 m) veneer across much of the Hanford Site, as well as the injection site. The Holocene deposits and exposed Hanford formation sediments have experienced some soil development and evolved into identifiable soil types. However, construction of the nearby disposal crib in 1967 obliterated any identifiable soil horizons at the injection site.

HYDROGEOLOGIC CHARACTERISTICS OF THE VADOSE ZONE

Between 1946 and 1998, annual precipitation at the Hanford Site averaged 174 mm and varied between 76 and 313 mm. During the same period, average monthly temperatures ranged from -0.9°C in January to 24.6°C in July. The plant community is

shrub-steppe, consisting of a combination of sagebrush and bunchgrasses. Prior to the injection experiment, the site was grubbed (that is, shrubs and other vegetation were removed), possibly as early as 1967. Since then, vegetation at the injection site has consisted of annual grasses and forbs and non-native weedy species such as cheatgrass, tumblemustard, and tumbleweed.

Natural recharge rates in shrub-steppe communities typically range from 0 to 5 mm/yr. After shrub removal, rates can increase to values between 10 and 20 mm/yr. Movement of this recharge water will be controlled by the properties of the sediments. The depositional environment of the sediments (flood waters) led to the formation of distinct, mostly-horizontal layers in portions of the vadose zone. These large-scale sediment differences influence the rate and direction of water movement.

The local, unconfined aquifer is located about 100 m below the soil surface. The injection and subsequent monitoring all occurred more than 80 m above the water table, so groundwater impacts (if any) should be negligible.

CONTAMINANTS: TYPE AND DISTRIBUTION

Unlike most case studies involving leaks, spills, and waste disposal, a known quantity of contaminants was injected during each injection event. The solutions contained calcium chloride, calcium nitrate, barium chloride, rubidium nitrate, and two radioactive ions, ^{134}Cs and ^{85}Sr . Table 1 provides information on these tracers, including estimated R_d values (an R_d value is an empirically-determined sorption parameter) and the average solution concentrations.

TABLE 1 Tracers used in the injection fluid.

Tracer	Atomic Weight	Valence	Half Life	Average R_d for Hanford (mL/g)	Suggested R_d Range (mL/g)	Average Injection Concentration (Activity)
Ba	137.3	+1	—	50	—	2.1×10^{-5} M
Ca	40.1	+2	—	10	—	6.0×10^{-3} M
Cl	35.5	-1	—	0	—	164 ppm
^{134}Cs	132.9	+1	2.05 yr	50	64 to 1360	1.6×10^{-11} M (2.8 $\mu\text{Ci/L}$)
NO_3	62.0	-1	—	0	—	320 ppm
Rb	85.5	+1	—	unknown	—	1.0×10^{-5} M
^{85}Sr	87.6	+2	64 d	1	0.3 to 42	1.2×10^{-11} M (24 $\mu\text{Ci/L}$)

GENERAL DESIGN AND METHODS USED

OVERVIEW OF FIELD DESIGN

A solution containing multiple tracers was injected on eleven separate occasions at a single point in the vadose zone. The resulting spread of the water and tracers was monitored in wells that surrounded the injection point. The injection experiment was carried out during a 16-month period from June 1980 to October 1981. Limited sediment analyses were conducted in 1993. All 32 boreholes were logged in 1995 for water content, bulk density, and ^{134}Cs . The reports containing these data include Sisson and Lu (1984) and Fayer *et al.* (1993, 1995).

METHODS USED

A 2.5-cm-diameter galvanized steel pipe was cemented within a 0.15-cm-diameter schedule-40 steel casing such that the bottom of the smaller pipe protruded slightly from the casing. The smaller pipe delivered the injection solution. The tip of the smaller pipe was 4.57 m below ground surface and served as the injection point. Thirty-two 18.3-m-deep monitoring wells (0.15-cm-diameter schedule-40 steel casing) were installed within eight concentric rings arranged from 1 to 8 m from the injection well (Figure 1). Thus, the total monitored domain was 16 m in diameter and 18.3 m deep. Initial water contents were measured at 0.3-m intervals prior to the first injection.

Eleven injection tests were performed. The first eight injections occurred on a weekly basis from September 22 to November 10, 1980. These injections included the radioactive tracers. The remaining three injections occurred on November 18 and 24, 1980, and February 2, 1981, and did not include radioactive tracers. Each injection solution was mixed in the tank located outside the monitoring area and delivered by pipe to the injection point using a stainless-steel gear pump that controlled the delivery rate. The volume of solution injected during each a test ranged from 3,000 to 5,500 L. The injection rates ranged from 270 to 420 L/h.

Water content was measured with hand-held neutron probes and the concentrations of the two radioactive tracers were measured with a gamma-energy-analysis probe. These measurements occurred on an *ad hoc* basis at various depths and times throughout the experiment. Most measurements occurred near the injection point. Only as the wetted zone expanded were measurements conducted in the outer boreholes. The frequency of data collection in the outer wells was sparse. Measurements of ^{85}Sr and ^{134}Cs during the experiment were infrequent and limited to those wells located within 2 m of the injection well. The other tracers were not monitored.

Nineteen samples of drill cuttings were collected during emplacement of some of the monitoring wells. These samples were analyzed in 1993 for particle density and size distribution, water retention, and hydraulic conductivity, using repacked samples.

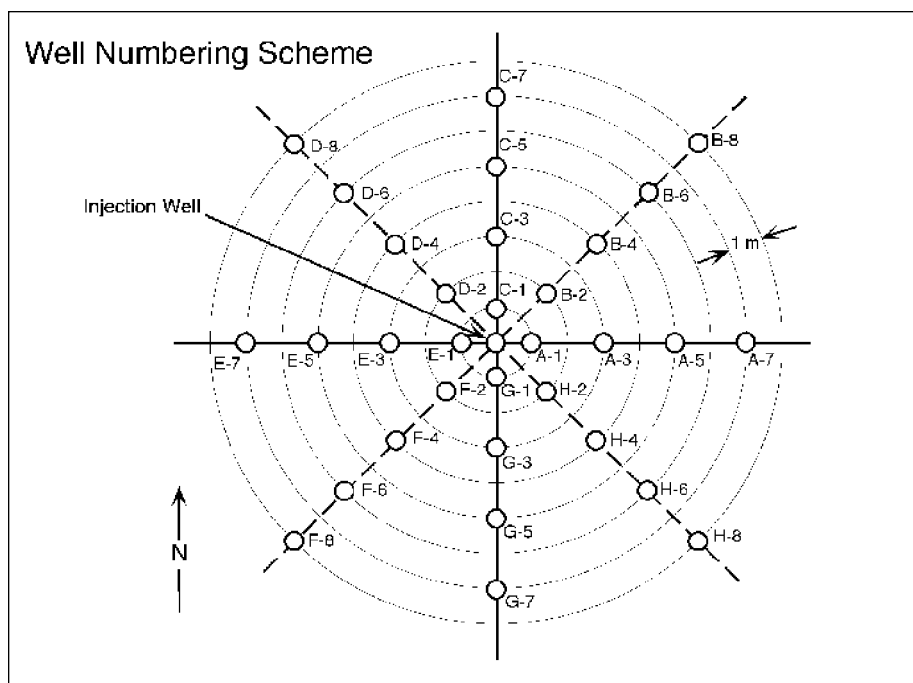


Figure 1. Plan view of the monitoring and injection wells.

In 1995, all 32 boreholes were logged every 0.15 m with a neutron tool for water content, a gamma tool for bulk density, and a spectral gamma tool for ^{85}Sr and ^{134}Cs ^a. Three boreholes near the injection well were logged with a high-selectivity, spectral gamma probe specifically for ^{134}Cs ^b.

RESULTS

Figure 2 shows depth profiles of the radioactive tracers and water content on several dates in one monitoring well located 1 m from the injection well. The peak activity of ^{85}Sr occurred at a depth of around 5.74 m. In time, the peak broadened vertically both upward and downward to depths between 4.9 and 7.3 m. The avail-

^aLogging was conducted using the CNT-G, LDS, and HNGS tools, Schlumberger Wireline Services, P. O. Box 2175, Houston, Texas.

^bLogging was conducted using a 70%-efficient HPGe scintillation detector, Three Rivers Scientific, 3659 Grant Court, West Richland, Washington.

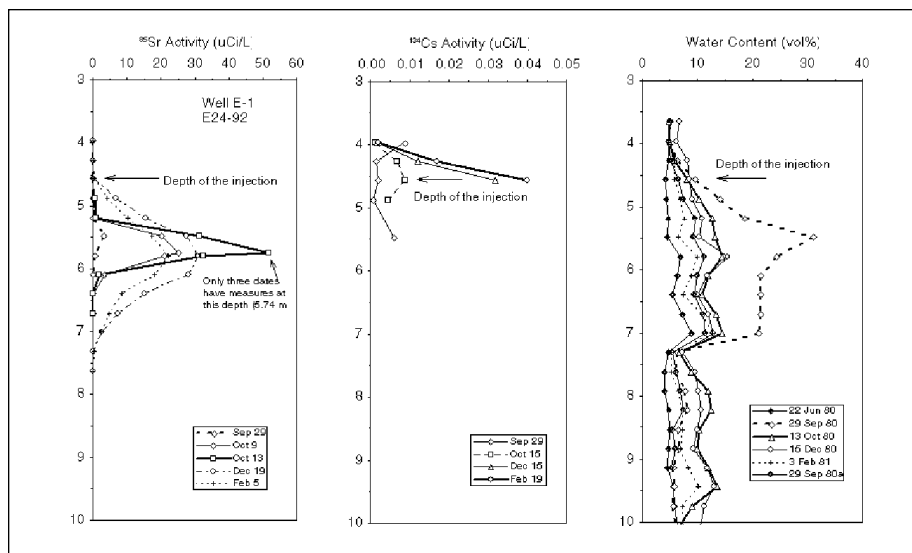


Figure 2. Depth profiles of ^{85}Sr , ^{134}Cs , and water content 1 m from the injection well on selected dates

able data suggest that ^{85}Sr moved beyond the 2-m wells. For example, elevated levels of ^{85}Sr were detected in the 2-m wells as early as the date of the fifth injection. However, no tracer measurements were made beyond the 2-m wells.

As Figure 2 shows, the profile of ^{134}Cs was not well defined. Throughout the 1980 experiment, ^{134}Cs was detected in only three wells, all located 1 m from the injection well. The depths of observation ranged from 4.0 to 5.5 m. The fourth well, located 1 m from the injection well, showed no ^{134}Cs . In contrast, all four monitoring wells at the 1-m distance showed elevated levels of ^{85}Sr .

The water-content profiles in Figure 2 show that water moved vertically quite rapidly throughout the system. Data from other wells showed that water left the monitored domain laterally and vertically before the end of the experiment.

In 1983, the 32 monitoring boreholes were surveyed for gross gamma counts. Pre-experiment gross gamma counts were used to delineate those regions that most likely had residual ^{134}Cs from the injection experiment. The results showed that ^{134}Cs still existed in all four 1-m monitoring wells at depths ranging from 3.9 to 6.6 m. The results also showed that ^{134}Cs existed in two of the four 2-m monitoring wells at depths ranging from 5.7 to 6.4 m. None of the other wells showed detectable ^{134}Cs .

Figure 3 shows a cross-section of the wet-bulk-density data derived from borehole logging. These data indicate the large-scale layered nature of the sediments. The data also reveal that the gross layers are not necessarily laterally uniform, continuous, or exactly horizontal, assumptions that are typically invoked in the traditional view of vadose zone sediments. The 1995 logging data also indicated the presence of minute amounts of residual ^{134}Cs in three of the four 1-m monitoring wells at depths within 1 m of the injection point depth. No ^{134}Cs was detected in any of the other wells.

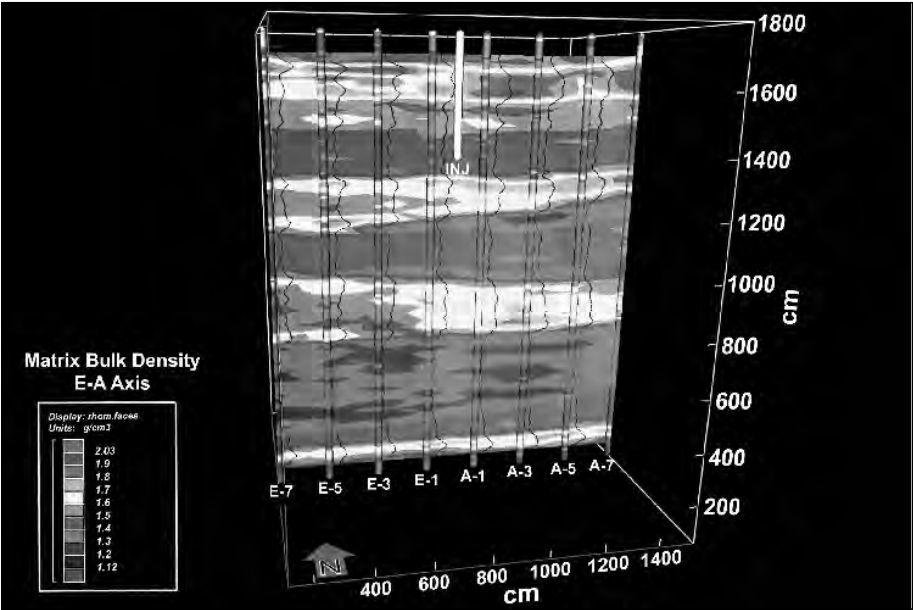


Figure 3. Cross section through the monitored domain showing bulk density estimated from logging data.

In the latest effort to model this experiment, Rockhold *et al.* (1997) used the initial water contents, logging-derived bulk densities, and the sediment soil hydraulic properties to parameterize a numerical model. They created a 3-D geologic model using geostatistical-indicator simulation techniques for spatial interpolation, and a conditional simulation method based on similar media scaling for estimating hydraulic properties from a set of scale-mean parameters and the initial water content and porosity distributions. They determined effective model parameters from the geologic model using an upscaling algorithm.

Figure 4 shows that the simulated water content distributions compared well with the measured distributions for two cross sections of the experiment domain on 4 December 1980, just eleven days after the tenth injection. The range of water content differences ($[\text{predicted}] - [\text{measured}]$) for the simulation on that date was from -0.096 to $0.103 \text{ cm}^3/\text{cm}^3$. The root-mean-square error (RMSE) in water content for that date was $0.034 \text{ cm}^3/\text{cm}^3$. To demonstrate sensitivity, Rockhold *et al.* (1997) adjusted three of the four scale-mean parameters and reduced the RMSE to $0.028 \text{ cm}^3/\text{cm}^3$.

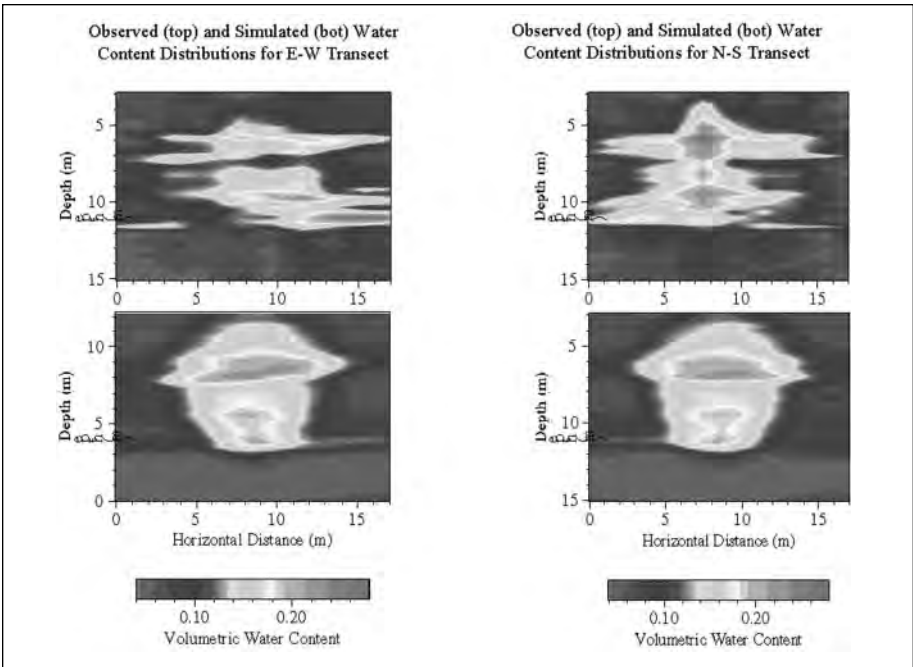


Figure 4. Observed water content distributions for (a) east-west and (b) north-south cross sections through the monitored domain, and simulated distributions along (c) east-west and (d) north-south cross-sections (after Rockhold *et al.* 1997).

DISCUSSION

The 1980 injection experiment was a unique vadose zone test that used two radioactive tracers and multiple injections. The test lasted 1 year (with a 15 year follow up) and had a 3-D domain size approaching the scale of waste sites. The monitoring scheme allowed for the detection of changes in water contents and tracer

concentrations in all directions around the central injection point. The results demonstrated that the experimental design was reasonable.

The 1995 borehole logging at the site showed that the ^{85}Sr tracer was no longer detectable (as expected, given the 64-d half-life), but that residual ^{134}Cs still remained in the vicinity of the injection well. Given the logging results from 1980 to 1995, the injected ^{134}Cs apparently remained within the monitored domain. The fact that ^{134}Cs never left the monitored domain verified the high sorption potential of cesium for these sediments.

The reports on the injection experiment contained recommendations for improvements in measurement techniques and frequency, equipment calibration, duration of experiment, support measurements, geologic model construction, and transport modeling. The use of neutron probes to monitor water content made it difficult to obtain something close to a concurrent measurement of water content throughout the domain. This problem was most acute just after an injection, when water contents were changing rapidly. To alleviate this problem, the researchers opted not to monitor certain wells and depths until the wetting front reached those zones. This time-saving solution is only useful if the wetting front is well-known. Otherwise, the experimenter runs the risk of missing the arrival of water at certain locations – as happened during the experiment.

All instruments must be reliably calibrated. If an experiment utilizes multiple probes and sensors, then efforts must be made to cross-calibrate the instruments to verify the comparability of the data collected. Field sampling is needed to verify indirect measurements (such as water content, bulk density, and cesium concentrations inferred from logging data).

The essence of the injection experiment was focused on following the short-term impacts of the injections rather than the long-term consequences. Only by serendipity (for example, the 1983 gross gamma logs) and post-mortem activities (for example, the 1995 logging) was the full value of the injection experiment realized. Trying to understand an experiment conducted more than a decade earlier revealed how difficult it is to continue an experiment if no attempt was made to prepare the original experimental details and results for posterity. Waste disposal facilities will be foci of concern for durations ranging from decades to millennia. Experiments should be designed and documented with that time frame in mind.

There is always pressure to reduce or eliminate tests to reduce costs. However, certain support tests are important and vitally needed. For example, the soil hydraulic data used for modeling activities came from loose sediment collected during the air-rotary drilling of three of the boreholes. Hydraulic properties are much more useful if derived *in situ*, or at least on undisturbed cores. The logging data were very helpful, but no samples were available to verify the lithology of the geologic model or to calibrate the geophysical logging tools.

Some of the data indicated features at a vertical scale finer than 0.15 m. Such features may play an important role in sorption and transport. In addition to 0.15 m spacing, the density tool collected information on a 2.5 cm spacing. This level of detail, with field verification, could be used to construct a more highly-resolved geologic model.

Many vadose zone modeling studies use the simple layered approach to describe vadose zone sediments. An effort could be made to repeat the simulations using several of these simpler models and comparing and contrasting the results using the geologic model constructed by Rockhold *et al.* (1997). The results could be used to evaluate the benefits derived from using the progressively more detailed, expensive, and computationally-intensive geologic models. In addition, an effort should be made to simulate the transport component of this experiment. Granted, the tracer data are spatially and temporally sparse, but the effort will highlight whether current capabilities are even capable of reproducing the observed behavior of the two radioactive tracers.

CONCLUSIONS

The 1980 injection experiment at the Hanford Site was a unique vadose zone test that included radioactive tracers and a 3-D domain size approaching the scale of waste sites. The monitoring scheme allowed for the detection of changes in water contents and tracer concentrations in all directions around the central injection point, although not always at the desired spatial and temporal frequency. The results demonstrated that the experimental design was reasonable, but could be improved.

Borehole logging in 1983 and 1995 demonstrated that the ^{134}Cs tracer was completely retained within the experimental domain. This result suggests that this tracer could be useful for other vadose zone studies.

The logging data proved valuable for constructing a 3-D geologic model of the experimental domain. Numerical simulations using that geologic model were reasonably successful at reproducing water content changes within the vadose zone. Transport simulations were not completed.

Recommendations for future vadose zone experiments were provided. One of the more important recommendations is to design longer-term experiments that are more similar to actual disposal conditions. If such experiments are attempted, they should be supported fully and in a fashion that maintains continuity and data integrity for the duration of the test. To be kept in mind is the distinct probability that those who finish the experiment a decade or more from now will not be those who start the experiment.

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INVERSE ESTIMATION OF UNSATURATED SOIL HYDRAULIC AND SOLUTE TRANSPORT PARAMETERS USING THE HYDRUS-1D CODE

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INTRODUCTION

A variety of field methods are currently available for direct measurement of the unsaturated hydraulic conductivity, K , as a function of the pressure head, h , and/or the water content, θ (Klute and Dirksen, 1986, Green *et al.* 1986, Dirksen 1991). Popular field methods include the instantaneous profile method, various unit-gradient-type approaches, sorptivity methods following ponded infiltration, and the crust method based on steady water flow. While relatively simple in concept, these direct measurement methods have a number of limitations that restrict their use in practice. For example, most methods are very time-consuming to execute because of the need to adhere to relatively restrictive initial and boundary conditions. This is especially true for field gravity-drainage experiments involving medium- and fine-textured soils. Methods requiring repeated steady-state flow situations or other equilibrium conditions are also tedious, while linearizations—and other approximations or interpolations to allow analytic or semi-analytic inversions of the flow equation—may introduce additional errors. Finally, information about uncertainty in the estimated hydraulic parameters is not readily obtained using direct inversion methods.

A much more flexible approach for solving the inverse problem is the use of parameter optimization methods (Kool *et al.* 1987, Hopmans and Simunek, 1999). Optimization procedures make it possible to simultaneously estimate the retention and hydraulic conductivity functions from transient flow data. While many possible scenarios exist for the application of parameter optimization methods, numerical inversion of the Richards' equation has thus far been limited only, or nearly exclusively, to one-dimensional experiments (Kool *et al.* 1985, Russo *et al.* 1991), mostly in conjunction with one-step or multi-step outflow experiments (Kool and Parker 1988; van Dam *et al.* 1992, 1994; Eching *et al.* 1993). Nevertheless, other types of experiments, such as upward infiltration (Hudson *et al.* 1996) or evaporation methods (Ciollaro and Romano 1995, Santini *et al.* 1995, Simunek *et al.* 1998b), have also been reported.

This case study documents our experience with a parameter estimation procedure which combines the Levenberg-Marquardt nonlinear parameter optimization method involving weighted least squares with a one-dimensional numerical model, HYDRUS-1D (Simunek *et al.* 1998a), simulating variably-saturated water flow and solute transport. We demonstrate parameter estimation procedure on laboratory and

field data, and briefly summarize several other applications of the HYDRUS-1D model.

THE FORWARD PROBLEM

VARIABLY-SATURATED WATER FLOW

The governing equation for two-dimensional isothermal Darcian water flow in a variably-saturated rigid isotropic porous medium is given by the following modified form of the Richards equation:

$$\frac{\partial \theta}{\partial t} = \frac{\partial}{\partial z} \left[K \left(\frac{\partial h}{\partial z} + 1 \right) \right] - S \quad (1)$$

where z is the vertical coordinate positive upwards, t is time, S is a sink term, and K is the unsaturated hydraulic conductivity function given as the product of the relative hydraulic conductivity, K_r , and the saturated hydraulic conductivity, K_s .

Equation (1) can be solved numerically for a given set of initial and boundary equations. The HYDRUS-1D code implements three different types of boundary conditions: specified pressure head (Dirichlet type) conditions of the form

$$h(z, t) = \psi(z, t) \quad (2)$$

with specified flux (Neumann type) conditions given by

$$-K \left(\frac{\partial h}{\partial z} + 1 \right) = \sigma(z, t) \quad (3)$$

and specified free drainage conditions as follows

$$\frac{\partial h}{\partial z} = 0 \quad (4)$$

where ψ and σ are the prescribed Dirichlet and Neumann type boundary conditions, respectively, as functions of t .

The above boundary conditions can be implemented in HYDRUS-1D in several ways: as (a) constant boundary conditions (either flux or head), (b) variable boundary conditions (again either flux or head), (c) seepage faces, (d) atmospheric boundaries, and (e) free or deep drainage boundaries. Boundary classes (a) and (b) represent system-independent boundary conditions, while (c), (d), and (e) are system dependent, that is, they depend on the prevailing transient soil moisture or flux conditions.

While different functions for the unsaturated soil-hydraulic properties may be used in the inverse problem, the expressions adopted in HYDRUS-1D are those of van Genuchten (1980):

$$S_e(h) = \frac{\theta(h) - \theta_r}{\theta_s - \theta_r} = \frac{1}{(1 + |\alpha h|^n)^m} \quad (5)$$

$$K(\theta) = K_s S_e^l [1 - (1 - S_e^{1/m})^m]^2 \quad (6)$$

and Brooks and Corey (1966):

$$S_e(h) = \frac{\theta(h) - \theta_r}{\theta_s - \theta_r} = \begin{cases} \frac{1}{|\alpha h|^n} & h < -1/\alpha \\ 1 & h \geq -1/\alpha \end{cases} \quad (7)$$

$$K(\theta) = K_s S_e^{l+2+2/n} \quad (8)$$

where S_e is the effective water content, θ_r and θ_s denote the residual and saturated water contents, respectively, and α , n , $m (= 1 - 1/n)$, and l are empirical parameters. The hydraulic characteristics defined by (5) through (8) contain 6 unknown parameters: θ_r , θ_s , α , n , l , and K_s . Of these, θ_r , θ_s , and K_s have a clear physical meaning, whereas α , n and l are essentially empirical parameters determining the shape of the retention and hydraulic conductivity functions (van Genuchten 1980).

For the hysteretic case the HYDRUS-1D code uses the formulation of Kool and Parker (1987) who coupled the van Genuchten-Mualem model with a simplified scaling approach proposed by Scott *et al.* (1983) to describe the scanning curves. Scott *et al.* (1983) assumed that the shape parameters α and n for all drying scanning curves are the same as those for the main drying curve and, similarly, the shape parameters for all wetting scanning curves are the same as those for the main wetting curve. Scanning curves are then calculated by varying the residual and saturated water contents for the wetting and drying scanning curves, respectively. Kool and Parker (1987) further assumed that the shape parameter n is the same for both wetting and drying, thus decreasing the number of required parameters. Using the additional restrictions that θ_r and θ_s are the same for both drying and wetting, the only extra parameter describing hysteresis is a third shape parameter α_d for the drying retention curve (we use α_w for wetting).

Equation (1), subject to initial and boundary conditions (2), (3) and (4), was solved numerically using the finite element method. The employed solution scheme is an

extension of the mass-conservative numerical iterative scheme used by Celia *et al.* (1990).

SOLUTE TRANSPORT

We assume that solutes can exist in all three phases (liquid, solid, and gaseous) and that production and decay processes can be different in each phase. We further assume that solutes are transported by convection and dispersion in the liquid phase, as well as by diffusion in the gas phase. The partial differential equations governing nonequilibrium chemical transport of solutes involved in a sequential first-order decay chain during transient water flow in a variably saturated rigid porous medium are taken as (Simunek *et al.* 1998a):

$$\begin{aligned} \frac{\partial \theta c_k}{\partial t} + \frac{\partial \rho s_k}{\partial t} + \frac{\partial a_v g_k}{\partial t} = & \frac{\partial}{\partial z} (\theta D_k^w \frac{\partial c_k}{\partial z}) + \frac{\partial}{\partial z} (a_v D_k^g \frac{\partial g_k}{\partial z}) - \frac{\partial q c_k}{\partial z} - \\ & - (\mu_{w,k} + \mu'_{w,k}) \theta c_k - (\mu_{s,k} + \mu'_{s,k}) \rho s_k - (\mu_{g,k} + \mu'_{g,k}) a_v g_k + \mu'_{w,k-1} \theta c_{k-1} \\ & + \mu'_{s,k-1} \rho s_{k-1} + \mu'_{g,k-1} a_v g_{k-1} + \gamma_{w,k} \theta + \gamma_{s,k} \rho + \gamma_{g,k} a_v - S_{c_r,k} \quad k \in (2, n_s) \end{aligned} \quad (9)$$

In equation (9) c , s , and g are solute concentrations in the liquid, solid and gas phases, respectively; q is the volumetric flux density; μ_w , μ_s , and μ_g are first-order rate constants for solutes in the liquid, solid and gas phases, respectively; μ'_w , μ'_s , and μ'_g are similar first-order rate constants providing connections between individual chain species; γ_w , γ_s , and γ_g are zero-order rate constants for the liquid, solid and gas phases, respectively; ρ is the soil bulk density, a_v is the air content; S is the sink term in flow equation (1); c_r is the concentration of the sink term; D^w is the dispersion coefficient for the liquid phase; and D^g is the diffusion coefficient for the gas phase. The subscripts w , s , and g correspond with the liquid, solid and gas phases, respectively. Subscript k represents the k th chain number and n_s is the number of solutes involved in the chain reaction. The nine zero- and first-order rate constants in (9) may be used to represent a variety of reactions or transformations, including biodegradation, volatilization, and precipitation. Single-ion transport is simulated by simply setting k equal to 1.

HYDRUS-1D may be used to simulate both equilibrium and nonequilibrium interactions between the solution (c) and adsorbed (s) concentrations, and equilibrium interaction between the solution (c) and gas (g) concentrations of the solute in the soil system. The equilibrium adsorption isotherm relating s and c is described by a generalized nonlinear equation of the form

$$s = \frac{k_s c^\beta}{1 + \eta c^\beta} \quad (10)$$

where k_s , β and η are empirical coefficients. The Freundlich, Langmuir, and linear adsorption equations are special cases of (10). The concentrations g and c are related by a linear expression of the form

$$g = k_g c \quad (11)$$

where k_g is an empirical constant, often referred to as Henry's constant.

The concept of two-site sorption (Selim *et al.* 1977, van Genuchten and Wagenet 1989) is implemented in the HYDRUS-1D code to permit consideration of nonequilibrium adsorption-desorption reactions. The two-site sorption concept assumes that the sorption sites can be divided into two fractions. Sorption, s^e , on one fraction of the sites (the type-1 sites) is assumed to be instantaneous, while sorption, s^k , on the remaining (type-2) sites is considered to be time-dependent. The mass balance equation for the type-2 sites in the presence of production and degradation is given by

$$\frac{\partial s^k}{\partial t} = \omega \left[(1-f) \frac{k_s c^\beta}{1 + \eta c^\beta} - s^k \right] - (\mu_s + \mu'_s) s^k + (1-f) \gamma_s \quad (12)$$

where ω is the first-order rate constant and f is the fraction of exchange sites assumed to be in equilibrium with the solution phase.

The HYDRUS-1D model also implements the concept of two-region, dual-porosity type solute transport (van Genuchten and Wierenga 1976) to permit consideration of physical nonequilibrium transport. The two-region concept assumes that the liquid phase can be partitioned into mobile (flowing), $\theta_{m'}$, and immobile (stagnant), $\theta_{im'}$, regions and that solute exchange between the two liquid regions can be modeled as a first-order process, that is, as

$$\left[\theta_{im} + \rho(1-f) \frac{k_s \beta c_{im}^{\beta-1}}{(1 + \eta c_{im}^\beta)^2} \right] \frac{\partial c_{im}}{\partial t} = - \left[\theta_{im} (\mu_w + \mu'_w) + \rho (\mu_s + \mu'_s) (1-f) \frac{k_s \beta c_{im}^{\beta-1}}{1 + \eta c_{im}^\beta} \right] c_{im} \quad (13)$$

$$+ \omega (c - c_{im}) + \gamma_w \theta_{im} + (1-f) \rho \gamma_s$$

where c_{im} is the concentration of the immobile region and w the mass transfer coefficient.

By selecting certain values (including zero) of the parameters $\gamma_w, \gamma_s, \gamma_g, \mu_w, \mu_s, \mu_g, \mu'_w, \mu'_s, \mu'_g, \eta, k_s, k_g, f, \theta_{im}, \beta$ and ω in (9) through (13), the entire system can be simplified significantly.

FORMULATION OF THE INVERSE PROBLEM

The objective function Φ , minimized during the parameter estimation with HYDRUS-1D, is defined as (Simunek *et al.* 1998a):

$$\begin{aligned} \Phi(\mathbf{b}, \mathbf{q}, \mathbf{p}) = & \sum_{j=1}^{m_q} v_j \sum_{i=1}^{n_{qj}} w_{i,j} [q_j^*(z, t_i) - q_j(z, t_i, \mathbf{b})]^2 + \\ & \sum_{j=1}^{m_p} \bar{v}_j \sum_{i=1}^{n_{pj}} \bar{w}_{i,j} [p_j^*(\theta_i) - p_j(\theta_i, \mathbf{b})]^2 + \\ & \sum_{j=1}^{n_b} \hat{v}_j [b_j^* - b_j]^2 \end{aligned} \quad (14)$$

where the first term on the right-hand side represents deviations between the measured and calculated space-time variables (for example, observed pressure heads, water contents, and/or concentrations at different locations and/or time in the flow domain, or actual or cumulative fluxes versus time across a boundary). In the first term, m_q is the number of different sets of measurements, n_{qj} is the number of measurements within a particular measurement set, $q_j^*(z, t_i)$ represents specific measurements at time t_i for the j th measurement set at location z , $q_j(z, t_i, \mathbf{b})$ represents the corresponding model predictions for the vector of optimized parameters $\mathbf{b}$ (e.g., θ_r , θ_s , a , n , l , K_s , D_r , k_g , ...), and v_j and $w_{i,j}$ are weights associated with a particular measurement set or point, respectively. The second term on the right-hand side of (14) represents differences between independently measured and predicted soil hydraulic properties (for example, retention $[q(h)]$ and/or hydraulic conductivity $[K(\theta)$ or $K(h)]$ data), while the terms m_p , n_{pj} , $p_j^*(\theta_i)$, $p_j(\theta_i, \mathbf{b})$, $\bar{v}_j$ and $\bar{w}_{i,j}$ have similar meanings as for the first term, but now for the soil hydraulic properties. The last term of (14) represents a penalty function for deviations between prior knowledge of the soil hydraulic parameters, b_j^* , and their final estimates, b_j , with n_b being the number of parameters with prior knowledge and $\hat{v}_j$ representing pre-assigned weights.

SOLUTION OF THE INVERSE PROBLEM

The parameter optimization scheme in HYDRUS-1D is based on Marquardt's (1963) method which has proved to be very effective in many applications involving non-linear least-square fitting. The method represents a compromise between the inverse-Hessian and steepest descend methods by using the steepest-descent method when the objective function is far from its minimum, and switching to the inverse-Hessian method as the minimum is being approached. Details are given in the HYDRUS-1D manual (Simunek *et al.* 1998a).

HYDRUS-1D EXAMPLES

Because of a very general formulation of the inverse problem and the possibility to use different combinations of boundary conditions, the HYDRUS-1D model can be used for a wide variety of parameter optimization problems. Typical applications include one-step (Kool *et al.* 1985) and multistep (van Dam *et al.* 1992, 1994; Echling *et al.* 1993) outflow experiments, upward infiltration experiments (Hudson *et al.* 1996), evaporation experiments (Ciollaro and Romano 1995, Santini *et al.* 1995, Simunek *et al.* 1998b), and combinations of the above experiments (e.g., infiltration followed by evaporation or redistribution). The general nature of the parameter estimation in HYDRUS-1D makes the code also a very flexible tool for inverse analysis of more complex, transient field experiments. Below we demonstrate the use of HYDRUS-1D by first estimating the soil hydraulic parameters from multistep outflow data, followed by analysis of a consecutive horizontal infiltration and redistribution experiment. The latter example demonstrates the use of HYDRUS-1D for evaluating water flow involving hysteresis. We will also use HYDRUS-1D here to estimate nonlinear parameters for solute transport involving Freundlich adsorption by analyzing a measured breakthrough curve.

INVERSE ANALYSIS OF A MULTISTEP OUTFLOW EXPERIMENT

In this example we analyze a multistep outflow experiment with simultaneous measurement of the pressure head inside the soil sample (Hopmans, personal communication). The experimental setup consisted of a 6-cm long soil column in a Tempe pressure cell modified to accommodate a microtensiometer-transducer system. A tensiometer was installed in the soil core, with the cup centered 3 cm below the soil surface. The soil sample was saturated from the bottom and subsequently equilibrated to an initial soil water pressure head of -25 cm at the soil surface. Pressures of 100, 200, 400, and 700 cm were subsequently applied in consecutive steps at 0, 12.41, 48.12, and 105.92 hours, respectively. Figure 1 compares the measured and optimized cumulative outflow curves for the soil sample, while Figure 2 compares measured and optimized pressure heads. Excellent agreement was obtained for both variables. The final fit for the optimized soil hydraulic parameters ($\theta_r=0.197$, $\theta_s=0.438$, $\alpha=0.0101 \text{ cm}^{-1}$, $n=1.43$, $l=3.80$, and $K_s=0.521 \text{ cm h}^{-1}$) had an r^2 of 0.9995. The resulting soil hydraulic functions are plotted in Figure 3.

HORIZONTAL INFILTRATION FOLLOWED BY REDISTRIBUTION

This example demonstrates the use of HYDRUS-1D for analyzing transient hysteretic flow. Data used for this example were published by Vachaud (1968). A horizontal soil column of 60 cm length and having an internal diameter of 9 cm was used. The initially air-dry silty soil was subjected to a zero pressure head at one end of the column for 620 minutes, after which water was allowed to redistribute. Although water

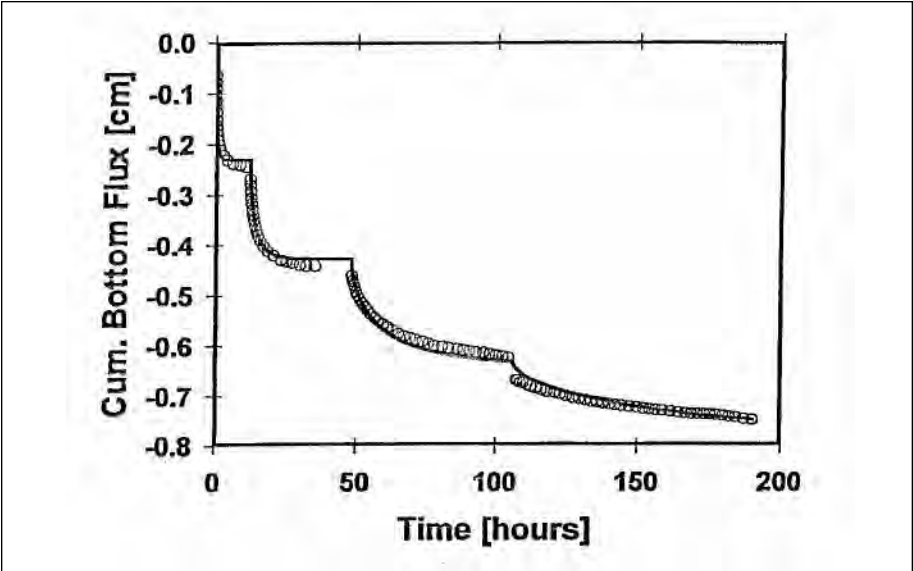


Figure 1. Measured and optimized cumulative bottom flux during a multistep outflow experiment.

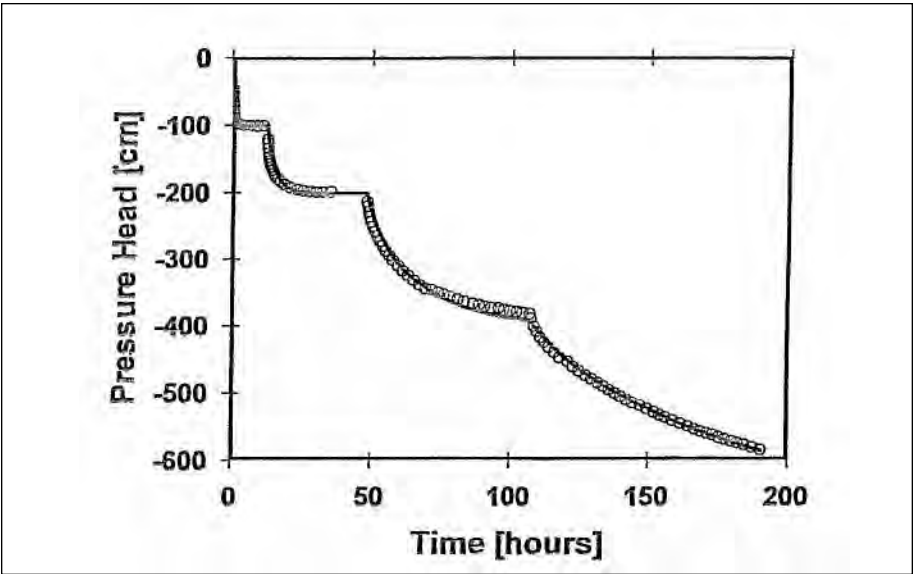


Figure 2. Measured and optimized pressure heads inside the soil sample during a multistep outflow experiment.

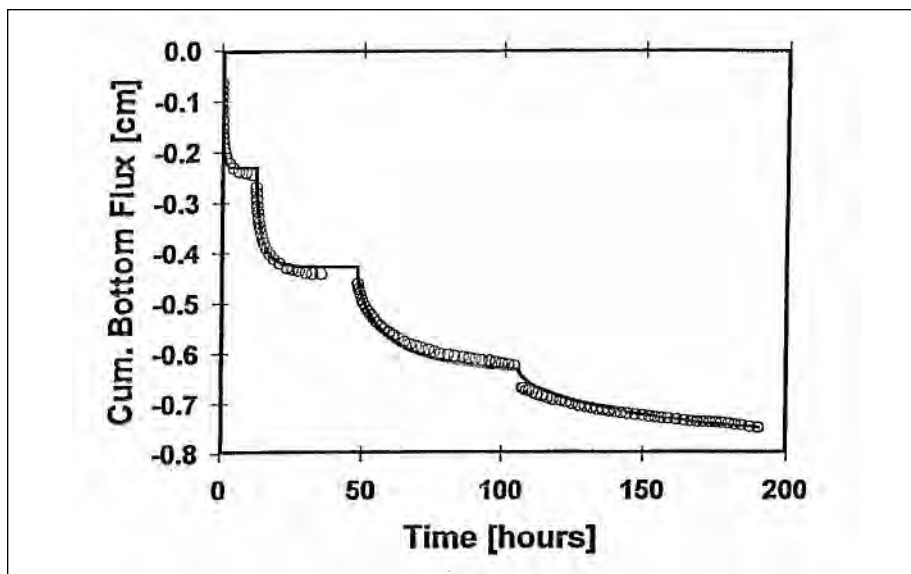


Figure 3. The resulting soil hydraulic functions, $\theta(h)$ and $K(h)$, for a multistep outflow experiment.

contents were measured at about 20 points in the column for about 25 days using a γ -ray attenuation techniques, we used data from only 10 points for the inversion. We optimized the soil hydraulic parameters in the hysteresis model of Kool and Parker's (1987) which assumes different α values for the wetting and drying curves (α_w, α_d). Figure 4 shows measured and fitted water contents during the entire experiment. An excellent fit could be obtained only when hysteresis was considered. The following soil hydraulic parameters were obtained: $\theta_r=0.009$, $\theta_s=0.423$, $\alpha_d=0.0637 \text{ cm}^{-1}$, $\alpha_w=0.0910 \text{ cm}^{-1}$, $n=3.86$, $l=1.47$, and $K_s=0.0202 \text{ cm min}^{-1}$. Figure 5 shows the resulting unsaturated soil hydraulic functions.

NONLINEAR SOLUTE TRANSPORT

This example demonstrates the use of HYDRUS-1D for estimating nonlinear solute transport parameters from column breakthrough curves. A 10.75-cm long soil column was first saturated with a $10 \text{ mmol}_e\text{L}^{-1}$ CaCl_2 solution. The experiment consisted of applying a 14.26 pore volume pulse ($t=358.05 \text{ h}$) of a $10 \text{ mmol}_e\text{L}^{-1}$ MgCl_2 solution, followed by the original CaCl_2 solution. The adsorption isotherm was determined independently with the help of batch experiments (Selim *et al.* 1987), and fitted with the Freundlich equation to yield $k_s=1.687 \text{ cm}^3\text{g}^{-1}$ and $\beta=1.615$.

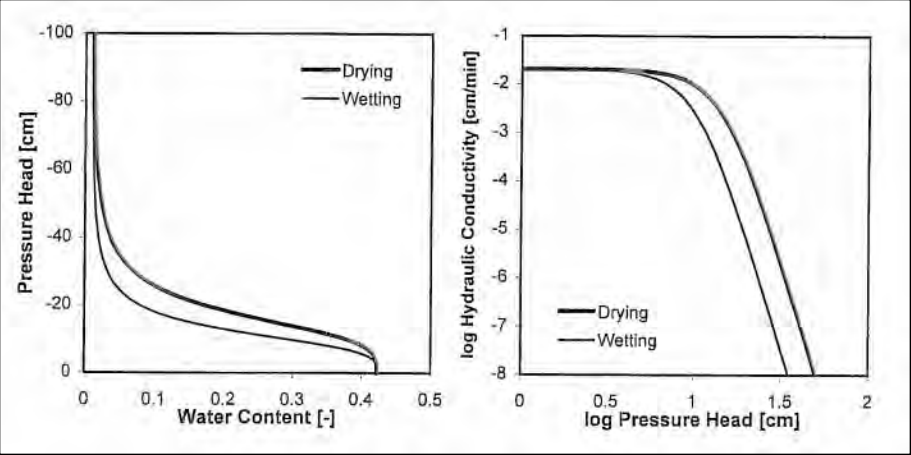


Figure 4. Measured and optimized water contents at 10 locations in a soil column during a horizontal infiltration followed by redistribution.

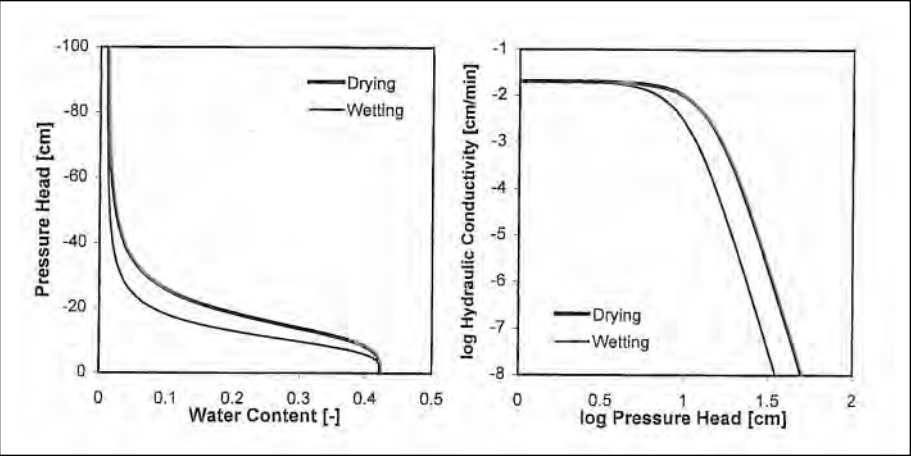


Figure 5. The resulting soil hydraulic functions, $\theta(h)$ and $K(h)$, for an experiment involving horizontal infiltration followed by redistribution.

Only the coefficients of the Freundlich isotherm (i.e., k_s and the exponent β) were optimized. Since the governing solute transport equation is nonlinear, in this case, one can not use an analytical solution, but must resort to a numerical model. The observed Mg breakthrough curve is shown in Figure 6, together with the fitted breakthrough curve obtained with HYDRUS-1D. The results indicate a reasonable prediction of the measured breakthrough curve for the final estimates of the optimized solute transport parameters ($k_s=0.943$, and $\beta=1.774$).

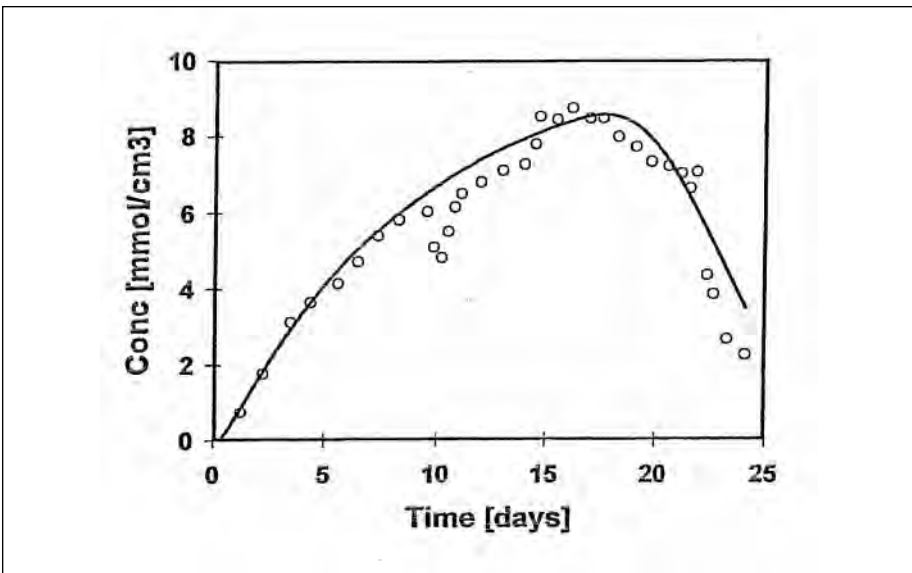


Figure 6. Measured and optimized breakthrough curve for a nonlinear solute transport problem.

CONCLUSIONS

A numerical code (HYDRUS-1D) was developed for identifying soil-hydraulic and solute transport parameters from unsaturated flow and transport data in a one-dimensional porous media. The utility of the code was demonstrated using data typically obtained during multistep outflow experiment, horizontal infiltration followed by redistribution, and a column miscible displacement (breakthrough) study. Because of its generality (in terms of the definition of the objective function, the possible combination of different boundary and initial conditions, and options for considering multi-layered systems), HYDRUS-1D is an extremely useful tool for analyzing a broad range of steady-state and transient laboratory and in-situ field flow and transport experiments.

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6

Biogeochemical Considerations and Complexities

C.C. Ainsworth, F.J. Brockman,
and P.M. Jardine

INTRODUCTION

Geochemical and microbiological processes influence the transport of any contaminant in either unsaturated or saturated environments. The physical characteristics, mineralogy, and aqueous chemical composition of an environment determine the extent and rate of geochemical and microbial processes that influence contaminant transport. Ultimately, this influence will reduce or enhance contaminant mobility, or transform the contaminant to one with a different toxicity and an entirely different set of chemical properties and mobility.

As discussed in Chapter 5, chemical influences on species mobility are normally described in terms of partitioning between the solid and liquid phases. It is also important to understand the reaction that occurs when the liquid phase concentration is increased or decreased and the extent to which this change is modified by precipitation sorption or desorption reactions. *Sorption* is defined here as a surface process by which a contaminant is removed from solution. It was once thought that contaminants were “sorbed,” equilibrium was rapidly attained, and

desorption was simply a reversible reaction (Barrow 1989). Through research, it is now conversely recognized that sorption is not a simple process, equilibrium is not rapidly reached, and desorption is not necessarily reversible. Further, microbial processes are often an important part of sorption, linked with geochemical processes whereby the interactions may impact contaminant mobility.

Multiple interrelated and interacting biogeochemical processes influence contaminant mobility. These include precipitation, coprecipitation, sorption, desorption, cation exchange, redox, complexation, and colloidal interactions. These processes are ongoing topics of intense study and discussion. Similarly, microbiologic processes such as biodegradation, transformation, hydrolysis, and redox also impact contaminant mobility. While the potential for these processes to affect contaminant mobility is axiomatic, quantitatively isolating the effect of a certain process in a simple monomineralogic system is difficult. In a mixed mineralogic porous media or especially when steady-state saturated flow or variable unsaturated flow is considered, this difficulty increases. However, steady advances in the geochemistry and microbiology of natural environments have provided a basis for understanding the potential behavior of contaminants in the saturated zone and to a lesser extent in the vadose zone.

Geochemical and microbial principles that govern contaminant behavior in the vadose zone are the same as those in saturated zone environments. However, the complexity of the vadose system increases with the presence of a third phase (gas), variable water content, and variable flow paths. This chapter reviews our current understanding of vadose zone geochemistry and microbiology and their relationship with unsaturated hydrologic processes common to the vadose zone. The first part of this chapter explores the major geochemical processes and reactions that affect contaminant behavior and the impacts specific to or accentuated by vadose zone characteristics. This is followed by a similar examination of the microbiology of the vadose zone. The third section covers the complexities of linked biogeochemical and hydrologic processes in the vadose zone. Current scientific and technical issues and challenges are identified to better understand and describe contaminant transport in the vadose zone.

GEOCHEMICAL REACTIONS AND PROCESSES

Chemical species occur as soluble-free, inorganic-soluble-complexed, organic-soluble-complexed, adsorbed, precipitated, coprecipitated, or solid structural. These species can be either contaminant or noncontaminant and may be found in soil, groundwater, or sediment environments. While the total chemical concentrations in the aqueous and solid phases indicate the extent of contamination, they give little insight into the forms in which metals are present in the soil and soil water, their mobility, or their bioavailability in the environment. The distribution of the possible species and solids is the result of geochemical processes that dictate their formation. Traditional transport modeling employs a lumped parameter for quantifying attenuation of contaminants regardless of biogeochemical process. The distribution coefficient (K_d) is a generic term, devoid of mechanism, that describes the partitioning of aqueous phase constituents to the solid phase and is defined as

$$K_d = \frac{q_i}{C_i} \quad (6.1)$$

where q_i is the amount of constituent sorbed, and C_i is the concentration of constituent in the equilibrium aqueous phase that is in contact with the solid phase (Sposito 1984). In simple cases in which K_d can adequately describe the partitioning of a contaminant, its relationship to retardation factor, R_f , and groundwater flow is shown by (Freeze and Cherry 1979)

$$R_f = \frac{v}{v_c} = 1 + \frac{\rho_b}{n} \cdot K_d \quad (6.2)$$

where v is the average linear velocity of the groundwater, v_c is the velocity of the $C/C_0 = 0.5$, ρ_b equals the bulk density, and n equals the porosity.

An implicit characteristic of K_d is fast, reversible reactions, or more precisely, attainment of equilibrium. While there are cases where these criteria are met or at least approximated, these reactions are often slow and/or nonreversible, which makes the use of K_d questionable (Barrow 1989). As it is traditionally used, the K_d is a purely empirical, “conditioned” measure that requires experimental determination for every soil and each variation in chemical environment, such as effects of changes in pH, ionic composition, and ionic strength. While physical-chemical

variations throughout a soil profile are often ignored, they are not always second-order effects (Suarez and Šmušnek 1996). For instance, the measured K_d for Sr in the presence of variable Ca and Mg concentrations ranged from 12 to 85 mL/g, increasing with decreasing Ca and Mg (Bunde *et al.* 1997). The difficulty is in knowing, *a priori*, which processes or shifts in environmental parameters are second- and third-order effects, and which will significantly affect a K_d measurement. Despite these severe limitations, the K_d approach is simple and computationally efficient, and does not require complete geochemical process descriptions (Suarez and Šmušnek 1996).

Figure 6-1 shows a conceptual model of geochemical processes that could affect the mobility of contaminants in the vadose zone from high-level radioactive storage tank leaks at the DOE Hanford reservation. Such tanks contain dense, high-temperature waste that has extreme (that is, high) pH and ionic strength. This complex chemistry may significantly alter transport in the “near field,” with fewer influences at greater distances from the release. In general, adsorption, precipitation, and oxidation/reduction (redox) tend to retard transport when they are operative. Conversely, aqueous complexation and colloid production tend to facilitate transport of contaminants. Because of the complex nature of the tank wastes and their interaction with the underlying soil material, it is conceivable that all the processes depicted in Figure 6-1 could significantly affect contaminant transport. Contaminant transport modeling of the system in Figure 6-1 (Ward *et al.* 1997) experienced varying degrees of success, depending on the subsurface structure detail used and the contaminant that was simulated. In all cases, a distribution coefficient represented the retardation potential of the system. While a single distribution coefficient approach was successful (for example, reproducing many features of overall contaminant distribution) for the more mobile, less reactive contaminants (TcO_4^- , NO_3^-), time-dependent, variable coefficients were required to achieve a similar level of success for Cs. At present, the geochemical processes altering the Cs K_d with time are not fully understood, but clearly those processes produce significant effects. The next section briefly explains major geochemical processes that may effect contaminant mobility.

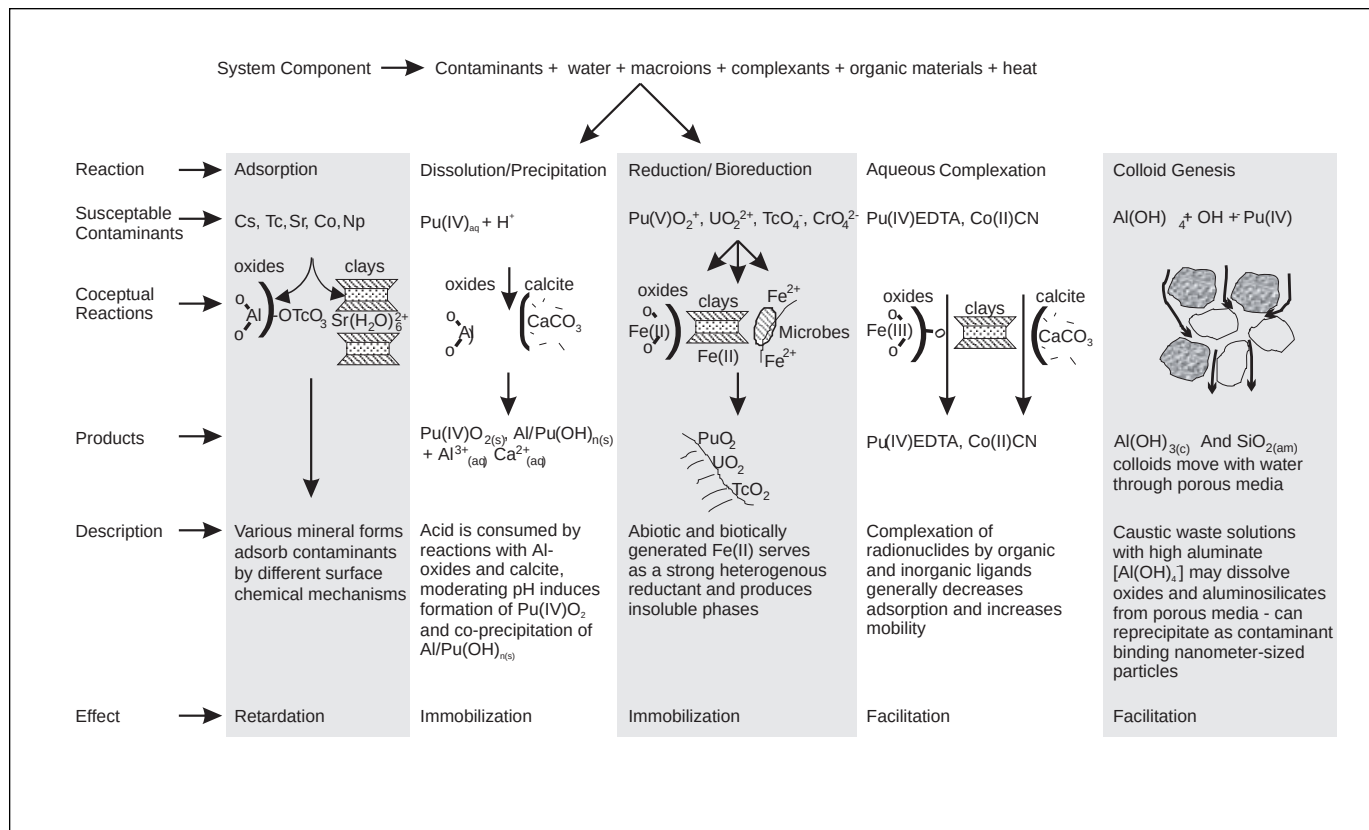


Figure 6-1. A conceptual model of the potential geochemical processes that could influence high level waste (HLW) mobility underneath the leaking HLW storage tanks at the DOE Hanford site in Richland, Washington (John Zachara, PNNL unpublished).

COMPLEXATION

Complexation is a process during which ions and molecules bond together and lose their separate identities by forming ion pairs or complex ions. Table 6-1 summarizes the essential elements of complexation equilibrium and kinetics and lists selected topical references. Sposito (1994) suggested that a typical soil solution may contain 100 to 200 different soluble complexes. The speciation in soil solutions is dependent on its chemical composition, pH, redox potential, and ionic strength. Simply changing pH, for instance, significantly impacts speciation. Table 6-2 shows the principal species found in well-aerated soil solutions. Comparing the acid and alkaline soil complexes in Table 6-2, the effect of pH is to favor the free metal species (M^{2+}) and protonated anions under acidic conditions, and carbonate and hydroxyl species under basic conditions. Competition, as seen here for protons, is an integral part of aqueous phase geochemistry and can alter the mobility of contaminants (Sposito 1994).

Because complexation substantially alters the sorptive behavior of the contaminant, complexed contaminants often exhibit enhanced mobility. Thus, with a given metal species, complexation causes the metal concentration in solution to increase, thus enhancing its apparent solubility. Similarly, complexation typically reduces adsorption, compared to the free metal species (uncomplexed), due to changes in its charge and size. For example, UO_2^{2+} adsorption to iron oxides and smectites has been shown to be extensive in the absence of CO_3^{2-} (Kent *et al.* 1988; Hsi and Langmuir 1985; Ames *et al.* 1982; McKinley *et al.* 1995). However in the presence of CO_3^{2-} or organic complexants, adsorption is substantially reduced or severely inhibited (Bond *et al.* 1991; Kent *et al.* 1988; Hsi and Langmuir 1985; Ames *et al.* 1982). These simple concepts—higher effective solubility combined with a reduced tendency to associate with mineral surfaces—reduce the “conditional” K_d . By understanding the nature of relative changes, we might improve estimates of liquid, solid partitioning and mobility.

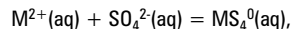
As indicated in Figure 6-1, complexation is expected to decrease attenuation of selected contaminants from leaking tanks at the Hanford reservation. The K_d for U(VI) ranges from 0.08 to 79.3 mL/g in Hanford soils (Kaplan *et al.* 1995). The major reasons for this observed variation are the distribution of fine-grained materials and complexation with

TABLE 6-1 Essential elements of aqueous complexation.

Complexation is a process whereby ions and molecules bond together, losing their separate identities by forming complex ions or ion pairs. If the central group and ligands in a complex are in direct contact, the complex is called "inner-sphere." If one or more water molecules are interposed between the central group and a ligand, the complex is called "outer-sphere." Inner-sphere complexes usually are much more stable than outer-sphere complexes.

CHEMICAL EQUILIBRIA

Consider the formation of a neutral sulfate complex with a bivalent metal cation M^{2+} as the central group:



where M represents a divalent metal (Ca, Sr, Co, Mn, Pb etc.).

The conditional stability constant is defined as:

$$K_c = \frac{[MS_4^0(aq)]}{[M^{2+}(aq)][SO_4^{2-}(aq)]}$$

Where [] represents the concentration of the species.

The thermodynamic stability constant is defined as:

$$\log K_s = \log K_c + \log \left(\frac{\gamma_{MS_4^0}}{\gamma_{M^{2+}} \gamma_{SO_4^{2-}}} \right)$$

Where γ represents the ion activity coefficient, and the activity of a species (a) is related to its concentration C by: $C\gamma = a$.

- Stability constant governs reversibility/competition
- Complexation alters geochemical behavior of free solute
- Complexation generally increases rate and extent of transport of free solute

Common soil ligands

HCO_3^-/CO_3^{2-} , Cl^- , SO_4^{2-} , PO_4^{3-} , possibly F, organic acid anions (oxalate, citrate, salicylate, phthalate etc.), amino acids (arginine, lysine, etc.), siderophores, and higher molecular weight poorly understood humic substances.

Anthropogenic ligands

CN, ethylenediaminetetraacetate (EDTA), nitrilotriacetic acid (NTA), cyclohexylenediaminetetraacetate CDTA and other chelates

COORDINATION KINETICS

The rate of formation and disassociation of complexes dependent on:

- The initial speciation of both the central group and the ligand
- The relative concentrations of the reacting species
- The strength of the central group-ligand interaction
- The type of perturbation
- The ligand structure
- The rate of chelate disassociation generally slower

Equilibrium or pseudo-equilibrium commonly assumed in natural systems, but the rates of biogeochemical reactions can be influenced or controlled by complexation. reactions.

Selected Topical References:

1. Chemical Equilibria—Denbigh 1981; Sposito 1994,1981; Lindsay 1979; Stumm and Morgan 1981
2. Coordination Kinetics—Margerum et al. 1978; Sposito 1994; Hering and Morel 1990ab; 1989

TABLE 6-2 Representative chemical species in soil solutions^a (after Sposito 1994).

PRINCIPAL SPECIES		
Cation	Acid Soils	Alkaline Soils
Na ⁺	Na ⁺	Na ⁺ , NaHCO ₃ ⁰ , NaSO ₄ ⁻
Mg ²⁺	Mg ²⁺ , MgSO ₄ ⁰ , org ^b	Mg ²⁺ , MgSO ₄ ⁰ , MgCO ₃ ⁰
Al ³⁺	Org, AlF ²⁺ , AlOH ²⁺	Al(OH) ₄ ⁻ , org
Si ⁴⁺	Si(OH) ₄ ⁰	Si(OH) ₄ ⁰
K ⁺	K ⁺	K ⁺ , NaSO ₄ ⁻
Ca ²⁺	Ca ²⁺ , CaSO ₄ ⁰ , org	Ca ²⁺ , CaSO ₄ ⁰ , CaHCO ₃ ⁺
Cr ³⁺	CrOH ²⁺	Cr(OH) ₄ ⁻
Cr ⁶⁺	CrO ₄ ²⁻	CrO ₄ ²⁻
Mn ²⁺	Mn ²⁺ , MnSO ₄ ⁰	Mn ²⁺ , MnSO ₄ ⁰ , MnCO ₃ ⁰ , MnHCO ₃ ⁺ , MnB(OH) ₄ ⁺
Fe ²⁺	Fe ²⁺ , FeSO ₄ ⁰ , FeH ₂ PO ₄ ⁺	FeCO ₃ ⁰ , Fe ²⁺ , FeHCO ₃ ⁺ , FeSO ₄ ⁰
Fe ³⁺	FeOH ²⁺ , Fe(OH) ₃ ⁰ , org	Fe(OH) ₃ ⁰ , org
Ni ²⁺	Ni ²⁺ , NiSO ₄ ⁰ , NiHCO ₃ ⁺ , org	NiCO ₃ ⁰ , NiHCO ₃ ⁺ , Ni ²⁺ , NiB(OH) ₄ ⁺
Cu ²⁺	Org, Cu ²⁺	CuCO ₃ ⁰ , Org, CuB(OH) ₄ ⁺ , Cu[B(OH) ₄] ₂ ⁰
Zn ²⁺	Zn ²⁺ , ZnSO ₄ ⁰ , org	ZnHCO ₃ ⁺ , ZnCO ₃ ⁰ , org, Zn ²⁺ , ZnSO ₄ ⁰ , ZnB(OH) ₄ ⁺
Mo ⁶⁺	H ₂ MoO ₄ ⁰ , HMoO ₄ ⁻	HMoO ₄ ⁻ , MoO ₄ ²⁻
Cd ²⁺	Cd ²⁺ , CdSO ₄ ⁰ , CdCl ⁺	Cd ²⁺ , CdCl ⁺ , CdSO ₄ ⁰ , CdHCO ₃ ⁺
Pb ²⁺	Pb ²⁺ , org, PbSO ₄ ⁰ , PbHCO ₃ ⁺	PbCO ₃ ⁰ , PbHCO ₃ ⁺ , org, Pb(CO ₃) ₂ ²⁻ , PbOH ⁺

^a The ordering of free-ion and complex species in each row from left to right is roughly according to decreasing concentration typical of either acid or alkaline soils.

^b org = metal-organic complex

inorganic and organic ligands. The aqueous U(IV) ion tends to form strong complexes with inorganic O-containing ligands such as hydroxide, carbonate, and phosphate. Aqueous UO₂²⁺ hydrolyzes to form a number of aqueous hydroxo complexes, including UO₂OH⁺, (UO₂)₂(OH)₂²⁺, (UO₂)₃(OH)₅⁺, and UO₂(OH)₃⁻. In solutions equili-

brated with air or higher $p\text{CO}_2$ waters at near neutral to high pH, the carbonate complexes (UO_2CO_3^0 , $\text{UO}_2(\text{CO}_3)_2^{2-}$, $\text{UO}_2(\text{CO}_3)_3^{4-}$) will dominate, but at lower pH, the hydrolysis species will dominate as $\text{CO}_2(\text{g})$ solubility in water decreases. Under near neutral pH conditions (pH 6 to 8), the concentration of the uncomplexed UO_2^{2+} species is expected to be insignificant (Carroll and Bruno 1991; Grenthe 1992). Complexation of UO_2^{2+} by dissolved fulvic acid has been suggested to facilitate U transport both to and in groundwaters (Bonotto 1989). The stability of a U(VI)-humic acid aqueous complex has been determined to be at least 10^3 greater than that of a Ca^{2+} -humic complex (Shanbhag and Choppin 1981 as reported by Idiz *et al.* 1986). In an organic-rich environment, even with a considerable difference in Ca to U concentrations, U complexation could be significant. However, the carbonate ligand is very competitive above pH 6. In fact, Shanbhag and Choppin (1981) concluded that the humic acid complexes with uranyl would not be important in seawater because of the significant presence of bicarbonate and carbonate at pH 8. Likewise, solutions of Na-bicarbonate-carbonate at pH 7 to 10 proved to be very effective at leaching U(VI) out of Holocene peat (Zielinski and Meier 1988), suggesting that U(VI)-carbonate complexes compete well with humic substances. In a study of purified Pettit peat bog humic acid, Idiz *et al.* (1986) found the adsorption of UO_2^{2+} increased as pH increased until about five, then decreased as a result of the formation of carbonate complexes.

The case study, "Observations of Multiple Actinide Species With Distinct Mobilities," by Robert A. Fjeld, John T. Coates, and Alan W. Elzerman of Clemson University, and James D. Navratil, Lockheed Martin Idaho Technologies Company, reviews the results of experiments conducted to determine whether high-mobility forms of radionuclides were possible under the influence of groundwater and perched water stimulants. See page 924.

While it is evident that the carbonate-U(VI) complexes are important species in uranium geochemistry, it has also been suggested that carbonate can be equally important to other actinides such as Pu(IV), Th(IV), Am(III), and Np(IV) (Kim *et al.* 1989). The geochemical characteristics of selected radionuclides, including potentially important lig-

ands, are listed in Table 6-3. The presence of carbonate-metal complexes in alkaline soils (Table 6-2) suggests that this ligand is important in the speciation and transport of a number of contaminants.

While naturally occurring organic and inorganic ligands affect the mobility of metal/radionuclide contaminants, chelating agents (EDTA, NTA, DTPA and others), commonly codisposed with metals/radionuclides, are equally effective at altering metal contaminant mobility. Field observations of unpredicted migration of Co(II) from waste disposal trenches through soils was suggested to be the result of EDTA complexation of the otherwise strongly sorbing free metal species (Means 1978). However, simply accounting for speciation is often only a starting consideration. Szecssody *et al.* (1998) found that eleven reactions required consideration in the transport of Co^{II}(EDTA) through a heterogeneous sediment; reactions included the sorption of the initial solute [Co^{II}(EDTA)] to Fe oxides, two competing surface reactions, oxidation of Co^{II}(EDTA) to Co^{III}(EDTA), and Fe oxide dissolution. To further complicate a K_d approach for Co transport, Jardine *et al.* (1993b) found that Co^{III}(EDTA) appeared to be controlled by time-dependent solid-phase sorption reactions. EDTA and other chelates have been shown to similarly effect the mobility of selected transition metals and actinides as a result of complexation (see Kim 1986, and the case study by Fjeld *et al.*).

In a soil solution, the equilibrium speciation (as seen in Table 6-2, for instance) is the culmination of a series of competition reactions (Spósito 1994). The final outcome can be predicted if the relevant thermodynamic stability constants are known. However, if the time scale for the relevant complexation reactions is longer than the time scale of interest (for example, the residence time of the soil solution at given location in a soil column), then the kinetics of complex formation/disassociation becomes important. Generally, the monodentate-ligand complexes (nonchelatate ligands) exhibit relatively rapid formation and disassociation kinetics; hence, local, or psuedoequilibrium, assumptions are probably valid. The relative lability/inertness of chelate complexes, however, may limit the validity of psuedoequilibrium assumptions (Hering and Morel 1990a,b, 1989). For instance, the degradation of NTA has been related to its aqueous speciation. However, the NTA degradation rates of a variety of NTA-metal complexes were not correlated to the stability constants; rather, the observed differential degradation rates of NTA

TABLE 6-3

List of selected isotopes[†], their oxidation states, soil/water processes that impact transport in soils and sediments[‡], important complexes and complexing ligands[§], and an estimate of their soil mobility[¶] (after Fellows *et al.* 1998).

Isotope(s) (half-lives)	Common Oxidation States	Important Processes in Soil/Water Systems	Important ligands in Aqueous speciation	Soil Mobility (K _d , mL/g)	References
^{235,238} U (7.1×10 ⁸ , 4.51×10 ⁹ yr)	U(IV)	Hydrolysis, Precipitation (insoluble; present in reducing environments)	U(OH) _n ⁴⁻ⁿ ; humic, fulvic acids and other organic ligands	Low (1000, est.)	(Grenthe, 1992) (Parks and Pohl, 1988) (Rai <i>et al.</i> 1998)
	U(VI)	Hydrolysis, Cation Exchange, Surface Complexation, Precipitation potential SO ₄ ²⁻ , F ⁻ , and Cl ⁻ species	UO ₂ ²⁺ , UO ₂ (OH) ⁺ , polynuclear hydrolysis species [i.e., (UO ₂) ₃ (OH) ₅ ⁺]; multiple CO ₃ ²⁻ and PO ₄ ³⁻ species;	Medium-High (0.08-79.3) 1981)	(Grenthe, 1992) (Idiz <i>et al.</i> , 1986) (Shanbhag and Choppin, Zachara and McKinley, 1993)
^{57,60} Co (270 d, 5.26 yr)	Co(II)	Hydrolysis, Cation Exchange, Surface Complexation, Precipitation	Co ²⁺ and its hydrolysis species, CO ₃ ²⁻ , SO ₄ ²⁻ , Cl ⁻ , humic and fulvic acids, and other organic ligands	Low (1200-12500)	(Trischen <i>et al.</i> , 1981) (Morel, 1983) (Ainsworth <i>et al.</i> , 1994) (Zachara <i>et al.</i> , 1994) (Zachara <i>et al.</i> , 1991)
	Co(III)	unstable in uncomplexed form	forms very stable organic complexes	High	(Trischen <i>et al.</i> , 1981) (Jardine <i>et al.</i> , 1993) (Szecsody <i>et al.</i> , 1998)
^{134,137} Cs (2.05, 30.23 yr)	Cs(I)	Cation Exchange	Cs ⁺ forms weak complexes with SO ₄ ²⁻ , Cl ⁻ , NO ₃ ⁻ , and organic ligands	Low (540-3180)	(Bruggenwert <i>et al.</i> , 1979) (Gast, 1969) (Gee <i>et al.</i> , 1983)

continued

TABLE 6-3

List of selected isotopes[†], their oxidation states, soil/water processes that impact transport in soils and sediments[‡], important complexes and complexing ligands[§], and an estimate of their soil mobility[¶] (after Fellows *et al.* 1998) (continued)

^{89,90} Sr (52 d, 28.1 yr)	Sr(II)	Cation Exchange, Precipitation	Sr ²⁺ forms weak complexes with SO ₄ ²⁻ , Medium-High Cl ⁻ , NO ₃ ⁻ , CO ₃ ²⁻ and organic ligands (5-173)	(Zachara <i>et al.</i> , 1991) (Gee <i>et al.</i> , 1983)
²³⁹ Pu (2.44x10 ⁴ yr)	Pu(III)	Hydrolysis, Precipitation (insoluble; only present in extremely reducing environments)	Low (1000 est.)	(Cleveland, 1979) (Rai and Serne, 1977)
	Pu(IV)	Hydrolysis, Precipitation (insoluble; stable over a wide redox range)	OH ⁻ , CO ₃ ²⁻ , and organic Chelates (EDTA) Low (1000 est.)	(Gee <i>et al.</i> , 1983) (Cleveland, 1979) (Rai and Serne, 1977)
	Pu(V)	Cation exchange (stable in highly oxidizing environments)	PuO ₂ ⁺ , forms only weak inorganic and organic complexes Medium [¶] (80->1980)	(Cleveland, 1979) (Rai and Serne, 1977)
⁹⁹ Tc (2.12x10 ⁵ yr)	Tc(IV)	Precipitation (insoluble; stable only in highly reduced	Soluble organic matter low molecular wt. Organic acids environments) Low (1000 est.)	(Kaplan, <i>et al.</i> , 1995) (Gu and Shultz, 1991)
	Tc(VII)	Anion Exchange	TcO ₄ ⁻ , does not form strong complexes High (0-1.3)	(Kaplan, <i>et al.</i> , 1995) (Gu and Shultz, 1991)

[†] The radionuclides listed are the most often associated with environmental concerns at DOE sites such as Hanford, Oakridge, Los Alamos, Rocky Flats, and others. This table provides an overview of selected radionuclide species interactions in soils, soil water components, and potential mobilities. Readers are directed to the listed references for more detailed discussion.

[‡] The soil/water mechanisms considered here are precipitation (and coprecipitation), surface complexation (to oxides, carbonates, organic matter, and clay edge sites), cation exchange, and anion exchange. No attempt is made to distinguish between particular sorbing surfaces, precipitates/coprecipitates, or other mechanisms such as solid phase incorporation, micropore diffusion, and solid phase diffusion.

[§] The formation of aqueous complexes can greatly influence the total aqueous concentration of a given element and its mobility. We have attempted to give the reader a sense for the aqueous ions typically associated with soil environments that could impact the total aqueous concentration of a given element. It is beyond the scope of this discussion to detail the association constants of these complexes; readers are directed to the listed references for more detailed discussion.

[¶] The soil mobility classification is purely empirical and is based on K_d values reported in Kaplan *et al.*, 1995. All the K_d values were determined or estimated for the Hanford Sediment in neutral-to-high pH, low salt (ionic strength < 0.01M), low organic, oxic solutions except U(IV), Pu(III,IV), and Tc(IV) which were estimated under anoxic conditions. The K_d measurement is dependent on the mineralogic components of the sorbent, pH, Eh, ionic strength, ionic composition of the aqueous phase, and often the equilibration time. Changes in any of these factors can greatly influence the magnitude of the K_d; however, in general, the mobility classification will not be affected in a relative sense. For instance, at higher salt concentrations (+ 0.01 M) the listed K_d values tend to decrease: Cs 64 - 1360, Pu(V) 10->98, U(VI) 0 - 4, Co(II) 222 - 4760, Tc(VII) 0 - 0.01, Sr 0.3 -42. The Pu(V) values listed at both ionic strengths may be overestimations due to reduction to Pu(IV); therefore, the lower value only was used to classify its soil mobility.

were related to the lability of the complex. In the simplest terms, the more inert the complex, the slower the degradation (Bolton *et al.* 1996).

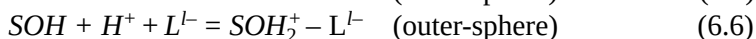
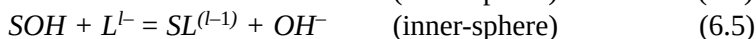
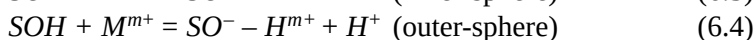
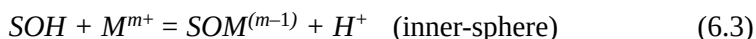
Calculation of chemical speciation that would yield results similar to those in Table 6-2 is typically accomplished by using one of a number of computer chemical equilibrium codes. While it is beyond the scope of this chapter to discuss the codes or the application of the codes, it is important to recognize that chemical equilibrium is the underlying assumption of most of these codes. While this may be a reasonable assumption in laboratory studies, application to natural systems without justification may be inappropriate (Suarez 1995; see Loeppert *et al.* 1995 for a thorough discussion of chemical equilibrium and reaction models).

CONTAMINANT-SURFACE INTERACTIONS

Sorption is broadly defined as the transfer of ions from the solution phase to an interface resulting in a surface excess without alteration of the solid (Parks 1990). Adsorption may be viewed as an interaction of an ion with the soil surface, culminating in the formation of a complex with a surface functional group. These complexes include the following: (1) formation of an inner-sphere complex, (2) formation of an outer-sphere complex that has a solvation shell (at least one water molecule between it and the surface), and (3) a solvated ion that does not form a complex with a charged surface functional group, but instead neutralizes surface charge only in a delocalized sense, and is said to be adsorbed in the diffuse-ion swarm (Figure 6-2[a,b]). The diffuse-ion swarm and the outer-sphere surface complexes are formed almost exclusively through electrostatic bonding; formation of these complexes is termed nonspecific adsorption. Whereas the formation of an inner-sphere complex is likely to involve ionic as well as covalent bonding, its formation is termed specific adsorption, or chemisorption (Sposito 1989). Key surface functional groups in soils include: (1) hydroxyl groups on Al, Fe, Mn, and Si oxides, (2) siloxane cavities on the surfaces of 2:1 layer silicates with fixed negative charge arising from isomorphic substitution, (3) hydroxyl groups associated with exposed Al and Si groups on clay mineral edges, and (4) carboxyl and phenolate sites on soil organic matter. In certain soils, the partially coordinated sites on surfaces of

carbonate and sulfate minerals may also be important specific adsorption sites.

Analogous to aqueous complexation, surface complex formation can be described as a chemical reaction between an aqueous species and a surface functional group leading to a surface complex. For example, anion (L^-) and cation (M^{m+}) adsorption to the hydroxylated surface sites (SOH) on metal oxides or layer silicate edges leading to either an inner- or outer-sphere complex may be written as (Mattigod and Zachara 1996, Figure 6-2[b]):



Similarly, cation exchange may be seen as a general surface complexation reaction involving the formation of outer-sphere and ion swarm complexes (Figure 6-2[a]). The cation exchange reaction is the replacement of one adsorbed, readily exchangeable ion with another. These ions are adsorbed solely through the outer-sphere complex and diffuse-ion swarm mechanism. The permanent charge sites of layer silicate clays, such as montmorillonite and vermiculite, retain cations by nonspecific electrostatic forces via a typically reversible and very rapid reaction with ion diffusion as the rate limiting step. In the cation-exchange reaction



Sr^{2+} replaces Ca^{2+} from an exchange site, X. Numerous ion-exchange models are described by Sposito (1989) and Stumm and Morgan (1981), and the molecular and thermodynamic considerations are discussed by Sposito (1981).

The coulombic nature of cation exchange suggests mass action reversibility without preference for ions of equal valence. However, slight preferential selectivity has been observed for many cation exchange pairs (Sumner and Miller 1996). Greater selectivity is observed for those ions that form weak inner-sphere complexes with the siloxane cavities of layer silicates. It has long been recognized that inter-lattice fixation of cations is the result of certain cations dehydrating and fitting into the siloxane cavities along the exterior oxygen plane of the

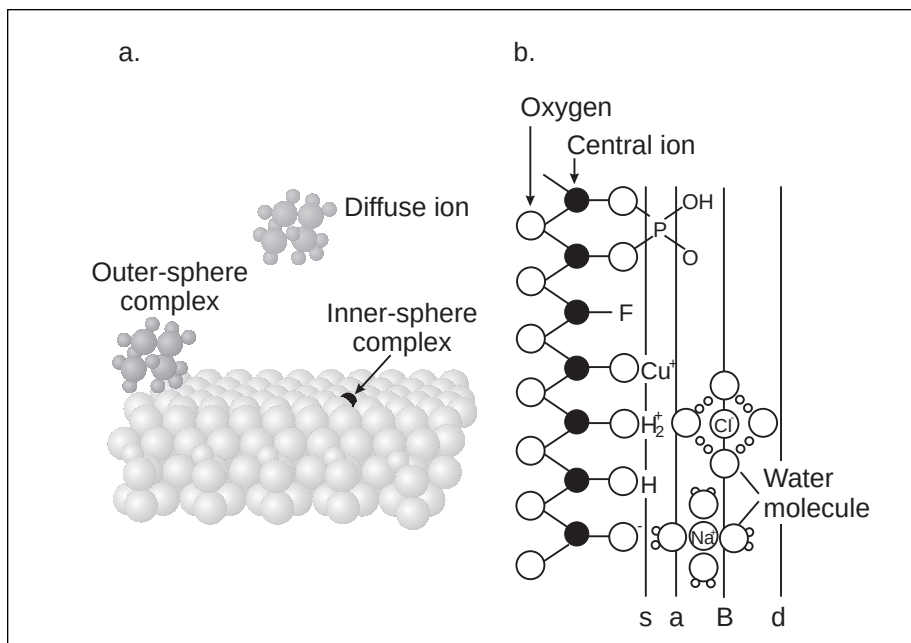


Figure 6-2. Schematic of possible surface complex formation on a) the siloxane surface of a layer silicate (e.g., montmorillonite) (after Sposito 1989) and b) an inorganic hydroxyl surface, showing planes associated with surface hydroxyl groups ("s"), inner-sphere complexes ("a"), outer-sphere complexes ("B"), and the diffuse ion swarm ("d") (after Stumm 1992, modified from Sposito 1984).

tetrahedral layer of layer silicate minerals (Bruggenwert and Kamphorst 1979). This creates the formation of a weak inner-sphere complex as seen in Figure 6-2[a]. The energy gain associated with this fixation, in the form of electrostatic attraction, must be balanced against the energy loss due to the dehydration process. Generally, cations that have the largest ionic radii and lowest hydration energy adsorb most strongly to the permanent charges of clay minerals. For the Group IA cations, the selectivity can be seen as a series with increasing stability in exchange reactions with clays (Sposito 1984):



The importance of this observed selectivity series, with regard to contaminant transport, is seen in the behavior of Cs in soils. For instance, a series of experimental plots, in a sandy loam soil (~4% clay) located on the DOE Hanford site, were established to determine native vegetation uptake of ^{90}Sr and ^{137}Cs in an arid environment. Over 22 years, ^{90}Sr had migrated approximately 40 cm (center of mass), but the ^{137}Cs has remained in the top 15 cm of soil where it was originally placed (Cline and Cadwell 1984; Cline 1981; Cline and Rickard 1972). Because of its propensity to interact with the siloxane cavities of layer silicates and frayed edge sites of mica, cesium is generally not mobile and is rarely found as a groundwater contaminant.

As stated previously, the term sorption has been applied to avoid any interfacial mechanistic implication. Frequently, sorption is quantified through the use of a sorption coefficient or other empirical adsorption isotherms such as Langmuir, Freundlich, and Temkin; however, adherence of sorption data to any of these adsorption isotherms does not provide evidence of an actual mechanism (Sposito 1984). Molecular adsorption models are mathematical paradigms of surface complexation at the aqueous-mineral interface that are based on hypotheses about the interactions between the surface functional groups and the aqueous species of interest. It is generally expected that these hypotheses are based on spectroscopic information about the adsorbent-adsorbate interaction and the formed surface structure. These models formulate the reactions in a similar manner as those represented by Equations (6.3) through (6.6). Intrinsic equilibrium constants are formulated in a similar manner as aqueous complexation, but with an additional term describing the electrostatics at the interface. Several models, each with its own set of conditions, are widely used to describe ion adsorption. These models include the Constant Capacitance Model, Diffuse Layer Model, and the Triple Layer Model (for a full discussion of these models, see Sposito [1984], Mattigod and Zachara [1996], Dzombak and Morel [1990], Davis and Kent [1990], Goldberg [1995], and references therein).

Our understanding of surface complexation theory has developed almost exclusively through laboratory experimentation with well-characterized single mineral systems. However, the use of surface complexation theory in soil and geochemical applications is slowly developing. Davis and Kent (1990) reviewed the application of surface complexation

theory to more complicated systems such as soils. The primary concern of these systems was the array of surface functional groups in mixed mineralogic systems, the nature of their interactions, and the concentration of surface functional groups. A similar conclusion was voiced by Goldberg (1995) in discussing the current limitations in applying surface complexation to soil systems quantitatively by using various interfacial models. Currently, there is no governing paradigm for the application of surface complexation theory to natural systems. Two basic approaches have been used. First, the entire soil is treated as a composite, integrated surface protonation, and adsorption reactions are described as complexation with average surface functional groups. In this case, all the intrinsic surface complexation constants (protonation-disassociation constants and background electrolyte complexation constants) are determined for the whole soil (Charlet and Sposito 1987, 1989; Davis *et al.* 1998; Wen *et al.* 1998; Wang *et al.* 1997). Second, a specific mineral surface should be considered in the soil that is proposed to dominate adsorption. Here, a soil mineralogically dominated by goethite was used, and the necessary constants were identified from experiments using a synthetic goethite (Zachara *et al.* 1989). In the latter study, however, estimating effective surface site density (or effective surface area, since these two variables are covariant) was problematic. A variant of the latter approach is the use of literature compilations of constants for various reference minerals (Goldberg and Sposito 1984; Goldberg and Glaubig 1986, 1988; Sposito *et al.* 1988).

To this point, the adsorption discussion has centered on the formation of mononuclear surface species, as illustrated by Equations (6.3) through (6.6), which are likely dominant at low levels of adsorbate surface coverage on stable, well-crystalline metal oxides and hydroxides. Recent evidence suggests that at intermediate to high concentrations of sorbate, a progression of surface species appears from the mononuclear species to nucleation of small adsorbate clusters, to mixed metal oxides, to precipitation of separate mineral phases of surface sorption products (McBride 1994).

PRECIPITATION-DISSOLUTION

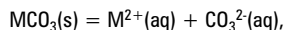
Table 6-4 summarizes the principles of mineral solubility and the use of the saturation index (SI) as a tool for investigating solubility. The sol-

TABLE 6-4 Essential elements of precipitation-dissolution equilibrium.

The overall reaction describing a dissolution or precipitation for a two component solid is simply a special case of a complexation reaction, except in this case the complex is a solid.

CHEMICAL EQUILIBRIA

Consider the formation of a divalent metal carbonate:



where M represents a divalent metal (Ca, Sr, Co, Mn, Pb etc.)

The dissolution equilibrium constant is defined as:

$$K_{dis} = \frac{(M^{2+})(CO_3^{2-})}{(MCO_3)}$$

where () represents the activities of the species.

The solubility product is closely related to the K_{dis} by:

$$K_{sp} = (MCO_3)K_{dis}$$

If the solid is in its standard state,

$$\text{then } K_{dis} \equiv K_{sp}$$

Two useful criteria for dissolution-precipitation equilibrium are the ion activity product (IAP) and its ratio to the K_{sp} , the saturation index (SI):

$$IAP = (M^{2+})(CO_3^{2-}) \text{ and } SI = \frac{IAP}{K_{sp}}$$

The SI value is often used as a measure of whether equilibrium between solid phases and the soil solution exists (see discussion in Sposito 1984; 1994, Suarez 1995).

- SI value is < 1 or > 1 the solution is termed undersaturated or oversaturated with respect to the solid phase.

- Whenever SI value is < 1 or > 1 , one of the following conclusions can be made:

- The reaction is not at equilibrium
- No solid phase corresponding to the reaction is present
- The reaction is at equilibrium, but the solid phase is not in the standard state assumed in computing K_{sp}

- If the solid phase has been identified as present in soil, the SI can be followed with time solubility equilibrium determined.

- Without evidence of the presence of the solid phase of interest and an understanding of the kinetics of dissolution and precipitation, the interpretation of SI as a measure of equilibrium or disequilibrium is problematic.

Selected Topical References:

Denbigh 1981; Sposito 1994, 1981; Lindsay 1979; Stumm and Morgan 1981

ubility product approach outlined in Table 6-4 is most successful in determining ion solubility for ions (Fe, Al, Ca, Si, and others) exhibiting fairly high total concentrations in the soils. Even for these elements, if metastable phase's solubility product is unknown, the presence of metastable products with a higher solubility than the more thermodynamically stable phase may affect the above approach. For example, Fe precipitation as the Fe oxide ferrihydrite is common in soils and sediments. Even though goethite or hematite (depending on environmental conditions) is thermodynamically favored in many soil environments, ferrihydrite often precipitates first and exists in soils for long time periods (Cornell and Schwertmann 1996). Additionally, the ferrihydrite transformation rate varies with surface and solution chemistry including contaminant surface loading; ferrihydrite transformation rates have been observed to decrease with increased surface metal loading (Giovanolli and Cornell 1992; Cornell and Schwertmann 1996; Ford *et al.* 1999). Similarly, Al solubility is often complicated in the case of gibbsite precipitation, because of the formation of metastable Al-hydroxy polymers that transform slowly in the aqueous phase and structural disorder in the solid phase (Sposito 1994; Bertsch and Parker 1996; Lindsay and Walthall 1996).

While pure (or nearly pure) phases may control the solubility of the major cations in soil solution, unless the soil is highly contaminated, it is less likely that the solubility of contaminant ions (Cd, Cu, Mn, Ni, and others) will be controlled by the formation of pure solid phases. More likely, if solubility is controlled by a precipitation-dissolution process, the controlling solid phases will be coprecipitates. Coprecipitation is the simultaneous precipitation of a chemical element with other elements, without regard to mechanism or rate (Sposito 1981, 1994). The three broad types of coprecipitation have been identified in soils as: (1) mixed solid formation, (2) adsorption, and (3) inclusion.

Coprecipitation, through the formation of a solid solution, requires the solid phase to be a homogeneous mass with a uniform distribution of the minor constituent. This tends to constrain solid solutions to free diffusion and high structural compatibility of the minor constituents within the precipitate. Examples of solid solutions in soils include secondary minerals (like montmorillonite or calcium carbonate minerals) that precipitate from the soil solution (Sposito 1981). For contaminants, the principal effect of coprecipitation through the formation of a solid

solution is on the solubility of the minor constituent of the solid phase; the activity of the aqueous phase minor constituent ion is often significantly lower than if it were in equilibrium with its own pure solid phase. While there are many examples of possible solid solutions in soils, their prevalence and importance in controlling contaminant ion solubility have not been addressed (McBride 1994). (The concept and theory of solid solutions are thoroughly discussed in Sposito 1981 and McBride 1994.)

Divalent metals are known to sorb to the surface of calcite via an adsorption reaction (Fuller and Davis 1987; Zachara *et al.* 1991). Once at the calcite interface, Cd and Mn appear to dehydrate and form a phase that behaves like a surface precipitate. Zn, Co, and Ni appear to form surface complexes that remain hydrated until the ions are incorporated into the structure via recrystallization (Zachara *et al.* 1991). While the eventual formation of a Cd, Co, or Mn substituted calcite surface layer (near-surface $(\text{Ca,Me})\text{CO}_3$ solid solution) has been observed (McBride 1979; Davis *et al.* 1987; Stipp *et al.* 1992; Xu *et al.* 1996), the mechanism is highly complex, reflecting the dynamic nature of the calcite surface and the dependence on the aqueous phase composition. Similarly, Ni, Co, and Cd adsorbed to the surface of ferrihydrite are incorporated into a recrystallizing oxide (presumably goethite) structure (Ainsworth *et al.* 1994; Ford *et al.* 1999). However, unlike calcite, the pathway for ferrihydrite to recrystallize to goethite is via a slow dissolution and reprecipitation mechanism. As goethite formation continues, Ni, Cd, and Co become increasingly isolated against desorption. Additionally, Pb adsorbed to the ferrihydrite surface does not incorporate into the slowly forming goethite (Ainsworth *et al.* 1994; Ford *et al.* 1999) presumably because its size (ionic radii) is incompatible with the structure of goethite. Since the distribution of the minor metal component in these systems is unknown, it is unclear if the forming goethite is a true solid solution. However, the process and the observed behavior of the metals suggest this type of coprecipitation.

Coprecipitation via adsorption is an extension of mixed metal oxide formation as a result of adsorption at relatively high sorbate concentration (detailed in the preceding paragraph). Generally, it can be expected that coprecipitation through adsorption will be much more dependent on the kinetics of precipitation and the composition of the soil solution than it would be in solid solution formation. Additionally, conditions that

favor this process would be rapid precipitation initiated under pronounced supersaturation conditions and a relatively high degree of incompatibility between the adsorbing species and the bulk structure of the precipitate (Sposito 1981). An ideal example of this type of an environment is underneath the high pH, high aluminate concentration (1 to 5 M) waste tanks on the DOE Hanford reservation. Laboratory studies with high level waste supernatants and high level waste simulants document active Al-oxide precipitation when the temperature is decreased when the solutions contact Hanford geologic materials (Serne and Burke 1997). Massive precipitation of Al phases is expected under these conditions, and the presence of strongly hydrolyzing actinide and metal contaminants, which are highly incompatible with expected Al oxides because of size, suggests ideal conditions for this type of coprecipitation.

OXIDATION-REDUCTION

Oxidation-reduction (redox) reactions can profoundly influence aqueous phase speciation and ion and organic contaminant mobility. Even within an aerobic environment, where the redox potential of the soil solution is strongly oxidizing, the potential for oxidation reactions to substantially influence ion mobility is present (Stucki *et al.* 1995). While it is recognized that transient O₂ depletion may occur in the vadose zone and that microenvironments exist where O₂ is often depleted, the bulk vadose zone is generally an aerobic, oxidizing environment.

The electron is a very useful conceptual device for describing the redox status of aqueous systems, just as the aqueous proton is useful for describing the acid-base status of solutions. Similar to pH, the propensity of a system to be oxidized can be expressed by the negative common logarithm of the free-electron activity

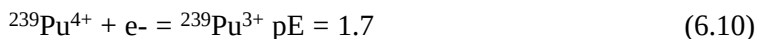
$$\text{pE} = -\log(e^-) \quad (6.9)$$

The range of pE values (at pH 7) in aerobic soil systems varies between approximately 12.0 to 2.0 (Sposito 1989). C, N, O, S, Mn, and Fe are the most important chemical elements affected by redox reactions. In contaminated systems, this list would include As, Co, Cr, Hg, Np, Pu, Se, Tc, and U.

As the soil pE value drops into the range of approximately 7.0 to 5.0, electrons become plentiful enough to support the reduction of Fe and

Mn in solid phases. Reduction of Fe does not occur until O_2 and NO_3^- are depleted, but Mn reduction can be initiated in the presence of NO_3^- . In the case of Mn and Fe, decreasing pE results in solid-phase dissolution because the stable forms of Mn(IV) and Fe(III) are solid species. Besides Mn and Fe solubility increasing due to lowered pE, a marked increase in the aqueous-phase concentrations of metals like Cu, Zn, or Cd, and of ligands like $H_2PO_4^-$ or $HMoO_4^-$, accompanying Mn and Fe reduction, is usually observed. The principal cause of this secondary phenomenon is the desorption of metals and ligands occurring when adsorbents such as Fe and Mn oxides to which metals are bound become unstable and dissolve. Detailed discussions of the concepts and theory of redox reactions in the natural environment may be found in McBride (1994), Sposito (1981, 1989), Stumm and Morgan (1981), and Lindsay (1979).

Redox chemistry also has a direct effect on radionuclide chemistry in soils. The oxidation state of Co, Np, Pu, Tc, and U is affected. For example, the reduction of Pu



makes ^{239}Pu appreciably less reactive toward complexation (that is, $^{239}Pu^{3+}$ stability constants are much less than those of $^{239}Pu^{4+}$) and sorption reactions (Kim 1986). The reduction of U(VI) as the UO_2^{2+} ion to U(IV) has the opposite effect; that is, U(IV) forms stronger complexes and insoluble solid phases, and sorbs more strongly to surfaces than U(VI).

Aside from homogeneous aqueous phase redox reactions, clays and oxides can promote redox reactions. These surface reactions are preceded by an adsorption step, and the surface is often catalytic. Soil constituents known to act as electron acceptors are Mn- and Fe-oxides and Fe^{3+} -bearing layer silicate clays. The oxidation of organic compounds, particularly amines, at the surface of clay minerals occurs in the presence of exchangeable or structural Fe^{3+} (Furukawa and Brindley 1973; Ainsworth *et al.* 1991; Szecsody *et al.* 1993). Mn oxides have been shown to be extremely important solid phase oxidants. They can oxidize Co(II) to Co(III), Cr(III) to Cr(IV), As(III) to As(VI), Pu(III) to Pu(IV), and phenols and aromatic amines to polymeric products (McBride 1994; Zachara *et al.* 1995; Crespo *et al.* 1992; Szecsody *et al.* 1998; McBride 1989; Whelan *et al.* 1995). In many cases where structural or adsorbed

Mn and Fe act as oxidants, the mineral is only the catalyst due to O_2 ultimately reoxidizing the reduced metal species. The presence of the mineral surface increases the rate of the reaction, as a catalyst typically does, over that observed in aqueous solution. The resulting change in speciation, as observed by Szecsody *et al.* (1998) and Jardine *et al.* (1993b) for the oxidation of Co(II) to Co(III) by Mn oxides, can have a substantial effect on contaminant mobility.

ORGANIC CONTAMINANT-SOIL INTERACTIONS

While the discussion to this point has centered on inorganic contaminants, organic compounds are also important contaminants in the saturated and unsaturated zone [for a complete discussion of soil-organic compound interactions see Cheng (1990) and Sawhney and Brown (1989)]. Interaction of dissolved organic contaminants to soils and subsurface materials has been intensively studied, and sorption mechanisms have been formulated for a variety of compounds. The sorption of ionizable compounds (organic bases, acids, chelates) can undergo exchange reactions with lattice layer silicates (Ainsworth *et al.* 1987; Zachara *et al.* 1986, 1987), specific adsorption with variable charge oxide surfaces (Ainsworth *et al.* 1998; Zachara *et al.* 1990; Kummert and Stumm 1980; Stumm *et al.* 1980), and sorption to organic matter (Chiou *et al.* 1979; Hassett *et al.* 1980; Means *et al.* 1982). The magnitude and intensity of ionizable compounds and HOC sorption have been related to: (1) chemical and physical properties of the compound (solubility, octanol/water partition coefficient, pKa, dipole moment, molecular surface area, and delocalization of charge; (Kenaga and Goring 1980; Karickhoff *et al.* 1979; Zachara *et al.* 1986, 1987, 1990); (2) soil and subsurface properties (Zachara *et al.* 1986; Ainsworth *et al.* 1989); and (3) pore fluid properties [fluid composition (the presence of cosolvent or cocontaminant); Ainsworth *et al.* 1989; Nkedi-Kizza *et al.* 1985; Zachara *et al.* 1986, 1987)].

Nonpolar and polar compounds [hydrophobic organic compounds (HOC)] largely undergo partitioning into the organic matter associated with the solid matrix or dissolved organic matter in pore waters (Chiou *et al.* 1979, 1983, 1986). While HOC sorption is generally associated with the organic carbon (OC) fraction of the soils and sediments, they have been observed to sorb to the mineral fraction of the solid matrix at

low OC levels (Luthy *et al.* 1997; Shwartzbach and Westall 1981; Curtis *et al.* 1986; Karickhoff *et al.* 1979; Nkedi-Kizza *et al.* 1983a). Additionally, in most soils and sediments, the HOC sorption isotherms are linear and yield an OC normalized sorption constant (K_{OC}) that is well predicted from a compound's solubility (Chiou *et al.* 1979, 1983) and octanol/water partition coefficient (Kenaga and Goring 1981; Shwartzbach and Westall 1981; Hassett *et al.* 1980). Deviations from sorption linearity have been observed at low concentrations. The reasons for these deviations center on proposed structural differences in the soil OC and surface area differences in OC (Chiou and Kile 1998 and references therein).

The sorption/desorption kinetics of HOCs is often characterized by a rapid initial uptake (or release) followed by a slow approach toward equilibrium (Wu and Gschwend 1986; Leenheer and Ahlrichs 1971; Brusseau and Rao 1989). This slow reaction (sorption or desorption) can occur on a time scale of days to months and longer (Coates and Elzerman 1986). The long equilibration and release times observed during sorption/desorption studies have been characterized as diffusion-controlled sorption/desorption resistance and are suggested to be a result of micropore diffusion in aggregated materials (Wu and Gschwend 1986; Steinburg *et al.* 1987). The higher a compound's partition coefficient (K_p ; which is related to the fraction of OC and the hydrophobicity of the compound), the slower the rate of sorption or desorption (Brusseau and Rao 1989); also, the rate will be dependent on the length of the micropores in a solid matrix. It is evident, however, that micropore diffusion becomes increasingly important as the solubility of HOCs decreases. For example, a series of PCB congeners exhibiting a decreasing solubility also shows a concomitant decrease in the rate of desorption (Girvin *et al.* 1997). The slow desorption has often been seen to control HOC microbial degradation and, hence, a compound's bioavailability (Carmichael *et al.* 1997; Guthrie and Pfaender 1998; Nam *et al.* 1998; Chung and Alexander 1998).

THE EFFECT OF COLLOIDS

Colloids, insoluble solids, suspended in the soil solution have the potential to significantly affect contaminant mobility (Liang and McCarthy 1995). Colloids are small, having a particle diameter between

0.01 μm and 10 μm . They can be mineral grains (like clays, Fe/Al/Mn oxides, SiO_2 , CaCO_3), particulate organic matter (POM), or bacteria or viruses. Generally, they have similar composition and surface characteristics as the immobile solid phase. Hence, they can originate from clay-sized minerals from the original parent material, or they can be formed through the geochemical alteration of primary minerals. Colloidal particles, such as secondary hydrous oxides, layer silicates, silica and complex solid mixtures, form on the surfaces of larger grain-sized minerals. Additionally, secondary minerals may form from homogeneous nucleation as a result of local changes in geochemistry, such as pH, pCO_2 , Eh ionic composition, or ionic strength (McCarthy and Zachara 1989). For instance, Gschwend and Reynolds (1987) found precipitates of ferrous phosphate colloids in groundwater down gradient of a sewage infiltration. Strongly hydrolyzing radionuclides like Pu have been shown to form discrete submicrometer-sized particles under natural soil conditions (Rai *et al.* 1980) and have been suggested to behave as their own colloids (Litaor *et al.* 1996).

Colloid-assisted transport has been implicated in the mobility of $^{239/240}\text{Pu}$ in the groundwater at the Nevada Test Site (NTS) and in the soils of Rocky Flats, Colorado (Buddenmeier and Hunt 1988; Kersting *et al.* 1999; Litaor *et al.* 1996; Ryan *et al.* 1998). At the NTS, the Pu as well as other radionuclides appears to be associated with clay mineral assemblages likely dominated by illite and mordenite, which is a zeolite. Clays and zeolites are common secondary minerals in altered rhyolitic tuff, smectite, clinoptilolite, and mordenite, and have been specifically identified in the rocks at the NTS. Transport of discrete PuO_2 particles was suggested to be the transported colloid at Rocky Flats. Champ and Merritt (1981) observed apparently accelerated transport of ^{137}Cs from buried glass blocks at Chalk River, Ontario. Using undisturbed soil columns taken adjacent to the buried blocks, they found evidence of colloid assisted Cs transport.

To facilitate transport, colloids must be mobile over significant distances and immune to filtration while passing through porous media. Colloid stability, or the ability to remain as a dispersed suspension, is a complex combination of particle size, density, surface chemistry, water chemistry, and flow rate (Ryan *et al.* 1998; Roy and Dzombak 1997; Johnson *et al.* 1996; Kretzschmar and Sticher 1997). However, according to DLVO theory (see Stumm and Morgan 1981), the stability of col-

loidal suspensions is governed by van der Waals attractive forces, which promote aggregation, and electrostatic forces, which promote dispersion. Hence, colloid stability is significantly influenced by particle mineralogy, those chemical factors controlling surface charge, and the extent of the electrical double layer (McCarthy and Zachara 1989; also see the case studies associated with this chapter). For a more complete explanation of colloidal phenomena and the aforementioned chemical and mineral factors influencing colloid stability, see Stumm and Morgan (1981) and Sposito (1994).

The case study, "The Effect of Colloid Size, Colloid Hydrophobicity, and Volumetric Water Content on the Transport of Colloids Through Unsaturated Porous Media," by Maureen McGraw, Los Alamos National Laboratory, breaks down the results of a series of experiments to test the extent of colloid mobility through Unimin sand under various factors such as colloid size, surface property, and volumetric water content. *See page 928.*

The case study, "Summary of Colloid Generation and Stabilization in Response to Induced Water Chemistry Changes," by B. B. Looney, Savannah River Technology Center; R. N. Strom, Savannah River Technology Center; J. C. Seaman, Savannah River Ecology Laboratory; and P. M. Bertsch, Savannah River Ecology Laboratory, summarizes tests conducted to support reinjection of treated groundwater into sediments and the resultant effect on subsurface systems. *See page 939.*

The case study, "Understanding the Fate and Transport of Multiphase Fluid and Colloidal Contaminants in the Vadose Zone Using an Intermediate-Scale Field Experiment," by Charles R. Carrigan, Lawrence Livermore National Laboratory, investigates contaminant transport issues in a semi-controlled environment during an intermediate-scale field infiltration experiment. *See page 943.*



UNIQUENESS OF THE VADOSE ZONE—IMPACT ON GEOCHEMISTRY

Thus far in the chapter, the discussion has centered on major geochemical processes affecting contaminant mobility in the natural system, regardless of environment. The discussion is valid whether the context is saturated or unsaturated zones, lakes, oceans, or the near surface or deep vadose zone. The vadose zone, however, is an environment with certain unique attendant properties. This uniqueness can affect the

rate and extent of biogeochemical processes. These properties include transient and variable water flow, variable water content, and the presence of a gas phase.

The presence of a gas phase in the vadose zone can have significant effects on contaminant behavior. First, there is a connection to the atmosphere (albeit via a tortuous path) that will generally maintain a pO_2 level that minimizes the potential of anoxic conditions to exist, or at least persist, for long periods of time as discussed earlier. Second, pCO_2 will fluctuate due to CO_2 production and transport: in the near surface vadose zone, plant root respiration and organic matter decomposition/microbial activity can cause pCO_2 levels to be orders of magnitude greater than atmospheric levels. Third, volatile organic compounds (VOCs) like carbon tetrachloride, TCE, benzene, and others partition between the gas, liquid, and soil solids; the volatility of VOCs has been used in several remediation techniques (such as vapor extraction etc.). Similarly, water movement in the vapor phase can occur as a result of osmotic potentials or thermal gradients. Vapor movement of VOCs and water is discussed in other chapters.

The pCO_2 level is often an important component in inorganic contaminant geochemistry. Under circumneutral to alkaline conditions, the precipitation/dissolution of $CaCO_3$ may control CO_2 gas concentrations and the bicarbonate and carbonate aqueous species. This factor is probably more important in the deeper subsurface environment below the major CO_2 production zone (Suarez and Simunek 1996, 1997). More importantly, however, the precipitation/dissolution of $CaCO_3$ can affect the solubility of contaminant ions via adsorption to the carbonate surface and formation of coprecipitates. Suarez and Simunek (1996, 1997) argue that under many conditions, the local equilibrium assumption regarding $CaCO_3$ precipitation/dissolution may not be valid and that kinetic expressions may yield results closer to field measurements. If this is true for major ion geochemistry (for example, $CaCO_3$), then local equilibrium assumptions for ionic contaminants that form surface complexes and coprecipitates with carbonate minerals may also be inappropriate. This is particularly important in light of the temporal component of metal adsorption to carbonates and their propensity, as a result of carbonate recrystallization, to form time-dependent solid solutions.

Vapor phase transport of VOCs in the vadose zone is one of the important pathways in the distribution and attenuation of these organic

compounds. The presence of three phases (gas, aqueous, and solid—not considering a nonaqueous phase liquid) complicates an already complex system. A fundamental understanding of the partitioning of VOCs between the aqueous-solid, aqueous-gas, and the gas-solid interfaces is key to effectively modeling a VOC three-phase system. These relationships are complex due to several physical-chemical constraints that influence VOC partitioning (see Chapter 1). The aqueous-gas phase partitioning, or volatilization, of organics is favored for those organics with a high Henry's law constant and low aqueous phase solubility. While the partitioning between the gas and liquid phase may be determined from Henry's law constants and the rate of partitioning is fast (Washington 1996), the presence of the other phases will affect local equilibrium. In addition, the applicability of the local equilibrium assumptions depends on the scale and resolution of the mathematical model used (see the case study in Chapter 7 "Scale-Dependent Mass Transfer During SVE" by Clifford K. Ho, Sandia National Laboratories). Moisture content is an important factor among those physical-chemical characteristics of the vadose zone that may impact vapor phase transport. There is potential for deviation from Henry's law behavior for dilute VOC concentrations, resulting from capillary tension, and high ionic solute concentrations are possible in drier or drying soils. These deviations, however, have been shown to be small for most soil conditions (Washington 1996). The major impact of moisture content and its variability is on the partitioning between the gas and solid phases.

At extremely low moisture contents, vapor-solid sorption onto mineral surfaces dominates and has been correlated to the soil's surface area. At the opposite extreme, in a saturated system there is no vapor phase sorption; sorption reactions occur through dissolved VOC sorption onto soil surfaces. (See the recent review by Luthy *et al.* [1997] for a discussion of sorption-sequestration of hydrophobic organic contaminants [HOC]; also see Cheng [1990] and Sawhney and Brown [1989] for thorough discussions of HOC-soil interactions.) In between these two extremes, VOC sorption exhibits a complex multiphase equilibria between the solid, gas, and aqueous phases (Ong and Lion 1991a,b; Ong *et al.* 1992; Unger *et al.* 1996). At higher water content, water effectively competes with VOC sorption to mineral surfaces, minimizing gas-solid phase partitioning. However, as moisture content decreases, VOC gas-solid partitioning increases. For example, TCE sorption from the

gas phase, in soils with water contents equivalent to surface coverages of about 8 water layers, can exhibit partition coefficients 2 to 4 orders of magnitude larger than those at higher moisture contents (Ong and Lion 1991a). While typical of most vadose zone soils, these low moisture content conditions could prevail in arid and semi-arid regions, and desiccated surface soils.

Sorption of VOCs (compounds with high Henry's Law constants and low aqueous phase solubility) to soils is generally thought to occur via the following processes: (1) adsorption at the mineral/water interface, (2) adsorption at the gas/water interface, (3) partitioning into soil organic matter, and (4) partitioning into the adsorbed water located at the soil mineral surface. Farrell and Rienhard (1994a) found that for unsaturated soils, adsorption into water-filled micropores (pores smaller than several adsorbate diameters in width) can significantly contribute to, and even dominate, sorption of VOCs. Importantly, micropore sorption has been implicated in a slow desorption process that could affect remediation estimates for VOCs. For instance, Farrell and Reinhard (1994b) observed that desorption in unsaturated soil occurs at two time scales. The first is very rapid, but the second was suggested to be extremely slow, requiring months and possibly years. Hence, identifying dominant sorption mechanisms may be critical in determining if a local equilibrium model is a reasonable approximation in modeling. Unfortunately, there is no *a priori* predictive capability currently available on which to base local equilibrium assumptions.

As covered in the adsorption section of this chapter, the use of surface complexation theory to explain and understand adsorption from a more molecular perspective is superior to the more traditional K_d approach. However, the two approaches both suffer from limitations particularly exacerbated in unsaturated systems. In the component additivity approach (Zachara *et al.* 1989; Davis *et al.* 1998), the difficulty in identifying the important or dominant surfaces and their respective surface areas and site densities creates a need for very detailed and exhaustive characterization. The generalized composite approach treats the whole soil or sediment as a composite adsorbent, and requires the determination of soil specific mass action equations and stability constants (Davis *et al.* 1998; Wen *et al.* 1998; Wang *et al.* 1997; Charlet and Sposito 1987). The latter approach is more direct and requires less descriptive characterization, while still maintaining a link between surface and

aqueous speciation. However, it loses the molecular insight on which the surface complexation theory is based (Davis *et al.* 1998). The latter approach depends on surface area and an estimate of “soil site densities,” typically 2 to 10 sites/nm², to estimate stability constants. The estimation of surface area or site density in both approaches is difficult in saturated and unsaturated systems. Because contaminant movement is coincident with water movement, the active surface area in unsaturated systems is not the same as the total surface area. This problem in the application of surface complexation theory is equally attendant to cation exchange reactions, where the “effective” cation exchange capacity is necessary to quantify exchange reactions in unsaturated soil. In fact, the character of interfacial surfaces and their quantification, whether it is a mineral-water, water-air, or air-solid interface, is important for estimating rates and extents of reactions at those surfaces.

In essence, the problem of site density is an example of a bigger challenge—heterogeneity. Briefly, heterogeneity is a catchword for the ubiquitous spatial variability in soil physical, chemical, and microbial properties and the multitude of processes that can occur. Physical heterogeneity is commonly associated with preferential flow and contaminant migration paths and similar hydrologic phenomena affecting the movement of water and contaminants. Microbial heterogeneity is related to the spatial variability of microbial populations, activity, and ecology. Chemical heterogeneity is related to the nonuniform distribution of reactive minerals or conditions that can affect contaminant speciation and overall mobility in the soil.

Although it is only briefly covered in this chapter, heterogeneity’s influence on contaminant transport can be substantial. The extent of its influence on contaminant biogeochemistry of the vadose zone is only now being addressed. For an overview on heterogeneity and its influence in contaminant transport, see Thompson and Jackson (1996).

VADOSE ZONE MICROBIOLOGY

OVERVIEW

Microorganisms exist in the vadose zone and perform a variety of biochemical transformations that impact the chemistry of the zone’s gas, solid, and aqueous phases. The primary differences between the microbiology of the saturated zone (aquifers and aquitards) and the vadose

zone are related to (1) differences in nutrient flux and nutrient availability and (2) differences in the energy potential of water and the relative role and scale of nutrient advection and diffusion.

Oxygen is rarely limiting in the bulk vadose zone due to the presence of the air phase, although specific microsites and small zones may be anaerobic. In contrast, dissolved oxygen concentrations are less than 10% of maximal in many saturated environments, and zones ranging from lenses to entire strata are anaerobic. For nutrients other than oxygen, nutrient flux is primarily controlled by the groundwater recharge rate and the type and concentration of soluble nutrients. Gas-phase flux of some nutrients by diffusion and advection, such as natural barometric pumping, may also be important. In high precipitation climates, recharge rates are typically large, with high plant biomass resulting in the input of large quantities of plant-derived organic matter. Conversely, in arid climates recharge is often very low, plant communities are very sparse, and the input of organic matter becomes extremely small. Typical vadose zone recharge rates vary over four orders of magnitude, from 0.03 to 500 mm yr⁻¹ (Driscoll 1985). Assuming that the input of soluble organic material varies approximately three orders of magnitude, nutrient flux in different vadose zone environments may, therefore, vary by as much as seven orders of magnitude. Moreover, preferential flow often occurs in the vadose zone and can result in total bypass of moisture and soluble nutrients to large regions of the vadose zone.

In the vadose zone, capillary and adsorptive forces of the solid matrix (that is, matric potential) attract and bind water and lower its potential energy compared to the reaction in saturated systems. While the matric potentials commonly present in the vadose zone do not result in desiccation stress to microorganisms, they can severely limit microbial transport and the transport of soluble nutrients to microorganisms (Wong and Griffin 1976; Kieft *et al.* 1993). In addition, moisture content and texture of the solid phase play a critical role in determining the pore-scale distribution of water and contaminants. In general, the vadose zone possesses discontinuous water films and wedges except at low air-filled porosities and very fine textures (Wong and Griffin 1976). These discontinuities fragment the vadose zone into isolated diffusion-controlled entities. The scale of these entities is controlled by sediment texture, layering, and moisture content. Fragmentation becomes permanent in the

absence of hydrologic events that increase the water content and continuity. In the presence of major recharge events, only a small fraction of the vadose zone may be affected due to preferential flow. Thus, while movement of nutrients in aquifers is dominated by advection, diffusion is the dominant mechanism in most of the sediment volume in vadose zone environments. Although both aquitards and low recharge vadose zones are diffusion-controlled systems with low water and nutrient flux, the degree of hydrologic continuity and the dominant scale of diffusion is smaller in low recharge vadose zones. In summary, the presence of an air phase alters the amount, type, and scale of nutrient movement, which profoundly impacts the population density, activity level, spatial heterogeneity, and transport of microorganisms in the vadose zone.

MICROBIOLOGICAL PROCESSES IN THE VADOSE ZONE

Microbially mediated chemical reactions may have major impacts on the chemistry of the vadose zone and contaminant mixtures when moisture and nutrient concentrations and fluxes are relatively high. Conversely, microbially mediated reactions may have little or no impact on the chemistry of the vadose zone and contaminant mixtures when moisture and nutrient concentrations and fluxes are low. This section covers the current knowledge of the population density, activity level, spatial heterogeneity, and transport of microorganisms in the vadose zone as a function of hydrologic and geochemical properties. It also highlights gaps in our current understanding of microbial transformations of contaminants in the vadose zone.

Microbial Abundance

Studies during the last 10 years have shown that viable microorganisms exist in a variety of deep (10–450 m) vadose zones, including both porous media and fractured and matrix rock. Direct microscopic counts vary from 10^4 – 10^7 cells g^{-1} . Direct counts are typically lowest in low recharge vadose zones. Very low percentages of the direct count cells can be cultured in vadose zone materials. Heterotrophic plate counts are orders of magnitude higher in shallow vadose zones ($<10^1$ – 10^3 CFU g^{-1} to 10^4 – 10^6 CFU g^{-1}) than in deep, low recharge vadose zones ($<10^1$ – 10^2 CFU g^{-1} to $<10^1$ – 10^4 CFU g^{-1}), (Balkwill *et al.* 1998; Brockman *et al.*

1992, 1997b; Colwell 1989; Fredrickson *et al.* 1994; Haldeman and Amy 1993; Haldeman *et al.* 1993; Kieft *et al.* 1993, 1998; Severson *et al.* 1991; Zhang *et al.* 1998). Based on other studies, the median percent of microscopically visible cells (after staining with the dye acridine orange) that could be cultured and the median percent of viable cells (estimated by measuring microbial phospholipid fatty acid extracted from the sediment) that could be cultured were 0.0003 percent and 0.01 percent, respectively, for deep vadose zones with low recharge. The equivalent values were approximately three orders of magnitude higher for deep vadose zones from the eastern coastal plain where recharge is much higher (Figure 6-3). The lower percentages for the acridine orange cells that could be cultured were likely due to the presence of intact dead cells as, in a separate study, the DGA:PLFA ratio (diglyceride fatty acid [indicative of dead cells] to phospholipid fatty acid [indicative of viable cells]) increased with increasing depth from the surface to 37 m deep (Kieft *et al.* 1998).

At contaminated vadose zone sites, microscopic counts and heterotrophic plate counts are typically orders of magnitude higher than at uncontaminated sites (Kieft *et al.* 1993; Fredrickson *et al.* 1994). The highest densities are obtained when contaminants are present at relatively high but not highly toxic concentrations. Under these conditions, microscopic counts and heterotrophic plate counts approach or exceed those found in uncontaminated aquifers and surface soils.

Microbial Activity

Consistent with lower nutrient flux in the vadose zone than in aquifers or surface soil, microbial activity is lower in the vadose zone. For example, slower rates of metabolism and longer lag times were observed in the unsaturated zone than in either the surface soil or the underlying aquifer using ^{14}C -labeled organic compounds (Konopka and Turco 1991). The detection of microbial activity in laboratory incubations of vadose zone material is highly dependent on factors such as incubation time, substrate, type of assay, and sample storage prior to initiation of the assay. Extended incubations (weeks to months) and addition of inorganic nutrients are often required to detect microbial activity, even when ^{14}C -labeled substrates are supplied. For example, at uncontaminated low recharge sites, the median percent glucose mineralization

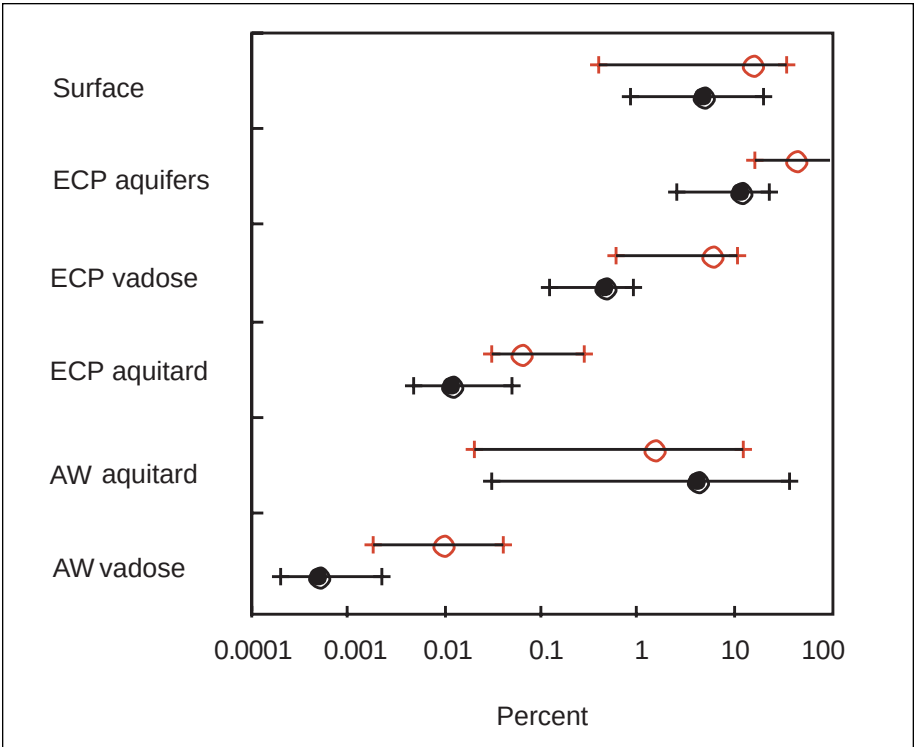


Figure 6-3. Percent of viable and total cells that were cultured in various subsurface ecosystems in the USA. The number of viable cells can be estimated by extracting and measuring the cellular phospholipid fatty acids, and using an empirical conversion factor to convert mass of phospholipid to number of viable (cultured plus uncultured) cells. Cultured cells are the sum of aerobic and anaerobic heterotrophs and autotrophs grown on approximately 10 to 15 media. Open circle, median percent of viable cells that were cultured. Closed circle, median percent of acridine orange direct count cells that were cultured. Error bars represent the 25th percentile and 75th percentile. ECP, eastern coastal plain; AW, arid western regions. Data for these calculations was provided by over 20 investigators in the U.S. Department of Energy Subsurface Science Program.

in positive samples after 2 months is typically 1 percent to 5 percent, with less than 20 percent of the positive samples showing greater than 10 percent mineralization (Brockman *et al.* 1997b). Substrate was primarily unutilized, as nearly all of the glucose was leachable (Brockman, unpublished). This situation is exacerbated when assays use difficult to degrade substrates. Some radiotracer assays are more sensitive than others. For example, ^3H -acetate incorporation into microbial lipids is more sensitive than trapping mineralized $^{14}\text{CO}_2$ in KOH (Brockman 1998b) (Table 6-5). Physical disturbance and chemical alteration of vadose zone sediments, which is inherent to sampling even when samples are not mixed, can stimulate microbial activity and populations (Brockman *et al.* 1992, 1998a; Haldeman *et al.* 1994, 1995; Fredrickson *et al.* 1995). Therefore, samples should be analyzed immediately to minimize laboratory artifacts. Stimulation results from bringing microorganisms into contact with previously unavailable nutrients, induced moisture gradients that cause advection of nutrient solutes, and increased diffusion of oxygen into the sediment.

In situ rates of microbial activity in uncontaminated vadose zones are very low and have been estimated using geochemical mass balance models. At a shallow vadose zone site in Canada, microbial CO_2 production was estimated to be $7.1 \text{ g CO}_2 \text{ m}^{-3} \text{ year}^{-1}$ at a depth of 6.5 to 7.5 m immediately above the capillary fringe (Wood *et al.* 1993). This rate was at least 100 times larger than in the vadose zone between 1.0 and 6.5 m, and is likely due to diffusion of electron donors from the underlying saturated zone and increased advection of nutrients by seasonal fluctuation in the water table. Microbial CO_2 production in the zone between 1.0 and 6.5 m was, therefore, less than 1.6 millimoles (less than 0.07 g) $\text{CO}_2 \text{ m}^{-3} \text{ year}^{-1}$. In comparison to this shallow site, activity in deep vadose zones has been estimated to be less than 0.1 nanomoles $\text{CO}_2 \text{ L}^{-1}$ porewater year^{-1} (Kieft and Phelps 1997). These extremely low rates of metabolism are due to lower availability of carbon in older, deeply buried sediments and low (less than 1 millimeter year^{-1}) levels of moisture recharge through the vadose zone. Such low levels of microbial activity indicate that the vadose zone probably contains a higher fraction of dormant microorganisms than other subsurface environments.

Contaminants that can serve as an electron donor, electron acceptor, or nutrient source to microorganisms will increase microbial activity unless they are present in toxic concentrations or at very low concentra-

TABLE 6-5

Microbiological and pore water characteristics of a surface soil B horizon and eight subsurface paleosol B horizons.

Depth (m)	PORE WATER		³ H-ACETATE INCORPORATION ¹		¹⁴ C-GLUCOSE MINERALIZATION ²		CFU ³
	Age (yrs)	Organic C (ppm)	Positive samples	Mean ⁴ of positive samples	Positive samples	Mean ⁵ of positive samples	Positive samples
<i>Site A</i>							
0.3	0	1800	100%	2.0 x 10 ⁵	100%	36%	100%
5.0	50	1920	100%	1.1 x 10 ⁵	100%	38%	100%
8.0	110	450	66%	1.2 x 10 ⁴	14%	0.3%	92%
9.5	170	270	100%	3.8 x 10 ⁴	46%	19%	100%
<i>Site B</i>							
4.1	50	100	18%	1.9 x 10 ³	8%	0.6%	4%
17.7	640	160	12%	4.5 x 10 ²	4%	0.3%	4%
18.4	720	120	22%	6.9 x 10 ²	6%	0.4%	4%
19.1	780	150	20%	1.8 x 10 ²	0%	—	0%
25.8	1,000	100	10%	3.1 x 10 ³	0%	—	0%

¹ Incorporation of ³H-acetate into microbial lipids. 28 d assay, except 2 d for the 0.3 m sample and 7 d for the 5.0 m sample. n=50 for each sample.

² Conversion of ¹⁴C-glucose to ¹⁴C-CO₂. 28 d assay, except 7 d for the 0.3 m sample. n=50 for each sample.

³ Heterotrophic colony forming units growing on 10% RZA medium. Detection level = 100 CFU/g sediment. Counts performed periodically during 42 d incubation at room temperature. n=25 for each sample.

⁴ Mean expressed as disintegrations per minute, measured in a scintillation counter.

⁵ Mean expressed as a percentage by calculating (disintegrations per minute as ¹⁴C-CO₂/ disintegrations per minute initially added as ¹⁴C-glucose) x 100.

tions. Because most contaminants reach the vadose zone in solution, the increased moisture improves availability of indigenous nutrients and contributes to increased activity. Methods of measuring microbial activity in contaminated vadose zones are addressed in Chapter 3.

Microbial Heterogeneity

The gas phase controls the availability and movement of moisture and nutrients in the vadose zone. At the pore scale, a myriad of isolated chemical microenvironments exist in discontinuous water films and wedges. Chemical microenvironments are conditioned by natural distributions of nutrients and partitioning of contaminants to specific mineralogies and/or pore classes. At the field scale, layers and strata with different properties can generate microbial spatial heterogeneity. For example, interfaces between sedimentary layers often generate localized regions of greater saturation where microorganisms may exhibit increased numbers or activity due to improved access to sediment-associated nutrients. Similarly, differences in water and nutrient (indigenous or as contaminants) flux in flow bypass versus preferential flow regions will generate heterogeneity in microbial populations and activity. The generally low populations of viable microorganisms in the vadose zone may also contribute to spatial heterogeneity, as microbes may have become extinct or rare in regions of the vadose zone that were not conducive to survival. Moreover, a specific microbial contaminant transformation activity is likely to display greater spatial heterogeneity than the ability to degrade a simple sugar. Little research has been devoted to systematic examination of microbial spatial heterogeneity in the vadose zone and its impact on contaminant transformation. Similarly, the presence and distribution of specific microbial functional types, such as different types of chemolithotrophs and strict anaerobes, has rarely been addressed.

In one study, the impact of water flux, and by extension nutrient flux, on microbial distribution was examined by comparing sites receiving 15 μm , μm to mm , and 20 cm average annual recharge. At each site, several 50-sample transects (5 to 10 cm sample spacing) were performed, and 1-g aliquots from a 15-g homogenized sample were assayed for ^{14}C -glucose mineralization and ^3H -acetate incorporation into membranes in 2- to 3-month unsaturated incubations. Samples were treated with acid at

the end of the incubation to recover residual ^{14}C - CO_2 . ^3H -acetate incorporation is highly sensitive and able to detect metabolic activity when cells are limiting their energy. Microbial activity was not detected in 60 percent to 70 percent of the samples in the low-recharge sites compared to 0 percent to 25 percent at the 20-cm recharge site (Brockman *et al.* 1999). Incubation of the low-recharge samples with low levels of inorganic nutrients did not increase the frequency of detection. Lastly, samples at the low-recharge sites were four- to eight-fold more likely to have detectable activity in silts than in the lower water content sands. Because the silt and sand had similarly low organic carbon content, this result is likely attributable to greater water connectivity at the pore scale in the silt and, thus, greater survival due to improved diffusion of nutrients to isolated microorganisms.

The large percentage of samples lacking detectable activity at the low-recharge sites suggests that large volumes of sediment (several tens of cubic cm) can be devoid of microorganisms capable of metabolism, or at minimum there were very few if any microorganisms able to metabolize the substrate and/or grow under the conditions of the assay. This pattern may be explained by the gradual death of most microorganisms over time, except in rare microsites where conditions permit long-term survival (Brockman *et al.* 1997b) and by higher mortality with decreasing recharge (Brockman *et al.* 1998b). This conclusion was also supported by activity assays of replicate 0.1-, 1-, 10-, and 100.0-g samples removed (without sample homogenization) from the same core. These assays used vessels in which sediment, headspace, and ^{14}C trap volumes and surface areas were kept nearly constant for all sample sizes. In the low-recharge sites, activity was rarely detected in the small samples, and the frequency of detection of activity increased with increasing sample size (Brockman and Murray 1997a). In contrast, at the 20-cm recharge site, activity was detected and approximately equal in all eight replicates for all sample sizes (Figure 6-4). Measurements of viable biomass by PLFA on 75-g samples showed a spatially averaged density of approximately 10^4 viable cells g^{-1} at all three sites. Thus, microbial colonization was more evenly distributed at the high-recharge site. This pattern likely results from higher concentrations and fluxes of bioavailable nutrients in pore water (due to higher precipitation and higher plant biomass) and possibly increased transport of microorganisms from higher in the profile.

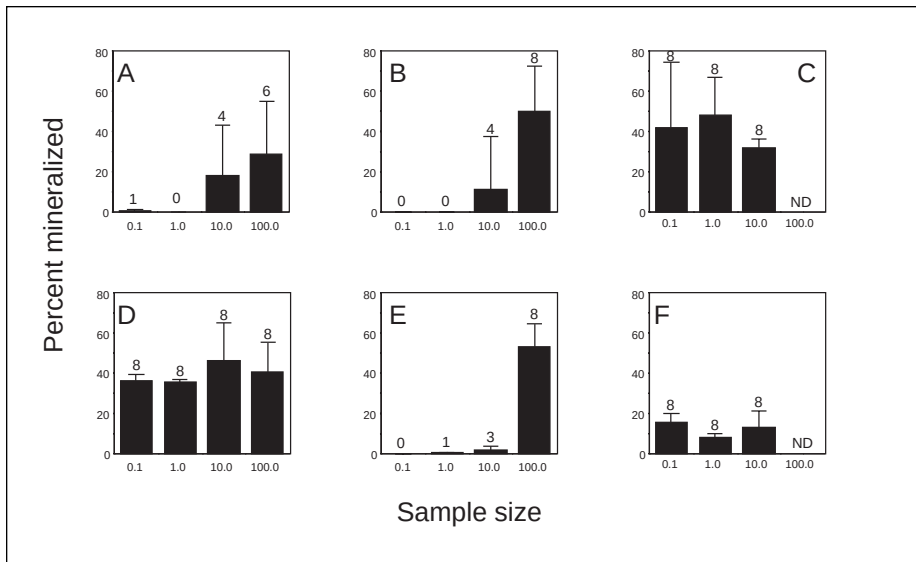


Figure 6-4. Microbial activity (mean and standard deviation) in 8 replicate 0.1-, 1.0-, 10.0-, and 100.0-g samples from a core at different sites. Values above bars indicate the number of replicates in which activity was detected. Panel A: recharge of 15 μm , 60 d aerobic incubation. Panels B and E: recharge of μm to mm, 60 d aerobic and anaerobic incubations respectively. Panels C and F: recharge of 20 cm, 3 d aerobic and 26 d anaerobic incubations respectively. Panel D: surface soil B horizon, 7 d aerobic incubation (for purpose of comparison). ND = assay not done.

In a separate study, the role of depth, sediment age, pore water age, and pore water organic carbon on fine-scale microbial spatial heterogeneity was examined in a sediment sequence containing multiple ancient buried soils, or paleosols. Sediments were deposited by wind from the same source area and of the same general composition over approximately 1 million years. Cores from eight paleosol horizons, with similar degrees of soil development, were studied to examine microbial distribution in a setting where geochemical and geohydrologic parameters were as similar as possible. Fifty individual 1-g samples were removed every 0.3 cm in each of the eight cores, and ^3H -acetate incorporation and ^{14}C -labeled substrate mineralization were measured. Pore water organic carbon showed the strongest positive correlation to the

amount of substrate used and the percent of samples in which activity was detected (Brockman *et al.* 1998b) (Table 6-5). Activity assays conducted on eight replicate 0.1-, 1-, 10-, and 100-g samples in cores showed a continuum, from activity being detected in all replicates of the 1-, 10-, and 100-g samples in cores with a pore water age of 50 years and high pore water organic carbon, to as few as one of the 100-g replicates having detectable activity in cores with old pore water and low pore water organic carbon. Thus, expanding upon the results from the low- versus high-recharge sites, the results at this site (recharge of 0.1 to 0.8 cm) demonstrate that pore water age and organic carbon are important determinants of the presence of microorganisms capable of metabolism. The rare microsite/large extinction volume phenomenon may have important implications for bioremediation in the vadose zone.

Microbial Transport

Laboratory investigations of microbial transport under unsaturated conditions have typically been performed in homogenous sand columns or in simulated porous media such as micromodels. These experiments have generally used high concentrations of bacteria and/or nutrients. Such experimental conditions don't accurately represent most vadose zones. Bacterial transport in agricultural soil microcosms has been well studied. However, soils are structurally and chemically different from the vadose zone; they possess high microbial populations, and high concentrations of "marked" bacteria are typically added to conduct experiments. Although these laboratory and field studies poorly represent most unsaturated zones, several controlling processes are evident and have relevance to vadose zone microbial transport. The potential for transport of microorganisms in the vadose zone is primarily controlled by transient saturated flow, the amount of air- and water-filled porosity, and the concentration of nutrients (natural, or as contaminants) available for microbial growth and partitioning of cells into the liquid phase. Cell size, shape, hydrophobicity, and motility are less important factors, and because few results exist on their impact in the vadose zone, they will not be discussed. A predominance of pore throats smaller than the average size of cells or occlusion of a high fraction of the pore throats by cementation will prevent or greatly restrict microbial transport. The geochemistry of sediment coatings can also inhibit microbial transport due to selective sorption of cells onto specific minerals.

Microbial transport in soils occurs primarily by preferential (saturated or near-saturated) flow within soil channels or macropores (Smith *et al.* 1985; Madsen and Alexander 1982; Natsch *et al.* 1996; Breitenbeck *et al.* 1988; Hagedorn *et al.* 1978) and matrix flow during transient saturated conditions (Rahe *et al.* 1978). While channels and macropores rarely exist in the vadose zone below the rooting and burrowing zone, vadose zones may become transiently or locally saturated and experience preferential flow in pore networks or fracture systems in regions receiving high recharge from snowmelt, storm events, or high annual precipitation. Increasing saturation reduces the adsorption of unattached cells to surfaces. High water velocities in preferential flow paths will transport unattached cells, and can detach attached cells. Most transport of microorganisms in the vadose zone occurs during these events. In the absence of these events, the degree of saturation plays an important role. Water flow under unsaturated conditions occurs in water films by capillary forces, and microorganisms could theoretically be transported or actively move in water films. However, adsorptive forces and air-water interfaces greatly retard microbial movement in water films. Wong and Griffin (1976) concluded that both active bacterial movement (via cell division or chemotaxis) and passive movement (via advection and diffusion) are unlikely at matric potentials below approximately -0.05 MPa (-0.5 bars). This is because of discontinuities in water lenses and films (for coarse textures) and very high adsorption and/or filtration (for fine textures that may retain continuous films at much more negative matric potentials).

In laboratory experiments with unsaturated porous media, bacteria preferentially adsorbed to air-water interfaces over solid-water interfaces (Wan *et al.* 1994; Powelson and Mills 1998) and adsorption increased with decreasing saturation (Wan *et al.* 1994; Schafer *et al.* 1998). Adsorption to the air-water interface appears to be irreversible and controlled by the degree of cell hydrophobicity (Wan *et al.* 1994). Thus, microbial transport in an oligotrophic (that is, low nutrient) environment at low water saturation and in the absence of preferential flow or transient matrix flow appears close to impossible. Balkwill *et al.* (1998) studied the distribution of indigenous microorganisms in vertical (4 to 15-m deep) unsaturated flow paths at 5 semi-arid field sites characterized by low recharge, high recharge accompanied by rare saturated (preferential) flow, and high recharge via solely unsaturated flow. They found strong

evidence suggesting transport of microbial cells at the high-recharge sites with preferential flow, but no evidence of microbial transport at the high-recharge unsaturated flow site and low-recharge sites.

There is high potential for microbial colonization and transport in contaminated vadose zones. This is due to contaminants typically being delivered by a transient saturation event or percolation of contaminated water (or free hydrocarbon). Colonization and transport will be highly stimulated if the contaminant supports microbial growth and is present at high, nontoxic concentrations. In saturated columns without water movement, colonization may occur via the displacement of daughter cells into adjacent pore spaces as cells divide (Reynolds *et al.* 1989; Sharma *et al.* 1993). Detachment rates from biofilms in liquid bioreactors are growth-rate dependent (Peyton 1996) and not significantly affected by shear stress (Peyton and Characklis 1993). While similar data are lacking for unsaturated systems, it is reasonable to assume that the same growth-dependent colonization and transport processes can occur in contaminated vadose zones, particularly at high pore saturations and in the presence of relatively high rates of growth. Cells are also transported between saturated pores by gas bubbles generated by fermentation (Reynolds *et al.* 1989), and a similar process may occur in the vadose zone during bioventing and in the capillary fringe during biosparging.

CONTAMINANT BIOTRANSFORMATION IN THE VADOSE ZONE

Vadose zone bioremediation approaches are important for protecting groundwater quality, because contaminants often reside in the vadose zone and are released over time to underlying aquifers. Vadose zone contaminants can be biotransformed as a result of natural or intrinsic processes, or by accelerating the processes through delivery of nutrients (electron acceptors, electron donors, or inorganic nutrients). In the majority of cases, biomass and/or activity in the vadose zone must be increased many orders of magnitude above the levels that occur via natural processes to have a significant impact on attenuation of contaminant transport. Criteria for proving that bioremediation is occurring, or has previously occurred, have been established (National Research Council 1993).

Extensive literature exists on bioventing, the controlled injection of air to stimulate aerobic biodegradation of petroleum hydrocarbons in the vadose zone. Bioventing promotes biodegradation of both liquid- and

vapor-phase petroleum hydrocarbons by volatilizing components with high vapor pressures, distributing vapors through the vadose zone to maximize biodegradation, and overcoming any existing oxygen limitation. An excellent review of bioventing is provided by Norris *et al.* (1994), and compendia of articles exist in Hinchee *et al.* (1995) and Alleman and Leeson (1997). Bioventing can be supplemented with injection or infiltration of water to increase the bioavailability of sediment-associated nutrients or, if required, water supplemented with inorganic nutrients to further increase biodegrading populations (Dupont *et al.* 1991). Rates of petroleum hydrocarbon biodegradation during bioventing typically range from 0.2 to 20 mg/kg/day (Norris *et al.* 1994). A number of factors control biodegradation rates, including: (1) the type of petroleum hydrocarbon mixture, (2) site physical and geochemical properties such as permeability, redox status, content of reduced minerals that can be oxidized, and availability of microbial inorganic nutrients, (3) the length of time since contamination, which impacts the population density of degraders and the chemical form and bioavailability of the contaminant and, (4) toxicity from high petroleum hydrocarbon concentrations, which can include pure hydrocarbon partially or entirely filling pore spaces at many sites. Bioventing has been successful at depths of 20 m in low-recharge vadose zones (Dupont *et al.* 1991), demonstrating that at least some of these microbially sparse environments can be transformed to high-population, high-activity “underground bioreactors” in the presence of readily available carbon and electron donors. Biosparging is the injection of air into the saturated zone. The books previously cited for bioventing also have excellent information on biosparging. Movement of bubbles of air and gaseous metabolites (potentially volatile fatty acids, hydrogen, and methane) from the saturated zone into the capillary fringe and higher regions of the vadose zone can achieve results similar to bioventing.

The genetic potential to aerobically biodegrade components of petroleum hydrocarbons is essentially ubiquitous in all natural aerobic environments. In contrast, biotransformation of other classes of contaminants in the vadose zone is more difficult, as detectable rates of biotransformation may require delivery of exogenous nutrients to increase populations and activities by orders of magnitude, and/or injection of biotransforming microorganisms. These refractory contaminant classes include highly chlorinated hydrocarbons, metals and/or radionu-

clides, synthetic chelating agents, and complex contaminant mixtures containing several contaminant classes (Riley and Zachara 1992). It is possible that in some vadose zones, biotransformation of certain contaminants will not occur, will occur so slowly that it cannot be measured, or occur more slowly than desired by policy makers.

In addition to incomplete knowledge of microbial transformations for several of these contaminant classes and the complex interactions between the microbiological, geochemical, and hydrogeological systems, several other issues add to the difficulty in successfully bioremediating the aforementioned recalcitrant contaminant classes:

1. Before contamination, the percentages of the microorganisms in the vadose zone with the genetic potential to perform these biotransformations are orders of magnitude lower than for petroleum hydrocarbons. In addition, reductive dechlorination and reduction of metals and radionuclides require anaerobic metabolisms, and populations of anaerobes (facultative and obligate) are low in pristine vadose zones. If nutrient and redox conditions imposed during engineered bioremediation are favorable, expression of genetic potential and populations of degraders can increase through microbial growth, selection, and population dynamics.
2. The initial distribution of contaminant transformers and the degree and speed with which they colonize surrounding volumes of “barren” sediment by growth and/or microbial transport is a critical issue. Microorganisms appear to exist in rare microsites in uncontaminated low-recharge vadose zones. For contaminants that are difficult to transform, the distribution of contaminant-degraders is also likely to occur in rare microsites, even in high-recharge uncontaminated vadose zones. Because microbial colonization and transport in discontinuous or continuous water films and partially filled pores is very slow in the presence of contaminants, bioremediation may be unsuccessful or very slow.
3. Approaches for enhancing the co-location of contaminant-transforming microorganisms and requisite nutrient amendments to regions where contaminants exist are problematic in the vadose zone. This co-location is critical because contaminants may exist primarily in fine-grained materials with low biomass, low permeability, and small pore throats that preclude or limit advective flows of

nutrient amendments and transport of microorganisms. Aqueous injection of nutrients or microbes is not considered feasible for some contaminant classes because it can spread contaminants in the vadose zone and potentially drive contaminants to the underlying aquifer. Injection of gas phase carbon nitrogen and phosphorous nutrients will be required in such cases; however, the efficacy of this approach in a variety of vadose zone settings has not been assessed. Successfully injecting contaminant-transforming microorganisms into the vadose zone is restricted by very poor transport of microbes in systems of low water saturation, as described earlier.

4. Diffusion of nutrients and contaminants to microorganisms may be more limiting to the rate of contaminant biotransformation in unsaturated than in saturated systems. For example, the diffusion coefficient for toluene through an unsaturated biofilm (an air-biofilm interface lacking a significant layer of free water exterior to the biofilm) was approximately two orders of magnitude lower than toluene diffusivity in water (Holden *et al.* 1997). Thus, mass transfer and biotransformation rates may be very sensitive to whether biotransforming microorganisms exist as isolated cells, microcolonies, or biofilms, and the extent to which the latter morphologies are covered by water films. This concept may explain the observation that TCE and toluene were not degraded in unsaturated soil at 5 percent moisture and below, but were degraded at 16- to 30 percent moisture (Fan and Scow 1993).
5. Avoiding chemical toxicity may be more difficult in the vadose zone, especially in the presence of mixtures of contaminants and contaminant classes. Microorganisms and contaminants may become concentrated by physical and chemical processes unique to the dynamics of an air-water-solid system; for example, microorganisms and contaminants may concentrate together at air-water interfaces.

Notwithstanding these potential limitations, significant progress has been made in co-metabolic bioventing of chlorinated contaminants in the vadose zone. Gaseous nutrient delivery of electron donor and acceptor (and nitrogen and phosphorus, if necessary) has the potential to pro-

mote widespread zones of microbial stimulation in the vadose zone and minimize mobilization of contaminants. Although focused on the saturated zone, biosparging of methane, nitrous oxide, and triethyl phosphate stimulated microbial populations and their TCE- and PCE-degrading ability in the overlying vadose zone (Hazen *et al.* 1994; Brockman 1994). Presumably, this was by means of the movement of moist air, unused methane, and possibly gaseous microbial metabolites into the vadose zone. There is ample evidence that anaerobic microsites and/or regions exist in the vadose zone, and these are likely due to two factors: (1) protection of anaerobic bacteria from oxygen diffusion through high oxygen uptake by immediately adjacent aerobic microorganisms (obligate and facultative), and (2) reduced oxygen diffusion into soil aggregates and fine-grained strata possessing high tortuosity. Anaerobic reductive dechlorination of PCE was shown in a large water-saturated column containing vadose zone sediment (Enzien *et al.* 1994). This anaerobic process occurred even though the column was run with oxygen at saturation in the influent and no lower than 12 percent of saturation in the effluent.

Sayles and co-workers have been very active in developing co-metabolic bioventing of chlorinated hydrocarbons in the vadose zone (Sayles *et al.* 1997a, 1997b; Moser *et al.* 1997). If air is injected, chlorinated compounds can be biodegraded aerobically (such as TCE to TCE epoxide) or anaerobically (such as PCE to ethylene) in microsites or regions stimulated and/or expanded by the higher levels of substrate and activity or biomass. Successful field-scale aerobic co-metabolic bioventing of chloroform, TCE, and 1-1-1-trichloroethane has been demonstrated (Cox *et al.* 1998). If contaminants require initial dechlorination before aerobic metabolism, an alternative strategy is injection of anaerobic electron donor and acceptor (hydrogen and carbon dioxide) in an anaerobic carrier (nitrogen, plus helium as a tracer) while still allowing aerobic degradation (Sayles *et al.* 1997a). Aerobic degradation would then occur at the margins of the engineered anaerobic zone or by halting injection and allowing oxygen to diffuse periodically into the injection wells. Thus, with either of these co-metabolic bioventing approaches, aerobic and anaerobic processes may co-occur, or be separated, in space and/or time. While these studies have been conducted at high-recharge sites with relatively shallow vadose zones, they suggest the possibility of establishing anaerobic microsites and/or larger anaerobic zones when

nutrients are injected into low-recharge and deep vadose zones. Other gaseous nutrients, namely propane, butane, propylene, and ammonia, have been shown to greatly stimulate microbial populations and activity in saturated microcosm studies (Kim *et al.* 1997, Moser *et al.* 1997, Palumbo *et al.* 1995, Tovanabootr *et al.* 1997) and could also be useful in the vadose zone.

Some metals and radionuclides are transported in the vadose zone because of increased mobility resulting from microbial or geochemical transformations, chemical associations with particulates, or complexation with synthetic or natural organic ligands. Microbially mediated oxidation-reduction reactions, biodegradation of organic-radionuclide complexes, microbial production of complexing or sorbing agents, and microbially induced changes in pH and Eh are all microbial transformations that affect mobility. Understanding metal and radionuclide biotransformations is critical for minimizing the risk of transport to sources of domestic water and irrigation and to plant rooting zones, as well as the risk of long-term storage of nuclear waste in deep vadose zones in arid environments. Possible scenarios for vadose zone bioremediation of metals and radionuclides include: (1) immobilization by microbially assisted mineral formation, (2) mobilization by microbially assisted reductive dissolution by flooding and removing the inorganic contaminants by pumping, and (3) biodegradation of organic ligands. Reductive dissolution of metals/radionuclides would require locally anaerobic conditions in the vadose zone. This can be achieved by adding easily metabolized organic substrate, reducing agents, and, possibly, in-well lifting of anaerobic groundwater and injection into the vadose zone. Although bioremediation concepts and processes for metals and radionuclides have been applied to *ex situ* treatment and, in some cases, evaluated for application to the saturated zone, they have not been tested or evaluated for the vadose zone. This is an important knowledge gap that should be addressed in the future.

Vadose zone numerical reactive transport models that incorporate biological processes are advancing (see Chapter 5); however, they are far less developed than similar models applied to the saturated zone. While simple reactive transport models have been applied to bioremediation of petroleum hydrocarbons in the vadose zone, the uncertainties are much greater when attempting to apply these models to other contaminant classes. From the perspective of biological processes, major

sources of uncertainty include: (1) a sufficient knowledge of the kinetics of the biotransformation of interest and, if any, the associated microbial growth, (2) the initial distribution of the biotransforming microorganisms and activity of interest, (3) spatial and temporal dynamics of microbial colonization and transport in response to contaminants in the presence and absence of nutrient addition, and (4) how these processes link to spatially variable hydrogeologic and geochemical processes. Laboratory experiments should be conducted under environmentally relevant conditions to address these sources of uncertainty and provide empirical information for developing mathematical expressions that describe the important processes and links. Major benefits of working toward the development and validation of such models in the future include the ability to perform sensitivity analyses, explore and evaluate the effect of changing parameters (for example, different alternative nutrient injection strategies), predict outcomes at a site with a higher level of certainty, and, ultimately, extrapolate from studied sites to similar unstudied sites.

INFLUENCE OF HYDROLOGIC PROCESSES ON ALL BIOGEOCHEMICAL REACTIONS IN THE VADOSE ZONE

The extent and magnitude of subsurface biogeochemical reactions is often controlled by the spatial and temporal variability in vadose zone hydrologic processes. The physical properties of the media (for example structured or layered), coupled with the duration and intensity of precipitation events, dictate the avenues of water, solute, and microbe movement through the subsurface. In humid environments where structured media is commonplace, transient storm events invariably result in the preferential migration of water (Shuford *et al.* 1977; Shaffer *et al.* 1979; Jardine *et al.* 1988, 1989, 1990a, 1998, 1999a; Wilson *et al.* 1989, 1993, 1998a; Hornberger *et al.* 1991). Highly conductive voids within the media (such as fractures or macropores) carry water around low permeability, high porosity matrix blocks, or aggregates. Recent field observations and numerical studies suggest that subsurface preferential flow is also a key mechanism controlling water and solute mobility in arid environments (Ritsema *et al.* 1993, 1998; Porro *et al.* 1993; Hendrickx and Yao 1996; Liu *et al.* 1998; Ho and Webb 1998). Lithologic discontinuities and sediment layering promote perched water tables and

unstable wetting fronts that drive both lateral and vertical subsurface preferential flow. Water that preferentially flows through media often remains in intimate contact with the porous matrix, and physical and hydrologic gradients drive the exchange of mass from one pore regime to another. Mass exchange is time-dependent and often controlled by diffusion to and from the matrix. The preferential movement of water and mass through the subsurface, therefore, significantly impacts geochemical and microbial processes by controlling the extent and rate of various reactions within the solid phase. It imposes kinetic constraints on biogeochemical reactions and limits the surface area of interaction by partially excluding water and mass from the matrix porosity.

MECHANISMS OF PREFERENTIAL FLOW AND MATRIX DIFFUSION

Preferential flow in porous media can be attributed to one of three broad-based generic categories: (1) short-circuiting flow, (2) finger flow, and (3) funnel flow. In the unsaturated zone, the preferred flow of water and mass is often dictated by the structure of the media. Interbedded layers of material with distinctly different characteristic pore size, such as a coarse sand layer embedded as a lens within a fine sand or the occurrence of voids and fractures, promote the accelerated movement of water. In structured media, near-saturated flow results in short-circuiting flow through macropores or fractures that bypasses a significant portion of the soil matrix. Macropores are operationally defined as pores greater than 1 mm in diameter that are capable of channel flow as a result of surface ponding or perched water tables. As the capillary pressure head (ψ) and subsequently the water content (θ) of the media decreases, the dominant mechanism responsible for preferential flow shifts from macropore flow to mesopore flow (Figure 6-5). Mesopores are pores within the range of 0.01 to 1.00 mm in diameter. As the capillary pressure head decreases further, the characteristic pore size through which flow is directed becomes less heterogeneous (micropore flow through pores less than 0.01 mm diameter), thereby decreasing the importance of preferential flow. This is experimentally observed in Figure 6-6, which shows Br effluent concentrations at three different steady-state pressure heads on a structured soil. The increasing asymmetry of the breakthrough curves with increasing saturation (less negative pressure head) is indicative of enhanced preferential flow coupled with mass loss to the matrix

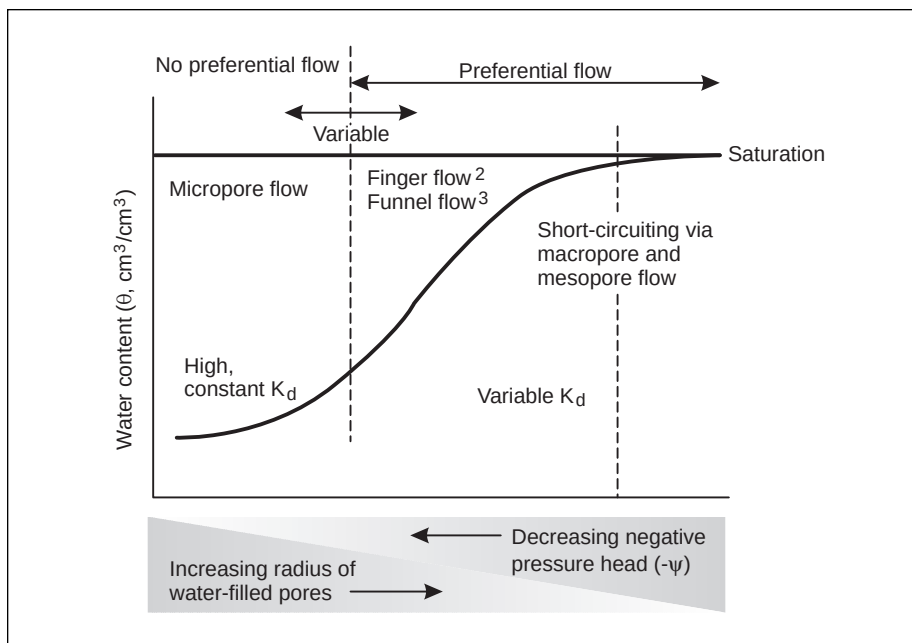


Figure 6-5. Idealized representation of a water content versus capillary pressure head curve (θ versus ψ curve, or moisture characteristic). At high water content, preferential flow via macropore flow occurs. As the capillary pressure head decreases, alternate forms of preferential flow become operable, such as mesopore flow, finger flow, and funnel flow. Below a certain threshold where there is less heterogeneity in characteristic pore size, preferential flow is inoperable. To the extent that the versus curve is related to mineralogical differences, one might expect that there will be a relationship between geochemical retardation and soil water content. (Wilson and Luxmoore, 1988; Wilson *et al.*, 1992; Ritsema *et al.*, 1998; Kung, 1990b).

porosity via diffusion. As the soil becomes increasingly unsaturated (more negative pressure head), the breakthrough curve tailing becomes less significant because of a decrease in the participation of larger pores involved in the transport process. Thus, flow and transport are restricted to a smaller, more homogeneous set of pore regimes. Transport processes within various pore regimes do not act independently. Pressure-head differences in various sized pore regimes create hydraulic gradients that drive inter-region advective mass transfer. Also, solute

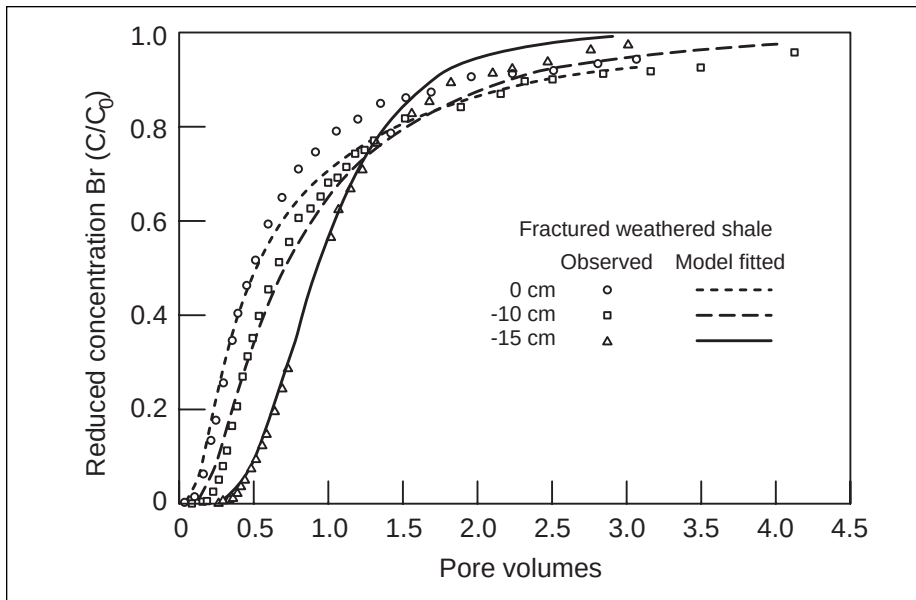


Figure 6-6. Observed and modeled Br effluent concentrations at three different steady-state pressure-heads (i.e. water contents) for an undisturbed column of structured soil. These experiments show the dependence of water content on preferential flow and time-dependent mass-transfer between various pore regimes of different size (from Jardine *et al.*, 1993a).

concentration differences among various sized pores create concentration gradients that drive time-dependent inter-region diffusive mass transfer (Jardine *et al.* 1988, 1990a, 1993 a,b, 1998; Wilson *et al.* 1993, 1998a; Gwo *et al.* 1996, 1998).

In arid environments where the subsurface is typically less structured, sediment layering and lithologic discontinuities typically promote localized perched water tables that drive vertical and lateral preferential flow. One mechanism of preferential water and solute migration within non-structured porous media is finger flow that results from wetting front instability (Jury *et al.* 1986a,b; Ghodrati and Jury 1990; Ritsema *et al.* 1993, 1998; Hendrickx and Yao 1996; Kapor 1996). Because arid granular soils are difficult to wet during precipitation events, like rainfall and snowmelt, water and solutes are often distributed laterally, resulting in transient perched water tables that eventually drain to lower horizons as

localized channels or fingers (Ritsema *et al.* 1998; Ho and Webb 1998). Ritsema *et al.* (1998) have shown that finger formation results from hysteresis in the water retention function of the porous media (Figure 6-7). Once fingers are established, hysteresis causes fingers to recur along the same pathways during subsequent infiltration of water and solutes to deep subsurface arid environments. Another mechanism of preferential water and solute migration in structureless porous media is

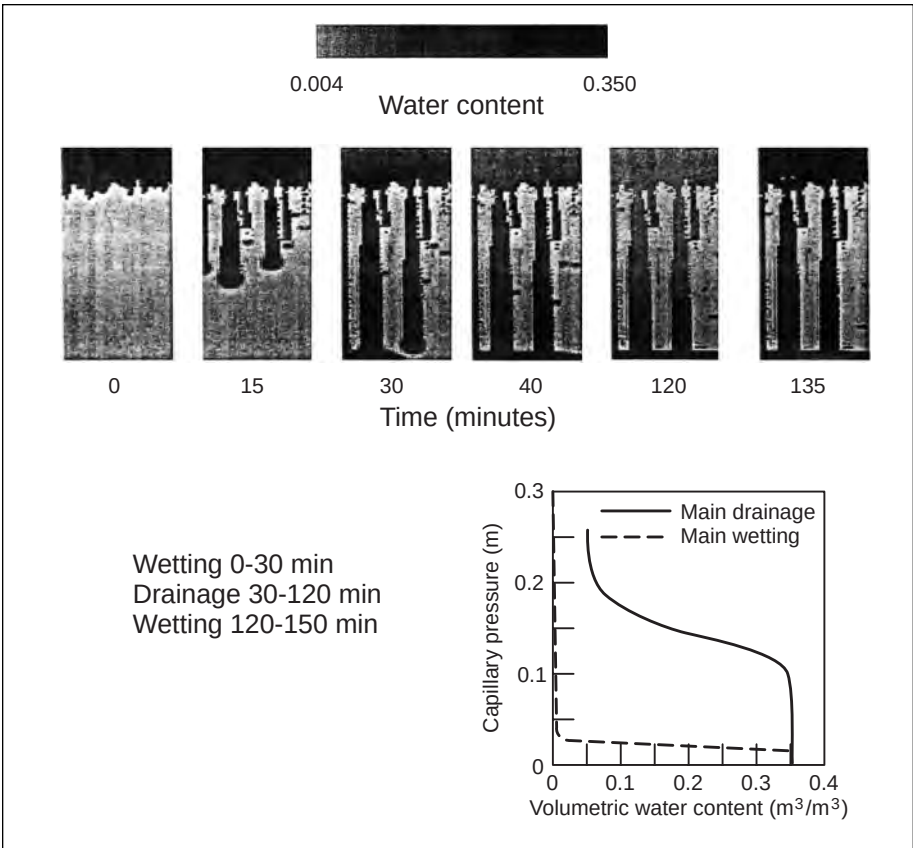


Figure 6-7. Illustration of fingered flow in a soil during alternating wetting and drying cycles. The main wetting and main drainage branches of the water retention function for the soil are provided in the graphic inset. The results convey that finger formation results from hysteresis in the water retention function, and that fingers recur along the same pathways during wetting and drying cycles (from Ritsema *et al.*, 1998).

funnel flow (Kung 1990a,b). Interbedded structures and abrupt textural discontinuities that are inclined within a soil profile can trigger preferential funnel-flow in unsaturated systems (Figure 6-8). Coarse sand layers or densely packed fine layers that are interbedded can behave as a wall of a funnel, which can concentrate an initially unsaturated flow into an irregularly spaced column. Water flows laterally across the lithological barrier, or funnel wall, and eventually becomes a more concentrated column flow after passing the lower edge of the layer (Figure 6-8). Four factors contribute to funnel flow: (1) conductivity of the upper fine layer, (2) the slope of the inclined layer, (3) the retention potential of the upper fine layer, and (4) the ponding potential of the media. One other possible mechanism of preferential flow in arid environments is film flow

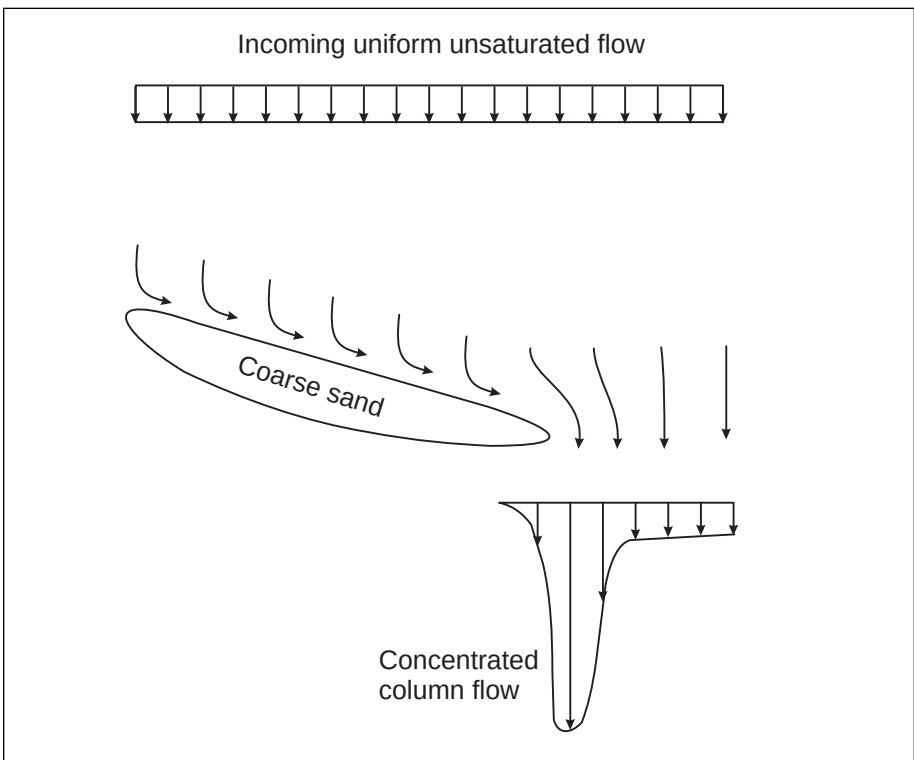


Figure 6-8. Schematic diagram of funnel preferential flow that may result during unsaturated transport in stratified media with distinct lithological contrasts (from Kung 1990b).

along fracture surfaces (Figure 6-9) (Tokunaga and Wan 1997). Laboratory studies using idealized fractures have shown that film velocities ranged from 2 to 40 m d⁻¹, which was approximately 1,000 times faster than saturated flow at unit gradient. These findings are consistent with recent evidence suggesting enhanced infiltration rates and recharge at Yucca Mountain, Nevada (Davis *et al.* 1998; Liu *et al.* 1998). In general, preferential vertical flow in the arid vadose zone is driven by lithological discontinuities, where tension-dependent anisotropic water flow

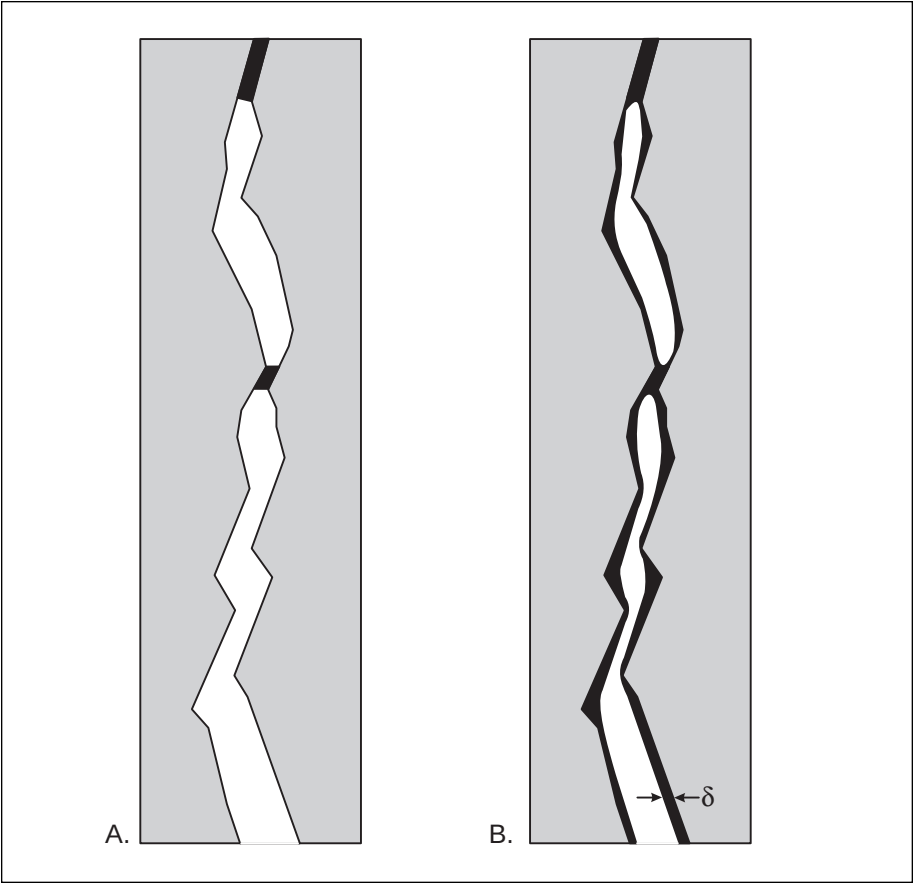


Figure 6-9. Two conceptual models of fluid distributions in subsurface voids (a) aperture based and (b) inclusion of surface films with thickness that result in film flow (from Tokunaga and Wan, 1997).

creates perched water zones that intersect vertical conduits, such as clastic dikes, or create unstable wetting fronts resulting in localized channel flow, like finger flow or funnel flow.

Because arid zone porous media consist of interbedded and mixed coarse and fine sediments that vary in porosity and reactive surface area, the media exhibit multiporosity, multipermeability characteristics where pore regime conductivity is governed by the water content of the system (Jardine *et al.* 1993b; Vogeler *et al.* 1997; Maraqa *et al.* 1999). If the water content is sufficient to induce preferential flow, hydraulic and physical gradients develop between flow regimes, resulting in nonequilibrium mass transfer processes (Gwo *et al.* 1995, 1996; Wilson *et al.* 1998a; Jardine *et al.* 1999a). Pressure-head differences caused by multiple fluid velocities in different sized pore regimes create hydraulic gradients which drive time-dependent inter-region advective mass transfer. Solute concentration differences between various sized pores create concentration gradients that drive time-dependent inter-region diffusive mass transfer. The implications of nonequilibrium mass transfer on subsurface solute migration beneath the subsurface are significant, because rapid transport of small amounts of mass may be occurring along preferred flow paths, while the majority of mass resides within the microporosity of the fines, which greatly retards bulk mass migration rates.

INFLUENCE OF SUBSURFACE HYDROLOGIC PROCESSES ON BIOGEOCHEMICAL REACTIONS

Subsurface geochemical and microbial reactions are directly linked to hydrodynamics. Soil moisture conditions that promote the onset of preferential flow, and thus higher volumetric flux per unit area, will minimize geochemical and microbial interfacial reactions due to decreased residence times during transport and potential bypass of the soil matrix (Jardine *et al.* 1988, 1993a; Kung 1990a, b; Estrella *et al.* 1993; Maraqua *et al.* 1999). In addition, these conditions will minimize geochemical retardation mechanisms because the mass of solute per unit weight of soil solids will greatly exceed estimates (by a factor of 10 to 1000, Kung 1990b) based on areal or volumetric averaging. Conversely, soil moisture conditions that do not promote preferential flow will generally enhance geochemical retardation and microbial interfacial reactions. In the presence or absence of preferential flow, water content variations

affect the extent and rate of geochemical vs. microbial reactions very differently. The extent of contaminant retardation by the solid phase via geochemical mechanisms, such as sorption, redox alteration, and complexation, will be more pronounced when flow is restricted to smaller pore size regimes like mesopores or micropores. The larger surface area and potential reactivity of these pore regimes versus macropores allow geochemical reactions to proceed to a more significant extent in the subsurface media. Microbes cannot reside within the entire pore structure of subsurface media as do solutes, and are typically excluded from micropore regions due to their size (Smith *et al.* 1985; Champ and Schroeter 1988; Bales *et al.* 1989; Harvey *et al.* 1989, 1993; Wilson *et al.* 1993; McKay *et al.* 1993a; Harton 1996; Jardine *et al.* 1998). Thus, microbial processes are shut down or become exceedingly sluggish when flow is restricted to the micropore domain.

Hydrologic Influences on Subsurface Geochemical Reactions

Organic and inorganic solute transport in the subsurface is often controlled by interfacial reactions with the soil solid phase. Coulombic exchange, chemisorption, hydrophobic sorption, redox alterations, transformation like N dynamics or Al polymerization, precipitation/dissolution, and complexation are typical chemical processes that govern the reactivity of solutes in the subsurface. Both the extent and rate of these processes can be significantly influenced by variations in water content (θ) and the degree of pore regime connectivity. The physical heterogeneities that cause preferential flow are also likely related to differences in mineralogy (for example, a fine-grained caliche layer embedded in a coarse sand and gravel formation). To the extent that these physical/chemical heterogeneities exist and form the underlying basis for preferential flow, one might reasonably expect that just as the causes and manifestations of θ -dependent preferential flow exist, there is also θ -dependent solute reactivity with the solid phase (for example, θ -dependent K_d , which implies a θ -dependent solute retardation). A few examples in the literature demonstrate this concept (Shaffer *et al.* 1979; Seyfried and Rao 1987; Jardine *et al.* 1988, 1990b, 1993a,b; Gaber *et al.* 1995; Vogeler *et al.* 1997; Heng *et al.* 1999). Jardine *et al.* (1988, 1993 a,b) have found that the reactivity of reactive contaminants and chelated radionuclides increased dramatically when the pressure head or water

content decreased slightly. This was the result of a decrease in preferential bypass when large pores were empty, and a greater contact time between the high surface area matrix. When preferential macroporous flow was prevalent, batch sorption isotherms overestimated solute retardation during transport by a factor of 2. In unsaturated conditions, when macropore flow was eliminated, batch sorption isotherms provided an excellent description of solute retardation during transport. Similar results were observed by Vogeler *et al.* (1997) during the unsaturated transport of cations through a structured aeolian silt loam. Numerous studies have also found that batch K_d values for reactive organic and inorganic solutes are significantly larger than those obtained from saturated undisturbed columns where macropore flow is prevalent (Seyfried and Rao 1987; Southworth 1987; Southworth *et al.* 1987; O'Dell *et al.* 1992). Langner *et al.* (1998) found that the rate and extent of 2,4-D degradation in soil decreased with increasing pore water velocity (v), where large values of v typically resulted in higher water contents. Variations in the degradation rate were thought to be caused by enhanced microbial attachment and distribution as well as more rapid nutrient desorption rates from the soil at lower pore water velocities.

Preferential flow rarely bypasses the soil matrix entirely. The various pore regimes of subsurface media are connected through time-dependent mass exchange processes. Thus, if given enough time, solute concentrations within the soil matrix would eventually achieve equilibrium with those in the larger pore regimes, even during macropore flow. In reality, equilibration between the various pore regimes rarely occurs since precipitation and flow-through subsurface media are transient in nature. Thus, pore regime disconnection and reconnection to the primary flow field is an ongoing process. Likewise, time-dependent mass exchange between the various pore regimes is an ongoing process controlled by the pore water flux and the water content of the system. The rate of mass-transfer between pore regimes has been shown to be proportional to the pore water flux, with larger rate coefficients being present at larger fluxes (Nkedi-Kizza *et al.* 1983b; Akrotanakul *et al.* 1983; Jensen 1984; Kookana *et al.* 1993; Reedy *et al.* 1996). This can be attributed to larger concentration gradients between pore domains at higher fluxes. Under these circumstances, one might expect that equilibrium between pore regimes would be established more rapidly under sustained macropore flow. The scenario is actually more complicated: (1) calculated rate

coefficients should be time-dependent and decrease as the concentration gradient between pore regions diminishes (Gwo *et al.* 1998); and (2) hydraulic gradient can develop during transient flow due to pressure-head differences between pore classes, thereby driving water from macropores to mesopores and micropores—opposite the concentration gradient (see Gwo *et al.* 1996 and Wilson *et al.* 1998a). Thus, the rate of geochemical reactions in subsurface media can be significantly impacted by the complex time-dependent interaction of water between the various pore regimes of the media. Gaber *et al.* (1995) found that both physical and geochemical nonequilibrium processes controlled atrazine transport in an undisturbed structured soil. Because preferential flow processes dominated under these conditions, atrazine sorption and diffusion into the soil matrix was limited by higher water contents and more rapid pore water velocities. Lower water contents resulted in more symmetric breakthrough curves that were indicative of increased interaction between preferential flow paths and the soil matrix.

Hydrologic Influences on Subsurface Microbial Reactions

Physical and chemical interactions with the solid phase, as well as the availability of nutrients, sources of carbon, and possible electron acceptors, control microbial activity and transport in the subsurface. Bio-transformation, biosorption, and electron transfer reactions are typical processes that govern the fate and transport of microbes in the subsurface. Unlike solutes that can reside within nearly all of the pore structure of subsurface media, microbes like bacteria and viruses, are too large to reach a significant fraction of the micropore regime and are restricted to the mesopore and macropore domains. Usually, less than 5 percent to 10 percent of the void volume in structured media is accessible to bacteria (Smith *et al.* 1985; Champ and Schroeter 1988; McKay *et al.* 1993a; Harton 1996; Palumbo *et al.* 1995; Jardine *et al.* 1998) because most of the soil porosity is contained within the micropore domain. Because the greatest mass of solutes is found within the micropore region where microbes are too large to penetrate, biological reactions and bioremediation efforts targeted at organic and inorganic contaminant removal have limited efficiency. Fortunately, the pore structure of most subsurface media is hydrologically interconnected, and contaminants move from one pore class to another via hydraulic and

concentration gradients (Schaefer *et al.* 1998; Seyfried and Rao 1987; Jardine *et al.* 1990a,b, 1993a,b, 1998; Hornberger *et al.* 1991; Wilson *et al.* 1991a,b, 1993, 1998a; Reedy *et al.* 1996). This process is slow, however, and is often the rate-limiting factor governing the success of contaminant bioremediation or nutrient removal from the micropores.

Microbial activity may accelerate solute mass-transfer from micropores to larger meso- and macropores. Although bacteria cannot physically access most of the micropore regime, they can form biofilms around the soil aggregates and matrix blocks. These biofilms are permeable to the transfer of water and solutes between the various pore domains. It is possible that active biofilms surrounding micropore domains accelerate the mass-transfer of contaminants and solutes to the more biologically active pore regions. This may occur since microbial processes maintain a steep concentration gradient between the small and the large pores.

For structured and unstructured media, the mechanisms and rates of bacteria retention in unsaturated subsurface media are proportional to the degree of gas saturation. This is because bacteria preferentially sorb to the gas-water interface versus the solid-water interface (Wan *et al.* 1994; Powelson and Mills 1996, 1998; Schafer *et al.* 1998; Jewett *et al.* 1999). The extent of bacterial retardation in the subsurface increases markedly with decreasing water content of the porous media, because of the tendency of bacteria to accumulate at the air-water interface. This retention is enhanced by the corresponding loss or decrease of preferential flow and the corresponding increase in available surface area of both the solid surface and the air-water interface. The degree of sorption to the air-water interface is controlled mainly by the hydrophobicity of the cell surface, and the sorption process is essentially irreversible because of capillary forces (Wan *et al.* 1994).

Depending on the water content of the subsurface media, unsaturated preferential flow may result in a significant portion of microbial transport bypassing the soil matrix (Powelson and Gerba 1994; Powelson and Mills 1998; Schafer *et al.* 1998; Jewett *et al.* 1999). Wilson *et al.* (1999) found that only 6 percent to 15 percent of the cross-sectional area of an undisturbed block of structureless coastal plain sandy sediment exhibited flow during unsaturated bacterial transport, with 88 percent of this flow occurring through just 4 percent of the area. Because areas dominated by fine sand tended to accumulate bacteria, particle size distribu-

tion, rather than porosity, was the most significant property controlling microbial transport. Thus, subtle variations in particle size and arrangement (for example, media structure) control unsaturated preferential flow paths and the degree of gas saturation, which allows for the accumulation of bacteria within the subsurface. Powelson and Gerba (1994) found that virus removal by soil was three times more effective during unsaturated flow relative to saturated conditions; however, the column displacement retardations of virus transport were only 0.8 percent to 8 percent of that predicted by adsorption coefficients determined from batch studies.

TECHNIQUES FOR QUANTIFYING THE EFFECTS OF PREFERENTIAL FLOW AND THE INFLUENCE OF NONEQUILIBRIUM PROCESSES

The rate and extent of subsurface geochemical and microbial processes are highly dependent on the preferential movement of water and mass through the media. A variety of flow and tracer techniques are available to confirm and quantify whether preferential flow and time-dependent pore-regime interactions significantly impact subsurface biogeochemical reactions. These techniques are described in detail by Jardine *et al.* (1998) and will be summarized in this section. The techniques include: (1) controlling flow path dynamics with manipulation of pore water flux and soil-water tension, (2) isolating diffusion and slow geochemical processes with flow interruption, (3) using multiple tracers with different diffusion coefficients, and (4) using multiple tracers with grossly different sizes.

Controlling Flow-Path Dynamics

Variations in Pore Water Flux

A simple technique for confirming and quantifying preferential flow and physical nonequilibrium in subsurface involves tracer displacement experiments performed at a variety of experimental fluxes using a single representative tracer. Alteration of the experimental flux or specific discharge through a soil system perturbs the rate of approach toward equilibrium by changing the hydraulic or concentration gradient. In heterogeneous systems that exhibit a large distribution of pore sizes, an increase in the overall pore-water flux should result in greater system

nonequilibrium due to a decrease in solute residence time within the porous media. This is usually the case since solute movement into the matrix is a combination of advective and diffusive processes, and is typically the rate-limiting step as the system approaches equilibrium. This condition can be observed in Figure 6-10, which shows the breakthrough of a nonreactive Br⁻ tracer at several different pore water fluxes through an undisturbed column of weathered fractured shale. As is typical of heterogeneous media, tracer displacement is characterized by an initial rapid solute breakthrough followed by extended tailing to longer times. In this system, the fracture network of the weathered shale controls the advective transport of solutes, which is coupled with diffusion into the surrounding matrix blocks. The largest and smallest flux experiments were conducted over 0.25 d and 94 d, respectively, with the relative amount of tracer mass remaining in the column at the end of each pulse ranging from 22 percent (fast flux) to 38 percent (slow flux). These results indicate that the system became increasingly removed from equilibrium as the pore-water flux increased. At faster flux, the tracer residence times in the mobile fracture regions were significantly decreased, and not as much mass was lost to the matrix. Controlling flow-path dynamics at the field scale through variations in pore water flux was also performed by Hornberger *et al.* (1991) on a structured forest soil. This study confirmed the utility of multiple pore water fluxes for quantifying preferential flow and nonequilibrium processes at larger scales.

Variations in Pressure Head

Controlling flow-path dynamics by manipulating the soil water content with pressure-head variations is an excellent technique to assess nonequilibrium processes (Seyfried and Rao 1987; Jardine *et al.* 1993a). The basic concept of the technique is the collection of water and solutes from select sets of pore classes to determine how each set contributes to the bulk flow and transport processes observed for the whole system. In heterogeneous systems, a decrease in pressure-head (more negative) will cause larger pores, such as fractures, to drain and become nonconductive during solute transport. Because advective flow processes tend to dominate in large pore regimes, a decrease in pressure-head, which will restrict flow and transport to smaller pores, will limit the disparity of solute concentrations among pore groups. By minimizing the concentration gradient in the system, the extent of physical nonequilibrium

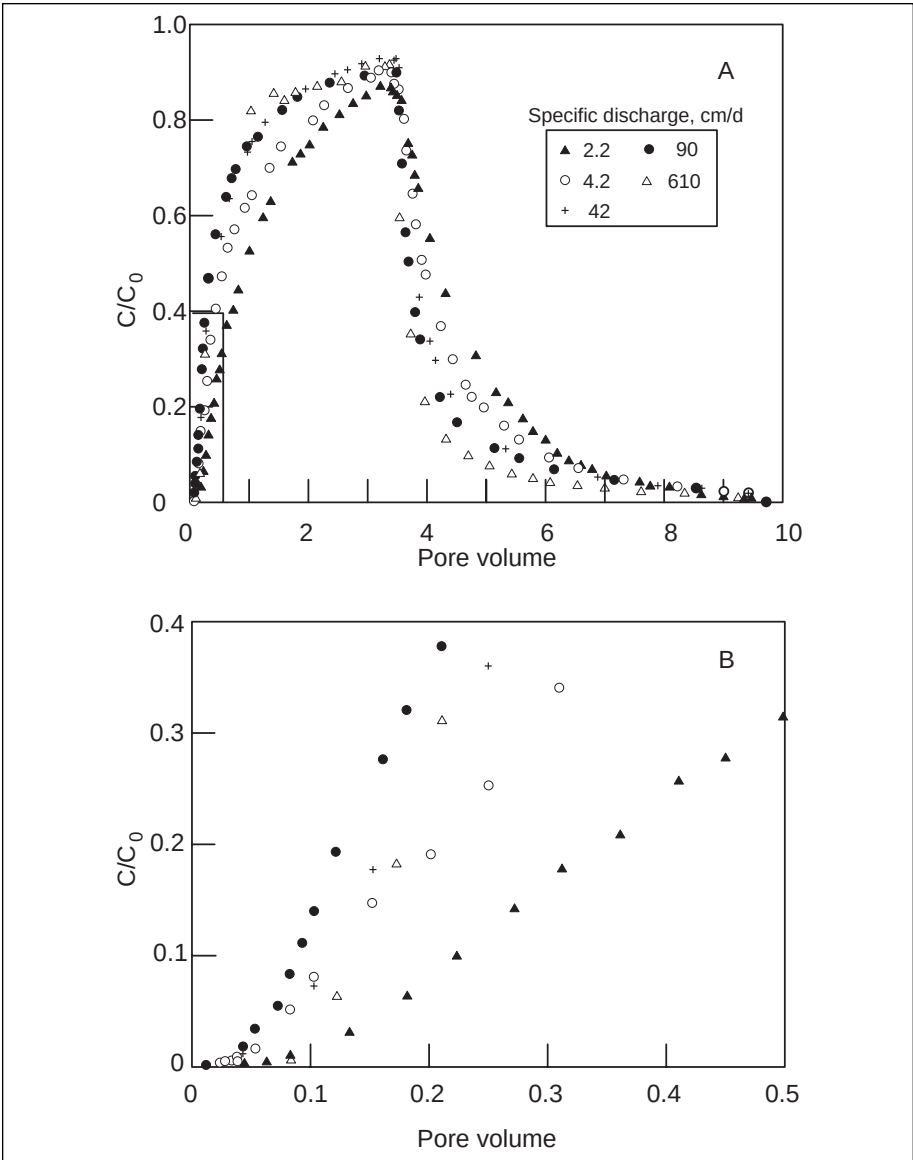


Figure 6-10. (a) Bromide breakthrough curves for a series of steady-state specific discharges in an undisturbed column of fractured weathered shale. The largest and slowest flux experiments were conducted over periods of 6 and 2200 hrs., respectively. The rectangle in the lower corner defines the expanded portion of the plot shown in (b). Breakthrough curves at higher fluxes are significantly more asymmetric which is indicative of greater system nonequilibrium (O'Brien, R., 1994, ORNL, unpublished data).

decreases. Figure 6-6 shows the breakthrough curves of a nonreactive Br tracer at three different pressure-heads in an undisturbed column of weathered fractured shale. As described earlier in this chapter, the increasing asymmetry of the breakthrough curves with increasing saturation (less negative pressure head) indicates enhanced preferential flow coupled with mass loss into the matrix. As the soil becomes increasingly unsaturated, breakthrough curve tailing becomes less significant because of a decrease in the participation of larger pores (fractures) involved in the transport process. These findings suggest that mass-transfer limitations (nonequilibrium conditions) become less significant for these unsaturated conditions because fracture flow has been eliminated. The application of -10 and -15 cm pressure heads resulted in 5- and 40-fold decreases in the mean pore water flux, respectively, with relatively little change in soil water content relative to saturated conditions ($0.55 \text{ cm}^3/\text{cm}^3$ at $h=0$ to $0.51 \text{ cm}^3/\text{cm}^3$ at $h= -15\text{cm}$). This suggests that most of the water flux may be channeled through pores that hold water with tensions less than 10 cm (primary fractures, macropores), even though their surface area and contribution to the total system porosity is very small (Wilson and Luxmoore 1988; Wilson *et al.* 1989).

These results, and the results of Seyfried and Rao (1987), Gaber *et al.* (1995), and Wilson *et al.* (1998b) differ markedly from unsaturated flow investigations, which failed to consider that the average pore water flux *in situ* decreases as θ decreases. The findings of Krupp and Elrick (1968), who investigated Cl^- transport in variably saturated glass bead media, showed breakthrough asymmetry was more pronounced during unsaturated conditions relative to saturated flow. This observation resulted from the uniformity of the media and the use of a constant volumetric flow rate for both saturated and unsaturated conditions, which caused the development of a wider pore water velocity distribution during unsaturated flow. Under natural drainage scenarios in the field, the volumetric flow rate does not remain constant as θ changes; thus, the findings of Krupp and Elrick (1968) are a special case of variably unsaturated flow at constant volumetric flux. Likewise, studies that use the newly developed unsaturated/saturated flow apparatus (UFA, Conca, and Wright 1998), which is based on centrifugal acceleration, commonly investigate the unsaturated transport of solutes and colloids at different water contents using the same pore water flux (see McGraw case study). This results in enhanced solute breakthrough curve asymmetry at

low water contents, which may not be representative of unsaturated conditions in the field. The UFA method is a powerful technique for measuring unsaturated transport processes at very low water contents and care should be taken to design experiments such that the centrifugal force is varied to provide pore water fluxes that are proportional to changes in water content.

At the field scale, tension infiltrometers have been used to assess infiltration rates as a function of soil porosity (Watson and Luxmoore 1986; Wilson and Luxmoore 1988; Clothier *et al.* 1992; Jaynes *et al.* 1995). The technique is similar to that described earlier for columns, where new water infiltrates into the soil surface under tension, thereby controlling the flow-path dynamics of the system. This technique is useful for estimating macroporosity and mesoporosity distributions in the field and the prevalence of preferential flow processes. Tracers can also be added to the infiltrating solution to quantify nonequilibrium processes in the field (Clothier *et al.* 1992; Jaynes *et al.* 1995).

By using negative pressure-head or tension to withdraw water and solutes from different pore regimes within the subsurface media, it is possible to assess the effects of preferential flow and nonequilibrium mass transfer at the field scale (Jardine *et al.* 1990a,b). Strategic extraction of water from the various advective flow domains and the soil matrix can be accomplished by samplers with different porosities or bubbling pressures.

Flow Interruption

Flow interruption during a tracer displacement experiment is another useful technique for isolating diffusion or slow time-dependent geochemical reactions. The technique involves inhibiting the flow process for a designated period of time and allowing the approach of a new physical or chemical equilibrium state. When physical nonequilibrium processes are significant in a soil system, the resumption of the interrupted flow will cause an observable concentration perturbation for a conservative tracer. Interrupting flow during tracer injection will decrease tracer concentration when flow is resumed, whereas interrupting flow during tracer displacement (washout) will increase tracer concentration when flow is resumed. The concentration perturbations observed after flow interruptions indicate solute diffusion between pore

regions of heterogeneous media. Conditions of preferential flow create concentration gradients between pore domains (physical nonequilibrium), resulting in diffusive mass transfer between the regions. Therefore, during injection, tracer concentrations within advection-dominated flow paths such as fractures and macropores are higher than those within the matrix. Upon flow interruption, the relative concentration decrease that is observed indicates that solute diffusion is occurring from larger, more conductive pores, into the smaller pores. During tracer displacement, or washout, the concentrations within the preferred flow paths are lower than those within the matrix. Thus, solute diffusion is occurring from smaller pores into larger pores, and a concentration increase is observed during flow interruption.

The utility of the flow interruption method for confirming and quantifying physical nonequilibrium can be observed in Figure 6-11. This figure shows Br^- breakthrough curves at two fluxes in an undisturbed column of weathered fractured shale. The observed concentration perturbations on the ascending and descending limbs of the breakthrough curves are the result of prolonged flow-interrupt and the system's approaching a new state of physical equilibrium. The concentration perturbations that are induced by flow interruption are significantly more pronounced at larger fluxes (Figure 6-11[b]) than at smaller fluxes (Figure 6-11[a]). This is because the system is further removed from equilibrium at the larger fluxes since a greater concentration gradient exists between advection-dominated flow paths and the soil matrix.

Multiple Tracers with Different Diffusion Coefficients

The simultaneous use of multiple tracers with different diffusion coefficients is another useful technique for quantifying preferential flow and nonequilibrium processes in structured subsurface media. In general, when the technique is used to quantify physical nonequilibrium processes in soils and rock, two or more conservative tracers with different diffusion coefficients are simultaneously displaced through the porous media. When physical nonequilibrium processes are significant in porous media, tracers with larger molecular diffusion coefficients will be preferentially lost from advective flow paths, such as fractures, due to more rapid diffusion into the surrounding solid phase matrix. Likewise, tracers with smaller molecular diffusion coefficients, like larger molecules, will remain in the advective flow paths for a longer time due to slower diffusion into the matrix porosity. When advective processes

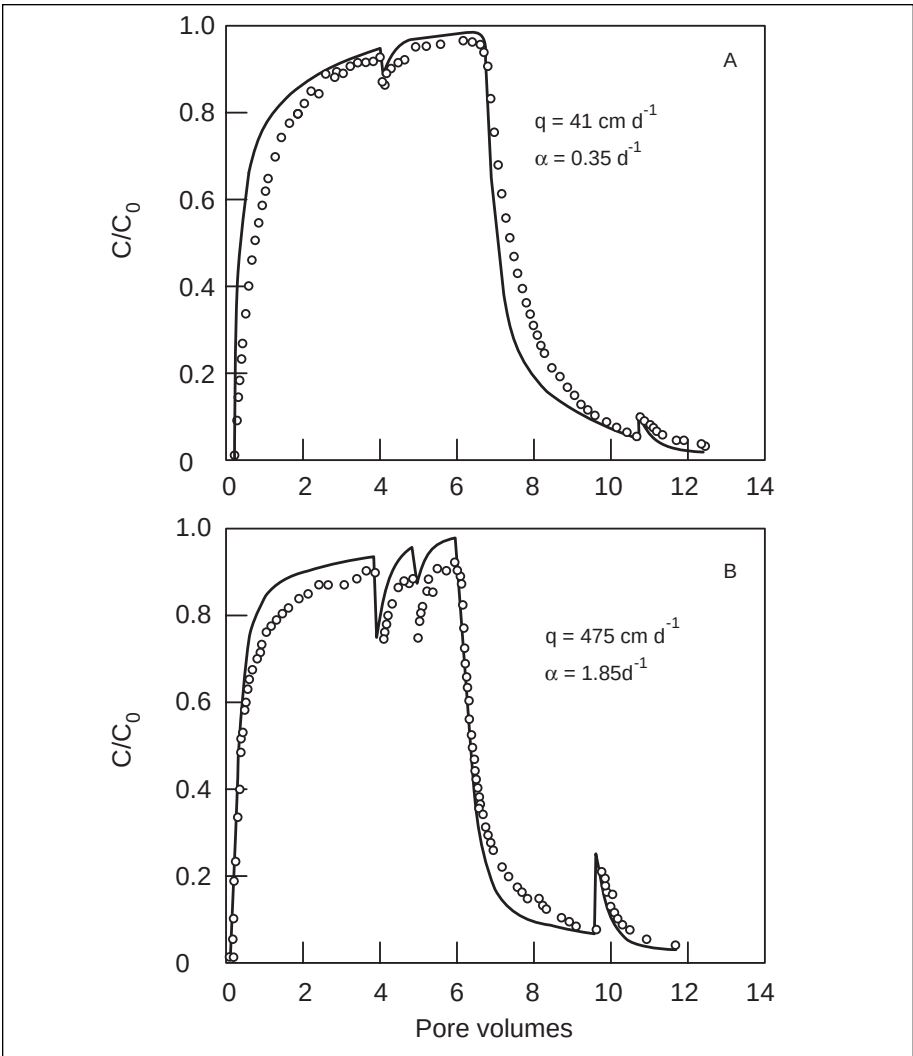


Figure 6-11. Breakthrough curves with flow interruption, at two specific discharges for a nonreactive Br⁻ tracer in an undisturbed column of fractured weathered shale. Flow interruption was initiated for 7 days after (a) approximately 4 and 11 pore volumes of tracer were displaced at a flux of 41 cm d⁻¹ and (b) approximately 4, 5, and 10 pore volumes of tracer were displaced at a flux of 475 cm d⁻¹. The observed concentration perturbations following flow interrupt are the result of a reequilibration of mass between different pore regions. The solid lines represent simulations using a two-region model with optimization of the mass transfer coefficient that accounts for mass exchange between different pore regions (modified from Reedy *et al.*, 1996).

are dominant in a system and matrix diffusion is negligible, multiple tracer breakthrough profiles will not differ considerably.

Figure 6-12 illustrates the advantage of multiple tracers for quantifying physical nonequilibrium processes in structured media. In this example, the simultaneous transport of two nonreactive tracers, Br⁻ and PFBA, was investigated in large undisturbed columns of fractured weathered shale at two different pore water fluxes. The molecular diffusion coefficient for PFBA is 40 percent smaller than that for Br⁻ (Bowman 1984). Differences in the breakthrough curves for these solutes can be attributed to differences in the rates of tracer diffusion into the soil matrix. Because it diffused more slowly into the weathered shale matrix, the PFBA's breakthrough at the column exit was initially more rapid than Br⁻, but required longer times to approach equilibrium ($C/C_0=1$). Thus, Br⁻ had a larger mass loss to the matrix at any given time and exhibited a more retarded breakthrough relative to PFBA. However, the approach to equilibrium was more rapid for Br⁻ relative to PFBA, and the tracer breakthrough curves eventually crossed at longer times. In contrast, the mobility of these two nonreactive tracers would be identical in a column of unstructured media because pore class heterogeneity would be minimal, thus limiting the significance of physical nonequilibrium during transport. Using multiple tracers with different diffusion coefficients is also ideal for quantifying preferential flow and nonequilibrium processes at the field-scale (Jardine *et al.* 1999b).

Multiple Tracers with Grossly Different Sizes

The use of multiple tracers with distinctly different sizes is a sensitive technique for confirming and quantifying the preferential flow of microbes and the accompanying physical nonequilibrium processes in heterogeneous soil and rock systems. This technique uses both dissolved solutes and colloidal tracers for controlling flow-path accessibility. Viruses, bacteria, fluorescent microspheres, DNA-labeled microspheres, radiolabeled Fe-oxide particles, and synthetic polymers have all been used as colloidal tracers in various subsurface media (Barraclough and Nye 1979; Gerba *et al.* 1981; Smith *et al.* 1985; Bales *et al.* 1989; Harvey *et al.* 1989, 1993, 1995; Toran and Palumbo 1991; McKay *et al.* 1993a,b; Hinsby *et al.* 1996; Yang *et al.* 1996; Reimus 1996). Colloidal particles are typically large enough to be excluded from the matrix

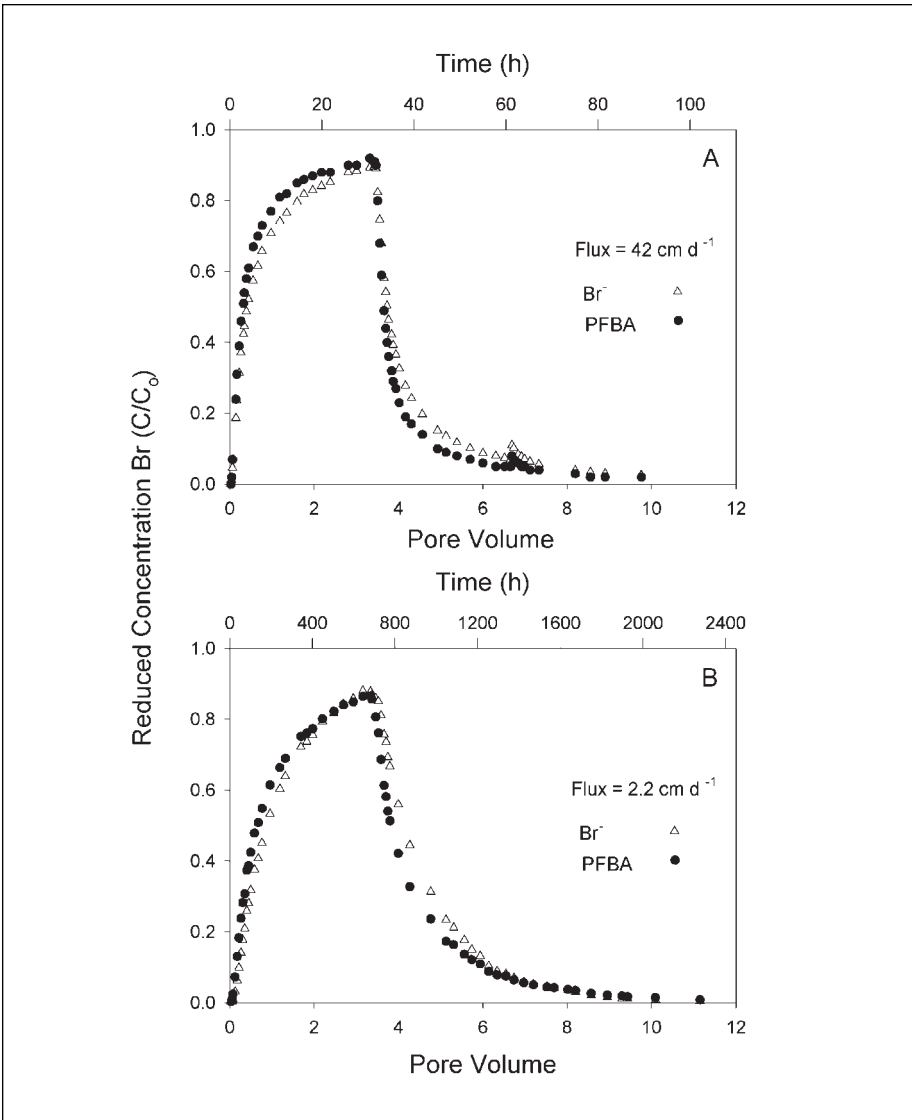


Figure 6-12. Breakthrough curves for the simultaneous injection of two nonreactive tracers, Br^- and PFBA, at a flux of (a) 42 cm d^{-1} and (b) 2.2 cm d^{-1} in an undisturbed column of fractured weathered shale. The free water diffusion coefficient for Br^- is 40% larger than that of PFBA, thus resulting in the accelerated breakthrough of the latter. The differences in the solute breakthrough curves confirm nonequilibrium mass transfer between different sized pore classes (O'Brien, R., 1994, ORNL, unpublished data).

porosity of soils and geologic material (McCarthy and Zachara 1989). If they are not severely retarded by the porous media, colloidal particles serve as excellent tracers for quantifying advective flow velocities in systems conducive to preferential flow. They also provide important information about bioremediation strategies, biofacilitated transport of pollutants, and the dispersal of pathogenic microorganisms (Schaefer *et al.* 1998). When colloidal tracers are coupled with dissolved solutes that can interact with the matrix porosity, a unique technique emerges for assessing physical nonequilibrium processes in subsurface media.

The utility of using multiple tracers of different size can be seen in Figure 6-13, which shows the assessment of physical nonequilibrium

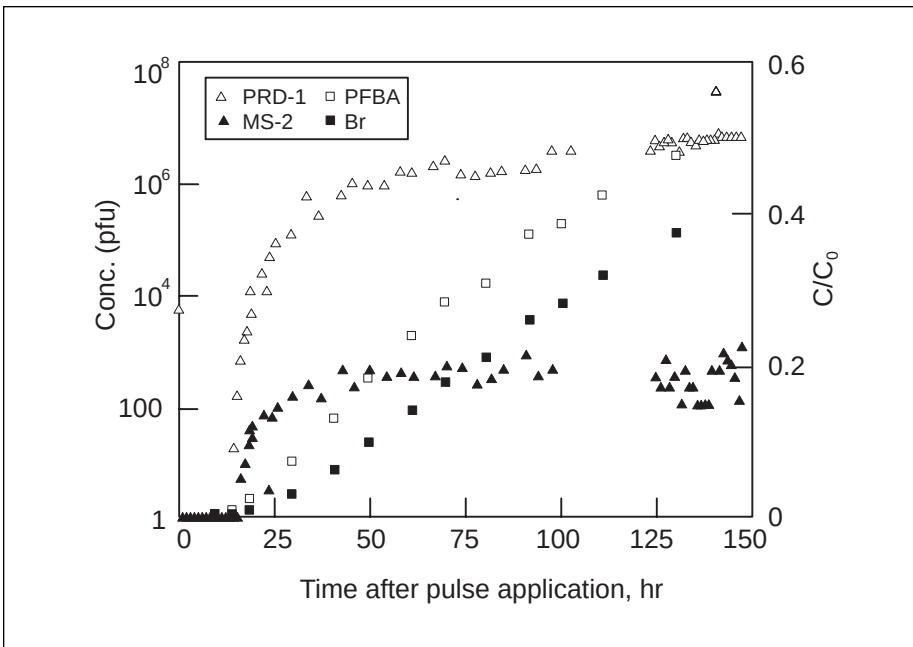


Figure 6-13. Effluent concentrations of two bacteriophage strains (PRD-1 and MS-2, with a mean size of 0.062 and 0.026 μm , respectively) and reduced concentrations of the dissolved tracers PFBA and Br-, that were simultaneously injected at 2.2 cm d^{-1} into an undisturbed column of fractured weathered shale. Note the different concentration axes used for each of the two tracer types. The bacteriophage are rapidly transported through the larger pore regimes and are too large to diffuse into the matrix porosity as do the dissolved solutes. (O'Brien, R., 1994, ORNL, unpublished data).

processes by simultaneous injection of two strains of bacteriophage (PRD-1 and MS-2) and two dissolved solutes (Br^- and PFBA) into a column of fractured weathered shale. The bacteriophage travel times were significantly faster than the dissolved solutes and exhibited substantially less total dispersion in their transport, as evidenced by steeper breakthrough characteristics relative to PFBA and Br^- . The larger bacteriophage were preferentially transported through the large pore regimes and were minimally affected by diffusion into the matrix porosity. The dissolved tracers subsequently were influenced by diffusive mass transfer processes between fractures and the matrix. These experiments present many results: (1) they provide visual evidence of preferential flow and physical nonequilibrium processes in structured media; (2) they provide advective flow velocities that are useful for parameterizing numerical models designed to simulate the observed data; and (3) they enable us to estimate the fate and transport of microbes through the subsurface media.

The choice of colloidal particles as tracers in subsurface media depends on a number of factors (McKay *et al.* 1993a): (1) loss due to matrix diffusion, (2) loss due to sorption, (3) loss due to decay or inactivation, and (4) detection limits. Bacteriophage turn out to be an excellent tracer for quantifying preferential flow and time-dependent mass-transfer processes at the field scale because (1) many are sufficiently hydrophobic to discourage sorption on mineral surfaces, (2) bacteriophage inactivation is slow at normal groundwater temperatures, thereby permitting use in long-term field experiments, and (3) the detection limits are reasonably low to allow several orders of magnitude dilution during a tracer study. McKay *et al.* (1993a,b, 1995) used bacteriophage in field experiments to quantify advective flow velocities and physical nonequilibria phenomena in a fractured clay till and a fractured shale saprolite. The transport velocity of the bacteriophage was several orders of magnitude greater than nonreactive tracers at both field facilities. The large contrast in transport velocities between the bacteriophage and the conservative tracers was due to extensive diffusion of the dissolved solutes into the matrix porosity.

CONCLUSIONS

Over the last two to three decades, major progress has been made in understanding fundamental geochemical and microbiological reactions and processes that dictates contaminant behavior in geologic materials and the complexities inherent with linking these with hydrologic processes. Yet, there are still numerous technical issues and challenges; addressing these will greatly increase our understanding of contaminant transport in the vadose zone. Each subsection has pointed out limitations of our understanding in microbiology, geochemistry, and hydrology related to the saturated and vadose zone contaminant transport. However, there are several overarching issues that encompass many of the challenges of the individual disciplines.

One of the more technically challenging issues that arose from these discussions is time-dependence of reactions and processes and the validity of local equilibrium assumptions. Water flow impacts geochemical and microbial processes by controlling the extent and rate of various processes; it imposes kinetic constraints on biogeochemical reactions. These constraints are often observed at different scales and appear to be controlled different processes. At a molecular scale, the rate-controlling step of a complexation reaction may limit the extent an organic ligand degradation reaction or desorption of a surface species. At the pore scale, these reactions may be considered mass exchange and are often controlled by diffusion to and from the matrix. Contaminant retardation via geochemical processes is often more pronounced at low water content because flow is slower and restricted to smaller pore size regimes. At these lower water contents, residence times increase, and local equilibrium assumptions (in some cases) are observed to provide excellent descriptions of contaminant retardation. Yet, even with increased residence times, microbial reactions are often restricted at low water content because the microbes are excluded from the micropores where the substrates and contaminants reside.

Hence, a fundamental knowledge of reactions and the properties governing extent and rates of reaction are required. Yet, this information needs to be linked with a quantifiable understanding of soil structure and how variations in water content influences the rate and mechanisms of geochemical and microbial processes; this is crucial to linking biogeochemical processes with hydrologic processes. This multidisciplinary

understanding is required so that laboratory observations can be scaled to the field, allowing improved assessment of reaction rates and processes at that scale. While it is crucial to develop a fundamental base for geochemical and microbial reactions and their rates at the molecular and microscopic scale, it is not yet clear how this information may be used (upscaled) at larger scales.

While briefly covered in this chapter and others, the effects of spatial heterogeneity are crucial to understanding contaminant retardation, microbial transformation, and transport in the vadose zone. Spatial (physical, chemical and microbial) heterogeneity is omnipresent in natural porous media and can be manifest on a hierarchy of scales from the sub-pore (microns) to the field (meters or more). These heterogeneities are not isolated one from another; rather they are interrelated and connected. For instance, at the pore scale, isolated microenvironments exist in discontinuous water films and isolated pores. These chemical microenvironments are conditioned by natural distributions of water and nutrients and partitioning of contaminants to specific mineralogies and/or pore classes, which generate microbial spatial heterogeneity. At the field scale, microbial spatial heterogeneity can exist where layers and strata with different properties create regions of greater saturation, yielding increased populations and/or activity. As stated by Tompson and Jackson (1996), in terms of reactive phenomena in the subsurface, their true dimensions cannot be understood without regarding the fluid flow processes and their relationship to heterogeneity. Contaminant migration, dilution, speciation, retardation, and other reaction and mobility issues will be affected by spatial heterogeneity.

These issues are only two of many that could be put forth, but they highlight the current limitations in biogeochemistry as related to vadose zone contaminant transport. They are very broad, encompassing a number of disciplines that require investigations at a number of experimental levels (basic and applied) and scales (molecular to the field scale). Addressing these issues (and others) will require concerted efforts from research teams working closely to enhance interactions between mathematicians, modelers, and experimentalists.

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CASE STUDIES



OBSERVATIONS OF MULTIPLE ACTINIDE SPECIES WITH DISTINCT MOBILITIES

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The Subsurface Disposal Area (SDA), within the Radioactive Waste Management Complex (RWMC) at the Idaho National Engineering and Environmental Laboratory (INEEL), contains shallow pits, soil vaults, and trenches where a variety of low-level, mixed, and transuranic wastes are buried. The Snake River Plain aquifer is separated from the RWMC by a 180 m thick vadose zone consisting of a layered sequence of fractured volcanic rocks (primarily basalt) and sedimentary interbeds. Traditional modeling approaches, where contaminant mobility is based on batch sorption studies, imply very slow movement of important contaminants such as plutonium and americium through the interbed layers. However, field data suggest the possibility of high mobility forms of these radionuclides. Consequently, a series of laboratory column experiments were undertaken to determine if high mobility forms were possible under the influence of groundwater and perched water simulants.

The column apparatus consisted of reservoirs for the groundwater or perched water simulant and the spiked simulant, a peristaltic pump, the column packed with either crushed basalt or sedimentary interbed, and a fraction collector. The spiked and unspiked simulants were introduced at the bottom of the vertically oriented column, and effluent fractions were collected at the top. Analyses of the effluent fractions were performed with an alpha/beta discriminating liquid scintillation counter. This made it possible, in a single test, to simultaneously measure tritium (used as a non-reacting tracer to check for channeling in the column), a higher energy beta emitter such as ^{137}Cs , and an actinide. The test procedure was as follows. The spiked simulant was introduced into the column as a finite step of approximately one pore volume in width. Following the spike, the column was eluted with anywhere from 200 to more than 1000 pore volumes of unspiked simulant. The column effluent was collected by a fraction collector and the fractions were analyzed with the liquid scintillation counter. Breakthrough curves, such as normalized effluent concentration versus time (expressed as displaced pore volume, DPV, which is the integrated volumetric flow divided by the pore volume), were plotted for the contaminant.

Figure 1 presents the breakthrough curves for tritium and cesium in basalt. The tritium breakthrough curve revealed no evidence of channeling in the column. The

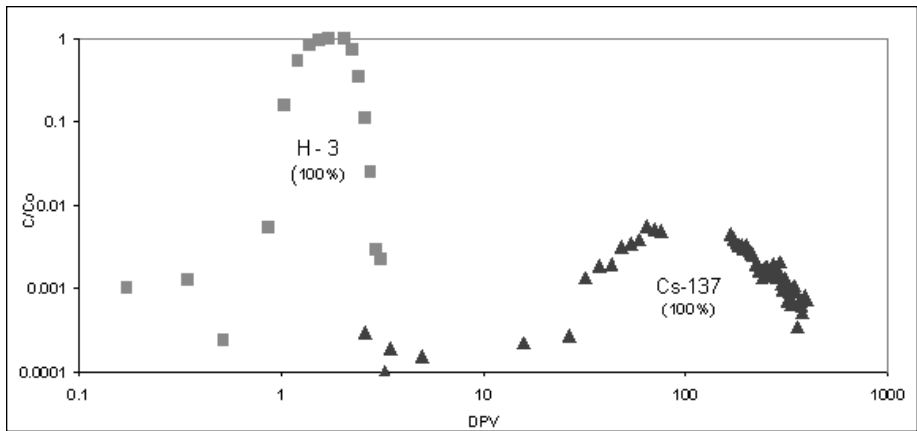


Figure 1. Breakthrough curves for hydrogen-3 and cesium-137 in basalt under the influence of the groundwater simulant.

cesium curve was characterized by a single peak containing essentially all of the activity that was in the spike. Uranium and strontium breakthrough was also characterized by a single peak containing all of the activity. This behavior is consistent with predictions based on classical advection/dispersion/retardation models. The cobalt behavior, however, was quite different, as shown in Figure 2. There was a small fraction (2 percent to 3 percent) with high mobility ($R^1 = 1$), a large fraction (65 percent to 70 percent) with moderate mobility ($R = 34$), and the remainder (≈ 30 percent) retained in the column with very low mobility. Americium and plutonium also exhibited high and very low mobility forms. This behavior suggests that multiple physical/chemical forms having distinctly different mobilities are possible. The implication of the results, if they are representative of processes that occur under actual field conditions, is that transport models based on a single retardation factor inferred from batch distribution coefficient measurements are not appropriate in some situations.

Multiple mobility fractions were also observed in interbed. These experiments were conducted to determine if high mobility forms of selected radionuclides might occur under the influence of a perched water simulant containing elevated concentrations of potential complexing agents such as carbonate, fluoride, sulfate, and EDTA. The experimental protocol was similar to that used for the basalt experiments with one exception. In the basalt experiments, the one pore volume spike was introduced into

¹ R is the retardation factor. It is the ratio of the mean linear groundwater velocity to the mean linear contaminant velocity.

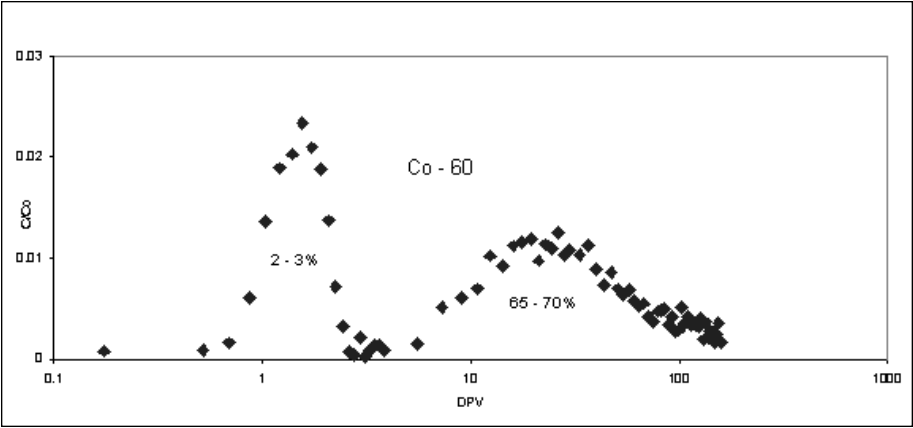


Figure 2. Breakthrough curve for cobalt-60 in basalt under the influence of the groundwater simulant.

a pre-wetted column. In the interbed experiments, it was introduced into a dry column. Figure 3 presents breakthrough curves for thorium(IV) and neptunium(V), which are often used as surrogates for plutonium(IV) and plutonium(V), respectively. The solid symbols are the curves obtained under the influence of the complete perched water simulant. The open symbols are curves obtained for the simulant without EDTA. For the complete perched water simulant, the behavior of both thorium and neptunium was very similar to that observed for cobalt in basalt. The breakthrough curves were characterized by a small fraction with high mobility, a

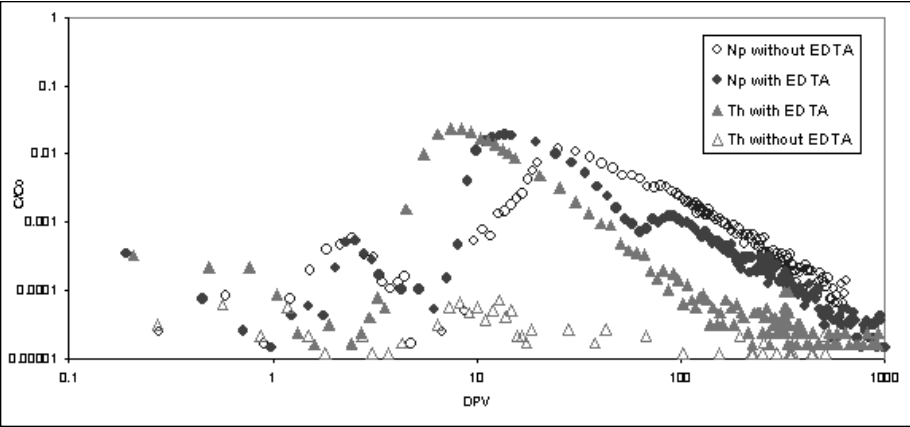


Figure 3. Breakthrough curves for neptunium-237 and thorium-230 in sedimentary interbed under the influence of the perched water simulant with and without EDTA.

large fraction with moderate mobility, and a large fraction retained in the column. With EDTA removed from the simulant, the breakthrough curve for neptunium changed very little. The curve for thorium, however, changed dramatically. The moderate mobility fraction was no longer present. Similar behavior was observed for americium(III) and plutonium(IV). These results suggest that the intermediate mobility fractions observed were due to an actinide-EDTA complex. From this, it is tempting to conclude that EDTA would have a significant impact on the mobilities of americium(III), thorium(IV), and plutonium(IV). However, the spikes were prepared within an hour of the start of the experiments. In spikes that were allowed to age for a relatively short time (24 hours), these actinides were predominantly in a colloidal, rather than soluble, form. In column tests with the aged spikes, the moderate mobility fraction did not appear, suggesting that the colloids were sufficiently large to be filtered by the soil matrix.

The occurrence of multiple mobility fractions was also inferred from experiments with uranium in sedimentary interbed (Figure 4). Under the influence of the perched water simulant (without EDTA), all of the uranium in the spike appeared between 1 and 100 DPV. Upon removal of carbonate from the perched water simulant, there was a large decrease in the fraction appearing between 1 and 100 DPV, suggesting that uranium mobility was dominated by a carbonate complex. In addition, there was the appearance of a fraction between 100 and 1000 DPV, which was due either to UO_2^+ or complexation with one of the predominant anion complexants, F^- , SO_4^{2-} , or OH^- .

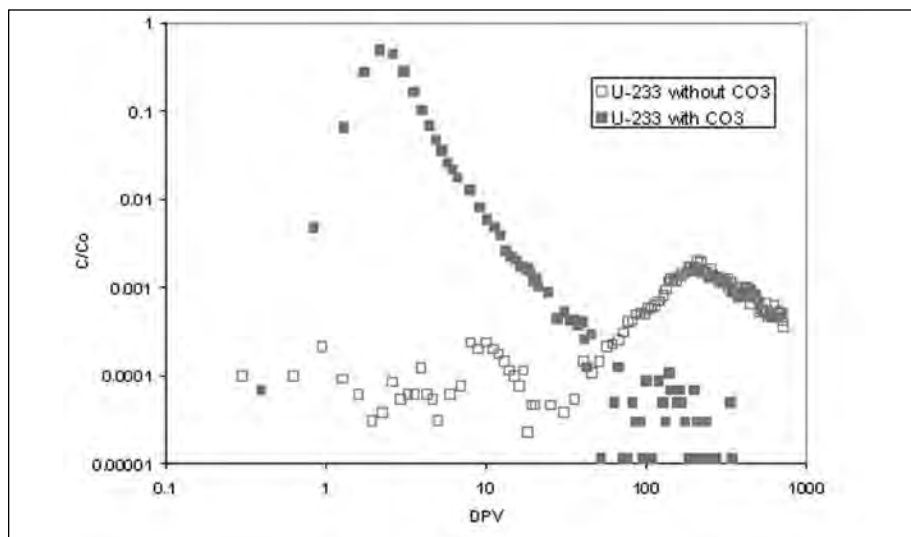


Figure 4. Breakthrough curves for uranium in sedimentary interbed under the influence of the perched water simulant (without EDTA) with and without added carbonate.



THE EFFECT OF COLLOID SIZE, COLLOID HYDROPHOBICITY, AND VOLUMETRIC WATER CONTENT ON THE TRANSPORT OF COLLOIDS THROUGH UNSATURATED POROUS MEDIA

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Colloids may facilitate the transport of radionuclides, hydrophobic organic contaminants, and heavy metals that are considered relatively immobile because of their high sorption capacity onto the soil or rock matrix. The extent of colloid mobility is investigated with two different sets of experiments through Unimin sand. The sand is composed of 90 percent quartz, 9 percent Na-, K-, and Ca-feldspar, and 1 percent mica with a calculated mean grain size of 650 μm . The first set of experiments examines colloid mobility as a function of size (52 nm to 1900 nm). This range was used to select various colloid sizes that were likely to be mobile. In the second set of experiments, the breakthrough of hydrophobic and hydrophilic colloids as a function of size (20 nm to 280 nm) and volumetric water content (θ) were compared relative to the breakthrough of a conservative tracer, potassium bromide (KBr). Fluorescent latex microspheres were used as idealized colloids for these experiments.

In the first set of experiments, the colloids contained no surface functional groups and represented hydrophobic natural minerals (for example, talc, sulfur, graphite, molybdenite, and galena) or natural minerals that become hydrophobic because they are coated with contaminants, such as immiscible oil (Cary *et al.* 1994). In the second set of experiments, the hydrophobic colloids contained sulfate (SO_4) functional groups, and the hydrophilic colloids were carboxyl-modified latex (CML). The colloid sizes, fluorescent dye used for detection, surface charge density, and other surface properties are shown in Table 1. Additional information about the colloids is available in McGraw (1996).

Saturated colloid experiments were used as an upper boundary for colloid mobility. It was assumed that if the colloids were not mobile under saturated conditions, they would not be mobile under partially saturated conditions. The saturated experiments were conducted in glass chromatography columns (5 cm inside diameter x 10 cm long), with the diameter at least 50x larger than the mean grain size to minimize the influence of flow along the column walls (Relyea 1982). The column was saturated by imbibing water and flushing the column from the bottom at 20 ml/hr for a minimum of 24 hours to purge large air bubbles from the system.

The unsaturated column experiments were conducted using a centrifugal technique that has been used to measure hydraulic conductivity (Conca 1993; Nimmo *et al.* 1992; Nimmo *et al.* 1987), estimate recharge rates (Nimmo *et al.* 1994), study

TABLE 1 Surface properties of colloids.

Colloid Size (nm)	Surface Groups	Fluorescent Dye	Surface Charge Density ($\mu\text{C}/\text{cm}^2$)	Zeta Potential ¹ ζ (mV)	Relative Contact Angle ²
52	None	Yellow G	NA	-44	<10°
189	None	Coumarin 153	NA	-48	74°
545	None	Yellow G	NA	-44	85°
910	None	Acridine Orange	NA	-49	<10°
1900	None	DCM Orange	NA	-10	21°
20	SO ₄	Crimson	5.5	-45	82°
30	CML	Blue	.6	-50	<10°
93	CML	Blue	102	-54	<10°
120	SO ₄	Crimson	.9	-47	81°
190	CML	Blue	221	-39	19°
200	SO ₄	Crimson	1.1	-48	79°
270	SO ₄	Crimson	1.67	-55	<10°
280	CML	Blue	140 ³	51	20°

¹ Measured on a Malvern Zeta Sizer 3² Measurement technique described in McGraw (1996).³ Approximated based on similar batches of colloids.

solute transport (Lindenmeier 1995), and measure hydraulic properties of carbon tetrachloride (Shields 1995). Specifically, a modified Beckman J-6 ultracentrifuge and a HySed 3.0 rotor were used for these experiments. This configuration is known as the unsaturated flow apparatus (UFA). The columns (3.3 cm inside diameter x 5 cm long) were run in duplicate under steady-state conditions. The development of the application of centrifugal techniques to monitor colloid transport and a detailed description of the experimental set up is described in McGraw (1996).

In the first set of experiments, the transport of five different colloid sizes was examined under saturated and unsaturated conditions. For the unsaturated conditions, the average volumetric water content, θ_{avg} , was 6 percent, or about 15 percent saturation. This low value was selected to represent very arid sites and to serve as a worse case scenario for transport of the different colloid sizes. Figure 1 shows the percent mass recovered for the different colloid sizes under saturated conditions as a function of pore volumes. At five pore volumes, the colloid suspension was changed to water. Under saturated conditions, more than 70 percent of the colloids

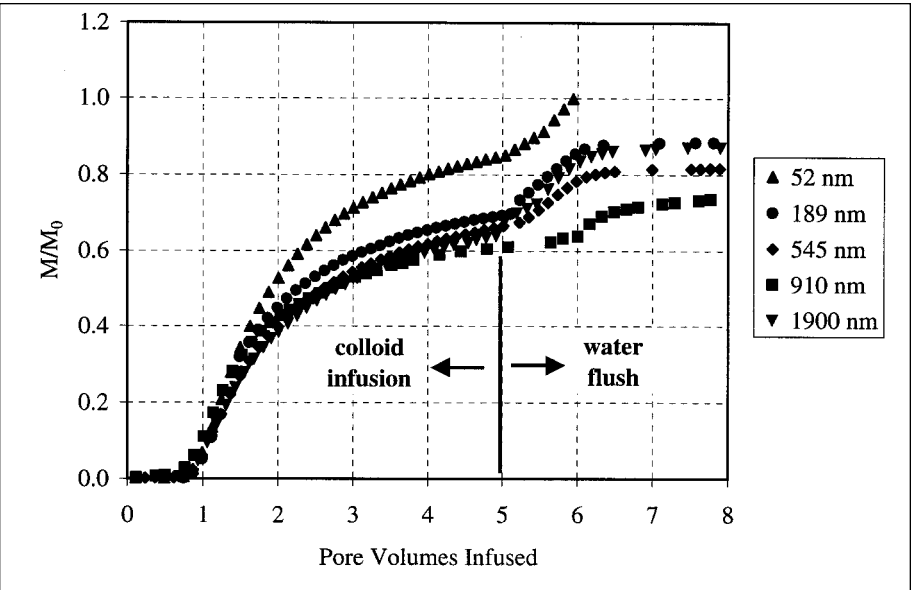


Figure 1. The effect of colloid size on the cumulative mass recovered for latex colloids without surface functional groups from duplicate experiments under saturated conditions.

were recovered for each size considered. Specifically, the 52 nm colloid was completely recovered; the 189, 545, and 1900 nm colloids had similar recoveries; and the lowest recovery was for the 910 nm colloids. Under unsaturated conditions, the percent mass recovered depended on the colloid size (Figure 2). If the cumulative percent mass recovered at 50 pore volumes is plotted as a function of colloid size, there is an exponential decrease in the cumulative percent mass recovered as the colloid size increases (Figure 3). The correlation coefficient, R^2 , for the exponential function indicates that 98.91 percent of the variability in the cumulative percent mass recovered can be explained by the colloid size. Variations between the experiments are expected because of differences in the volumetric water content and column packing. The volumetric water content can be normalized by calculating the water film thickness (t_w), using equation (4.1), which assumes that the water distribution around the sand grain is uniform (Mitchell 1993).

$$t_w = \frac{\theta}{\rho_b A_{ss}} \quad (4.1)$$

where

- θ = volumetric water content
- ρ_b = density of sand (g/cm^3)
- A_{ss} = specific surface area (cm^2/g)

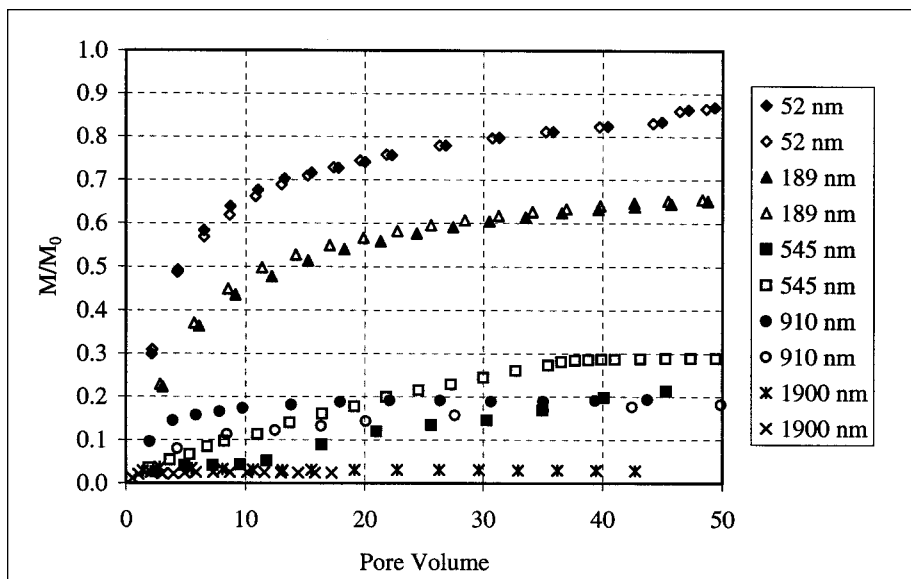


Figure 2. The breakthrough of latex colloids without surface functional groups at $\theta_{\text{avg}} = 6\%$ to examine the effect of size on colloid mobility.

The value calculated is approximate and does not account for local variations in the film thickness due to water meniscus between particles. The effect of the water film thickness can be seen schematically in Figure 4, which shows the colloid size relative to the average film thickness (115 nm) for these experiments. The figure shows that for 52 nm colloids, the water film thickness does not affect transport. However, the 189 nm colloids are larger than the film thickness, but the contact angle of the particle to the air-water interface allows the colloids to move along the interface and minimize the effects of the water film. For the larger colloids, the percent mass recovered decreases significantly because the water film thickness affects colloid transport. Based on these experiments, it was determined that colloids smaller than 325 nm had the greatest potential for migration under steady-state unsaturated conditions, which was defined as at least 50 percent breakthrough. The 325 nm size was used to select the colloid sizes for the second set of experiments.

In the second set of experiments, the breakthrough of KBr and colloids was examined under saturated and unsaturated conditions. These experiments used pairs of hydrophobic and hydrophilic colloids that were transported simultaneously through the columns. This transfer required that each colloid had a distinctly different excitation and emission spectra, and that the presence of one colloid did not interfere with the detection of the other colloid. Details about this technique are described in McGraw (1996). Figure 5 shows the breakthrough curves for KBr at three different

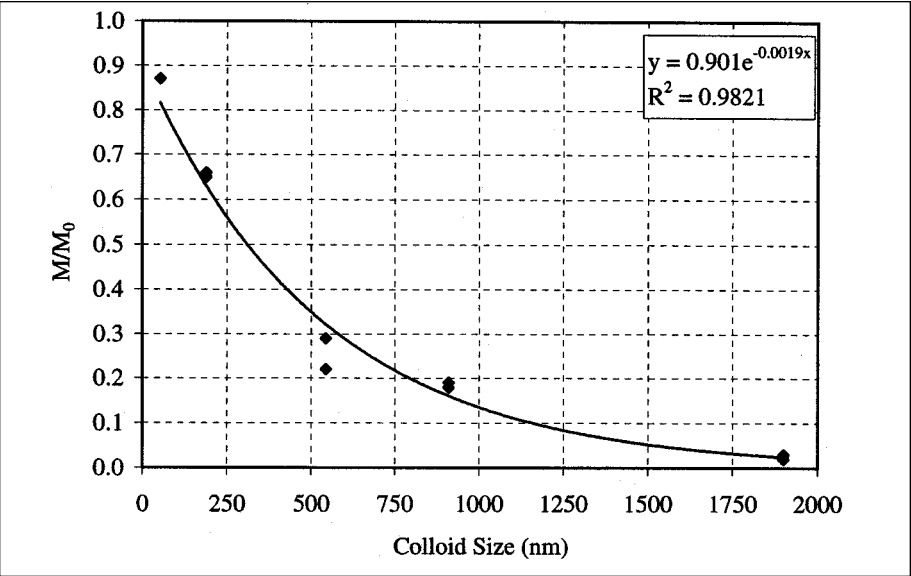


Figure 3. Cumulative mass recovered at 50 pore volumes for latex colloids without surface functional groups as a function of size at $\theta_{\text{avg}} = 6\%$. The solid line represents an exponential relationship between the percent recovered and colloid size.

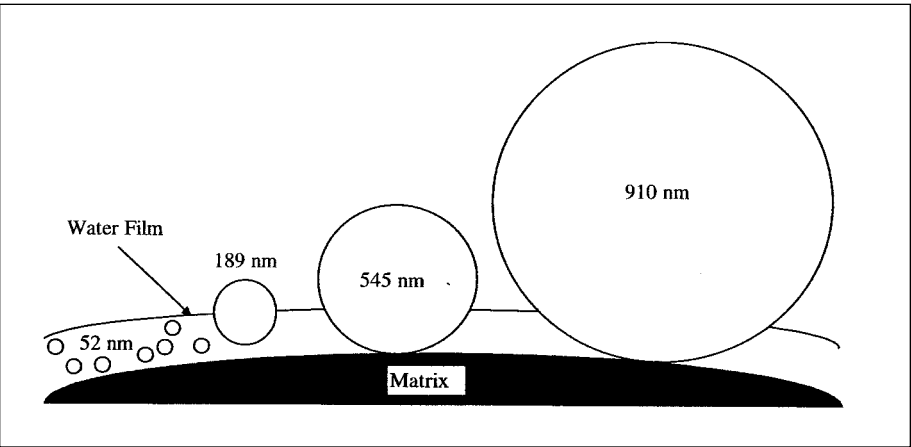


Figure 4. Proportional schematic of different sized colloids without surface functional groups in a 115 nm water film ($\theta_{\text{avg}} = 6\%$).

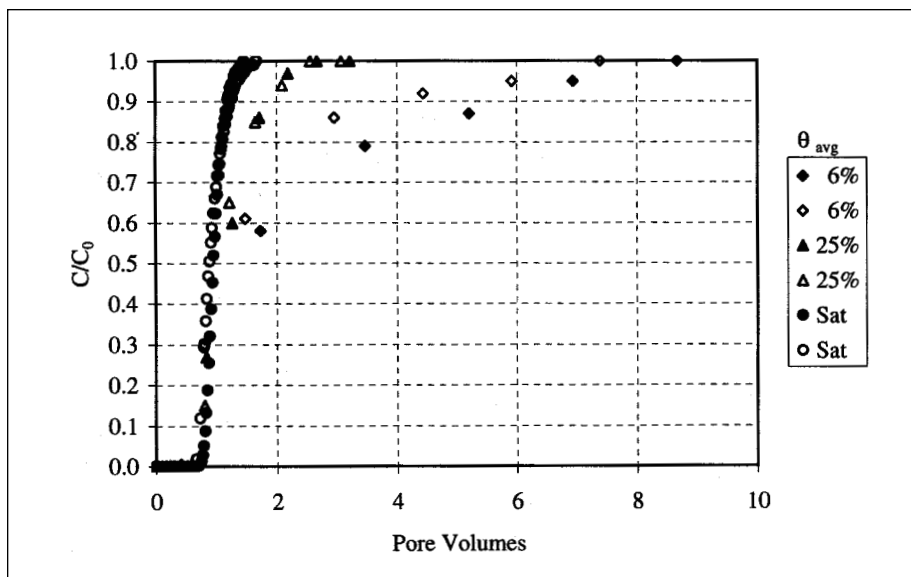


Figure 5. Normalized breakthrough of KBr for different volumetric water contents.

volumetric water contents. As the volumetric water content decreased, the number of pore volumes required for complete breakthrough of KBr increased. This result indicates that the path traveled by the KBr under unsaturated conditions was longer or more tortuous than it was under saturated conditions. Therefore, it was expected that a similar trend would be observed for the colloids.

The 93 nm hydrophilic and the 120 nm hydrophobic colloids were selected as a representative pair to examine the breakthrough behavior as a function of volumetric water content. Figure 6 shows the cumulative percent mass recovered at three different volumetric water contents for the 93 and 120 nm colloids, respectively. Under saturated conditions, the breakthrough of the colloids is similar. However, as the volumetric water content decreases, the time required for breakthrough increases for both colloids. The effect is more pronounced for the hydrophobic colloids. This fact indicates that there is a mechanism, in addition to an increase in path length, which affects the transport of the hydrophobic colloids relative to hydrophilic colloids and/or KBr.

Mechanisms considered in these experiments include the colloid surface charge density, the volumetric water content, and the water film thickness, although other mechanisms are possible. For these experiments, the hydrophilic colloids showed no relationship to the surface charge density, and only a slight trend was observed for the hydrophobic colloids. However, the range of values considered was too small to draw any definite conclusions.

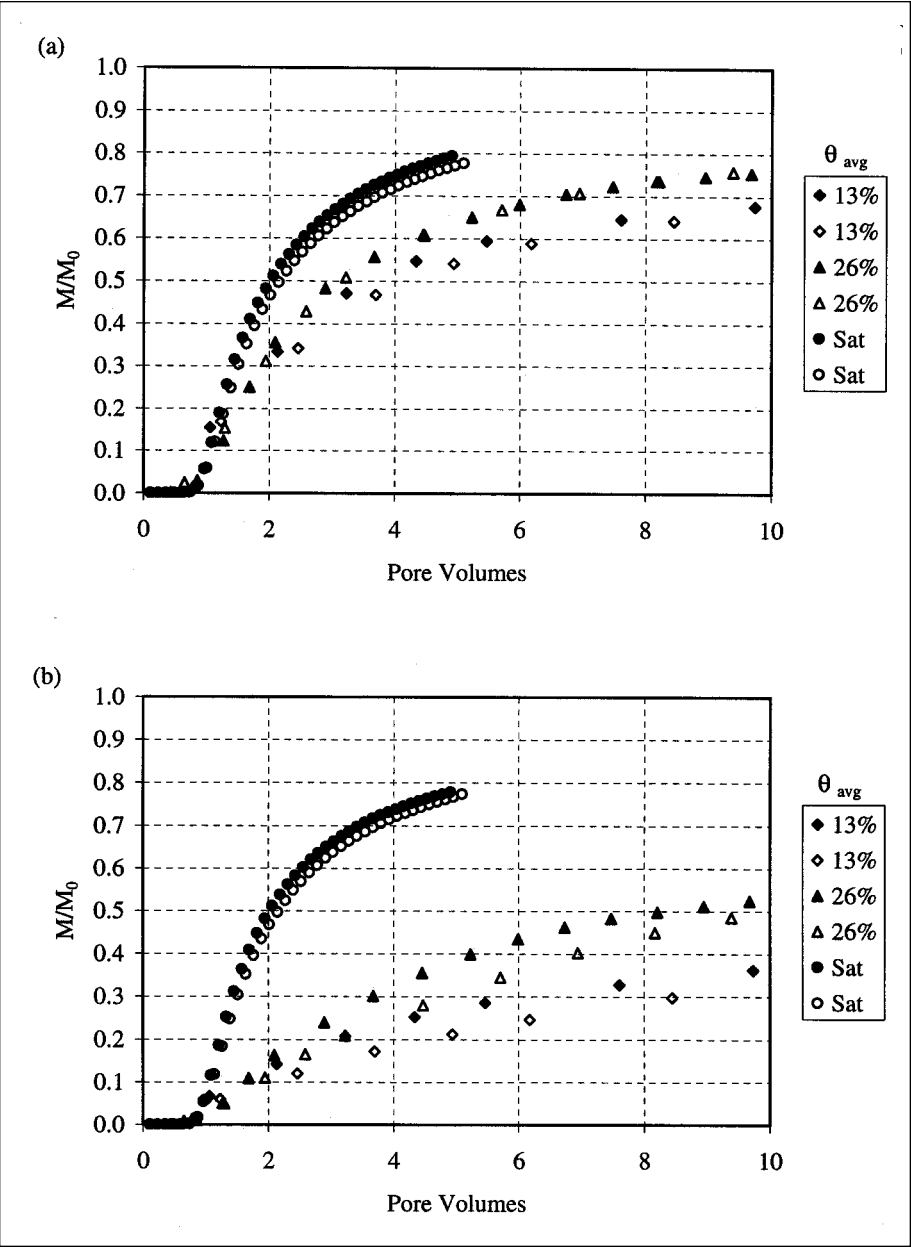


Figure 6. Cumulative percent mass recovered for (a) 93 nm hydrophilic and (b) 120 nm hydrophobic colloids at different volumetric water contents.

Figure 7 shows the effect of the volumetric water content on the cumulative percent mass recovered after the colloid breakthrough reached a plateau for the hydrophilic and hydrophobic colloids, respectively. The mass recovered was taken at 10 pore volumes for the saturated experiments and 20 pore volumes for the unsaturated experiments. This comparison is not ideal and is made for illustrative purposes only, with the *caveat* that the saturated and unsaturated experiments were conducted in different columns and with different techniques. Therefore, the data should not be compared. However, the illustration shows a linear trend among the hydrophilic colloids as a function of volumetric water content that is absent from the hydrophobic colloids. If the data from only the unsaturated experiments is plotted as a function of the water film thickness divided by the colloid size, then a trend is observed for the hydrophobic colloids and no trend is observed for the hydrophilic colloids (Figure 8).

These experiments demonstrate that colloids are mobile under steady-state unsaturated conditions, and they consider the physical mechanisms of transport in the absence of chemical affects. For hydrophilic colloids, the transport was most strongly related to the decrease in volumetric water content, which was also observed for the KBr data. This relationship suggests that the behavior of the hydrophilic colloids is related to changes in the advective flow as the column becomes unsaturated. As the water content decreases, a water film forms around the matrix grains that increases the tortuosity of the flow path and the distance that must be traveled through the column. In addition, as the columns become unsaturated, the percentage of immobile water increases. For the sand used in these experiments, the percentage is expected to be small, but it can be significant for fine-grained material. Therefore, these results indicate that the steady-state transport of small hydrophilic colloids that are not subject to filtration can be modeled as equivalent to aqueous phase.

In contrast, the transport of hydrophobic colloids was affected by the ratio of the water film thickness to the colloid size. However, this ratio did not completely account for the retardation and retention of the hydrophobic colloids. The surface charge density had a slight effect, but the range of values examined was insufficient to draw any definite conclusions relative to other mechanisms. In addition, this study did not account for or distinguish among rapped air bubbles that would be expected to increase colloid retention or a continuous gases phase in the column. Therefore, the steady-state transport of hydrophobic colloids must be modeled in relationship to the water film thickness, and other experiments are necessary to further understand other variables that affect transport of hydrophobic colloids.

In summary, colloids can move under steady-state unsaturated conditions. Although a range of colloid sizes was observed to be mobile, smaller colloids had the greatest mobility. These results demonstrate that the unsaturated zone is not a barrier to colloid transport, and that colloid facilitation should be considered at contaminated sites.

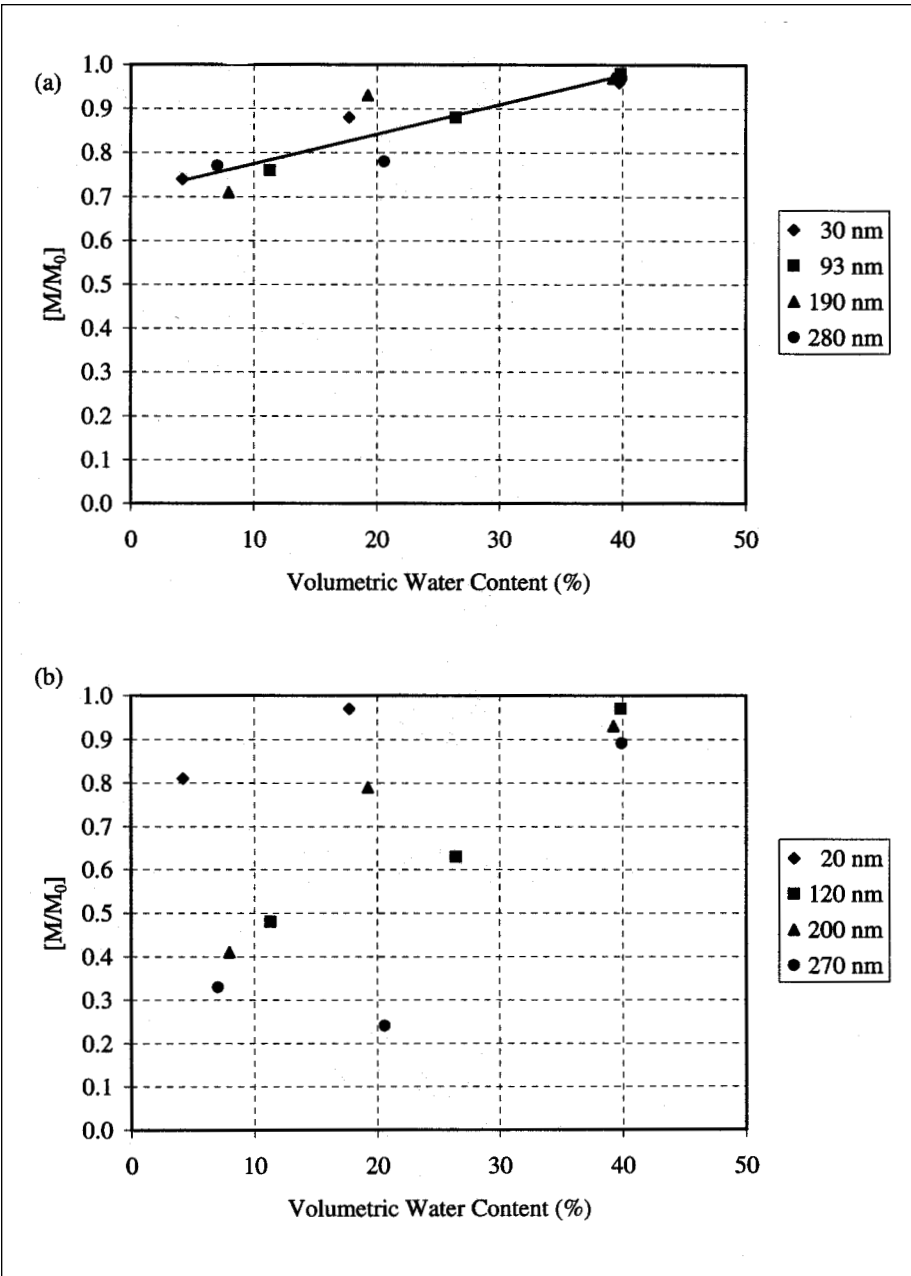


Figure 7. Cumulative percent mass recovered for the (a) hydrophilic and (b) hydrophobic colloids as a function of the volumetric water content.

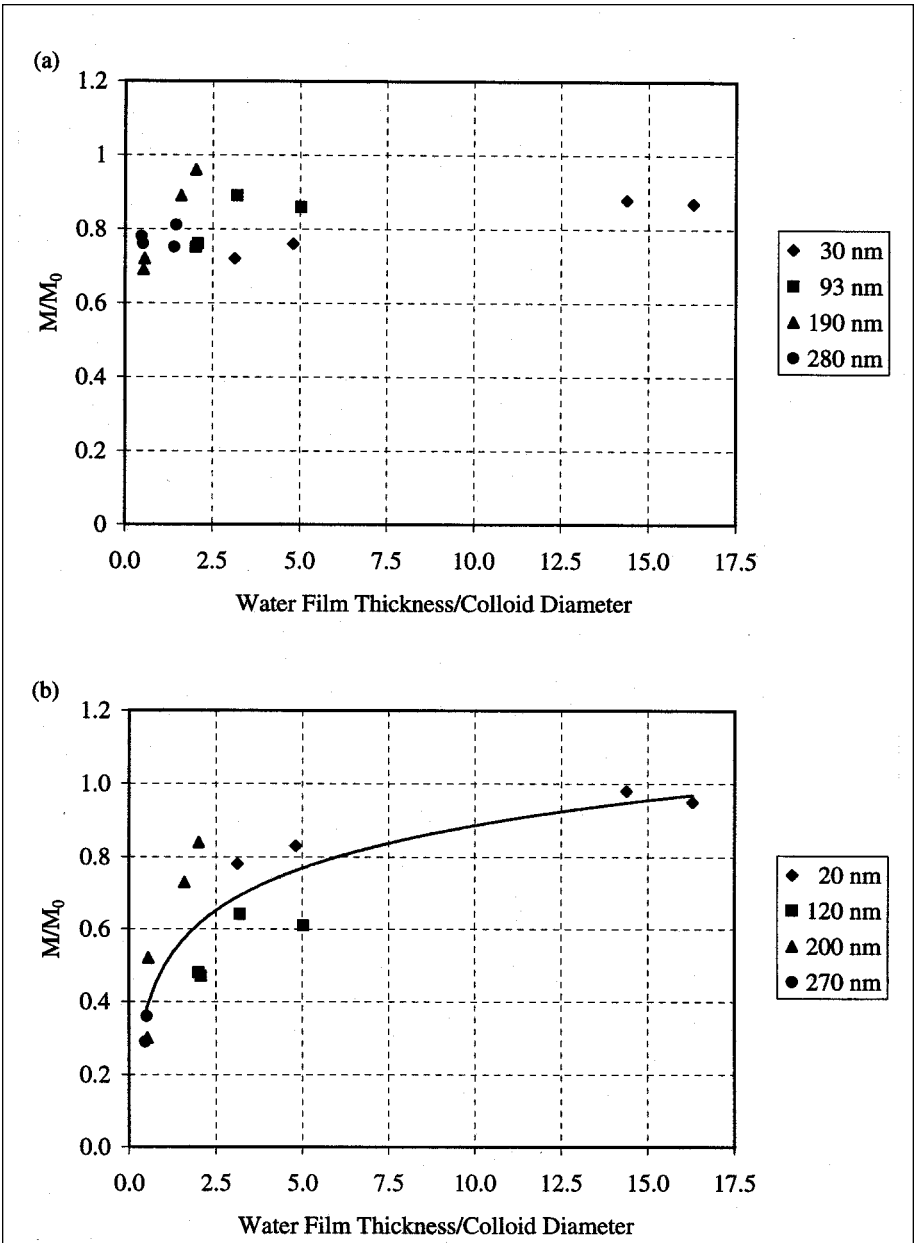


Figure 8. Cumulative percent mass recovered for (a) hydrophilic and (b) hydrophobic colloids as a function of the water film thickness/colloid size.

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SUMMARY OF COLLOID GENERATION AND STABILIZATION IN RESPONSE TO INDUCED WATER CHEMISTRY CHANGES

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Induced water chemistry changes, such as those resulting from waste disposal or through operation of injection or circulation wells, can significantly impact subsurface systems. Possible effects include generation and/or mobilization of colloidal solids and dispersal of matrix materials. The potential indirect results of these effects are to increase turbidity or suspended solids, increase apparent “aqueous concentrations” of native elements, facilitate contaminant migration, and alter matrix permeability.

A study to support reinjection of treated groundwater into sediments of the Southeastern Coastal Plain of the United States (Strom *et al.* 1994) provided significant insight into the impacts of induced chemistry changes. This work consisted of detailed analyses of bulk (batch) dispersibility experiments and column studies conducted under a variety of conditions. While the work performed was to be representative of shallow groundwater (that is, saturated conditions), the results and observations should generally apply to vadose zone sites where induced water chemistry changes are imposed in a system of sands and weathered clays.

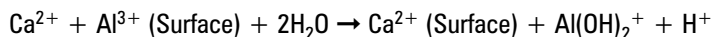
The most fundamental observation from the work is that the interaction between natural sediments and solutions, even relatively dilute solutions, is a dynamic process and that the chemistry of both phases is altered by the interaction. The results were consistent with a few broad mechanistic principles. A brief description of the work, examples of specific observations, the broad principles, and sample recommendations based on the results follow. A detailed description of the methods and comprehensive results are presented in the work of Strom (1994).

The dispersibility tests were used as indicators of probable conditions where clogging, or reduced hydraulic conductivity, can occur. Additionally, dispersive geochemical regimes were identified as probable conditions under which colloidal solids are mobilized for downgradient transport. The column studies were designed to further investigate various geochemical regimes identified in the bulk tests and to examine colloid mobilization and matrix changes under dynamic flow conditions. The column studies also allowed us to identify specific behaviors of individual ions as the injected water interacted with the geologic matrix. To be consistent with the literature, we use the term “stable” to describe colloids and conditions where the particles remain in solution rather than flocculating and/or depositing on matrix surfaces.

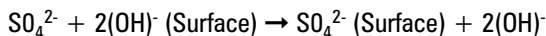
The data from both types of experiments indicated that natural colloids in pore water remain at low levels within a relatively narrow injectate pH range—a range close to that of the natural system. Significant levels of stable colloids were released under two different chemical regimes: at high sodium concentrations in conjunction with elevated pH, and at low pH in conjunction with specific ion interaction with the oxide phases.

The column experiments indicated that both the pore water chemistry and the surface charge of the aquifer matrix are sensitive to small changes in the injection solution composition. The chemical changes result primarily from surface chemical reaction between the aquifer matrix materials and the injected waters. Ion exchange reactions play a prominent role in these reactions. Calcium, for example, displaces aluminum and magnesium from exchange sites and results in changes in the column effluent composition. Sodium, however, appears to be ineffective in displacing either magnesium or aluminum in the column experiments. For the anions, chloride and bromide are not significantly involved in surface reaction except in extremely low ionic strength solutions. Sulfate, though, appears to participate in ligand reaction with hydroxyl ions on surface coatings.

Interestingly, the exchange reactions induced significant shifts in solution pHs (>1 pH unit) in poorly buffered solutions. Influent sulfate raises the pore water pH, and Ca exchange lowers the pH. The researchers inferred from their data that the reduction in pH was due to hydrolysis of displaced aluminum. The acidogenic reaction for calcium exchange can be summarized as



The sulfate reaction is presumed to be a direct displacement of hydroxyl ions:



Specifically, adsorbed oxy-anions (for example, arsenate and phosphate) exhibited similar but stronger increase in solution pH as water moved through the sediments. The various anions may also act in solution to reduce the hydrolysis of aluminum by forming ion pairs. Either mechanism has the net effect of reducing the extent of acidogenic reactions. In dilute sodium chloride solutions, neither the cations nor anions have sufficient displacing power to influence solution pH through ion exchange reaction.

Table 1 shows the effects of the tested ions on solution diagenesis grouped with ions that are predicted to have similar effects on the solutions.

The column experiments corroborated the results of the batch experiments at the high pH range. In addition, they demonstrated that, in a low pH regime, dilute stable colloid suspensions of positively charged particles are formed in low ionic strength solutions. Adding calcium to the solutions increased the stability of the colloids, contradicting classical colloid theory, which predicts decreased stability. The pH effects

due to the hydrolysis of displaced aluminum appear to outweigh the flocculating effects of divalent ions on colloids in poorly buffered solutions. The colloids generated in the low pH regime ranged in size from 400 to 660 nm in diameter and had the characteristics of positively charged surface. The characteristics of the dispersed phase in the high pH regime were not reported. However, the behavior is consistent with negatively charged colloids and dispersed clay minerals.

TABLE 1		Acid and base producing ions in reaction with mineral surfaces for the Savannah River Site in South Carolina.	
Ion Type	Acidogenic	Weak or Neutral	Alkalinogenic
Cations	<i>Ca</i> ²⁺ , <i>Mg</i> ²⁺ , <i>Sr</i> ⁺ , <i>Cs</i> ⁺ , <i>K</i> ⁺	<i>Na</i> ⁺ , <i>Li</i> ⁺ , <i>NH</i> ₄ ⁺	
Anions		<i>Cl</i> ⁻ , <i>Br</i> ⁻ , <i>NO</i> ₃ ⁻ , <i>HOCl</i>	<i>SO</i> ₄ ²⁻ , <i>HPO</i> ₄ ²⁻ , <i>F</i> ⁻ , <i>As</i> ₄ ³⁻

Notes: Ions listed in bold italic type were tested. Other listed ions are examples that are expected to be similar based on the ion exchange properties of kaolinite as a model surface (Grim 1968).

Figure 1 summarizes conditions under which stable colloidal systems (that is, elevated mobile colloids) formed in the studies. The pH and ionic strength of the effluent solutions seemed to have the greatest influence. Within the native pH range, Ca. 4-5.5, the colloid system remains flocculated in natural sediments. In the column experiments, large quantities of colloids were generated/dispersed during transient conditions as pore water of one type or chemical characteristic was being replaced by another water type (that is, when high ionic strength water was being replaced by low ionic strength water). Also, it is important to point out that a much greater quantity of colloids was mobilized under the high pH regime than under the low pH regime. Because of the concentrated nature of the resulting suspension, the high pH regime was observed to lead to long-term reduction of the permeability of the materials.

Based on the results, we developed detailed recommendations related to the chemistry of water for injection to the subsurface. A few examples follow:

- The safest target pH range for field injection is approximately 5.5 to 6.5. This range can be expanded to lower values (approximately 4 to 6.5) if cations and anions are selected to avoid post-injection pH reduction as the water flows away from the system.
- The preinjection water treatment should balance ions that either elevate or reduce pH of the influent solution through reaction with subsurface materials to avoid undesirable downgradient deviations from the target pH range. Simple balancing of acidogenic and alkalinogenic ions can moderate the potential negative impacts of post-injection pH changes.

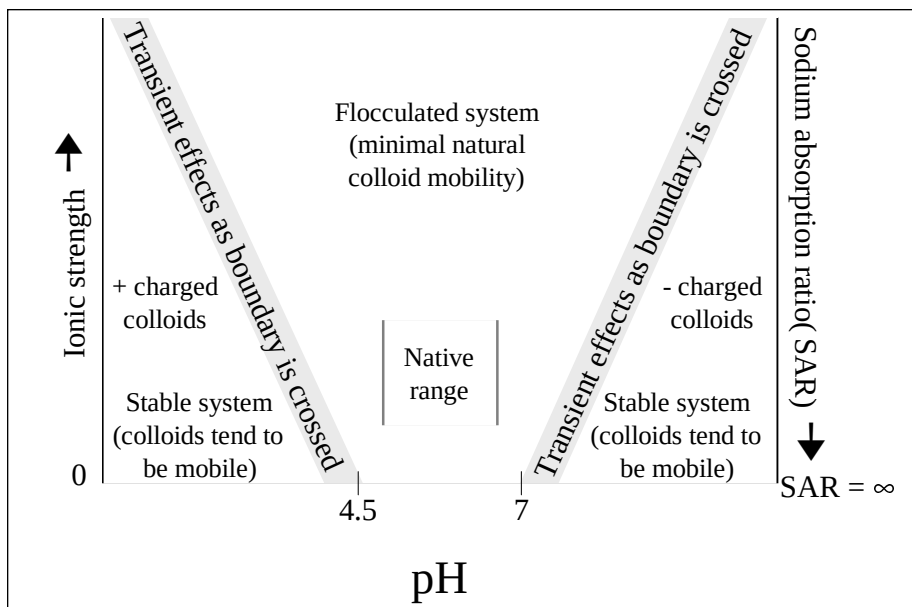


Figure 1. Summary of colloid characteristics and stability as a function of chemical conditions based on batch and column experiments.

- Except for extreme conditions, the most significant periods of colloid generation were transients associated with influent chemistry changes. Thus, low to moderately low ionic strength solutions are most suitable for injection. These solutions are similar to the natural chemistry and minimize the potential for long-term groundwater quality degradation and undesirable transients at the end of treatment as native groundwater reenters the treatment zone. Higher ionic strength solutions behaved predictably, but such solutions may not be consistent with clean-up objectives (for example, replacing low concentrations of contaminants with high concentrations of salt).
- Because of the transient nature of some of the impacts, system start-up monitoring and field monitoring of geochemistry and formation changes are prudent to support start up and operation of any large-scale injection system.

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UNDERSTANDING THE FATE AND TRANSPORT OF MULTIPHASE FLUID AND COLLOIDAL CONTAMINANTS IN THE VADOSE ZONE USING AN INTERMEDIATE-SCALE FIELD EXPERIMENT

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INTRODUCTION

Scientists, stakeholders, and regulators alike often hope that the vadose zone will serve as a barrier to the downward transport of contaminants to the water table. Unfortunately, both the degree to which this is true and the conditions under which the vadose zone functions or fails as a barrier to different kinds of groundwater contamination are often not well-known. Experiments of intermediate scale (for example, somewhere between bench-scale and field-scale) offer the opportunity to investigate contaminant transport issues in at least a semi-controlled environment to better determine and quantify the important physical and chemical processes associated with contaminant infiltration across the vadose zone.

THE VADOSE ZONE OBSERVATORY

The Vadose Zone Observatory (VZO) at Lawrence Livermore National Laboratory is an example of an intermediate-scale facility that is well-characterized by field-scale standards and allows a high degree of monitoring of infiltration events. The facility uses a variety of monitoring methods to track controlled infiltration experiments. The unsaturated regime is approximately 60 to 70 feet thick and consists of silt, silty-sand and silty-gravel deposits. The observatory consists of about 20 instrumented boreholes and monitoring wells that traverse the 70-foot unsaturated zone, including 8 wells containing electric resistance tomography (ERT) arrays and 4 boreholes with multilevel gas-sampling ports, soil temperature sensors, gypsum blocks, tensiometers, and lysimeters (Figure 1). Several multichannel data loggers continuously store information about surface barometric pressure, subsurface gas-phase pressure, subsurface temperature, capillarity, and water-table levels; this information is downloaded into portable computers for analysis.

The facility is ideal for carrying out infiltration experiments designed to elucidate how vadose zone characteristics such as preferential pathways, heterogeneities, multiple phases of flow, and relative permeabilities influence the transport of contamination in liquid, gas, and colloidal phases to the water table. The capabilities of the VZO allow us to continuously monitor the progress of an infiltration event. In addition, we can also directly take samples of moisture and gases for analysis from

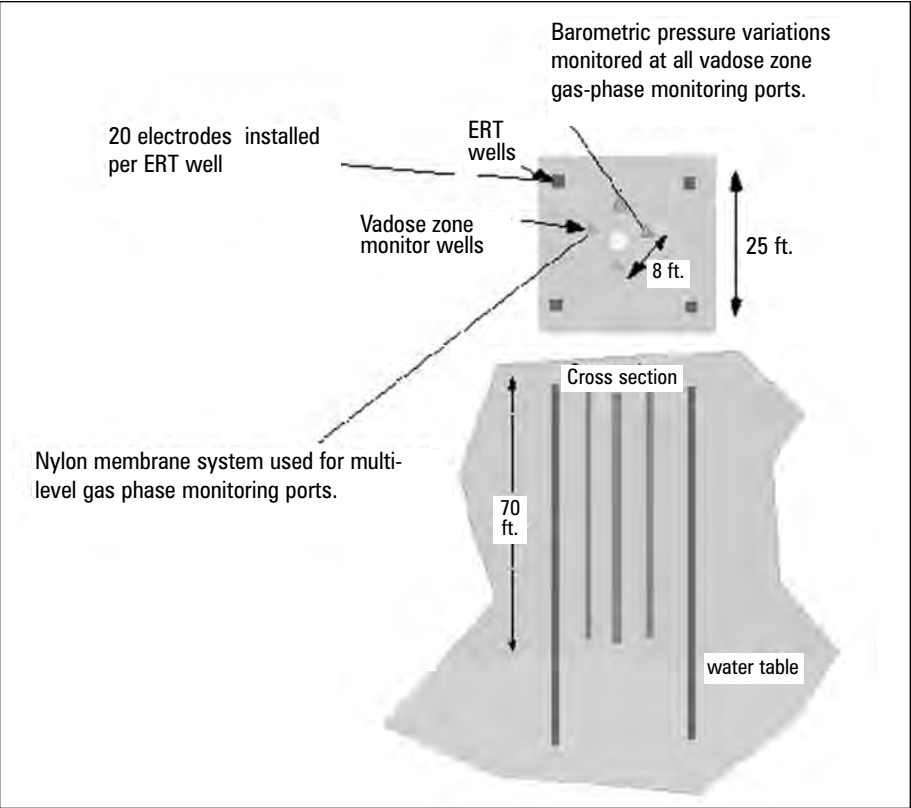


Figure 1. A schematic of the Vadose Zone Observatory shows orientations of several ERT and monitoring wells (not all shown). The infiltration well in the center allows point-source release of infiltration water at a depth of approximately 14 feet in a vadose zone that is 65-70 feet thick.

many different depths in the vadose zone as well as from the underlying water table. The ability to sample is critical to our infiltration experiments, which include gas- and liquid-phase tracers and tagged particles simulating colloids.

**MONITORING LIQUID-PHASE, COLLOIDAL,
AND GAS-PHASE INFILTRATION EVENTS**

To date, infiltration events have simulated leaks from tanks or subsurface pipes that might have occurred beneath the single-walled tanks at Hanford. Either the flow rate or head are controllable from such near-surface point sources. Typical experiments involve releasing 1,600 to 80,000 liters of water with typical zero-head injection

rates of 2–3 liters/min. The ERT arrays measure electrical conductivity changes resulting from plume-induced chemical changes to the groundwater as well as saturation changes. Figure 2 illustrates a typical sequence of ERT images obtained from an early infiltration event (Carrigan *et al.* 1998). The 3-D images obtained from inversion of the conductivity measurements of the soil bounded by the vertical electrode arrays show structure corresponding to electrical conductivity increases down to the water table. In addition to the vadose zone conductivity enhancements associated with saturation changes, tensiometers detect saturation increases throughout the whole vadose zone regime. Further, both liquid- and gas-phase tracers have been used to track the downward chemical progression of the plume (Ekwurzel *et al.* 1999), and allow an interesting comparison to be made with the ERT results.

Simulations of infiltration at the site, assuming a multi-layered-soil (2-D) structure with hydrologic properties determined from lab tests on soil cores, suggest that the vadose zone will function as a formidable barrier to contamination of the water table by a near-surface leak. However, the ERT results show that saturation changes

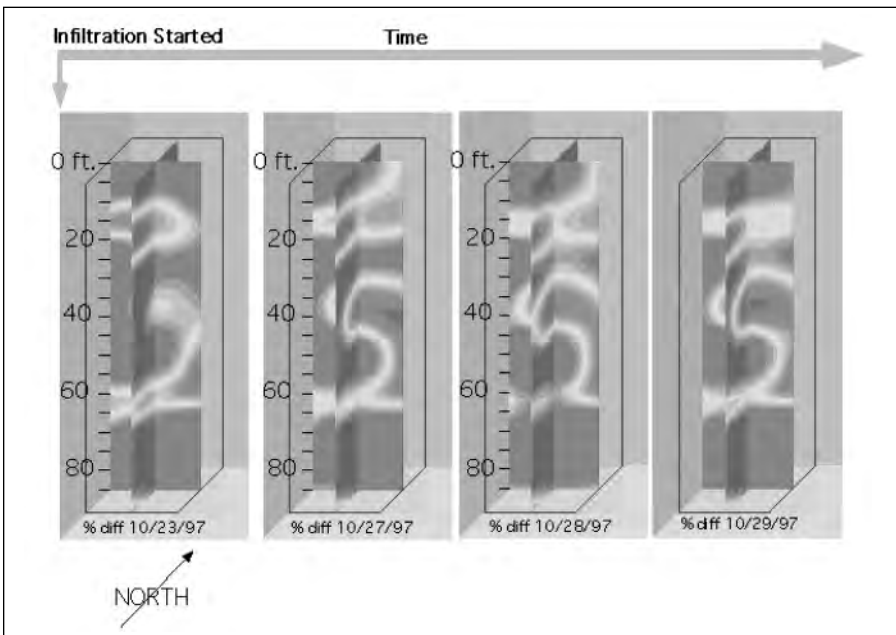


Figure 2. A sequence of ERT images shows that a rapid change in saturation occurs throughout the vadose zone within hours after infiltration is initiated. ERT images indicate changes in electrical conductivity of soil which is related to saturation changes in the vadose regime resulting from infiltration. Changes in images with time indicate evolution of saturation at different levels in the vadose zone.

occur down to the water table within hours. Similar results are obtained from gypsum-block tensiometers placed at different levels in a monitoring well near the central infiltration well. A 3-D heterogeneous model with high-permeability pathways more closely fits the observations of rapid saturation change down to the water table than the layered model mentioned previously (Carrigan *et al.* 1998). However, the results of our attempts to track the migration of chemical tracers across the vadose zone show that a significant time lag (approximately a month) exists between the detection of saturation changes near the water table and the detectable arrival of the tracers at the water table. During this interim period, water was infiltrated periodically until approximately one pore volume had been flushed through the vadose zone. Similar time lags have been observed in our numerical simulations. We attribute this time-lag between the detection of saturation and chemical changes near the water table to be largely a result of displacement and dilution effects.

Colloidal transport represents one possible mechanism for the migration of contamination across the vadose zone. The saturated zone readily permits the transport of colloids in a fractured medium subject to the appropriate chemical conditions (McCarthy *et al.* 1998). At the VZO, a preliminary and ongoing experiment to test the ability of the vadose zone to permit the transport of micron-sized colloids (simulated by microspheres tagged with fluorescent dye) has not resulted in the detection of these particles at the water table or at any monitoring level in the unsaturated regime to date. During this infiltration experiment, we removed the flexible liners in several wells surrounding the central infiltration well and examined the borehole walls for evidence of groundwater seepage. After days of infiltration, there was no evidence of seepage into the boreholes or flow along desiccation cracks that intersect the boreholes. The lack of seepage in boreholes or in any observable cracks in the vadose zone may have significant implications for the prevention of contaminant migration by colloidal transport.

Transport by the gas phase represents another potential mode by which contaminants can spread through the vadose zone and ultimately reach the underlying water table. In addition to spreading contamination, movement of the gas phase can also influence estimates of contaminant inventories that are based on gas sampling at different levels in a monitoring well. We are currently evaluating the role of gas-phase transport in the vadose zone at our facility. Despite the dominating volume of nearly saturated silty soils at the site, some combination of diffusion and barometric pumping appears to have dispersed tracer gases both vertically and horizontally over the site in a period of months (Carrigan *et al.* 1998). Using the NUFT multiphase flow-and-transport program developed at Lawrence Livermore National Laboratory (LLNL) (Nitao 1995), we are currently evaluating the role of barometric pumping and diffusion upon gas-phase transport in a variety of subsurface soil environments with and without fractures (Ralston *et al.* 1999).

MODELING: THE FRAMEWORK FOR FIELD OBSERVATIONS

The different monitoring techniques used at the VZO produce very different “snapshots” of an infiltration event. Numerically modeling these events is an important part of understanding, or reconciling, the results of the different techniques. Another way of viewing modeling is that it provides a quantitative framework that can connect observations obtained from the VZO. Sometimes observations do not fit into the framework of a given model. An example already mentioned is the 2-D-layered model for infiltration which cannot explain the rapid saturation changes occurring at the water table. On the other hand, the behavior of a 3-D heterogeneous model with preferential pathways more closely resembles the saturation observations provided by ERT as well as the fundamentally different chemical transport observations provided by the tracer studies.

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7

Remediation of Organic Chemicals in the Vadose Zone

Larry Murdoch

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INTRODUCTION

The remediation of organic chemicals in the vadose zone has been blessed by remarkable success, but it has also been cursed by challenges to even our most advanced capabilities. This spectrum of outcomes to the remedial process is a result of the diversity of conditions encountered at contaminated sites. Organic chemicals are rarely stored or intentionally placed beneath the water table, so the source of most organic contamination is at the ground surface or in the shallow vadose zone. As a result, nearly all sites containing organic contaminants have at least some problems in the vadose zone, and commonly the greatest concentrations of contaminants occur in the vadose zone near the source.

The large number of sites requiring vadose zone remediation presents a broad range of conditions and circumstances, including factors related to geologic conditions, properties of the contaminants, and the ability to access the subsurface. All are critical to the performance of the remedial technique, and currently no single technique addresses all the factors found at contaminated sites. Instead, an array of techniques has been developed, some to target widespread problems and others to address the more difficult niches.

The development of soil vapor extraction (SVE) in the mid-to-late 1980s provided a method that can significantly reduce the mass of volatile compounds at sites underlain by relatively dry, sandy sediments, in areas readily accessed by conventional drilling. A significant number of sites meet those criteria, and SVE has been used to close many of them. SVE is widely available and, along with several companion techniques, it forms the backbone of our organic chemical remediation capabilities.

A variety of conditions impede SVE performance. Organic contaminants may partition into the vapor phase only sparingly, or the underlying material may be tight or marked by significant heterogeneities, or the contaminated region may be beyond the influence of conventional wells. These factors reduce the effectiveness of SVE, delaying the completion of remediation and increasing costs.

Performance improvement and cost reduction motivated the development of at least a dozen other technologies for remediating organic chemicals in the vadose zone. Each of these innovative technologies either stretches the limitations caused by geology, contaminant properties, or access, or reduces the equipment and operating costs of conventional SVE. Some are designed to improve SVE performance itself, for example, by heating the ground to accelerate the contaminant evaporation and increase the recovery rate. Others draw on different physical or chemical processes for remediation.

Contaminant recovery is by no means the only remediation method for the vadose zone. Bioremediation of hydrocarbons has been widespread and successful in many vadose settings. Other possibilities include chemically altering contaminants to benign compounds, or injecting chemicals to markedly reduce the mobility of contaminants and limit their ability to migrate to potential receptors. At some sites, naturally occurring processes may reduce the concentrations of contaminants so that subsurface monitoring is sufficient to ensure remediation.

The purpose of this chapter is to identify the current state of our capability to remediate organic chemicals in the vadose zone. The first part of the chapter describes the remedial technologies that are currently available. The second part of the chapter compares the performance of these technologies under a variety of conditions at contaminated sites. Most of the remediation methods considered here fall unambiguously into one of four major classes of remedial methods: recovery, destruc-

tion, immobilization, and natural processes, and the chapter is organized around these classes. However, a few of the technologies are capable of more than one type of action; for example, heating the subsurface will improve recovery but it can also destroy some contaminants by oxidation or pyrolysis.

All of the technologies described in the following pages have advanced through the development process and are now offered as a service by private companies. Some are widely available, while other methods are more specialized. A variety of other methods currently show promise in the laboratory, and it is expected that they will soon be added to the list of commercially available techniques.

REMEDICATION TECHNOLOGIES

CONVENTIONAL VAPOR EXTRACTION*

Soil vapor extraction (SVE) is the benchmark process for remediation in the vadose zone. Its widespread application since it was developed in the 1980s is probably responsible for cleaning up more sites than any other *in situ* remedial method. SVE is achieved by inducing air flow through the contaminated zone (Figure 7-1) to extract the contaminant-laden vapors and promote vaporization/volatilization and subsequent removal of liquid, dissolved, and sorbed contaminants. The pore-scale situation depicted in Figure 7-1 can occur wherever air flow can be maintained in the subsurface. Subsurface air flow is induced in a manner analogous to pumping groundwater: vacuum blowers attached to SVE vents serve the same purpose as pumps in water wells and reduce pressures in extraction vents. SVE extraction vents resemble water wells completed in the vadose zone. Air flows downward from the ground surface towards the lower pressure in the extraction vents. Subsurface flow could likewise be induced by injecting air under pressures greater than atmospheric, but applying negative pressures (suction) allows the contaminated vapors to be captured and treated.

The subsurface flow of gases can be analyzed using a continuity equation with Darcy's law to relate volumetric flux to potential gradient,

*This section was contributed by J.S. Gierke.

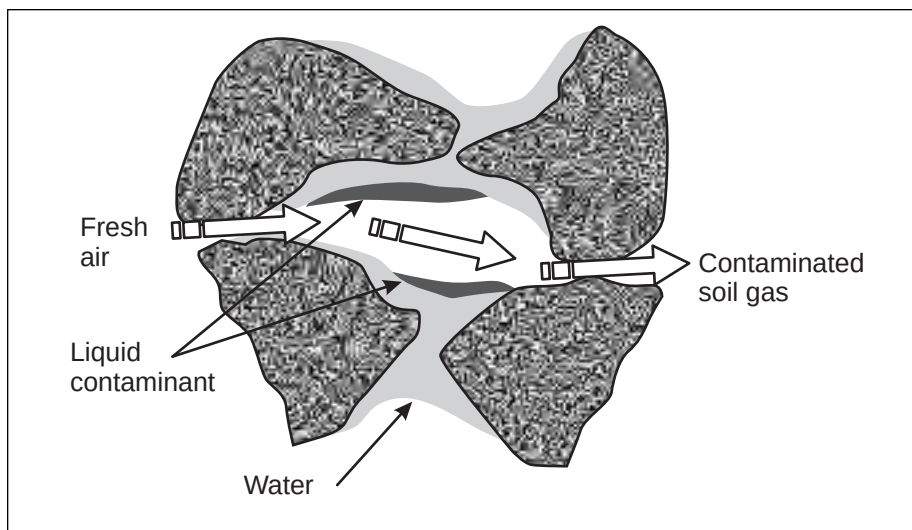


Figure 7-1. Grain-scale view of soil vapor extraction process: fresh air drawn into contaminated zone under induced vacuum displaces soil gas previously equilibrated with the contaminant, causing vaporization/volatilization of liquid, dissolved, and sorbed contaminants, potentially until chemical equilibrium is achieved. The soil gas becomes progressively more contaminated and eventually is extracted and treated.

and the ideal gas law to describe the equation of state (see Chapters 1, 3, and 5; Jordan *et al.* 1995). Because gas density is small, the gravitational component of the fluid potential is typically ignored and flow is induced primarily by pressure gradients. Analytical solutions exist for idealized flow conditions (such as homogeneous, steady-state, and axisymmetric) in either one- or two-dimensional configurations (Johnson *et al.* 1990a; Shan *et al.* 1992; Falta 1996). Numerical models account for non-ideal flow geometries and heterogeneities. By ignoring compositional effects on gas density and viscosity, and linearizing the gas flow equation, groundwater flow models can be used to simulate air flow induced by SVE (Baehr and Joss 1995).

The SVE contaminant removal process can be analyzed using a continuity equation approach with phase-partitioning (Henry's law for air-water, Raoult's law for NAPL-air and NAPL-water, and linear sorption)

between the organic, aqueous, gaseous, and sorbed phases (see Chapters 1 and 5; Baehr and Hoag 1988). Nonequilibrium mass transfer is important for chemical removal at a range of scales (Hiller and Gudemann 1989; Brusseau 1991; Gierke *et al.* 1992; Armstrong *et al.* 1994). Different stages of the removal process are characterized according to the dominant mechanisms: initially, removal is dominated by advection, which later transitions to diffusion-dominant (nonequilibrium) removal (Jordan *et al.* 1995). The advection-dominant phase is shorter as the degree of heterogeneity (in either the contaminant distribution or soil permeability) increases.

The effectiveness of SVE in removal of vadose zone contamination is due to the volatility of the contaminants, and the gas permeability of the contaminated soil. SVE also enhances *in situ* biodegradation of many organic contaminants, especially petroleum hydrocarbons. Biodegradation associated with induced air flow (*bioventing*) is discussed in more detail later.

Contaminant Volatility

The property of volatility is characterized by the pure vapor pressure of a contaminant present as a nonaqueous phase liquid (NAPL), or by the Henry's constant if it is present only in dissolved and sorbed phases. Vapor pressure can be translated in terms of the carrying capacity of the gas phase of the contaminant. For example, a compound with a vapor pressure of 0.1-mm Hg at 25°C can achieve a vapor concentration up to 5.4 micromoles per liter of air, corresponding to the minimum vapor pressure for which SVE is practical (Hutzler *et al.* 1989). However, this lower limit of vapor pressure may be optimistic because the maximum concentration is rarely reached in field applications for reasons described below.

When contamination is present as a NAPL mixture, the capacity of the vapor phase for each contaminant is reduced to an amount directly proportional to its mole fraction in the NAPL phase (Chapter 1). Johnson *et al.* (1990a) discuss applications of Raoult's law to SVE performance. The contaminant removal observed by monitoring the SVE offgas may appear similar to the hypothetical curve shown in Figure 7-2.

The volatilization of a compound from the aqueous phase is primarily a function of its Henry's constant, which depends on the compound

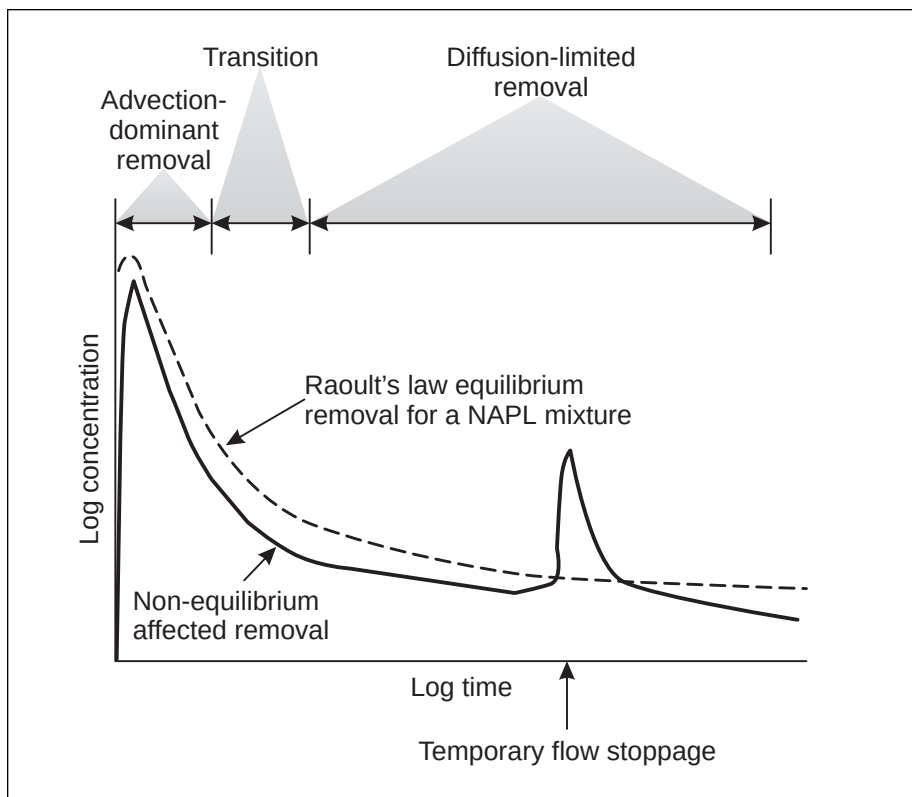


Figure 2. Characteristic offgas concentrations observed during SVE in conventional configurations in permeable soils with NAPL contamination. Adapted from Hiller and Gudemann (1989) and Johnson *et al.* (1990a).

vapor pressure and aqueous solubility. In general, compounds with what is considered sufficiently high vapor pressure usually also have a high enough Henry's constant for SVE to be effective, that is, greater than 1 L atm/mole. (Jordan *et al.* 1995). Notable exceptions are miscible organic compounds, such as many alcohols, phenol, and acetone, all of which have high vapor pressures (greater than 80 mm Hg) but low Henry's constants (less than 0.04 L atm/mole) due to their high solubility in water.

Mixtures of dissolved contaminants increase, slightly, the volatility of most of the individual constituents, as their solubilities often decrease in the presence of other compounds. This effect is minimal and exceptions

exist when substances (such as surfactants or cosolvents) are present that increase solubility.

Contamination is always present in a heterogeneous distribution. Moreover, air flow follows the paths of least resistance (such as the shortest distance or highest permeability). Therefore, not all of the induced air flow will contact contamination. This bypassing of the contamination leads to offgas concentrations that are lower than the ideal concentration based on equilibrium calculations as illustrated in Figure 7-2. Grain-scale mass transfer processes also cause concentrations to be lower than equilibrium values. Both causes will result in abrupt increases in offgas concentrations when SVE flow is interrupted. From a practical view, differentiation between causes of nonequilibrium is unnecessary, but it remains an area of active research for development and testing of mathematical models for SVE performance prediction.

Permeability

Permeability is the key factor determining whether a sufficient vapor flow for practical achievement of cleanup goals can be achieved. In SVE operations, soil permeability is the ability of air to flow through the vadose zone. Gas density and viscosity also affect gas flow, but to a much lesser extent for typical SVE applications (Johnson *et al.* 1990a; Falta *et al.* 1989). Gas permeabilities are a complex function of gas-filled porosity and pore size distribution. The gas permeability is the product of the intrinsic permeability, k , and the gas phase relative permeability, k_{rg} . In the vast majority of SVE projects, gas permeabilities are estimated *in situ* by applying suction to a venting well, much like aquifer permeabilities use pumping tests.

The minimum level of soil-gas permeability at which SVE is practical is difficult to establish because it depends on the extent of contamination and the degree of anisotropy and heterogeneity of the soils, among other factors. Shallow contaminated zones of limited areal extent can be treated more efficiently than large zones of contamination. A highly heterogeneous soil may have a high permeability measured in a pilot test, but most of the flow is concentrated in localized, high-permeability layers, and flow through the lower permeability matrix blocks is negligible. In this case, remediation is limited by the rate of

diffusion from the low permeability zones and may be quite slow, despite the high bulk permeability.

Implementation

SVE is considered a presumptive remedy for volatile organic chemical (VOC) contamination in the vadose zone, where the flow of air can be induced at a rate sufficient to flush the gas-filled porosity in the treatment zone on, at most, a daily basis. This qualitative criterion is consistent with the limited performance data available to date. For example, based on the projects listed in Table 7-1, several hundred to hundreds of thousands of gas pore volume flushes are required to reduce contamination levels to meet risk-reduction objectives. Quantitative guidance is not yet readily available because of a lack of predictive tools. Nevertheless, despite the lack of rigorously based approaches, design and operation of SVE has been successful at many sites (Table 7-1).

Table 7-1 lists a range of SVE applications that have been implemented for various site and contaminant conditions. The volume of treated soil at SVE sites ranges from 650 cubic yards to more than 200,000 cubic yards. Chlorinated solvents and/or fuel contaminants are the most common problem, and concentrations range from low values, where probably only dissolved and sorbed phases were present, to sites where substantial NAPL contamination was present (upwards of 40 pounds of contaminants per cubic yard of soil). Reported costs vary from a few dollars per cubic yard at large sites with low levels of contamination, to more than a thousand dollars per cubic yard at sites with severe geological limitations and heavy contamination. Moreover, some of the projects were completed while others are works in progress. The information in these reports is useful for compiling evidence of the feasibility of SVE for many sites.

Historical Development

SVE was developed in the early 1980s. Identifying the “first” application is controversial and was the subject of at least one patent suit in the mid-1980s. The rapid acceptance of SVE as a soil treatment technology was due in part to the relative simplicity of the governing principles (as outlined above), the early development of straightforward

TABLE 7-1 Summary of SVE performance at field sites in the U.S. from USEPA (1996 and 1998).

Site Name	Contaminant Type	Maximum Soil Concentration (mg/kg)	Quantity of Contaminants (lbs)	Quantity Removed (lbs)	Treatment Volume (yd ³)	Soil Type(s)	Treatment Depth (ft)	Minimum Permeability (cm ²)	Maximum Permeability (cm ²)
Commencement Bay, South Tacoma Channel Well 12A Superfund	chlorinated aliphatics	19,000	571,000	n/a	98,200	sand, gravel	40	4.2E-07	5.4E-07
Fairchild Semi-Conductor Corporation Superfund	chlorinated aliphatics, xylenes	4,500	700,000	16,000	42,000	sand, gravel, w/silt and clay layers	60	1.8E-05	1.2E-04
Hastings Groundwater Contamination Superfund	chlorinated aliphatics	n/a	n/a	600	185,000	upper clayey silt, below fine to very fine sand	125	1.9E-10	6.2E-08
Hill AFB Site 914	jet fuel (JP-4)	10,200	200,000	211,000	5,000	sand, gravel w/clay lenses	50	4.7E-08	7.8E-08
Luke AFB North Fire Training Area	waste fuels & JP-4	1,400	n/a	12,000	n/a	silty sands, clean sands, inorganic silts	60	1.5E-08	4.5E-07
McClellan AFB Operable Unit D, Site S	chlorinated aliphatics	3,000	n/a	113,000	n/a	silty sands, fine sand, silty/clayey sand and gravel	100	1.0E-11	1.7E-08
Rocky Mountain Arsenal, Motor Pool Area	chlorinated aliphatics	n/a	n/a	70	34,000	lenses, 1-3 foot clay layer	60	1.7E-06	2.9E-05
Sacramento Army Depot Operable Unit 3 (Tank 2)	chlorinated aliphatics, waste fuel	11,000	n/a	500	650	silt	20	2.6E-11	9.3E-09

continued

TABLE 7-1

Summary of SVE performance at field sites in the U.S. from USEPA (1996 and 1998) (continued).

Site Name	Contaminant Type	Maximum Soil Concentration (mg/kg)	Quantity of Contaminants (lbs)	Quantity Removed (lbs)	Treatment Volume (yd ³)	Soil Type(s)	Treatment Depth (ft)	Minimum Permeability (cm ²)	Maximum Permeability (cm ²)
Verona Well Field Superfund, Thomas Solvent Raymond Road (OU-1)	chlorinated & nonchlorinated aliphatics	n/a	16,500	45,000	26,700	fine to medium sand w/gravel and silt/clay	20	1.0E-07	2.0E-07
Camp LeJeune Military Reservation, Area A	chlorinated aliphatics, benzene	n/a	n/a	n/a	17,500	fine to medium sand w/traces of silt and clay	12	1.2E-07	2.8E-07
Davis-Monthan AFB Site ST-35	fuel	320,000	n/a	587,000	63,000	sandy clay with interbedded gravels and sands	n/a	n/a	n/a
Fort Richardson Bldg. 908 South	diesel fuel	17,000	n/a		4,600	glacial deposits	55	n/a	n/a
Holloman AFB Sites 2 & 5	fuel	17,500	n/a	44,000	9,500	clean to silty sands interbedded w/silt & clay	15	n/a	n/a
Intersil-Siemens Superfund	chlorinated aliphatics	11,000	n/a	3,000	280,000	interbedded sand and gravel with silt and clay	100	n/a	n/a
Seymour Recycling Corporation Superfund	chlorinated aliphatics	>1,000	200,000	29,000	200,000	sands, silts	6	n/a	n/a
Tyson's Dump Superfund	chlorinated aliphatics	250,000	n/a	200,000	30,000	clayey sand to silty sand	10	n/a	n/a

continued

TABLE 7-1

Summary of SVE performance at field sites in the U.S. from USEPA (1996 and 1998) (continued).

Site Name	Maximum Design Flow (cfm)	Vertical Vents	Horizontal Vents	Offgas Treatment	Capital Cost	Annual O&M Cost	Total Cost	Status	Operating Duration (years)	Literature Reference	Est. Pore Volume Flushes
Commencement Bay, South Tacoma Channel Well 12A Superfund	3,000	22		GAC w/regeneration	\$5,314,000	\$100,000	n/a	Ongoing 1994	2.5	USEPA (1995)	14,868
Fairchild Semi-Conductor Corporation Superfund	9,000	39		GAC	\$2,100,000	\$1,350,000	n/a	Cleanup Complete	1.3	USEPA (1995)	55,480
Hastings Groundwater Contamination Superfund	860	10		GAC	\$210,000	\$160,000	\$370,000	Cleanup Complete	1.0	USEPA (1995)	905
Hill AFB Site 914	1,500	7		catalytic incinerator	\$335,000	\$132,000	\$599,000	Cleanup Complete	2.0	USEPA (1995)	116,800
Luke AFB North Fire Training Area	95	1		thermal oxidation	\$297,000	\$210,000	n/a	Cleanup Complete	1.2	USEPA (1995)	n/a
McClellan AFB Operable Unit D, Site S	2,500	17		catalytic oxidation	\$692,000	\$937,200	n/a	Ongoing 1994	1.0	USEPA (1995)	n/a
Rocky Mountain Arsenal, Motor Pool Area	340	2		GAC	n/a	n/a	\$74,600	Cleanup Complete	1.4	USEPA (1995)	2,758

continued

TABLE 7-1**Summary of SVE performance at field sites in the U.S. from USEPA (1996 and 1998) (continued).**

Site Name	Maximum Design Flow (cfm)	Vertical Vents	Horizontal Vents	Offgas Treatment	Capital Cost	Annual O&M Cost	Total Cost	Status	Operating Duration (years)	Literature Reference	Est. Pore Volume Flushes
Sacramento Army Depot Operable Unit 3 (Tank 2)	365	8		GAC	\$216,000	\$808,800	n/a	Cleanup Complete	0.4	USEPA (1995)	45,547
SMS Instruments Superfund	300		2	catalytic oxidation w/acid gas scrubber	\$267,800	\$182,700	\$450,521	Cleanup Complete	2	USEPA (1995)	93,440
Verona Well Field Superfund, Thomas Solvent Raymond Road (OU-1)	1,600	23		catalytic oxidation, GAC	n/a	n/a	\$1,645,281	Cleanup Complete	4.0	USEPA (1995)	46,662
Camp LeJeune Military Reservation, Area A	500	8	1	GAC	\$222,400	\$247,500	\$469,900	Cleanup Complete	0.7	USEPA (1998)	3,708
Davis-Monthan AFB Site ST-35	123	6		burned as fuels in engines used to operate blowers	\$162,000	\$24,545	\$207,000	Ongoing 1996	1.8	USEPA (1998)	697
Fort Richardson Bldg. 908 South	220	2		none	\$116,900	\$13,530	\$252,200	Ongoing 1998	1.1	USEPA (1998)	10,086
Holloman AFB Sites 2 & 5	70	22		none	\$343,000	\$205,000	\$610,000	Closure Pending 1998	3.0	USEPA (1998)	4,303
Intersil-Siemens Superfund	38	7		GAC	\$550,000	\$41,905	\$770,000	Cleanup Complete	5.3	USEPA (1998)	139
Seymour Recycling Corporation Superfund	123		19	GAC	\$1,200,000	\$750,000	n/a	Ongoing 1996	4.0	USEPA (1998)	479
Tyson's Dump Superfund	15,000	90		GAC	\$22,000,000	\$5,350,000	\$43,400,000	Cleanup Complete	4.0	USEPA (1998)	389,333

design guidance (Johnson *et al.* 1990b; U.S. EPA 1991; Michaelson 1993), and the standardization of equipment and materials (Hutzler *et al.* 1989).

SVE gained acceptance more rapidly than any other innovative treatment technology (Gierke and Powers 1997). Two factors contribute to the continued popularity of SVE: its successful remediation of many sites where effective flows are established (see more in the “Status” section below, and in U.S. EPA 1995 & 1998), and its effectiveness in reducing health risks to an acceptable level, so that treatment is no longer necessary. Demonstrations of complete removal of contaminants are few.

The basic design, installation, and operational practices have not changed substantially since those described by Johnson *et al.* (1990b), U.S. EPA (1991), Michaelson (1993), and, more recently, in a comprehensive text by Holbrook *et al.* (1998). Design refinements and new developments focus on improvements in offgas treatment, blower performance and durability, and efficiency of screens. Predictive tools for forecasting SVE performance and optimizing system design have been developed but are not yet fully proven (Jordan *et al.* 1995).

Design Considerations

The basic design considerations for SVE are the number and placement of extraction vents, selection of blower(s) to achieve desired flow rates, and selection of the offgas treatment system (Figure 7-3). When suction is applied using a blower, air flows from the ground surface, through the contaminated zone, and to extraction vents. An impermeable barrier at the ground surface may impede the flow of atmospheric air and is sometimes used to affect air flow pattern to vents. Where the treatment area is covered or where heterogeneities/anisotropic conditions exist that limit vertical air movement, subsurface flows can be modified by either allowing air to flow into inlet vents (vents open to the atmosphere) or by injecting air or treated offgas into vents. Sparge wells, which inject air below the water table, are also sometimes used in SVE. Inlet vents are usually sufficient to prevent stagnant zones and encourage flow deep into heterogeneous/anisotropic soils. Air injection can cause contaminant vapors to move away from the treatment zone. It is

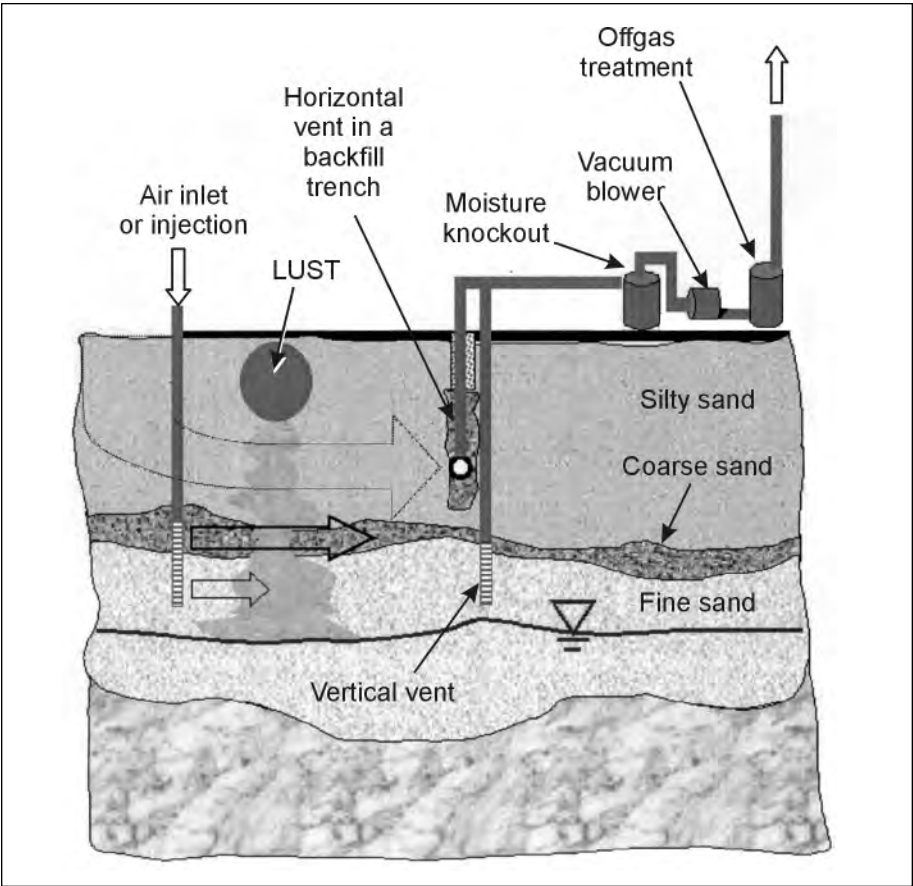


Figure 7-3. Conventional SVE configurations for removal of volatile contaminants from the vadose zone shown for a leaky underground storage tank (LUST) situation.

common to configure extraction vents so they can operate as either extraction or inlet vents.

Vents

Most SVE vents utilize water-well screens and casing that are installed vertically in the vadose zone, much like water wells in aquifers. Preferably, the screen on the vent is located below the contaminated zone (U.S. EPA 1991; Shan *et al.* 1992). In shallow settings (less than

4-m deep), installation of horizontal vents to obtain more efficient vapor flow is feasible and sometimes more practical (U.S. EPA 1991; Aiken 1992).

The number of vents is usually determined by the size of the contaminated area and the radius of influence (ROI) of the extraction vents. Vents are situated so that their ROI overlap and encompass the contaminated area (Johnson *et al.* 1990b and U.S. EPA 1991). This oversimplified approach is increasingly recognized as inappropriate because it ignores gas residence times (flushing rates) and hence the contaminant removal rates. A more appropriate approach is to define the treatment zone around an extraction vent based on a desired flushing rate, which can be determined for homogeneous conditions using analytical approaches (Shan *et al.* 1992) or for more general conditions using numerical models (Jordan *et al.* 1995). In either case, induced subsurface air flow is affected by heterogeneities, and rarely will actual flow patterns follow idealized predictions. Site capping, proper vent installation, and inlet/injection venting are useful methods for flow pattern control.

Vertical vent installations are predominantly completed in unconsolidated deposits using hollow-stem augers and either pea-gravel or coarse-sand filterpacks, as depicted in Figure 7-4a. Proper grouting near the ground surface is necessary to minimize “short-circuiting” of air through the filterpack. Direct-push technologies can be used to install vents in high-permeability, coarse-grained soils, but precautions need to be taken to ensure that screens do not become plugged with fine-grained sediments. There are no development methods to flush well screens in the unsaturated zone like those for wells in the saturated zone. Also, short-circuiting is likely when the top of the screen is near the ground surface. Horizontal vents can be installed in a back-filled trench as shown in Figure 7-4b, or with directional-drilling techniques. Directional-drilling installations are susceptible to screen-plugging unless precautions are taken to minimize screen contact with fines, or clog removal procedures are performed. Stainless steel wire-wrap screens are least susceptible to chemical attack and are more pneumatically efficient than slotted screens. High-density polyethylene and polyvinyl chloride slotted screens are more economical than stainless steel and are chemically resistant to petroleum hydrocarbons and chlorinated organics when concentrations are low. Steel and polyvinyl chloride are the two most

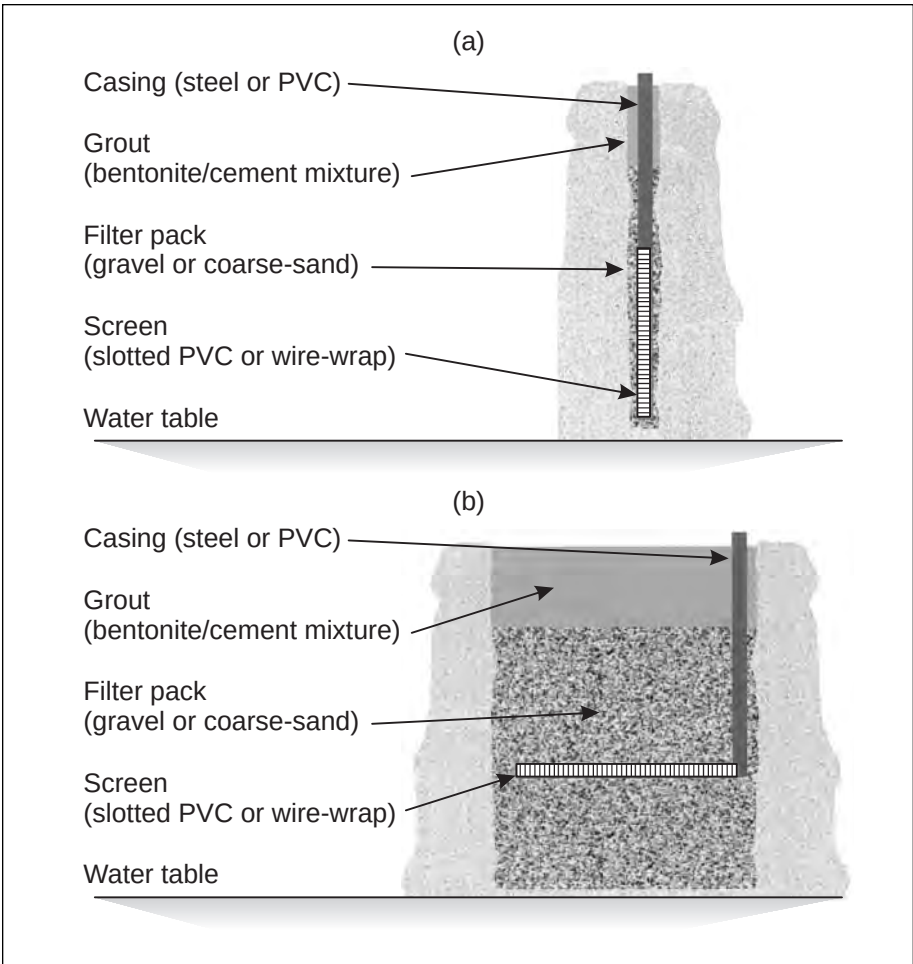


Figure 7-4. Vent configurations in Unconsolidated Deposits: (a) vertical and (b) horizontal trench.

common materials for vent casing and above-ground plumbing. Nominal diameters for screens, casing, and piping are usually between $\frac{3}{4}$ and 4 inches.

The above-ground plumbing should include valves and ports to allow flexibility in flow configurations, flow metering (rates and pressures), and ports for concentration monitoring to optimize system performance.

Because there is no readily available design guidance for the above-ground plumbing specific for SVE, refer to a fluid mechanics handbook that includes gas flows. Pressure losses in the piping and fittings can be significant and should be considered (Peramaki 1993).

Blower Selection

Blower selection is critical to power requirement minimization. In permeable soils, dynamic-displacement blowers typically are used to induce gas flow. Positive-displacement blowers, usually rotary-lobe, are used where the soil permeability is low. Dynamic-displacement blowers can provide high flows at low suctions, but blower performance diminishes rapidly as suction increases. Positive-displacement blowers operate at a constant flow rate over a wider range of suction, but their maximum flow rate is less than that of dynamic-displacement blowers.

In order to determine blower size for a full-scale operation, a pilot test measures *in situ* gas permeabilities. It is common to rent a blower for the pilot test and size the blower(s) that will be required for the full-scale remediation based on the pilot performance measurements (flows and vacuums), adjusted for the full-scale plumbing configurations. At sites where the soils are highly heterogeneous, such as glacial deposits, several pilot tests in different locations are performed to ensure that the desired flows can be achieved across the entire treatment area.

Thermally protected, intrinsically safe, explosion-proof equipment should be used. Blowers should not be throttled to control flow rates but rather plumbed to bleed in air from above-ground; however, this condition can be avoided altogether by properly selecting a blower to minimize power usage. Blowers must be protected from dust by filters and from liquid droplets by moisture separators or knockout drums, as illustrated in Figure 7-3. Systems are configured with a float switch to shut down the blower so that the moisture separator can be drained when it fills with water. The blower, moisture separator, and associated electrical controls are purchased as a complete system and configured to the site requirements. Three-phase 230/460-voltage blower motors are the most efficient and should be used if the appropriate electrical service is available.

Offgas Treatment

The offgas treatment system can be the most expensive part of the remediation system. Granular activated carbon has the lowest capital cost, but it can be rapidly saturated, and is a poor choice where chemicals are recovered at high concentrations. Combustion and thermal/catalytic oxidation units are more expensive to purchase than granular, activated carbon but are cheaper to operate when offgas concentrations are high and if the contaminants are combustible and/or can be oxidized. Offgas treatment units/systems can be rented and some vendors provide pilot-scale units to be tried during permeability tests. Pilot tests tend to over-predict contaminant removal rates. Therefore offgas treatment should be considered over the long term by providing for flexibility to either adjust operating conditions when concentrations diminish or to switch to other treatment options.

Costs

Extraction vent installation and the purchase of an offgas treatment system and blower(s) comprise the majority of capital costs. Operating and maintenance (O&M) costs include the costs of supplying power for the blower(s) and for operation of the offgas treatment system (such costs include fuel replenishment, replacement/regeneration of carbon, etc.). Initial site characterization, performance assessment, and monitoring costs are often close to the costs of remediation alone.

Augmenting Technologies

Conventional SVE performs well at sites where the contaminants are relatively volatile and soils are relatively permeable to air. Augmenting technologies can be implemented to enhance both volatility and permeability at sites where these factors are limiting. There are four important methods for increasing the volatility of contaminants by heating soils: thermal conduction, radio-frequency, 6-phase joule, and steam injection; these technologies are described in the following pages. Soils also are heated by injecting hot air into vents, and this simple augmentation increases SVE performance. Hot air injection is a straightforward modification of conventional SVE and it is not described as a separate technology .

SVE usually performs poorly in low-permeability soils, especially those containing clays, because air flow rates are too slow to flush out contaminants. Rock and soil formations can be fractured to enhance their permeability. Pneumatic fracturing increases SVE performance in glacial drift as well as fractured shale (Murdoch *et al.* 1994; Frank and Barkley 1995), and hydraulic fracturing also enhances SVE in a variety of low-permeability formations (Murdoch *et al.* 1994). The efficacy of fractured systems for long-term complete cleanup is unknown because diffusion of contaminants from the unfractured matrix to the fractures may require a longer time than is known (Grathwohl 1998).

Deep soil mixing disrupts the soil fabric with a large auger, markedly increasing air flow rates within the mixed volume. Hot air or steam also can be injected to increase the volatility of contaminants, further increasing SVE recovery (Siegrist *et al.* 1995).

Large-scale, small-pressure disturbances associated with weather systems can cause gas flow into and out of the subsurface; this process is called “barometric pumping.” Barometric pumping is used as a long-term, low-operating-cost form of SVE for slow removal of diffusion-limited contamination through a combination of volatilization and enhanced bioremediation.

Monitoring

SVE is monitored *in situ* by measuring pressures, obtaining gas samples from vents, or obtaining soil samples at various times during the project. It is monitored aboveground by measuring pressures, flow rates, and compositions of gases at the access ports in the process equipment. The variables typically monitored during SVE operation are listed in Table 7-2, but some of these variables are not necessarily representative of subsurface conditions. For example, subsurface gas pressures are needed during pilot tests for determining gas permeabilities; however, during full-scale operation they are not necessarily indicative of subsurface gas velocities, nor even useful for identifying areas where flow is occurring, because suction can be observed at vents even where the air is stagnant. A more effective measure of vent influence is change in concentrations of contaminants, oxygen, or tracers in soil gas.

Concentrations of contaminants are difficult to measure at sites where contaminants are present as mixtures. Typically, several constituents are

TABLE 7-2		Variables monitored during SVE design activities and operation.	
Property	Measurement Location	Data Purpose	Operational Phase
Gas Pressure	<i>In situ</i> at vents	Establish radius of influence	Pilot test(s)
		Determine subsurface pressure gradients and flow directions	Pilot test(s) & Full-scale operation
		Quantify gas permeabilities	Pilot test(s)
	Above-ground piping	Size blower(s) Ensure operation consistent with blower capabilities	Pilot test(s) Full-scale operation
Gas Flows	Vent(s)	Control system flow	Full-scale operation
		Determine air permeability and blower performance required	Pilot test(s)
		Quantify contaminant mass removal	Pilot test(s) & Full-scale operation
Vapor Concentrations (total & contaminants of concern)	<i>In situ</i> at vents	Measure performance	Full-scale operation
	Above-ground piping	Measure performance	Pilot test(s) & Full-scale operation
	Offgas treatment discharge	Measure offgas treatment system performance & Discharge safety and permit compliance	Full-scale operation
Soil Concentration (total and contaminants of concern)	Soil Samples	Delineate contaminated area Establish treatment performance and compliance	Pre-treatment characterization
Temperature	Flow meters	Calculation of gas flow rates and concentrations corresponding to operating conditions	Pilot test(s) & Full-scale operation
Soil moisture	Soil samples	Establish initial conditions	Vent installation

selected as contaminants of concern (COC), such as benzene, toluene, ethylbenzene, and xylene (BTEX). Equivalent and comprehensive measures are also used, such as total hydrocarbons/VOCs (gasoline range organics) or total petroleum hydrocarbons (diesel range organics). Reductions in COC concentrations do not necessarily correlate to overall contaminant removal.

Flow rates and concentration measurements help to monitor system performance and can be used, potentially, to improve operations. When removals are dominated by advection but are transitioning towards diffusion-limited, rising extraction rates increase mass removal rates even though offgas concentrations may decrease as a result of a higher proportion of bypassing or reduction in gas residence times (allowing less time for equilibration). When the removal rate is diffusion-limited (Figure 7-2), increasing the extraction rate provides a negligible increase in the mass removal rate. Combustion and catalytic oxidation methods for offgas treatment benefit from high vapor concentrations, so monitoring concentrations (in terms of fuel value) from individual extraction vents can be used to optimize the performance of offgas treatment.

Comprehensive site characterization of permeability and contaminant distributions helps to locate extraction vents in the most permeable, highest-concentration areas, and maximizes extracted vapor concentrations, leading to maximum offgas treatment efficiency.

Status

SVE is a mature technology with thousands of applications. A selection of detailed case studies (U.S. EPA 1995 & 1998) summarizes site and contaminant characteristics, system configuration and key design criteria, operational performance, capital and O&M costs, regulatory issues, lessons learned, technical contacts, and additional references.

The case studies "Modeling the Performance of a SVE Field Test," by M.E. Beshry, J.S. Gierke, and P.B. Bedient (*see page 1157*), and "Scale Dependent Mass Transfer During SVE" by C.K. Ho, describe applications of this technology in more detail (*see page 1170*).



BAROMETRIC PUMPING: PASSIVE SOIL VAPOR EXTRACTION*

SVE installation and equipment operation is impractical at many locations where it could benefit remediation. An inexpensive system using a renewable energy source and operating in the gas phase can fill the gap in these locations. Natural variations in atmospheric pressure, due to diurnal temperature fluctuations or weather changes associated with major fronts, can cause gases to flow to or from wells completed in the vadose zone. This process, called “barometric pumping,” induces large enough flow rates to provide meaningful remediation effects and can also be used for subsurface characterization.

Barometric pressure, an important, easily measured property of the near surface atmosphere, is the force per unit area generated by the weight of an air column extending upward 160 km to the top of the stratosphere (Hodgman 1952). It can be accurately measured using a simple pressure gauge, or *barometer*. The weight of the air column reflects the column’s air density, which varies markedly from the ground to the stratosphere. Air density is a strong function of temperature and it responds to heat radiated from land surfaces or water, or absorbed directly from solar radiation. Density also varies with changes in humidity, atmospheric chemistry, or other dynamic factors associated with weather systems. As a result, records from barometers show regular fluctuations or cycles. The daily cycle of sunlight and darkness causes temperature changes in the atmosphere to produce a diurnal cycle of barometric pressure that typically varies by less than a percent of the total average pressure. A complicated interplay of thermal and chemical effects in many areas cause even larger fluctuations in barometric pressure, typically a few percent of the total pressure, which occur every few days or weeks in response to major weather systems.

The fluctuating barometric pressure is transmitted into the subsurface to cause variations in the pressure of vadose zone gases, resulting in air flow from areas of high pressure to areas of low pressure in the subsurface, just as in the atmosphere. The pressure differences between adjacent zones in the subsurface that drive these flows are small and the flows that they produce are modest, often only detectable under special

*This section was contributed by J. Rossabi.

conditions. As a result, the subsurface flow caused by barometric fluctuations, until recently, has been overlooked by an environmental community eager for quick solutions to vadose zone contamination. However, when specific subsurface zones are connected directly to the surface by a vadose zone well, pressure differences are much larger and can produce flows as large as 700 liters per minute from 10 cm-diameter wells. Barometric pumping can move significant volumes of air, it occurs regularly, and it is free.

Barometric pumping was recognized as an interesting phenomenon long before it was used for remediation. Native Americans used “blow-holes” (areas that mysteriously drew in or blew out air at different times) to forecast weather and as the focal point of rituals (Fisher 1992). Speleologists recognized that some blowholes were actually caves, and they showed that the air flow in “breathing” caves varied periodically as a result of barometric cycles, wind-driven pressures, preferential solar heating, or a combination of these processes. Hydrologists have recognized barometric effects since at least 1896, when Fairbanks described a well that intermittently released natural gas when barometric pressure decreased and drew air in when pressure increased (Science 1896). He noted that the rate of gas flow increased during periods of changing weather. An early monograph describing the release of carbonic acid from soil and its replacement with oxygen from the atmosphere also mentions this effect (Buckingham 1904). Among other important observations, Buckingham predicted that the pressure fluctuation in the subsurface would lag behind fluctuations in the atmosphere, and the lag time should increase with depth.

Several processes related to barometrically-derived subsurface flow are environmentally important. Pressure fluctuations resulting from barometric effects were observed in the subsurface during experiments at the proposed Yucca Mountain, Nevada, repository for nuclear waste (Ahlers *et al.* 1998). Gas flow accompanying the pressure fluctuations can change the subsurface moisture content, which could significantly affect the flow and transport of contaminants over long periods. Thus, barometrically induced flow could affect the performance of the nuclear waste repository. The naturally induced flow of radon gas through the vadose zone and into buildings hits closer to home. Many researchers (Owczarski *et al.* 1990; Narasimhan *et al.* 1990; Tsang and Narasimhan 1992; Garbesi *et al.* 1993; Robinson and Sextro 1995) have shown that

barometric pressure fluctuations affect the transport of radon gas into houses. Other investigators in the environmental field (Little *et al.* 1992; Massman and Farrier 1992; Pirkle *et al.* 1992; Forbes *et al.* 1993; Shan 1995; Auer *et al.* 1996; Ellerd *et al.* 1999; Rossabi 1999) examined the potential effects of barometric fluctuations on the transport of VOCs. They describe effects on shallow soil gas surveys, the transmission of the surface pressure to depth, and resultant gas transport in natural sediments with organic contamination.

Barometric pumping for remediation purposes has led to two primary applications: the injection of air to increase the oxygen content and stimulate aerobic biodegradation (Zachary 1993; Zwick *et al.* 1994), and the recovery of air and contaminated vapors (Rohay and Cameron 1992; Rossabi *et al.* 1994; Riha and Rossabi 1997; Ellerd *et al.* 1999). Both applications have counterparts, bioventing and SVE, that use mechanical pumps to move air, so the basic remedial processes employed by the applications are well known. Both passive vapor extraction and passive vapor injection can be used under the right conditions to control the migration of subsurface gas (such as landfill gas). Barometric pumping sacrifices the high flow rates achieved by pumps for the cost of operating and maintaining them. This tradeoff is attractive in circumstances where contaminants occur at low, but significant, concentrations. However, it is important to be able to estimate the potential effects of barometric pumping before it can be used for remediation.

Characterizing The Effect

At the Savannah River Site in South Carolina, significant flow of contaminated air out of vadose zone wells was observed following drops in barometric pressure. The conceptual model explaining this occurrence indicates that the air flow in and out of wells is a result of the difference in pressure between the formation at the screened zone of the well and the atmosphere at the surface. Atmospheric pressure fluctuations are damped and delayed during transmittal through the subsurface. The delay and attenuation of pressure changes in the subsurface with respect to the surface pressure produces a pressure differential that drives flow through wells between the subsurface and the atmosphere.

A test well was instrumented and monitored in detail to evaluate the conceptual model and to provide data to assess the effectiveness of the-

oretical predictions. The well was completed with a 2-m-long screen at a depth of 30 m in partially saturated sands and silts. Barometric pressure and the gas pressure at 30 m depth were recorded along with the gas flow rate into and out of the well during a 30-day test period in the spring of 1994.

The barometric pressure varied diurnally by a few mbar, but it varied by several tens of mbar over periods of three to five days during the test (Figure 7-5). The subsurface pressure showed little diurnal variation, but it always lagged approximately 12 hours behind the three- to five-day-long barometric fluctuations. That lag produces a pressure differential between the atmosphere and pore gases at a depth of 30 m. The pressure differential was commonly 5 mbar, with the greatest being about 12 mbar (Figure 7-5). In general, the differential was positive (atmospheric pressure is greatest, indicating that air flows into wells) when the barometer was rising, and it was negative when the barometer was falling (Figure 7-5).

Pressure differentials were sustained for approximately three to five days before changing sign. This defined periods of several days when the flow was either into or out of the well. For example, the pressure differential indicated that air was flowing out of the well on days 0-4, 6-7,

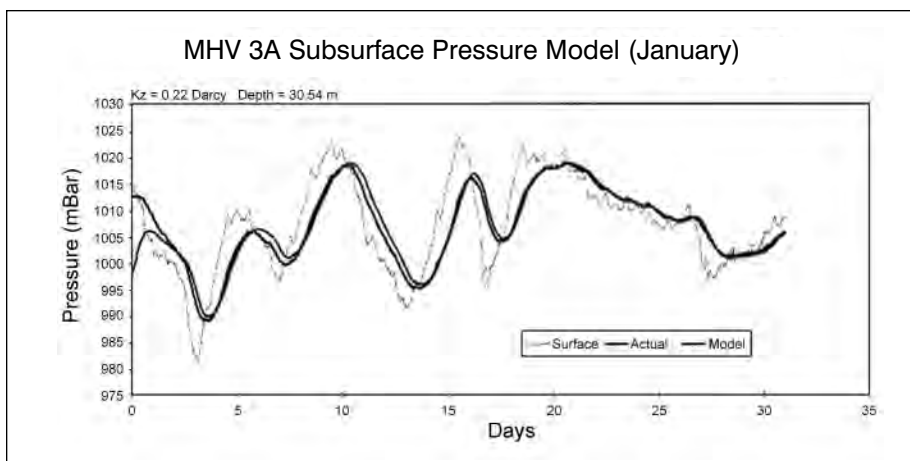


Figure 7-5. Barometric pressure, observed subsurface pressure, and predicted subsurface pressure in a well 30.5 m deep with a 2-m-long screen at Savannah River Site.

10-14, 16-17, and 21-26, whereas it flowed into the well on days 4-6, 7-10, 14-16, and 17-21. These flow periods and changes in barometric pressure corresponded to major weather systems that passed through east-central South Carolina every three to five days. Barometric pumping at this test well was driven by major weather changes, while it was largely unaffected by diurnal variations.

Improving Performance

Clearly, barometric pumping can transfer substantial volumes of gas between the atmosphere and subsurface. The natural process exchanges gas equally in both directions; that is, the volume of gas that flows into a well equals the volume that flows out when averaged over several cycles. However, most applications only require transfer in one direction (injection for bioventing or recovery for passive SVE), and transfer in the other direction may actually reduce effectiveness.

At least two check valves have been developed to limit barometric pumping to unidirectional flows (U.S. Patents No. 5,641,245 and 5,697,437). The valve discussed here is a lightweight ball about 3 cm in diameter that sits in a conical seat. It functions like a common ball-type check valve with an exceptionally small cracking pressure, markedly improving the performance of barometric pumping for remediation.

During the demonstration at the Savannah River Site, a check valve prevented air from flowing into the well during the first two flow cycles, and then it was removed for the next few cycles (Figure 7-6). During the flow cycles using the check valve, concentrations of contaminants increased rapidly and were nearly constant. However, after the check valve was removed, the contaminants showed a markedly different history. They started at dilute concentrations and increased through the recovery cycle, but they never reached the concentrations that occurred during the check valve cycles, because clean air flowed into the well and diluted contaminant vapors in the subsurface. Eventually the clean air equilibrated with contaminants in the subsurface, but the gas flow cycle was faster than the contaminant equilibration process during the Savannah River Site test. Clearly, more mass is recovered when a check valve prevents unnecessary injections of air.

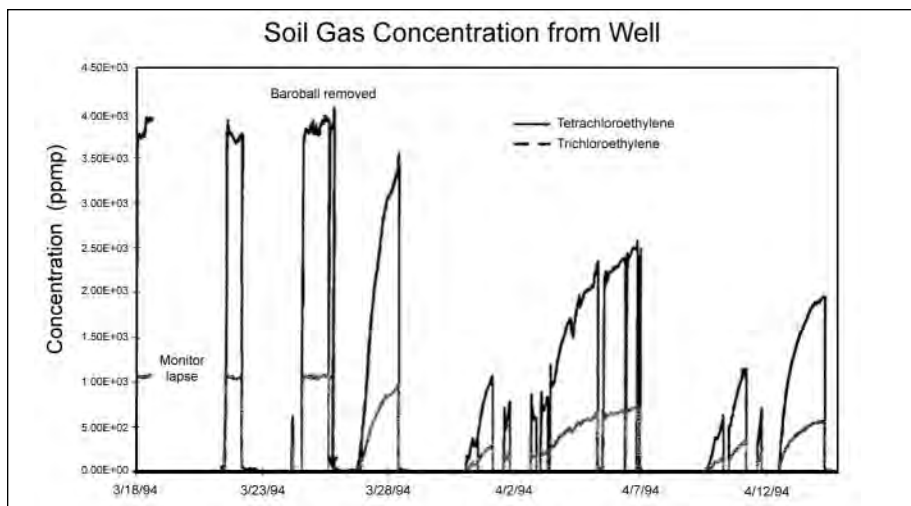


Figure 7-6. Concentrations of contaminants recovered from test well CPT RAM 16 by barometric pumping before and after removal of Baroball check valve.

Predicting Performance

Theoretical models described by Weeks (1978), Shan (1995), and Rossabi (1999) played an important role in establishing the viability of barometric pumping. A simple analytical model (Rossabi 1999) using the pressure observed at the ground surface as a boundary condition precisely predicted the pressure observed during the test described above (Figure 7-5). A similar analytical model also predicts the volumetric flow rate into and out of the subsurface (Figure 7-7). Numerical models were used to predict the effects of a check valve on the flow rate and concentration at the well (Ellerd *et al.* 1999; and Rossabi 1999). All of the predictions are remarkably similar to field observations.

Those modeling efforts have shown that barometric pumping follows well-known principles, and that the effects can be readily predicted. The performance of barometric pumping can be forecast based on the characteristics of a particular site. Barometric pumping also can be adapted as a tool for site characterization; for example, by using the analysis with a parameter estimation to determine pneumatic conductivity, or using field data to determine the distribution of contaminants. These advances pave the way for useful applications of barometric pumping.

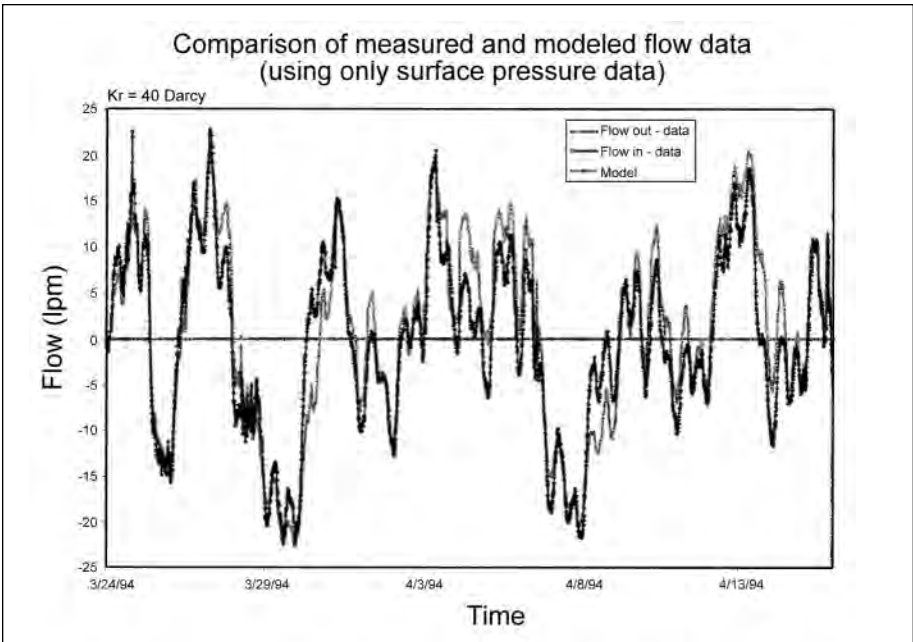


Figure 7-7. Volumetric flow rates as observed at test well CPT RAM 16 and as predicted using analyses described by Rossabi (1999).

Implementation

Barometric pumping has three primary applications in the environmental field: (1) recovery of contaminants, (2) air injection to stimulate aerobic biodegradation, and (3) characterization of the subsurface. The performance of applications that recover contaminants or inject air are both improved using a check valve at the ground surface. Those applications directly parallel SVE or bioventing processes using mechanical pumps. Commonly, barometric pumping applications are labeled “passive” SVE or “passive” bioventing. Barometric pumping moves air at slower rates than mechanical pumps, so it is inappropriate for sites where remediation must be achieved quickly, or where the rate of remediation is strongly dependent on the rate of air flow through the subsurface. At many sites, the rate of contaminant mass transfer to a mobile vapor phase is relatively slow. The rate of remediation is limited by this slow rate of mass transfer, rather than by the rate of vapor flowing

through the subsurface. In such cases, the higher rates of flow that can be achieved with mechanical pumps may contribute little to the overall rate of remediation. This type of mass transfer limitation will occur at sites where SVE has already been operating for a considerable period, or where the initial concentrations are relatively low, such as at the periphery of a plume. At sites where only modest reductions in concentration are required to meet regulatory requirements, barometric pumping can successfully remediate while reducing operating costs.

Some sites are well suited to remediation by SVE or bioventing, but the economics of installing a pumping system are intractable; for example, at remote locations lacking a connection to electrical utilities, or at sites where there is not an economically viable, responsible party. Economic issues block any meaningful remedial action around the edges of many active sites, where monitoring wells penetrate contaminated ground but are not attached to an SVE system. Barometric pumping is ideal for these circumstances because it can be implemented quickly and inexpensively, and it provides a remedial process at locations that would otherwise be neglected.

The case study "Passive Soil Vapor Extraction at the SRS Miscellaneous Chemical Basin," by B. Riha and J. Rossabi, describes an application of barometric pumping at the Savannah River Site. *See page 1177.*



Barometric pumping is also used for subsurface characterization. Flow rates from a well and the accompanying barometric record can be used to deduce the pneumatic conductivity of the subsurface (Rossabi 1999). Moreover, chemical analyses of the vapors expelled during barometric pumping can provide insights into the amount and distribution of contaminant mass, and the rate of mass transport in vapor phase. The concentrations of vapors expelled during the first two cycles of barometric pumping shown in Figure 7-6 (check valve installed) are representative of actual subsurface conditions, whereas the concentrations during subsequent cycles (no check valve) do not accurately represent ambient subsurface conditions, because the air flowing into the well diluted the concentration of vapors. Therefore, check valves are

recommended to improve the characterization of distribution and concentration of contaminants.

Passive soil vapor injection can be used to stimulate aerobic degradation of contaminants in the subsurface by providing oxygen from the atmosphere to zones where oxygen has been depleted by chemical or biological activity. In these cases, surface air is unable to adequately penetrate the subsurface because of physical permeability limitations or because of depletion in shallower zones. A well is used to transmit air directly to subsurface zones by barometric pumping.

Important Factors

Barometric pumping like SVE and bioventing is best suited to formations that are relatively permeable with relatively low moisture contents. (Like SVE, barometric pumping is hindered by sorption in extremely dry clays.)

Barometric pumping should be considered at sites where the rate of contaminant recovery is limited by the rate of mass transfer to a mobile vapor phase, rather than by the rate of air flow through the site. It also should be considered at sites that could benefit from SVE, but where the cost of installing an SVE system cannot be justified. Finally, the use of barometric pumping as an interim measure, for example, when permit or design issues delay the installation and operation of more aggressive treatment methods, is an option that is often overlooked.

Several factors uniquely affect barometric pumping performance. The process relies on a lag time between the barometric pressure and the pressure at the depth of the well screen to produce a differential that drives flow. Generally, the duration of the lag, and the magnitude of the pressure differential, increases with the depth of the well screen. As a result, the effectiveness of barometric pumping will usually increase with depth (assuming other factors are independent of depth).

Effectiveness is improved by the presence of a confining layer, such as a bed of fine-grained sediment, above the well screen. The ROI of the well increases, just as it does for a vapor extraction well, but also the rate of recovery increases by slowing the transmission of the pressure signal and increasing the pressure differential between the well and the atmosphere. Other factors, such as seasonal moisture changes or ice forma-

tion, that affect the permeability in layers between the surface and the target zone in the subsurface impact barometric pumping performance.

Status

Barometric pumping has been used to create passive SVE systems at DOE, DoD, and private sites in the United States and abroad. Since 1990, hundreds of sites have used barometric pumping to augment more aggressive remediation systems or as standalone systems. Few careful studies of the removal effectiveness have been conducted because the chemical analysis costs are usually far greater than the system operating costs, or even the system installation costs (Riha and Rossabi 1997). At least two check valves with a small cracking pressure designed to improve the performance of barometric pumping have been patented (US Patent Nos. 5,641,245 and 5,697,437). One is commercially available under the tradename Baroball, and the other should be available soon. Published methods for designing barometric pumping applications are available largely as a result of research during implementations at DOE sites. *The Passive Voice*, an electronic newsletter edited by V. J. Rohay, was started in 1993 and continues to be an important source of information describing remedial applications for barometric pumping.

HEATING TECHNOLOGIES

Four methods of heating the subsurface to improve remediation are currently available. All of them are intended to increase the partitioning of organic chemicals into vapor phases where they can be recovered by SVE processes. In addition, one of the heating methods, conductive heating, creates temperatures, of 500°C or higher that will oxidize contaminants in place. Six-phase resistive heating and RF heating can also create subsurface temperatures above 100°C, but they have primarily been used to heat the subsurface to the boiling temperature of water. This amount of heating will increase the rates of both degradation and recovery. Hydrous pyrolysis may oxidize organic contaminants under some conditions, and the rate of biodegradation can increase markedly with a rise in temperature.

The four heating methods draw on significantly different physical processes to transport energy into the subsurface, and, as a result, each

is particularly appropriate for certain site conditions. Thermal conduction potentially creates the hottest temperatures and is relatively insensitive to material properties, but it will only affect a small region around each heating element. Radio-frequency heating uses electromagnetic radiation that readily penetrates subsurface formations, extending the size of the region that can be heated. Steam flooding uses a hot fluid to carry heat into the subsurface. Steam follows high permeability pathways through the subsurface, however, so it preferentially heats those paths and leaves the tighter areas relatively cool. Electrical resistive heating passes an electrical current through the subsurface, heating formations where the electrical current flow is the greatest. Interestingly, electrical current flows through clays and silts more readily than through sand, so electrical resistive heating preferentially warms the clay-bearing horizons that are avoided during steam injection.

- **Effect Of Heat On Chemical Properties**—Heating improves the performance of SVE by changing the partitioning and transport properties of contaminants. For example, the following processes accompany an increase in temperature:
 - Vapor pressure of free-phase NAPL increases (Lyman et al. 1990).
 - Henry's law constant may increase due to the rise in vapor pressure, but can be constrained by smaller increases in water solubility (Davis 1997).
 - Liquid-solid sorption and vapor-solid sorption typically decrease (Ong and Lion 1991).
 - Soil moisture content decreases and very dry conditions can cause a marked increase in vapor-solid sorption (Ong *et al.* 1992)
 - Removal of soil water opens new flow paths, decreasing diffusion lengths for dead-end pore-space-trapped contaminants (Davis 1997)
 - Diffusivity in water and air increases (Lyman *et al.* 1990)
 - Volatilization of water induces steam distillation, increasing the volatilization rate of chemical species (Davis 1997)
 - Water expansion from liquid phase to vapor phase induces advection flow and mixing (Davis 1997)

- **Energy Requirements For Heating the Vadose Zone**—The four heating technologies are methods for delivering thermal energy to the subsurface, and the final temperature that is achieved will depend on the amount of heat that is delivered. The ambient temperature at a depth of 10 m is roughly 10°C in most areas. Adding thermal energy will first increase subsurface temperatures from ambient conditions to 100°C, the boiling temperature of water. Adding more heat will boil pore water and warm the surrounding region, but the maximum temperature will be maintained at 100°C until the liquid water has been removed from the vicinity of the heaters. After liquid water has been completely removed by boiling, temperatures may rise above 100°C.

The energy required to warm porous materials from ambient conditions to 100°C depends on the heat capacity. In general, the effective heat capacity is a weighted average of the heat capacities of soil solids, C_R , and water, C_w . The weighting depends on the porosity, ϕ , densities of solids, ρ_R , and water, ρ_w , and the degree of water saturation, S_w . The heat required per unit volume to change the temperature of a porous material by ΔT is

$$\Delta M_{\Delta T} = [C_R(1 - \phi)\rho_R + C_w\phi\rho_w S_w] \Delta T \quad (7.1)$$

neglecting the change of heat in the gas and non-aqueous phases. This shows that the heat required to change the temperature will depend on the degree of saturation; it will decrease as the initial saturation becomes drier. For example, consider a material with a porosity of 0.35 containing solids with a density of 2.6 gm/cm³. The heat capacity of common minerals is roughly 0.2 cal/g°C, and water is 1.0 cal/g°C. The energy required to heat that soil from ambient conditions to the boiling point of water ($\Delta T = 90^\circ$) is 62 cal/cm³ when the soil is initially saturated, 52 cal/cm³ when the degree of saturation is 0.7, and 30 cal/cm³ when the soil is initially dry ($S_w = 0$).

Temperature will be maintained at 100°C while water is evaporated. The latent heat of vaporization of water, $u_{\text{vap,water}}$, is 540 cal/gram, and the energy required to boil all the water initially present in the soil is

$$\Delta M_{\text{vap}} = u_{\text{vap,water}} \phi \rho_w S_w \quad (7.2)$$

Boiling all the water in the soil cited above, for example, will require 189 cal/cm^3 when the soil initially is saturated, and 132 cal/cm^3 when the initial degree of saturation is 0.7. The energy required to boil water from soil decreases as the initial degree of saturation diminishes, but clearly, several times more energy may be required to boil all the water than to raise the temperature from ambient conditions to the boiling point.

All heating technologies must deliver thermal energy of the amounts described above to change the temperature or boil water in the subsurface. The technologies differ in the mechanism used to transfer the thermal energy through the subsurface, and these differences in the mechanism of heat transfer are the primary factor affecting their relative performances under different conditions.

- **Soil Vapor Recovery And Treatment**—Heating increases the performance of SVE, but it can also increase the cost of the SVE operation. One factor affecting costs is related to the increase in mass of water caused by heating air. The saturated humidity of air at 10°C is $10 \text{ gm of water/m}^3$, but increasing the temperature to 40°C raises the saturated humidity by a factor of 5 to $50 \text{ gm of water/m}^3$. The increase in water content in recovered air needs to be managed by processing equipment associated with the SVE system. This typically includes equipment to condense and treat the recovered water. In addition, water may condense in cooler, low-lying areas along the SVE pipes. This can restrict vapor flow through the pipes, and the water may freeze in cold weather. Those problems can be addressed by including heat tracing or other modifications in the above ground treatment system.

Conductive Heating*

One of the more straightforward methods of improving SVE is to warm the subsurface by inserting rods containing electrically resistive heaters. The rods radiate heat from their outer surface and the heat is conducted through the enveloping soil (Figure 7-8). The rate of heat transfer, or heat flux, during conduction is proportional to the tempera-

*This section was contributed by J. Reed and D. Conley.

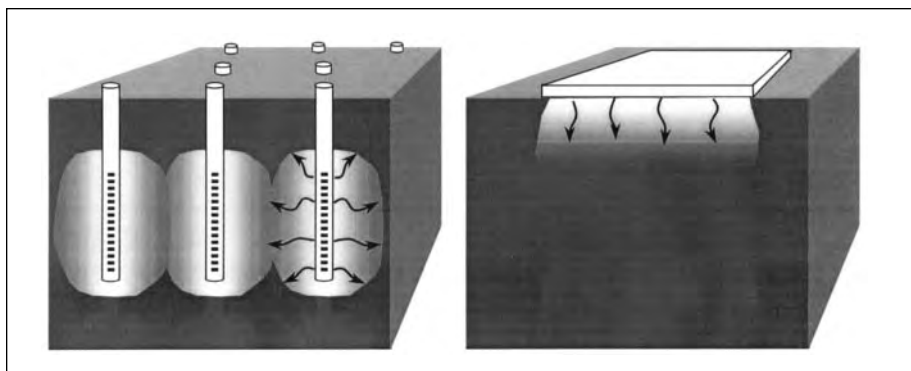


Figure 7-8. Thermal wells and blanket heaters used to raise subsurface temperatures by heat conduction.

ture gradient in the soil. Water near the heaters may be vaporized and the resulting steam will cause some convective heat transfer into the formation. This effect is relatively minor, however, with most heat transfer occurring by thermal conduction.

Thermal conduction from a heated rod produces a temperature profile that decreases with radial distance from the rod (Figure 7-9a). This is an inevitable consequence of the geometry of a rod-like heater, and it is analogous to the change in hydraulic head radially away from a well in an aquifer. Temperatures are greatest in the vicinity of the rod and are limited only by the thermal integrity of the heating element. As a result, this process is capable of developing extremely hot temperatures, in excess of 500°C, particularly when an array of heaters is used. Most organic compounds are destroyed in the presence of oxygen at those temperatures. The *in situ* temperature decreases with distance from the heater, however, so the zone where oxidization of organic compounds occurs is confined to within a few feet of the heater. Significant temperature increases occur beyond the zone where organic compounds can be oxidized. In this region the important remedial effect is evaporation of organic chemicals, increasing their availability for vapor extraction.

Temperatures in the vicinity of a heated rod will depend on the power of the heater, the radiant heat transfer between the rod and the soil, the thermal conductivity and heat capacity of the soil, and the spacing of neighboring heaters. The heating rate increases with thermal conductivity and decreases with heat capacity of the heated material. Both thermal conductivity and heat capacity depend on water content, but they

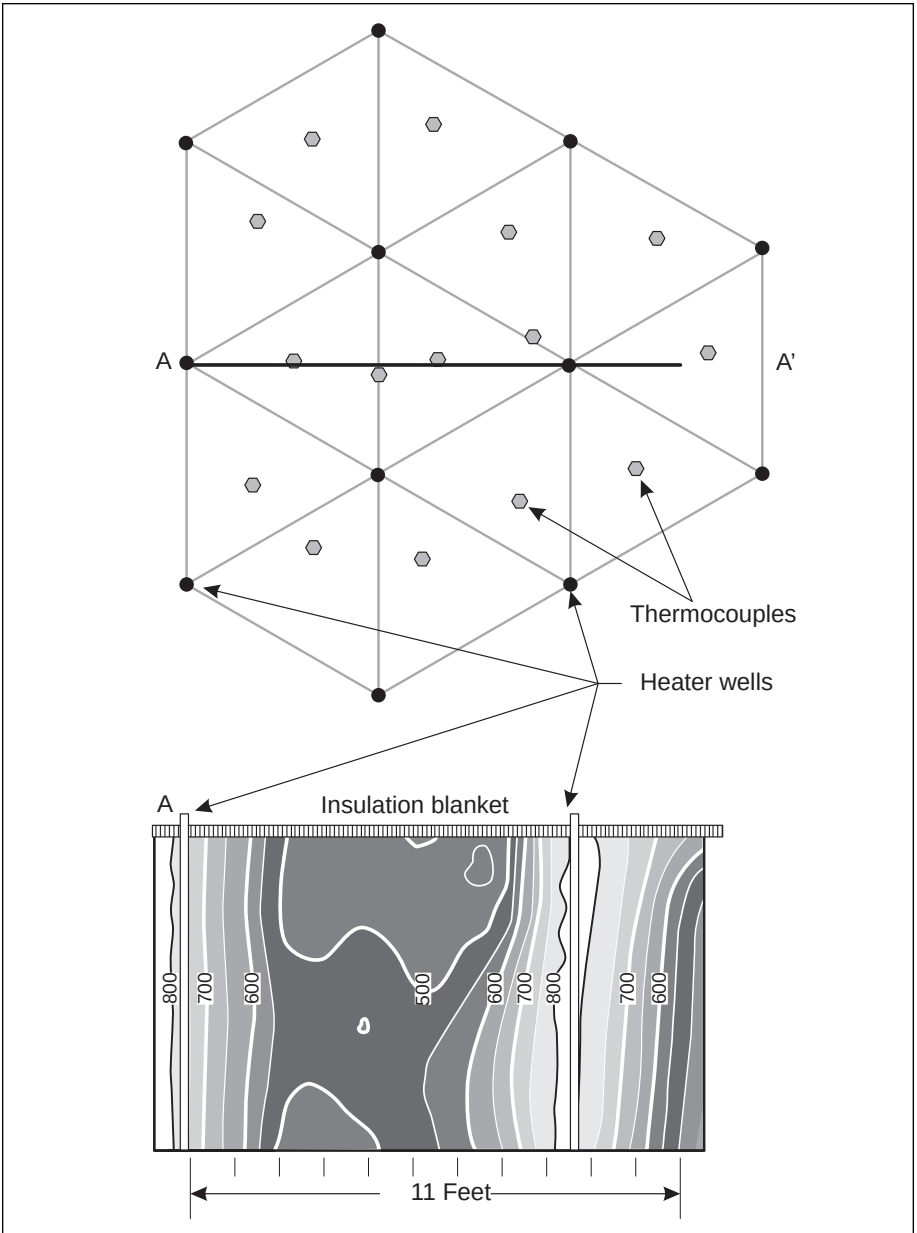


Figure 7-9a. Maximum observed temperatures in °C along a cross-section through an array of heater wells arranged in a hexagonal pattern (above). Temperature field based on measurements at thermocouples spaced every 1 to 3 ft. Data from Vinegar *et al.* (1998; fig. 5).

are relatively insensitive to grain size or mineral content. As a result, temperature changes resulting from conductive heating will be relatively independent of the type of sediment or rock being heated. Moreover, the change in temperature will be relatively uniform even in formations that are heterogeneous, such as interbedded sands and clays or fractured rock. The temperature field resulting from conductive heating depends primarily on the distance and geometry of the heat source, not on variations in geologic conditions.

Water content plays an important role in conductive heating because it changes the thermal conductivity and heat capacity of the formation. In general, as the water content decreases, the thermal conductivity diminishes much more rapidly than the heat capacity. As a result, steeper temperature gradients are required to conduct a unit of heat through a dry formation than through a saturated one. This has several important consequences during conductive heating in the subsurface. Boiling of water in the vicinity of the heater can markedly dry the formation and decrease the thermal conductivity, steepening the temperature gradient and elevating the temperature in the vicinity of the heater. Thus, drying near the heater causes temperatures to be even higher than they would otherwise be in a uniformly saturated material, which is an important asset where hot temperatures are desired to oxidize contaminants *in situ*.

Below the water table, or in large perched zones, water readily flows toward the heater if the formation is permeable, so the effects of drying in the vicinity of the heater may be negligible. Convection increases the rate of heat transfer in such cases, so the temperature increase will be smaller, but spread over a larger area compared to conductive heating in the vadose zone.

Implementation

Thermal conduction can be implemented as a remedial technique either in the subsurface using rod-like heaters that function as thermal wells, or at the ground surface using slab heaters or thermal blankets (see Figure 7-8). Rod and slab heaters were used for remediation in approximately 10 full-scale demonstrations by TerraTherm Environmental Services. All of the examples in this section are based on the TerraTherm data. *In Situ* Thermal Desorption (ISTD), the process used by TerraTherm, is used as a trade name describing a particular implementation of thermal conduction heating (Vinegar *et al.* 1993, 1994).

Heating by thermal conduction offers two important effects that improve remediation. Like other heating methods, conduction increases SVE effectiveness by accelerating evaporation. Unlike the other methods, conduction is particularly effective at creating a zone of hot temperatures (greater than 500°C) near the heating elements. Organic contaminants can be destroyed in the presence of oxygen at those temperatures, so conduction heating can both destroy and accelerate the contaminant removal. As a result, the ISTD process is particularly robust, effectively remediating a variety of organic contaminants, which can be present initially at high concentrations. For example, ISTD has been used to remove free-phase NAPLs in the vadose or saturated zones. Perhaps even more significantly, it has also been used to effectively remediate regions containing organic contaminants with low vapor pressures, such as polychlorinated biphenyls (PCBs), which defy remediation by conventional SVE.

Thermal Wells

The petroleum industry developed the technology of thermal wells to increase recovery from oil reservoirs as deep as 600 m. A thermal production well contains a casing and well screen, much like a conventional SVE well, and also an electric heater. Gas and vapors are recovered by connecting the casing to a suction source, and the heater increases volatilization. Another type of thermal well contains only an electric heater in a solid casing. It is designed to heat the ground, but it lacks a well screen, so no fluids can be recovered from a heater-only well. Thermal wells are installed using conventional drilling methods, and they have been used to depths of 30 m to improve remediation (although greater depths are possible).

Thermal wells are typically arranged in a hexagonal pattern (see Figure 7-9a), with a thermal production well surrounded by a ring of six heater-only wells. The area between the wells is covered with an impermeable vapor barrier and insulating blanket. Thermal energy heats the soil, water, and contaminants, and the targeted treatment zone is maintained under suction. Vapors and gases generated by the process flow through the heated soil and are recovered at the production wells. The impermeable barrier increases the depth of air flow and inhibits fugitive emissions of contaminants.

The positions of the well screens and heaters are determined by the distribution and type of contaminant. The spacing of the wells is determined by the temperature required, the rate at which water can flow to the heated region, and other factors. Well spacings for most applications that require high temperatures are on the order of 5 to 8 ft (see, for example, Figure 7-8).

The process uses electrical heaters that can produce temperatures of 800°C or more. The thermal blankets apply 100 kW of radiant energy to the soil. Electrical heaters used in the thermal wells typically radiate several tens of kW each.

The effects of heating by conduction are illustrated by an example of the ISTD process where 12 thermal wells were used to heat PCB-contaminated ground at the Cape Girardeau site in Missouri (Vinegar *et al.* 1998). An array of 14 temperature monitoring wells with thermocouples spaced every 0.3 m with depth was used to determine heating effectiveness. The process was operated for 41 days, and there were 3 distinct periods of heating. Temperatures increased from ambient conditions to 100°C as the soil and water was heated during the first 10 days of the project (Figure 7-9b). Boiling of pore water occurred throughout the

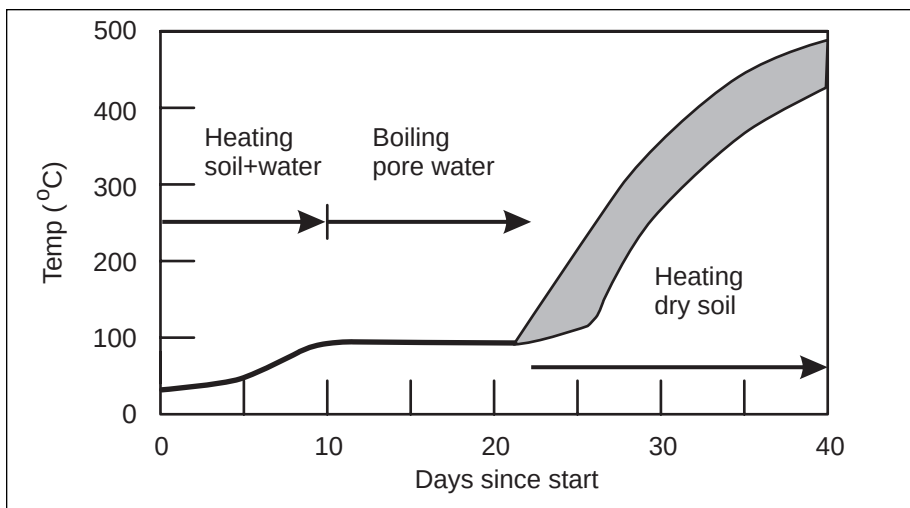


Figure 7-9b. Temperature as a function of time at a depth of 2 m at the 14 thermocouple locations shown in a. Temperatures were relatively uniform prior to day 21, but they ranged over about 100° C after that time. Based on Vinegar *et al.* (1998).

region for the next 12 to 16 days, and temperatures were maintained at 100°C. The temperatures increased again between days 22 and 26, apparently because liquid water was removed completely in that time frame. Temperatures increased from 100°C to more than 400°C during the last two weeks of the project (Figure 7-9b).

Thermal Blankets

Thermal blankets are slab-like heaters that are placed on the ground surface. They consist of a network of heating elements that form a panel 2.5 m by 6 m (8 by 20 ft), with a layer of high-temperature insulation 0.3 m (1 ft) thick used as backing to the heaters. The area in the vicinity of a thermal blanket is sealed with sheets of silicone rubber. Access piping within or beneath the heaters is attached to a suction source to recover vapors generated during heating.

Thermal blankets are designed to address contamination at shallow depths. While they are particularly effective at creating temperatures as high as 800°C within a few days to weeks, the treatment depth is limited to the upper 0.5 m. Organic contaminants are destroyed by pyrolysis and oxidation within the high temperature region beneath the heating elements. In addition, contaminant gases and volatile decomposition products flow upward into the high temperature region as a result of applied suction, destroying some mobile contaminants *in situ*. The remaining contaminants are collected and treated above ground.

Above-ground Treatment

Process and control equipment is used to maintain temperatures in the heating modules and to collect and treat vapors from the treatment area. Process gases removed from the heated soil matrix typically contain original contaminants, oxidation products, water vapor, and atmospheric gases. These gases are treated as required using appropriate technology. For example, the risk associated with PCB releases requires that a flameless thermal oxidizer and granulated activated carbon filter be used to treat off-gases at PCB sites.

Monitoring And Control

The temperature distribution in the subsurface is the single most important quantity affecting the subsurface remediation. Temperatures

are monitored using *in situ* thermocouples. The resulting data gives the temperature distribution in the treatment area (Figure 7-9a) or the temperatures as a function of time (Figure 7-9b).

Factors Affecting Performance

The ISTD process is remarkably robust and it appears to be effective over a wide range of geologic conditions and contaminant properties. Nevertheless, it is by no means a technology that is suited to every case of contamination in the vadose zone. The technique is equipment- and power-intensive, and so it is relatively expensive. As a result, it is best suited to relatively small areas with high concentrations of recalcitrant compounds that defy remediation using other methods. Sites containing high concentrations of PCBs are good candidates, but a variety of other compounds have been remediated with remarkable efficiency.

The technique is particularly well suited to shallow depths where thermal blankets can be used. The cost of installing heater wells at the close spacings required to raise temperatures to several hundred °C may be prohibitive at substantial depths. The economics of this application depend on the magnitude of improvement that can be achieved and what alternatives are available, and so they should be evaluated on a site-by-site basis. This technique will be infeasible at some sites, however, where sensitive structures at the ground surface preclude the installation of either thermal wells or blankets.

The ISTD process is remarkably effective at removing organic compounds from the vadose zone. For example during one of the applications of the ISTD process, the concentration of PCBs in soil was reduced from more than 500,000 ppb to an average of 0.003 ppb (Vinegar *et al.* 1998).

Status

The ISTD technology covered by U.S. Patents No. 5190405 and 5318116 has been used to treat formations contaminated with chlorinated VOCs, aliphatic and aromatic hydrocarbons (BTEX), and PCBs. The results of approximately 10 demonstrations have shown that ISTD reduces the concentration of PCBs from more than a few percent initially in a soil to less-than-detectable after treatment. Based on data from the demonstrations, ISTD was issued an interim or “draft” permit by the

U.S. EPA Office of Pollution Prevention and Toxics, as an alternative treatment for soils containing PCBs.

The status of the ISTD process has taken an important turn during the time this book has been in preparation. TerraTherm, the company that developed the process, has been dissolved and the patent rights have been transferred to the University of Texas. Licensing arrangements are currently being developed and the technology should be available from several vendors in the near future.

The case study "PCB Destruction and Removal," by John Reed and Denis Conley, describes an application of this technology. *See page 1178.*



Heating Using Radio Frequency Energy*

Heating earth materials using radio frequency (RF) energy was first explored during the oil crisis of the 1970s, when tar sands were heated to recover petroleum products. This process was later refined to improve the remediation of vadose zone soils (Smith and Hinchee 1993; Davis 1997; Jarosch *et al.* 1994; Weston 1992; EPA 1995a, 1995b; Phelan *et al.* 1997).

RF heating occurs as a changing electromagnetic field interacts with molecules in the subsurface. Water is a primary target molecule, but interactions with other molecules can also be important. Water is heated in an RF field because its polar molecules rotate when the polarity of the electromagnetic field reverses. The rate at which the rotation occurs depends largely on the dipole moment of the molecule, but other factors, such as attraction to different molecules, may also be important. The dipole moment is important because optimal heating occurs when the frequency with which the electromagnetic field reverses is tuned to the rate at which the molecules can rotate. When the electromagnetic field changes polarity much faster than the molecules can rotate, then the effect of the field on the molecule is subdued. Similarly, when the change in polarity is slow compared to the rotation rate, the molecules may realign themselves and return to their original state. When the frequency of the electromagnetic field is tuned to the rotation rate, how-

*This section was contributed by J. Phelan.

ever, the molecules resonate and move rapidly. Molecules other than water can also be heated by RF energy. The mechanisms will be somewhat different, but, in general, the mechanisms all produce rapid molecular motions that are manifested as an increase in temperature.

Tuning the RF transmitter to the proper frequency is important to effective heating. Microwave ovens transmit electromagnetic radiation with a frequency of 2450 MHz because water molecules are strongly influenced by this frequency. However, the depth of penetration of electromagnetic field radiation is inversely proportional to the frequency, and microwave ovens use relatively high frequencies that have limited penetration in soils. The optimum frequency range to both penetrate and interact with molecules in soils is 2 to 40 MHz, and RF transmitters that will generate this range of frequencies are typically used for soil heating.

The dielectric constant of the soil is an important property affecting optimum frequency. The dielectric constant of water is 78, whereas it is between 4 and 6 for most minerals, and it is 1 for air. The bulk dielectric constant of a soil is an average value weighted to the proportions of water, minerals, air and other components (for example, contaminants) in the soil. The dielectric constant of water is much greater than the other common components of soil, so the volumetric water content is an important control of the bulk dielectric constant of soil. This means that the bulk dielectric constant will decrease as water is removed from the soil during heating. This change can be significant because it complicates the impedance matching required to optimally tune the RF transmitter to soil conditions.

Initial application of RF energy warms both soil and minerals and causes subsurface temperatures to increase to 100°C. This is followed by a period where the maximum temperatures are maintained at 100°C as pore water boils. RF heating continues to be effective after the liquid water has been removed, so the maximum temperatures may increase above 100°C. Maximum temperatures of 250°C have been achieved using RF heating, but 100°C is the design temperature for many remedial applications.

Field Implementation

Two approaches have been developed for applying RF energy to soils. IIT Research Institute in Chicago, IL, uses a tri-plate array. Beginning

with a totally enclosed rectangular wave-guide, the narrow side and bottom walls are removed and the three plates are then converted into electrode arrays (Figure 7-10). The center row of electrodes is used as an exciter array and the outer row is used as guard electrodes, to reflect energy back into the central cavity. Vapor recovery occurs through one or more of the center electrodes. Electrode length and spacing depends upon the area requiring restoration. Electrode lengths demonstrated to date have been up to 8.5 m (28 ft) long with interelectrode spacing of 1.2m (4 ft) and row spacing of 3.5 m (10 ft). A single transmitter feeds all of the electrodes in the tri-plate array and is sized according to the required heating rates. An impedance-matching network between the transmitter and the electrode array is periodically adjusted as the soil heats up and soil water is removed. The exciter array electrodes are connected aboveground by the center conductor of the RF feed. A specially designed structure shields this element to keep free-field RF emissions below occupational health and communications interference criteria.

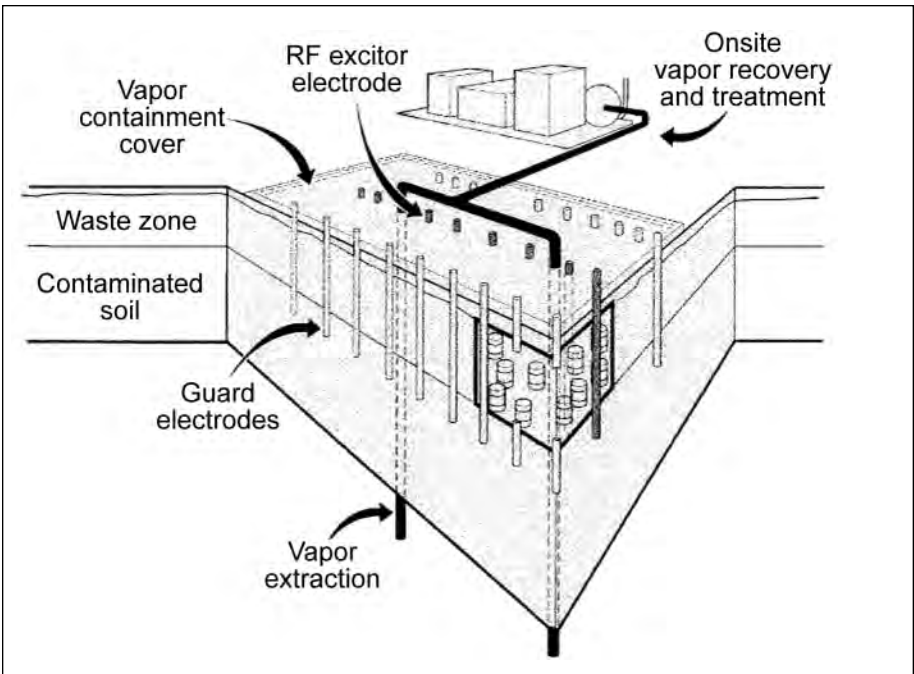


Figure 7-10. Tri-plate array for applying RF energy to soils.

KAI Technologies, Inc., in Woburn, MA, uses a dipole antenna. RF energy is directed through a flexible coaxial transmission line to a down-hole antenna or applicator (Figure 7-11). The dipole antenna can be from 2.5 to 15 cm (1 to 6 in) in diameter and 1.5 to 15 m (5 to 50 ft) long. The borehole must be completed with a non-metallic casing that can withstand the near-field temperatures induced by the RF energy. Vapor phase contaminant removal is performed with SVE, through the antenna borehole or an adjacent borehole. The antennae are spaced 10 to 20 feet apart to achieve uniform heating of soils in a given area. Antennas that are placed in near-surface soils must be shielded to limit radiative emissions.

Monitoring

Measurement systems for RF heating include diagnostics for the RF forward and reflected power, and the impedance-matching network. Measurement of soil temperature is complicated because RF power interferes with standard temperature measurement technologies (resistance temperature devices, thermocouples, and thermistors). Temporarily turning off the RF power and making the temperature measurements with traditional technologies, or using fiber-optic-based temperature sensors while the RF energy is applied, are two options available. Moisture and contaminant monitoring are also important when evaluating system performance during operation.

Limiting Conditions

Due to the bulk heating nature of RF energy, there are few instances where application of RF heating technology is not appropriate. Soil heterogeneities and moisture content variability are not significant issues since the RF energy is able to reach all areas. However, geographic areas with high precipitation rates may be problematic due to the increased energy requirements for heating and volatilization of the additional water. This will be true for all the heating technologies, however, and probably can be mitigated by covering the area to be heated.

Economics

The cost of RF heating will include energy costs to power the system, as well as the cost to deploy and monitor the operation. Energy costs

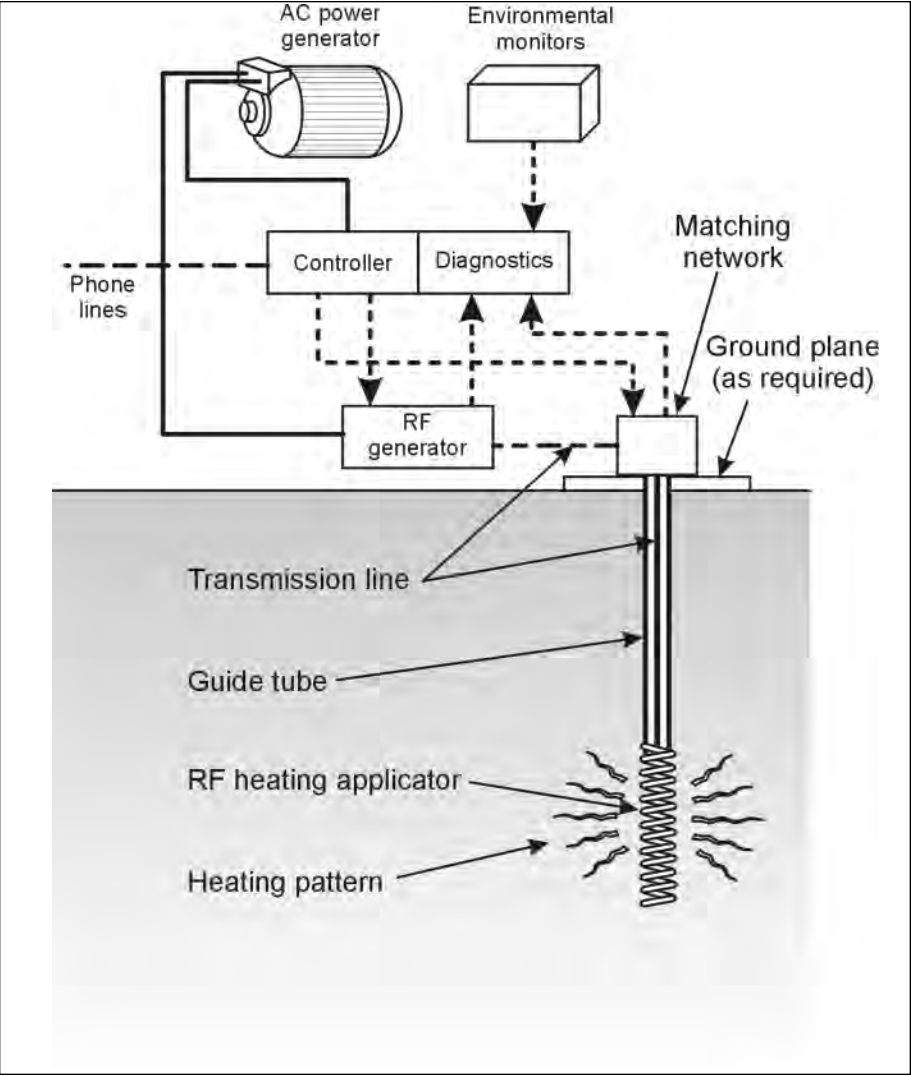


Figure 7-11. Dipole antenna for applying RF energy to soils.

depend on the soil type and degree of saturation (Figure 7-12), as well as the amount of heating required. The mass of water in soils varies significantly with the type of soil, and hence, porosity and the percent saturation of the soil pore space (Table 7-3). The amount of water in soils plays a critical part in the energy balance because it affects the bulk heat

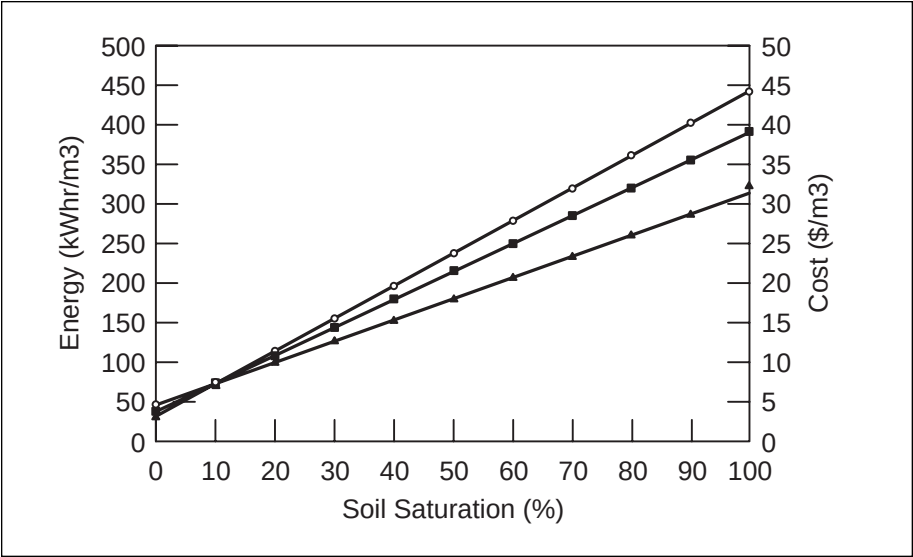


Figure 7-12. Energy and cost to heat and evaporate soils of variable saturation.

TABLE 7-3		Water Content of Soils (kg/m³)		
	Saturation (%)	Clay	Silt	Sand
	100	547	472	358
	90	492	425	323
	80	438	377	287
	70	383	330	251
	60	328	283	215
	50	274	236	179
	40	219	189	143
	30	164	142	108
	20	109	94	72
	10	55	47	36
	0	0	0	0

capacity (equation 7.1) and the bulk heat of vaporization. Figure 7-12 shows the energy requirements to heat one cubic meter of soil (clay, silt, and sand) to 100°C, with varying soil moisture saturation levels to the point where all soil moisture has been evaporated. Even with no soil water, about 50 kWhr/m³ is needed to warm the soil from ambient temperatures to 100°C. This figure can be used to estimate the energy costs of heating to this point.

Steam Flooding*

Controlled steam injection can be a rapid and effective NAPL source remediation technique for many vadose zone sites. The process involves the injection of steam in one or more injection wells, with extraction of water, NAPL, and vapors from one or more extraction wells (Figure 7-13). Steam flooding can be used both with LNAPL and with DNAPL,

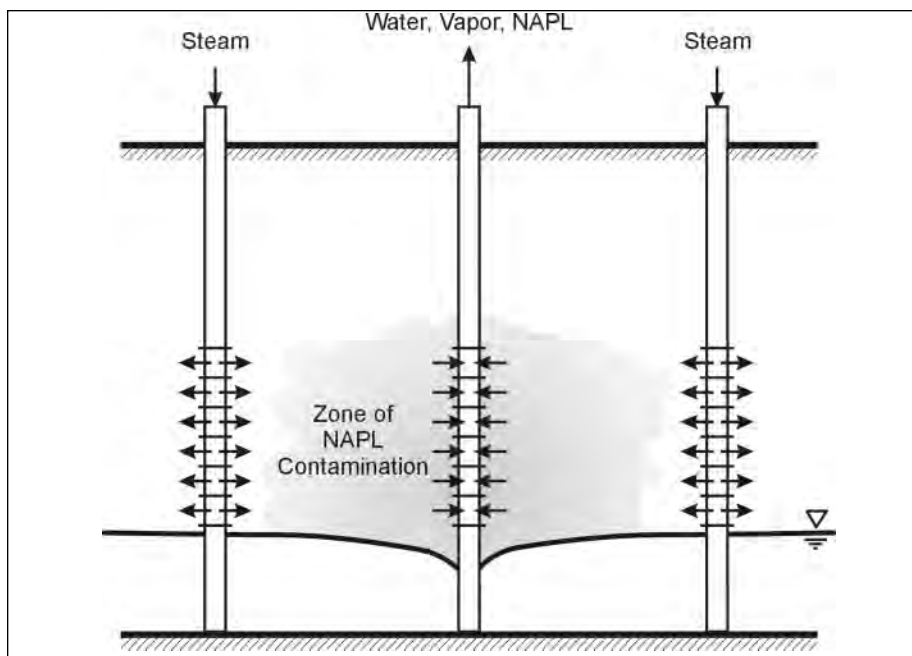


Figure 7-13. Simplified diagram of the steam injection process for remediation of NAPL source zones.

*This section was contributed by R.W. Falta.

although issues of unwanted NAPL migration can arise at DNAPL sites. Although Figure 7-13 shows a NAPL with steam injection above the water table, steam remediation can also be performed below the water table in systems where there is strong layering or anisotropy (Newmark and Aines 1997; Newmark 1994).

Steam injection for the recovery of NAPL is a well-established practice in the petroleum industry. Steam flooding has been used for enhanced oil recovery (EOR) since the 1930s (Stoval 1934). Texts by Prats (1982), Burger *et al.* (1985), Boberg (1988), and Baibakov and Garushev (1989) are among those included in an extensive literature base on steam flooding for EOR.

Experience with steam injection for EOR projects, along with related developments in geothermal reservoir engineering, has helped promote the use of the steam injection application for environmental remediation. However, there are substantial differences between the application of steam injection for environmental purposes and for EOR applications. Vadose zone NAPL source areas are usually in shallow, unconfined systems, and are limited in scale to a few acres or less. In contrast, a typical EOR steam injection application might involve a tightly confined formation, located at a depth of a thousand feet or more, with an overall injection/extraction pattern covering tens or even hundreds of acres. In the EOR case, the oil is uniformly distributed over a large area, at high phase saturations in the range of approximately 50 percent. On the other hand, typical NAPL source zones involve much smaller quantities of NAPL at lower saturations, with a highly heterogeneous and often unknown distribution.

The goals of EOR and environmental remediation differ as well. The goal of an EOR project is to economically produce oil, and a small amount of oil left in the formation after a steam flood is inconsequential. A NAPL source zone remediation project will have a completely different objective, to remove all, or nearly all, of the NAPL from the treatment zone.

Physical Processes

Steam flooding for remediation depends on the delivery of energy to a targeted zone, and on the subsequent mobilization and recovery of contaminants in that zone. The processes of energy delivery and con-

taminant removal are quite different, although they are equally important to successful remediation.

Energy Delivery

Energy delivery can be done either through the injection of hot fluids, such as steam, hot air, or hot water, or through the direct addition of energy. Examples of direct energy addition include radio frequency heating, microwave heating, and resistive heating. These direct energy techniques can be used in conjunction with steam injection to target zones, which are not effectively heated by the steam (Newmark and Aines 1997).

The heat energy required to raise the temperature in a subsurface volume depends on the heat energy content of the volume before and after the heating, and on heat losses from the volume. The heat content consists of contributions from the soil grains or rock, and from the various fluid phases present in the porous media: gas, aqueous, and NAPL. The heat content of a unit volume of vadose zone material was given in Chapter 1 as:

$$M^h = (1 - \phi)\rho_R C_R T + \phi S_g \rho_g u_g + \phi S_w \rho_w u_w + \phi S_n \rho_n u_n \quad (7.3)$$

As shown earlier in this chapter, the amount of energy required to raise a unit volume of the treatment zone from ambient conditions to steam zone conditions is computed by subtracting the value of M^h for the ambient conditions from the value for the steam zone conditions. The energy requirement calculated above corresponds to fairly modest energy costs, on the order of a few dollars per cubic meter. In general, the cost of energy is usually not a limiting economic consideration in the design of a steam flood.

Energy delivery by hot fluids can be accomplished through the injection of steam, hot water, hot air, or some combination of the three. For a given mass injection rate, the rate of energy input is determined by the injected fluid's specific enthalpy. As discussed in Chapter 1, the specific enthalpy of fluids varies dramatically depending on whether they are liquids, condensable gases (such as steam), or noncondensable gases (such as air). For example, the specific enthalpy of liquid water at 100°C is 419 kJ/kg, while the specific enthalpy of steam at this temperature is much higher, 2676 kJ/kg (Sonntag and van Wylen 1982). The difference

is heat of vaporization, which is the energy required to evaporate a unit mass of the liquid. Steam has a very high specific enthalpy due to the high heat of vaporization of water, 2257 kJ/kg at 100°C. For this reason, a large amount of energy is used to convert liquid water into steam initially, in the boiler. This energy is released when the steam condenses at the steam front. The steam condensation at the steam front forms the basis for a very efficient heat transfer mechanism.

The steam condensation front velocity and the steam Darcy velocity in the steam zone are important features of a steam flood. The steam front velocity is the speed at which the leading edge of the steam zone advances. The steam front is characterized by an exponential decline in the temperature from the steam zone temperature, which is nearly constant (Menegus and Udell 1985; Stewart and Udell 1988; Hunt *et al.* 1988). These profiles, as well as the pressure profile and the steam front velocity, can be determined analytically for one-dimensional conditions (Menegus and Udell 1985; Stewart and Udell 1988). Typical field steam front velocities are in the range of a few meters per day, depending on the geometry and injection rates.

Behind the steam condensation front, the steam Darcy velocity is very high. From a simple mass balance, the maximum steam Darcy velocity behind the condensation front is:

$$V_s = \frac{\dot{m}_{in} X}{\rho_g} \quad (7.4)$$

where $\dot{m}_{in}$ is the injected water mass flux (kg/m²s), X is the injected steam quality (the mass fraction of steam in $\dot{m}_{in}$), and ρ_g is the steam density, about 0.6 kg/m³. The steam Darcy velocity behind the steam front is about two orders of magnitude larger than the advancing front velocity due to the change in volume that occurs as steam condenses back to liquid water. A noncondensable gas such as air would not have this property, and the magnitudes of the advancing gas front velocity and the gas velocity behind the front would be much closer.

Fingering of the injected steam may occur due to heterogeneities in the vadose zone. Interestingly, steam floods have properties that may substantially reduce this effect, especially compared to the injection of a noncondensable gas such as air. The rate of advance of a steam front is largely controlled by the rate of heating that occurs at the front. If a

small finger of steam forms, it is subject to large heat conduction losses and tends to collapse back into liquid water, stabilizing the front (Miller 1975; Stewart and Udell 1989; Lake 1989). The large pressure gradient in the steam zone compared to the pressure gradient ahead of the steam front provides additional stability to the front (Lake 1989; Udell 1994).

While the mechanisms discussed above stabilize the steam front, it is still affected by permeability heterogeneity. This behavior has been observed in two-dimensional laboratory studies by Basel (1991), and in the field tests reported by Udell and Stewart (1989) and Newmark and Aines (1997). The heat conduction mechanism discussed above also reduces this effect for small-scale heterogeneities. Thus, it is expected that mainly the larger scale heterogeneities will influence the steam front propagation (Udell 1994).

Contaminant Removal

The primary means by which steam injection improves NAPL recovery from a source zone is through a greatly increased rate of evaporation in the steam zone (Stewart and Udell 1988). This occurs, in part, because of the strong increase in chemical vapor pressures with increasing temperature, and, in part, because of the high steam velocities which are generated in the steam zone. Over the temperature range of interest, about 10°C to 100°C, a chemical's vapor pressure can increase by a factor of 50 or more. For a given gas phase velocity through the NAPL zone, the rate of evaporation of a single component NAPL is a linear function of its vapor pressure. The evaporation of a multi-component NAPL such as gasoline is somewhat more complicated. The effective vapor pressure of each chemical component in a multi-component NAPL is a function of the product of the component's mole fraction in the NAPL, with its pure vapor pressure. Nonetheless, the vapor pressure of all of the components in the multi-component mixture will increase with increasing temperature. This distillation effect has been investigated by Hunt *et al.* (1988), Basel (1991), and Adenekan (1992), among others.

The high steam velocity behind the condensation front provides an efficient mechanism for NAPL evaporation. While it is obvious that contaminants with boiling points lower than the steam temperature will be removed, contaminants with higher boiling points also can be removed efficiently, as long as the NAPL evaporation front velocity is as large as

the steam condensation front velocity (Falta 1992b; Yuan and Udell 1993). Using a numerical analysis, Falta *et al.* (1992b) concluded that steam flooding would operate most efficiently for chemicals with boiling points less than about 175°C. Yuan and Udell (1993) arrived at a similar conclusion using a theoretical analysis which included the effects of mass-transfer-limited NAPL evaporation.

These theoretical results are consistent with the experiments of Basel (1991), which demonstrated efficient steam removal of xylene from a two-dimensional sand pack, and with the experiments of Stewart and Udell (1988), Basel (1991), and Yuan and Udell (1993), using mineral oil, diesel fuel, and dodecane, where the removal was much slower.

Experiments by Hunt *et al.* (1988); and Basel (1991) have shown that volatile or semi-volatile NAPL evaporated from the steam zone can condense into a high saturation NAPL bank at the steam condensation front. This concentration of the NAPL at a high saturation results in an increase in the NAPL relative permeability, making it mobile. Other features of a steam flood which help improve separate phase NAPL displacement at and ahead of a steam front include: reduction of NAPL viscosity with increased temperature; high displacing pressure gradients, due to the high steam zone velocities, and reduced capillary effects, due to lower surface tension at high temperatures.

If the NAPL in the treatment zone is an LNAPL, this mobilization is likely to be beneficial to the steam flood efficiency, and there is probably little danger in unwanted mobilization. However it may not be desirable to concentrate and mobilize a DNAPL ahead of the steam front. Since most DNAPL chemicals (for example, PCE, TCE, DCE, TCA, carbon tetrachloride, and chloroform) have boiling points below 175°C, they can be expected to form a mobile bank ahead of the steam front. Unless there is some type of confining unit below the steam zone, it is possible that the DNAPL bank ahead of the steam front might migrate downward, out of the treatment zone. The downward mobilization of NAPL can be reduced by using special steam flood designs.

The large steam Darcy velocity behind the steam front provides a powerful stripping effect for a chemical dissolved in the pore water. Due in part to the volume reduction that occurs when steam condenses back to liquid water, hundreds of pore volumes of steam are injected for each pore volume of porous media swept by the steam condensation front. This steam stripping is enhanced by the increase in the Henry's constant

that takes place when the pore water is heated to the steam temperature. The combination of these effects makes it unlikely that much dissolved chemical remains far behind the steam front unless it has a very low Henry's constant, or unless it is strongly adsorbed (at the steam temperature).

Udell (1994) shows that a large reduction of dissolved VOC concentrations can result from vaporizing the pore water in the steam zone. Boiling off only a few percent of the pore water in a steam zone (by dropping the pressure) could lead to a reduction of the aqueous VOC concentration by several orders of magnitude, due to the volume change which occurs when the liquid water vaporizes into a gas, followed by equilibration of dissolved VOC with the gas.

Other possible mechanisms for contaminant removal by steam injection include enhanced thermal desorption of adsorbed compounds (Udell 1994), dilution of dissolved nonvolatile contaminants (Vaughan *et al.* 1993), and hydrous pyrolysis/oxidation of dissolved organic compounds (Knauss *et al.* 1997; Leif *et al.* 1998). The long-term effects of steam flooding on biodegradation rates are not well known, but the results of a field test conducted at Lawrence Livermore National Laboratory showed the presence of microbial communities in all soil samples from the steam zone, including samples collected at a temperature greater than 90°C (Newmark and Aines 1997).

Predictive Capabilities

The complexity of the steam flood process limits the applicability of analytical solutions to one-dimensional systems, so numerical models are typically used to model field applications. At least seven numerical steam flood simulators have been presented in the environmental literature. The codes include T2VOC (Falta *et al.* 1995; Falta *et al.* 1992a; b), M2NOTS (Adenekan *et al.* 1993), NUFT (Nitao 1993), MAGNAS (Panday *et al.* 1995; Huyakorn *et al.* 1994), COMPFLOW (Unger *et al.* 1995; Forsyth and Shao 1991; Forsyth 1994a; b), MUFTE (Helmig *et al.* 1994) and STOMP (White and Oostrom 1996a, b). All of these codes are fully implicit, three-dimensional, three-phase flow simulators that can handle anisotropic, heterogeneous, porous media properties. All of the codes assume local thermal and chemical phase equilibrium, and they allow for complete phase appearance and disappearance. Several of these codes have been validated with steam flood experimental data, and

they are useful tools for steam flood design and analysis. The mathematical basis for these codes is described in Chapter 5.

Field Studies

The first field test of steam injection for source zone remediation was performed in 1988 by Udell and Stewart (1989) at an industrial site in San Jose, CA. An industrial solvent treatment facility was located on this site beginning in 1973, and investigations begun in 1983 indicated widespread VOC contamination in the upper 20 feet of soil. These contaminants, which included xylenes, ethylbenzene, 1,2-dichlorobenzene, 1,1,1-trichloroethane, TCE, PCE, and acetone, were found at total concentrations exceeding 10,000 mg/kg in some locations. The site hydrogeology consisted of a shallow unconfined aquifer perched on continuous clay aquitard at a depth of 19 ft. The aquifer consisted of interbedded sands, silts and clays, with a 2- to 5-ft thick sand layer near the base of the aquifer. The depth to groundwater was about 17 feet, and the formation permeability was measured with a vacuum extraction test at 8.7 Darcys.

Six steam injection wells were installed in a hexagonal pattern around a central recovery well, with five-foot spacing between the injection and recovery wells. The 18-inch diameter injection wells were drilled to a depth of 19 feet, and screened over the bottom 5 feet. The recovery well was drilled to a depth of 21 feet and was screened from the bottom to the ground surface, and the ground surface around the pattern was sealed. Prior to steam injection, a 40-hour vapor extraction study was performed at a flow rate of 23 scfm. The contaminant concentrations were high, approximately 60 grams/m³ of gas. The total recovery of contaminants from the vapor extraction test was estimated at 222 lbs.

Following the vapor extraction test, steam was injected for 140 hours at an average rate of 250 lb/hr, with an injection pressure of about 6 psig. The recovery well contained a submersible liquid pump at the bottom and was also used as a vapor extraction well. The steam broke through in the recovery well after 20 hours of injection. After three days of steam injection, the steam was found in the bottom 5 feet of the flood zone, but as the test progressed, the steam zone grew vertically. Following the 140-hour steam injection, the system was shut down for eight days. Finally, the system was cycled with steam and vacuum for about two

weeks. By the end of the test, the steam zone extended to the ground surface.

A total of 540 lbs of contaminants were removed during the steam flood part of the experiment, with about 95 percent of the recovery occurring in the vapor phase. Udell and Stewart (1989) report a reduction in total contaminants from about 1,200 mg/kg to 23 mg/kg in the high permeability parts of the treatment zone, with lower recovery in the low permeability regions.

A full-scale field demonstration of steam flooding with supplementary electrical heating was performed at the Lawrence Livermore National Laboratory, Livermore, CA, in 1993 (Newmark 1992; Newmark 1994; Udell 1994; Newmark and Aines 1997). The contaminant at this site was gasoline, which leaked into the subsurface from underground tanks. The site hydrogeology consists of alluvial deposits, with strong layering. These layers range from coarse gravels to fine silts and clays, with large variations in permeability in adjacent units. Site characterization results yielded an estimate of 6,200 gallons of gasoline, located both above and below the water table. The gasoline was found as far as 30 feet below the water table due to past water table fluctuations. Figure 7-14 from Udell (1994) is a cross section of the site showing the initial gasoline distribution. As shown in the figure, there were two continuous high permeability layers in the contaminated zone, one above and one below the water table, separated by a contaminated clay layer.

The steam treatment system consisted of six steam injection wells, and three extraction wells, as illustrated in Figure 7-15. The injection wells surrounded the contaminated zone in a rough hexagonal pattern, with the extraction wells located near the center of the zone. The spacing between the injection and extraction wells ranged from about 35 to about 90 feet. The six steam injection wells had special completions, with screened zones in the permeable layers and electrodes in the clay layer. Three electrical heating wells were also installed in the pattern, with electrodes in the clay between the high permeability zones, and above the upper high permeability zone. The recovery wells were screened across the contaminated zone. Figure 7-14 illustrates the various well completions.

The remediation operation included three phases: (1) an initial electrical heating of the clay zones and an initial steam flush, (2) a second

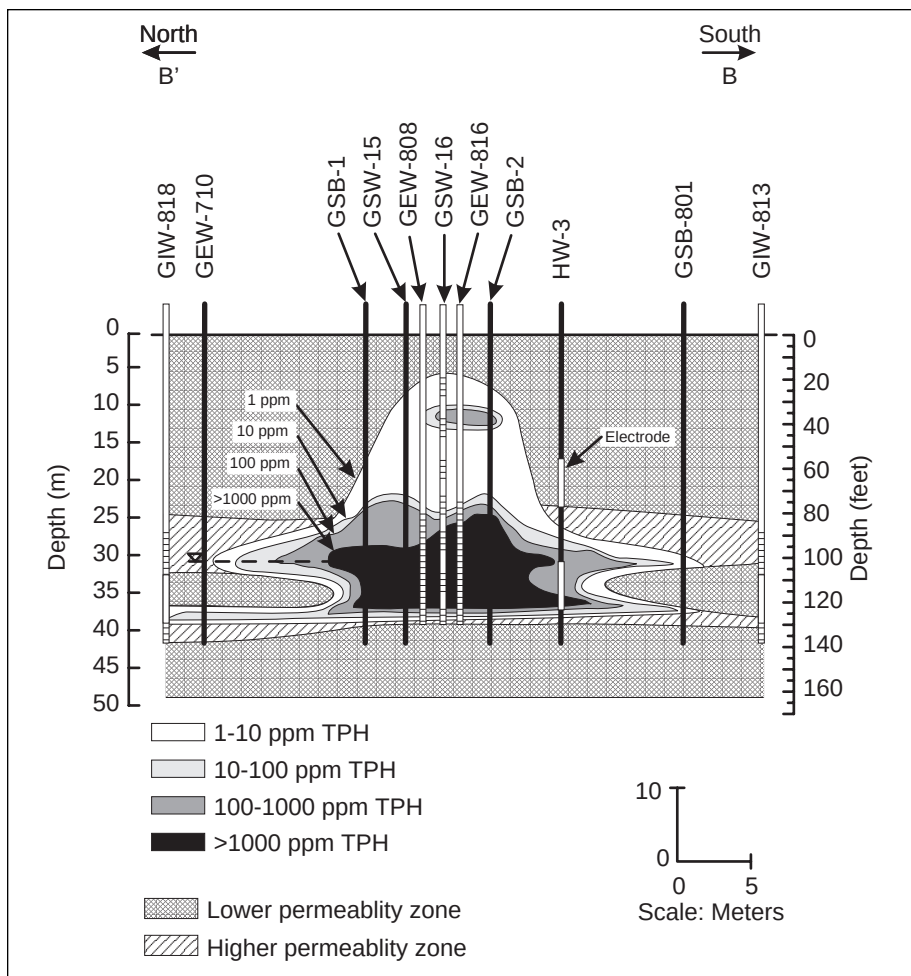


Figure 7-14. Cross section through the Lawrence Livermore gasoline site prior to steam flood (from Udell 1994).

steam flush, and (3) a final electrical heating and vapor and ground water extraction (Newmark and Aines 1997).

The electrical resistance heating involved a power input of up to 800 kW, with each electrode applying several hundred amps at up to 600 volts. In this operation, the clay zones are preferentially heated due to their higher electrical conductivity compared to the gravel zones. This heating was performed for a period of about two months, with a total

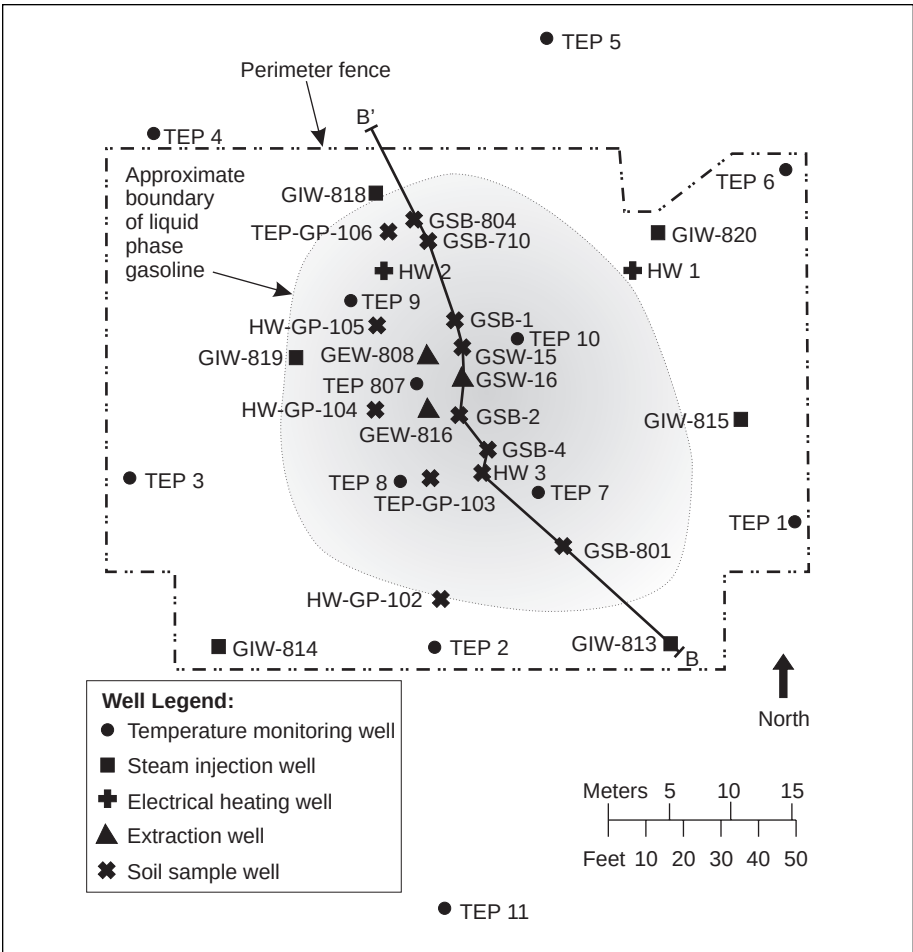


Figure 7-15. Site layout for the Lawrence Livermore steam flood demonstration (from Udell 1994).

energy input of about 202 MW-hours, heating some areas of the clay above 70°C.

The first steam injection operated for 37 days, with a steam injection rate of 11,000 kg/hour. This was generated using an 8 MW gas-fired boiler. Steam first broke through in the extraction wells after 12 days of injection. Following this initial breakthrough, the individual injection well rates were adjusted so the gasoline would continue to be driven

towards the center of the pattern without excessive steam losses outside the pattern. During this initial steam flood, about 1,700 gallons of gasoline were removed from the subsurface, mainly (about 85 percent) in the form of a vapor (Newmark and Aines 1997).

During the first steam flood, the gasoline vapor recovery was limited by the capacity of the treatment system. Following the first steam flood, the system was shut down for three months, and the vapor treatment system capacity was increased. The second steam flood operated for 46 days in a cyclical manner. The highest rates of gasoline vapor recovery occurred before the start of steam injection and immediately following the termination of steam injection periods, when the system was depressurized by the vapor extraction (Udell 1994). The total gasoline recovery during this phase of operations was about 5,000 gallons. Soil concentrations in the treatment zone after the second steam flood indicated that the NAPL had been removed from most of the treatment zone, except for part of the clay between the high permeability zones. This clay was cooler than the steam zone, and it was estimated that about 750 gallons of gasoline remained there. Figure 7-16 shows the distribution of gasoline after the second steam flood.

The final stage of operations involved electrical heating, groundwater extraction, and vapor extraction, without steam injection. This phase removed an additional 1,000 gallons of gasoline, for a total recovery of about 7,700 gallons. In 1995, termination of groundwater pump-and-treat and vapor extraction operations at the site were approved, and in 1996, the San Francisco Bay Region Regional Water Quality Control Board determined the remediation effort to be complete (Newmark and Aines 1997).

A field demonstration of steam flooding for chlorinated solvent removal was performed at Hill Air Force Base, Utah by Stewart *et al.* (1998). This site, known as Operable Unit 2, is located on a hillside and contains two former trenches used to dispose of spent solvents. These DNAPL liquids (trichloroethylene, Freon 113, 1,1,1-trichloroethane, and tetrachloroethylene) accumulated along a subsurface channel located on a clay layer at a depth of about 15 m below the ground surface. Prior to the demonstration, nearly 100,000 liters of DNAPL had been recovered from the site by pumping.

A series of extraction wells were installed along a 16.8 m segment of the subsurface channel, with a central steam injection well screened near

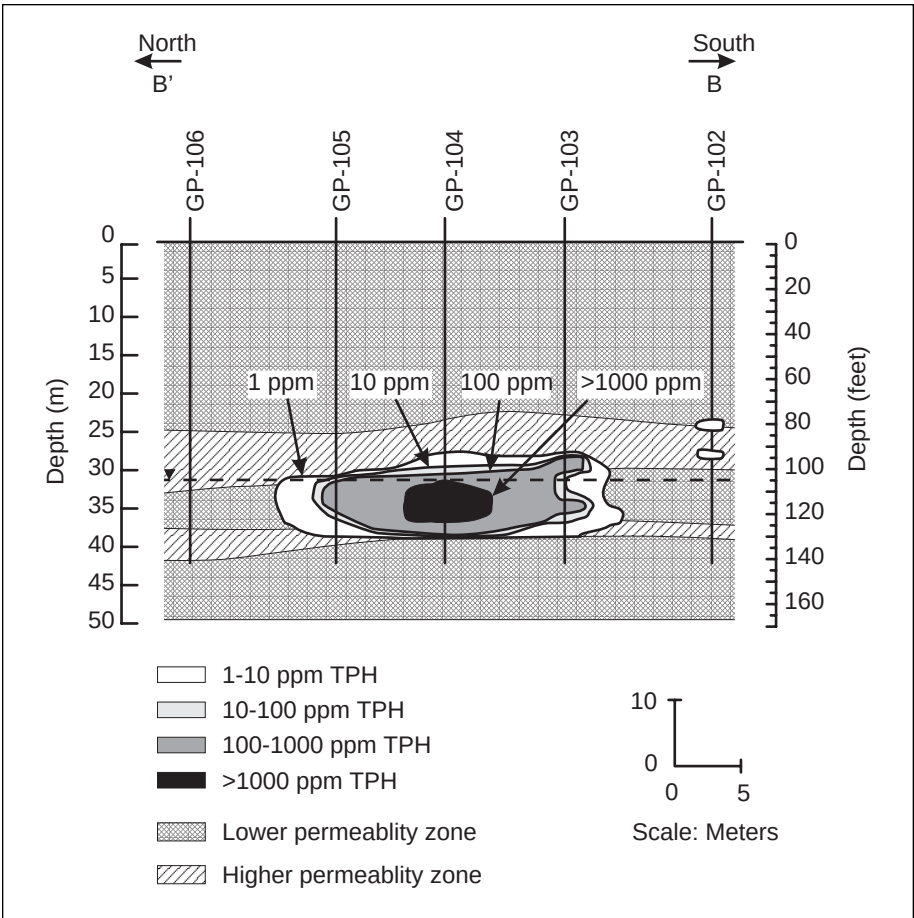


Figure 7-16. Cross-section through the Lawrence Livermore gasoline site after the second steam flush, but before final treatment (from Udell 1994).

the bottom of the channel (Figure 7-17). These wells were initially used to dewater the site, and about 5,300 liters of DNAPL were removed during this activity. Next, SVE was performed for several days. Initial SVE extraction rates were about 27 kg/hr, but these rates decreased by an order of magnitude within six days.

Steam was injected into the central well, with groundwater and vapor extraction from the outer wells. Following steam breakthrough after three days, the steam was injected at a reduced rate for eight days. A

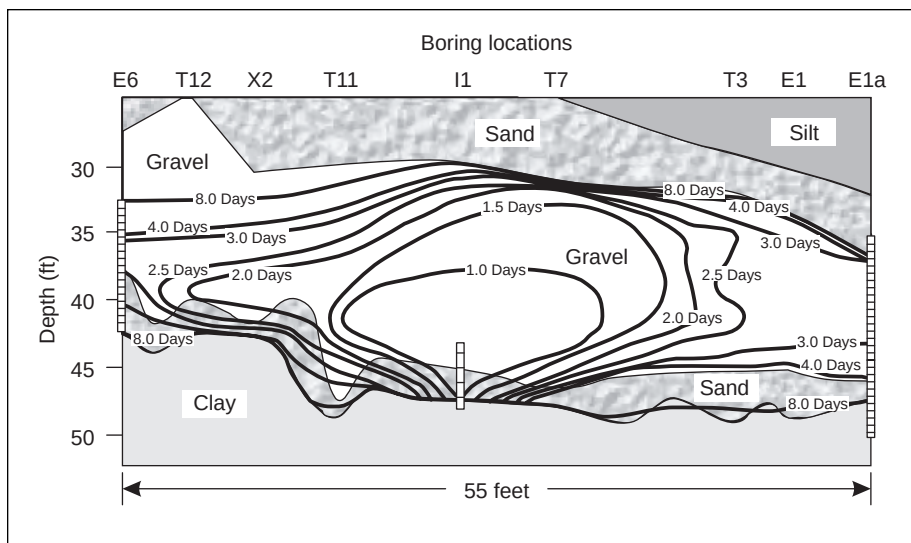


Figure 7-17. Cross-section through the Hill AFB OU2 steam flood experiment (from Stewart *et al.* 1998).

DNAPL bank was produced ahead of the thermal front, and about 1,900 liters of DNAPL were produced from the test zone in the first five days of the test. Figure 7-17 shows the approximate locations of the steam condensation front during the test. The experiment concluded with 12 days of ambient air injection and SVE, along with groundwater pumping for an additional week. The total volume of DNAPL removed was 3,440 liters.

Post-test soil sampling showed 96 percent reduction of contaminant concentrations in the treated zone, and 50 percent reduction of concentrations in the underlying clay zone. Stewart *et al.* (1998) report that the cost for the demonstration was \$230 per cubic yard treated, and \$165 per gallon of DNAPL removed. They conclude that future applications could be conducted for about one-half of this cost.

The largest environmental steam flood to date is currently underway at a utility pole treating facility in Visalia, California. This full-scale application of vadose zone steam flooding is described in the accompanying case study.

"A Case Study of Steam Flooding: The Visalia Project," by R.L. Newmark, R.D. Aines, K.G. Knauss, R.N. Leif, M. Chiarappa, G.B. Hudson, C. Carrigan, J.J. Nitao, A. Thompson, J. Richards, C. Eaker, R. Weidner, and T. Sciarotta, describes a steam injection/vacuum extraction operation at Southern California Edison's Visalia Pole Yard site. See page 1181.



Heating Using Electrical Resistance*

Earth materials can be heated by electricity, just as an element on an electric stove is heated when an electric current flows through it. This process of *electrical resistive heating* will increase temperatures throughout a region between electrodes in the ground. Electrical resistive heating can raise the temperature of the subsurface to the boiling point of water, which creates an *in situ* source of steam to strip contaminants from the subsurface. As the contaminants are converted to vapors, they are captured and removed using standard SVE techniques. The ability to produce steam *in situ* between electrodes can produce a more uniform distribution of temperatures than steam flooding and conductive heating, where heat moves outward from wells.

Electrically, the soil and groundwater behave as a distributed matrix of resistors. As an electrical current I is passed through a soil of resistance R , the resulting power P , is $P = I^2R$. The heating rate is equivalent to the power dissipated in the subsurface, so heating will be greatest where the current flow is greatest. The applied voltage, rather than the current, is adjusted in the field to produce the current that is needed to induce resistive heating at whatever rate is required to accomplish timely remediation. Ohm's law states the relationship between the applied voltage and the induced current is $V = IR$.

The configuration of electrodes is critical to creating a uniform distribution of heat. The optimal configuration uses six metal electrodes placed in a circle around a central neutral electrode. Conversion of three-phase electricity from standard power lines into six electrical phases using standard electrical transformers powers this array. The six phases are used to energize the six metal electrodes, and the electrodes

*This section was contributed by W. Heath.

are connected in a spatially phase-sequenced pattern so that each electrode conducts to every other electrode in the formation, as shown schematically in Figure 7-18, with the central electrode acting as an electrical neutral. This electrical configuration produces a remarkably uniform heating pattern, as shown by the infrared thermal image in Figure 7-19. Figure 7-20 shows a typical field installation.

Six-phase heating appears to be an effective method to uniformly heat soil and groundwater. This technique was originally developed by Battelle Memorial Institute for the U.S. Department of Energy as a method to enhance the removal of VOCs from low-permeability soils. It is now commercially available from Current Environmental Solutions, a joint venture with Battelle Memorial Institute.

Because the soils are heated internally, low-permeability clay soils and complex heterogeneous soil formations can be effectively treated with six-phase heating.

The current generated by six-phase heating concentrates within zones having higher electrical conductivity in the subsurface. The electrical conductivity depends primarily on moisture content and the concentration of free ions. As a result, low-permeability zones like silts and clays are heated preferentially because they exhibit higher moisture contents than permeable sands. This natural effect aids the treatment process by focusing heat on formations that resist advective flushing.

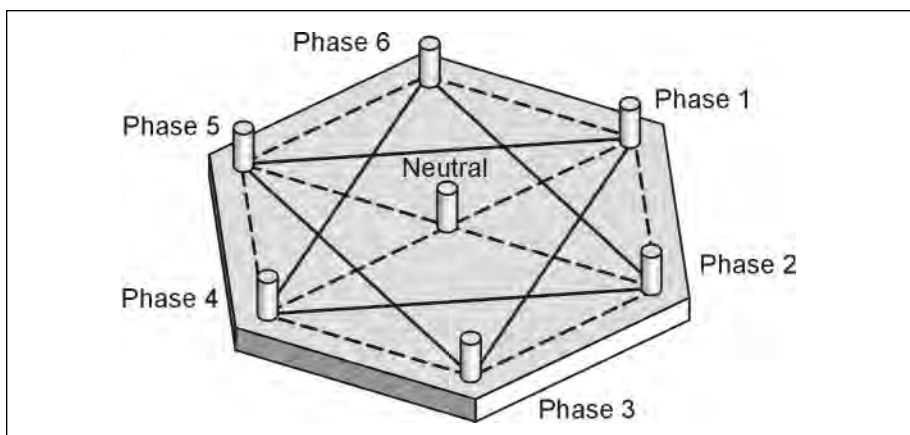


Figure 7-18. Electrode configuration and current flow paths for six-phase heating.

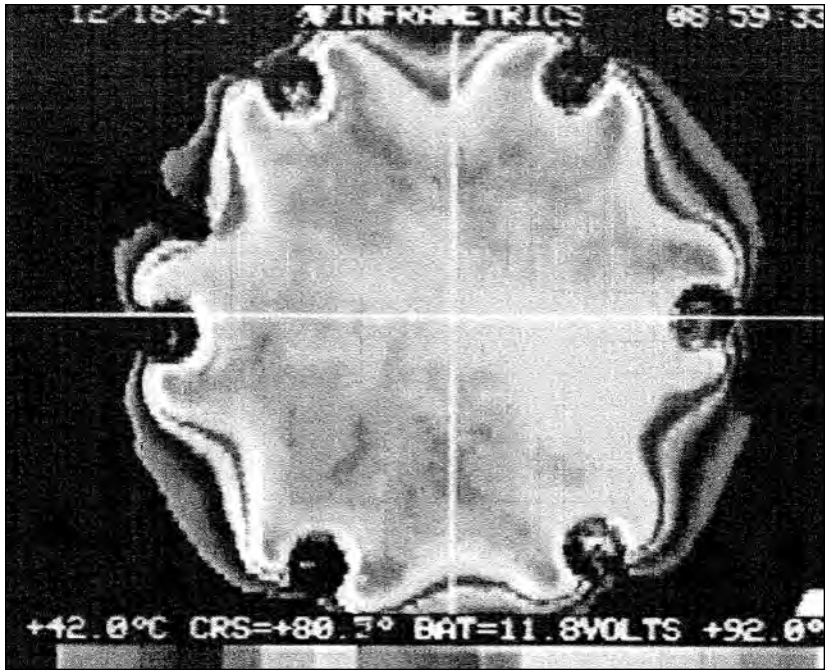


Figure 7-19. Infrared photograph of heating pattern.

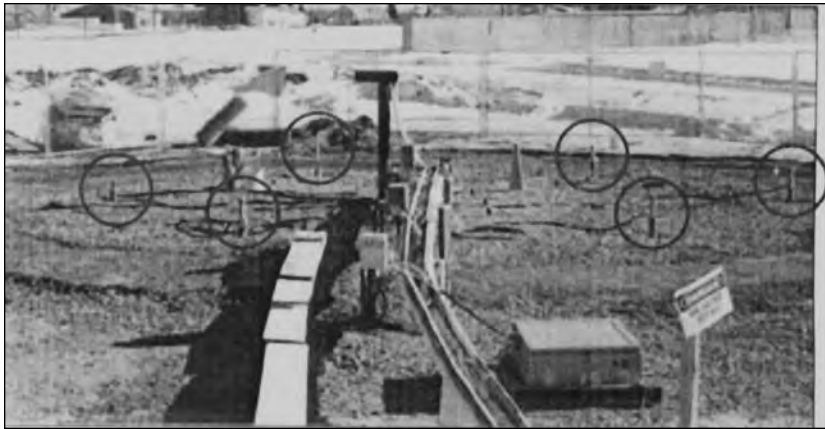


Figure 7-20. Six-phase electrode array in a typical field installation.

For large-scale remediation efforts, multiple arrays of electrodes are operated simultaneously to treat large volumes of soil. In general, the design and placement of the six-phase heating electrodes are optimized for each site based on the following criteria:

- Size and shape of the remediation area, and total depth of site impact
- Site lithology and depth to groundwater
- Total organic carbon content and electrical resistivity of site soil
- Buried utilities and immediately adjacent surface structures

In addition to the electrodes and power supply, the major components of a six-phase heating treatment system are:

- Vapor extraction vents and monitoring wells (temperature and pressure) installed subsurface
- An off-gas collection and treatment system (including piping, a blower, a steam condenser, a condensate holding tank, and an off-gas treatment unit)
- A computer control and data acquisition system with fully remote communication

During the heating process, subsurface vapor extraction wells are used to remove steam and contaminant vapors as they are produced. A steam condenser separates the mixture of soil vapors, steam, and contaminants, which is extracted from the subsurface into condensate and contaminant-laden vapor. If these waste streams require pre-treatment before discharge, standard air abatement and water treatment technologies are utilized. Figure 7-21 shows a typical process scheme used for offgas treatment.

The case study "Vadose Zone Remediation Using Six-Phase Heating," by W. Heath describes an application of this technology. See page 1187.



The remote communication system enables complete system control (including startup, shutdown, and voltage and power adjustments) from

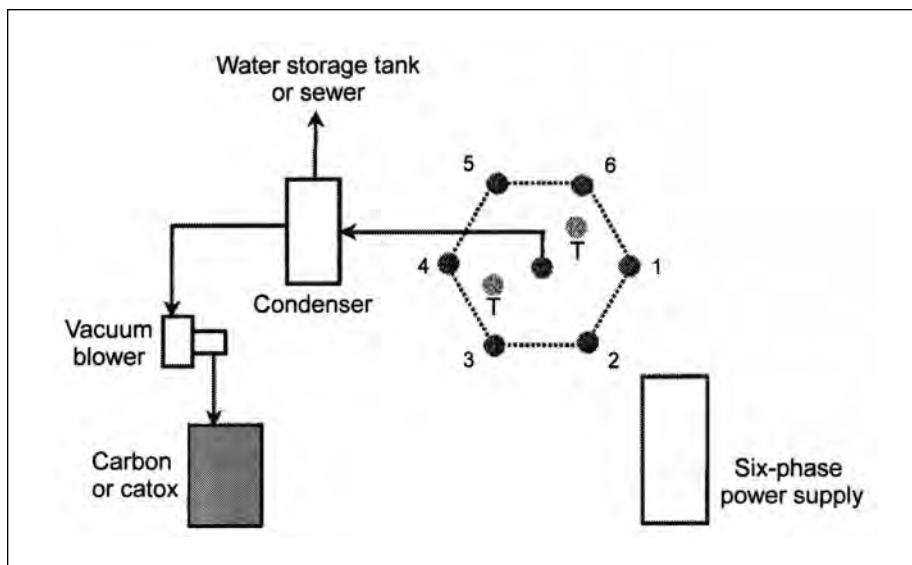


Figure 7-21. Simplified process schematic for 6-phase heating with SVE.

a remotely located computer via phone lines. The system also transmits the operational status of the six-phase heating power supplies and data from *in situ* and aboveground sensors. During system operations, the six-phase heating equipment is remotely monitored and controlled in consultation with onsite personnel.

Case Studies

Six-phase heating technology has been deployed at the time of this writing on both pilot-scale (single electrode array) and full-scale (multiple arrays) to treat the following contaminated sites:

- Savannah River—chlorinated solvents in tight clay in vadose zone
- Dover Air Force Base—DNAPL in flowing aquifer
- Niagara Falls—groundwater heating
- Ft. Richardson—recalcitrant compound demo
- Fort Wainwright—bio/cold region demo
- Skokie Site I—full-scale DNAPL cleanup

- Cincinnati Site—LNAPL smear-zone demo
- Skokie Site II—full-scale DNAPL cleanup
- Seattle Site—full-scale groundwater cleanup

BIOREMEDIATION*

Contaminants can be transformed to harmless compounds during biochemical reactions orchestrated by microbes in the subsurface, and bioremediation is an engineered action that will increase the rate at which the transformation process takes place (Figure 7-22). Some organic contaminants, such as petroleum hydrocarbons, are oxidized as microbes use them as a source for carbon and energy. Other compounds, such as chlorinated solvents, are degraded by enzymes produced by microbes, even though those compounds offer no known benefit to the microbes. In other cases, metals and radionuclides can be transformed to other valence states or compounds, directly, by the microbes' use of them as electron acceptors, or indirectly, by oxidation of chelators. Both inorganic and organic compounds can be made more mobile or less mobile by stimulating production of biological surfactants or by degrading surfactants. Thus, bioremediation of contaminants can result in the complete mineralization of the contaminants, transformation to less toxic forms, immobilization, or mobilization in the vadose zone. Bioremediation is described in more detail by Hazen (1997) and McCullough *et al.* (1999). Terminology related to bioremediation is defined in Table 3.1 in Chapter 3.

Biotransformation is any alteration of the molecular or atomic structure of a compound by microorganisms. Biodegradation is the breakdown of organic substances by microorganisms into smaller organic or inorganic components. Mineralization is the complete biodegradation of a contaminant into inorganic constituents, such as carbon dioxide and water. Under anaerobic conditions, the ultimate product of biodegradation may be methane. This complete degradation of a compound is the end result of numerous biodegradation steps. These transforming and degrading processes result from the microorganisms' use of the contam-

*This section was contributed by T. Hazen.

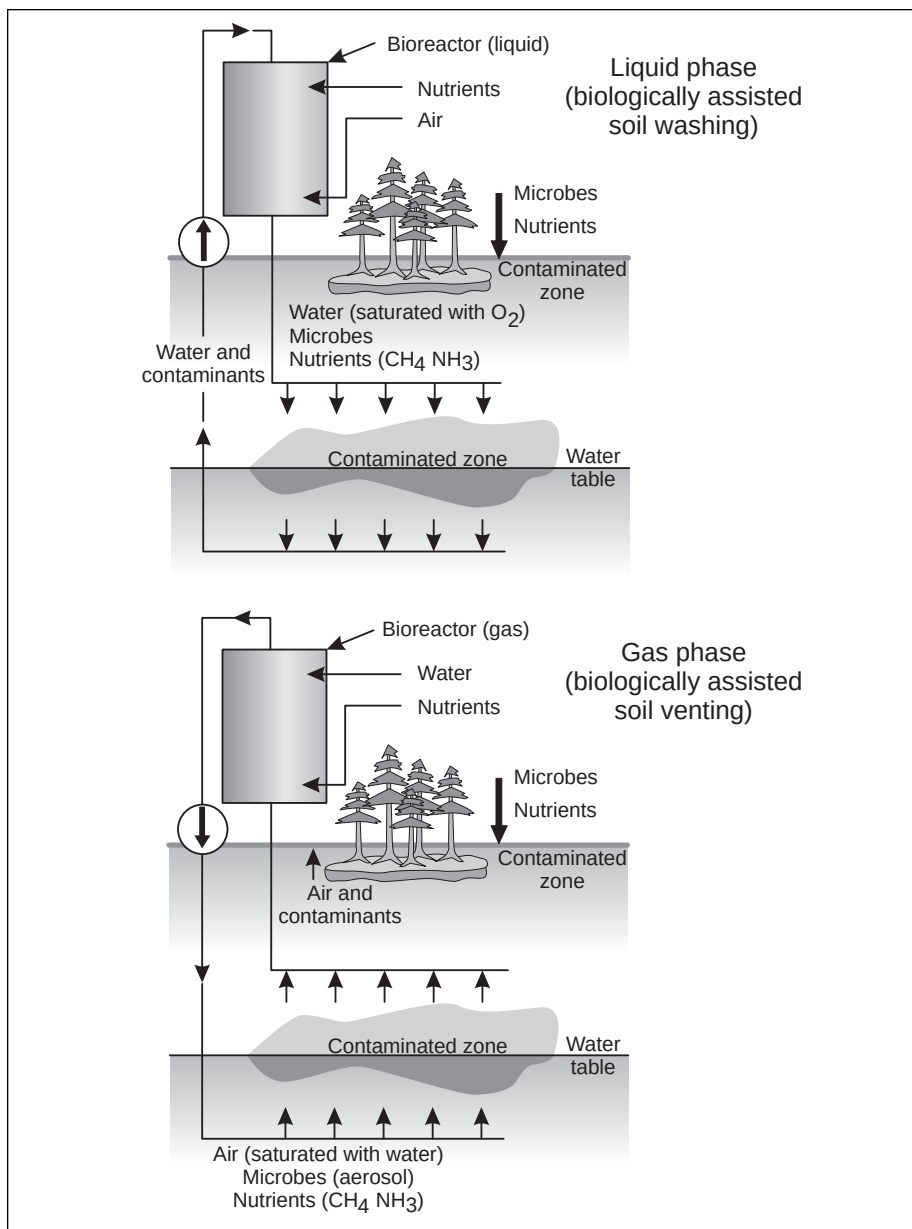


Figure 7-22. Both *ex situ* and *in situ* technologies use either liquid or gas to treat the vadose zone and can use horizontal wells (shown) and infiltration galleries (not shown) with strategies for biofilters, bioremediation, bioventing, biosparging, bioimmobilization, bioreactors, phytoremediation, biomobilization, biocurtain, bioaugmentation, and biostimulation.

inants as a source of nutrients or energy, changing them through various metabolic reactions. Microorganisms also can interact with contaminants and transform them from one chemical form to another by changing their oxidation state. In some cases, the solubility of the altered species increases, increasing the mobility of the contaminant and allowing it to be flushed more easily from the environment. In other cases, the opposite occurs, and the contaminant is immobilized *in situ*, thus reducing the risk to humans and the environment. Both kinds of transformations present opportunities for bioremediation of metals and radionuclides—either to lock them in place or to accelerate their removal.

Although bacteria are usually the agents in most types of bioremediation, fungi, protozoa, algae, and higher plants also can transform and degrade contaminants. Bioremediation depends on the presence of the appropriate organisms or their products in the correct amounts and combinations, and under the appropriate environmental conditions. Optimum environments for microbe growth typically consist of temperatures ranging between 15 and 45°C; pH values between 5.5 and 8.5, and nutrient ratios of 120:10:1 (carbon: nitrogen: phosphorous or C:N:P). Atmosphere and moisture also must be conducive to many types of microbial growth, and the contaminants must be close enough to the microbes, in a form that they can utilize.

Engineered bioremediation involves either adding nutrients to encourage the growth of indigenous organisms in a process called *biostimulation*, or adding specialized organisms themselves in a process called *bioaugmentation*. Both processes may be useful depending on the requirements of the site. A dozen or more specific techniques are associated with engineered bioremediation, and they are briefly described in a lexicon at the end of this section.

Biostimulation

Biostimulation, the most common method of bioremediation in the vadose zone, requires that indigenous organisms capable of degrading contaminants already exist at the site, and that their activity can be increased to achieve a useful effect. Many contaminants, especially organic compounds, are naturally occurring or have natural analogs in the environment. As a result, indigenous organisms in most terrestrial

subsurface environments have been exposed to contaminants for extended periods of time and have adapted, or have even been naturally selected, to utilize the contaminants in their normal metabolic functions. Rarely can a terrestrial subsurface environment be found that is free from organisms that degrade or transform any compound present. Indeed, even pristine environments have bacteria that degrade contaminants. It has been shown in deep drilling studies that plasmids of bacteria living in the sediment increase as depth increases. Plasmids are exogenous pieces of DNA code for enzymes that can break down complex organics, like contaminants. Thus, as the environment becomes increasingly hostile with depth, the ability of bacteria to degrade more recalcitrant compounds increases. (Fredrickson *et al.* 1988).

Biostimulation involves first identifying the compounds that limit the activity of organisms capable of degrading contaminants, and then implementing a method for delivering those compounds to the subsurface. Water, oxygen, carbon, nitrogen, and phosphorus are essential for microbial activity, and shortages of one or more of these compounds limit biochemical degradation reactions at most sites. Not only must the compounds be present in the subsurface, but, typically, they must occur within a certain range of concentrations, and they must be in a chemical form that is available to microbes.

All significant biochemical reactions occur in the aqueous phase, so water is a key ingredient for biostimulation. Water is usually present in sufficient quantities to sustain biodegradation in most natural settings, although it must be added in some cases where previous actions, such as heating, have desiccated the subsurface.

Oxygen is often limiting since the contaminant can be used as a carbon and energy source by the organisms, and the contaminant concentration greatly exceeds the oxygen input rate from natural sources in that environment, such as diffusion from the surface. Oxygen is used as a terminal electron acceptor in respiration, allowing production of much greater amounts of energy from metabolism of organics than simple fermentation processes. Aerobic respiration is the organism's preferred mechanism of metabolism, resulting in complete scavenging of oxygen from the environment. Oxygen is commonly introduced to the vadose zone by injecting air into wells, or by tilling when contaminants are near the ground surface. Barometric pumping or wind turbines can increase air flow into the subsurface without the use of pumps. Applications in

the saturated zone use air or oxygen injected into sparge wells, or hydrogen peroxide injected into wells or distributed through infiltration galleries, a process that stimulates aerobic organisms, which are extremely effective at degrading petroleum hydrocarbons (Thomas and Ward 1992).

A C:N:P ratio of 30:5:1 is generally accepted as ideal for unrestricted growth of soil microbes (Paul and Clark 1989). However, the ratio of these compounds in pore water may differ markedly from the ideal.

Carbon can be a limiting nutrient in settings where the contaminant is a poor carbon or energy source. For example, tetrachloroethylene is a double-bonded, 2-carbon compound with 4 chlorine atoms attached. The energy required to break the double bond and cleave the chlorine atoms prevents the organism from gaining energy during degradation of this compound (Horvath 1972). A source of organic carbon other than the contaminant also is required if the total organic carbon concentration in the environment falls below 1 ppm and the contaminant clean-up levels still have not been met. As a result, fluids with a C:N:P ratio of 50:5:1 are injected for biostimulation, to slightly enrich pore fluids in carbon compared to the idealized ratio cited above (Litchfield 1993). Methane, methanol, acetate, molasses, sugars, agricultural compost, phenol, and toluene all have been added as secondary carbon supplements to the terrestrial subsurface to stimulate bioremediation (National Research Council 1993). Methane can be injected as a gas and is suited to applications in the vadose zone; the other compounds are liquids or solids and are best suited either to applications at the ground surface, such as mixing with soils by tilling, or to injection into wells in the saturated zone.

Nitrogen may be depleted where anaerobic conditions persist for extended periods of time and where the contaminant has a high carbon content. Such conditions promote denitrification and may cause nitrogen to limit the biodegradation rate. Denitrification in the saturated zone is more common than in the vadose zone. Nitrogen has been successfully introduced into the terrestrial subsurface for biostimulation by injecting ammonia, nitrate, urea, or nitrous oxide (U.S. EPA 1989).

Phosphorus is an important nutrient, but it is only required in small concentrations relative to the other nutrients. This is fortunate because phosphorus concentrations are quite low in natural waters. Phosphorus occurs most commonly in the mineral apatite, but this compound is

Bioventing—A Simple Example of Bioremediation Design

By Brian B. Looney

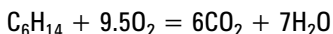
Two common bioremediation methods, bioventing and biosparging, rely on the engineered movement of air through the soil and shallow groundwater to deliver oxygen and other necessary materials. When implemented as bioventing, the method directly targets vadose zone hydrocarbon contaminants. Bioventing is closely related to soil vapor extraction and provides a good example of simple bioremediation design principles. Bioventing is distinguished from vapor extraction by incorporating modifications that maximize the role of biological destruction/detoxification (using lower airflow rates, for example). Bioventing can be implemented using either air injection or soil gas extraction, depending on site needs. Injection systems are typically less expensive and more popular because they are simpler to design and minimize offgas emission or treatment issues. This process has proven robust at a large number of sites and provides an instructive example of general bioremediation design concepts (Leeson and Hinchey 1996).

Bioventing implementation is normally customized for each site based on straightforward field tests. Also, as noted below, bioventing concepts can be modified and expanded for other classes of contaminants and other objectives (for example, cometabolism for chlorinated solvents destruction, redox manipulation for metals stabilization/detoxification, and the like.). Such modifications include innovative delivery systems, alternative reagents, and intro-

duction of alternative microorganisms. In each case, it is critical to develop a simple and consistent design concept that accounts for heterogeneity to maintain reliable performance.

In situ treatment methods, particularly *in situ* bioremediation, require controlled, uniform delivery of amendments to the contaminated zone. In many cases, microbial activity and contaminant destruction rate are limited by a lack of oxygen and other nutrients. In bioventing, air is injected to transport oxygen into the vadose zone.

The amount of air required to degrade hydrocarbons can be estimated by assuming a representative compound (typically hexane) is degraded according to a respiration equation:



This reaction indicates that 9.5 moles of oxygen are required to degrade 1 mole of hexane. This stoichiometric relationship is combined with soil properties and subsurface conditions to estimate rates of contaminant destruction and oxygen utilization. Details of these calculations are given in EPA (1995a) and EPA (1995b).

The degradation reaction cited above identifies a molar ratio between the utilization of carbon and oxygen. As a result, the rate at which oxygen is depleted from soil gases immediately after a bioventing system is shut down can provide a measure of performance. This type of "field respirometry" test

continued

provides an integrated measure of hydrocarbon destruction in the vadose zone (in units of mg of hexane equivalent hydrocarbon per kg of soil per day) according to

$$\text{Hydrocarbon destruction rate} = k_B = (0.68) (\text{oxygen depletion rate})$$

where oxygen depletion rate is measured in units of % O₂ per day

The equation was derived using typical values for porosity, moisture content, bulk density, oxygen density, and the like. Extreme conditions can be evaluated using the full equation presented in EPA (1995b).

Bioventing and biotransformation have been used successfully under a wide range of conditions. Typical system designs generally fall into the following ranges, but there are no theoretical limits on system size:

- Typical site size = 1000 to 6000 m² (0.25 to 1.5 acres)
- Air injected into vadose zone using blower/compressor (1 to 10 hp)
- Typical total air flow = 0.6 to 2.8 m³/min (20 to 100 scfm)
- Typical radius of influence for each well = 6 to 23 m (20 to 75 feet)

System performance and the ability to reach closure criteria are commonly enhanced by increasing the density of wells to overcome mass transfer and heterogeneity limitations. Traditional bioventing relies on the interaction of microorganisms, oxygen (electron acceptor), moisture, nutrients, and aerobically degradable contaminants (electron

donor). Each of these conditions must be present, or supplied, for successful cleanup. A phased implementation normally is used to ensure viability and efficient use of resources. The typical phases are:

1. Assessment of biodegradation potential (are organisms present and active)
2. Assessment of air flow and *in situ* respiration rates
3. System design
4. Full scale operation
5. System monitoring and verification

Many sites can be remediated by bioventing alone, but the presence of recalcitrant compounds (such as chlorinated solvents), nutrient limitations, or other chemical conditions may inhibit the effectiveness of bioventing. Recent research has shown that the addition of alternate carbon sources, redox modifiers, or macronutrients may be able to overcome some site-specific limitations. One example developed by the DOE is the addition of gas-phase phosphorus to overcome limitations caused by the scarcity of this nutrient. This example is described in more detail below to show how general design concepts can be adapted to implement "new" technologies.

While bioventing design has traditionally been related to respiration stoichiometry, characterization of the hydrocarbon utilization by the biological community can be expanded to include an equation for microbial growth. The

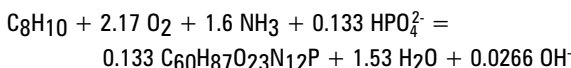
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equations below show the biomass formation stoichiometry for a representative contaminant (in this case ethylbenzene). Maximum contaminant degradation rates are generated when biomass is increased and overall site respiration rates are concurrently

increased. The equation for biomass presented below includes all of the primary macronutrients represented in cell mass. The equation is expanded to facilitate discussion of technology limitations and development potential.

Biomass Formation (Growth)

hydrocarbon + oxygen + nitrogen + phosphorus = biomass + water + other products



It is clear that oxygen is the primary element limiting both respiration and microbial growth during aerobic biodegradation. Microbial growth rates at hydrocarbon-rich sites can be further limited by nitrogen (N) and phosphorus (P). Bioventing and biosparging provide both oxygen and nitrogen (via fixation) as air moves through the soil and shallow groundwater. This leaves phosphorus as a rate-limiting nutrient at some bioventing sites. Phosphorus can be injected into the vadose zone as an aqueous fertilizer solution; however, liquid injection increases costs and complexity and has not reliably increased performance (EPA 1995a and 1995b). Liquids injected into the vadose zone decrease the gas-phase permeability and tend to affect relatively small areas near the injection locations, whereas the

bioventing process is a large-scale volumetric process that occurs throughout the contaminated vadose zone with minimal impacts of typical levels of heterogeneity.

To overcome these limitations, scientists working for DOE developed a process that exploits the vapor pressure of alkyl phosphate esters to deliver phosphate as a component of the injected air. This process provides process control and accelerated cleanup (by increasing biomass) for bioventing and biosparging applications where phosphorus is a limiting nutrient. As with many new environmental technologies, this example shows that scientific advances are generally made in a disciplined fashion in which the baseline is improved in a step-wise manner.

nearly insoluble and effectively eliminates the bioavailability of the phosphorus it contains. Several inorganic and organic forms of soluble phosphate have been successfully used for biostimulation where phosphorus is a limiting nutrient (U.S. EPA 1989).

Even plants, such as poplar trees, have been used to biostimulate remediation of subsurface environments (Schnoor *et al.* 1995). In this case, the plants act as solar-powered nutrient pumps stimulating rhizosphere microbes to degrade contaminants (Anderson *et al.* 1993).

Biostimulation can be measured and monitored in the vadose zone using a number of direct and indirect techniques, including measurement of degradation products, like daughter products and carbon dioxide, or changes in degrading organism density. See Chapter 3 for discussion of techniques that can be used.

Bioaugmentation

Bioaugmentation is used where indigenous microbes suitable for degrading contaminants are absent, or where non-indigenous microbes are particularly well-suited to degrading a contaminant under conditions that can be established at the site (Hazen, 1997). This approach may be particularly well-suited where:

1. Contaminants were released recently and the indigenous bacteria have not had time to adapt to the contaminant
2. Contaminants are particularly recalcitrant so that only a limited number of organisms are capable of transforming or degrading them
3. Harsh environmental conditions inhibit the establishment and maintenance of a critical biomass
4. The project objective is to cause growth that will plug the pores of a formation for contaminant containment
5. The environment can be carefully controlled, as in bioreactors, prepared beds, composting, bioslurry reactors, and land farming, so that specific inocula of high rate degraders is effective.

Novel organisms injected into the subsurface have successfully enhanced the *in situ* bioremediation of compounds that are recalcitrant

to degradation by indigenous organisms such as PCBs, chlorinated solvents, polycyclic aromatic hydrocarbons (PAHs), and creosote (National Research Council 1993). Surface applications of bioaugmentation for petroleum contaminants in prepared beds and land farming are routine since they help jump-start the bioremediation process. For controlled and carefully optimized environments, such as bioreactors, biofilters, biopiles, and bioslurry reactors, bioaugmentation is ideal, since it is relatively easy to control conditions that maximize rates of biochemical transformation or degradation.

Bioaugmentation may cause rapid growth that clogs pores and restricts additional fluid flow. This is certainly a problem where it occurs mistakenly, but it can be an important method for rapidly creating a barrier that contains contaminants. The oil industry has used bioaugmentation to plug certain zones in order to enhance oil recovery (Cusack *et al.* 1992), and similar processes have been applied to improve containment of contaminant plumes.

The relative merits of bioaugmentation and biostimulation can become blurred when the details of the processes are scrutinized. Microorganisms are commonly present in the nutrients used for biostimulation, particularly when the nutrients are in liquid form, and those organisms may augment indigenous populations when they are injected. Likewise, dead organisms are an excellent source of nutrients for most indigenous organisms. Specialized organisms injected for bioaugmentation may quickly die only to provide nutrients for indigenous organisms, which degrade contaminants. As a result, it is nearly impossible to determine if the augmentation of organisms provides a significant advantage over nutrient stimulation alone. Even some of the best controlled bioaugmentation field studies, such as caisson studies of PCB biodegradation in Hudson River sediment, failed to show that bioaugmentation was superior to biostimulation alone (Harkness *et al.* 1993).

Due to the high cost of organism production, and the lack of proof of its effectiveness, bioaugmentation probably is limited to applications where exceptional improvements are possible. For example, this is the case with genetically engineered microorganisms. It is possible that a genetically engineered microorganism could be constructed with unique combinations of enzymes to facilitate a sequential biotransformation or biodegradation of a contaminant. This would be particularly helpful for contaminants that are extremely recalcitrant, such as PCBs, or for con-

taminants that can now only be degraded under restricted conditions, such as tetrachloroethylene and carbon tetrachloride. In addition, genetically engineered microorganisms could be modified to have unique survival or adherence properties, making them better suited to the environment where they are used. Genetic engineering has been used to create microbes that will emit light when degrading contaminants, so that the rate of *in situ* biodegradation can be measured using fiber optic probes (Ripp *et al.* 1999). The effectiveness of genetically engineered, light-emitting microbes to signal the biodegradation of naphthalene was proven during field studies in large lysimeters at a DOE site (Ripp *et al.* 1999). Permitting was once thought to be prohibitive to the release of genetically engineered microorganisms, but experience and many agricultural examples have eased these concerns, and regulators in many states are willing to consider these options.

Factors Affecting Performance

The major factors affecting the performance of bioremediation in the vadose zone include the following:

1. Site Evaluation—Ambient biochemical processes and other subsurface conditions, such as contaminant concentration or permeability distribution, must be assessed at the site.
2. Biochemical Process—Biochemical processes must be identified that will occur under conditions that can be sustained at the site and are capable of degrading contaminants of concern.
3. Delivery—Materials required to sustain degradation reactions, or microbes themselves, must be delivered to the location of the contaminants.
4. Monitoring—Subsurface conditions must be monitored to determine the location of the desired biochemical processes, and to adjust the process as required.

Biochemical processes can be identified that are capable of degrading all but the most recalcitrant compounds. However, those biochemical processes may require conditions that are challenging to achieve at many sites. For example, some chlorinated solvents can be degraded

under anaerobic conditions using biochemical processes that are currently well understood. Such conditions are common in the saturated zone, but anaerobic conditions suitable for the degradation of chlorinated solvents rarely occur naturally in the vadose zone. Experimentally, it is possible at some sites to create and sustain anaerobic conditions by infusion of high-oxygen-demand organics like lactate. In addition, some chlorinated solvents can be degraded quite effectively under aerobic conditions if a carbon source, like methane, is mixed with air and injected. (Hazen 1999b, Hazen *et al.* 1997). Correct assessment of ambient site conditions and evaluation of a feasible biochemical pathway for degrading contaminants are critical factors for successful bioremediation.

Biochemical reactions are restricted to compounds dissolved in water, and the concentration of the dissolved compounds is an important factor affecting performance. Some compounds may be toxic to microbes when present in high concentrations, even though lesser concentrations can be readily degraded. This means that bioremediation efforts cannot degrade NAPLs directly, and the high dissolved concentrations that accompany NAPL occurrence may also inhibit bioremediation. Typically, it is necessary to remove NAPLs that are floating on the water table or smearing the capillary fringe zone before biostimulation is successful (Keet 1995). This strategy greatly increases the biostimulation response time by lowering the highest concentration of contaminant the organisms are forced to transform.

The delivery of compounds to increase biochemical reaction rates is an essential part of nearly any bioremediation effort. Biostimulation and bioaugmentation have specific delivery problems, because the factors affecting transport of chemical nutrients in the vadose zone and groundwater are somewhat different from those affecting transport of organisms (Alfoldi 1988). Both bacteria and chemicals can be retarded during flow through porous materials, but even the smallest bacterium has different transport properties than dissolved chemicals. For example, the pores in clayey soils may be smaller than bacteria and physically prevent their movement, whereas this type of physical filtering never affects dissolved nutrients. Clays also may electrostatically bind negatively charged microbes, where divalent metals form cationic bridges that create a local positive charge, which will then attract microbes. Dissolved chemical nutrients also may be electrostatically attracted to the surfaces

of clay minerals, but this interaction can go well beyond simple sorption. Inorganic chemicals injected for biostimulation may precipitate metals, swell clays, change redox potentials, and modify either or both the hydraulic or electrical conductivity, all changes that can have major effects on water flow and biochemistry.

The permeability of the contaminated formation is the single most important site characteristic affecting delivery. The minimum average hydraulic conductivity is generally 10^{-4} cm/sec where conventional methods are used to deliver nutrients to the saturated zone (Thomas and Ward 1989). The lower limit for successful bioaugmentation is even greater, 10^{-3} cm/sec or greater, depending on the size and adherence properties of the organism being applied (Baker and Herson 1990). Recent studies have shown the less adherent strains of some contaminant-degraders can be isolated and produced to improve formation penetration (DeFlaun *et al.* 1994). Such innovations make it feasible to inject microbes into tighter formations.

Pneumatic conductivity, which decreases with increasing water content, as described in Chapter 1, affects the average delivery rate of nutrient gases in the vadose zone. Heterogeneity in the subsurface markedly affects bioremediation by influencing the flow paths of fluids or microorganisms. In general, heterogeneities cause preferential flow paths to develop so that delivery is concentrated in certain regions and avoided in others. Unfortunately, remediation will follow a similarly patchy pattern, leaving significant regions contaminated. Bedded sedimentary formations and fractured rock, or fine-grained sediments, will be particularly susceptible to this problem.

Infiltration galleries, ponding, or sprinklers are the primary method for liquid delivery to the vadose zone. Surface structures and land use prevent construction of infiltration galleries at many locations. Moreover, the flow of water from infiltration galleries downward through the vadose zone nearly always follows preferential pathways, either due to heterogeneities or from fluid instabilities at the wetting front. As a result, it is difficult (or perhaps impossible) to uniformly deliver liquids to the vadose zone where pores are partially saturated.

Delivering nutrients as a gas phase is one way to improve biostimulation in the vadose zone, largely because diffusion will smooth the irregularities in concentrations caused by preferential flow of gases much more quickly than it does in liquids. Oxygen, carbon, nitrogen,

and water can be injected as gas or vapor, and so most biostimulation in the vadose zone uses gas injection. Gaseous nutrient injection has also been used to remediate chlorinated solvents in fractured rocks at several sites (Hazen 1999a). Microbes are typically suspended in water when they are delivered, so bioaugmentation cannot use gases.

The effects of the biostimulant itself may change the permeability of the formation. Hydrogen peroxide is an excellent source of oxygen, but it can trigger such a dense growth of microbes that the pores around the injection well become plugged and block the flow of additional nutrients. Hydrogen peroxide will raise the redox potential, which may cause metals to precipitate and clog pores even further (Thomas and Ward 1989). Injecting ammonia also can be problematic because it decreases permeability by swelling clays around an injection well. Ammonia also rapidly sorbs to clays and can change the pH in poorly buffered environments.

Many of the liquid delivery problems in the vadose zone can be addressed by excavating the soil and treating it in a bioreactor, prepared bed, land farm, bioslurry reactor, biopile, or compost pile. In these cases, the permeability can be controlled or manipulated to allow better stimulation of the biotreatment process.

Where excavation is infeasible, alternative methods of delivering fluids *in situ* may improve the performance of bioremediation, particularly in formations where low permeability or heterogeneities present problems. Liquid nutrients can be injected laterally outward from a lance that is temporarily pushed into the subsurface (Siegrist *et al.* 1998). Fractures can be induced by injecting liquids or gases to increase the flow of fluids in the subsurface. Both pneumatic and hydraulic fracturing methods have been used to improve bioremediation in tight soils (Murdoch *et al.* 1994).

Status

Biostimulation is particularly effective at petroleum-hydrocarbon degradation under aerobic conditions in the vadose zone. This application is probably the most commonly used method for treating soils containing petroleum hydrocarbons at the ground surface. Bioventing is widely used to remediate petroleum hydrocarbons because it is an effective method for low-to-moderate concentrations, and it is relatively inex-

pensive. Bioventing is used as a specific design objective, and it also can be implemented inadvertently during vapor extraction.

Bioremediation of some chlorinated solvents requires anaerobic conditions when indigenous microbes are used. It is possible to create anaerobic conditions in the vadose zone by injecting inert gas to displace air or to markedly increase the water content. However, these conditions are difficult to maintain in the vadose zone, so this process rarely is attempted above the water table. Fortunately, many chlorinated solvents can be bioremediated under aerobic conditions by addition or use of some secondary carbon source like methane, propane, or petroleum co-contaminants. Co-metabolic bioventing and biosparging has been used to cleanup a large number of sites in the last 5 years.

Genetically engineered microorganisms (GEMs) have been demonstrated to remediate polycyclic aromatic hydrogen (PAH) compounds at DOE sites in lysimeters (Ripp *et al.* 1999). The next step, still in the planning stage, is a large-scale field application at a contaminated site. This technique holds great promise for both remediation and monitoring. A large number of agricultural releases of GEMs and several bioremediations using GEMs suggest that this could become an important remediation technique, especially as the public and regulators become more comfortable with the technology.

INJECTION OF LIQUID OXIDANTS*

In the 1990s, *in situ* chemical oxidation emerged as a promising remediation method for sites contaminated with organic chemicals (Siegrist 1998; U.S. EPA 1998). Its promise is because many toxic organic chemicals can be either completely destroyed or partially degraded as an aid to subsequent bioremediation. Early studies were primarily focused on hydrogen peroxide (H_2O_2) or Fenton's Reagent (H_2O_2 plus Fe^{+2}), applied to the *ex situ* treatment of individual organic chemicals in water (Barbeni *et al.* 1987; Bowers *et al.* 1989; Watts and Smith 1991; Venkatadri and Peters 1993). Subsequent research began to explore peroxide and Fenton's reagent oxidation in soil environments (Watts *et al.* 1990; Watts and Smith 1991; Watts *et al.* 1991; Tyre *et al.*

*This section was contributed by R.L. Siegrist, O.R. West, and M.A. Urynowicz.

1991; Ravikumar and Gurol 1994; Gates and Siegrist 1993; 1995; Watts *et al.* 1997). Research was also initiated into alternative oxidants, such as ozone (Bellamy *et al.* 1991; Nelson and Brown 1994; Marvin *et al.* 1998) and potassium permanganate (KMnO_4) (Vella *et al.* 1990; Vella and Veronda 1994; Gates *et al.* 1995; Schnarr *et al.* 1998; West *et al.* 1998; Siegrist *et al.* 1998a, b, 1999; Struse 1999). Field demonstrations and full-scale applications have evaluated alternative methods for delivering oxidants, including permeation by vertical lances (Jerome *et al.* 1997), flushing by vertical or horizontal groundwater wells (Lowe *et al.* 1999; Schnarr *et al.* 1998; West *et al.* 1998), and reactive zone emplacement by hydraulic fracturing (Murdoch *et al.* 1997; Siegrist *et al.* 1998a, b; Siegrist *et al.* 1999). This section presents the principles and practices of *in situ* chemical oxidation using peroxide and permanganate, including reaction chemistry and delivery systems. Figure 7-23 illustrates the types of systems being deployed while Table 7-4 highlights some of their key features and factors affecting performance.

Much of the research and many of the applications of liquid oxidants have been in the saturated zone. Nevertheless, there has been some important work done on vadose applications, and the technique is viable at least under some conditions in the vadose zone. One of the primary concerns with applications of this technology, or other remedial technologies where liquids are injected into the vadose zone, is the development of preferential flow paths that limit the contact between the oxidant and contaminants. These effects will be particularly important in strongly heterogeneous materials, or in coarse-grained sediments in the vadose zone where gravity dominates capillary forces. Effective methods for mitigating the development of preferential pathways, for example, by modifying well design, injection strategy, or other means, are important to the remedial performance of liquid oxidants in the vadose zone.

The case study "Case History of Liquid Oxidant Injection Into the Vadose Zone," by R.L. Siegrist, N.E. Kort, O.R. West, and M.A. Urynowicz, describes a field trial of liquid oxidant injection at the DOE Portsmouth Plant. *See page 1191.*



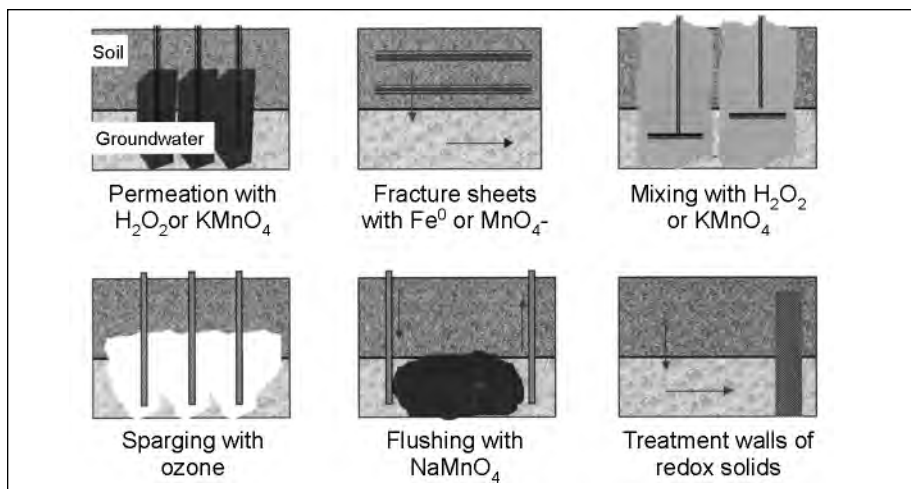


Figure 7-23. Applications of *in situ* chemical oxidation systems (Siegrist *et al.* 1999).

TABLE 7-4

Features of peroxide, permanganate, and ozone oxidants as used for *in situ* remediation.

	Features	Peroxide (Fenton's)	Permanganate	Ozone
Reagent	Form	Liquid	Liquid or solid	Gas
Characteristics	Point of generation	Offsite, shipped onsite	Offsite, shipped onsite	Onsite during use
	Quantities available	Small to large	Small to large	Small to large
Oxidation <i>In Situ</i>	Delivery Methods	GW wells, soil lances	GW wells, soil lances, fractur.	GW sparge wells
	Dose concentrations	5 to 50 wt. percent H_2O_2	0.02 to 4.0 wt. percent MnO_4	Variable
	Single / multiple dosing	Multiple is common	Single and multiple	Multiple
	Amendments	Fe^{+2} and acid	None	Often ozone in air
	Subsurface transport	Advection	Advection and diffusion	Advection
	Rate reaction / transport	High or very high	Moderate to high	Very high
	Companion technology	None required	None required	Soil vapor extraction

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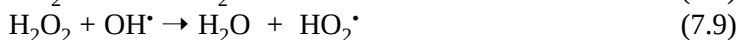
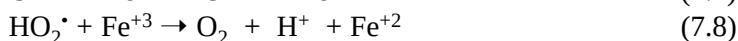
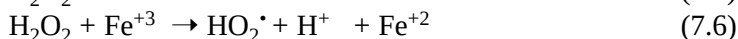
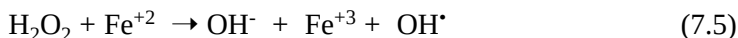
TABLE 7-4

Features of peroxide, permanganate, and ozone oxidants as used for *in situ* remediation (continued).

	Features	Peroxide (Fenton's)	Permanganate	Ozone
Oxidation Effectiveness	Susceptible organics	BTEX, PAHs, phenols, alkenes	BTEX, PAHs, alkenes	BTEX, PAHs, phenols, alkenes
	Difficult to treat organics	Some alkanes, PCBs	Alkanes, PCBs	Alkanes, PCBs
	Oxidation of NAPL	Direct oxidation possible	Direct oxidation possible	Direct oxidation possible
	Reaction products	Organic acids, salts, O ₂ , CO ₂	Organic acids, salts, MnO ₂ , CO ₂	Organic acids, salts, O ₂ , CO ₂
	Gas evolution	Substantial gas evolution	Minimal gas evolution	Minimal gas evolution
System Effects on Oxidation	Effect of NOM	Demand for oxidant	Demand for oxidant	Demand for oxidant
	Effect of pH	Most effective in acidic pH	Effective over pH 3.5 to 12	Effective over pH 3.5 to 12
	Effect of temperature	Reduced rate at lower temp.	Reduced rate at lower temps.	Reduced rate at lower temp.
	Effect of ionic strength	Limited effects	Limited effects	Limited effects
Oxidation Effects on System	pH	Lowered if inadequate buffering	Lowered if inadequate buffering	Lowered if inadequate buffering
	Temperature	Minor to high increase	None to minor increase	Minor to high increase
	Metal mobility	Potential for redox metals	Potential for redox/exch. metals	Potential for redox metals
	Permeability loss	Potential for reduction due to gas evolution and colloids	Potential for reduction due to MnO ₂ colloid genesis	Potential for reduction due to gas evolution and colloids

Principles

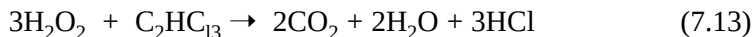
The chemical principles governing the degradation of toxic organic chemicals by peroxides were first recognized during studies focused on petrochemicals, such as naphthalene, phenanthrene, pyrene, and phenols, but later work included chlorinated solvents like TCE and tetrachloroethylene (PCE) (Watts *et al.* 1990; Watts and Smith 1991; Watts *et al.* 1991; Tyre *et al.* 1991; Ravikumar and Gurol 1994; Gates and Siegrist 1993; 1995; Watts *et al.* 1997). Oxidation using H_2O_2 in the presence of native or supplemental Fe^{+2} produces Fenton's reagent, which yields free radicals ($\text{OH}^\bullet$) that can rapidly degrade a variety of organic compounds (Table 7-4). However, the application of peroxide to soil and groundwater systems involves a variety of competing reactions as follows:



Hydrogen peroxide can also autodecompose in aqueous solutions with accelerated rates upon contact with mineral surfaces or carbonate and bicarbonate ions (Hoigne and Bador 1983) according to



The simplified stoichiometric reaction for peroxide degradation of TCE is

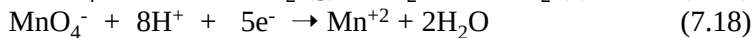
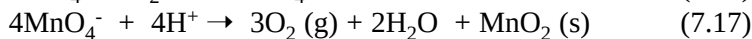
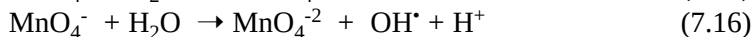
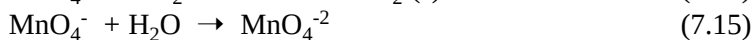
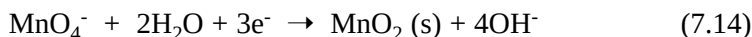


Fenton's Reagent oxidation is most effective under very acidic conditions, such as pH 2 to 4, and becomes ineffective under moderate to strongly alkaline conditions and/or where free radical scavengers like CO_3^{-2} are present. The reaction is strongly exothermic and can produce substantial gas and heat. The oxidative reactions are extremely rapid and follow second-order kinetics.

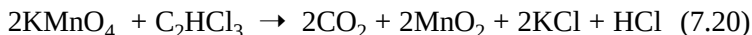
For application *in situ*, there are three processes that have been patented based on reaction chemistry and/or mode of delivery: the

CleanOX, GeoCleanse, and ISOTEC methods. While the specifics of an application will be very site-dependent, *in situ* chemical oxidation with peroxides has typically included H_2O_2 concentrations in the range of 5 to 50 percent by weight and where native iron has been lacking or unavailable, ferrous sulfate is often added at mM levels. In some cases acetic or sulfuric acids are also added to reduce the pH to a more favorable acidic range. Delivery methods include common groundwater wells or specialized injectors. In many cases, multiple doses or application cycles are used to facilitate more uniform delivery of reagents and efficiency of treatment.

Compared to peroxide, oxidation of soil and groundwater using permanganate has more recently been studied for *in situ* treatment of chlorinated solvents, such as TCE, PCE, and petrochemicals such as naphthalene, phenanthrene, pyrene, and phenols (Vella *et al.* 1990; Leung *et al.* 1992; Vella and Veronda 1994; Gates *et al.* 1995; Yan and Schwartz 1996; Schnarr *et al.* 1998; West *et al.* 1998; Siegrist *et al.* 1998a,b; Lowe *et al.* 1999; Siegrist *et al.* 1999; Struse 1999). The reaction stoichiometry and kinetics in natural systems are quite complex and are not yet fully understood. Permanganate (typically as KMnO_4 , but also available in Na, Ca, or Mg salts) can participate in several reactions as determined to a large degree by system pH. For example, between a pH of 3.5 and 12, permanganate ion reacts slowly to form manganese dioxide (equation 7.14). Above a pH of about 12, manganate ions (Mn(VI)) may be formed (equation 7.15). Hydroxyl radicals may also be formed in alkaline solutions (equation 7.16). In slightly acidic solutions, the permanganate ion can decompose slowly to form manganese dioxide with a release of oxygen (equation 7.17). Below a pH of about 3.5, Mn(II) cations are formed (equation 7.18). Under acidic conditions, the permanganate ion can then oxidize the Mn(II) to form manganese dioxide (equation 7.19).



The stoichiometric reaction for the complete destruction of TCE by KMnO_4 is



Under neutral or acidic pH, oxidation is speculated to occur through the formation of a cyclic ester with further reaction yielding organic acids and aldehydes as well as CO_2 and $\text{MnO}_2(\text{s})$ (Arndt 1981; Leung *et al.* 1992; Yan and Schwartz 1996). Halogenated substitution with Cl may facilitate C-C cleavage during oxidation, although the rate of reaction slows with increasing Cl substitution (Yan and Schwartz 1996). For example, PCE degradation is slower than TCE. The reaction appears to be second order with a rate constant of about $0.6 \text{ L mol}^{-1}\text{s}^{-1}$ (in clean groundwater). Solution pH between 4 and 8 has little or no effect on rate, but temperature does affect the rate as described by the Arrhenius equation (Case 1997). In alkaline solutions, hydroxyl radicals may be formed and contribute to oxidative destruction (equation 7.16). The reaction can include destruction by direct electron transfer or free radical advanced oxidation. The pH of the reacting system can decline to strongly acidic conditions, such as pH 2 to 3, depending on the buffering capacity of the system. Key reaction products can include intermediate organic acids along with production of manganese oxide solids and chlorides.

Pseudo first- or second-order kinetic models often describe the kinetics of oxidant reaction with target organic chemicals. For example, during the past year kinetic studies have been completed for treatment of TCE over a wide range of concentrations (0.5 to 800 mg/L) in simulated and site groundwaters using permanganate solutions or solids at stoichiometric dosages in the range of 5x to 10x. The reaction order and kinetic parameters have been examined using pseudo first- and second-order kinetic models fit to the data:

$$\text{First order} \quad d[C_1]/dt = -k_1[C_1] \quad (7.21)$$

$$\text{Second order} \quad d[C_1]/dt = -k_2 [C_1][C_2] \quad (7.22)$$

$$\text{Pseudo first order} \quad d[C_1]/dt = -k'[C_1] \quad (7.23a)$$

$$k' = k_2 [C_2] \quad (7.23b)$$

where, $d[C_1]/dt$ is rate of change in concentration of the target compound ($\text{ML}^{-3}\text{T}^{-1}$), k_1 is the first-order rate constant (T^{-1}), C_1 is the con-

centration of the target compound (ML^{-3}), k_2 is the second-order rate constant ($\text{L}^3\text{M}^{-1}\text{T}^{-1}$), C_2 is the concentration of the oxidant (ML^{-3}), and k' is the pseudo first-order rate constant (T^{-1}).

The degradation of TCE by KMnO_4 in the absence of natural organic matter (NOM) is clearly second order, according to a series of recent tests conducted using KMnO_4 solutions ranging from 0.6 to 6.3 mM. The tests determined that a second-order reaction model with $k_2 = 0.9 \text{ L mol}^{-1}\text{s}^{-1}$ could explain the all experimental data with a relative error of only 12 percent.

The kinetics of oxidation of a given target organic chemical are also affected by matrix conditions; most notably, temperature and the concentration of other oxidant-demanding substances such as natural organic matter (NOM). Temperature effects can be described by the Arrhenius equation (Case 1997). However, the effects of NOM or minerals on the rate and extent of oxidant demand is poorly understood. Limited research suggests that the rate of oxidant consumption is comparable or slower than that of most target chemicals and that only a fraction of the total NOM is susceptible to oxidation. It is clear, however, that the rate and extent of demand must be accounted for, or a kinetic model, such as equation (7.23), will grossly over-predict the rate of destruction of a target like TCE. Moreover, if the NOM demand is high, it may deplete the oxidant and cause the reaction with the target organic chemical to cease altogether.

Another factor affecting the kinetics of destruction is the phase of the target organic contaminant; for example, whether the organic chemical is dissolved, sorbed, or occurs as a nonaqueous liquid phase. Most research has been conducted with dissolved organic chemicals. Limited research with Fenton's reagent (Tyre *et al.* 1991; Li *et al.* 1997; Watts *et al.* 1997) and permanganate (unpublished CSM work) suggests that sorption is not rate-limiting under the usual high-oxidant doses and energetic reaction conditions. Research on the oxidative destruction of nonaqueous phase liquids is limited, but preliminary results indicate that the rate of pure phase dissolution and degradation is accelerated by permanganate in the bulk solution.

Implementation and Augmenting Technologies

The standard of practice for the design and implementation of *in situ* chemical oxidation technologies is still evolving. While there have been

numerous laboratory studies and an increasing number of field-scale trials and full-scale projects, there are still gaps in the current knowledge base and performance deficiencies have been observed. Engineering of *in situ* oxidation technologies must, therefore, be done carefully, with due attention to reaction chemistry and to delivery and transport processes. As illustrated in Figure 7-24, the design and implementation process should rely on an integrated effort involving screening-level characterization tests and reaction and transport modeling, combined with treatability studies at the lab and field scale.

The method of delivery and distribution throughout a subsurface region is of paramount importance due to the relatively indiscriminate and rapid rate of reaction of oxidants, and it is of particular importance in the vadose zone, where preferential flow may cause the oxidant to bypass much of the contamination. Oxidant delivery systems in the vadose zone often employ infiltration galleries or injection probes. These can be coupled with delivery in the saturated zone by vertical or horizontal wells. Forced advection should be employed in both cases if permeability is adequate to rapidly move the oxidant away from the initial point of entry into the subsurface region to be treated (Figures 7-23 and 7-24). In low permeability media such as silts and clays, or when

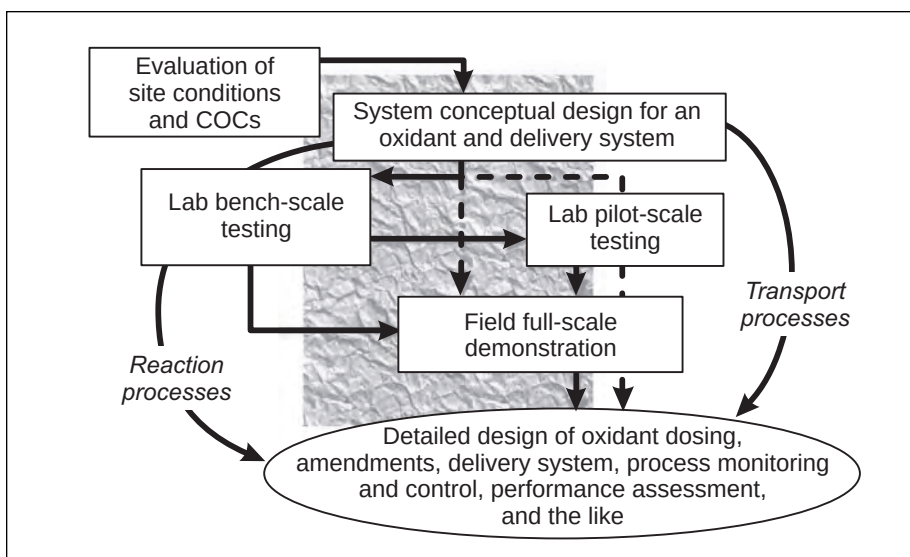


Figure 7-24. Process design approach for *in situ* chemical oxidation.

oxidant reaction rates are extremely high, oxidant delivery systems can employ vertical lance injection or sparging systems, enabling high-density delivery to minimize transport distances and enhance contact with target chemicals. In contrast to peroxide and ozone oxidants, permanganate is less prone to decomposition and is more stable. As a result, it can migrate by diffusive processes, albeit at slow rates of transport (Struse 1999).

Critical Factors Affecting Performance

Past experience and consideration of the current state of knowledge suggest that there are some key issues to carefully consider during design process (Table 7-5). These issues include:

- (1) The ability of the oxidant to degrade the target chemicals at a rate and to the extent required under given environmental matrix conditions.
- (2) The ability of the oxidant to be delivered to, and dispersed throughout, the contaminated region. This issue is particularly important in the vadose zone where preferential flow may limit the contact between oxidant and contaminants.
- (3) The rate and extent of natural oxidant demand.
- (4) Potential for adverse effects caused by the oxidant. Such effects include the formation of toxic by-products, gas evolution, impurities in the oxidant, precipitation of solids, permeability loss, and mobilization of metals.
- (5) Compatibility of oxidation with other technologies, like natural attenuation and post-treatment land use.

The relevance of these issues and the need for their accurate and complete delineation during system design depends on the site-specific conditions and context of the application being contemplated.

Monitoring

Monitoring of *in situ* chemical oxidation in the vadose zone should be designed to verify remediation effectiveness during application, includ-

TABLE 7-5 Representative list of organic chemicals successfully treated by chemical oxidants.

Organic contaminant	Media treated	Oxidant	References
Trichloroethylene	Water (spiked)	H ₂ O ₂	Bellamy <i>et al.</i> 1991
	Silica sand (spiked)	H ₂ O ₂	Ravikumar and Gurol 1992
	Silty clay soil (spiked)	H ₂ O ₂	Gates and Siegrist 1995
	Sand & clay soils (spiked)	H ₂ O ₂ or KMnO ₄	Gates, Siegrist and Cline 1995
	Ground water (spiked)	KMnO ₄	Case 1997, Yan and Schwartz 1996
	Ground water (field site)	KMnO ₄	West <i>et al.</i> 1998, Schnarr <i>et al.</i> 1998
	Ground water (field site)	NaMnO ₄	Lowe <i>et al.</i> 1999
	Silty clay soil (field site)	KMnO ₄	Siegrist <i>et al.</i> 1999
Tetrachloroethylene	Water (spiked)	H ₂ O ₂	Bellamy <i>et al.</i> 1991
	Silica sand (spiked)	H ₂ O ₂	Leung <i>et al.</i> 1992
	Sand, clay soils (spiked)	H ₂ O ₂ or KMnO ₄	Gates, Siegrist, and Cline 1995
	Ground water (field site)	KMnO ₄	Schnarr <i>et al.</i> 1998
	Ground water (spiked)	KMnO ₄	Yan and Schwartz 1996
	Ground water (field site)	Ozone	Dreiling <i>et al.</i> 1998
Carbon tetrachloride and t-1,2-DCE	Water (spiked)	H ₂ O ₂	Bellamy <i>et al.</i> 1991
Pentachlorophenol	Silica sand (spiked)	H ₂ O ₂	Ravikumar and Gurol 1992
	Natural soil (spiked)	H ₂ O ₂	Watts <i>et al.</i> 1990
2,4-dichlorophenol, dinitro-o-cresol	Water (spiked)	H ₂ O ₂	Bowers <i>et al.</i> 1989
Trifluralin, hexadecane, dieldrin	Soil (spiked)	H ₂ O ₂	Tyre <i>et al.</i> 1991
Naphthalene, phenanthrene, pyrene	Clay, sandy soils (spiked)	H ₂ O ₂ or KMnO ₄	Gates, Siegrist, and Cline 1995
Octachlorodibenzo(p)dioxin	Soil (spiked)	H ₂ O ₂	Watts <i>et al.</i> 1991
Motor oil / diesel fuel	Soil (field site)	H ₂ O ₂	Watts 1992
PAHs and PCP	Soil and GW (field site)	Ozone	Marvin <i>et al.</i> 1998
BTEX and TPH	Soil and GW (field site)	Ozone	U.S. EPA 1998

ing the absence of oxidation-induced adverse secondary effects. Characterization is also typically completed before application of chemical oxidation to verify suitability of the target compounds and matrix conditions, as well as to gather data to support engineering of transport and delivery methods. Remediation effectiveness is gauged by monitoring several factors: (1) oxidant distribution throughout the region of interest, (2) destruction of the target compounds, (3) production of undesirable fugitive emissions or daughter products, and (4) effects on co-contaminants, for example, redox metals. Ancillary monitoring in some applications can also include compatibility with post-oxidation processes such as bioremediation and changes in soil structure and geochemistry, which could affect subsequent land use.

Oxidant distribution can be monitored by direct measurement of oxidant concentrations, such as MnO_4^- or H_2O_2 , or the reaction byproducts, such as oxygen concentrations (pore water or vapor phase), chlorides (pore water), or ions (pore water). This can be complicated in the vadose zone, but suction lysimeters can be employed for pore water sampling and soil cores can be collected by direct push technology. Alternatively, soil sensors can be employed to detect changes in soil temperature (increases), pH (decreases), or Eh (increases), one or all of which can result from an oxidant entering the vadose zone. These measurements may or may not be sensitive enough in a given setting to detect chemical oxidation in progress and they do not verify that the oxidant is still present or at a level capable of degrading the target chemicals of concern. Destruction of target compounds, such as TCE and BTEX, and production of daughter compounds, such as chlorinated alkanes or chlorinated organic acids, can be determined by either vapor phase sampling and equilibrium partitioning calculations, or by direct sampling and analysis, with great care being taken for quantification of volatile organic compounds (Siegrist and Van Ee 1994). Monitoring of fugitive gaseous emissions, of greater concern with peroxide oxidants, can be assessed by quantifying pressure gradients and/or by analysis of gas composition at key points. This can be monitored by subsurface vapor probes with pressure transducers and sampling wells, by surface flux chambers above the treated region, and/or by sampling/analysis of air within sensitive areas. This monitoring is especially critical when there are nearby conduits for untreated chlorocarbon or petrochemical gases such as sewers, utility corridors, and basements. Monitoring of any

mobile co-contaminants is normally done by direct core collection and characterization, such as speciation of chromium between Cr^{+3} and Cr^{+6} or by sampling/analysis of groundwater wells under the treated region. Ancillary monitoring is normally accomplished by soil core collection and analyses for the relevant parameters of interest.

Status

In situ chemical oxidation is rapidly emerging as a viable remediation technology for mass reduction in the vadose zone as well as in the associated groundwater plumes. Tables 7-6 to 7-8 highlight several recent applications, illustrating the type of applications being pursued and the results being achieved. The oxidants most commonly employed to date include peroxide, permanganate, and ozone systems, with subsurface delivery in the vadose zone through vertical lance injectors, wells intersecting hydraulic fractures, or soil mixing techniques. In saturated zones, delivery has been achieved using vertical or horizontal wells, or sparge points.

Laboratory studies, field trials, and full-scale applications have generated considerable insight into the process, principles, and application of *in situ* chemical oxidation. In general, the oxidants have been shown to achieve high treatment efficiencies, for example greater than 90 percent, for unsaturated aliphatics like trichloroethylene (TCE) and aromatic compounds like benzene, with very fast reaction rates (90 percent destruction in minutes). Field applications have demonstrated very high reductions in the mass of contaminants, but only where adequate oxidants were able to be delivered and contacted with the target organic chemicals. These field applications have been particularly valuable in that they have clearly affirmed the control that field-scale reaction and transport processes exert on design and performance of *in situ* chemical oxidation.

The potential benefits of *in situ* oxidation include the following: (1) the rapid and extensive reactions with various COCs, applicable to many biorecalcitrant organic compounds and subsurface environments, (2) ability to be tailored to a site from locally available components and resources, and (3) facilitation of property development and transfer. Some potential limitations include: (1) requirement for handling large quantities of hazardous oxidants, (2) resistance of some COCs to oxi-

TABLE 7-6

Examples of *in situ* treatment applications using peroxide
(after U.S. EPA 1998; Siegrist 1998).

Location (date) Delivery	Media and COCs	Application method and results
Ohio (1993) <i>Deep soil mixing</i>	Silty clay soil with TCE and VOCs.	• H_2O_2 + compressed air injected during deep soil mixing to 15 ft. depth in 3 10-ft. diam. mixing zones. • Up to 100 mg/kg mass reduced by 70%, including 50% due to oxidation.
Colorado (1996) <i>Injectors into GW</i>	Ground water with BTEX.	• H_2O_2 + chelated Fe injected via 8 to 14 lances and 7 trenches over 100 ft. x 100 ft. area. Four cycles at 4 to 6 days each. • BTEX reduced from 25 mg/L to less than 0.09 mg/L. Property sold.
Massachusetts (1996) <i>Injectors into GW</i>	TCA and VC in groundwater.	• H_2O_2 + Fe + acid via 2 points over 3 days within 30 ft. D.W. • TCA reduced from 40.6 to 0.4 mg/L, VC 0.40 to 0.08 or ND mg/L.
Alabama (1997) <i>Injectors into GW</i>	Soil with high levels of TCE, DCE, and BTEX.	• H_2O_2 + FeSO_4 via 255 injectors into 8 to 26 ft bgs zone of clay backfill in 2 acre waste lagoons. 120 days treatment time. • 72,000 lbs. of NAPLs treated down to soil screening levels.
South Carolina (1997) <i>Injectors into GW</i>	Deep GW zone with PCE and TCE DNAPLs in sandy clay aquifer.	• H_2O_2 + FeSO_4 via 4 injectors into zone at 140 ft. bgs beneath old waste basin. 6-day treatment time. • Treatment achieved 94% reduction in COCs with GW near MCLs. GW TCE reduced from 21 to 0.07 mg/L; PCE from 119 to 0.65 mg/L.

TABLE 7-7

Examples of *in situ* treatment applications using permanganate (after U.S. EPA 1998; Siegrist 1998).

Location (date) Delivery	Media and COCs	Application method and results
Ohio (1997) <i>Horizontal well recirculation</i>	Ground water with TCE DNAPLs in a thin, sandy aquifer.	• KMnO_4 (2 to 4 wt.% feed) delivered by horizontal recirculation wells, 200 ft. long and 100 ft. apart at 30 ft. bags, to treat 10^6 L zone of ground water over 30 days. • TCE reduced from 820 mg/L to MCL in 13 of 17 wells. ~ 300 kg of TCE destroyed. Some MnO_2 particles generated. Aquifer heterogeneities noted.
Kansas (1996) <i>Deep soil mixing</i>	TCE and DCE in soil and ground water to 47 ft. depth.	• KMnO_4 (3.1 to 4.9 wt.%) delivered by deep soil mixing (8 ft. augers) to 47 ft. bgs during 4 days. • TCE reduced from 800 mg/kg by 82% in the vadose zone and 69% in the saturated zone (> 8 ft. bgs). MnO_4^- depleted. Microbes persisted. Comparison tests with mixed region vapor stripping yielded 69% reduction and bioaugmentation were 38% reduction.
Ohio (1998) <i>Vertical well recirculation</i>	TCE in silty sand and gravel ground water zone at 30 ft. bags.	• NaMnO_4 (250 mg/L) delivered by 5-spot vertical well recirculation system (ctr. well and 4 perimeter wells at 45 ft. spacing) for 3 pore volumes over 10 days. • TCE reduced from 2.0 mg/L to MCL. Oxidant gradually depleted in 30 days and no Microtox toxicity. No permeability loss in formation.
Ohio (1996) <i>Hydraulic fracturing</i>	VOCs in silty clay soil from ground level to 18 ft. bgs.	• KMnO_4 grout delivered by hydraulic fracturing to create multi-layered redox zones. Emplaced over 4 days but sustained oxidative zone for more than 15 mon. • Dissolved TCE reduced from equiv. of 4000 mg/kg by 99% during 1 hr of contact.

TABLE 7-8

**Examples of *in situ* treatment applications using ozone
(after U.S. EPA 1998; Siegrist 1998).**

Location (date) Delivery	Media and COCs	Application method and results
Colorado (1997) <i>GW wells</i>	Soil and GW with BTEX and TPH.	• Former gas station site. Sand/gravel to 43 ft. bgs with GW at 28 ft. 3 wells to 50 ft. depth cycling air/ozone with water recirculation. 12 cycles per day. SVE also continued. TPH in soil from 90 to 2380 mg/kg and BTEX at 7.8 to 36.5 mg/kg. TPH in GW at 490 mg/L to NAPL. • After 6 mon, GW below MCLs. No soils data. System shut down.
Kansas (1997) <i>Injectors into GW</i>	PCE in GW.	• Old dry cleaners site. GW at 14 to 16 ft. bgs in terrace deposits. One sparge point at 3 scfm at 35 ft. bgs. SVE wells in vadose zone. PCE in top 15 ft. of aquifer at 0.03 to 0.60 mg/L. • Reduced 91% within 10 ft. of well. Comparisons with air only indicated 66 to 87% reductions.
California (1998) <i>Injectors into GW</i>	Soil and GW with PAHs and PCP.	• Wood treater site 300 ft. by 300 ft. in area. Stratified sands and clays. 4 multilevel ozone injectors at up to 10 cfm. SVE wells in the vadose zone. • After 1 mon, PAHs at 1800 mg/kg reduced by 67 to 99% and PCP at 3300 mg/kg reduced 39 to 98%.

dation, and (3) potential for process-induced detrimental effects, including gas evolution, permeability loss, and mobilizing redox-sensitive and exchangeable sorbed metals. Full-scale deployment is accelerating, but care must be taken to avoid poor performance and unforeseen adverse effects. Matching the oxidant and delivery system to the COCs and site conditions is the key to achieving performance goals. Further development work is ongoing in many areas.

DELIVERY BY LANCE INJECTION*

Remediation methods that rely on chemical or biological processes typically require a compound to be delivered to the subsurface. The delivery mechanism is particularly important in formations that are highly heterogeneous or that have a low permeability. Delivery systems that can inject materials at closely spaced locations can facilitate remediation in these settings. Specialized drilling systems, or lances, have been developed to rapidly permeate a formation with treating compounds. This technique is also called “lance permeation.”

Principles

Lance permeation involves advancing small augers, or directly pushed casing, while injecting one or more reagents. The reagents migrate away from the lance by entering existing pore and fracture networks and creating a halo of reactivity. Slower diffusion processes can supplement this advective movement. To ensure complete coverage in a particular region, the lance injections are made with relatively close spacing, typically within 0.6 to 1.2 m of each other.

A particularly effective apparatus for this type of delivery consists of as many as four narrow augers mounted side-by-side on a frame attached to a tractor (Figure 7-25). The unit is mobile and can penetrate up to 10 m below the ground surface, with fluid flowing from all four augers simultaneously. Other equipment, such as cone penetrometers or GeoProbe™s, use static weight or hammers to push pipes that have been used as injection lances. The direct-push equipment generates less waste, and it can penetrate deeper than the multi-auger device. The simultaneous use of four augers, however, causes the multi-auger system to deliver reactive compounds considerably quicker than direct-push equipment. For this reason, much of the work described here will focus on applications of the multi-auger system.

The typical approach has been to inject, at relatively low pressures, 200 to 500 kPa (2 to 5 atm) to fill pores with injected fluid but avoid hydraulic fracturing. Agents can be injected up to the air-filled porosity of the media, but might be constrained in the range of 5 percent v/v. The

*This section was contributed by R.L. Siegrist.

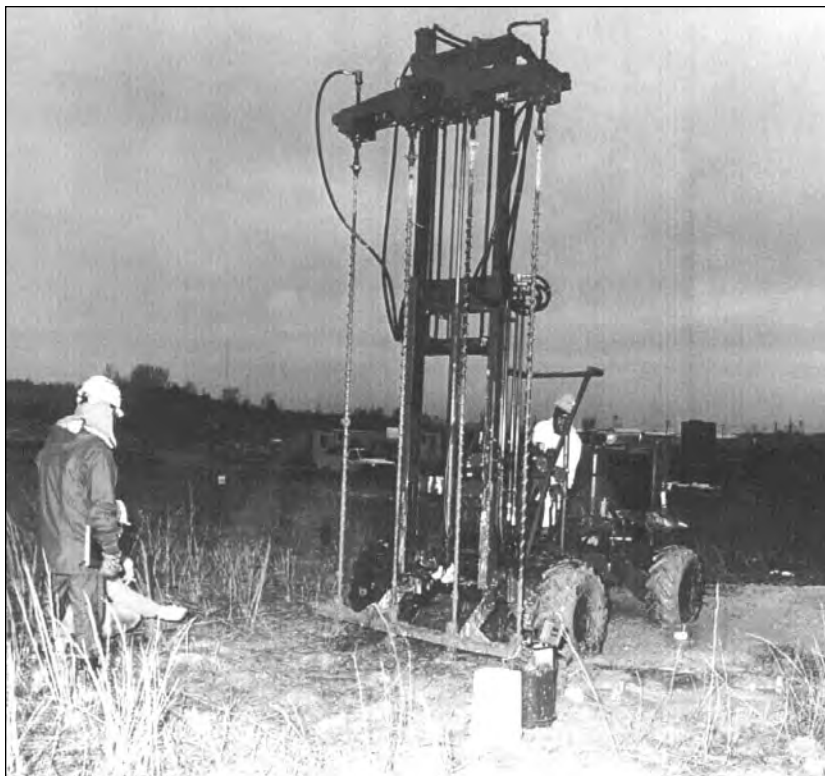


Figure 7-25. *In situ* reagent delivery using tractor-mounted multiple lance equipment.

following agents have been delivered under field trials or full-scale applications: (1) tracers that evaluate uniformity of delivery, (2) an alkaline slurry that increases soil pH and immobilizes metals, (3) KMnO_4 and H_2O_2 that oxidatively degrade organic chemicals, (4) zero-valent iron metal that reductively degrades chlorinated solvents, and (5) bionutrients that stimulate indigenous microbes and enable bioremediation of organic chemicals. In addition, compressed air has been injected at somewhat higher pressures to increase pneumatic permeability and facilitate soil vapor extraction.

Existing applications have injected fluid at relatively modest pressures, but an application scheduled for future deployment at the DOE Portsmouth Gaseous Diffusion Plant will utilize a somewhat different

approach. High pressure (50 to 100 MPa), low-flow jets will be used to carry reactive fluids away from a lance that is pushed into a low-permeability formation. This approach is expected to increase the radius that can be quickly permeated by a single bore.

Implementation

The implementation of lance permeation technologies relies on available equipment, treatment processes that are selected for the specific contaminants, and environmental conditions at the site. Site physical conditions need to be examined to ensure the proper penetration depth is possible and that the volume of fluid to achieve a treatment effect can be delivered. It is important that the contaminants of concern and the desired treatment goals be defined. Batch experiments with the site media and contaminants, along with the treatment agents to be employed, can reveal rate and extent of reaction data. Data gathered from diffusive transport tests in the lab reveal important information about real transport rates, extents, and any matrix interactions. A field pilot test is often required to verify laboratory results and field performance.

Critical Factors Affecting Performance

The contaminant and the deposit are singular factors affecting performance, but the interaction of the two also must be taken into consideration. Central among these issues is the flow of liquids injected by the lancing technique. In coarse-grain deposits, injected liquids may form unstable fingers that move rapidly downward and extend outward to limited distances. Jetting may help extend the radius of influence, and closely spaced injection points will reduce the volume of fluid injected into any particular location, but unstable flow or the development of preferential paths may limit the contact between reactive fluids and the contaminant.

If the formation is extremely tight, then dispersal using low pressure lance permeation may be ineffective. Some degree of advection away from the lance is important to yield a rapidly evolving halo around the lance. However, there are some advantages to applications of lance permeation methods in fine-grained formations. In fine-grained deposits, diffusive transport can expand and homogenize the treated region.

Moreover, capillary forces will dominate gravitational forces affecting fluid flow in fine-grained formations, and this will limit the effects of preferential flow.

The formation must be sufficiently unconsolidated and free of boulders or buried debris, such as underground utilities and conduits, so that a lance can penetrate the desired depth. None of the lance permeation techniques will work in crystalline rock. Surface obstructions, such as parking areas and buildings, preclude application or greatly increase costs. If contaminant concentrations are too high, the mass of treatment agent that can be delivered in the volume of fluid may be insufficient and may require multiple treatment cycles. The ability to retreat or increase delivery in hot spot areas is an advantage of multipoint lance injection. The groundwater zone and its susceptibility to contamination by leaching of contaminants or treatment agents during permeation of the overlying vadose zone must be considered.

Monitoring

Monitoring requirements include: (1) reagent delivery volumes and pressures, and depth of delivery, (2) subsurface biogeochemistry changes important to the treatment being implemented, and (3) changes in contaminant mass or mobility within the region treated. Available sensing devices and data acquisition systems perform monitoring. Soil core samples, which are used to analyze target constituents and relevant properties, can be acquired by direct push technology. Even with the monitoring technology to date, inaccurate quantification of treatment efficiencies in low permeability and heterogeneous systems still exist, and error and uncertainties, regardless of sample numbers, remain unacceptably high.

Status

Field trials involving multiple reagents were evaluated by Siegrist *et al.* at the DOE Portsmouth Gaseous Diffusion Plant beginning in 1994. A field trial in California evaluated lance injection and permeation dispersal of KMnO_4 to treat trichloroethylene in massive soils to a depth of 10 m. A site in Ohio contaminated by TCE and other halocarbons is com-

pleting a field test during 1999. Information to date suggests a treatment cost on the order of \$25 per c.y., somewhat independent of reagent costs.

INJECTION OF GAS-PHASE OXIDANTS: OZONE GAS*

Ozone (O_3) gas is a strong oxidizer (oxidation potential of 2.07 volts) that will degrade a variety of organic compounds. It is used to destroy organic contaminants in drinking water, wastewater, marine aquaria, and swimming pools. Recently, ozone has been injected into the subsurface to remediate recalcitrant organic contaminants *in situ*. Ozone can be injected directly into wells in the vadose zone, or it can be sparged into wells screened in the saturated zone. The gas is injected into pore spaces to contact contaminants, which are then degraded to daughter compounds. The technology has been used to treat regions containing dissolved, sorbed, and NAPL-phase contaminants, including pentachlorophenol (PCP) and polynuclear aromatic hydrocarbons (PAHs) (Fluor Daniel GTI 1998; Marvin *et al.* 1998; Brown *et al.* 1997; Nelson *et al.* 1997), and chlorinated solvents trichloroethene (TCE) and dichloroethene (DCE) (Clayton and Nelson 1995).

In situ ozonation may have several advantages over other oxidant-injection methods at some sites. The most significant advantage is that the gaseous nature of ozone promotes delivery through the vadose zone more readily than that of liquid oxidants. Volatilization and subsequent oxidation of residual NAPL may also occur during gas injection. Since ozone contains only oxygen atoms, it may impose less geochemical stress on the subsurface environment than oxidants containing ionic species such as Fe^{2+} , K^+ , Na^+ , or MnO_4^- . For this reason, ion exchange and solids precipitation are generally minimal during ozonation.

There can be significant limitations to *in situ* ozonation, primarily related to subsurface ozone transport, and competition for consumption among natural organic matter and other oxidizable species. While these limitations are common to all *in situ* oxidation technologies, they are expressed uniquely for each technology.

Managing the application of *in situ* ozonation involves the following primary issues: (1) determining that oxidation by ozone is a feasible

*This section was contributed by W. Clayton.

treatment mechanism for the specific contaminants, (2) delivering an appropriate mass of ozone to ensure complete treatment, and overcoming competing ozone consumption, such as by natural organic matter, (3) providing adequate subsurface transport of ozone gas so that injected ozone contacts all contaminated areas, and (4) implementing appropriate engineering and safety controls for ozone gas generation and handling.

The case study "Vadose *In Situ* Ozonation of Polynuclear Aromatic Hydrocarbons and Pentachlorophenol," by Wilson S. Clayton, describes an application of *in situ* ozonation in Sonoma County, California. See page 1200.



Treatment Mechanisms

In situ ozonation involves three primary treatment mechanisms: (1) direct oxidation, (2) advanced oxidation, and (3) combined chemical-biological oxidation. These mechanisms are interrelated and they can be difficult to distinguish in detail, even in carefully controlled aqueous- or slurry-phase reactors. A full understanding of these treatment mechanisms is particularly difficult in the subsurface, where geochemical reactions can be poorly resolved. The many possible interactions between contaminants, ozone, and native aquifer are poorly understood from a mechanistic viewpoint. Therefore, most of the generalizations about the treatment mechanisms are made by reference to the water treatment literature, and by observations from bench tests and *in situ* ozonation project sites.

Laboratory testing of ozone treatability is critical to determine site-specific feasibility. This testing is important despite published literature and previous experience and results to guide expectations. Ozone treatability work should include either slurry tests or column tests to account for the effects of soil matrix interactions. Laboratory treatability tests are especially critical for contaminant mixtures, where specific compounds may be preferentially oxidized.

Direct Oxidation

Contaminants susceptible to direct oxidation by ozone are generally organic chemicals that contain carbon-carbon double bonds (Rice and Browning 1980). Examples of double-bonded organics that should be read-

ily treatable by direct oxidation using ozone include: (1) nitroaromatic explosive compounds such as TNT, DNT, TNB, DNB, and tetryl, (2) aromatic hydrocarbons such as benzene, toluene, ethylbenzene, and xylene (BTEX), (3) PAHs such as benzo(a)pyrene, naphthalene, and pyrene, (4) vinyl chloride, (5) chlorinated ethenes such as DCE, TCE, and PCE, (6) phenols, and (7) chlorinated phenols such as PCP and dichlorophenol.

The oxidation of a complex organic molecule has factors affecting intermediate compounds. Research has shown that intermediate compounds are readily oxidized if sufficient ozone is delivered. For example, Qiu *et al.* (1999) studied the oxidation of DCP by ozone, showing that intermediate chlorinated compounds were further oxidized to produce chloride, acetic acid, and ethylacetate. The acetic acid and ethylacetate can be readily biodegraded under aerobic conditions, resulting in complete mineralization of the contaminant.

Advanced Oxidation

Ozone may form hydroxyl radicals (AOH) as a second reaction pathway. These can be produced by the decomposition of ozone in the presence of water or enhanced by addition of radical promoters such as hydrogen peroxide (H_2O_2). Oxidation by AOH is faster and more aggressive than direct oxidation by ozone, and can address a wider range of organic contaminants (Hoigne and Bader 1976). However, the degree of AOH produced during *in situ* ozonation is difficult to measure and is small to moderate unless H_2O_2 is added.

Combined Chemical-Biological Oxidation

In situ ozonation may enhance aerobic biodegradation, although the details of this process are still being resolved. Ozone degrades to oxygen gas, so the by-product of ozonation can provide an important ingredient for aerobic biodegradation. However, ozone is a powerful sterilizing agent with the capacity to destroy the microbes involved with aerobic degradation. This sterilizing potential apparently is incompletely realized, because unpublished field and laboratory data indicate that significant microbes survive and will flourish after cessation of ozone injection. Ozone may be unable to penetrate and sterilize the myriad pore spaces housing bacteria in the subsurface. Other research (Brown *et al.* 1997) suggests that ozone can transform some recalcitrant

contaminants into readily biodegradable daughter compounds, which may further enhance bioremediation.

Ozone Mass Delivery

Ozone consumption under both laboratory and field conditions appears to range from 3 to 10 grams of ozone per gram of organic contaminant, according to unpublished studies conducted by the author. These values include ozone demand by oxidizable native aquifer materials, such as humic matter or carbonates, although data are unavailable for materials with a wide range of naturally occurring organic material. Certainly, the mass of ozone required to completely oxidize contaminants in formations rich in native organic material, such as peat, lignite, or some shales, would be excessive. Bench-scale studies can be conducted to evaluate the ratio of the mass of ozone consumed to the mass of contaminants degraded in a particular material.

Ozone Transport and Mass Transfer

In situ oxidation will generally rely on effective transport of the oxidant to the contaminant. This is a contrast to many *in situ* remediation technologies that rely on mobilization and extraction of contaminants. For ozone injection, ozone reactions and mass transfer from the gaseous phase to the aqueous phase exert critical control over the ability to contact target contaminants.

A general conceptual model for ozone transport begins when ozone gas is transported by advection within gas-filled pores in the subsurface. It is then lost to the aqueous phase by mass transfer and reactions in all phases. The net result is the decrease of ozone concentrations along the flow path. Clayton (1998) used this conceptual model to develop an unsteady state numerical model of ozone and contaminant mass transfer and transport phenomena. The results of this modeling effort show that ozone degradation limits ozone transport, even in the absence of contaminants or other oxidizable material. During the early phase of treatment, second order reactions between ozone and contaminants or other oxidizable material near the injection well can deplete ozone gas concentrations. As contaminants and native materials near the injection well are oxidized, ozone gas is transported farther. Changes in ozone gas

distribution over time are controlled by the balance between gas flow velocity, and mass transfer and reaction rates. Increased ozone injection flow rates and concentrations help transport ozone farther. Ozone transport distances are also sensitive to the effective air saturation as a smaller effective air saturation results in a greater advective velocity and greater ozone transport distances.

In addition to the limitations on ozone transport imposed by ozone reactivity, subsurface heterogeneity can lead to preferential flow of injected gases in high permeability zones. In a severe case, advective gas flow avoids the low permeability zones. Ozone transport into the low permeability zones is then limited by diffusion, either in the gas phase or the aqueous phase.

In heterogeneous environments, geologic control over ozone transport is a primary design consideration. Injection well spacing and screened intervals should be selected based on careful geologic characterization. Multi-level injection wells may be required in some settings to obtain adequate ozone transport. Subsurface monitoring should also allow for the accurate characterization of the distribution of ozone in the gas phase and aqueous phase.

Engineering and Safety Controls For In Situ Ozonation

The engineering design of an *in situ* ozone injection system requires that the following criteria be met: (1) the ozone generator system must deliver a sufficient amount of ozone to destroy the required contaminant mass within a target time, (2) the system must deliver the ozone gas at sufficient pressure and flow to achieve adequate subsurface ozone transport, (3) the system must be constructed of materials which are chemically resistant to degradation by ozone, and (4) the system must include sufficient safety control systems to ensure that site personnel are protected from possible physical hazards and releases of liquid oxygen or ozone gas.

Ozone gas is created onsite using an ozone generator, which exposes oxygen to a high voltage electrical discharge. Ozone can be generated from air or from pure oxygen. Use of air typically generates an ozone concentration of about 1 percent, whereas use of pure oxygen as feed gas typically results in ozone concentrations of 4 to 6 percent.

Ozone generators typically operate within a narrow range of pressure and flow. Ozone gas distribution header systems must allow for independent pressure and flow control on multiple injection legs. This allows ozone injection at discrete pressures and flow rates in different injection points to accommodate heterogeneous environments.

Materials involved in the ozone delivery system should be constructed of Teflon or stainless steel. Alternate materials may be acceptable for components with limited ozone contact. Engineered safety controls should include system interlocks to shut down ozone generation in the event of a leak of ozone or oxygen gas.

Control and monitoring of subsurface gases is critical for safely implementing ozone injection. Impermeable covers and extraction vents can be used to maintain control of the injected ozone. Monitoring the pore gas compositions, both within and outside of the treated area, is also important to ensure that fugitive emissions of ozone are avoided.

Status

The general applicability of ozone injection has been established through several professional reports and non-peer-reviewed papers describing remedial action projects. The field demonstrations performed to date have focused on meeting remediation objectives for industrial clients, which has precluded obtaining detailed data typical of research projects. However, the results have been encouraging and this technology shows promise. Current experience with this new technique is limited to a few consulting companies.

REACTIVE BARRIERS*

Vertical reactive barriers have recently become a widely accepted method for remediation of dissolved contaminants in horizontally moving groundwater plumes. A companion technology has been developed that uses horizontal reactive barriers to degrade vertically moving contaminants in the vadose zone (Figure 7-26), but it has lagged behind

*This section was contributed by L.C. Murdoch and W.W. Slack.

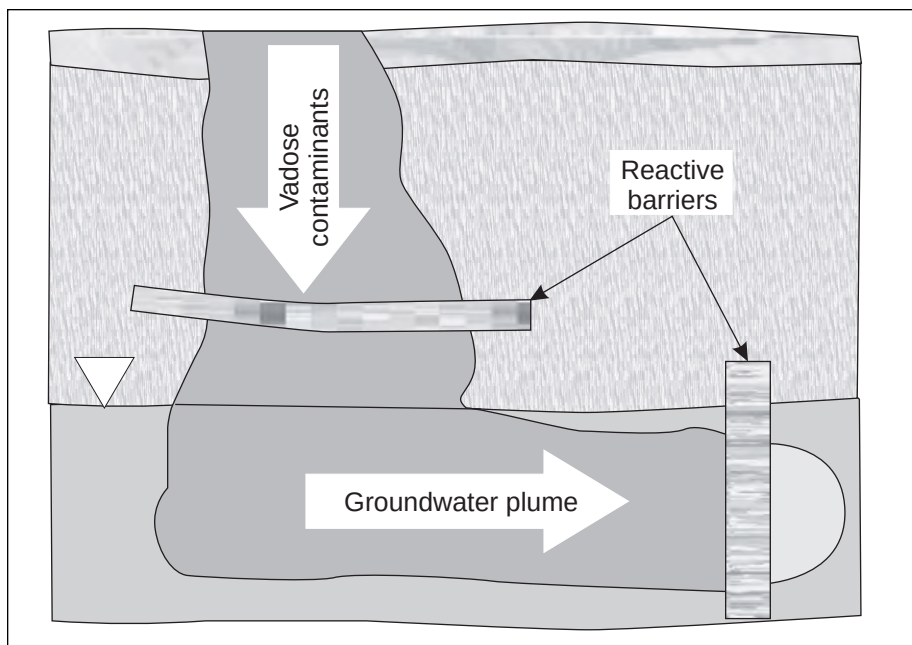


Figure 7-26. Reactive barriers in the vadose and saturated zones.

applications in the saturated zone. Research into the use of horizontal reactive barriers has indicated that they could have an important place in the search for increased remedial effectiveness at reduced costs.

The basic remedial approach using a reactive barrier, whether above or below the water table, is to first build a structure in the subsurface that will intercept the entire cross section of flowing contaminated water. Special material that will degrade or even immobilize contaminants on contact is placed in the structure, and the natural hydrologic system equilibrates. The barrier may contain impermeable panels to divert the subsurface flow, but the actual reactive zone is typically as permeable as the enveloping aquifer to ensure that water will flow through the material and not be diverted around it. When functioning properly, contaminants are carried by the ambient flow of water into the reactive zone where they are removed. Clean water emerges from the downstream side of the zone allowing water to pass unrestricted and barring the migration of contaminants. Orientation is a major difference between reactive barriers in the vadose zone and those in aquifers. Reactive barriers in the

saturated zone are typically vertical and positioned normal to the azimuth of ground water flow, whereas those above the water table must be nearly horizontal to intercept the predominantly downward moving water in the vadose zone.

The strategy for using reactive barriers is markedly different from most other methods that seek to reduce risk by removing or destroying all contaminants. Instead, reactive barriers are intended to degrade contaminants that are mobile, while having little effect on immobile compounds. Risk is reduced by placing reactive barriers upstream from potential receptors. The barriers prevent mobile contaminants from reaching receptors, but immobile contaminants may be left in place. In the vadose zone, reactive barriers are largely intended to intercept downward moving contaminants before they reach the water table where they could flow to a well or stream. Interestingly, soluble reactive compounds used in reactive barriers may diffuse through the vadose zone and destroy some compounds before they are mobile (Siegrist *et al.* 1999).

Several types of reactions can be used in barriers including aggressive chemical degradations, milder biochemical transformations, and sorption reactions. Zero-valent iron is currently the most widely used compound in reactive barriers in the saturated zone and has also been used above the water table (Table 7-9). Potassium permanganate is an aggressive oxidant that will degrade many organic compounds, although

TABLE 7-9	Some reactive materials, their mechanism of degradation, and the type of contaminant that could be degraded in a reactive barrier.	
Reactive Material	Mechanism	Target Contaminant
Zero-valent iron	Reductive dechlorination	Chlorinated solvents
Potassium permanganate	Oxidization Sorption	Organic chemicals, metals
Porous ceramic	Bioremediation	Hydrocarbons, solvents
Manganese peroxide	Aerobic biodegradation	Hydrocarbons
Sodium percarbonate	Aerobic biodegradation	Hydrocarbons
Lactate or similar	Anaerobic biodegradation	Solvents
Activated carbon	Sorption	Metals +/- Organics
Surface modified zeolite	Sorption	Metals

applications thus far have targeted chlorinated solvents. Manganese oxide produced when permanganate is reduced will sorb metals or radionuclides to the reactive barrier. This sorption suggests that this material may form a barrier suitable for mixed wastes. Porous ceramics are well suited as host media for microbes used to facilitate bioaugmentation. Manganese peroxide and sodium percarbonate are solid peroxides that react with water to release oxygen. They fuel aerobic biodegradation reactions, particularly of petroleum hydrocarbons. Lactate or similar compounds are used to enhance anaerobic reactions designed to degrade chlorinated solvents. Lactate and the peroxides are highly soluble in raw form, so they are processed with insoluble binders to delay their release. Granular activated carbon and surface-modified zeolites will sorb contaminants and are suitable for use in reactive barriers where immobilization is advantageous. For example, sorbants could arrest the migration of metals or radionuclides.

Reactive barriers must be thick enough to sufficiently degrade contaminants while they are in contact with the reactive material. Increasing thickness will increase material costs, which can be a significant component of the project cost. Barrier thickness can also influence implementation or method of construction. Determining the thickness required for a reactive barrier involves balancing the water flux and concentration of contaminants flowing into the barrier with the thickness and rate of degradation in the barrier itself. Many degradation reactions are essentially first order, where the reaction rate is proportional to the concentration of contaminants. Assuming that water is flowing normally to the barrier, and the vertical flow rate is uniform through the barrier, the concentration profile through the reactive barrier is

$$\frac{C}{C_o} = \exp \left\{ \frac{-S_w \phi_e k}{v_w} \right\} x \quad (7.24)$$

where C_o is the concentration entering the barrier, k is the first order constant of the decay reaction, v_w is the flux of groundwater in the x direction perpendicular to the barrier, and ϕ_e and S_w are the effective porosity and degree of water saturation of the barrier material, respectively. The concentration through the barrier will decrease as a negative exponential with distance (Figure 7-27), according to this simple analysis. Equation 7.24 can determine how thick the barrier should be to

reduce the incoming concentration by a certain fraction. The thickness required to reduce the concentration by one order of magnitude ($C/C_0 = 0.1$) is from equation (7-24) and Figure 7-27.

$$X_{0.1} = 2.3 \frac{v_w}{\phi_e S_w k} \quad (7.25)$$

Reducing a concentration in groundwater by two orders of magnitude ($C/C_0 = 0.01$) will require a reactive barrier twice as thick as indicated by equation 7.25. This relation (equation 7.25) shows that the thickness of a reactive barrier is directly proportional to the flux, and it is inversely proportional to the effective porosity and the reaction rate.

Equation (7.25) can be used to estimate thicknesses required for reactive barriers. The half-life of degradation reactions ranges from a few minutes for potassium permanganate to a day or longer for zero-valent

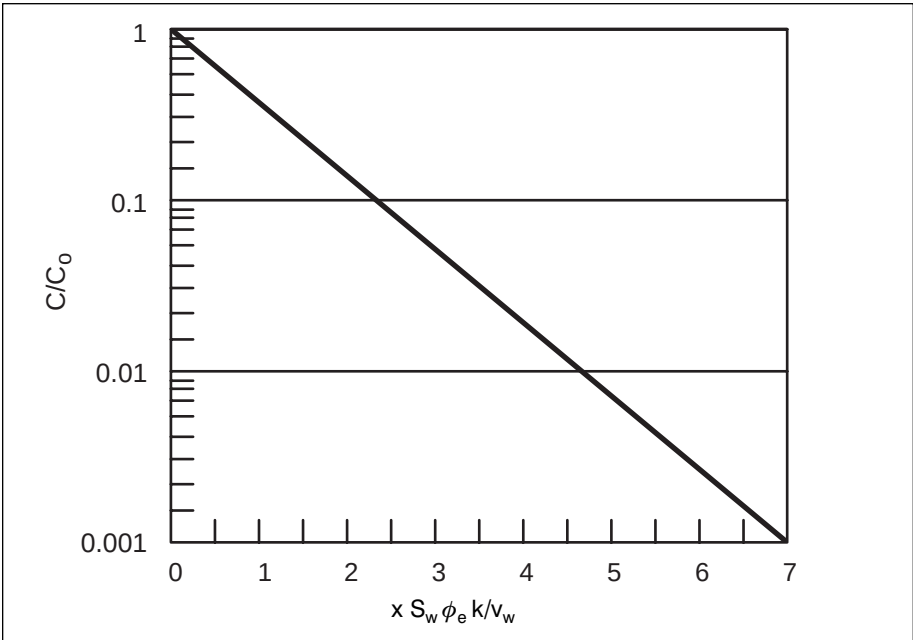


Figure 7-27. Concentration as a function of distance, reaction rate, effective porosity and flux through a reactive barrier. Assuming first-order decay reaction and flow in the positive x direction.

iron or other compounds. Expect from this that k will range from less than 10^{-5} to 10^{-3} s^{-1} . The average flux through the deep vadose zone is the rate at which the underlying aquifer is recharged. Recharge fluxes are on the order of 10^{-6} cm/s in the eastern United States, but they could be 2 orders of magnitude less (10^{-8} cm/s) in arid regions of the west, such as Sandia or Hanford. The effective porosity of reactive material that is granular is probably at least 0.15. Using those values and equation (7.25), the thickness of a reactive barrier required to reduce concentrations by a factor of 10 ranges from 10^{-4} cm for the fastest reactions and the slowest recharge flux to 1.5 cm for the slower reaction and the faster recharge flux. Those thicknesses would be doubled to reduce concentrations by a factor of 100.

The design considerations presented in the previous paragraphs have assumed that the water flow through the barrier is uniformly distributed; however, it is widely recognized that flow through the vadose zone can be localized along preferential paths. Certainly the occurrence of fast, localized flow through a barrier will reduce the residence time and change the thickness calculations based on equation (7.25). The severity of this issue is unclear, but probably depends on the permeability structures of the host formation and reactive barrier material, as well as the maximum water flux applied to the barrier. It should be feasible to use principles for capillary barriers to design the hydraulic properties of a material that would impede flow along a fast path long enough to ensure degradation. Of course, this would have to be done without excessively impeding flow and diverting water around the barrier. The details of this process have never been investigated with respect to reactive barriers in the vadose zone, but they should be amenable to available experimental and theoretical techniques.

Implementation

The two major issues affecting reactive barrier implementation in the vadose zone are: (1) constructing a barrier at the required location and (2) selecting a material that will safely treat the contaminants. Barrier construction requires creating a flat-lying layer of reactive material in the subsurface. Several methods based on horizontal wells have been proposed. Material can be permeated, or sediment can be eroded with a high-pressure jet to create panels between parallel horizontal wells (Sass

et al. 1997). A mechanical device has also been used to cut the formation between horizontal wells (Carter 1997). High pressure jets may be deployed from vertical wells to create flat-lying disk-shaped bodies in the subsurface. A continuous layer can be formed from this deployment by creating many neighboring disks at the same depth (Furth *et al.* 1997). Those methods typically have been used to create low permeability barriers, but they apparently have not been used to create permeable barriers from reactive material.

Hydraulic fracturing is another method for creating gently dipping layers of granular material, and, as far as is known, it is the only one that has been used to create reactive barriers in the vadose zone.

Hydraulic fracturing begins by injecting fluid into a borehole until the pressure exceeds a critical value and a fracture is nucleated. Granular material is injected as a slurry while the fracture grows away from the borehole. A viscous fluid, typically either an organic or inorganic gel, is used to facilitate transport of the granular material into the fracture. After pumping, the fracture walls close on the granules to form a thin layer or bed of reactive material in the subsurface (Murdoch *et al.* 1995).

Conventional methods of hydraulic fracturing generally produce a single parting (multiple fractures require repeated operations), and the form of the fracture depends on the state of stress, the degree of stratigraphic layering or fabric in the enveloping formation, and may include other factors. In overconsolidated or bedded sediments, hydraulic fractures, typically, are equant to slightly elongate in plan, and dip gently towards their parent borehole (Figure 7-28).

Hydraulic fractures have been created for environmental applications at depths of 12 and 16 m with the possibility of greater depths. Many of those fractures have been created in the vadose zone. Maximum dimensions of the fractures increase with depth, but are in the range of 7 to 15 m. Bulk volumes of granular material used to fill the fractures also increase with depth, ranging from 0.15 m³ (5 ft³) for shallow fractures to 1.25 m³ (44 ft³) for deeper ones. The average thickness of material filling a fracture ranges from 0.5 to 1.0 cm, but can be as much as 2.5 cm. Special methods (Brunsing 1987; Murdoch *et al.* 1997) are available to create fractures that are a decimeter or more thick.

Hydraulic fracturing methods have created reactive barriers in the vadose zone using most of the materials in Table 7-9. Lactate and zeolite are two exceptions only because environmental applications of those

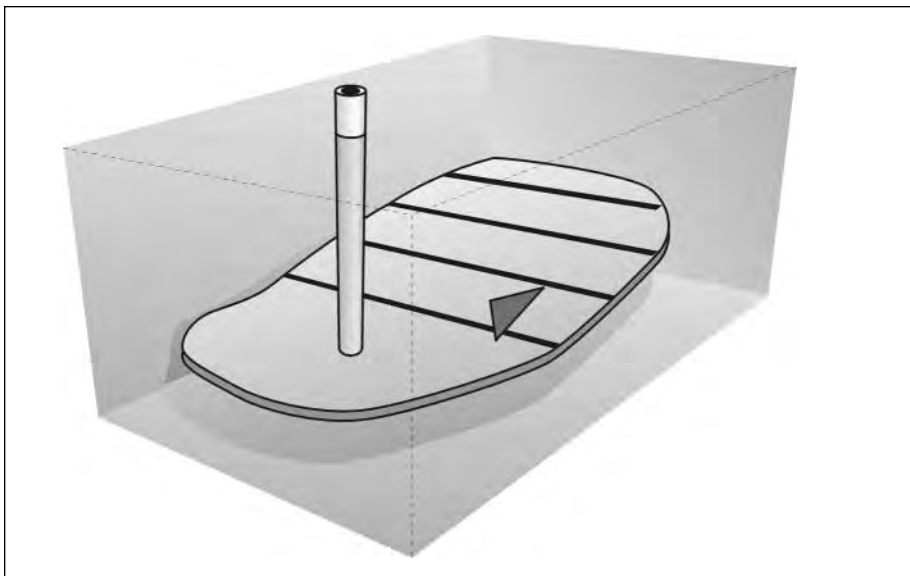


Figure 7-28. Idealized hydraulic fracture.

materials are relatively new. Conventional fracturing methods can be used to inject many reactive materials. Guar gum gel, a cellulose-based thickening agent, is typically used to suspend reactive material, although this gel is abruptly degraded by the oxidative capacity of raw potassium permanganate. An inorganic gel is used to inject potassium permanganate (Siegrist *et al.* 1999).

The case study, "Case History of Reactive Barriers Using Fe^0 Metal and KMnO_4 to Degrade Chlorinated Solvents," by R.L. Siegrist, K.S. Lowe, L.C. Murdoch, and T.C. Houk, describes a field trial of *in situ* remediation at the DOE Portsmouth Plant. See page 1206.

Monitoring

Reactive barrier monitoring in the vadose zone evaluates the creation of the barriers, as well as their performance. Determining the form of the fracture, particularly the size and location, is critical to ensuring that

potential downward pathways of contaminants are intercepted. This can be done using geophysical methods during or following fracturing. The ground surface over a flat-lying hydraulic fracture will lift to form a broad, gentle dome. The amount of uplift is similar to the fracture aperture above shallow, flat-lying fractures (Murdoch *et al.* 1995), but the uplift pattern becomes more complicated as the fracture becomes deeper. Theoretical analyses are available to estimate the geometry of hydraulic fractures based on the uplift pattern (Du *et al.* 1993; Davis 1983). Net ground displacements accompanying fracturing can be measured using optical leveling, or the inclination of the ground surface can be measured in real time using an array of tiltmeters. Resistivity measurements can also be used to estimate fracture location during propagation (Wang *et al.* 1991; G. Hocking, personal communication, 1998).

The performance of reactive barriers in the vadose zone can be evaluated using the standard vadose zone sampling and monitoring methods described in Chapters 3 and 4. Specialized methods (Murdoch *et al.* in press) have been developed to monitor critical parameters, such as moisture content, Eh, or fluid composition, at closely spaced depth intervals. Sensors can be embedded into a borehole sidewall at spacings of as little as 7 cm, to provide detailed resolution of subsurface processes.

Factors Affecting Performance

Reactive barriers must be able to intercept contaminants and provide enough residence time to accomplish sufficient degradation. The two primary factors that will affect these processes are the orientation and position of the barrier, and the properties of flow through the barrier. Reactive barriers in the vadose zone should be nearly flat-lying to intercept downward flow. The dip of barriers created using hydraulic fracturing methods depends largely on the state-of-stress and sediment anisotropy. A lateral compressive stress that is greater than the vertical compressive stress favors the creation of a flat-lying fracture because it is easier for the dilating fracture to lift against the vertical than to push against the lateral stress. This stress state occurs in over-consolidated sediments and many rocks.

Material anisotropy, particularly the fracture toughness, becomes important where the horizontal and vertical stresses are similar. Fracture toughness is the property that governs the propagation of an elastic

fracture, and it often differs with direction in natural materials. For example, some sediments part more readily parallel to bedding than they do perpendicular to it because the least fracture toughness is parallel to bedding. As a result, bedding planes or laminations may favor the creation of flat-lying hydraulic fractures in sediments where the vertical and horizontal stresses are similar, such as in normally consolidated sediments.

Reactive barriers must be capable of degrading contaminants while they reside in the reactive material. The simple approach outlined above indicates that for a sufficient residence time to elapse, the thickness of reactive barriers in the vadose zone should be at least a few mm to cm, and this thickness is readily achieved by hydraulic fracturing methods. However, it is likely that local fluxes could be markedly greater than the average yearly flux used in the calculations above. For example, this could occur if the contaminants move episodically along permeable paths in heterogeneous formations, or as unstable fingers in granular deposits. Little is known about the details of flow through reactive material in the vadose zone, so this issue remains unresolved. It may be possible that concepts developed for designing capillary barriers could be used to design material properties that would regulate flow through reactive barriers in the vadose zone.

Access to the subsurface is required to create a reactive barrier. Conventional drilling is typically used, but hydraulic fractures can be created using directional drilling when access by conventional rigs is impossible. Buildings or other structures overlying fractures should be capable of accommodating some displacements during the fracturing process.

The rate of the degradation reaction and the life of the reactive material affects the performance of the barrier. These issues depend on details of the type, concentration, and total mass of the contaminants in the vadose zone, as well as the subsurface geochemical setting. Materials are available to degrade or sorb many of the major contaminants (Table 7-9), and current information about their performance in the vadose zone is encouraging (Siegrist *et al.* 1999). However, only a handful of field trials have been attempted, so additional investigation is required before the scope of these factors can be assessed.

Status

The use of reactive fractures in the vadose zone is a new technology with only a handful of field examples. Flat-lying reactive barriers suitable

for the vadose zone have been created using granules of potassium permanganate, zero-valent iron (Siegrist *et al.* 1999), porous ceramics cultured with specialized microbes (Stavnes *et al.* 1996), oxygen-releasing sodium percarbonate (Vesper *et al.* 1994), and granular activated carbon (Davis-Hoover *et al.* 1999). All of those projects have been pilot tests involving one to several barriers that were created to evaluate the technology. The results from the tests are encouraging, suggesting that it should be feasible to use reactive barriers in source zones within the vadose zone, just as it is feasible to use them to degrade groundwater plumes downstream from those source zones. Nevertheless, the technology has not yet been applied at a full-scale nor has it been evaluated throughout the life of the reactive material. The technology is commercially available, but it has not yet been transferred beyond the original developers.

See case study "Case History of Reactive Barriers of Porous Ceramics Used to Enhance Biodegradation of Petroleum Hydrocarbons" by A. Yorke and T. Meiggs on page 1216.



DEEP SOIL MIXING: RECOVERY AND DESTRUCTION PROCESSES*

In situ remediation can be exceedingly slow or of limited efficiency due to adverse properties of the subsurface, such as high organic matter content, low permeability, or contaminants with low vapor pressures, high K_{oc}, or the presence of residual NAPL. A potential approach to rapid *in situ* treatment involves the use of deep soil mixing coupled with various physical or chemical treatment processes. In concept, soil mixing creates continuously mixed subsurface soil reactors where various treatment processes can be implemented (Figure 7-29). Vapor stripping, chemical oxidation and reduction, bioremediation, and solidification/stabilization processes have been evaluated under laboratory, and in some cases, field conditions (Table 7-10) (West *et al.* 1995a; Siegrist *et al.* 1995a,b; Gierke *et al.* 1995; DOE 1996; Cline *et al.* 1997).

This section describes *in situ* soil mixing treatment technologies coupled with either vapor stripping or chemical oxidation. Mixed region vapor stripping (MRVS) couples soil mixing with high pressure air injection and is potentially applicable at sites where contaminants are

*This section was contributed by R.L. Siegrist and O.R. West.

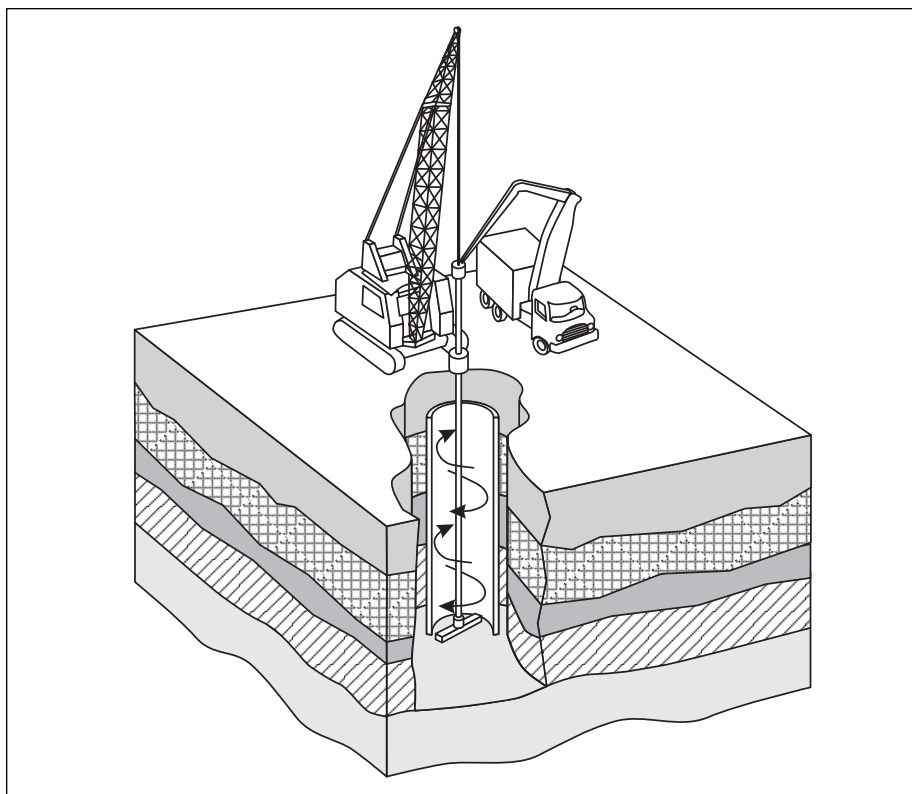


Figure 7-29. Subsurface soil reactor using mixed-region processes for *in situ* treatment.

relatively volatile (West *et al.* 1995a; Siegrist *et al.* 1995a; Gierke *et al.* 1995; DOE 1996). Mixed region chemical oxidation (MRCO) combines soil mixing with *in situ* chemical oxidation and is potentially applicable to sites with oxidizable target compounds, such as petrochemicals and chlorinated solvents. This section presents a general description of soil mixing technology first. Descriptions of vapor stripping and chemical oxidation processes coupled with soil mixing as the delivery system follow, with process, principles, and experience.

Principles

Soil mixing has evolved from construction drilling technologies to an approach for enabling remediation of contaminated sites by various *in*

TABLE 7-10 Possible mixed-region processes.

Mixed-Region Processes	References
Vapor stripping with air, hot air, and/or steam (volatile organics)	U.S. EPA 1989; Roy 1990; West <i>et al.</i> 1995a; Siegrist <i>et al.</i> 1995a; DOE 1996; Cline <i>et al.</i> 1997
Flushing with surfactants, acids, chelating agents (organics and metals)	
Chemical oxidation with peroxide or permanganate (organics, metals)	Siegrist <i>et al.</i> 1995a; DOE 1996; Cline <i>et al.</i> 1997
Chemical reduction with zero valent iron metal (organics, inorganics, metals)	
Biodegradation with bioaugmentation (organics)	
Solidification/stabilization by grout injection (organics, metals, radionuclides)	Stinson and Sawyer 1989; Siegrist <i>et al.</i> 1995(b)

situ processes. Soil mixing can be used to accomplish several treatment objectives including: (1) recovery by stripping or flushing, (2) *in situ* destruction by chemical or biological methods, or (3) *in situ* immobilization by solidification/stabilization. Soil mixing enables rapid and extensive treatment in the vadose zone by subsurface disruption and facilitation of treatment agent contact and mass transfer. Mixing does not fully homogenize a subsurface region, yielding limited soil and contaminant translocation inward and upward within the mixed region. In concept, continuously mixed subsurface soil reactors can be created in various soils and sediments, including the vadose and saturated zones.

MRVS involves injection of compressed gases at high volumetric flow rates, such as 1 soil reactor volume per minute, to volatilize and advectively remove organic chemicals from the subsurface. The removed chemicals are either released to the atmosphere or captured in a shroud or hood and managed by a variety of offgas treatment techniques such as carbon adsorption or catalytic oxidation. MRVS utilizes various auger designs. Gas injection is accomplished through orifices

along the auger blade(s) or out the bottom end of a mixing shaft. Removal efficiency is dependent on contaminant and media properties, such as pore size and continuity, water content, and sorption, as well as injected gas properties like flow rate and energy content (West *et al.* 1993a; West *et al.* 1995a; Siegrist *et al.* 1995a; Gierke *et al.* 1995).

MRVS treatment time is a function of several factors, including: (1) the chemical properties (for example, vapor pressure and Henry's constant) of the target contaminants, (2) the partitioning behavior within the contaminant/media system (K_d), (3) the physical properties of mixed soil/media, such as aggregate size and surface area, (4) the volume of soil to be treated, (5) the air flow rate and energy content, and (6) the required removal efficiency.

Laboratory and field tests of MRVS have shown that from 400 to 700 unit volumes of air (ambient temperature) per unit volume of soil (reactor volume, or *r.v.*) were required to reduce TCE concentrations in clay soils by at least 80 percent (West *et al.* 1995a). The treatment time for ambient air MRVS of a given mixed volume can be roughly estimated for a prescribed airflow rate. For example, for a treatment volume of 460 cu. ft (nearly equal to 6 ft diameter, 20 ft depth) and an air flow rate of 1,500 cfm, an estimated treatment time is obtained as follows:

$$\text{treatment time} = 400r.v. \times \frac{460 \text{ cu.ft.}}{1500 \text{ cfm}} = 123 \text{ min.} \quad (7.26)$$

This estimation procedure is thought to be valid for contaminants with vapor pressures similar to TCE, and for contaminant/soil systems that exhibit partitioning behavior similar to that of the TCE/soil system ($K_d = \sim 0.1 \text{ mL/g}$) studied by Siegrist *et al.* (1995a). For other contaminants, like gasoline or diesel, and other high organic content soil systems, laboratory tests and/or modeling, coupled with laboratory measurement, will be necessary to estimate required treatment times (West *et al.* 1995a; Gierke *et al.* 1995).

MRVS may enable secondary treatment through biological degradation in much the same manner that bioventing can during conventional SVE. This possibility was considered during a MRVS demonstration at a land treatment site in Ohio (Siegrist *et al.* 1995a). Comparisons of microbial activity before and after treatment revealed increases in total bacterial populations, (for example 1,000x) although the significance of this was not elucidated.

MRCO involves soil mixing that delivers an oxidizing agent to a subsurface region to achieve *in situ* destruction of organic contaminants. MRCO has been most commonly implemented with hydrogen peroxide (H_2O_2) and potassium permanganate (KMnO_4) oxidants (Table 7-11). However, other oxidants can be used, like ozone. Reductants are also feasible, such as zero-valent iron metal. (The principles and practices of chemical oxidation are discussed elsewhere in this chapter and are thus not described in detail here.) Depending on system pH, degradation of target organic chemicals and other reduced substances can occur by direct electron transfer or free radical processes (Siegrist *et al.* 1999). Since the reaction rates for most susceptible organic compounds are extremely fast, that is, in minutes, transport and distribution often control treatment efficiency and extent, assuming adequate oxidant is delivered to satisfy the demand of the target organic chemicals as well as natural organic matter and other reduced substances. Treatment efficiency appears to be a principal function of media properties, as in natural soil organic matter content and pH, oxidant concentration and mass loading rate, and uniformity of delivery and distribution. Oxidant solutions (H_2O_2 at 0.01-10 wt. percent or KMnO_4 at 1.0 to 4.0 wt. percent) have been mixed with contaminated soil to provide mass loadings that are 1,000 times greater than the stoichiometric requirements for degradation. The oxidant solutions are typically combined with soil at a ratio of 5 to 10 percent by volume (liquid volume per volume of treated media), which provides enough volume to disperse the oxidant without creating a slurry that produces free water. To enhance distribution of oxidant throughout the mixed region, hydrogen peroxide solution has been injected into an air stream, for example at 300 scfm, so that it enters the mixed region as a fine mist (Siegrist *et al.* 1995a; DOE 1996). In this approach, some organic compounds can be volatilized and advectively removed concurrently with the *in situ* oxidation processes. As in MRVS, any organic chemicals in the offgas are captured in a shroud covering the ground surface and managed by appropriate treatment techniques, for example, by carbon adsorption or catalytic oxidation.

Implementation and Augmenting Technologies

Soil mixing was first used as an *in situ* remediation method in the late 1980s. The early applications were designed to deliver solidification

TABLE 7-11**Example applications of *in situ* mixed-region processes for site remediation.**

Location (date) Process	Media and COCs	Application method and results
Florida (1988) <i>Solidification</i>	Sandy soil with PCBs to 5.5-m depth	EPA demonstration was completed at a PCB contaminated site in Florida where two, 10-ft by 20-ft areas were treated with cement-based solidification grout in 3-ft diameter columns to depths of 14 and 18 ft.
California (1989) <i>Steam stripping</i>	Soil with VOCs and SVOCs	At the San Pedro site over 8,000 yd ³ of soil was contaminated with up to 12,000 ppm of chlorinated hydrocarbons plus other volatiles and semi-volatiles from a few ppm to 50,000 ppm. Up to 99% removal of volatiles from the soil was achieved (efficiencies of removal ranged from 54% to 99+%). Semi-volatile organics (SVOCs) were removed with efficiencies ranging from 7% to 98%. Post-treatment concentrations of VOCs averaged 57, 53, and 71 ppm, respectively, in the three tests. For the SVOCs, 920 and 490 ppm remained after completion of two of the tests.
California (1989) <i>Steam stripping</i>	Soil with TPH to 6.1-m depth	At the Carson site, when the total petroleum hydrocarbon (TPH) concentration was less than or equal to about 1,000 ppm, removal efficiencies were 75 to 90% for a 15-ft deep soil column, with an average treatment time of 47 min. per column. When TPH was greater than 10,000 ppm, removal efficiencies were 90 to 95% in a 20-ft deep column, with an average treatment time of 78 min./column.
Ohio (1993) <i>Ambient and hot air stripping, Peroxide oxidation, and Solidification</i>	Silty clay soil with TCE and VOCs to	Comparative demonstration of soil mixing coupled with ambient (20°C) and hot air (120°C) stripping, chemical oxidation, or solidification to treat TCE and other halocarbons at 100 to 500 mg/kg. Use of a single 3-m augur to treat 3 overlapping columns to 4.6-m depth. Treatment time of 225 min yielded an average VOC removal efficiency of nearly equal to 92% for ambient air and nearly equal to 98% for heated air, while MRVS to 6.7-m depth with heated air was lower at approximately 88%. H ₂ O ₂ + compressed air injected during deep soil mixing to 15 ft depth in 3 10-ft diam. mixing zones. Up to 100 mg/kg mass reduced by 70% including 50% due to oxidation.
Kansas (1996) <i>Permanganate oxidation</i>	TCE and DCE in soil and ground water to 14.3-m depth.	Comparative demonstration of permanganate oxidation, bioaugmentation, and vapor stripping. KMnO ₄ (3.1 to 4.9 wt.%) delivered by deep soil mixing (8 ft augers) to 47 ft bgs during 4 days. TCE reduced from 800 mg/kg by 82% in the vadose zone and 69% in the saturated zone (greater than 8 ft bgs). MnO ₄ ⁻ depleted. Microbes persisted. Comparison tests with mixed region vapor stripping yielded 69% reduction with bioaugmentation yielding 38% reduction.

agents into the subsurface to immobilize contaminants such as PCBs (Table 7-11). During this same period, mixed region steam stripping emerged, and was evaluated at two sites in California (Treweek and Wogec 1988; Roy 1990). Three tests were conducted at a site in San Pedro, and the fourth was conducted at a petroleum-hydrocarbon-contaminated site in Carson. At that time, mixed-region processes involving ambient and hot air stripping as well as peroxide chemical oxidation and grout solidification were tested in Ohio (Siegrist *et al.* 1995a,b; DOE 1996). Later, permanganate chemical oxidation along with MRVS and bioaugmentation were evaluated during a field demonstration at a DOE site in Kansas City (Cline *et al.* 1997).

Today, implementation involves consideration of site conditions with respect to soil mixing technology (like depth and areal extent of contamination), site access and surface topography, surface or subsurface obstructions, and post-treatment land use, as well as treatment process chemistry and function (for example, soil texture and permeability, water and organic matter content, pH, type of contamination and treatment goals to be achieved). Implementation typically involves a series of activities from initial screening for site suitability and development of performance goals for the site, to development of a conceptual design. Site characterization data is gathered and used to verify design conditions. Laboratory bench-scale tests are recommended to verify or refine design parameters and document performance for a treatment process such as chemical oxidation. However, field-scale implementation remains uncertain until a field pilot-test is performed. This pilot-test can be performed before mobilizing to the field for a full-scale application, or as a shakedown test at the beginning of a full-scale application.

While soil mixing augments the implemented treatment process, there are other enhancements that might improve effectiveness. Thermophysical enhancements such as soil heating within low permeability deposits could enhance removal rates in some settings. Incorporating secondary treatment processes could also provide benefits. For example, passive volatilization and/or bioremediation enhancements could be implemented following MRVS or MRCO. Also, vegetative restoration techniques could be beneficially implemented following these processes. Finally, coupling could be envisioned for treatment of sites with mixtures of organic and metal contaminants, for example, MRVS followed by solidification/stabilization.

The cost and commercial availability of MRVS and MRCO technologies can be illustrated by considering a hypothetical site, 100 ft by 100 ft by 15 ft deep (nearly equal to 5,550 yd³). This site is characterized by stratified fine-grained media contaminated with gasoline that is diffused into the low permeability matrix blocks at a concentration of 1,000 mg/kg. The goal is to remediate the site to 200 mg/kg or lower. Based on full-scale data with chlorinated solvents like TCE, the estimated cost for MRVS (ambient or heated air) to achieve an 80 percent removal efficiency is approximately \$100-150/yd³; the cost for MRCO to achieve a 70 percent reduction is approximately the same. These costs are similar, because major costs are associated with mobilization/demobilization and mixing equipment operation. Coupling chemical oxidation with secondary processes might reduce the treatment costs. These data are projected based on a treatment cost of \$200/yd³ treatment of TCE, as determined during a full-scale field demonstration at a secured DOE site where higher costs are normally encountered (Siegrist *et al.* 1995a). This assumes that off-gas treatment constraints are nominal. The estimated treatment time for the site is 30 to 60 days based on a processing rate of 100-200 yd³/d (Siegrist *et al.* 1995a; DOE 1996). Both MRVS and MRCO are commercially available technologies.

The case study "Mixed Region Vapor Stripping in a Silty Clay Vadose Zone," by R.L. Siegrist and O.R. West, describes an MRVS field test at the DOE's Portsmouth Plant in Piketon, Ohio. See page 1224.



Critical Factors Affecting Performance

The soil mixing delivery system and the treatment process to be implemented, such as vapor stripping and chemical oxidation, are some of the critical factors affecting performance. There are many soil mixing factors to consider. Surface topography must be generally level (or be made so by grading) to provide a stable base for the mixing equipment. Surface obstructions such as parking lots, buildings, or overhead power or steam lines can limit access totally or make it exceedingly expensive. Subsurface obstructions such as buried utilities, boulders or rock, or construction debris can similarly limit application. The technique is unsuitable where contaminants occur in rock that cannot be disrupted

with an auger. Depth and areal extent of contamination are important, and, to date, most field applications have been accomplished at depths less than 16 m (50 ft), and in areas smaller than 1 hectare. Planned land use following mixed region treatment is very important because mixing causes a volume expansion of roughly 15 percent (1.5 m^3 within an above ground berm per 10 m^3 of media treated *in situ*). This means that the height of the ground surface will increase during mixing, and the use of the land must be able to accommodate this change. (Siegrist *et al.* 1995a).

Critical factors related to treatment processes vary with each process. For MRVS, target chemical vapor pressure, K_{oc} , and contaminant concentration are important. With lower vapor pressures, high K_{oc} 's and high contaminant levels, benefits can be gained by using heated air, and even steam, rather than simply ambient air. For MRCO, critical factors include the target organic compound and whether it is amenable to oxidative destruction by peroxide or permanganate. Many organic chemicals are amenable to oxidative destruction but some are more susceptible to peroxide or Fenton's reagent compared to permanganate (Siegrist *et al.* 1999). Soil system pH and natural organic matter content are also important. Low pH, for example a pH of 4 to 5, and low NOM, for example less than 0.5 percent by weight, are generally preferred. It is also important to clarify the presence of metal co-contaminants that might be mobilized by redox effects.

Monitoring

Several systems are used to monitor the MRVS processes. A sensor on the auguring tool can monitor auger depth. Offgas air flow rate and VOC concentrations can be monitored via flow meters and sampling ports in the shroud covering the mixed region. These measurements should be linked to the auguring depth record to enable interpretation of treatment progress. Offgas pressure and temperature provide insight into the operation of the system. These data can be readily tracked by sensors and recorded by a computerized data acquisition system (DAS) at intervals of approximately 0.5 to 3.0 minutes. In addition to this DAS sensor data, soil solid and soil gas samples can be collected before and after *in situ* treatment for analyses of physical, chemical, and biological properties. The treatment performance, such as total mass recovered and

residual organic concentrations, can be determined from the results of soil VOC analyses before and after MRVS (Figure 7-30) (Siegrist *et al.* 1995a; West *et al.* 1995b). The pre- and post-treatment data can be analyzed using statistical procedures employing classical descriptive statistics as well as stochastic simulation methods (West *et al.* 1995b). The estimated mass reduction calculated from soil concentration data can be compared to that calculated from the cumulative mass recovered in the offgas. MRCO is more difficult to monitor since chemical reactions occur within the mixed region during active mixing and reagent delivery, as well as during a period following cessation of mixing. Most of the above monitoring methods described for MRVS can also be employed for MRCO. In addition, analyses include reaction products, such as chlorides produced during oxidation of TCE.

Status

It is possible to identify relative advantages and disadvantages of the MRVS and MRCO systems, although the state of knowledge and practice is currently insufficient to give firm guidelines for selecting these processes in a given setting. MRVS has the advantage of providing high treatment efficiencies while being simpler and easier to implement. Because chemical solutions are not involved in MRVS, chemical handling equipment is not required, injection permits are unnecessary, and health and safety hazards decrease. Moreover, since MRVS physically removes organic contaminants from the subsurface, online process monitoring and control is feasible. Finally, since no liquids are introduced, there is no potential for contaminant leaching. In contrast, MRCO has the advantage of more rapid treatment of not only volatile but also semi-volatile organic compounds. The addition of hydrogen peroxide yields oxygen, thereby enhancing potential biodegradation of original or partially oxidized organic compounds. MRCO also may enhance mixing efficiency and reduce mixing energy requirements. Finally, MRCO may reduce the potential for post-treatment leaching of untreated contaminants, for example, of heavy metals, by reducing matrix and bulk deposit permeability as a result of increasing water content and site compaction.

This mixed region strategy is an aggressive approach to *in situ* treatment and is most appropriate for source areas characterized by either high contaminant concentrations, biorefractory compounds, and/or sites

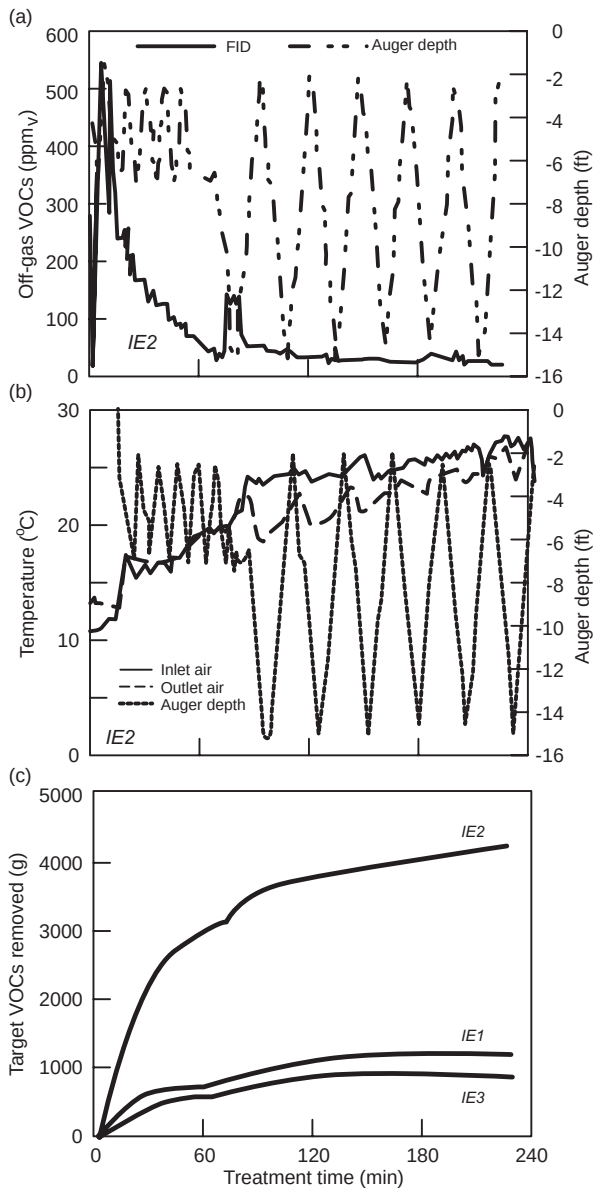


Figure 7-30. Results of MRVS using ambient air including (a) offgas VOC concentration, (b) offgas temperature, and (c) offgas VOC mass removal versus treatment time (Siegrist *et al.* 1995a).

with lower permeability media. Application to NAPL-contaminated low-permeability media is very attractive since it may offer the only way to rapidly and extensively disperse treatment agents and concomitantly remove/degrade contaminants in such settings. Much of the complexity and cost of a mixed-region treatment process (either MRVS or MRCO) is associated with mobilization/demobilization and operation of the soil mixing and delivery system. The costs associated with the treatment agents themselves, such as ambient air, heated air, and hydrogen peroxide, are relatively minor (less than 15 percent). Offgas treatment costs can represent minor or moderate costs, depending on the type and mass of contaminants, and treatment required.

The benefits of using heat (heated air or steam) in the MRVS process depend on the contamination properties; for example, concentration and solubility, and media properties like sorption and heat transfer. Benefits gained by injecting heated air are measurable and probably warranted for contaminant/media systems with relatively higher sorptive properties ($K_d > 0.1$ mL/g). Injection of steam is more uncertain, as it may result in saturation and water flooding prior to system drying and vapor stripping of NAPL.

There is potential for coupling MRVS with MRCO and other complementary technologies like fracturing systems and oxidation, and bioremediation. For example, MRVS could be employed to remove the accessible volatile fractions followed by MRCO to facilitate degradation of the remaining less volatile or entrapped organic chemicals.

IMMOBILIZING ORGANIC CONTAMINANTS BY STABILIZATION AND SOLIDIFICATION*

Solidification/stabilization (S/S) processes are among the most widely used methods for treating contaminated soils and waste materials in the United States today (U.S. EPA 1994). These processes have been used to remediate organic chemicals, but their primary application over the past 20 years has been to immobilize metals and other inorganic compounds in industrial sludges, contaminated soils, fossil-fuel fly ash, incinerator residues, and other hazardous wastes. The U.S. EPA now

*This section was contributed by P. Bishop and V. Hebatpuria.

recognizes S/S technology as an acceptable method for treating materials with metal contamination (U.S. EPA 1989), and the technology is used more often than any other hazardous waste management alternative. However, the ability of S/S methods to treat organic contaminants is more controversial.

Land-ban regulations (Anon 1985) prohibit disposal of hazardous liquids in landfills and require that the wastes be solidified, with a minimum of free water, before landfilling. This can be accomplished by S/S processes. Stabilization refers to techniques that reduce the hazard potential of a waste by converting the contaminants into their least soluble, mobile, or toxic form. The physical nature and handling characteristics of the waste are not necessarily changed by stabilization. On the other hand, solidification refers to techniques that encapsulate the waste in a monolithic solid of high structural integrity. It does not necessarily involve a chemical interaction between the waste and the solidifying reagents, but may mechanically bind the waste into the monolith (Conner *et al.* 1990). Together the S/S processes can transform liquid wastes so that they meet the requirements of land-ban regulations, allowing those wastes to be placed in landfills.

The most common S/S processes use Portland cement, lime/fly ash, or other pozzolanic materials as a binder for stabilizing contaminants into a relatively immobile form and solidifying them into a rigid mass. Cement-based techniques can cost-effectively stabilize heavy metals in sludges and soils. Unfortunately, many of these waste materials also contain toxic organic chemicals, which may not be immobilized as effectively as heavy metals. A great deal is known about the chemical processes involved with stabilizing metals in cement, but relatively little is known about the mechanisms involved with the release, or leaching, of organic chemicals from stabilized waste. This section provides an overview of organic compound leaching from S/S contaminated soils, reviews what is currently being done to improve the immobilization of these compounds, and describes what new techniques are being developed. Applications for S/S on metal-bearing wastes are described in Chapter 8.

Principles

Leaching from stabilized solids into water that percolates through the waste is the primary mechanism for release of contaminants to the envi-

ronment. As a result, the leaching rate is the major criterion for evaluating stabilized wastes (Conner *et al.* 1990). The leaching rate is typically estimated using one or more standardized laboratory tests, such as the Toxicity Characteristics Leaching Procedure (TCLP). A variety of such tests are available (Means *et al.* 1995) and most of them involve placing samples of the stabilized material in containers of water or weak acid (to simulate acid rain). The containers are agitated and the concentrations of contaminants in the water are measured either after a specific time has elapsed, or at several times during the test. The leaching rate can be estimated by comparing the concentration of the contaminant that leached into the water during the test to some reference concentration, such as the drinking water standard. Alternatively, the leaching rate can be characterized by fitting concentrations measured as a function of time using a transport model.

In typical S/S systems, most metals precipitate as insoluble carbonates, silicates, sulfates, and other salts, in the highly alkaline environment created by reactions with Portland cement. These metals are encapsulated in the gel-like structure of the binder matrix. Those processes significantly reduce the leaching rate of most metals (Bishop 1988).

Organic chemicals show no such behavior. They rarely precipitate due to an increase in pH, and, typically they fail to bind to cement. Organic chemicals may be sorbed or encapsulated in pores in some cement material, but this stabilization effect is often short-lived. While there are a few examples where organic compounds can be hydrolyzed, oxidized, or reduced due to reaction with cement (Conner 1990; Lear and Conner 1992), such cases are uncommon. In most cases, organic chemicals are released relatively rapidly from conventional S/S material, although the release rate does depend to some degree on water solubility, polarity, presence of functional groups, and volatility (U.S. EPA 1993). Most experts consider conventional S/S processes inappropriate for long-term containment of organic chemicals at moderate-to-high concentrations. This is particularly true for volatile chemicals, but also for most semi-volatiles (Battelle 1993).

The need to improve the organic chemical immobilization in S/S material has motivated a great deal of research, most of which has focused on materials that strongly sorb organic chemicals before being added to cement. For sorbants to be effective, however, investigators had

to address an even more insidious problem: organic chemicals may actively interfere with chemical processes within the cement itself.

Interferences Caused By Organics

Many organic chemicals may actually retard or accelerate the hydration of cement binders (Cartledge *et al.* 1990). This can reduce the strength of the solidified material, or it may prevent the cement from solidifying altogether (Cartledge *et al.* 1990; U.S. EPA 1993). Even low concentrations of organic chemicals in a mixed waste may reduce strength and interfere with hydration, (Pollard *et al.* 1990).

The interference effects are due to interactions at the molecular level. For example, Phenol is known to reduce the long-term strength of cement even at concentrations as low as 2000 mg/L (U.S. EPA 1993). Detailed examination shows that 3-chlorophenol inhibits cement hydration by stabilizing ettringite formation, retarding its conversion to monosulfate within the waste form (Montgomery 1989). Another microstructural study showed that methanol and phenol inhibited ettringite formation, but trichloroethylene appeared to stimulate it (El-Korchi *et al.* 1989). A potentially beneficial effect was observed with 1,3,5-trichlorobenzene, which decreased the pore diameters in the waste, causing entrapment and reduced leaching of the contaminant (Riaz and Zamorani 1989). Ethylene glycol, p-bromophenol, and p-chlorophenol also interact with cement (Tittlebaum *et al.* 1986). Ethylene glycol can inhibit hydration by occupying three distinct sites in the hydrated cement matrix, and can also alter the cement microstructure, producing grainy nodular surfaces that lack crystallinity. The ethylene glycol molecule is apparently small enough to substitute for water during hydration, but it deforms the resulting structure in the process. Both p-bromophenol and p-chlorophenol interact with the calcium-silicate-hydrate gel that forms during the hydration of cement, although the details of the interaction are slightly different for the two compounds (Tittlebaum *et al.* 1986). The potential interactions between organic chemicals and cement-based S/S systems (U.S. EPA 1993) are summarized in Table 7-12.

TABLE 7-12 Interference effects due to the presence of organics in S/S systems.

Compound	Potential Interference
Phenols	Decrease compressive strength for high phenol levels
Semi-volatile organics/PAHs	Interfere with bonding of waste materials
Polar organics (alcohols/ organic acids/glycols)	Impede setting of cement, decrease short-term and long-term durability. Alcohols may retard setting of pozzolans.
Solid organics (plastics, tars, resins)	Ineffective with urea formaldehyde polymers; may retard setting of other polymers.
Aliphatics hydrocarbons	Increase setting time for cement.
Chlorinated organics	Increase setting time and decrease durability of cement if concentration is high.
Non-polar organics (oil/ grease/PCBs)	Impede setting of cement, decrease long-term durability and allow escape of volatiles during mixing

Adsorbent

Adsorbents, which show promise as a material for organic chemical stabilization, have been used by the S/S industry for many years (Conner 1995), but most are proprietary and relatively expensive. The research community is investigating a variety of relatively inexpensive materials, including activated carbon, quarternary ammonium-exchanged clays (organophilic clays, or organoclays) and zeolites that could be used to absorb organic chemicals in wastes prior to cement-based solidification. In one study, fly ash, bentonite, virgin activated carbon, and soluble silicates were used to absorb various organic compounds (Caldwell *et al.* 1990). Activated carbon was the most effective of the sorbants tested. The insoluble, non-volatile compounds tested in this study were tightly bound in the S/S matrix. The distribution coefficient decreased and the leaching rate increased as solubility and volatility of the contaminants increased; however, volatile contaminants were poorly immobilized by the sorbants.

Several studies have identified activated charcoal as an important sorbant. Kyles *et al.* (1987) screened a range of conventional and novel processes for S/S of four wastes, including electroplating filter cakes

contaminated with chlorinated organics, a mixed waste containing dyes and pigments, an oil filter cake, and an acidic tar residue. The adsorbents used in the study were kiln dust, calcium oxide, and activated carbon. The study shows that activated carbon was the only compound to effectively immobilize the organic constituents. Sheriff *et al.* (1989) used decolorizing charcoal and quarternary-ammonium-exchanged clay for the cement-based fixation of 3-chlorophenol and 2,3-dichlorophenol (100 to 2000 mg/L). The charcoal rapidly adsorbed the contaminants and immobilized them in the S/S waste matrix, and the charcoal appeared to aid cement hydration and increase compressive strength. Another investigation showed that several materials could adsorb as much as 30 percent (w/w) of an oily waste and then be successfully solidified in ordinary Portland cement (Lin and Mackenzie 1983).

Modified Clays

Normally hydrophilic clay minerals can be modified to increase their capacity to adsorb organic chemicals. One method for creating organophilic clays is to substitute quarternary ammonium compounds for cations between the silica and alumina layers in the mineral structure of montmorillonite, the major clay mineral in bentonite. The quarternary ammonium compounds contain long-chain alkyl or aromatic groups that make the space within the clay less polar and more hydrophobic, increasing the attraction of the clay for many toxic organic compounds (Figure 7-31).

Organophilic clays composed of bentonite containing tetra-alkylammonium compounds were used to adsorb various phenols before being incorporated into the cementitious matrices in several studies (Montgomery *et al.* 1991a; Montgomery *et al.* 1991b; Sheriff *et al.* 1989; Mortland *et al.* 1986). The partitioning coefficients of the modified clay increased with the degree of polarity and the addition of chlorine; that is, the partitioning of phenol < chlorophenol < dichlorophenol < trichlorophenol.

Thermally treated but unexchanged clays have also been utilized for adsorption of organic chemicals. Escher and Newton (1985) used a mix of Portland cement and bentonite clay to solidify wastes contaminated with cyanide and phenol. In another study, spent clay from the edible oil industry was modified to a low-cost clay-carbon adsorbent by the chemical activation of residual oil on the mineral surface. Activated

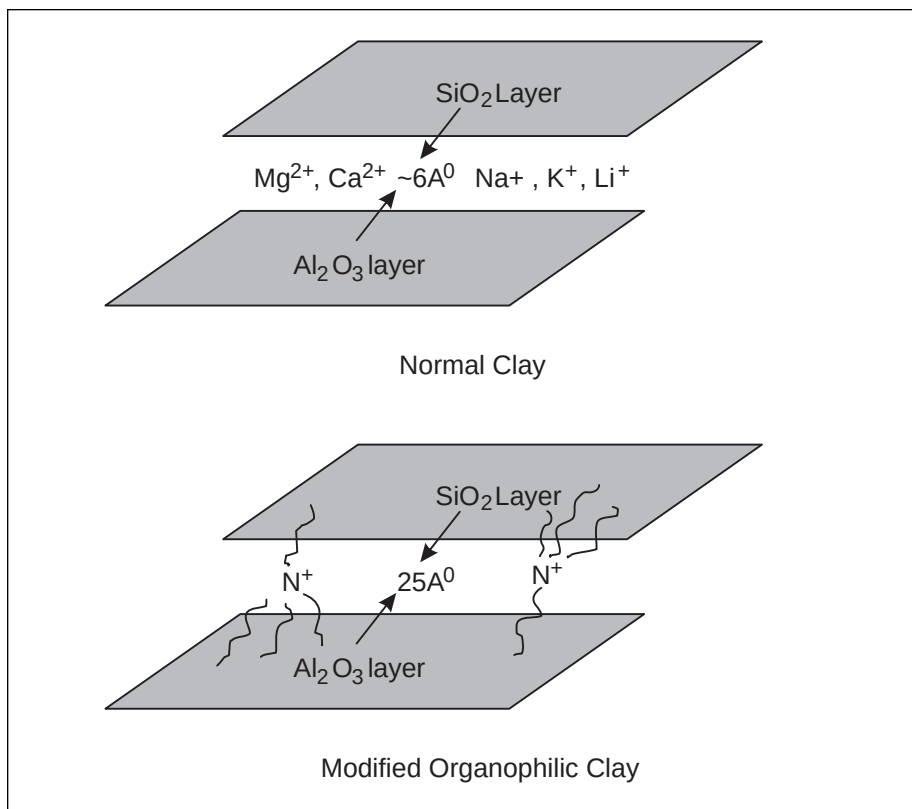


Figure 7-31. Modifying a clay with a quaternary ammonium compound.

bleaching earth was also evaluated for the cement-based S/S of an organically contaminated pickling acid waste, and its performance was compared with that of activated carbon used in drinking water treatment (Pollard *et al.* 1990). Adding 10 percent (w/w) of the modified clay reduced the leachable total organic carbon (TOC) by as much as 37 percent (w/w). Also, the pozzolanic activity of the clay increased the compressive strength of the waste by 2 to 3 times.

Fly Ash

Fly ash is one of several materials (including blast furnace slag and cement kiln dust) produced as an industrial byproduct that will react

with lime to form a pozzolanic cement. Many researchers (Davidson *et al.* 1958; Leonard and Davidson 1959; Thorne and Watt 1965) have proposed that reactive sites of fly ash will sorb unpyrolyzed organic compounds and prevent interaction with cementation reactions. Soils contaminated with PCBs were solidified by a commercial S/S process using fly ash and additives (Myers and Zappa 1987). The process produced negligible volatile and leachable TOC in leach test filtrates, but details of this proprietary process were not disclosed.

Pozzolans have been shown to solidify clay soil contaminated with simple alcohols and substituted aromatics with an organic content of 11.4 percent (w/w) (Thornton *et al.* 1975). The addition of 5 percent (w/w) lignite fly ash increased the compressive strength by 40 percent. Investigations of cement strength showed that aliphatic and dicarboxylic acids neutralized lime, and, therefore, interfered with pozzolanic hydration (Smith 1979).

Proprietary Additives

Many companies sell proprietary additives, which they claim, will effectively immobilize toxic organics in S/S matrices. It is often difficult to substantiate these claims because the stabilization ingredients are kept secret and leaching tests are generally only performed by the vendor. However, one validated study was performed in which two additives (KAX-50[™] and KAX-100[™]) containing rubber particles were compared with activated carbon, an organophilic clay, and untreated contaminated soil (Conner 1995). The two proprietary additives were found to be superior for stabilizing most of the organics tested, though the high cost of these additives may make their use uneconomical in many cases.

Activated Carbon

Activated carbon appears to be the most effective adsorbent in immobilizing organic contaminants in soils (Caldwell *et al.* 1990). However, virgin activated carbon is too expensive to use during large-scale S/S processes (Conner 1990). One way to realize the benefits of activated carbon but reduce costs is to use thermally reactivated carbon. The demand for this previously used, but regenerated, carbon is generally low, making it relatively inexpensive (only about 20 to 25 percent of the cost of virgin activated carbon).

An extensive study of the use of reactivated carbon to immobilize organics in S/S systems is currently underway (Arafat *et al.* in press; Hebatpuria 1998; Hebatpuria *et al.* in press-a; Hebatpuria *et al.* in press-b). Preliminary results show that contaminated soils containing a wide range of volatile and semi-volatile organic compounds (for example phenol, aniline, naphthalene, and 2-chlorobenzene), can be effectively immobilized in a cement-based S/S process using thermally reactivated carbon as the preadsorbent (Figure 7-32). Only 0.5 to 2 percent (w/w) reactivated carbon was needed. Adsorption was very rapid (Figure 7-33), so premixing of the soil with the reactivated carbon was not needed; it could be added to the contaminated soil along with the cement. Moreover, immobilization of the organic chemicals appears to be essentially permanent; leaching studies using aggressive leachants failed to remove the organics from the S/S matrix even after much of the cement gel structure had been dissolved, an effect probably due to the cement sealing the micropores of the activated carbon, which contain much of the contaminant.

Implementation

S/S processes can be used either *ex situ* or *in situ*. The *ex situ* process involves excavating contaminated soil and mixing it with suitable binders and additives (U.S. EPA 1993), and then placing this mixture into designated hazardous waste landfills. In most *ex situ* applications, the resultant slurry can be handled in several different ways: it may be (1) poured into containers or molds for curing followed by off-site disposal, (2) poured into cells or trenches for disposal onsite, (3) injected into the subsurface environment, or (4) reused as construction material, with appropriate regulatory approvals.

The *in situ* processes require the use of large augers, or similar devices, that can inject binder and mix it directly with the contaminated soil. *In situ* S/S processes can reduce costs by eliminating the need for excavation, but they can be less effective because of incomplete mixing. Figures 7-34 and 7-35 depict generic elements of typical *ex situ* and *in situ* processes (U.S. EPA 1993).

Feasibility Screening

The U.S. EPA has developed an approach that determines the feasibility of S/S for treating organically contaminated soils (Means *et al.*

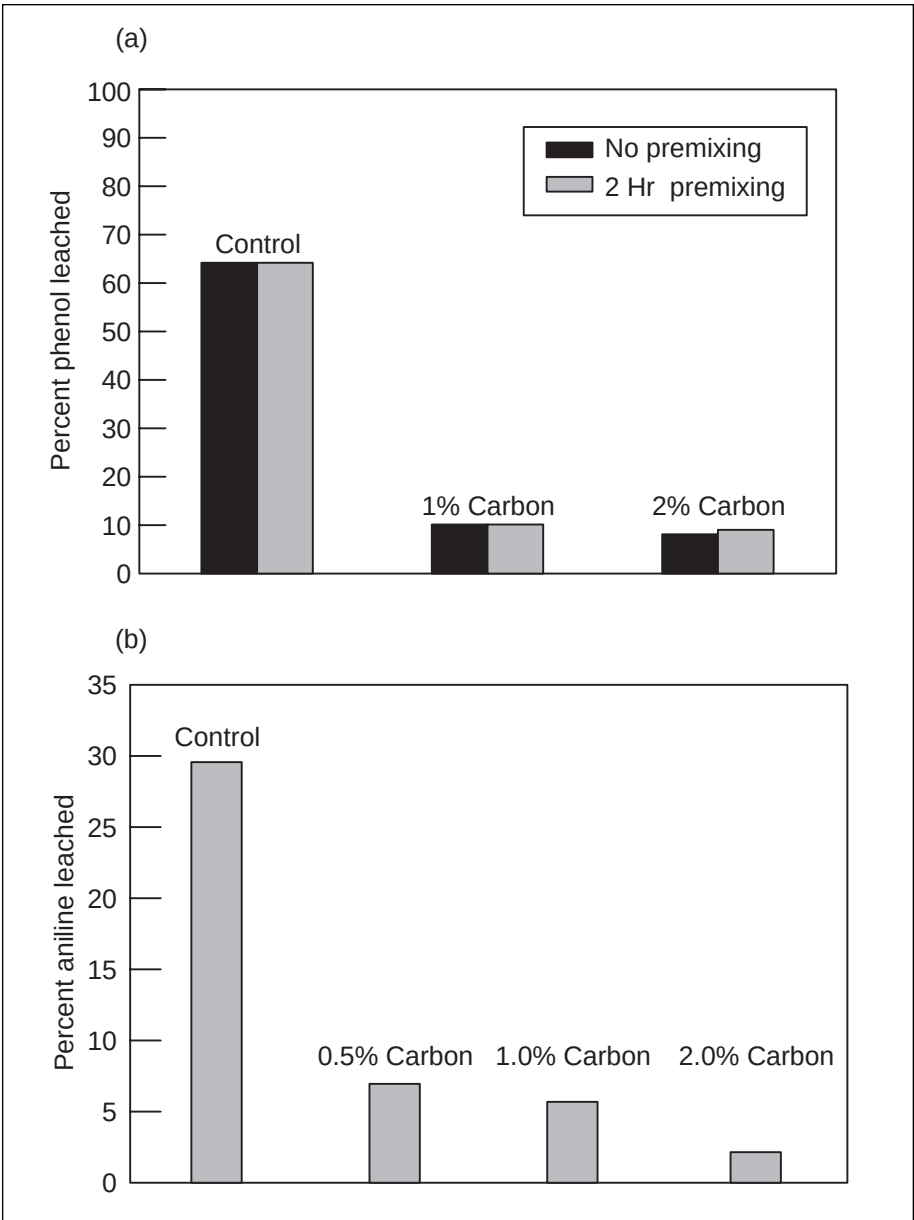


Figure 7-32. TCLP analyses of solidified/stabilized soils containing (a) phenol and (b) aniline using various carbon loadings. Specimens had a liquid:solids ratio of 10:1 and were cured for 7 days prior to testing.

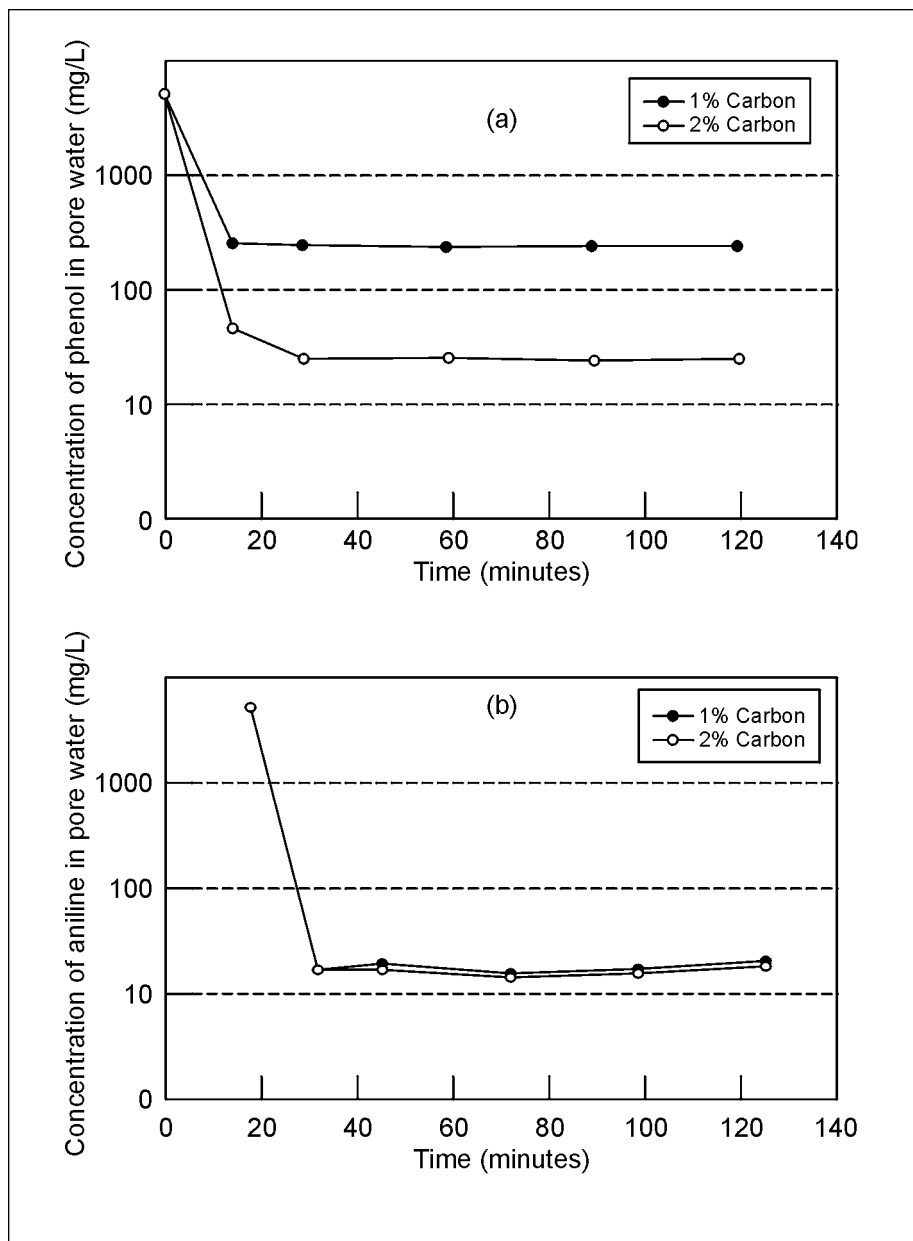


Figure 7-33. Time required for immobilization of contaminants using thermally reactivated carbon as the adsorbent.

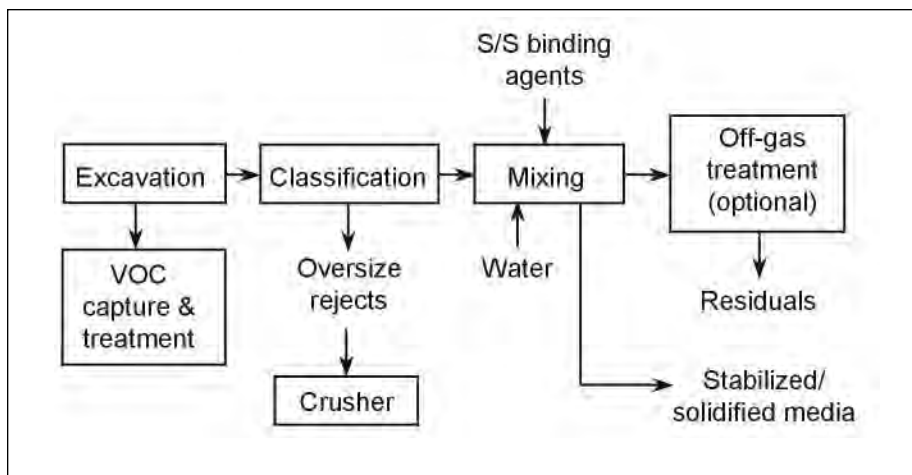


Figure 7-34. Generic elements of typical *in situ* S/S process.

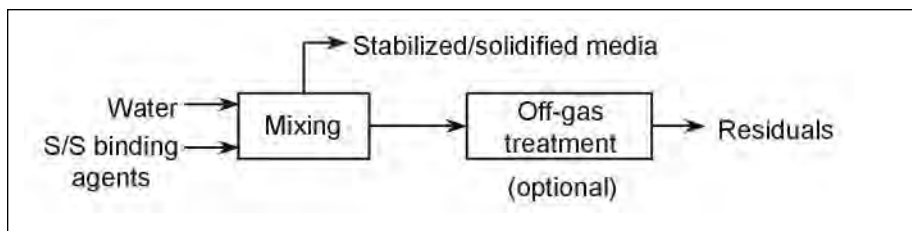


Figure 7-35. Generic elements of typical *ex situ* S/S process.

1995). The decision tree shown in Figure 7-36 is used to determine whether S/S technologies provide an acceptable alternative for treating a particular waste containing organics. This screening approach determines whether S/S treatment will destroy or remove the toxic organic components, release them to the air during treatment, or release them in solidified/stabilized waste leachate.

Augmenting Technologies

Recovery technologies such as SVE can be used to reduce concentrations of organic chemicals before S/S processes are used. This

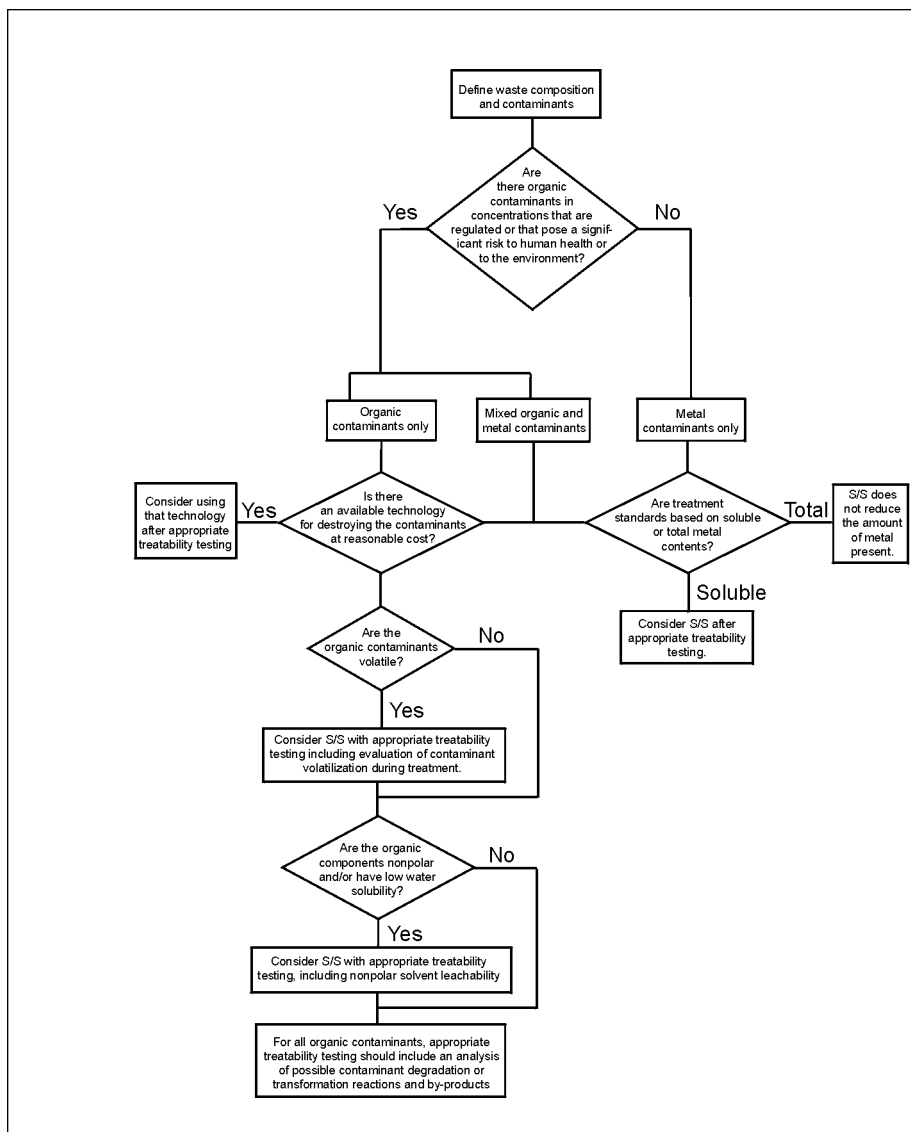


Figure 7-36. Decision tree for determining whether S/S technologies provide acceptable alternatives for treating particular organic waste.

preliminary step reduces potential interferences with organic chemicals and lessens the burden of preventing their mobilization. In some cases, *in situ* technologies can be used prior to stabilization, whereas in cases where S/S involves excavation, it may be feasible to pre-treat waste above ground to remove organic compounds. A two-step process of recovering or destroying organic contaminants and then using S/S to remediate metal contamination can be effective method for treating mixed waste.

Critical Factors Affecting Performance

The major determinants governing the performance of S/S processes for soils contaminated with organic compounds are the types and amounts of organics present, the type of soil being treated, the volume of contaminated materials requiring treatment, and the depth to which the contamination in the soil extends.

Organic compounds with low volatility and low solubility in water are most suitable for incorporation into a S/S matrix. Highly volatile (and even many semi-volatile) organic compounds may be lost to the atmosphere during excavation, mixing, and subsequent processing of the soil. These problems may be overcome by *in situ* S/S, where binder chemicals and water are injected into the soil and mixed in place using soil augers. Highly water-soluble organics may only be encapsulated within the S/S matrix and may readily leach out later. S/S treatment may be unsuitable for these compounds, although the addition of an adsorbent such as activated carbon or organophilic clay may immobilize the organics in the waste form. Some organics are incompatible with cement binders, causing accelerated or delayed setting, or no setting at all. Adsorbents may be successful in trapping the organics and preventing them from interfering with the cement setting reactions, but this has not been fully investigated. These factors can be evaluated using bench-scale tests.

The type of soil to be treated is also important. Clayey and some silty soils can act as strong sorbents and help to hold organic contaminants in the S/S matrix. These soils could be good candidates for S/S treatment. Sandy soils fail to sorb many organic contaminants and may be less suitable for S/S treatment unless an adsorbent is added along with the binders. Highly organic soils may interfere with the cement setting reactions.

Large amounts of binder chemicals are needed to effectively stabilize and solidify contaminated soils. Thus, the cost for processing large vol-

umes of soil may be prohibitive. Another drawback to this treatment is the volume increase exhibited by the treated soil, which may have a final volume that is 10 to 40 percent greater than the original. If the S/S material is kept onsite, provision must be made for the increase in elevation accompanying the volume change; if it is hauled to another disposal site, the resulting increase in volume must be considered when selecting the site.

The depth of contamination is also important. There are limits to how deeply binder chemicals can be effectively injected and mixed into the soil. There are claims that this can be done to a depth of 30 m, but most feel that *in situ* stabilization should be limited to the upper 10 to 15 m. *Ex situ* S/S requires excavation of all soil material. Obviously, the deeper the contamination, the more costly the excavation and total treatment costs.

Monitoring

Monitoring at S/S sites is often complex because the effectiveness of the process depends on chemical reactions that occur in the subsurface. Consequently, intensive testing to determine the treatability of the waste and proper mix formulations, and rigorous quality control and monitoring of the mixing process is needed. Commonly, with *ex situ* processing, the S/S waste is immediately placed back into the ground as an uncured slurry. Any problems with improper setting may go undetected. In a few instances, the waste form is placed in a mold after mixing and held until the waste sets, to insure that it is properly solidified, but this procedure is usually too expensive for large operations. Intermediate testing is typically impossible with *in situ* treatment. Here, the effectiveness of the soil mixing with the binders is of paramount importance, but reliable techniques for monitoring *in situ* mixing are currently unavailable. Once the soil has been treated and placed in the ground, the pore water in the solidified mass is also difficult to monitor. Typically, monitoring must be done at the perimeter of the site. Monitoring wells have been placed below the site, but they are uncommon.

Status

S/S of heavy metal-contaminated soils is a mature, well-accepted process, used at many hazardous waste sites as the sole treatment

process, or in combination with other technologies. Approximately 40 percent of all Records of Decision include S/S as part of the treatment process. Many of these sites also contain toxic organic chemicals. In some cases, immobilization of the organics has been effective; in others it has been less so. Few sites whose primary objective is treatment of organics have used S/S because better technologies are available. The exceptions are sites that are contaminated with heavy, non-volatile, low-solubility organics, such as coal tars or petroleum residues. Here, S/S processing may be suitable because it is unlikely that the organics will readily leach from the solidified waste form.

PHYTOREMEDIATION*

Natural processes accompanying plant growth affect the fate of organic contaminants in several ways (Fig. 7-37). Plants move water from the subsurface to the atmosphere, which transports vadose zone contaminants to the root zone (the rhizosphere), where microbes are usually concentrated. Organic compounds may be biodegraded by microorganisms in the rhizosphere, transported into the plants, and/or adsorbed to the organic matter associated with the vegetation. Some compounds are transformed, either in the plant or in the soil, to other organic forms that become part of the plants, microorganisms, or humic matter of the soil.

Principles

Phytoremediation includes all processes where plants play a leading role in remediation; some of these processes involve microbes associated with plants. As a result, phytoremediation is closely linked with bioremediation, which is described earlier in this chapter. Many phytoremediation processes relate to the ability of plants to move water through the vadose zone by evapotranspiration. This pumping effect removes as much as 2 meters of water per year ($2 \text{ m}^3/\text{m}^2/\text{yr}$). Evapotranspiration is significant as water and contaminants are moved to the root zone of the plants, where contaminants can be transformed by a

*This section was contributed by L.E. Erickson, L.C. Davis, and P.A. Kulakow.

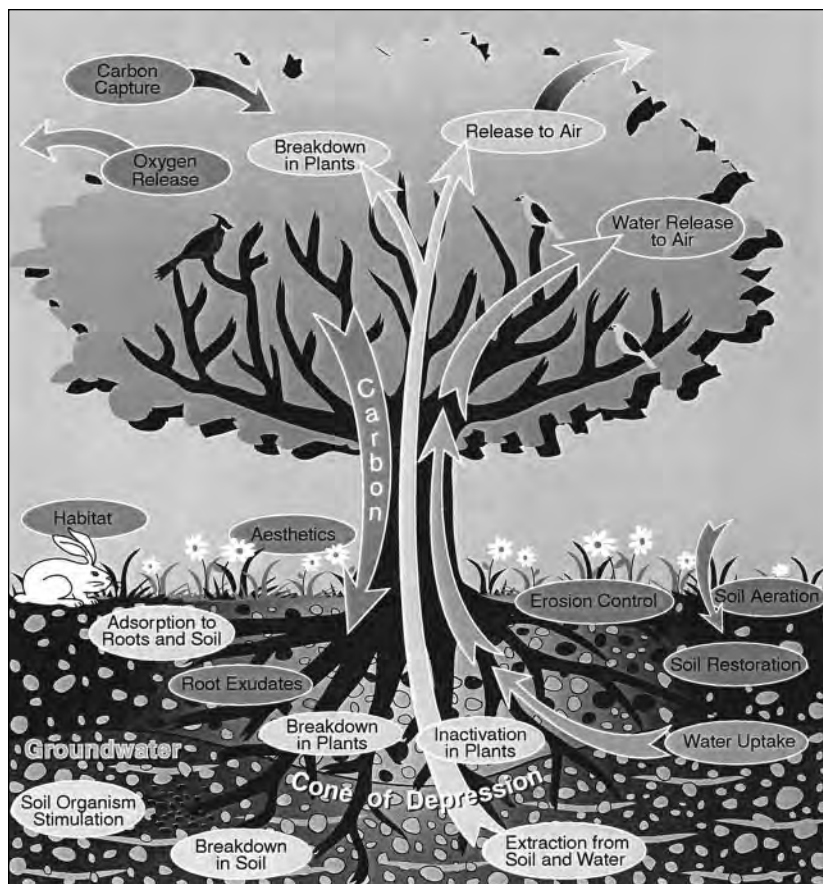


Figure 37. Processes involved during phytoremediation.

diverse microbial population in the rhizosphere. Some contaminants are transported into the roots and are transformed within the plants themselves. Volatile contaminants may be transported completely through the plant and released to the atmosphere either through leaves or through gas phase diffusion in the vadose zone.

Evapotranspiration reduces the amount of water in the subsurface and extends the depth of the vadose zone, allowing volatile contaminants to be released to the atmosphere and oxygen to diffuse to greater depths. Since many organic compounds are aerobically biodegraded, the gas phase diffusion of oxygen within the subsurface can significantly increase remediation.

Evapotranspiration can inhibit contaminants from moving below the root zone of plants. Since some plants have rooting depths of 10 meters or more, considerable moisture can be stored temporarily in the root zone. The soil moisture can range from field capacity to near wilting point conditions. Table 7-13 shows the estimated water storage capacity of several different soils. For example, a silt loam soil with 2-meter root depth can store 34 to 44 cm³/cm² of water. By combining the storage capacity of the soil with the pumping capacity of plants, a system is produced that limits the amount of precipitation extending past the root zone. This concept has been used to create vegetative caps that reduce infiltration and are less expensive than conventional caps used on landfills. Plants have also been placed near landfills and other contaminated sites to arrest the migration of plumes of contaminated groundwater. Plants can develop a cone of influence, similar to a well, such that shallow groundwater moves into the region where the vegetation is.

Plants contribute to the management of surface water at many contaminated sites. Vegetation reduces runoff and erosion, thereby limiting the movement of contaminants from the site in dissolved and suspended forms. In cases where plants are used to capture and evapotranspire precipitation, ensuring that there is surface runoff with appropriate treatment during periods of large amounts of rainfall will reduce the infiltration and enhance the probability of containing all of the infiltration in the root zone.

Complex processes involving microbes in the rhizosphere can destroy some organic contaminants. Microorganisms flourish in the root zone of many plants, where they are sustained by root exudates and organic mat-

TABLE 7-13

Approximate available water storage capacity of various soils based on differences between field capacity and wilting point. Data from various sources.

Textural Class	Estimated Storage Capacity, % Water
Silt loam	17-22
Loam	12-21
Silty clay	14-19
Sandy loam	4-16
Clay	11-15
Clay loam	5-10
Sand	2.5

ter from decaying roots (Table 7-14). The energetics of this process begin with solar radiation and can be quantitatively traced through the rhizosphere (Table 7-14). Microbes take advantage of the carbon and energy supplied by plants (Table 7-15). Microbial populations are often more than one order of magnitude larger near the root surface than they are elsewhere in the soil. The plant-supplied organic matter is a mixture of aliphatic and aromatic compounds, which either include or resemble compounds that are organic contaminants. Rhizosphere microbes often develop the capacity to degrade organic contaminants because similar compounds occur naturally in their environment. The degradation process is driven largely by microbial enzymes, but plant enzymes contribute as well.

TABLE 7-14

Bioenergetics of plant growth and energy flow to the rhizosphere. Approximate values from Erickson *et al.* (1995). For these processes, energy flows of enthalpy and free energy are of similar magnitude. Root exudates can sustain about 10^8 cells/g soil.

Process	Energy Flow
Solar energy transformed to:	
Chemical energy (0.7–3.2%)	1.5 kJ/kg soil day
Chemical energy in fixed carbon transported to root zone (30–50%)	0.45–0.75 kJ/kg soil day
Chemical energy supplied to soil as root exudates (40–70% of carbon flow to root zone)	0.18–0.52 kJ/kg soil day
Maintenance energy needed for aerobic vegetative cells	137 kJ/gmole microbial biomass carbon day or 1.6 nJ/cell day

TABLE 7-15

Sources of organic carbon that contribute to the diversity of biodegradation capability in the rhizosphere.

Root exudates including sugars, amino acids, organic acids, enzymes, and nucleotides
Mucilages consisting of mainly polysaccharides and polyglacturonic acid
Sloughed-off plant cells and their lysates
Root hairs that die and decay
Microbial cells that die and decay
Plant leaves and stems that fall to the soil surface

Organic compounds can also be sorbed and immobilized by organic matter in the rhizosphere, reducing the bioavailability of contaminants and their associated health risks. Contaminants that desorb from the organic matter become available to potential degradation by microbes, although some contaminants may escape degradation and migrate out of the rhizosphere.

Organic contaminants can enter plants, move up into the stems, and be evaporated from leaves as a natural analog to the pump-and-treat process. Interestingly, the pumping system utilized by plants can remove water held by capillary forces in the vadose zone much more effectively than mechanical pumps developed by man. Because contaminants can be toxic to plants, however, the vadose pumping system that they have developed does have drawbacks. Many commonly occurring VOCs can be transported through plants and evaporated from their leaves without significantly crippling the plant. However, details of this process are only beginning to be recognized. Toxicity studies and monitoring the concentration of contaminants should be part of any phytoremediation project.

Mathematical models describing the movement of contaminants into and through plants have been developed and used to explain experimental results by a variety of investigators, including Trapp and McFarlane (1995), Burken and Schnoor (1998), and Davis *et al.* (1998a, b). The fates of compounds such as toluene and TCE have been modeled by Narayanan and others (Narayanan 1998; Narayanan *et al.* 1998a, b; Davis *et al.* 1998a, b; Narayanan *et al.* 1998a, b;), who show that toluene is biodegraded aerobically in the root zone, whereas TCE diffuses into the atmosphere. The effect of plants and root exudates on biodegradation of polynuclear aromatic hydrocarbons has been modeled and compared with experimental data by Santharam *et al.* (1994). Their research found that biodegradation in vegetated plots achieved lower concentrations than it did in unvegetated plots due to rhizospheric processes.

The case study "Phytoremediation of Petroleum Contaminated Soil," by L.E. Erickson, P.A. Kulakow, and L.C. Davis, describes several field studies of phytoremediation at sites contaminated with petroleum hydrocarbons. See page 1234.



Implementation

Phytoremediation utilizes common agricultural and horticultural methods. In some applications, fertilizers are needed to provide nutrients for plant growth. Irrigation may also be provided if rainfall does not arrive when needed.

Details of the design of a particular implementation may vary considerably, depending on many factors including the following: (1) contaminant issues, such as biodegradability, bioavailability, plant toxicity, depth, and concentrations, (2) plant issues, such as properties of available native plants (root depth, evapotranspiration rate, potential degradation mechanism), climate, growing season, soil fertility, and (3) site issues, such as plume management objectives, future plans for the site, time for treatment, health risks to humans and animals during treatment, risk-based standards, and regulatory expectations and limits.

Poplar trees, cottonwood trees, and alfalfa are often used because of their high evapotranspiration rates. Since alfalfa fixes nitrogen, this crop has advantages where the contaminants or soil lacks nitrogen. Alfalfa can be planted inexpensively, and, in many cases, can be harvested and used as animal feed. Poplar and cottonwood trees can be planted as whips cut from growing trees. Trees should be planted in the spring while they are dormant. Cost is often \$2 or less per tree when thousands are planted. Recently about six thousand cottonwood trees were planted in about four hours, using approximately 25 volunteers who planted about 30 cm deep in prepared soil using shovels.

Augmenting Technologies

Several augmenting technologies can be used with phytoremediation, including irrigation to supply water, air sparging to move contaminants from the saturated zone to the vadose zone, bioventing to move contaminants below the root zone up into the rhizosphere, surfactant additions to solubilize contaminants to enhance biodegradation, other soil amendments (fertilizers) to enhance biodegradation, mechanical pumping to supplement evapotranspiration where plume control is needed, and fences or other barriers to control access to the site. Phytoremediation can be used as a polishing step in conjunction with other technologies, such as source removal, or integrated with other technologies as part of a site remediation. It is often an integral part of natural attenuation.

Critical Factors Affecting Performance

Environmental conditions affect plant growth and biodegradation of the contaminants. Soil moisture should be on the order of 50 percent of field capacity for aerobic biodegradation to be effective. Oxygen transfer is poor if the soil is near saturation, whereas microbial growth and substrate transport are inhibited under particularly dry conditions.

The biodegradation and transport characteristics of the contaminants during phytoremediation are important. Volatile, nonbiodegradable contaminants may be released to the atmosphere, where they can be dispersed or transformed by light-catalyzed gas-phase reactions. Organic contaminants that have very low solubility in water may be difficult to treat because of their low bioavailability. Vegetation provides additional opportunities for sorption, so phytoremediation does not always proceed at a faster rate than bioremediation.

Temperature is an important variable, with rate reductions expected in winter, especially in cold climates. In addition, evapotranspiration rates also depend on water availability and humidity of the air at the site.

Monitoring

There are several ways to monitor phytoremediation processes. Recently, Vroblesky *et al.* (1999) measured organic contaminants dissolved in fluids from core samples taken from trees. Their measurements demonstrated that the movement of contaminants into and through the vegetation proved that phytoremediation was occurring. Generally, it is difficult to detect contaminants in the atmosphere above the vegetation; however, contaminants in the gas phase have been measured in closed chambers and by using collection devices at the leaf surface or the soil surface. *In situ* monitoring methods using wells, lysimeters, or soil cores can also be used to monitor phytoremediation, just as they can be used to monitor other vadose remedial processes.

Status

Phytoremediation has been used at many field sites where the goals are simple and the chances for success are great. Applications include biodegradation of petroleum hydrocarbons in the vadose zone, use of

vegetation to consume water and prevent migration of contaminants from the site, closure of landfills with vegetated caps, disposal of landfill leachate as irrigation water for trees, utilization of ammonium and nitrates in nitrogen rich soils, and riparian buffers to protect streams from contamination by agricultural fertilizers and pesticides.

THE PERFORMANCE OF AVAILABLE REMEDIATION TECHNOLOGIES

The performance of *in situ* remedial methods depends on many factors, but geologic conditions, properties of the contaminants, and ability to access the subsurface are among the most critical. Many of these factors interact in complex ways to determine the viability of a particular remedial method at a particular site. Nevertheless, most remedial methods perform well under certain conditions but can be limited where geologic, contaminant, or access conditions differ from the ideal. The objective of this chapter is to identify the current state of remedial capabilities, the conditions that can be adequately addressed by current technology, and the conditions that represent gaps in remediation capabilities. To meet this objective, a list of the major critical factors affecting remedial performance has been compiled and evaluated to determine how each of these factors affects each of the available technologies. Table 7-16 summarizes the results of this evaluation.

Natural attenuation has recently been recognized as an important process for reducing risks associated with contaminants dissolved in ground water. This process is so important that natural attenuation is considered a viable option for remediating dissolved contaminants in some ground water plumes. The risk associated with some contaminants in the vadose zone probably also decreases with time due to natural processes, such as degradation by microbes, barometrically induced gas flow, or other processes. The state of knowledge about natural attenuation in the vadose zone is in its infancy compared to the understanding of processes in groundwater, however, and the extent to which this process may actually contribute to remediation is unclear. As a result, we have omitted natural attenuation as a remedial option in the following assessment. Additional research into this process may show that it is important and should be included as a viable alternative for remediation in the vadose zone.

TABLE 7-16 Effects of various factors on remedial performance (continued).

Effects of contaminant properties on remedial performance.

	Ptyro remediation	Solidification/ Stabilization	Reactive Barrier	Deep Soil Mixing	Liquid Oxidant	Gas-phase Oxidant	Bioremediated Bio	6-phase	Steam	Radio Frequency	Thermal Conduction	Passive SVE	SVE
Concentration in soil													
High (>20000 mg/kg)	☉	☉	☉		○	○	☉	●	☉	●	●	○	○
Moderate (10-20000)	☉	☉	●	●	○	☉	☉	●	☉	●	●	☉	☉
Low (<10 mg/kg)	●		●	●			●		●			●	●
Components													
Dissolved phases only	☉	☉						●	●	●	●	●	●
Single NAPL	☉	☉		●		☉		●	●	●	●	☉	☉
Multiple NAPL		☉		●	☉		○	●	●	●	●	☉	☉
NAPL and metals				●								○	○
Time since release													
Short (<1 yr)	☉	☉		●			☉	●	●	●	●	☉	☉
Moderate (1-10yrs)		●	●	●	☉								
Long (>10 yrs)	☉	☉			☉	☉	☉		●	●	●	☉	☉

Effects of chemical properties on remedial performance.

	SVE	Passive SVE	Thermal Conduction	Radio Frequency	Steam	6-phase	Engineered Bio	Gas-phase Oxidant	Liquid Oxidant	Deep Soil Mixing	Reactive Barrier	Solidification/Stabilization	Phyto-remediation
A. Vapor:NAPL													
High ($V_g > 5$ mm Hg)	●	●	●	●	●	●	●	●	●	●	●	●	●
Intermed. (0.05-5 mm Hg)	⊙	⊙	●	●	⊙	⊙	●	⊙	●	●	●	●	●
Low ($V_g < 0.05$ mm Hg)	○	○	●	⊙	●	●	●	○	●	●	●	●	●
B. Air:water													
High ($H > 0.12$)	●	●	●	●	●	●	●	●	●	●	●	●	●
Intermed. (0.01-0.12)	⊙	⊙	●	●	●	●	●	⊙	●	●	●	●	●
Low ($H < 0.01$)	○	○	●	●	●	●	●	○	●	●	●	●	●
C. Solid:water													
High ($\log K_{oc} > 3.1$)	○	○	●	●	●	●	●	○	●	●	●	●	●
Intermed. (2.0-3.1)	⊙	⊙	●	●	●	●	●	○	●	●	●	●	●
Low ($\log K_{oc} < 2.0$)	●	●	●	●	●	●	●	●	●	●	●	●	●
D. NAPL:water													
High ($\log K_{ow} > 3.5$)	●	●	●	●	●	●	●	●	●	●	●	●	●
Intermed. (2.5- 3.5)	⊙	⊙	●	●	●	●	●	⊙	●	●	●	●	●
Low ($\log K_{ow} < 2.5$)	○	○	●	●	●	●	●	○	●	●	●	●	●
E. Molecular weight													
High (>200 gm/mole)	○	○	●	●	●	●	●	○	●	●	●	●	●
Intermed. (110-200)	⊙	⊙	●	●	●	●	●	⊙	●	●	●	●	●
Low (<110 gm/mole)	●	●	●	●	●	●	●	●	●	●	●	●	●
F. Halogenation													
Hydrocarbon	●	●	●	●	●	●	●	●	●	●	●	●	●
1-3 halogens	⊙	⊙	●	●	●	●	●	⊙	●	●	●	●	●
>3 halogens	○	○	●	●	●	●	○	○	●	●	●	●	○

TABLE 7-16 Effects of various factors on remedial performance (*continued*).

Effects of access on remedial performance.

	SVE	Passive SVE	Thermal Conduction	Radio Frequency	Stream	6-phase	Engineered Bio	Gas-phase Oxidant	Liquid Oxidant	Deep Soil Mixing	Reactive Barrier	Solidification Stabilization	Phyto-remediation	Natural Attenuation
Depth														
Surficial (<0.3 m)	○	○	●	○	○	○	●	○	●	○	○	●	○	●
Shallow (0.3–3m)	○	○	●	○	○	○	●	○	●	○	○	○	○	●
Moderate (3–10m)	○	○	●	○	○	○	●	○	●	○	○	○	○	●
Deep (>10 m)	○	○	●	○	○	○	●	○	●	○	○	○	○	●
Areal Extent														
Small (<1 acre)	○	○	●	○	○	○	●	○	●	○	○	○	○	●
Medium (1–10 acres)	○	○	○	○	○	○	○	○	○	○	○	○	○	○
Large (>10 acres)	○	○	○	○	○	○	○	○	○	○	○	○	○	○
Vertical drilling restricted	○	○	○	○	○	○	○	○	○	○	○	○	○	○
Surface access restricted	○	○	○	○	○	○	○	○	○	○	○	○	○	○
Hazards to structures														
Displacement	○	○	○	○	○	○	○	○	○	○	○	○	○	○
Heat	○	○	○	○	○	○	○	○	○	○	○	○	○	○
EM Fields	○	○	○	○	○	○	○	○	○	○	○	○	○	○
Chemical	○	○	○	○	○	○	○	○	○	○	○	○	○	○
Duration until clean														
Short (<1 yr)	○	○	○	○	○	○	○	○	○	○	○	○	○	○
Moderate (1–5 yrs)	○	○	○	○	○	○	○	○	○	○	○	○	○	○
Long (>5yrs)	○	○	○	○	○	○	○	○	○	○	○	○	○	○

Legend

●	Technology performance is unaffected by this factor. Technology can remediate vadose contamination to MCLs or similar regulatory goals under these conditions.
○	Some effect on performance. Technology can significantly reduce mass contained in, or mass flux out of, the vadose zone.
○	Major performance reduction expected. The technology can be expected to produce a limited reduction in mass contained in, or mass flux out of, the vadose zone.

EVALUATION STRATEGY

The performance of each remedial method was evaluated by considering a hypothetical site where the technology could perform well. The effect of each factor was considered individually by estimating the extent to which it would diminish performance. Three levels of performance were considered in the evaluation of each factor. The highest level, which is indicated by a filled circle in Table 7-16, is where the factor has negligible detrimental effect on remedial performance when other conditions are favorable. The second level of performance, indicated by a circle and a central dot, recognizes some detrimental effect on performance that could lead to either significant delays or an inability to reach MCL-type goals. Nevertheless, significant reduction of mass or mobility of contaminants are possible using the technology under these conditions. The lowest level of performance, represented by an open circle, indicates a severe compromise of remedial capability. Typically, the technology is unable to provide a significant beneficial remedial effect under these conditions.

It is important to recognize that this evaluation strategy provides a simple way to match remedial technologies with the major factors affecting their performance, but it does so at the expense of overlooking a variety of important issues. Interactions between factors have been ignored, as have a variety of other circumstances that could influence performance at any particular site. In some cases, interactions of factors will conspire to reduce the performance more severely than indicated here. In other cases, several technologies could be combined synergistically to improve performance. Many current remedial actions combine several technologies in a sequence to maximize overall performance. The effects of interacting factors and the potential benefits of combining remedial technologies must be considered at any site, but such interactions and combinations are not considered here in order to limit the scope of the following summary. The evaluations were based on the results of field tests, where such results are known. However, field data are unavailable for many of the technologies under some of the conditions. In these cases, the performance of the technology was estimated based on lab experiments, theoretical estimates, or judgment.

The performance summary includes technologies that are described in the first part of this chapter. Documentation of the performance of

each technology is included in the previous sections and the reader should consult the papers cited in those sections for additional information about performance.

Hydrogeological Factors

The hydrogeological factors considered in the evaluation include major rock type and average permeability of materials underlying the site, the effects of heterogeneity, flux of water through the vadose zone, average water saturation, presence of perched water, thickness of the capillary fringe, and the magnitude of fluctuations of the water table.

Media Type

The type of rock or sediment that underlies a site affects remediation by influencing permeability, geochemistry, and access capabilities. These influences are considered explicitly themselves, but it is worthwhile to evaluate their effects as associated with rock type (Table 7-16). Clastic sediments underlie many sites. Grain size distribution is a major factor affecting remedial performance because it controls pore sizes and, hence, permeability. Fine-grained material implies low permeability and limited fluid flow, which may restrict the performance of remedial techniques based on gas or liquid flow. Thermal conduction and six-phase heating are exceptions as they can effectively heat clayey formations, and radio frequency (RF) heating will also heat any water-bearing horizon. Deep soil mixing is completely insensitive to grain size, and solidification/stabilization (S/S) of organics may actually benefit from the sorption of organic chemicals into fine-grained formations. Reactive barriers are well suited to fine-grained sediments because hydraulic fracturing performs well in this material, and because fine-grained formations typically have limited water flux. Plant growth may be limited in heavy clay, and natural attenuation may also be limited because of the relative isolation of contaminants in clays.

The performance of technologies that require fluid flow improves as the sediment coarsens. Most of the technologies that perform poorly in fine-grained sediments perform well in sand or gravel. Liquid oxidants may rapidly drain downward in gravel, limiting ability to maintain hydraulic control. The performance of hydraulic fractures in granular sediments has received limited investigation, so the effectiveness of

reactive barriers in sand and gravel is difficult to predict. Should hydraulic fracturing methods prove infeasible in coarse-grained unsaturated materials, jetting methods are an alternative.

Organic-rich sediments sorb contaminants, increasing the time required for remediation and affecting SVE and passive SVE, and also affecting heating technologies. The high temperatures developed during conduction heating should lessen the effect of sorption on organic-rich sediments. Bioremediation is affected because of organic-rich sediments' tendencies to reduce. Aerobic biochemical processes diminish as anaerobic ones are favored, so bioremediation could be either enhanced or diminished, depending upon the degradation reactions. Oxidants react with naturally occurring organic material, which diminishes the effectiveness of methods using oxidative fluids, as well as reactive barriers using oxidants. The ability for deep soil mixing to disrupt the subsurface is unaffected, but the potential limitations of SVE or oxidant injection used with deep soil mixing are similar to limitations for those processes separately. The performance of S/S can be diminished if organic-rich material interferes with the setting of cement. However, contaminants sorbed to organic material are less mobile than contaminants in clean soil, so the performance of S/S could improve. Phytoremediation probably is unaffected by the organic content of the soil. Natural attenuation may be affected by a decrease in contaminant mobility.

The performance of technologies involving fluid flow are affected by interbedded coarse- and fine-grained sediments, where recovery rates are limited by diffusion rates out of the fine-grained beds (contaminants are assumed to be distributed within both the fine- and coarse-grained beds). Electrical resistance heating is an exception, because it preferentially heats the fine-grained beds, accelerating the rate at which they release contaminants. RF heating also may perform well in interbedded sediments. The effects of thermal conduction are limited to the vicinity of the heating element, and so this technology is relatively insensitive to preferential flow in interbedded sediments. Deep soil mixing and S/S using excavation are insensitive to interbedded sediments. S/S done *in situ* may be severely affected by preferential flow, and probably will be ineffective in interbedded sediments.

The next three categories are hard rocks with different permeability structures. (Table 7-16). Volcanic rocks and lithified sedimentary rock

are expected to be relatively impermeable except along bedding planes and where they are cut by fractures. Unwelded tuffs are an exception, and they probably will behave more like clastic sediments during remediation. Crystalline rocks are expected to have even lower matrix permeabilities, and to be cut by fewer fractures than volcanic or clastic sedimentary rocks. Carbonate rocks have matrix permeabilities that range from moderate to low, but they commonly contain fractures enlarged by dissolution, and they may contain major karst conduits that will dominate flow.

All fractured rock materials are extremely difficult to remediate, and it is expected that remediation of karst will be infeasible using existing technologies. Deep soil mixing and S/S will be ineffective in hard rock due to difficulties with excavation. Conventional and passive SVE may be marginally effective in volcanic rock, but they probably will be ineffective in most hard rocks because of a high degree of heterogeneity. Heating should improve remedial performance, and there are a few cases where heating has apparently contributed to successful remediation in fractured rock. Bioremediation and the oxidant injection technologies will probably perform poorly because heterogeneities limit the ability to deliver fluids essential to performance. Gas and liquid phase oxidants probably will be ineffective in all three types of fractured rock because preferential flow will significantly increase the amount of oxidant required to react with the contaminants. It is feasible to create reactive barriers in rock using hydraulic fracturing methods, and it should be possible to create flat-lying barriers along flat-lying bedding planes. Therefore, it may be possible to create reactive barriers in some hard rocks, but there are no field data on this application. Phytoremediation and natural attenuation probably will be infeasible in fractured rock.

Gypsum-bearing strata are fairly common in the western United States, and sulfate-rich water is common in coal-mining areas throughout the United States. Gypsum-bearing rocks may contain solution cavities and channels that cause preferential flow much like karst does. However, gypsum may be present as a cement or as discontinuous bodies with limited solution channels. Remedial performance of the fluid flow technologies will be poor where solution channels are present. However, deep soil mixing, and, possibly, S/S should be feasible in gypsum, because it is friable and can be excavated or disrupted with an auger. Gypsum may interfere with the setting of cement, so the effects

on S/S are unclear. Sulfate-bearing water also affects organism growth and restricts the types of biochemical reactions that can be utilized during bioremediation. High sulfate concentrations may stunt or prevent plant growth during phytoremediation, and also may affect natural attenuation processes.

Peat is composed almost entirely of organic material that can strongly sorb organic contaminants (by contrast, it is assumed that organic-rich sediment is primarily clastic material with a subordinate fraction of organic substances). As a result, the effect of sorption reduces the performance of remedial technologies in peat even more than in organic-rich sediment.

Average Permeability and Heterogeneity

The effects of the average permeability and the degree of heterogeneity on remediation follow from the principles outlined in the preceding pages. The effect of water content on relative permeability is ignored here; it will be considered later. Nearly all of the remedial technologies perform well in homogeneous, permeable material (Table 7-16). Reactive barriers are the one exception because of the uncertainty regarding methods for creating reactive barriers in permeable material. The flow rate of air through the subsurface decreases with average permeability, reducing the performance of SVE and passive SVE. Passive SVE may be ineffective in low permeability materials, although conventional SVE can perform well in some tight formations using high-suction pumps. Heating can extend the effectiveness of recovery techniques to lower permeabilities. Electrical resistance heating is well-suited to clay-rich formations, but it may be poorly suited to low-permeability formations lacking clay, such as unweathered crystalline rock. The performance of engineered bioremediation and the oxidant technologies is reduced with the permeability due to fluid delivery problems. Hydraulic fractures filled with permeable material improve the yields of wells in low permeability formations and should extend the performance of all of the technologies that rely on the delivery or recovery of fluids. Hydraulic fractures as an augmenting technology was not considered in this evaluation because they have only been used with a few of the remedial technologies. The performance of deep soil mixing and S/S should be independent of formation permeability, although S/S

that is done by injecting stabilizing fluids will only be feasible in high-to-moderate permeabilities.

Heterogeneity is perhaps the single most important factor affecting *in situ* remediation in the vadose zone. All the technologies perform well in homogeneous materials, and all the ones that rely on fluid flow perform poorly in heterogeneous formations (Table 7-16). Thermal conduction will reduce the effects of heterogeneities, but it cannot eliminate those effects altogether.

Hydrologic Factors

Hydrologic factors control the amount and distribution of water at the site, affecting remediation in the vadose zone by influencing the relative permeability, accessibility, and natural flux of contaminants. The natural flux of water through the vadose zone, the typical air-filled porosity, presence of perched water, thickness of the capillary fringe, and extent of water table fluctuations are factors that can affect remediation (Table 7-16).

The dissolution of NAPL and migration of dissolved contaminants through the vadose zone increases with the average flux through the vadose zone. As a result, sites where the natural flux is relatively high are more vulnerable to groundwater contamination than sites with a low flux. This vulnerability may bias the consideration of clean-up time. Conventional and passive SVE, along with engineered bioremediation, phytoremediation, and natural attenuation may proceed at too slow a pace at sites that provide a significant and ongoing source of contaminants to the groundwater. The more aggressive technologies that can be applied quickly may be more appropriate. The thickness of reactive barriers must increase as the flux through the vadose zone increases, driving up the material costs.

Areas of particularly low flux will probably be relatively dry. A scarcity of water limits plant growth and may affect phytoremediation. Extremely dry conditions may slow SVE by increasing the sorption of contaminants, or it may slow bioremediation by limiting the availability of water. However, those effects are only important at extremely low moisture contents, which probably are rare even where the flux through the vadose zone is slow.

Volumetric Gas Content

Volumetric gas content, θ_a , (volume gas: total volume) is a critical factor affecting the movement and storage of gases in the subsurface, and it will control technologies that require gas flow, such as SVE, passive SVE, and gas-phase oxidant injection. Indeed, the performance categories of volumetric gas content in Table 7-16 were determined based on the performance of SVE; that is, $\theta_a > 0.1$ will not limit SVE, but $\theta_a < 0.05$ will severely limit SVE. The heating technologies are capable of changing the volumetric gas content, so they are relatively independent of this parameter. Most biostimulation processes in the vadose zone use gases to deliver nutrients, so the processes may be hampered by low values of θ_a . It may be possible to deliver nutrients as liquids at vadose zone sites where θ_a is small enough to preclude significant gas flow. The volumetric gas content is also called the air-filled porosity, and it can be estimated using the equation $\theta_a = \phi (1 - S_w)$, where S_w is the degree of water saturation and ϕ is porosity.

Perched Water

Perched water represents local saturated areas within the vadose zone where volumetric gas content and the gas-phase relative permeability are negligible. Contaminants in these areas are inaccessible to gas-flow methods. The performance of remedial methods based on gas flow are related to the amount of perched water at the site, and the methods probably will be ineffective where perched water is common. Heating may remove some perched water and improve performance compared to conventional SVE. Sites underlain by a vadose zone with many isolated zones of perched water may be difficult to remediate even using heating technologies unless characterization efforts are able to locate the perched zones (Table 7-16).

Capillary Fringe and Water Table

The capillary fringe is inaccessible to technologies that rely on gas flow, so both a thick capillary fringe and a water table that fluctuates greatly diminishes the performance of those technologies. Thick capillary fringes occur in fine-grained formations, so a thick fringe also implies relatively low intrinsic permeability. Heating improves performance at the capillary fringe for the same reasons that it improves per-

formance in perched water zones. The low intrinsic permeability tacitly implied by a thick capillary fringe is expected to reduce the performance of the heating technologies (Table 7-16).

Large fluctuations of the water table may indicate that there is a significant section where the degree of saturation varies seasonally. This will cause problems with the technologies that rely on gas flow. It also may cause problems with the delivery of nutrients during engineered bioremediation. Those potentially detrimental effects can probably be addressed by artificially limiting the change in the water table using wells or dewatering trenches. However, dewatering increases both the initial and operational costs of remediation. Large fluctuations of the water table may affect phytoremediation because it places an additional restriction on the plants that are used—they must be able to both accomplish remediation and tolerate large changes of saturation in the root zone.

Contaminant Factors

Clearly, properties of contaminants are among the most important factors affecting remedial performance. The location of contaminants is discussed in the previous section, where several geologic scenarios affecting location are evaluated. Location is also considered in the following section, where access issues related to the depth and size of the contaminated region are discussed. This section focuses on the contaminants themselves, the concentrations in which they occur, their basic components, age, and, most importantly, their basic chemical properties (Table 7-16).

The performance of remedial methods may depend on chemical factors that are interdependent; for example, the upper limit of concentration that can be remediated by a technology depends on key properties of the contaminant, such as vapor pressure. However, the evaluation method used here allows only one factor to be considered at a time. As a result, during the evaluation of each factor, assume that all the other factors, such as chemical properties, are typical of common contaminants that could be remediated by the technology; that is, the other factors will be non-limiting. It is beyond the scope of this summary to address all possible interactions, but some interactions between factors are presented where they are important.

Concentration In Soil

Concentrations of common organic contaminants greater than 500 to 1000 mg/kg suggests the presence of NAPL phases in the soil, whereas lesser concentrations indicate that most of the organic contaminants occur as dissolved or adsorbed phases. The indicator of NAPL presence will shift to higher or lower concentrations with the solubility and K_d of the contaminant, but it is an important marker for estimating remedial performance. All of the remedial techniques are expected to perform well when low concentrations of dissolved contaminants are present. The performance of several remedial methods will decrease with increasing contaminant concentrations, particularly where NAPL is common (Table 7-16).

SVE can effectively remediate relatively high concentrations, perhaps as great as 20,000 mg/kg, of contaminants that are relatively volatile. High concentrations imply the existence of NAPL, so volatility of a single-component NAPL will be determined by its vapor pressure (partitioning between NAPL and vapor). Three categories of vapor pressure are presented below, and the 20,000 mg/kg upper bound is for compounds in the highest category of vapor pressure.

Passive SVE is intended for use in areas of relatively low concentrations, either along the periphery of a major plume or during the late stages of a remedial project. However, it is certainly feasible that significant mass can be removed or degraded using passive SVE in areas with moderate contaminant concentrations. Indeed, passive SVE may be ideal for areas that are remote or where access to electricity needed to power SVE blowers is unavailable. Higher contaminant concentrations generally mean longer remediation times for SVE because the volume of air that must flow through the site increases with the mass of contaminants that must be removed. However, extremely high concentrations may indicate locations of NAPL saturation where the air-filled porosity is occluded by NAPL. Such regions may inhibit air flow and, hence, removal will be slower. Gas-phase oxidants may also be unable to access areas saturated by NAPL. High vapor concentrations of solvents may also damage PVC well screens, piping, or other plastic exposed to the vapors.

A similar problem exists for the delivery of gas-phase nutrients for bioremediation, but this is by no means the only problem that high con-

centrations pose for bioremediation. Microbes can only utilize chemicals dissolved in water, so NAPL must first dissolve before it can be degraded biologically. In addition, compounds that can be readily degraded as dissolved phases of modest concentration may be toxic to microbes at high concentrations. Plants also are unable to access NAPL directly, and may find high concentrations toxic, depending on the type of plant and contaminant. There is evidence that some plants can tolerate relatively high concentrations of some NAPLs. High concentrations of NAPLs will not preclude phytoremediation altogether. However, in general, the ability of both bioremediation and phytoremediation to significantly reduce concentrations of NAPL is probably limited.

Heat increases the volatility of organic compounds, so the heating technologies perform better than conventional SVE in soils with high concentrations (Table 7-16). Like SVE, however, the upper bound of concentration increases with the vapor pressure of the contaminant, so technologies that can achieve the highest temperatures will perform better on areas with high concentrations of contaminants with low vapor pressure. Heating may also destroy organic contaminants by pyrolysis or oxidization, and these effects will improve remedial performance in soils of any concentration. Heating by conduction achieves the highest temperatures of the heating technologies, so it probably will be the most effective remediation method for areas of high concentrations, particularly where the contaminants have a low vapor pressure. However, heating by conduction affects only a relatively small region in the vicinity of the heater, so the applicability of the technique is subject to access limitations.

Liquid phase oxidants may be capable of degrading NAPL, but the details of this application are still being evaluated. It is possible that injection of liquid oxidants can destroy some NAPL, but degradation of high NAPL saturations is probably impractical.

The capability of reactive barriers filled with solid oxidants to degrade NAPL probably is similar to that of liquid oxidants. However, reactive barriers are intended to be relatively long-lived and to degrade contaminants that are naturally mobile, whereas liquid oxidants are intended to degrade all organic contaminants that can be quickly accessed soon after injection. In vadose zones where NAPL is trapped as ganglia, the primary mobile phase is probably dissolved in downward moving water. As a

result, reactive barriers may perform well in material with high NAPL concentrations, if the NAPL phase itself is immobile.

High concentrations of organic chemicals may interfere with the setting of cement during S/S, potentially limiting the applicability of this technology. Sorbants such as activated carbon may sufficiently isolate even relatively high concentrations of organic chemicals from the cement. Deep soil mixing will be insensitive to concentrations; however, the location of high concentrations must certainly be considered when designing the treatment method and depth of penetration used during DSM.

Components

Contaminants may occur as single components, but commonly they exist as mixtures of multiple compounds. Such mixtures may affect remedial performance by diminishing the ability to target specific compounds that represent the major risk at a site. Moreover, many remedial technologies will rapidly recover or destroy contaminants with particular properties, while more recalcitrant compounds remain in the subsurface. This can be a serious issue where the recalcitrant compounds present serious risks, because the rapid reduction of overall contaminant mass may present an overly optimistic assessment of risk reduction.

The vapor pressure is greater over a single component NAPL than it is where the liquid occurs as a mixture. According to Raoult's Law, the depression of the vapor pressure is roughly proportional to the mole fraction of the NAPL in the mixture. As a result, volatile contaminants that occur as a minor component of a NAPL mixture may behave as if they have a significantly lower vapor pressure than the contaminant as a pure liquid. This effect of multi-component NAPL decreases the performance of both conventional and passive SVE, and it affects the performance of the heating techniques during recovery. The performance of conventional SVE is significantly curtailed, for example, where contaminants targeted for recovery occur at mole fractions of less than 0.01 (Table 7-16).

Bioremediation and phytoremediation are unable to access NAPL directly, and their performance is significantly diminished by the occurrence of either single components or NAPL mixtures. Moreover, both of those processes will selectively degrade some dissolved compounds while leaving other, more recalcitrant (and, perhaps, hazardous) com-

pounds behind. The oxidant injection technologies should be relatively insensitive to the components of NAPL because the strong oxidants used by those methods destroy many organic compounds. The occurrence of immobile NAPL should have a minor effect on the performance of reactive barriers, assuming that the barriers contain enough oxidant to react with whatever organic material becomes mobile. Some NAPLs may interfere with the setting of some S/S materials, but sorbants such as activated carbon can be used to effectively stabilize many NAPLs. Deep soil mixing is capable of performing well where both single component and mixtures of NAPL occur (Table 7-16).

The occurrence of hazardous metals, including radionuclides, along with NAPL is particularly problematic. Most of the vadose technologies are unable to remediate the metals in such mixtures. A two stage process, in which the NAPL is remediated by one technology (for example, by SVE) and the metals by another (for example, by S/S) is currently the most tenable approach to remediating areas containing mixed NAPL and metals. It is possible that deep soil mixing could be used to simultaneously remove organic chemicals and mix the resulting material with a stabilizing agent. Oxidants injected as a liquid, gas, or solid may also reduce the solubility and thereby immobilize some metals by changing their redox state. Furthermore, oxidants such as potassium permanganate can produce a residue (amorphous manganese oxide) that sorbs metals after they are reduced by reaction with organic compounds (Table 7-16).

Time Since Release

The longer a contaminant resides in the subsurface, the more difficult it can be to remediate. Compounds occupy major flow channels soon after they are released to the environment, but with time they diffuse away to occupy small pores within matrix blocks between flow channels. The slow pace of diffusion back out of the matrix blocks can be a major limitation to the recovery of contaminants from fractured materials or interbedded sediments. The time available for contaminants to diffuse into the matrix blocks plays a key role in how deeply they penetrate the blocks, and how quickly they will diffuse back out. As a result, the time since a contaminant release has occurred can be an important factor affecting remediation.

All of the remedial methods perform best on contaminants that have been released for less than one year (Table 7-16). Performance diminishes with increasing time since release for all of the technologies, except deep soil mixing and S/S. The time since release will be less sensitive to the heating technologies because they can improve recovery from matrix blocks.

Chemical Properties

The way in which a contaminant partitions among water, NAPL, vapor, and solid phases in the vadose zone is a factor that cuts across most of the other issues considered in this chapter. Technologies that access vapor phases perform better on compounds that readily partition into a vapor phase under almost any geologic condition. The following four partitioning coefficients, describing how a compound is distributed between any pair of either NAPL, water, vapor, or solid, are generally recognized to affect performance:

- Vapor pressure (NAPL:vapor)
- K_{ow} or C_w (NAPL:water)
- K_{oc} (water:solid)
- Henry's Law constant (water:vapor)

Vapor rarely contacts solids because most grain surfaces are covered by at least a thin film of water, and NAPLs generally fail to partition directly to solids, so the partitioning of vapor:solids and NAPL:solids is inconsequential during remediation.

Molecular weight and the number of halogen atoms in an organic molecule are important to some remedial processes; they also are evaluated.

The properties cited above span wide ranges of values among the common contaminants, and detailed evaluation of the properties was impractical. As a result, each of the properties is divided into three groups corresponding to large, intermediate, and small values, based on typical ranges. Thirty commonly occurring contaminants are listed in Table 7-17; their properties illustrate the three groupings of each property. The lists of contaminants are presented only as examples; they are by no means inclusive of all the chemicals in that range.

Vapor: NAPL Partitioning

Partitioning between vapor and NAPL is characterized by vapor pressure. Pressures of 5 mm Hg and 0.05 mm Hg define the boundaries of three classes of vapor pressure in Table 7-16, based on guidelines accepted for the performance of conventional SVE. This grouping gives a rather narrow intermediate range of values, with the upper boundary between the vapor pressures of 1,2 dichlorobenzene and ethylbenzene, and the lower one between nitrobenzene and PCB-1242 (Table 7-17a). The vapor pressure of water is approximately 10 mm Hg.

Conventional SVE performs well on compounds in the upper range of vapor pressure, where P_{vap} is the limiting factor (for example, where NAPL recovery by SVE is an important part of remediation). Significant

TABLE 7-17a Examples of major contaminants classified by vapor pressure
(from DeGrega et al. 1994; and EPA CFR Part 264, Appendix IX).

Compound	Vp mm Hg	Henry's Constant dimensionless	Log(K _{oc} (mg/L))	Log K _{ow}	Mw gm/mole	Halogens
Vinyl chloride	2,660	1.13E+00	1.76	1.38	62	1
1,1 DCE	600	9.27E-01	1.81	1.84	96	2
2,4,5 Trichlorophenol	400	7.16E-06	1.95	3.72	197	3
Acetone	270	1.74E-03	0.34	-0.24	58	0
1,1 DCA	180	2.39E-01	1.15	1.79	98	2
Chloroform	160	1.38E-01	1.49	1.97	119	3
Chlorobenzene	117	1.60E-01	2.52	2.84	112	1
1,1,1 TCA	100	1.66E-01	2.18	2.5	133	3
Benzene	95	2.26E-01	1.92	2.12	78	0
Carbon Tet	90	1.19E+00	2.04	2.64	153	4
MEK	77.5	1.90E-03	0.65	0.26	72	0
TCE	60	4.76E-01	2.10	2.38	131	3
PCE	60	1.09E+00	2.56	2.6	165	4
Toluene	22	2.41E-01	2.48	2.73	92	0
Xylene	10	1.70E-01	2.38	3.26	106	0
Ethylbenzene	7	3.27E-01	3.04	3.15	106	0
1,2 Dichlorobenzene	1	1.20E-01	3.23	3.60	147	2
Phenol	0.2	5.29E-05	1.15	1.46	94	0
Nitrobenzene	0.15	9.68E-04	1.56	1.85	123	0
PCB-1242	0.001	2.28E-02	3.73	4.11	261	6
Phenanthrene	9.60E-04	1.60E-03	4.15	4.46	178	0
Heptachlor	3.00E-04	6.02E-02	4.08	4.4	373	7
Pentachlorophenol	1.10E-04	1.14E-04	4.72	5	266	5
Hexachlorobenzene	1.90E-05	6.91E-02	3.59	5.23	284	6
Anthracene	1.70E-05	3.50E-03	3.15	4.45	178	0
Chlordane	1.00E-05	1.95E-03	5.15	3.32	409	8
Aldrin	6.00E-06	2.02E-02	3.98	5.3	364	6
DDT 4-4	1.90E-07	1.58E-03	5.39	6.19	354	5
Dieldrin	1.78E-07	2.38E-03	3.23	3.5	380	6
Benzo(a)pyrene	5.60E-09	1.99E-05	6.74	6.06	252	0

masses of contaminants in the intermediate range of vapor pressure can be recovered by SVE, but the time required to completely recover the NAPL may be excessive. SVE is generally ineffective at recovering NAPL with a vapor pressure less than 0.05 mm Hg. These guidelines are also generally applicable to the recovery of NAPL mixtures, where the mixture vapor pressure of a particular component is defined by Raoult's Law.

Vapor pressure increases with temperature, so the heating technologies perform better than conventional SVE when recovering contaminants with low vapor pressure. The effect of heating depends on the maximum temperatures that can be achieved by a particular technology, so conductive heating performs better than steam stripping on contaminants in the lowest vapor pressure category, since conductive heating creates hotter temperatures than steam stripping.

Technologies such as bioremediation, phytoremediation, liquid-phase oxidants and solid reactive barriers primarily act on dissolved contaminants. As a result, accessing contaminants that partition strongly into the vapor phase may be relatively difficult for these technologies.

The oxidant-based technologies are relatively new and, field data are sparse, so the details of their performance can only be inferred from basic principles. Deep soil mixing can be tailored to include processes that address a range of contaminant properties. As a result, deep soil mixing is less sensitive to vapor pressure to the other chemical properties as well.

Vapor phases are difficult to immobilize using S/S, so the performance of this technology probably will be poor where significant NAPLs occur with vapor pressures in the highest range.

Air:Water Partitioning

The constant from Henry's Law, the ratio of the concentration of the compound in air to its concentration in water, characterizes the partitioning of a compound between air and water. Dimensionless Henry's constants (expressed on a mass basis of 0.12 and 0.01) define the three classes of partitioning between water and vapor (Table 7-16). The upper boundary occurs between the properties of 1,2 dichlorobenzene and chloroform, and the lower one occurs between anthracene and aldrin (Table 7-17b). These values were selected based on the performance of conventional SVE. In general, the retardation of vapors transported

TABLE 7-17b

Examples of major contaminants classified by Henry's law constant
(from DeGrega et al. 1994; and EPA CFR Part 264, Appendix IX).

Compound	Vp mm Hg	Henry's Constant dimensionless	Log(Koc (mg/L))	Koc ml/gm	Mw gm/mole	Halogens
Carbon Tet	90	1.192	2.04	110	153	4
Vinyl chloride	2,660	1.131	1.76	57	62	1
PCE	60	1.090	2.56	364	165	4
1,1 DCE	600	0.927	1.81	65	96	2
TCE	60	0.476	2.10	126	131	3
Ethylbenzene	7	0.327	3.04	1,100	106	0
Toluene	22	0.241	2.48	300	92	0
1,1 DCA	180	0.239	1.15	14	98	2
Benzene	95	0.226	1.92	83	78	0
Xylene	10	0.170	2.38	240	106	0
1,1,1 TCA	100	0.166	2.18	152	133	3
Chlorobenzene	117	0.160	2.52	330	112	1
Chloroform	160	0.138	1.49	31	119	3
1,2 Dichlorobenzene	1	0.120	3.23	1,700	147	2
Hexachlorobenzene	1.90E-05	0.069	3.59	3,900	284	6
Heptachlor	3.00E-04	0.060	4.08	12,000	373	7
PCB-1242	0.001	0.023	3.73	5,370	261	6
Aldrin	6.00E-06	0.020	3.98	9,600	364	6
Anthracene	1.70E-05	0.0035	3.15	1,400	178	0
Dieldrin	1.78E-07	0.0024	3.23	1,700	380	6
Chlordane	1.00E-05	0.0019	5.15	1.40E+05	409	8
MEK	77.5	0.0019	0.65	4.5	72	0
Acetone	270	0.0017	0.34	2.2	58	0
Phenanthrene	9.60E-04	0.0016	4.15	14,000	178	0
DDT 4-4	1.90E-07	0.0016	5.39	2.43E+05	354	5
Nitrobenzene	0.15	9.68E-04	1.56	36	123	0
Pentachlorophenol	1.10E-04	1.14E-04	4.72	53,000	266	5
Phenol	0.2	5.29E-05	1.15	14.2	94	0
Benzo(a)pyrene	5.60E-09	1.99E-05	6.74	5.50E+06	252	0
2,4,5 Trichlorophenol	400	7.16E-06	1.95	89	197	3

through the subsurface is inversely proportional to H in materials where sorption is negligible, so three categories of Henry's constant correspond to different degrees of retardation during SVE. The degree of retardation also depends on the degree of saturation, according to $R = 1 + S_w / (S_g H)$. For example, where air occupies 50 percent of available pore space ($S_w = S_g = 0.5$), a value of $H = 0.1$ corresponds to a retardation factor of 11, whereas $H = 0.01$ corresponds to a retardation factor of 101.

Heating technologies can be particularly effective at recovering contaminants with relatively low Henry's constants. Increasing the temperature will increase Henry's constant, so warming the subsurface will increase the mass of contaminant in the vapor phase. This effect occurs for any amount of heating. All of the heating technologies are capable of

increasing temperatures to the boiling point of water, however, and this has an important additional effect. Boiling results in a roughly 1,000 fold increase in the volume of water. As a result, the mass of a contaminant that can be dissolved in one gram of water vapor is 1,000 times greater than the mass dissolved in one gram of liquid water. This effect causes dissolved contaminants with all but the very lowest Henry's constants to partition strongly into the vapor phase when pore water is heated to steam temperatures.

Air:water partitioning is rarely a factor during bioremediation. Biochemical reactions cannot directly access vapor phases, so contaminants with a high value of H may have significant masses beyond the reach of degradation reactions. This could be an issue where those vapors are naturally mobile, but in most cases vapors will partition back into the water phases as biodegradation takes place.

Gas-phase oxidant injection should perform best on contaminants with a high value of H . Liquid-phase oxidant injection and reactive barriers should perform best on contaminants with a low value of H , although these forecasts are speculative. S/S may perform poorly for contaminants with a high H , because it is unable to immobilize vapor phases.

Phytoremediation performs well for all values of H . Compounds with low values of H are dissolved where they are available for degradation by microbes in the rhizosphere, whereas compounds with high values of H are transpired through leaves and dissipated into the atmosphere.

Solid:Water Partitioning

Contaminant partitioning between solid surfaces and water is determined by sorption characteristics of the soil and contaminant. Most sorption of organic chemicals is assumed to occur on natural organic material, so the partitioning between organic carbon and water is used to predict sorption onto soil. The organic carbon partitioning coefficient, K_{oc} , is the ratio of the concentration of a compound sorbed to organic carbon in equilibrium with a dissolved phase, and the partitioning coefficient of the soil itself is the product of K_{oc} and the organic fraction of the soil.

Sorption contributes to the retardation of vapor transport. For example, the retardation factor due to sorption alone is $R = 1 + .13 K_{oc}/H$ for a sediment where density = 2.0 gm/cm³; porosity = 0.3; saturation = 0.5;

and organic carbon fraction=0.01. Previously it was assumed that the effects of H on retardation of this typical soil were small where H is greater than 0.12, and that SVE performance could be affected where R is greater than 10, suggesting that the retardation of contaminants could be significant where K_{oc} is greater than 10 mg/l. Almost all of the contaminants have a K_{oc} greater than 10 mg/l, and some of them are many orders of magnitude greater than that, so it is clear that sorption could be an important limitation to SVE performance. The intermediate category of K_{oc} is bounded $2.0 < \log K_{oc} \text{ (mg/l)} < 3.1$ (Table 7-17c). In general, R depends on both K_{oc} and H , and these two partitioning coefficients are independent. As a result, the retardation factor of compounds in the high category of K_{oc} are all quite large, but R cannot be predicted from K_{oc} alone in the intermediate and low values of K_{oc} , due to the effect that H has on R .

TABLE 7-17c Examples of major contaminants classified by organic carbon partitioning coefficient (from DeGrega eta l. 1994; and EPA CFR Part 264, Appendix IX).

Compound	Vp mm Hg	Henry's Constant dimensionless	Log(Koc[ml/g])	Log Kow	Mw gm/mole	Halogens
Acetone	270	1.74E-03	0.34	-0.24	58	0
MEK	77.5	1.90E-03	0.65	0.26	72	0
1,1 DCA	180	2.39E-01	1.15	1.79	98	2
Phenol	0.2	5.29E-05	1.15	1.46	94	0
Chloroform	160	1.38E-01	1.49	1.97	119	3
Nitrobenzene	0.15	9.68E-04	1.56	1.85	123	0
Vinyl chloride	2,660	1.13E+00	1.76	1.38	62	1
1,1 DCE	600	9.27E-01	1.81	1.84	96	2
Benzene	95	2.26E-01	1.92	2.12	78	0
2,4,5 Trichlorophenol	400	7.16E-06	1.95	3.72	197	3
Carbon Tet	90	1.19E+00	2.04	2.64	153	4
TCE	60	4.76E-01	2.10	2.38	131	3
1,1,1 TCA	100	1.66E-01	2.18	2.5	133	3
Xylene	10	1.70E-01	2.38	3.26	106	0
Toluene	22	2.41E-01	2.48	2.73	92	0
Chlorobenzene	117	1.60E-01	2.52	2.84	112	1
PCE	60	1.09E+00	2.56	2.6	165	4
Ethylbenzene	7	3.27E-01	3.04	3.15	106	0
Anthracene	1.70E-05	3.50E-03	3.15	4.45	178	0
1,2 Dichlorobenzene	1	1.20E-01	3.23	3.60	147	2
Dieldrin	1.78E-07	2.38E-03	3.23	3.5	380	6
Hexachlorobenzene	1.90E-05	6.91E-02	3.59	5.23	284	6
PCB-1242	0.001	2.28E-02	3.73	4.11	261	6
Aldrin	6.00E-06	2.02E-02	3.98	5.3	364	6
Heptachlor	3.00E-04	6.02E-02	4.08	4.4	373	7
Phenanthrene	9.60E-04	1.60E-03	4.15	4.46	178	0
Pentachlorophenol	1.10E-04	1.14E-04	4.72	5	266	5
Chlordane	1.00E-05	1.95E-03	5.15	3.32	409	8
DDT 4-4	1.90E-07	1.58E-03	5.39	6.19	354	5
Benzo(a)pyrene	5.60E-09	1.99E-05	6.74	6.06	252	0

The performance of SVE in most sediments is expected to be largely unaffected by sorption of compounds in the lowest category of K_{oc} . However, sorption of even those compounds in the lowest category of K_{oc} may significantly affect SVE performance in soils that are particularly rich in organic carbon. At the other end of the scale, sorption significantly retards recovery and may severely reduce the effectiveness of conventional SVE for contaminants in the highest category of K_{oc} . Sorption of contaminants in the intermediate group can delay remediation goals. This is a particularly important factor during the late stages of a project when the change of concentration is relatively slow.

Heating enhances desorption of contaminants, so the performance of heating technologies with SVE is better than conventional SVE (without heating). This effect is most important for contaminants with low-to-intermediate K_{oc} values. High temperatures may be required to desorb compounds with a high K_{oc} , so conductive heating may perform better than the other heating technologies when recovering strongly sorbed contaminants.

The performance of bioremediation and phytoremediation diminishes as K_{oc} increases because bioavailability can be significantly diminished where contaminants are strongly sorbed to organic matter. The performance of oxidant injection technologies is expected to diminish with the degree of sorption. Remediation of strongly sorbed contaminants could be accomplished by oxidizing all the organic material available for sorption, but this would increase the amount of oxidant required.

The performance of deep soil mixing and *in situ* reactive barriers are insensitive to sorption characteristics. Deep soil mixing has enough flexibility to address strongly sorbed contaminants. Reactive barriers are designed to degrade mobile compounds, so strongly sorbed contaminants take longer to contact the reactive material.

Sorption is actually an advantage to S/S systems, where sorbents such as activated carbon are used to bind organic chemicals as part of the remediation process. This is the only remedial technology in which performance improves as K_{oc} of the target contaminant increases.

Organic chemicals may sorb directly to the surfaces of minerals such as clays. This effect may be particularly important in clayey formations with a minute fraction of organic carbon. The degree of sorption to minerals cannot be gauged by K_{oc} values, so it is possible that sorption to clays will delay remediation even more than suggested here. The rela-

tive performance of the remedial methods should be independent of the site of sorption.

Solubility and NAPL:Water Partitioning

Partitioning of a compound between an NAPL and aqueous phase can be described by several parameters, but the octanol:water partitioning coefficient, K_{ow} , is used here. This value gives the ratio of equilibrium concentrations of a compound dissolved in octanol to that dissolved in water. The solubility of an organic chemical is related to K_{ow} , and an evaluation based on solubility is similar to one based on K_{ow} . High values of K_{ow} indicate the chemical is hydrophobic and correspond to low aqueous solubilities, whereas low values of K_{ow} correspond to high aqueous solubilities.

Octanol:water partitioning coefficients span more than six orders of magnitude, from less than 1 to more than 10^6 . An intermediate group of $\log(K_{ow})$ ranging from $2.5 < \log K_{ow} < 3.5$ splits the typical contaminants into three groups of roughly equal numbers of contaminants (Table 7-17d).

Engineered bioremediation and phytoremediation, the remedial methods most strongly affected by K_{ow} , perform well on contaminants with a low K_{ow} because these contaminants will be readily available in an aqueous phase. Contaminants with a high K_{ow} may not be bioavailable.

The performance of the other remedial methods are largely independent of the K_{ow} of target contaminants

Molecular Weight

Molecular weights of common contaminants range from 50 to more than 400 gm/mole. Contaminants with a molecular weight less than 110 gm/mole are considered light, whereas those with a molecular weight greater than 200 are considered heavy (Table 7-16). The upper boundary occurs between xylene and chlorobenzene, and the lower one occurs between 2,4,5-trichlorophenol and benzopyrene (Table 7-17e).

Molecular weight affects remedial performance because it is indirectly related to several other properties. In general, as molecular weight increases, the vapor pressure decreases, as does the Henry's constant. Both the K_{oc} and the K_{ow} typically increase with molecular weight. There are certainly exceptions to these generalizations. For example,

TABLE 7-17d

Examples of major contaminants classified by Octanol:water partitioning coefficient (from DeGrega et al. 1994; and EPA CFR Part 264, Appendix IX).

Compound	Vp mm Hg	Henry's Constant dimensionless	Log(K _{oc} (mg/L))	Log K _{ow}	Mw gm/mole	Halogens
DDT 4-4	1.90E-07	1.58E-03	5.39	6.19	354	5
Benzo(a)pyrene	5.60E-09	1.99E-05	6.74	6.06	252	0
Aldrin	6.00E-06	2.02E-02	3.98	5.30	364	6
Hexachlorobenzene	1.90E-05	6.91E-02	3.59	5.23	284	6
Pentachlorophenol	1.10E-04	1.14E-04	4.72	5.00	266	5
Phenanthrene	9.60E-04	1.60E-03	4.15	4.46	178	0
Anthracene	1.70E-05	3.50E-03	3.15	4.45	178	0
Heptachlor	3.00E-04	6.02E-02	4.08	4.40	373	7
PCB-1242	1.00E-03	2.28E-02	3.73	4.11	261	6
2,4,5 Trichlorophenol	400	7.16E-06	1.95	3.72	197	3
1,2 Dichlorobenzene	1	1.20E-01	3.23	3.60	147	2
Dieldrin	1.78E-07	2.38E-03	3.23	3.50	380	6
Chlordane	1.00E-05	1.95E-03	5.15	3.32	409	8
Xylene	10	1.70E-01	2.38	3.26	106	0
Ethylbenzene	7	3.27E-01	3.04	3.15	106	0
Chlorobenzene	117	1.60E-01	2.52	2.84	112	1
Toluene	22	2.41E-01	2.48	2.73	92	0
Carbon Tet	90	1.19E+00	2.04	2.64	153	4
PCE	60	1.09E+00	2.56	2.60	165	4
1,1,1 TCA	100	1.66E-01	2.18	2.50	133	3
TCE	60	4.76E-01	2.10	2.38	131	3
Benzene	95	2.26E-01	1.92	2.12	78	0
Chloroform	160	1.38E-01	1.49	1.97	119	3
Nitrobenzene	0.15	9.68E-04	1.56	1.85	123	0
1,1 DCE	600	9.27E-01	1.81	1.84	96	2
1,1 DCA	180	2.39E-01	1.15	1.79	98	2
Phenol	0.20	5.29E-05	1.15	1.46	94	0
Vinyl chloride	2,660	1.13E+00	1.76	1.38	62	1
MEK	78	1.90E-03	0.65	0.26	72	0
Acetone	270	1.74E-03	0.34	-0.24	58	0

phenol is relatively light but has an exceptionally low Henry's constant, and chlorobenzene is of intermediate weight but has a relatively high vapor pressure. Nevertheless, in most cases, increasing molecular weight increases partitioning into either NAPL phases or onto the surfaces of solids, markedly affecting remediation performance.

All of the technologies except S/S perform best on compounds with low molecular weight. The partitioning effects that accompany an increase in molecular weight slow conventional SVE, and relatively heavy compounds cannot be remediated by SVE. Heating helps partition molecules into the vapor phase, so the performance of SVE on heavier organic molecules can be improved using heating technologies. Some heavy compounds can be oxidized in place by high temperatures created by conductive heating. The bioavailability of heavy molecules is

TABLE 7-17e Examples of major contaminants classified by molecular weight (from DeGrega et al. 1994; and EPA CFR Part 264, Appendix IX).

Compound	Vp mm Hg	Henry's Constant dimensionless	Log(Koc (mg/L))	Log Kow	Mw gm/mole	Halogens
Acetone	2.70E+02	1.74E-03	0.34	-0.24	58	0
Vinyl chloride	2.66E+03	1.13E+00	1.76	1.38	62	1
MEK	7.75E+01	1.90E-03	0.65	0.26	72	0
Benzene	9.50E+01	2.26E-01	1.92	2.12	78	0
Toluene	2.20E+01	2.41E-01	2.48	2.73	92	0
Phenol	2.00E-01	5.29E-05	1.15	1.46	94	0
1,1 DCE	6.00E+02	9.27E-01	1.81	1.84	96	2
1,1 DCA	1.80E+02	2.39E-01	1.15	1.79	98	2
Ethylbenzene	7.00E+00	3.27E-01	3.04	3.15	106	0
Xylene	1.00E+01	1.70E-01	2.38	3.26	106	0
Chlorobenzene	1.17E+02	1.60E-01	2.52	2.84	112	1
Chloroform	1.60E+02	1.38E-01	1.49	1.97	119	3
Nitrobenzene	1.50E-01	9.68E-04	1.56	1.85	123	0
TCE	6.00E+01	4.76E-01	2.10	2.38	131	3
1,1,1 TCA	1.00E+02	1.66E-01	2.18	2.50	133	3
1,2 Dichlorobenzene	1.00E+00	1.20E-01	3.23	3.60	147	2
Carbon Tet	9.00E+01	1.19E+00	2.04	2.64	153	4
PCE	6.00E+01	1.09E+00	2.56	2.60	165	4
Anthracene	1.70E-05	3.50E-03	3.15	4.45	178	0
Phenanthrene	9.60E-04	1.60E-03	4.15	4.46	178	0
2,4,5 Trichlorophenol	4.00E+02	7.16E-06	1.95	3.72	197	3
Benzo(a)pyrene	5.60E-09	1.99E-05	6.74	6.06	252	0
PCB-1242	1.00E-03	2.28E-02	3.73	4.11	261	6
Pentachlorophenol	1.10E-04	1.14E-04	4.72	5.00	266	5
Hexachlorobenzene	1.90E-05	6.91E-02	3.59	5.23	284	6
DDT 4-4	1.90E-07	1.58E-03	5.39	6.19	354	5
Aldrin	6.00E-06	2.02E-02	3.98	5.30	364	6
Heptachlor	3.00E-04	6.02E-02	4.08	4.40	373	7
Dieldrin	1.78E-07	2.38E-03	3.23	3.50	380	6
Chlordane	1.00E-05	1.95E-03	5.15	3.32	409	8

generally poor, so the effectiveness of bioremediation and phytoremediation on heavy molecules is limited. Some methods of treating heavy organic molecules with oxidants or other compounds to break them into smaller molecular fragments show promise in improving bioavailability. The oxidant technologies may destroy large organic molecules, but there are issues related to the daughter products of these reactions that must be resolved.

Halogenation

The degree of halogenation ranges from hydrocarbons, which lack any halogens, through moderately halogenated molecules with as many as 3 halogens, to highly halogenated molecules with 4 or more halogen atoms in their molecular formula (Table 7-17f).

TABLE 7-17f

Examples of major contaminants classified by halogen atoms (from DeGrega et al. 1994; and EPA CFR Part 264, Appendix IX).

Compound	Vp mm Hg	Henry's Constant dimensionless	Log(Koc (mg/L))	Log Kow	Mw gm/mole	Halogens
Acetone	2.70E+02	1.74E-03	0.34	-0.24	58	0
Vinyl chloride	2.66E+03	1.13E+00	1.76	1.38	62	1
MEK	7.75E+01	1.90E-03	0.65	0.26	72	0
Benzene	9.50E+01	2.26E-01	1.92	2.12	78	0
Toluene	2.20E+01	2.41E-01	2.48	2.73	92	0
Phenol	2.00E-01	5.29E-05	1.15	1.46	94	0
1,1 DCE	6.00E+02	9.27E-01	1.81	1.84	96	2
1,1 DCA	1.80E+02	2.39E-01	1.15	1.79	98	2
Ethylbenzene	7.00E+00	3.27E-01	3.04	3.15	106	0
Xylene	1.00E+01	1.70E-01	2.38	3.26	106	0
Chlorobenzene	1.17E+02	1.60E-01	2.52	2.84	112	1
Chloroform	1.60E+02	1.38E-01	1.49	1.97	119	3
Nitrobenzene	1.50E-01	9.68E-04	1.56	1.85	123	0
TCE	6.00E+01	4.76E-01	2.10	2.38	131	3
1,1,1 TCA	1.00E+02	1.66E-01	2.18	2.50	133	3
1,2 Dichlorobenzene	1.00E+00	1.20E-01	3.23	3.60	147	2
Carbon Tet	9.00E+01	1.19E+00	2.04	2.64	153	4
PCE	6.00E+01	1.09E+00	2.56	2.60	165	4
Anthracene	1.70E-05	3.50E-03	3.15	4.45	178	0
Phenanthrene	9.60E-04	1.60E-03	4.15	4.46	178	0
2,4,5 Trichlorophenol	4.00E+02	7.16E-06	1.95	3.72	197	3
Benzo(a)pyrene	5.60E-09	1.99E-05	6.74	6.06	252	0
PCB-1242	1.00E-03	2.28E-02	3.73	4.11	261	6
Pentachlorophenol	1.10E-04	1.14E-04	4.72	5.00	266	5
Hexachlorbenzene	1.90E-05	6.91E-02	3.59	5.23	284	6
DDT 4-4	1.90E-07	1.58E-03	5.39	6.19	354	5
Aldrin	6.00E-06	2.02E-02	3.98	5.30	364	6
Heptachlor	3.00E-04	6.02E-02	4.08	4.40	373	7
Dieldrin	1.78E-07	2.38E-03	3.23	3.50	380	6
Chlordane	1.00E-05	1.95E-03	5.15	3.32	409	8

The degree of halogenation affects the susceptibility to bioremediation. Hydrocarbons are readily degraded by microbes, and compounds with a few halogen atoms in their structure may be degraded under some conditions. Compounds with many halogens are typically recalcitrant and are the most difficult to remediate biologically.

Increasing halogenation has effects on partitioning similar to molecular weight increase, affecting remediation in the same way as molecular weight. The degree of halogenation is expected to play a role in degradation reactions and to affect the performance of remediation by *in situ* oxidization. Details of the oxidization reactions are difficult to generalize based solely on the degree of halogenation.

Access

All of the remedial processes currently available require some type of access to the contaminated region. Typically, well boring provides access to contaminants, so many access issues are closely related to the cost and performance of wells. Several notable exceptions are outlined below and are considered in Table 7-16.

Depth

Contaminants in the vadose zone typically occur at depths less than 100 m, and most of them at less than 10 m. The shallowest contaminants, those in surficial sediments at depths less than 0.3 m, cannot be treated by many of the processes discussed here (surficial sediments can be excavated and treated using *ex situ* methods, which are not discussed in this chapter). Phytoremediation is an important exception, performing best at these shallow depths. Bioremediation using land-farming methods is ideally suited to surficial contamination, particularly when aerobic biochemical reactions can be used to degrade the contaminants. Surficial soils are effectively heated by conduction using thermal blankets, but this is the only heating technology that is intended for such shallow depths. S/S is well-suited to surficial soils because they can be readily accessed by excavation. A variety of other processes that treat excavated soil, such as thermal desorption and incineration, can be used to remediate surficial materials.

Shallow contaminants, at depths of 0.3 to 3 m, can be accessed by SVE vents. There can be problems sealing vents against leakage between the casing and the surrounding media at shallow depth. Moreover, the zone of influence of an SVE vent typically increases with depth, and shallow wells affect a relatively small area. A low permeability layer between the well screen and the ground surface extends the radius of influence, but constructing such a layer increases cost. Heating technologies are effective at shallow depths. Land-farming methods are inapplicable at depths below 0.3 m, but other methods can be used to deliver nutrients for engineered bioremediation. In general, bioremediation can be used with enough different delivery methods so that its application is independent of depth (Table 7-16).

Gas-phase oxidants can be used at shallow depths, but the radius of influence of wells used for oxidant injection may limit performance just

as it does for SVE. Macropores common near the ground surface may also affect the flow of gases and limit the performance of SVE and oxidant injection. Liquid oxidants are typically injected through a lance, which can be used at shallow depths. It is possible to apply liquid oxidants to surficial soils as well. Reactive barriers can be readily created in many shallow soils, but they generally are not applicable at depths less than about 1.5 m due to limitations of hydraulic fracturing. In principle, passive SVE can be used at shallow depths, but the short distance between the well screen and ground surface may be too small to sustain barometric pumping. Phytoremediation may be applicable at shallow depths (0.3 to 3 m), but the effectiveness at the bottom of this depth range requires the use of plants with relatively deep root systems.

Most of the technologies perform well at moderate depths (3-10 m). S/S is possible at these depths, but costs to mix the stabilizing material with the contaminants increases over this range. Phytoremediation is probably infeasible at moderate depths, except possibly under special circumstances where extremely deep-rooted plants are available (Table 7-16).

The same performance trends occur at depths below 10 m; all of the technologies except S/S and phytoremediation should perform well. It is technically feasible to conduct deep soil mixing below 10 m, but the cost of using equipment that can mix at these depths typically confines this technique to shallower regions.

Drilling costs can become a major factor as depth increases, so there will be a cost advantage to technologies that can minimize the number of wells required to treat an area. This will be particularly important at extremely deep sites, or where drilling is expensive for reasons other than well depth. The distance that can be affected by an individual SVE vent increases with depth and SVE requires fairly simple well completions that can be readily installed at any depth. It is not surprising, therefore, that SVE has been conducted at some of the deepest vadose zone sites. Steam injection is capable of affecting a larger volume of ground per well than the other heating technologies, so it will have advantages where wells are expensive.

Areal Extent

The areal extent of contaminants does not affect remedial performance, but it does impact cost. This is particularly relevant to the more

aggressive technologies that are designed to treat high concentrations in source zones within the vadose zone, where performance is obtained by relatively expensive methods. A detailed cost evaluation of the various technologies is beyond the scope of this chapter, but relative costs are reflected in the applicability to large contaminated areas.

All of the remedial methods are applicable at relatively small sites with areas less than 1 acre (Table 7-16). Conventional SVE and many of the heating technologies are applicable at intermediate-sized sites with areas between 1 and 10 acres. In general, the larger sites are best addressed by *in situ* techniques if they are underlain by a thick, permeable vadose zone with a low permeability layer near the ground surface, because such conditions increase the radius of influence of extraction vents. Conductive heating requires closely spaced wells, however, so it probably is limited to smaller sites. Applications of RF and six-phase heating have been limited to relatively small sites, so possible economies of scale are unclear. The oxidant injection technologies and reactive barriers are primarily intended to address small source zones, but could be used at intermediate-sized sites. Deep soil mixing is usually too expensive for intermediate-sized sites. S/S methods are widely used for intermediate-sized sites, but only where the soil can be excavated, mixed with the stabilizing material, and returned to the site.

It is feasible to use conventional SVE at some large sites because this technology is well known, and technology-specific surface equipment is widely available and robust. Passive SVE, however, is particularly well-suited to large sites because of its practically negligible operating costs. Steam stripping may be applicable to large sites under special circumstances, such as high NAPL saturations and low-volatility contamination. Bioremediation is applicable to large sites, particularly where land-farming methods can be used. Phytoremediation, where feasible based on other constraints, is also well-suited to large sites (Table 7-16).

Vertical Drilling Restrictions

Vertical drilling is restricted at many locations due to the presence of buildings, overhead electrical cables, or buried utilities. The adaptation of directional drilling technology from the utility installation industry during the past decade has provided a viable alternative to vertical wells. Horizontal wells are more expensive than vertical wells, but a single horizontal well can access a contaminated volume several times greater

than a vertical well, so the cost differences may be offset by the improved performance. Nevertheless, most applications of horizontal wells have been justified by their ability to access beneath structures, rather than by an improvement in performance.

Horizontal or directional wells can be used with many vadose remedial technologies where the contaminated region cannot be accessed by vertical wells. The use of horizontal wells may increase costs for initial installation and design of those technologies. However, it is a key enabling technology where structures restrict access to a vertical drill rig.

Several technologies are infeasible where vertical drilling is impossible (Table 7-16). Deep soil mixing relies on a large vertical auger that is impossible to use where vertical drilling is restricted. The closely spaced heating wells used during conduction heating are infeasible to install without vertical drilling, but it would be possible to use thermal blankets in some areas where vertical drilling was restricted. The standard configuration of six electrodes around a central well used for 6-phase heating would be impractical to use without vertical drilling. Liquid oxidants are typically injected from a lance driven vertically into the subsurface. It is possible to deliver liquid oxidants from a horizontal well, but the well spacing required to adequately disperse liquid oxidant in the vadose zone would be so small that the use of horizontal wells would be impractical in most situations. S/S would probably be impractical anywhere that vertical drilling is restricted. Drilling restrictions would have no effect on phytoremediation.

Surface Access Restricted

The ground surface cannot be accessed at all at some sites, placing even more restrictions on remediation (Table 7-16). Technologies that can use horizontal wells are still applicable, although the lack of any surface access will require the use of a more sophisticated location system during drilling. Conductive heating, S/S and phytoremediation will be infeasible without access to the ground surface.

Hazards To Structures

Remediation processes present a variety of hazards to structures in the vicinity. Displacements, heating, electromagnetic fields, and chemi-

cals are possible hazards to structures (buildings, utilities, storage tanks) or people working or living in nearby buildings (Table 7-16).

Displacements can be created by injecting fluid or by severe desiccation. Hydraulic fracturing methods used to create reactive barriers are known to create vertical displacements over the fractures. Other techniques involving fluid injection also cause displacement, but this is minor as long as injection pressures are low enough to prevent fracturing. Drying sediments during heating may cause subsidence in the overlying ground, particularly where the sediments are clay-rich. Thermal expansion could also result in unwanted displacements during heating.

The heating technologies clearly are impractical near structures that are sensitive to temperature changes, like fuel storage tanks.

RF heating is the only technology that is impossible to use near structures that are sensitive to electromagnetic fields. However, EM fields associated with the other electrical heating technologies may also eliminate them from use near sensitive structures.

Most of the remedial technologies present some risk of chemical exposure, but this factor probably significantly affects only those technologies involving fluid injection. In those cases, contaminants mobilized during injection could present a hazard to neighboring structures. Gas- and liquid-phase oxidant injection presents the most serious risk, since the oxidant itself is both highly mobile and potentially hazardous. Methods for containing injected fluids are well-known, and this issue should receive a great deal of attention during the design and implementation of remedial processes. As a result, the risks of chemical exposure during implementation of these remedial methods can generally be reduced by implementing the appropriate engineering measures.

Deep soil mixing and S/S can mobilize contaminant vapors that may present a risk to nearby structures. However, the installation methods required to implement those techniques are difficult to deploy near structures.

Acceptable Duration Until Clean

Remedial efforts are commonly driven by strict time schedules. Several of the technologies can be implemented in a few days to months, while others require several years or longer. Clearly, the time required to complete remediation depends on both type and amount of contaminant present, and a variety of other geologic factors.

All of the technologies can be effective if they are given a relatively long time to remediate conditions. Passive SVE and phytoremediation are the least energy intensive of the technologies considered, and they will probably take longest to clean a site (Table 7-16).

The time required for reactive barriers to clean a site will depend on the ambient rate of mass transfer within the site. It is possible that reactive barriers significantly reduce the flux of contaminants from the vadose zone quickly, even though immobile contaminants may remain above the barriers for much longer times. Data documenting the long-term performance of reactive barriers in the vadose zone are not yet available for this new technology.

Conventional SVE projects are commonly completed within 1 to 5 years, and many engineered bioremediation efforts are completed within this span as well. It is possible for those technologies to be effective more quickly at small sites containing low concentrations of contaminants.

All of the heating technologies, the oxidant injection methods, deep soil mixing, and S/S are completed within a short period of time, typically less than 1 year.

GAPS IN CURRENT CAPABILITIES

Currently available technologies can remediate many commonly occurring conditions, but gaps in these capabilities plague the efforts to reduce risks at contaminated sites. The performance review of remedial technologies presented in this section identified key factors related to geology, contaminant properties, and access that underlie these gaps in capabilities.

Heterogeneity is the single most important geological factor that limits the performance of remediation, because contaminants are slow to diffuse from low permeability matrix blocks between permeable pathways in heterogeneous materials. Karstified limestone and fractured rock are the most difficult formations to remediate because of their heterogeneities. Clay-rich sediments are also difficult formations to remediate, in part due to the effects of heterogeneities, and in part due to low permeabilities that limit the fluid flow necessary for many remedial techniques. Several methods have been developed to heat or fracture

clay sediments, but little headway has been made on methods for remediating karst or fractured rock.

Important secondary factors related to geologic conditions include perched water and the presence of organic-rich sediments. Organic-rich sediments retard recovery or bioavailability by sorbing contaminants, and they interfere with reactive chemicals, particularly oxidants, used to degrade contaminants. Perched water can defy remediation by many vadose zone techniques unless the locations of the perched zones can be identified.

Remarkably high concentrations of some contaminants can be remediated, but even modest concentrations of other compounds may challenge the best remedial capabilities. The presence of NAPL in the vadose zone increases the degree of difficulty, but NAPL with low vapor pressures are particularly difficult to remediate. Contaminants with a low vapor pressure and Henry's constant, and high K_{oc} and K_{ow} , are the most difficult to remediate when they occur in the vadose zone. Many compounds with a high molecular weight meet those criteria. NAPL mixed with toxic metals represent contaminant conditions that are most taxing to current remedial capabilities.

Access issues go hand-in-hand with problems associated with heterogeneity and low permeability. These problems are addressed by accessing the formation with closely spaced wells, but the cost of drilling many wells is prohibitive. New methods for creating vertical wells using direct push techniques have reduced costs, and directional drilling and hydraulic fracturing methods have improved performance during subsurface access. Many of the aggressive technologies are unsuitable in close proximity to buildings.

A variety of factors other than those related to technology performance also present major barriers to site remediation. Three important factors are rooted in the uncertainty regarding the outcome of the remedial process. The performance of many remedial methods under a variety of site conditions is uncertain; many of the evaluations cited above are based upon expected performance rather than field data. Moreover, the site conditions that characterize the regions underlying many contaminated sites are not completely known. In addition, we are uncertain as to how to assess the benefits of a particular remedial process, that is, to answer the question: "how clean is clean enough?" It is not surpris-

ing that managers are reluctant to commit the resources to move ahead with remediation in the face of these uncertainties.

These issues are certainly challenging, but they are far from insurmountable. There are three fundamental areas where additional research could fill significant gaps in current capabilities.

1. Demonstrations of remedial technology at the pilot-scale
2. Methods for monitoring and assessing remedial technology performance
3. Modeling fate and transport to evaluate risk of contaminants remaining after remediation

Pilot-scale field tests of remedial technologies under controlled conditions can provide the data needed to anticipate performance. Several *groundwater* remediation technologies have recently been tested and monitored in detail at Hill Air Force Base in Utah, and Dover Air Force Base in Delaware, under the Strategic Environmental Research and Development (SERDP) program jointly sponsored by the U.S. Environmental Protection Agency, Department of Defense, and DOE. A focused program, similar to the SERDP program, would provide essential data documenting the capabilities and limitations of technology in the vadose zone.

A research effort designed to improve methods for characterizing the vadose zone would improve capabilities by guiding the selection and design of remedial techniques. Moreover, improved monitoring and assessment capabilities would go a long way toward optimizing and controlling the implementation of any remediation method.

The fate and transport associated with contaminants that remain in the vadose zone after remediation has received little study, so it is currently unclear how much contamination can remain in the vadose zone and still have an acceptable risk. Theoretical modeling tools to make these types of predictions, which are currently available, are described in Chapter 5. The monitoring methods needed to validate such modeling efforts are among the suite of tools that is needed to characterize the vadose zone under any circumstances. Research into this issue would provide important guidance on how to prioritize remedial resources, where to evaluate remedial performance, and when to conclude that remediation is complete.

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CASE STUDIES



MODELING THE PERFORMANCE OF AN SVE FIELD TEST

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Soil vapor extraction (SVE) systems are usually designed by following published guidelines (Johnson *et al.* 1990b; USEPA 1991; Michaelson 1993). Quantitative tools that may improve the optimization of a design and/or operation of SVE exist as computer models varying in complexity and availability (Jordan *et al.* 1995). The lack of tested models for predicting SVE performance has limited the practice of using models in the design and operational phases of SVE systems. Until confidence in modeling full-scale SVE performance is attained, modeling will not be accepted in engineering and regulatory practices. Models that can predict SVE performance could be used to determine the feasibility of SVE, select vent spacings and extraction rates, design optimal offgas treatment, estimate cleanup times, and, ultimately, forecast capital and operational costs.

One cause for the lack of model testing for full-scale performance is the fact that many field operations lack the comprehensive monitoring and characterization data that are needed to fully test the validity of sophisticated mathematical models. A detailed understanding of vapor movement using mathematical modeling is essential in evaluating the appropriateness of SVE for remediation and for assessing the hazards caused by vapor migration and the potential for groundwater contamination. Mathematical models help in evaluating the extent of pollution and the effectiveness of remedial actions. The lack of knowledge on how to select the appropriate model and use it properly for field settings is a major obstacle limiting the usage of existing codes. Analogous to the current state of remediation system design, where many innovative techniques exist but are not used because of a lack of performance data (Gierke and Powers 1997), a number of software programs are available to simulate SVE, but they are not often used in practice because they have not been shown to be appropriate for simulating field performance. The most common practice is to

model the gas flow separately from the vapor transport and then simulate the vapor transport with a different code for an idealized flow field that may, in fact, be different than the one generated for the gas flow estimates.

The chronology of model developments for SVE began with studies solely of gas flow, ignoring the transport of individual components. Later, transport codes were developed with the assumption that the flow aspect (that is, velocities) would be prescribed separately. Early attempts to model subsurface gas flows started by modifying groundwater flow models to utilize the similarities between the governing equations for air and water flow (Rathfelder 1995; Baehr and Joss 1995). Subsequently, many analytical and numerical models were developed to account for the physical and chemical processes affecting vapor movement. In terms of the transport aspects, most models have the flow and transport aspects decoupled and assume equilibrium partitioning between phases (gas-liquid-solid), while other, more sophisticated, approaches allow for non-equilibrium partitioning, density-driven flows, and vapor phase sorption (Jordan *et al.* 1995; Rathfelder 1995).

Coupled flow and transport models have been developed in order to describe the interdependent processes affecting transport in the vadose zone. Since most models are one or two dimensional, their applicability to field settings is not certain. Three-dimensional models may provide a more accurate representation of field settings; however, they are more complex to use, require more input data, and are computationally intensive. Few three-dimensional models have been developed to date.

The applicability of models for field settings has not been tested due to a lack of available and comprehensive field data suitable for proper model validation. Most of the existing codes have been tested either by generating a hypothetical setting or by verifying the models against other solutions. A few have been compared to observations from laboratory experiments.

We identified a field study where the most complete characterization was available (DePaoli *et al.* 1991). We then selected a model that would allow for testing the most sophisticated approaches, and, subsequently, a variety of practical simplifications (for complete details, see El-Beshry 1998; El-Beshry *et al.* 1998; and El-Beshry *et al.* 1999).

This case study examines the applicability of a three-dimensional model to a set of field tests. VENT3D is a three-dimensional vapor flow and transport model for multi-component mixtures developed by David Benson at the University of Nevada, Reno (Benson, 1994). It is used for this model application demonstration because VENT3D represents at present the most sophisticated, commercially available SVE model suitable for multiple vent configurations and contaminant mixtures. The model was tested against data obtained from a soil vapor extraction study conducted at a JP-4 jet fuel spill site at Hill Air Force Base, Utah (DePaoli 1991). The model is used to estimate the mass removed during SVE and the distribution of contaminants remain-

ing in the soil after venting. Our intention was to demonstrate the appropriateness of the modeling approach and the use of field data to determine model input.

SETTING

The site selected for this study was a fuel storage area at Hill Air Force Base (HAFB), in Utah, where some 27,000 gallons (100,000 liters = 76,000 kg) of jet fuel (JP-4) were spilled onto the ground in 1985, after an automatic filling system malfunctioned and storage tanks overflowed (DePaoli *et al.*, 1991). SVE had been selected as the remediation method, since fuel constituents are volatile at ambient temperatures, and SVE was considered the most inexpensive and efficient method for cleanup. A field study of SVE was performed at HAFB by Oak Ridge National Laboratory (ORNL) in order to determine the long-term effectiveness for removing JP-4 from unsaturated soils. A number of pilot tests and a full-scale SVE study were carried out at the site to demonstrate the cleanup effectiveness attainable using soil venting for remediation of fuel contaminated sites. This is the only study with a data set comprehensive enough to provide adequate input to test the predictive capabilities of the commercially available SVE models.

A site schematic is shown in Figure 1. After the spill, the tanks and some of the underlying soils were removed. The excavated soil was placed in a pile on a flexible membrane liner. The spilled fuel had flowed from the tanks (denoted as the excava-

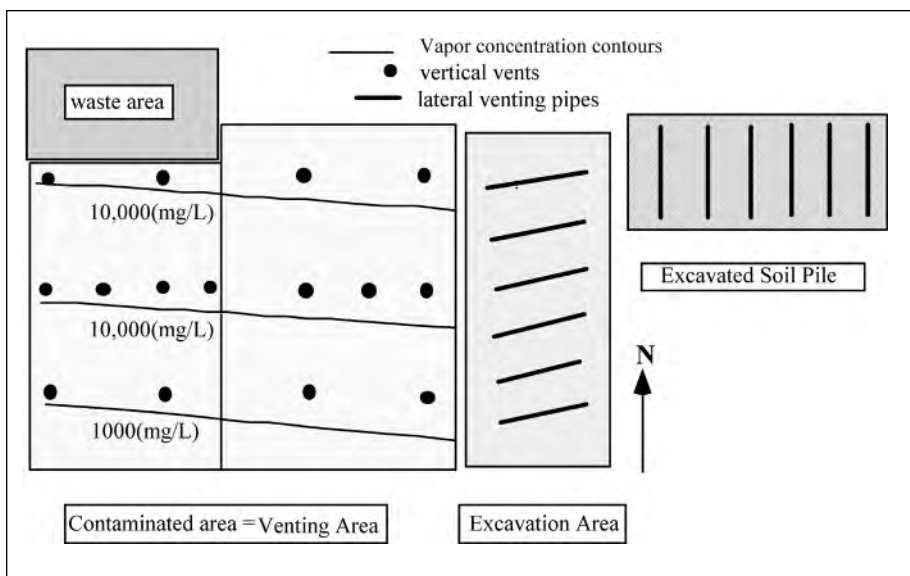


Figure 1. Site map of Hill AFB SVE study area (adapted from DePaoli *et al.* 1991).

tion area) to the west, infiltrating along the way. Venting was planned for the contaminated area shown in Figure 1. Five pilot tests were carried out at the site, followed by a full-scale soil venting that lasted for 10 months. The vent system consisted of 15 vertical vents as shown in Figure 1, some spaced at 40 ft along the upper and lower line and at 20 ft along the center line. During operation, several extraction rates and multiple well configurations were tested in twenty five consecutive flow tests. During the study, soil gas concentrations, hydrocarbon mass removals, and soil gas pressure data were collected. At the end of the study, a total of 48,000-54,000 kg of hydrocarbons were removed from the soil over the 10-month operation. Table 1 lists all of the events during the pilot tests and the full-scale operation that were included in the model simulations.

MODELING APPROACH

VENT3D is a 3-dimensional, finite-difference code for vapor flow and transport of a multi-component mixture (Benson 1994). The model computes the movement of compounds in the vapor phase and keeps track of the phase distribution of each compound in the other three phases (NAPL, dissolved, and sorbed). The model domain is divided into blocks (Figure 2), to which unique properties of permeability

TABLE 1 Chronology of vapor extraction flow rates during Hill AFB SVE study.	
Date	Activity
Pilot Tests	
January 18, 1988	Extraction from Vent 7 at 62 cfm for 2 hours
January 19,1988	Extraction from Vent 7 at 127 cfm for 2 hours and then extraction from Vent 7 at 202 cfm for 2 hours
January 20,1988	Extraction from Vent 7 at 172 cfm for 4 hours and then extraction from Vent 7 at 209 cfm for 8 hours
Full-scale Operation	
December 18–March 11, 1988	Extraction from Vent 7 at 250 cfm with occasional system shutdown
March 11-April 2, 1989	Extraction from Vent 10 at 250 cfm
April 2-April 22, 1989	Extraction from Vent 9, 10, & 11 at 350 cfm.
May 15-May 26, 1989	Extraction from Vent 5, 6, 7, 8, 9, 10, & 11 at 500 cfm, followed by 14 days of shutdown
June 10-August 15, 1989	Extraction from Vent 5, 6, 7, 8, 9, 10, & 11 at 918 cfm

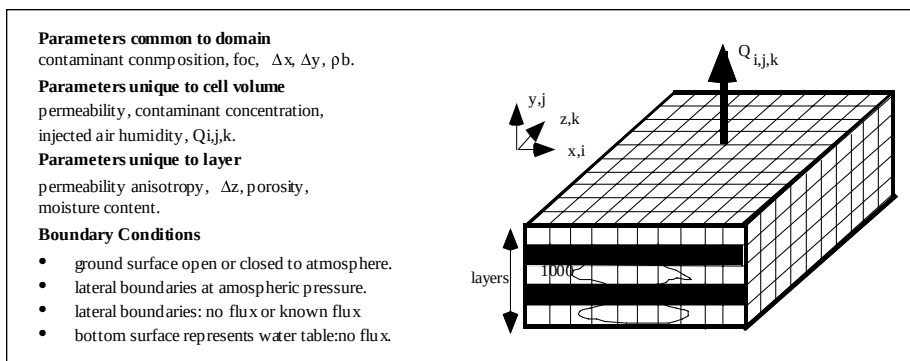


Figure 2. Schematic of VENT3D structure (after Benson 1994).

and contaminant concentration can be assigned. Extraction and injection vents can be simulated. Components of the contamination can be present in different proportions and have different properties. Thermophysical properties of the components, such as boiling point, molecular weight, solubility, vapor pressure, and octanol/water partition coefficient, are entered in the model. The soil temperature is assumed to be constant. Molecular diffusion is calculated as a function of the air diffusion coefficient and air saturation. The gas phase is the only moving phase. Equilibrium partitioning is assumed between the gas phase and all other phases (NAPL, dissolved, and sorbed). The model uses the linear sorption relationship and assumes constant gas viscosity. Air is considered to be incompressible, and elevation head is ignored, compared to pressure head, in the formulation of soil gas head. The model solves the three-dimensional, steady-state vapor flow equation for pressure. The bottom surface of the bottom layer is always assumed as a no-flow boundary, the top layer is specified either as a no-flow boundary (sealed surface) or open to the atmosphere boundary, and the lateral boundaries can be either open or closed to the surroundings. Knowing the gas pressure, the interblock gas flow is determined by Darcy's law.

Vapor transport is described by the advection-dispersion equation for each compound in the mixture. The model keeps track of the distribution of each compound in the three immobile phases (NAPL, aqueous, and sorbed). The total molar concentration of each compound is expressed as a function of the vapor concentration and the sum of the molar concentrations in the four phases. Where NAPL is present, the constituent mole fractions must sum to 1. Between time steps, mole fractions of each compound are moved into and out of each cell block. The transport

equations are solved iteratively, and equilibrium is re-calculated at the end of each time step.

MODEL SETUP AND ASSIGNMENT OF CHEMICAL PROPERTIES

The model domain was divided into an orthogonal grid in the x and y directions and into several layers in the z direction as shown in Figure 2. The contaminated soil volume was divided into 11 layers, each having different initial contaminant concentrations. The distribution of the soil concentrations was determined from the soil core analyses performed by DePaoli *et al.* (1987). Each layer was divided into a 16 by 12 orthogonal grid. Each grid cell was 10-ft wide by 10-ft long. Figure 3 shows the grid representing vent wells and soil boring locations for each layer in the vertical vent area. The grid shows the sub-areas into which the vertical vent area was divided. Each sub-area is represented by a soil boring (V1 to V15). The vent wells were installed at the boring locations. Soil samples were collected at 3-ft intervals up to a depth of 15 ft, and every 5 ft thereafter. The total depth was divided into

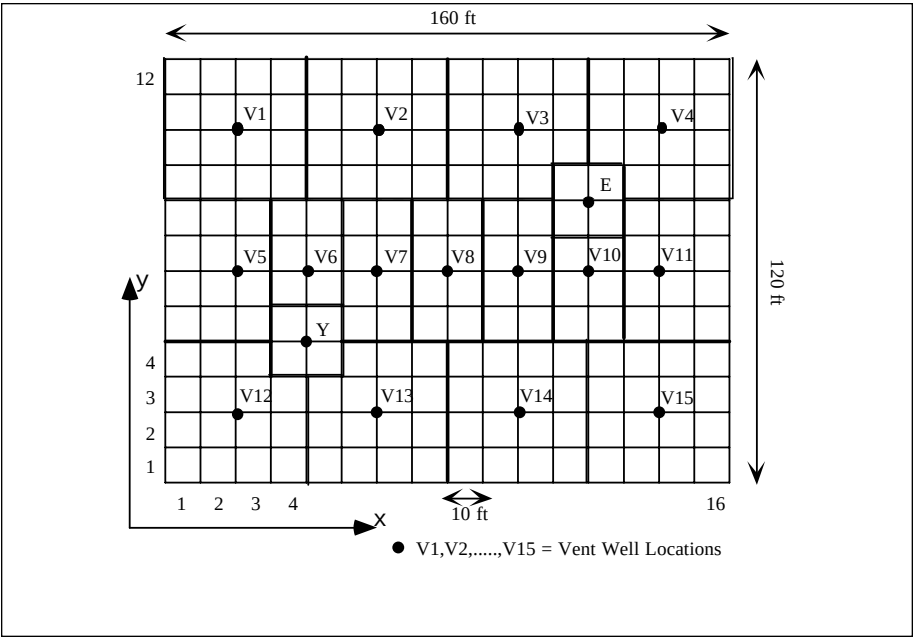


Figure 3. Grid used to represent the study area: (a) horizontal grid where each boring location is centered in an area to which the concentrations with depth are ascribed uniformly in the horizontal direction, and (b) depiction of how the soil profile was subdivided into model layers according to the sampling interval.

layers 3-ft thick for the upper 15 ft and 5-ft thick from the 15- to 50-ft depth. Each layer is represented by a soil sample.

In 1985, the volume of fuel spilled was estimated at 87,000 L (23,000 gallons). In 1987, 465 soil samples were collected. The total hydrocarbon mass in the vertical vent area was estimated, based on the soil samples concentrations, at less than 14,000 kg, which was much lower than the spill estimate. This could be attributed to the loss of volatile components from samples due to the sampling procedure used and/or a lack of representativeness of the sampling.

Comprehensive analysis of JP-4 using gas chromatography/mass spectrometry will yield a suite of some 100 components. For modeling purposes, the 104 components were reduced to 10 classes of components, as listed in Table 2, to reduce the computational intensity required with a large number of components. Moreover, the SVE monitoring provided only measures of hydrocarbon classes based on carbon number.

DETERMINATION OF PERMEABILITY

A software program called GASSOLVE (Falta 1996) computes the horizontal and vertical permeability of the unsaturated zone by fitting an analytical solution for gas flow to pressure data collected from field air-permeability tests. Given observed

TABLE 2

Composition of JP-4 estimated by Southern Petroleum Laboratories, Inc.

Number of Carbon Atoms	Mass Fractions
<C ₅	0
C ₅	0.005
C ₆	0.05
C ₇	0.15
C ₈	0.225
C ₉	0.145
C ₁₀	0.11
C ₁₁	0.12
C ₁₂ +C ₁₃	0.16
C ₁₄	0.025
C ₁₅	0.01
>C ₁₅	0

pressures from air-permeability tests—in which usually one extraction well screened in the unsaturated zone is operating and pressures are recorded at one or several locations—and assuming a homogeneous medium, GASSOLVE adjusts the horizontal and vertical permeabilities to achieve a minimum residual sum of squares between calculated and observed pressures.

Pressure data from four of the pilot tests conducted at the site were used by GASSOLVE to determine the air permeability of the formation. Table 3 lists the permeabilities determined by GASSOLVE for each pilot test.

TABLE 3 Horizontal and vertical permeabilities determined with GASSOLVE and pilot-test data.				
Pilot Test Flowrate (m ³ /s)	0.029	0.059	0.080	0.094
Horizontal Permeability (darcys)	35	40	43	42
Vertical Permeability (darcys)	1	1.3	1.1	1.02
Residual Sum of Squares	2.1e-5	4.7e-5	7.1e-5	1e-4

RESULTS

The flow rates calculated with the model are prescribed as model input. Therefore, it is more appropriate to test measured and predicted gas vacuums. Both soil-gas and vent pressures were measured, and these are shown in comparison to the model predictions using the pilot-test-calibrated permeabilites in Figure 4. The agreement shows that VENT3D was able to appropriately simulate the flow patterns during SVE at the Hill AFB site.

Mass removals were obtained from the field measurements by summing the removal of the different carbon-number class compounds listed in Table 2 during the various flow configurations shown in Table 1. The observed removals are compared to VENT3D predictions in Figure 5.

DISCUSSION

The agreement between the VENT3D preditions and the observed SVE performance is remarkable when one considers the complexity of the model input and how independent approaches were used to gather this information (El-Beshry, 1998). There are important factors that favor this agreement, and that may permit extrapolation to other sites. First, the chemical spill is relatively recent and relatively limited in

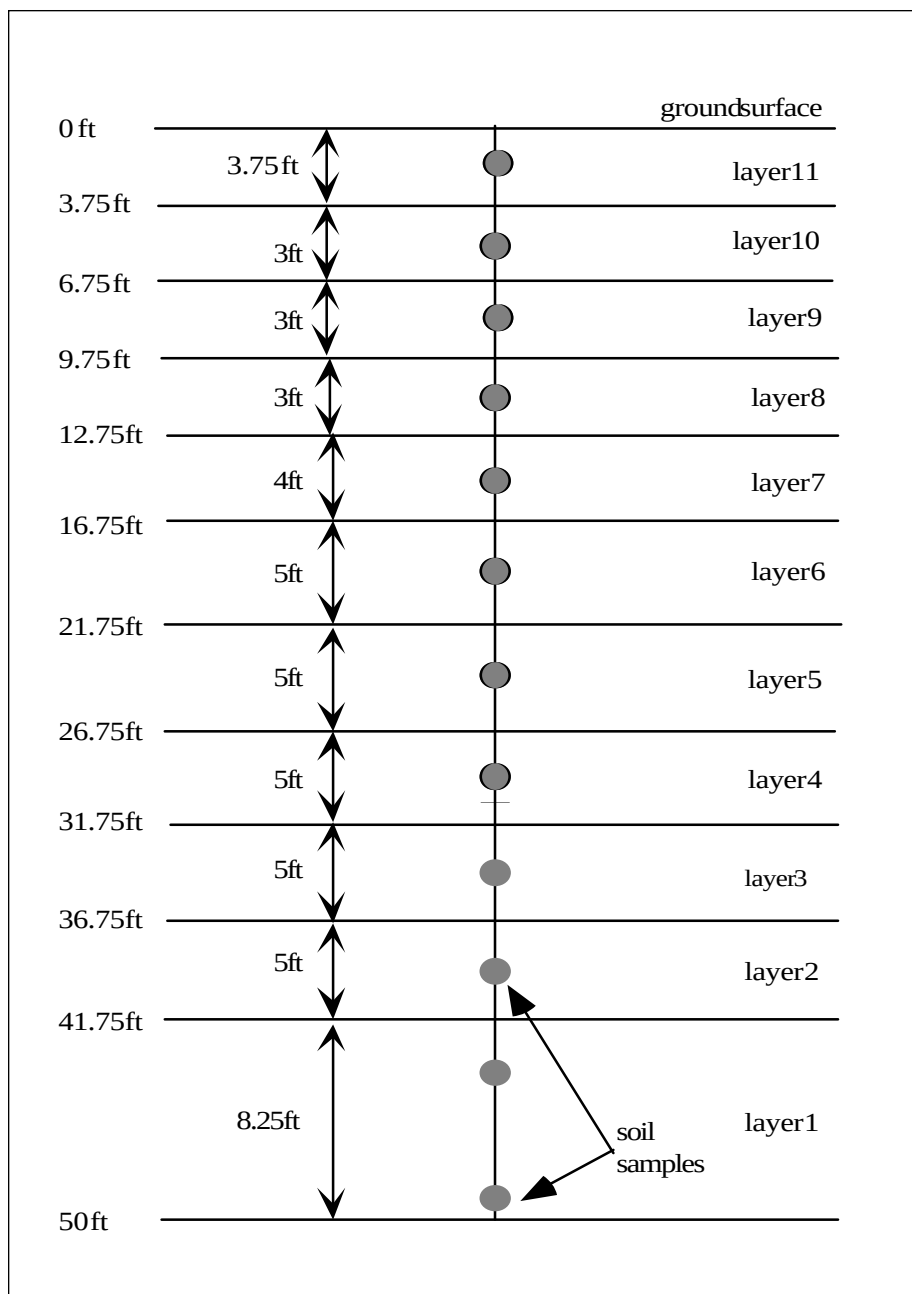


Figure 3b. Schematic of VENT3D structure (after Benson 1994).

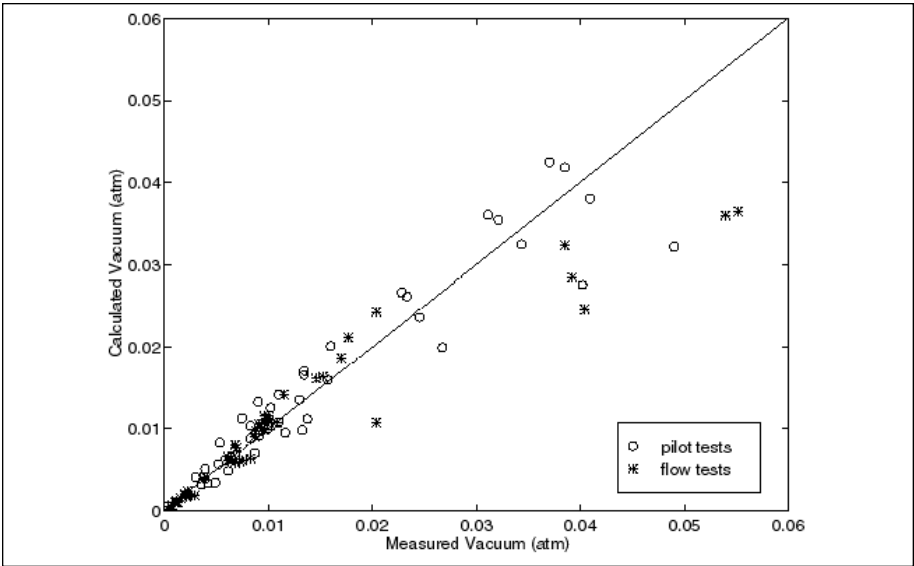


Figure 4. Comparison of measured soil-gas vacuums and VENT3D predictions using permeabilities obtained from GASSOLVE calibration to pilot test data.

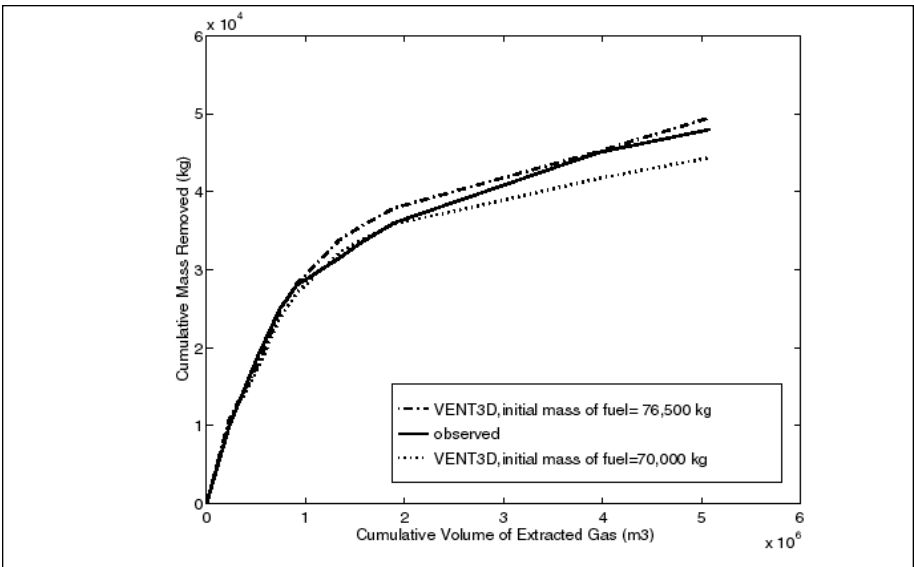


Figure 5. Comparison of measured total mass removal of JP-4 during Hill AFB SVE demonstration to VENT3D predictions using different estimates of the total initial mass of contamination.

areal extent. The NAPL phase was the predominant form of the contamination, and the removal depicted in Figure 5 is still advection-dominant removal. The ability of VENT3D to simulate complete removal was not tested because there was no data available to us for this purpose.

The model simulations were most sensitive to the initial total mass of contamination, which was not known. We used soil-core data first, and this underestimated the mass removal by a factor of more than 5. Our next option was to use the estimate of the total spill, which also was not well defined. Therefore, the initial mass really became a fitting parameter. The distribution of the contamination was assumed to follow the soil core data, assuming the volatile losses during the sampling was proportionally the same.

Other results that we obtained, are reported elsewhere (El-Beshry 1998; El-Beshry et al. 1998 and 1999). They include evaluations of simplifications, such as averaging the flow variations, treating the soil profile as homogeneous instead of multiple layers; and treating the fuel as an equivalent single-component. All of these simplifications led to results that were appropriate from a design standpoint.

TABLE 4

Steady-state extraction vent vacuums observed during pilot and field tests compared to vacuums predicted by VENT3D (adjusted for near-vent characteristics).

Extraction (m³/sec)	Observed Vacuum Rate (inches H₂O)	VENT3D Vacuum (inches H₂O)
<i>Pilot Tests</i>		
0.029	5.4	4.1
0.059	10.9	8.4
0.080	16.0	11.6
0.094	20.0	13.6
<i>Flow Tests</i>		
0.029	8.3	4.5
0.080	22.0	15.1
0.080	22.5	15.2
0.074	15.7	13.6
0.050	16.0	11.8
0.048	16.5	10.1

TABLE 5

Properties of components for the multi-component simulations and the equivalent properties for the single-component simulations.

Hydrocarbon Class	Mass Fraction %	Molecular Weight (gm/mole)	Boiling Point (°C)	Vapor Pressure (atm)	Aqueous Solubility (mg/l)	K_{ow}
C ₅	0.005	72	36	5.7e-1	40	2.5e3
C ₆	0.05	86	60	2.2e-1	13	6.5e3
C ₇	0.15	100	90	6.4e-2	3	2.2e4
C ₈	0.225	114	112	3.0e-2	1.5	5.8e4
C ₉	0.145	128	133	1.0e-2	0.3	1.9e5
C ₁₀	0.11	142	174	1.3e-3	0.01	4.0e6
C ₁₁	0.12	156	196	4.0e-4	0.007	6.3e6
C ₁₂ +C ₁₃	0.16	170	216	1.0e-4	0.004	7.9e6
C ₁₄	0.025	198	253	1.0e-5	0.002	1.5e7
C ₁₅	0.01	212	270	4.0e-6	0.0015	9.2e7

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SCALE-DEPENDENT MASS TRANSFER DURING SVE

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A number of studies have investigated local equilibrium assumptions and mass-transfer limitations associated with contaminant transport during remediation methods such as soil vapor extraction, air sparging, and steam injection (Fischer *et al.* 1998; Fischer *et al.* 1996; Wilkins *et al.* 1995; Ho *et al.* 1994; Ho and Udell 1995; Falta *et al.* 1992a; Falta *et al.* 1992b; Baehr *et al.* 1989). Several of these studies concluded that heterogeneities at various scales dictate whether local equilibrium assumptions can be used. For example, Ho and Udell (1992) showed experimentally that if contaminants are trapped in stagnant low-permeability zones during soil vapor extraction, the recovered effluent gas concentrations were significantly less than the saturated equilibrium gas concentration of the contaminant. While the presence of heterogeneities invalidates the use of local equilibrium assumptions, this case study demonstrates that local equilibrium assumptions are still valid if the representative elementary control volumes used in the system modeling are sufficiently small to capture the salient processes. Using the experimental results of Ho and Udell (1992), this case study demonstrates that mass transfer processes modeled at different scales yield significantly different results and interpretations, but that the use of local equilibrium assumptions at sufficiently small scales can adequately represent the physical behavior of the system.

EXPERIMENTAL BACKGROUND

Ho and Udell (1992) performed the experiments described here to determine the effects of heterogeneities on soil vapor extraction of volatile organic contaminants. In those experiments, a two-dimensional sand-filled apparatus was emplaced with benzene, toluene, and/or o-xylene. Air was vented through the system and the effluent gas concentrations were monitored using gas chromatography (Figure 1). Different sand configurations were used in order to produce varying degrees of heterogeneities. The system considered in this case study consists of 5 ml of toluene emplaced in 48-65 mesh sand, which fills the apparatus only halfway. Figure 2 illustrates the system and its associated parameters. Because the sand did not fill the apparatus entirely, air flowed preferentially through the open air space above the contaminated sand. The purpose of this configuration was to represent a system in which air preferentially channeled around (rather than through) a contaminated region because of heterogeneities in the soil. The outline of the visible liquid toluene in the sand was recorded at different times during the soil venting (Figure 2). The effluent gas concentrations of the toluene were also recorded as a function of time

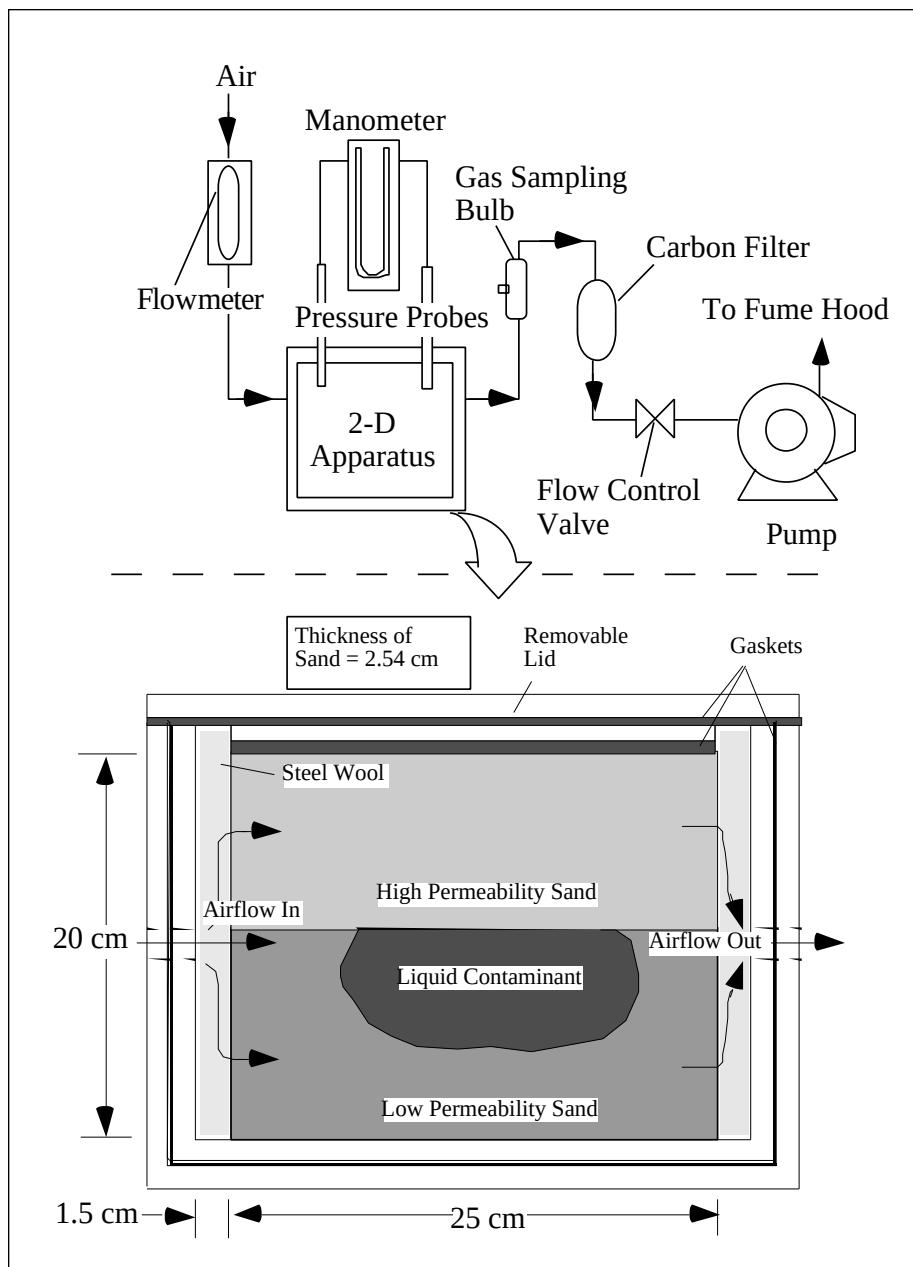


Figure 1. Sketch of the experimental apparatus for two-dimensional soil venting used in Ho and Udell (1992).

and are presented, along with the results of the models, developed at two different scales, later.

THEORETICAL DEVELOPMENT

There are two models of the experimental system presented previously. The first model assumes that the representative elementary control volume is the size of the entire test cell and that macro-equilibrium conditions exist within the test cell. The second model assumes that the representative elementary control volume is no larger than the boundary layer that develops over the contaminated region. Local equilibrium conditions are assumed to exist at the surface of the contaminant pool, but mass transfer can occur between the contaminant pool and the advective air-flow via diffusion.

Macro-Scale Equilibrium Model

The mass transfer of toluene in a macro-scale equilibrium model where control volume is the size of the entire test cell shown in Figure 2 can be described by the following equation:

$$\frac{dm}{dt} = -QC_{sat}$$

where the left-hand side is the time derivative of the mass, m [kg], of liquid toluene in the control volume, Q is the air flow rate [m^3/s], and C_{sat} is the saturated toluene gas concentration coming out of the control volume.

Assuming macro-scale equilibrium, the effluent gas concentration of toluene is obtained using the ideal gas law:

$$C_{sat} = \frac{P^0 M}{RT} \quad (2)$$

where P^0 is the saturated vapor pressure of toluene [Pa], M is the molecular weight of toluene [kg/kmol], R is the universal gas constant [8,300 J/kmol-K], and T is the system temperature [K]. Table 1 shows the relevant parameters for (1) and (2). The effluent gas concentration of toluene using this macro-scale equilibrium model is 0.11 kg/m^3 . Integration of (1) yields a simple expression for the time required to remove the total mass of toluene ($m^0 = 0.022 \text{ kg}$) in the system:

$$T = \frac{m^0}{QC_{sat}} \quad (3)$$

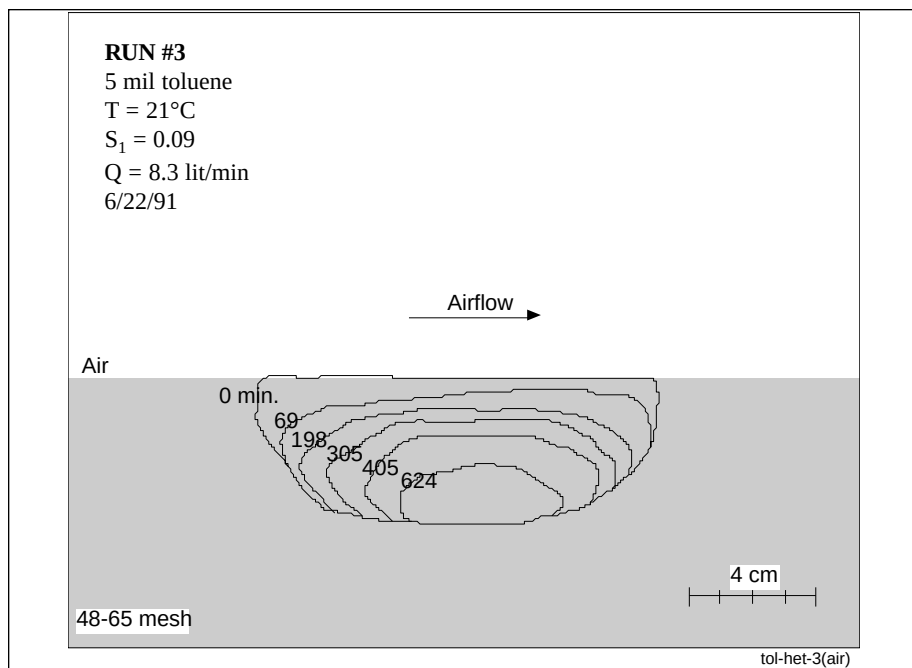


Figure 2. Air venting of toluene in a heterogeneous configuration consisting of sand filled halfway up the test cell so that air flows preferentially in the air space above. The outlines depict the shape of the toluene pool as a function of time (Ho and Udell, 1992).

TABLE 1	Properties of toluene at 20°C and parameters used in the models (Ho and Udell 1992).
Molecular weight (kg/kmol)	92.1
Density (kg/m ³)	867
Saturated vapor pressure (Pa)	2910
Binary diffusion coefficient of vapor in air, D_o (m ² /s)	7.9×10^{-6}
Vapor diffusion tortuosity factor, τ^*	0.29
*The vapor diffusion tortuosity factor accounts for the effects of moisture and porosity in porous media. The effective diffusion coefficient, D , is given as $D = D_o\tau$ where D_o is the diffusion coefficient of the vapor in air.	

Thus, the macro-equilibrium scale model yields an effluent concentration that is equal to the saturated concentration of toluene and that lasts for an amount of time given by (3).

Local-Scale Equilibrium Model

The second model uses a control volume that is small enough to capture the boundary layer development and stagnant diffusion layer over the contaminant pool in the sand (Figure 3). In this model, local equilibrium between liquid- and gas-phase toluene is assumed to exist, but because of the fine resolution of the model, local equilibrium only occurs at the surface of the contaminant pool. The equilibrium gas concentration at the surface encounters additional resistance in the stagnant diffusion layer and the convective boundary layer above the contaminant pool. Thus, the average effluent concentration leaving the test cell (and monitored by gas chromatography) is less than the saturated toluene gas concentration given in (2). Appropriate mass balances within a control volume in the boundary layer and across the interface of the high- and low- permeability zones yield relations for the average effluent concentration, C_{ave} , and vapor-phase diffusion length, d . Ho and Udell (1991) describe this model and the solution procedure in detail, and the results for the average effluent concentration of toluene using this local-equilibrium scale model are presented graphically in the next section.

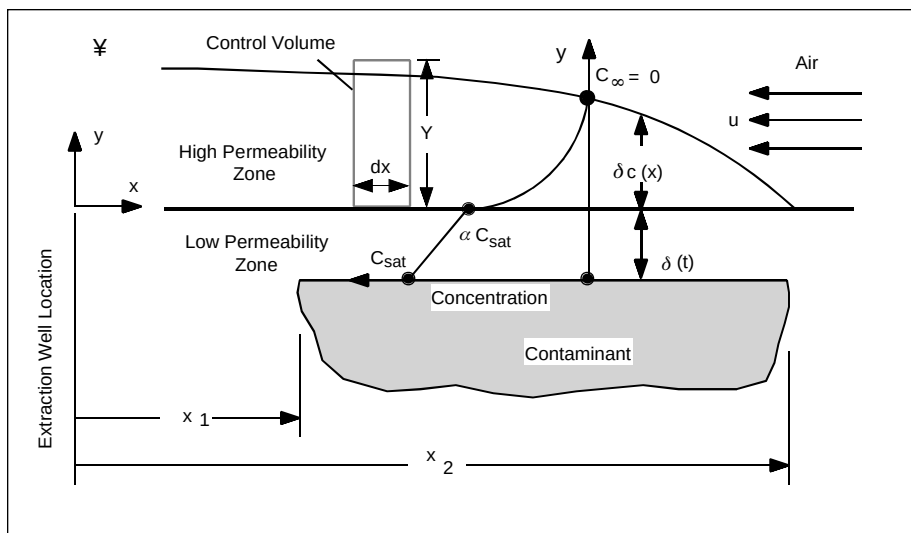


Figure 3. Sketch of the local-scale equilibrium model that considers the development of a concentration boundary layer and a stagnant diffusion layer over the contaminant pool. (Ho and Udell, 1991)

RESULTS AND DISCUSSION

The observed effluent concentrations of toluene during the experiment illustrated in Figure 2 are plotted in Figure 4, along with the predicted results of the macro-scale and local-scale equilibrium models. The results of the macro-scale model over-predict the observed concentrations by nearly an order of magnitude during the first few minutes of the experiment. The macro-scale equilibrium model predicts that by 5 minutes, all of the toluene will have been removed from the system. The vast difference between the predicted and observed remediation times is due to the assumed saturated equilibrium concentration of the effluent gas in the macro-scale model. However, because the toluene lies in the stagnant low-permeability zone, the airflow actually carries only a small fraction of the toluene vapor. This behavior is more accurately captured in the local-scale equilibrium model, which approximately predicts the tailing and long-term behavior of the system.

These results indicate that mass transfer limitations and equilibrium assumptions are scale-dependent. The assumption of local-scale equilibrium may be adequate if the resolution of the model is sufficient to capture the salient processes. In this case study, the processes included diffusion through the stagnant low-permeability zone and the development of a concentration boundary layer. The size of the control

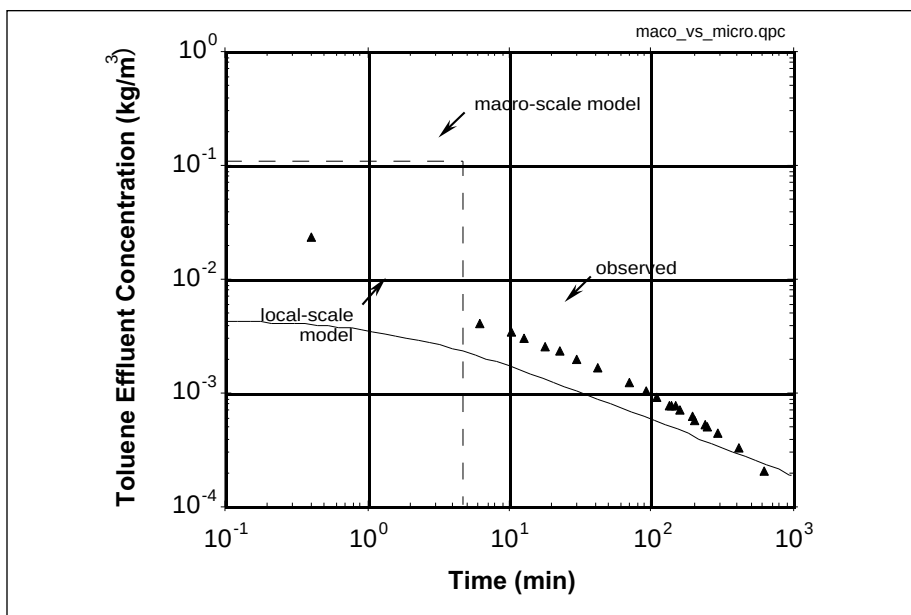


Figure 2. Air venting of toluene in a heterogeneous configuration consisting of sand filled halfway up the test cell so that air flows preferentially in the air space above. The outlines depict the shape of the toluene pool as a function of time (Ho and Udell, 1992).

volume used in the local-scale equilibrium model was small enough to represent these processes. In contrast, if the model cannot be refined to yield control volume sizes that capture important transport processes, then mass transfer limitations will have to be captured through analytical or empirical mass transfer coefficients and other phenomenological methods.

ACKNOWLEDGEMENTS

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PASSIVE SOIL VAPOR EXTRACTION AT THE SRS MISCELLANEOUS CHEMICAL BASIN

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A passive soil vapor extraction (PSVE) has been occurring since September 1996 in the interbedded sands, silts, and clays underlying the Miscellaneous Chemical Basin at the Savannah River Site (SRS). During this time, more than 200 pounds of chlorinated organic contaminants (166 lbs of TCE and 66 lbs of PCE) have been removed by natural barometric pumping of 25 wells fitted with low-pressure check valves (BaroBall® valves). According to contour maps of samples obtained from monitoring wells, the extent of the gas plume has decreased significantly over the past 2 years (Figure 1). Records from the recovery wells show that the concentration of recovered gases has decreased exponentially with time. Extrapolation of this trend indicates that using PSVE alone, concentrations at a majority of the wells will be less than 10 ppmv in approximately 3 years, and less than 1 ppmv in approximately 10 years.

Mass removal during this time frame is attributed to recovery by air flowing through coarse-grained sediments. Some of the recovered contaminants were originally in the coarse-grained sediments, whereas others diffused from fine-grained interbeds to the coarse-grained sediments, where they were advected by flowing air. Removal from the fine-grained sediments will be limited by the mass transfer rate to the coarse-grained beds.

PSVE requires minimal operation and maintenance. Sampling and analysis of well vapor requires approximately 8 hours per month. For this study, characterization and well installations were performed in three weeks at 25 locations using cone penetrometer technology, at a cost of approximately \$60,000. The characterization included continuous geologic profiles through the entire vadose zone (95 ft depth), depth-discrete gas sampling for volatile organic contaminants, and sediment samples.

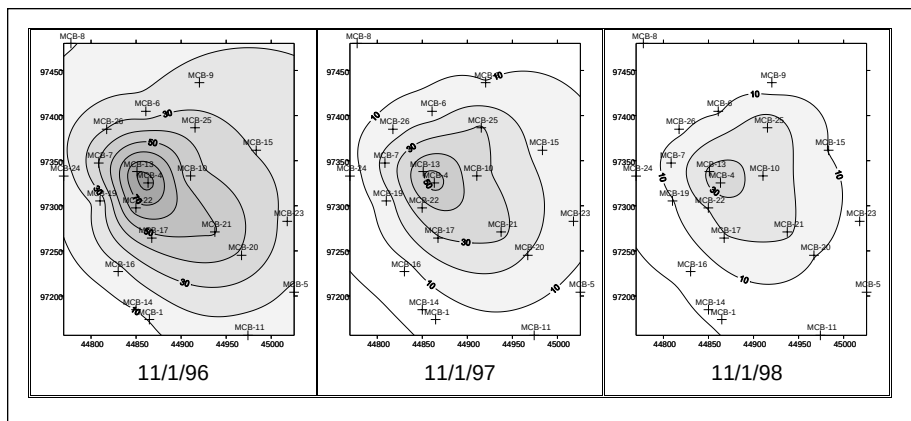


Figure 1. Concentration (ppmv) of TCE in PSVE wells as a function of time at the Miscellaneous Chemical Basin, Savannah River Site.



CASE HISTORY: PCB DESTRUCTION AND REMOVAL

John Reed and Denis Conley, TerraTherm

A demonstration of the ISTD process was conducted at the Missouri Electric Works Superfund Site, Cape Girardeau, MO to evaluate the destruction and removal efficiency (DRE) of PCBs (Vinegar *et al.* 1998). This demonstration is particularly significant because PCBs have resisted *in situ* remediation using conventional methods. Scientists from USEPA National Program Chemicals Division participated in the evaluation.

SAMPLING AND MONITORING

Forty soil samples were collected from boreholes at depths of up to 16 feet and analyzed for PCBs by a certified laboratory. The arithmetic mean of the 40 samples was used to determine the average concentration in the entire volume of contaminated soil. Concentration decreased with depth, so subsets of the samples were used to determine the average concentration in different depth intervals prior to treatment. After remediation, another 40 samples were taken from similar locations and analyzed to determine the average concentrations remaining in the soil.

A stack test for PCBs and breakdown products was conducted during 28 hours of the Thermal Well system operation. Stack sampling for PCBs, polychlorinated dibenzo dioxins (PCDDs), and polychlorinated dibenzo furans (PCDFs) was conducted by an independent contractor in accordance with EPA Method 5. Stack sample analyses were conducted by a certified off-site laboratory as prescribed by EPA Method 23 for PCDDs/PCDFs, and modified EPA Method 680 for PCB homologues.

RESULTS

The average concentration of PCBs in the upper 4 feet of soil was 4,600 mg/kg, and the maximum concentration was 19,900 mg/kg before remediation. The concentrations in all of the samples taken from this depth interval after treatment were less than 0.033 mg/kg, which is the detection limit for the analytical procedure. Therefore, nearly all of the PCBs appear to have been either removed or destroyed during remediation.

Based on a mean PCB concentration of 4,600 mg/kg, a soil density of 43.2 kg/ft³, and a treated soil volume of 200 ft³, the mass of PCBs treated was determined to be at least 40 kilograms (kg).

The total mass of PCBs detected in the stack sample by EPA Method 680 was 400 nanograms (ng). The volume of effluent collected for analysis during the test was 24.5 cubic meters (m³). The air flow determined by EPA Method 2C within the stack during sampling was 123 standard cubic feet per minute (scfm). With these values, the total mass of PCBs emitted during the 42-day demonstration was calculated to be 0.00343 grams.

The destruction and removal efficiency for the overall process was calculated as the difference between the initial mass in place (40,000 grams) and the mass released to the atmosphere (0.00343 grams) divided by the initial mass. This indicates that 99.999998 percent of the PCBs initially in the soil at the Cape Girardeau site were either destroyed *in situ* or recovered and destroyed above ground during the remediation process.

OTHER CASES

Additional projects using conductive heating implemented in the ISTD process have been completed in Indiana, Oregon, California, and on the Island of Saipan. A variety of contaminants have been remediated at those sites, including volatile and semi-volatile organic compounds and PAHs. These have occurred in sediments ranging from sand to silty clay. The initial and final average concentrations for each of the contaminants are summarized in Table 1.

TABLE 1

**Average concentrations of contaminants in soil before and after
in situ remediation using conductive heating and SVE in the ISTD process.**

Contaminant	Average Initial Concentration	Average Final Concentration	Matrix
Octachlorodibenzo-p-dioxin	6.9 ppb	0.014 ppb	Silty Clay
Chlordane	41 ppb	<0.033 ppb	Sandy Silt
4,4'-DDT	3,500 ppb	<0.033 ppb	Sandy Silt
Lindane	476 ppb	<0.066 ppb	Sandy Silt
4,4'-DDE	920 ppb	<0.033 ppb	Sandy Silt
4,4'-DDD	510 ppb	<0.033 ppb	Sandy Silt
PCB 1260 *	20,000 ppm	< 0.300 ppm	Clay
PCB 1248 *	5,200 ppm	< 0.950 ppm	Sand
1,1-DCE *	650 ppb	< 0.53 ppb	Clay
TCE *	79 ppm	<0.500 ppm	Clay
PCE *	3,500 ppm	<0.500 ppm	Clay
Diesel *	9,300 ppm	<100.000 ppm	Silt
Naphthalene	18,000 ppm	<0.033 ppm	Coal Tar
Acenaphthylene	1,300 ppm	<0.033 ppm	Coal Tar
Acenaphthene	750 ppm	<0.083 ppm	Coal Tar
Fluorene	3,200 ppm	<0.083 ppm	Coal Tar
Phenanthrene	7,600 ppm	<0.033 ppm	Coal Tar
Anthracene	2,100 ppm	<0.033 ppm	Coal Tar
Fluoranthene	4,500 ppm	0.091 ppm	Coal Tar
Pyrene	3,700 ppm	0.160 ppm	Coal Tar
Dibenzofuran	15 ppm	<0.033 ppm	Sandy Silt
Chrysene	1,300 ppm	0.200 ppm	Coal Tar
Benzo (a) anthracene	1,000 ppm	0.130 ppm	Coal Tar
Benzo (b) fluoranthene	960 ppm	0.410 ppm	Coal Tar
Benzo (k) fluoranthene	390 ppm	0.140 ppm	Coal Tar
Benzo (a) pyrene	1,100 ppm	0.360 ppm	Coal Tar
Dibenzo (a,h) anthracene	44 ppm	<0.033 ppm	Coal Tar
Benzo (g,h,i) perylene	690 ppm	0.570 ppm	Coal Tar
Indeno (1,2,3-cd) pyrene	400 ppm	0.380 ppm	Coal Tar
1-Methylnaphthalene	2,700 ppm	<0.066 ppm	Coal Tar
2-Methylnaphthalene	8,000 ppm	<0.066 ppm	Coal Tar

* field results

< indicates contaminant present at less than detection limit of analytical instrument

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A CASE STUDY OF STEAM FLOODING: THE VISALIA PROJECT

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Craig Eaker, Randall Weidner, and Terry Sciarotta, *Southern California Edison Co.*

Southern California Edison's Visalia Pole Yard site (Figure 1) was designated a Superfund site in 1987, and currently contains dense nonaqueous phase liquid (DNAPL) product composed of pole-treating chemicals (primarily creosote and pentachlorophenol) and an oil-based carrier fluid. Bioremediation of the free-organic liquids is expected to be prohibitively slow; enhanced bioremediation was predicted to take 120 years. Thermal treatment via steam injection with vacuum extraction, similar to that used in the Lawrence Livermore (LLNL) demonstration (Newmark 1994, Newmark *et al.* 1997), was chosen for removal of the free product contaminant. The overall objectives of the thermal remediation of the Visalia Pole Yard are to (1) remove a substantial portion of the DNAPL contaminant at the site (thereby enhancing the bioremediation of remaining contaminant), (2) significantly shorten the time to site closure, and (3) improve the accuracy of the time-to-closure prediction.

As part of the final removal process, the Southern California Edison Company (Edison) is testing hydrous pyrolysis (HPO), an experimental *in situ* method of destroy-

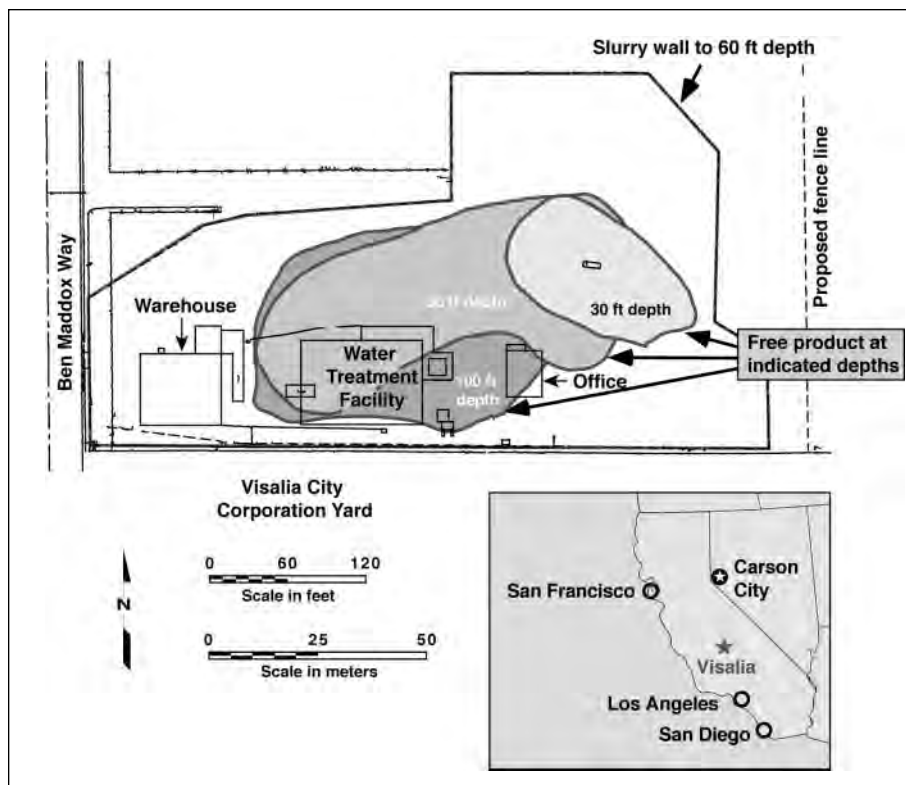


Figure 1. Site map, showing the location of the Visalia Pole Yard. Contours indicate the lateral extent of free product contamination at depth (Geraghty and Miller 1993; Weidner, personal communication).

ing organic contaminants using small amounts of supplemental air or oxygen (Knauss *et al.* 1998). By introducing both heat and oxygen, this process has destroyed petroleum and solvent contaminants in laboratory experiments (Knauss *et al.* 1997, 1998a, b; Leif *et al.* 1997a, b, 1998a). The primary use of the HPO method at this site could be for destruction of residual pentachlorophenol, which will not readily steam-strip due to high solubility and low vapor pressure.

Bioremediation is an important final step in soil and groundwater cleanups because the microorganisms destroy residual contaminants missed during the initial cleanup process. In 1994, the LLNL researchers discovered an unexpected benefit of steam flooding: it may encourage bioremediation (Newmark *et al.* 1994). Heating the soil at a gasoline spill site to temperatures above 100°C was expected to sterilize it, with the micro-organisms that use petroleum products as food expected to return slowly as the soil cooled. But soil samples taken soon after the cleanup was completed

revealed large numbers of microbes that thrive in high temperatures (known as thermophiles), apparently because predators and competition had been eliminated.

OPERATIONS

The operational plan was to remove as much of the free-product pole-treating compounds as possible by steam injection/vacuum extraction. It is estimated that between 40,000 and 80,000 gallons of pole-treating chemicals are in the soil.

During the first six weeks of thermal remediation operations, between June and August 1997, approximately 300,000 pounds (135 metric tons) of contaminant were either removed or believed to have been destroyed in place, a rate of about 46,000 pounds (22 metric tons) per week. For nearly 20 years, Edison has been removing contaminant from the subsurface using the standard pump-and-treat cleanup method, most recently at a rate of just 10 pounds (0.03 metric ton) per week. By comparison, the amount of hydrocarbons removed or destroyed in the six weeks of thermal remediation operations at the Visalia Pole Yard was equivalent to 600 years of pump-and-treat methods, or about 5,000 times the previous removal rate. LLNL scientists performed field tests to help verify the presence of hydrous pyrolysis/oxidation in the field, and to validate predictive models and monitoring strategies (Newmark *et al.* 1999). The results of field experiments help constrain the apparent destruction rates throughout the site, and allow estimates of total *in situ* destruction based on the recovered carbon dioxide.

Substantial contaminant reduction was achieved in the vadose zone during thermal remediation operations, which were primarily focused on the underlying saturated soils. At the Visalia Pole Yard, there is dense, non-aqueous phase liquid (DNAPL) contamination in three distinct water-bearing zones (Figure 1) (Geraghty and Miller 1992). During initial site characterization, contaminant concentrations indicated that DNAPL had first settled along an aquitard at a depth of about 60 feet. A slurry wall built around the site in the 1980s was designed to surround this area of high concentration (Geraghty and Miller 1992). The shallowest contamination (above 35 feet in depth), was not directly targeted for thermal methods, as bioremediation efforts were already active in the oxygenated shallow sediments. Since the shallow vadose zone was not considered a hazard to groundwater, bioremediation was deemed adequate to address this part of the site. The most important ground water resource is found in the deep aquifer, below about 120 feet. The thermal remediation system was designed to remove contaminant from the intermediate and shallow aquifers without disturbing the deep aquifer, which is a source of drinking water.

Prior to thermal treatment, a cone penetrometer survey verified the presence of contaminants in both the shallow vadose zone (above 60 ft) and in deeper units. This was supported by historical soil sampling in the area. In May of 1998, limited sampling was performed on a boring drilled in the vicinity of one of the cone penetrom-

eter pushes. The results indicate substantial contaminant reduction in the shallow vadose zone, despite the fact that steam operations had not yet been focused above the water table (Figure 2). Since then, limited steam injection has been conducted into the lower vadose zone to more uniformly heat the shallow aquifers and mobilize contaminant residing there.

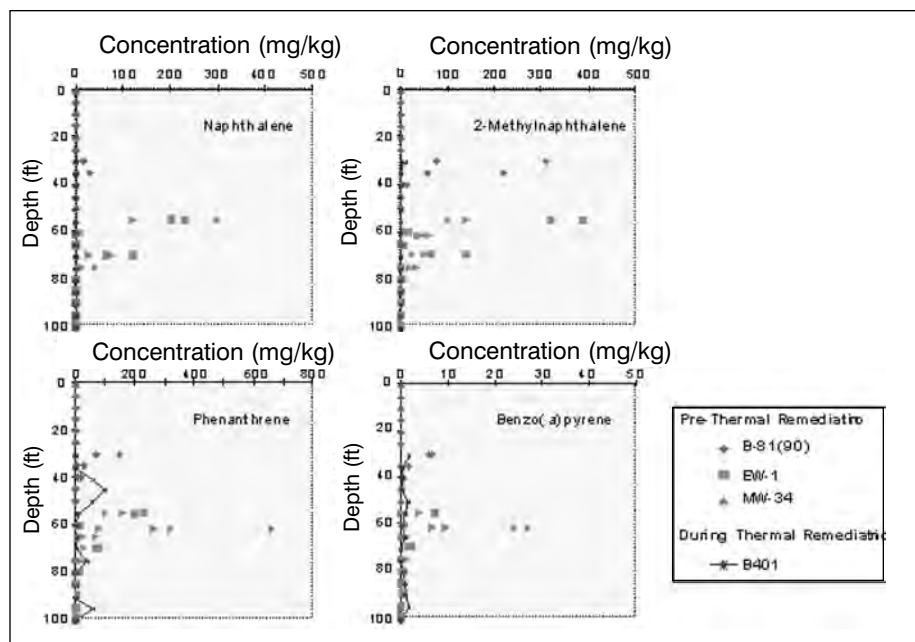


Figure 2. Soil concentrations measured in samples obtained in the treatment zone (above 100 ft) prior to thermal remediation (solid symbols) indicate substantial contamination, particularly in the 25-80 ft zone. Samples obtained in May 1998 (crosses with connecting lines) show substantial contaminant reduction. Water table is at 60 ft.

Edison achieved full initial heating of the Visalia site by the end of July, 1997 (approximately 500,000 cubic yards at a temperature of 100° C or above), including uniform heating of both aquifer and aquitard materials (Figure 3). At this point, about 20,000 gallons of free-product liquid had been removed. Vapor and water streams continued to be saturated with product. Continued destruction of the contaminant was inferred from high levels of carbon dioxide (0.08 - 0.12% by volume) removed through vapor extraction. Initial destruction, estimated from the carbon dioxide levels, was equivalent to about 300 pounds of contaminant per day. At this point, Edison adopted a "huff-and-puff" mode of operation, where steam is injected for about

a week, and then injection ceases for about a week while extraction continues. Maximum contaminant removal is obtained during this steam-off period, as the formation fluids flash to steam under an applied vacuum. In September 1997, Edison began providing supplemental oxygen as compressed air into the peripheral wells, along with steam injection. Increased carbon dioxide concentrations in the offgas suggested increased destruction rates of 800 pounds per day (Figure 4). As of October, 1998, over 900,000 lbs of contaminant were either removed, or believed to have been destroyed.

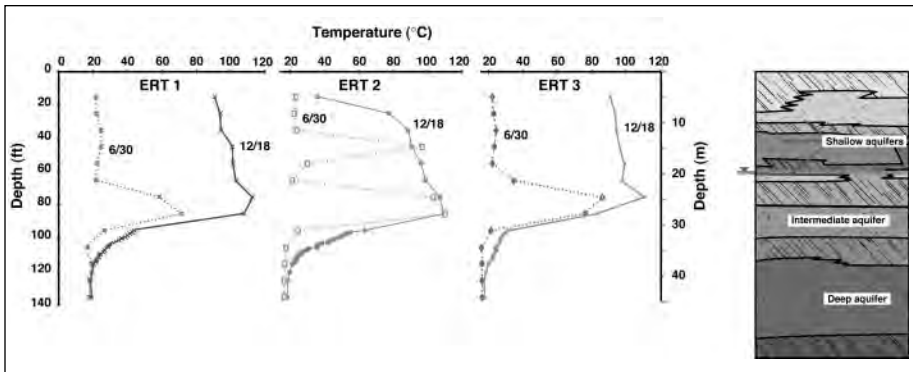


Figure 3. Temperature profiles in ERT-3 show uniform heating of the soil column from 95 ft to the surface.

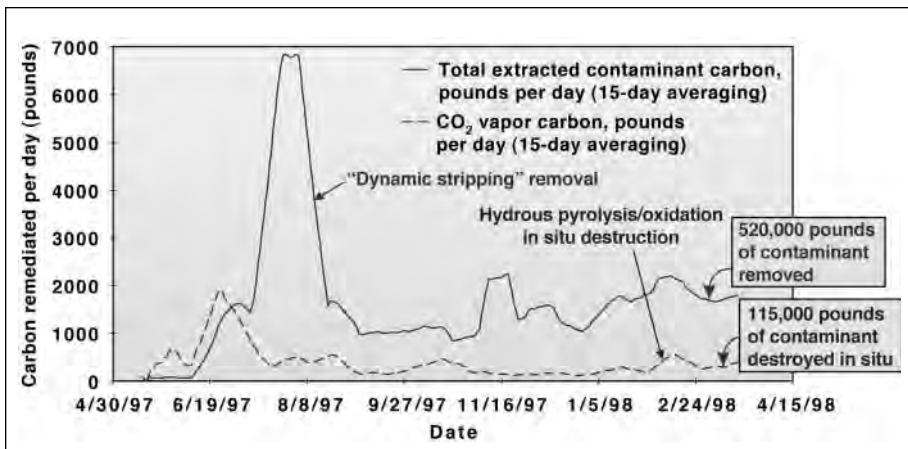


Figure 4. Visalia recovery, May 1997-May 1998. Contaminant removed is determined from total free-product recovery, vapor and groundwater concentration(s) and flux rates. HPO destruction estimated from extracted carbon dioxide in excess of geochemical balance (inflow-outflow).

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VADOSE ZONE REMEDIATION USING SIX-PHASE HEATING

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Six-Phase Heating (SPH) was first demonstrated at a Department of Energy (DOE) site in 1993 for heating low-permeability soils containing volatile organic contaminants in the vadose zone. Testing was performed over a 25-day period as part of the Volatile Organic Compounds in Non-Arid Soils Integrated Demonstration (VOC Non-Arid ID) at the Savannah River Site. The soil at the integrated demonstration site is contaminated with perchloroethylene (PCE) and trichloroethylene (TCE). The highest soil contamination occurred in a 10-foot-thick clay lens with an extremely low hydraulic conductivity of 10^{-12} cm/sec. Figure 1 shows the dimensions of the single SPH array that was used, as well as where the heated zone was located with respect to the site lithography. Figure 2 is a plot of soil temperatures showing that the clay zone (containing higher moisture content and residual chloride ions) was heated preferentially, followed by heating in the sand above and below the clay a few days later.

The demonstration sought to heat the clay zone and enhance the performance of conventional soil vapor extraction. Thermocouples at thirty locations quantified the areal and vertical heating within the treated zone. Soil samples were collected before and

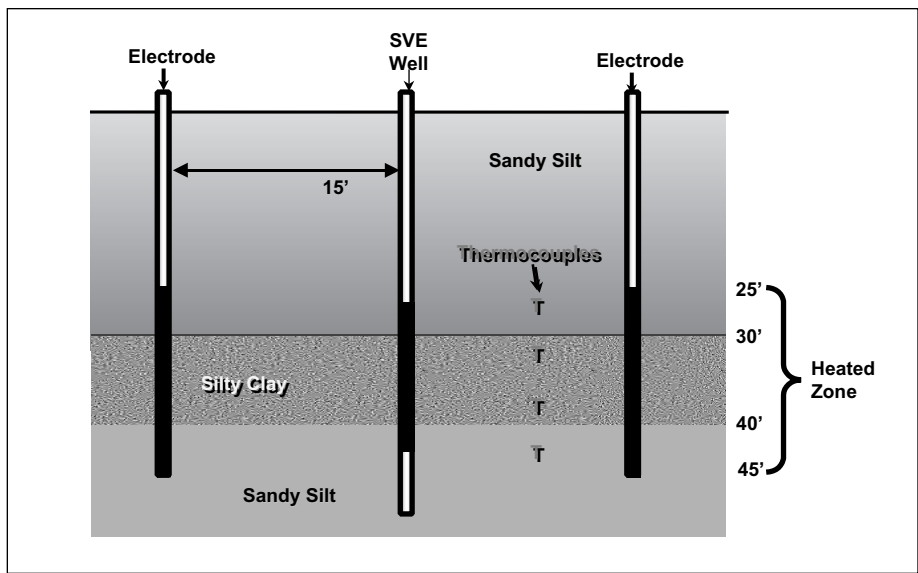


Figure 1. Site cross-section at Savannah River.

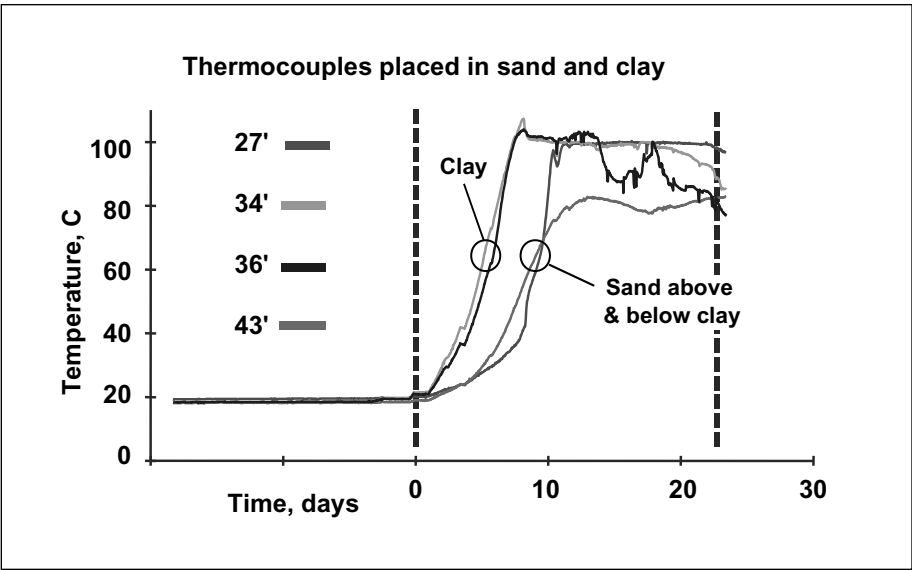


Figure 2. Heating rates and temperatures in clay and soil layers.

after heating to quantify the efficacy of heat-enhanced vapor extraction of PCE and TCE from the clay soil. Samples were taken (approximately every foot) from six wells prior to heating, and adjacent to these wells after heating. Contaminant levels in soil samples obtained before and after remediation are shown in Figure 3.

One objective of the demonstration was to evaluate the effect of soil heating on increasing the permeability of the soil by: pressure induced fracturing, desiccation fracturing, or, simply, by drying the soil (reducing the pore volume of water). The permeability of the vented soil can be determined from the flow of air and steam into the vent and the pressure at the vent. The steam flow was estimated from the rate of condensate collection, assuming an ideal gas; the air flow was measured by two specially designed orifice meters. During the heating phase, the majority of gas flow from the vent was steam. Determining the permeability of the soil is complicated because the steam is generated within the soil. However, the change in permeability can be determined qualitatively by calculating the ratio of total flow over an appropriate pressure drop. Figure 4 shows this ratio with the pressure drop appropriate for compressible gas flow (Dullien 1992). Clearly, the permeability increased during the demonstration. Because the permeability of the soil increased due to soil drying, the mass rate of contaminant removal increased, even though the offgas concentration varied little. In particular, the removal rate of PCE increased by a factor of 3 from an initial rate of about 5 g/min to a final rate of 15 g/min.

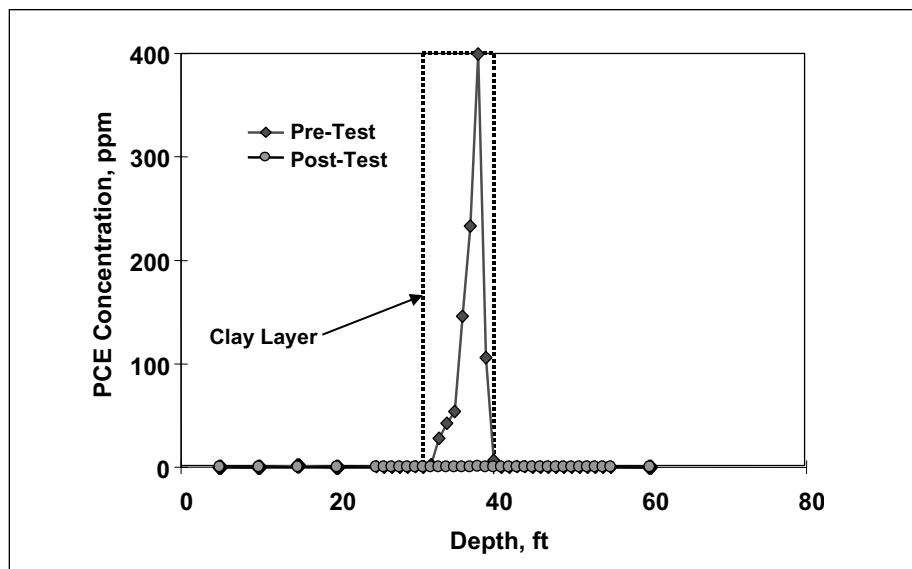


Figure 3. Contamination levels in soil samples before and after remediation.

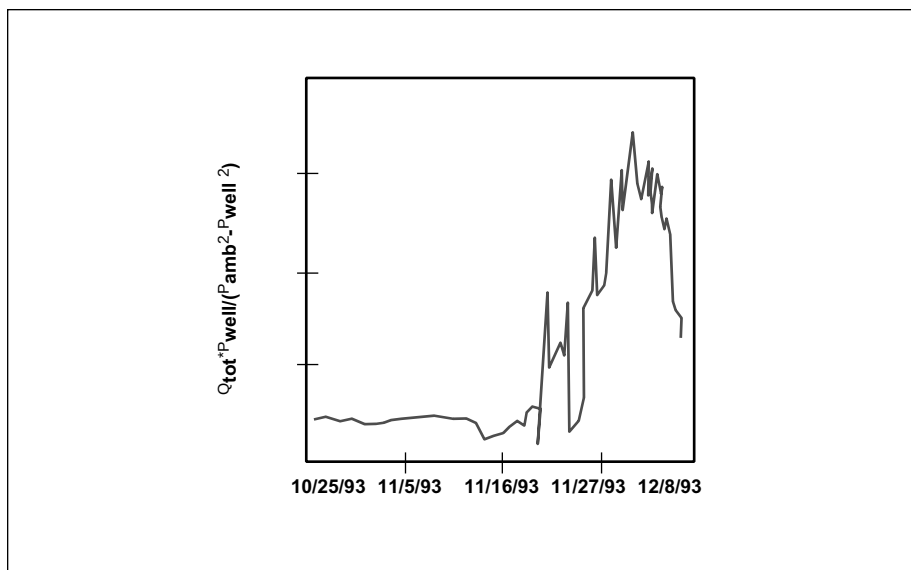


Figure 4. Effect of heating and drying on the permeability of the vented soil.

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CASE HISTORY OF LIQUID OXIDANT INJECTION INTO THE VADOSE ZONE

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In situ treatment of contaminants in the vadose zone can be accomplished using vertical lances to inject treatment agents such as chemical oxidants, reductants, or bionutrients. This approach is possible to depths of 50 meters or more, particularly if small hot spots are to be treated. However, this method is practically constrained to shallower depths if the area to be treated is larger (for example, hectares). A field trial was initiated to demonstrate permeation dispersal of reactive fluids in a shallow, silty clay vadose zone. This test was completed by Oak Ridge National Laboratory (ORNL) in collaboration with Hayward Baker Environmental, Inc. (HBE) at the DOE Portsmouth Gaseous Diffusion Plant in central Ohio. Supporting experimentation and modeling were conducted at ORNL and the Colorado School of Mines (CSM).

SETTING

At the DOE Portsmouth Plant, *in situ* remediation technologies were being evaluated to determine their viability for full-scale application at the plant (Siegrist *et al.* 1995; Siegrist *et al.* 1999). As part of this program of evaluation, a test area was established in an uncontaminated, but representative location near several contaminated land treatment units (Figure 1). The use of a clean test site was deemed appropriate to permit controlled hydrodynamic and biogeochemical studies of subsurface manipulation methods without the health and safety, waste management, and environmental concerns associated with a contaminated site. The test area was 5 hectares in size and underlain by a silty clay fluvio-lacustrine deposit from ground surface to a depth of 8 meters (Minford member). The bulk permeability of this silty clay deposit was $\sim 10^{-7}$ to 10^{-5} cm s⁻¹, although a fine platy structure with cross-cutting fractures provided preferential transport pathways that permitted vertical migration of contaminants released during land treatment of wastes. The air-filled porosity was estimated at 5 percent v/v due to a zone of groundwater saturation at a depth of 3 to 4 meters. Underlying the Minford is a moderately permeable sand

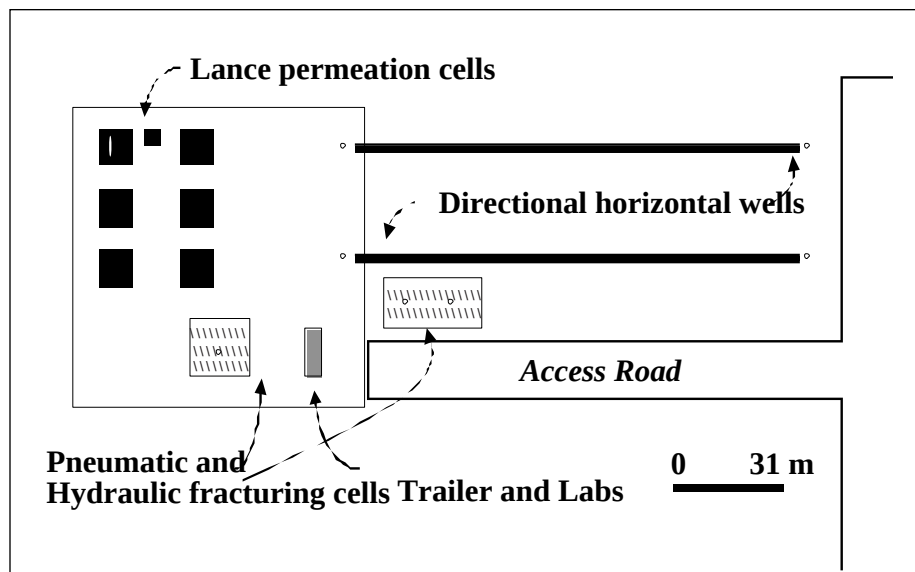


Figure 1. Field test area used for permeation trials (other demonstration plots are also shown).

known as the Gallia member, which consists of pebbles and gravel in a fine-grained silty-sand matrix that is 1 to 2.5 meters thick. Precipitation percolates through the Minford member to a zone of permanent saturation at a depth of about 4 meters, and it eventually reaches the Gallia member, where flow is predominantly horizontal. Subsurface features of the test area were representative of several contaminated land treatment sites at the plant. Previous characterization activities at these sites revealed total volatile organic compounds (VOCs) in soil (predominantly trichloroethylene [TCE]), ranging to as much as 300 mg/kg, whereas ground water at the site contained variable concentrations of TCE, including some dense nonaqueous phase liquids (DNAPLs).

REMEDICATION APPROACH

The goal of field testing activities was to explore the potential for rapid but relatively non-disruptive injection and dispersal of treatment fluids into and throughout the shallow vadose zone to achieve *in situ* treatment of organic and metal contaminants by physiochemical or biological processes. If successful, this permeation technology could enable rapid and extensive treatment in source areas and plumes associated with land treatment sites, impoundments, and tank and transfer line areas. A multi-point injection technology developed by HBE was chosen as the best available technology based on its relative simplicity and low cost, as well as its potential for effective performance.

The field trial included injections of different agents into seven unconfined test cells (six cells were 60 m² by 4 m deep and one was 3 m² by 4-m deep) (Fig. 1, Table 1) (Siegrist *et al.* 1999). The following agents were selected to achieve the stated purposes: (1) tracers to evaluate uniformity of delivery; (2) an alkaline slurry to increase soil pH and immobilize metals; (3) KMnO₄ and H₂O₂ to oxidatively degrade organics; (4) zero valent iron metal to reductively degrade chlorinated solvents; (5) bionutrients to stimulate indigenous microbes and enable bioremediation of organics; and (6) compressed air to increase pneumatic permeability and facilitate soil vapor extraction. The agents were injected at a volumetric loading rate in the range of 5 percent v/v and at pressures of 2 to 5 atm using a four-lance, vertical injector system (Figure 2). Injections were made on a 60-cm horizontal spacing to a depth of 3.2 meters. Each test cell was injected with either (1) a mixture of solute and colloidal tracers (that is, bromide- and ice-nucleating bacteria), (2) hydrogen peroxide (~7 percent by weight), (3) potassium permanganate (~4 percent by weight), (4) calcium hydroxide (~12 percent by weight), (5) bionutrients, (6) colloidal iron (~10 percent by weight), or (7) compressed air (~17 m³ min⁻¹). The operation of the dispersal system was monitored and the effects of the injected reagents on subsurface biogeochemical characteristics were monitored through analyses of pre- and post-treatment soil cores and solution samples. The injections were completed during the Fall of 1994, and monitoring of test cell characteristics was conducted for several years thereafter.

Monitoring devices included vadoze zone sensors for temperature and water content, suction lysimeters for soil pore water composition, and observation wells for monitoring water quality in the underlying saturated zone beneath each cell (Figure 3). Soil core samples were collected before and after and analyzed for pH, Eh, temperature, water content, organic carbon content, and elemental composition. (Figure 4). Microbial analyses were also conducted in the bionutrient cell and tracer cell.

To evaluate the permeation dispersal of KMnO₄ and H₂O₂ to destroy trichloroethylene (TCE) in the silty clay soil, laboratory-scale experiments were conducted at CSM using intact soil cores recovered from the test area (Urynowicz and Siegrist 1999). The soil cores were collected in a manner that did not alter the preferential pathways vital to hydrogeologic processes. They were transported to the pilot laboratory at CSM, where each was setup with a tension plate and porous polyethylene permeation tube, instrumented with soil moisture tensiometers, Eh electrodes, an Eh reference electrode, and encased with an ethyl vinyl acetate/paraffin wax thermoplastic (see Figures 5 and 6). The intact core study had four distinct phases: (1) a bromide tracer study to determine the hydrologic properties of the media; (2) contamination of each core with TCE dyed red with 1 ppm Sudan IV (a nonvolatile dye which does not visibly partition from TCE to the water phase); (3) lance injection of cores M1 and M2 with approximately one air-filled pore volume (~1000 mL)

TABLE 1**Summary of injection system operations for each test cell.**

Characteristic	Tracer (T1)	Lime (T2)	Peroxide (T3)	Permang. (T4)	Biotreat (T5)	Air (T6)	Iron (T7)
Cell area (ft ²)	24 x 24	24 x 24	24 x 24	24 x 24	24 x 24	24 x 24	8 x 8
Cell depth (ft)	10.4	10.4	10.4	10.4	10.4	10.4	10.4
Injection date	Nov. 12	Nov. 13	Nov. 15	Nov. 16	Nov. 18	Nov. 19	Nov. 19
Injection start time	13:54	11:21	09:50	13:50	13:35		
Injection end time	17:46	16:04	13:09	17:35	17:39		
Injection time (min)	232	283	199	225	245		
Injection vol. (gal)	2,870	2,330	2,420	2,260	2,220	~5,520 cf	310
Loading rate (v/v)	0.064	0.052	0.054	0.050	0.050	-0.90	0.47
Injection passes	1	1	1	1	1	1	1
Injector spacing (ft.)	2	2	2	2	2	12	2
Injector setups	36	36	36	36	36	4	4
Time/setup (min)	4-5	4-5	4-5	4-5	4-5	1	4-5
Interval volume (gal)	2.5	2.0	2.0	2.0	2.0	N/A	
Setup volume (gal)	79	64	68	62	64	1,380 cf	77
Injector Q (gpm)	4-5	4	4	4	8	~10 cfs	
Injector P (psig)	40-100	40-100	40-100	40-100	40-100	100-120	40-100
Batch size (gal)	6 @ 500	5 @ 500	Bulk tank	5 @ 500	2 @ 1000 1 @ 500	Air comp.	1 @ 500

Batch makeup:

Tapwater (gal)	500	500	—	500	—	—	500
KBr (kg)	0.72	—	—	—	0.42	—	—
Snomax (kg)	0.27	—	—	—	0.22	—	—
Lime (lb)	—	500	—	—	—	—	—
H ₂ O ₂ (~10%; gal)	—	—	Bulk	—	—	—	—
KMnO ₄ (~4%; kg)	—	—	—	~100	—	—	—
Biotreat (~5%; gal)	—	—	—	—	500	—	—
Air (600 cfm)	—	—	—	—	—	Air comp.	—
Iron (5 um; lb)	—	—	—	—	—	—	400
Guar gum (lb)	—	—	—	—	—	—	25



Figure 2. The HBE multipoint injection system during field trials at the DOE Portsmouth Plant.



Figure 3. Monitoring vadose zone sensors and lysimeters in the zero valent iron cell.

of 10,000 ppm KMnO_4 and 30,000 ppm H_2O_2 solutions, respectively (note that M3 remained untreated for the purpose of experimental control); and (4) core dismantling and sampling to compare treatment efficiencies and evaluate the media-specific geochemical effects of each reagent.

RESULTS AND DISCUSSION

During the field trial, all reagents were successfully delivered with commercially available equipment to a total depth of approximately 4 meters below ground surface. The effects on the vadose zone varied with the different agents, due to differ-



Figure 4. Intact soil core collected from the permanganate cell illustrating presence of oxidant (redox along the entire core length was elevated above 800 mv).



Figure 5. Intact core collected from the shallow vadose zone by perimeter carving and wax encapsulation.



Figure 6. Intact cores established in the laboratory at CSM on porous tension plates and instrumented with moisture and redox sensors.

ences in their reactivities as well as their amenability to permeation away from the point of injection from the lance. An illustration of this is shown in Figure 7, which depicts the redox potential with depth in each cell. The effects of the oxidants are clear, with permanganate having a greater effect than the peroxide. The H_2O_2 reacted rapidly and degraded within a few days to 2 weeks. The KMnO_4 appeared to react more mildly, permeate further, and persist for several months. $\text{Ca}(\text{OH})_2$ injection effectively elevated the soil and ground water pH to over 10 and this was sustained over 12 months. Lysimeter water sample results showed a slight pH decrease and a significant increase in manganese concentrations. Manganese concentrations remained elevated for approximately 5 weeks.

During the field-scale tests, soil sample total organic carbon (TOC) concentrations showed a significant decrease within the first 2 feet of ground surface as a result of peroxide injection; however, little or no change was observed at greater depths. Peroxide injection also increased dissolved oxygen (DO) concentration in lysimeter water samples. Post-injection field test soil sample results for KMnO_4 indicated a dramatic increase in Eh throughout the entire soil profile. Lysimeter water sample

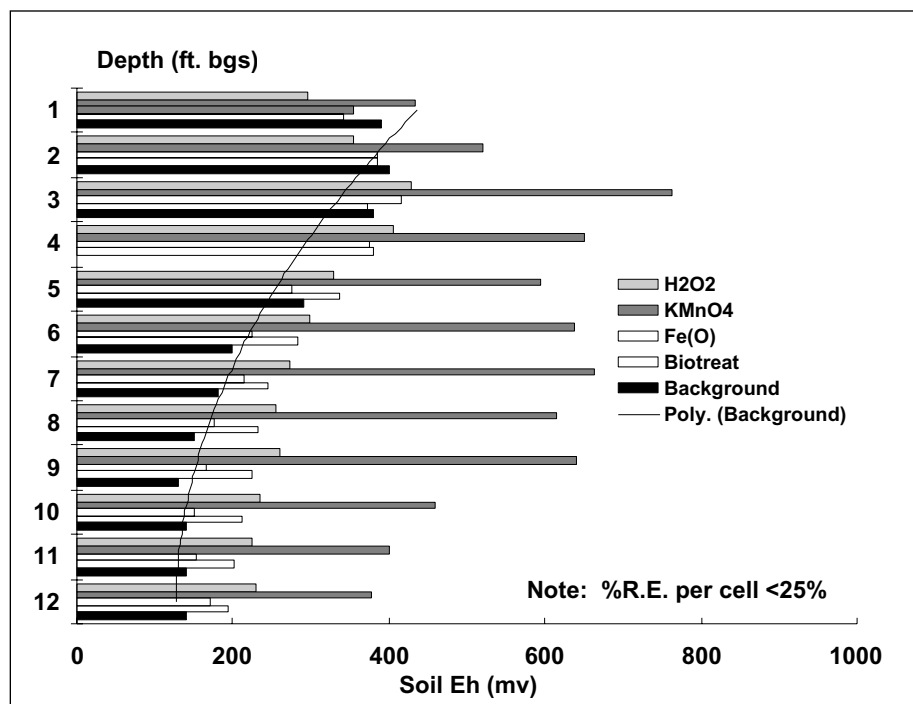


Figure 7. Redox potential changes within two months of permeation of dispersal of different treatment agents in a silty clay vadose zone.

results showed a slight pH decrease and a significant increase in manganese concentrations. Manganese concentrations remained elevated for approximately 5 weeks.

During the post-experimental sampling and characterization phase of the laboratory study, manganese dioxide solids [$\text{MnO}_2(\text{s})$] deposition was observed on soil surfaces adjacent to major preferential pathways such as the top of the monolith, the injector borehole, and large fractures. Permeation dispersal of H_2O_2 within M2 appeared to be more limited. Visual evidence of soil pore alteration was only observed on soil surfaces adjacent to the top of the core and injector borehole. Migration of H_2O_2 along large fractures does not appear to have occurred. Extreme TCE and Cl^- residual variability was observed in each core. Based on the sample volume (~ 1 mL) and frequency (168 discrete samples and 21 composite samples), it appears that core heterogeneity was on the order of millimeters or less.

Although approximately 2,628 mg of TCE was injected into cores M1 and M2 during the contamination phase, the post treatment mass balances accounted for less than 20 percent of the total TCE. It appears that core heterogeneity led to a biased low measure of TCE and Cl^- residual. Treatment efficiencies were determined based on monolith effluent and residual TCE and Cl^- concentrations assuming 70 percent of the TCE degraded by KMnO_4 and H_2O_2 was converted to chloride ions. The treatment efficiencies were between 67.6 and 83.6 percent and 60.6 and 75.7 percent for M1 (KMnO_4) and M2 (H_2O_2), respectively. The treatment efficiency range for each monolith was the result of discrete and composite data discrepancies.

CONCLUSIONS

The results of the field trial and laboratory core studies indicate that volumes of different treatment agents can be introduced into a relatively low permeability deposit and can dramatically impact subsurface properties (for example, raising Eh to >800 mV or elevating pH to >10). While pronounced effects were observed in the test cells, there was substantial short-range spatial variability in the effects on biogeochemical properties. This variability is believed to be due to the injected agents following existing preferential pathways in the subsurface and then, depending on fluid reactivity, their permeation to varying degrees into the finer pore and matrix structure. The nature and extent of the biogeochemical changes observed suggested that permeation dispersal could facilitate the transformation and degradation/immobilization of many contaminants, despite their presence in low permeability media. However, questions remain regarding the uniformity of distribution that can be achieved as a function of subsurface characteristics, fluid properties, dispersal system operation, the mobility and risk of any untreated contaminants, and the risk-reduction requirements for uniformity of dispersal and effect in order to ensure adequate *in situ* treatment effectiveness. These questions are still under study

through further field testing by ORNL and through supplementary controlled laboratory studies at CSM.

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VADOSE ZONE *IN SITU* OZONATION OF POLYCYCLIC AROMATIC HYDROCARBONS AND PENTACHLOROPHENOL

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The largest and most intensively monitored field-scale application of *in situ* ozonation conducted to date was performed at a former wood treatment and cooling tower manufacturing facility, located in Sonoma County, California. Primary contaminants are pentachlorophenol (PCP) and creosote (that is, polycyclic aromatic hydrocarbons [PAHs]). The site subsurface consists of stratified silty sands and clays, and the depth to water varies from 4 to 15 feet seasonally. Field operation and monitoring of the *in situ* ozonation system was conducted from December 1997 through December 1998.

Maximum pretreatment soil contamination was 220 mg/kg PCP and 5,680 mg/kg total PAHs. High levels of dissolved contamination and non-aqueous phase liquid (NAPL) existed in the vadose zone prior to treatment. For example, one lysimeter produced liquid NAPL and water which contained >20,000 ug/l total dissolved PCP and PAH.

TREATABILITY TEST WORK

A laboratory treatability study was performed using site aquifer materials. The primary objective of this test was to assess the ability of ozone addition to destroy PCP and PAHs in impacted soils from the site, and to determine if native aquifer materials imposed an excessive oxidation demand.

The laboratory test was conducted using a slurry of 20 percent soil and 80 percent groundwater in a 5 liter reactor vessel. Ozone laboratory treatability test results are shown in Figure 1. After 50 hours of ozonation, greater than 97 percent of the PCP and PAH mass was destroyed. The results also indicated that PAHs and PCP were preferentially oxidized over total organic carbon (TOC). The preferential oxidation of contaminants over TOC showed that competing ozone reactions with TOC do not impede contaminant remediation at this site. Temporary increases in dissolved TOC were observed in the ozonation reactor, indicating solubilization of partially oxidized compounds. Dissolved TOC levels were reduced as ozonation proceeded. While the experimental setup did not optimize ozone consumption efficiency, ozone consumption was observed to be approximately 10 grams of ozone per gram of contaminant.

OBJECTIVES AND DESIGN

The goals for the field study were to determine the level of contaminant reductions achievable by *in situ* ozonation, assess subsurface ozone transport and mass

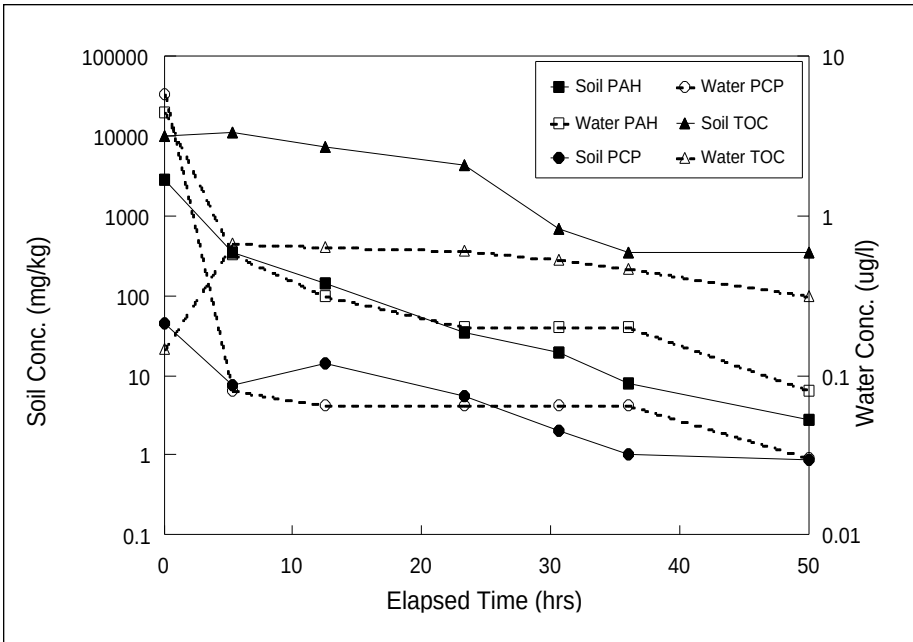


Figure 1. Contaminant reductions from laboratory treatability testing of ozone treatment of PCP and PAHs. Soil concentration data represent contaminants present in soil solids centrifuged from slurry samples. Water data represent the aqueous phase centrifuge fraction.

transfer, and determine appropriate well spacing and other site-specific operating parameters for a full-scale implementation. Two separate treatment areas were equipped with a pattern of multiple, vertical levels of ozone injection points and sampling plots (Figure 2). In one area, the injection points were installed in a 5-spot pattern, and in the second area, the injection points were installed in a 3-spot pattern. This layout allowed for flexibility of injection in a variety of patterns.

Subsurface monitoring instruments were installed in the sample plots at depths which match soil sampling depths to evaluate the phase distribution of contamination before, during, and after *in situ* ozonation treatment. These instruments included soil moisture sensors, pressure vacuum lysimeters to sample soil moisture, piezometers for groundwater sampling, thermocouples for monitoring subsurface temperature, and soil vapor probes for soil gas monitoring (Figure 3).

IN-SITU OZONATION RESULTS AND DISCUSSION

Approximately 8,000 lbs. of ozone were injected into the subsurface over a 12-month period. Water levels rose significantly during the project due to the El Niño

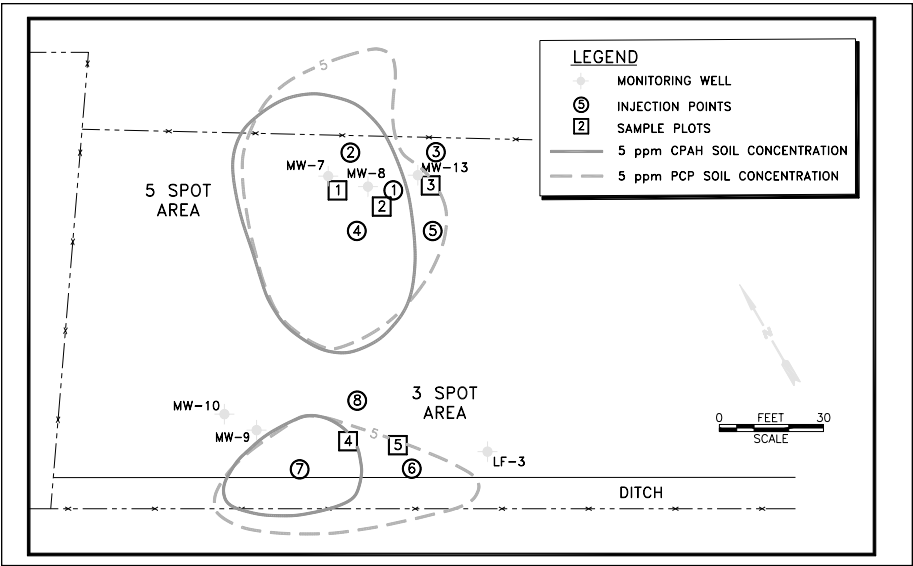


Figure 2. Configuration of injection and monitoring system.

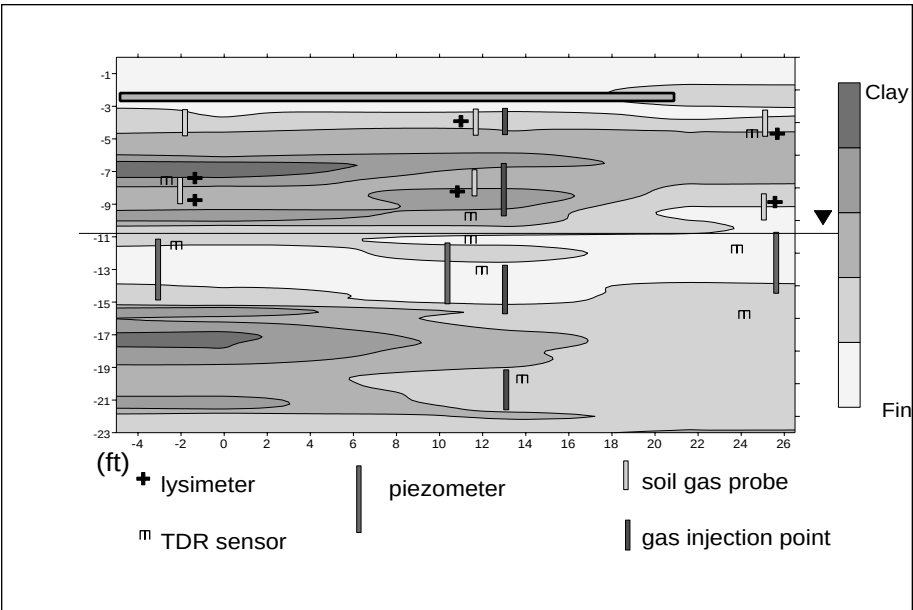


Figure 3. Cross-section of 5-spot treatment zone depicting heterogeneous geology and in situ monitoring systems.

rains of 1998, and some shallow injection points became submerged and functioned as sparge points. Soil moisture measurements collected using Time Domain Reflectometry (TDR) indicated that the vadose zone soils were initially highly water saturated (30 percent to 40 percent volumetric moisture content). The TDR data did not show significant change in water saturation in response to ozone injection.

In general, effective ozone transport and ozone gas mass transfer to the aqueous phase were observed. Ozone concentrations ranging from less than 1 ppm to several hundred ppm were measured in soil gas over the entire area of the monitoring network. These concentrations were several orders of magnitude below the injection concentration of 5 percent (50,000 ppm), which reflects rapid subsurface ozone reaction and degradation. Dissolved ozone concentrations up to 1.4 ppm were measured in soil moisture samples collected from pressure-vacuum lysimeters.

Soil samples collected at paired locations prior to *in situ* ozonation, and during February, June, and October 1998 (Figure 4) showed an average 93 percent reduction in PCP and PAHs.

The maximum pretreatment soil contamination was reduced greater than 98 percent, from an initial value of 220 mg/kg PCP and 5,680 mg/kg total PAHs, to below detection limits.

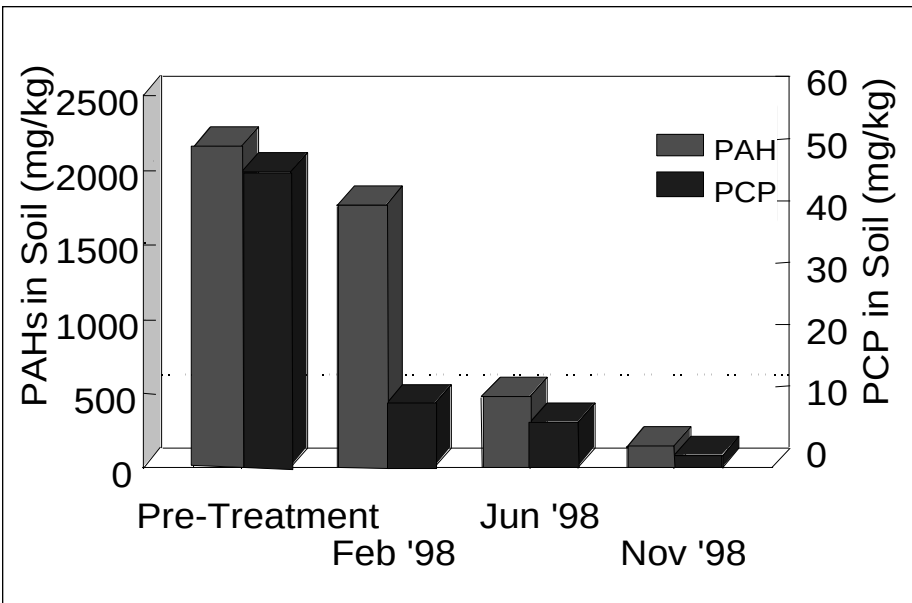


Figure 4. Decrease in average contaminant concentration in upper five feet of soil within cross-section shown in Figure 3.

Significant contaminant mass reduction was reflected not only in soils data, but in substantial reductions in aqueous-phase concentrations of PCP and PAHs. The lysimeter data (Figure 5) showed several orders of magnitude reduction in dissolved PCP and PAHs at the first sampling event, conducted after approximately one month of ozone injection in the 5-spot area. Also, lysimeter LY-2A produced liquid NAPL at the beginning of the project but not after one month of treatment. Several lysimeters located at the southern edge of the treatment area showed an increase in dissolved contaminants from January 1998 to February 1998. They apparently received additional input of contaminant mass from outside the treatment zone as a result of precipitation infiltration during the El Niño rains of 1998.

Lysimeter LY-2A was evaluated to assess rebound of dissolved contaminants in February and June of 1998 (Figure 5). The rebound sampling consisted of a second set of samples collected approximately 7 days after site-wide sampling. During the 7-day interim period, *in situ* ozonation was discontinued to allow soil moisture to re-equilibrate with soil and NAPL (if present). Significant rebound occurred in February 1998, while in June 1998, little rebound occurred. While the lysimeter data collected under conditions of active ozonation showed little decrease from February to June of 1998, the samples collected under rebounded conditions showed a substantial

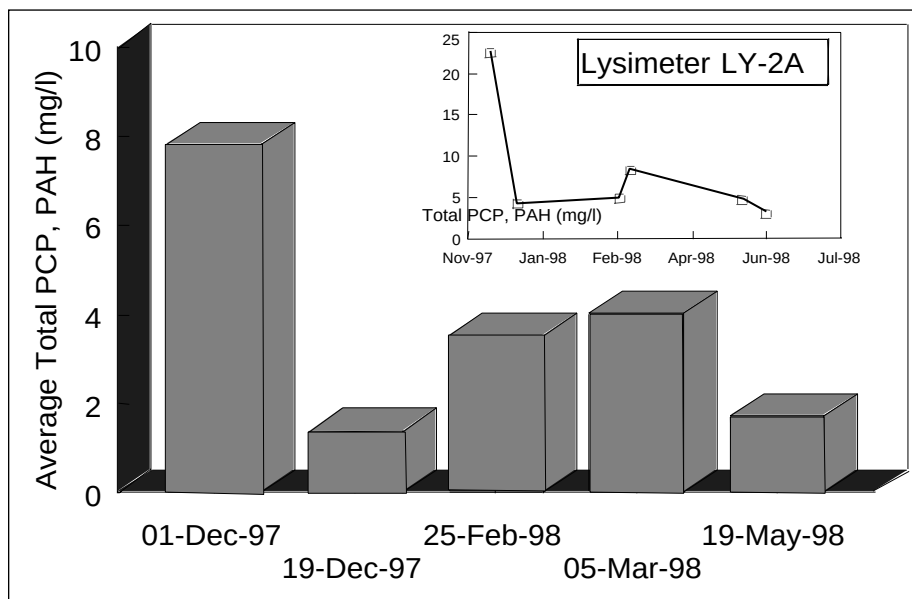


Figure 5. Changes in soil moisture contaminant concentrations. Bar chart shows average soil moisture contamination from all lysimeters across the cross-section in Figure 3. Inset shows contaminant concentrations at lysimeter LY-2A.

reduction. This indicates that the reservoir of dissolved NCPAH (that is, NAPL and sorbed phases) was significantly reduced during this period.

Figure 6 depicts a series of pie charts of the relative fraction of PCP, and 2-, 3-, 4-, and 5-ring PAHs in soil at two locations before treatment and after greater-than-95-percent treatment. These pie charts indicate that the ozonation treatment process was non-selective; that is, all contaminant compounds were treated at similar rates. This implies that the *in situ* ozonation process is not strongly limited by contaminant mass transfer from NAPL and sorbed phases into the aqueous phase. If contaminant mass transfer were limiting, we would expect to see highly preferential treatment of more soluble compounds such as PCP and 2- and 3-ring PAHs, relative to less soluble compounds such as 4- and 5-ring PAHs. Since this was not the case, and since most of the contamination was present in either NAPL or sorbed phases, we can infer that the oxidation reactions occurred largely at the interface between dissolved or gaseous ozone and NAPL or sorbed contaminants.

Ozone consumption was calculated at approximately 7 pounds of ozone per pound of PCP and PAH contaminant destroyed. This number is highly conservative, because the system was optimized for maximum ozone loading, and not for efficient ozone usage. Combining *in situ* ozonation and bioremediation can significantly decrease ozone consumption.

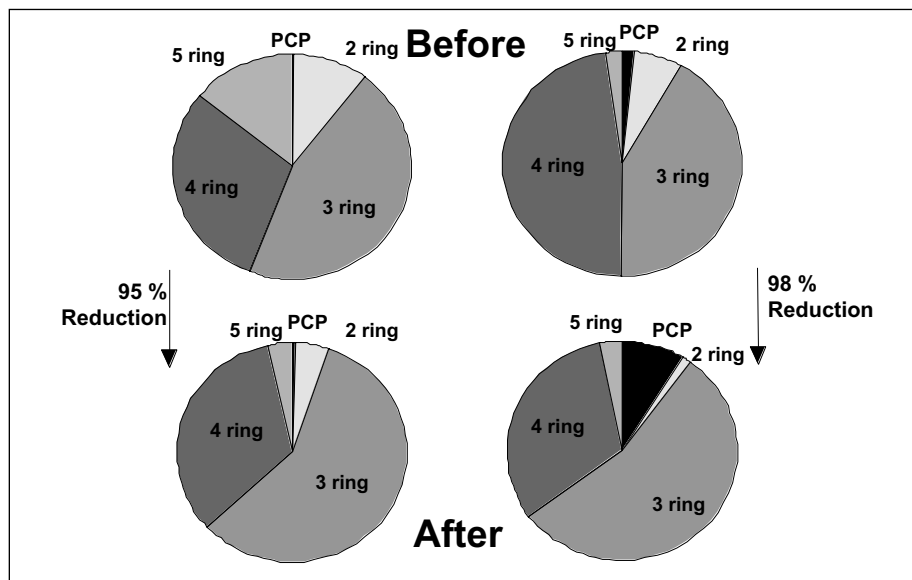


Figure 6. Changes in soil moisture contaminant concentrations. Bar chart shows average soil moisture contamination from all lysimeters across the cross-section in Figure 3. Inset shows contaminant concentrations at lysimeter LY-2A.



CASE HISTORY OF REACTIVE BARRIERS USING Fe^0 METAL AND KMnO_4 TO DEGRADE CHLORINATED SOLVENTS

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A field trial was completed to evaluate *in situ* remediation using hydraulic fracturing to emplace zero valent iron metal and potassium permanganate solids in a silty clay vadose zone to chemically treat trichloroethylene (TCE) (Siegrist *et al.* 1999) (Figures 1 and 2). This trial was completed by Oak Ridge National Laboratory (ORNL) and FRx, Inc. in collaboration with Lockheed Martin Energy Systems (Murdoch *et al.* 1997a, b; Siegrist *et al.* 1999). Supporting experimentation and modeling were conducted at ORNL and the Colorado School of Mines (CSM) (Case 1997; Struse 1999).

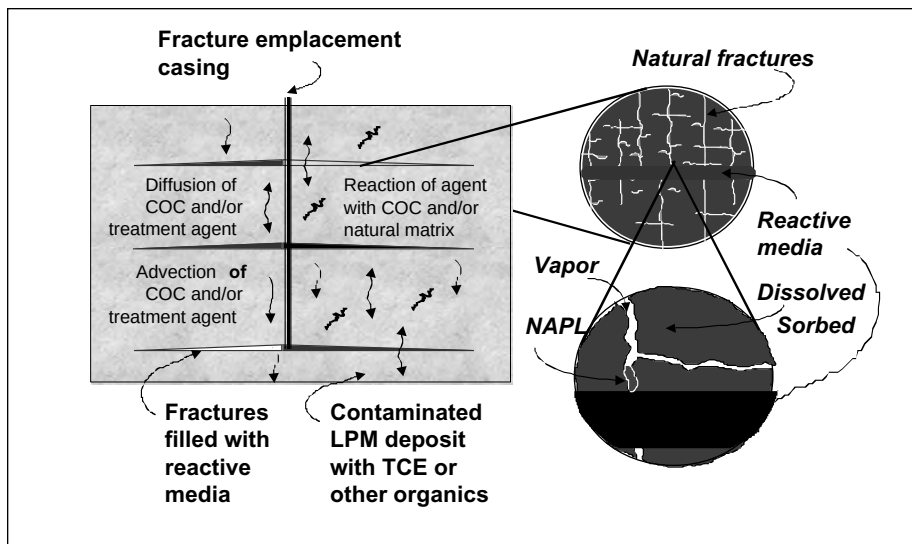


Figure 1. Chemical treatment zones installed using hydraulic fracturing and reactive solids (Siegrist *et al.* 1999).

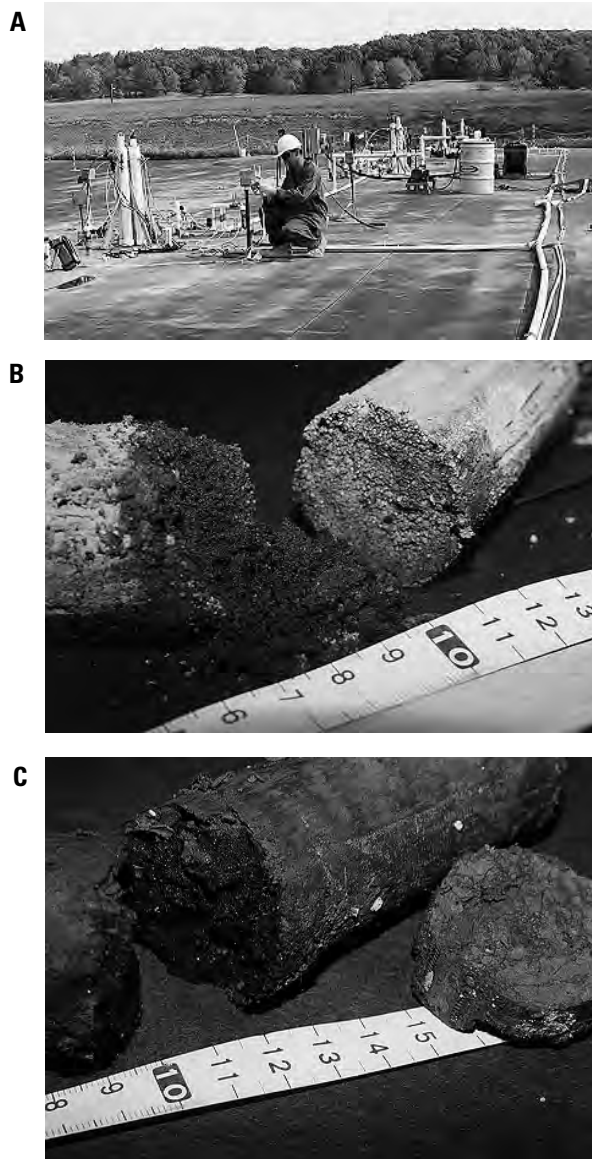


Figure 2. Overview of the X-231A site (a) and photographs of intact cores taken across fractures filled with zero valent iron metal (b) and potassium permanganate mixture (OPM) (c) 10

SETTING

The demonstration was completed at the X231-A land treatment site located at the DOE Portsmouth Gaseous Diffusion plant in central Ohio (Table 1). The 2.2 hectare site was used for disposal of waste oils and solvents during the 1970's until its use was terminated around 1980, and it was capped with a temporary geomembrane. Composed of unconsolidated Quaternary-age deposits, the site is underlain by 6 to 8 meters of low-permeability clays and silts ($K_{\text{sat}} < 10^{-6}$ cm/s) known as the Minford member. The Minford has naturally occurring platy structure and vertically dipping fractures that provide pathways for vertical migration of contaminants released during land treatment of wastes. Underlying the Minford is a moderately permeable sand known as the Gallia member, which consists of pebbles and gravel in a fine-grained silty-sand matrix that is 1 to 2.5-m thick. Precipitation percolates through the Minford member to a zone of permanent saturation at a depth of about 4 meters, and it eventually reaches the Gallia member, where flow is predominantly horizontal. Previous characterization activities at the site revealed total volatile organic compounds (VOCs) in soil (predominantly TCE), ranging to as much as 300 mg/kg, whereas groundwater at the site contained variable concentrations of TCE, including some dense nonaqueous phase liquid (DNAPL).

REMEDIATION APPROACH

Hydraulic fracturing was used to emplace zero valent iron metal in one cell and a new potassium permanganate mixture (OPM) in a second cell (Figure 1). Each of the test cells were comprised of five horizontal fractures stacked one over the other within a subsurface region roughly 6 meters in diameter and 5 meters deep (Table 2). Sand-filled fractures were propagated at nominal depths of 1.2 and 4.9 meters, with fractures containing reactive media propagated at depths of 1.8, 2.4, and 3.6 meters. The saturated zone was encountered at 3.6-meter below ground surface (bgs). In one test cell, iron metal in the form of 0.2-mm diameter Fe^0 particles (Master Builder) was suspended in guar gum gel, and this slurry was used to create three iron-filled fractures. In another test cell, an oxidative particle mixture (OPM) consisting of 0.1 to 0.3 mm diameter KMnO_4 particles (Carus Chemical) suspended in a mineral-based gel was used to create three permanganate-filled fractures. In each test cell, the shallowest fractures were created first, followed by successively deeper ones. For each fracture, steel casing was driven to depth and used to inject the reactive slurry, and then left in place for future access following procedures similar to those described in Murdoch *et al.* (1994). Forms of the fractures were estimated by measuring displacements of the ground surface during fracturing as well as via direct observation of intact cores collected from 8 boreholes made after fracture emplacement.

TABLE 1 Summary of the test site characteristics (Siegrist *et al.* 1999).

Characteristic	Units	Conditions
Soil type and genesis	Minford silty clay deposit of fluvio-lacustrine origin. Typically with a 4.6 m thick upper clay unit (CH) transitioning to a lower 3.0 m thick silt unit (CL).	
Soil particle size distribution		
–Sand (0.050 - 2.000 mm)	dry wt. %	~05
–Silt (0.002 - 0.050 mm)	dry wt. %	~60 to 85
–Clay (<0.002 mm)	dry wt. %	~10 to 35
Soil mineralogy	In the Minford, the sand fraction consists of mainly quartz with minor geothite. The silt fraction consists of quartz and minor feldspars but no geothite. The clay fraction is a mixture of illite (~33%), quartz (~29%), kaolinite (~26%), and smectite (~12%).	
Soil biogeochemical properties		
–Bulk density	g/cm ³	1.8
–Water content	wet wt. %	20%
–Liquid limit, plastic index	%	~60 and 35
–Total fractional porosity	v/v	0.40
–Water-filled porosity	% pores	90
–pH (in water)	–	6.0
–Organic carbon	mg/kg	500 to 1,500
–Iron oxides - free	mg/kg	23,000
–Iron oxides - amorphous	mg/kg	1,350
–Cation exchange capacity	meq/100g	17.5
–Total bacteria	org./g	100 to 10,000

The test cells were established during September 1996 and left in a passive mode of operation for the next 15 months. Since there was a geomembrane over the site, there was limited infiltration, although minor amounts of moisture did enter through perforations made in the cover for instrumentation and soil coring. Fracture emplacement was monitored and soil and ground water conditions were characterized. At 3, 10, and 15 months of emplacement, continuous cores were collected and morphologic and geochemical data were taken across the fracture zones. Controlled degradation tests were completed using site ground water with TCE concentrations near 53, 144, and 480 mg/L, equivalent to 0.5, 1.2, and 4.1 grams TCE per kilogram of media, respectively. Laboratory and modeling studies have been focused on per-

TABLE 2 Test cell installation features.

Test cell characteristic	Iron-filled fractures for dechlorination	Permanganate-filled fractures for oxidation
Method and time of installation	Iron metal and guar gel; 2 to 3 hr	Permanganate OPM; 2 to 3 hr
Fracture depth -		
proppant - amount	1.2 m - Sand - 0.14 m ³ 1.8 m - Fe ⁰ - 1,000 kg 2.4 m - Fe ⁰ - 1,300 kg 3.6 m - Fe ⁰ - 2,600 kg 5.0 m - Sand - 0.57 m ³	1.2 m - Sand - 0.14 m ³ 1.8 m - KMnO ₄ - 400 kg 2.4 m - KMnO ₄ - 600 kg 3.6 m - KMnO ₄ - 600 kg 5.0 m - Sand - 0.57 m ³
Cell size	6 m diam. by 5 m deep	6 m diam. by 5 m deep

manganate oxidation chemistry and delivery/transport processes since a body of research was already available and/or in progress regarding Fe⁰ metal reduction. Laboratory studies have included (1) batch tests to define permanganate oxidation kinetics, (2) development and testing of a permanganate oxidative particle mixture, and (3) intact core studies to quantify permanganate diffusive transport and matrix interactions.

RESULTS

In general, the fractures were flat-lying around the point of initiation but gradually climb upwards to form a gently bowl-shaped form, in some cases interacting with overlying fractures. The iron-filled fractures formed a discrete reactive seam less than 1 cm thick, where the Eh decreased and reductive dechlorination could occur; effects in the adjacent silty clay soils were negligible (Figures 2b and 3). While the zero valent iron exhibited some surface corrosion after extended emplacement in the subsurface, its reactivity was unaffected. Iron from the fractures degraded TCE at efficiencies of as much as 36 percent after 24 to 48 hours of contact, which is consistent with Fe⁰-packed bed degradation half-lives of 1 to 2 hours. The permanganate-filled fractures yielded a diffuse reactive zone that expanded over time, reaching 40 cm in thickness after 10 months (Figures 2c and 4). Throughout this oxidizing zone, the degradation efficiency was greater than 99 percent after 2 hours of contact for dissolved TCE at 0.5 and 1.2 mg TCE per gram of media. When exposed to higher TCE loadings (such as, 4.1 mg per gram), degradation efficiencies after 10

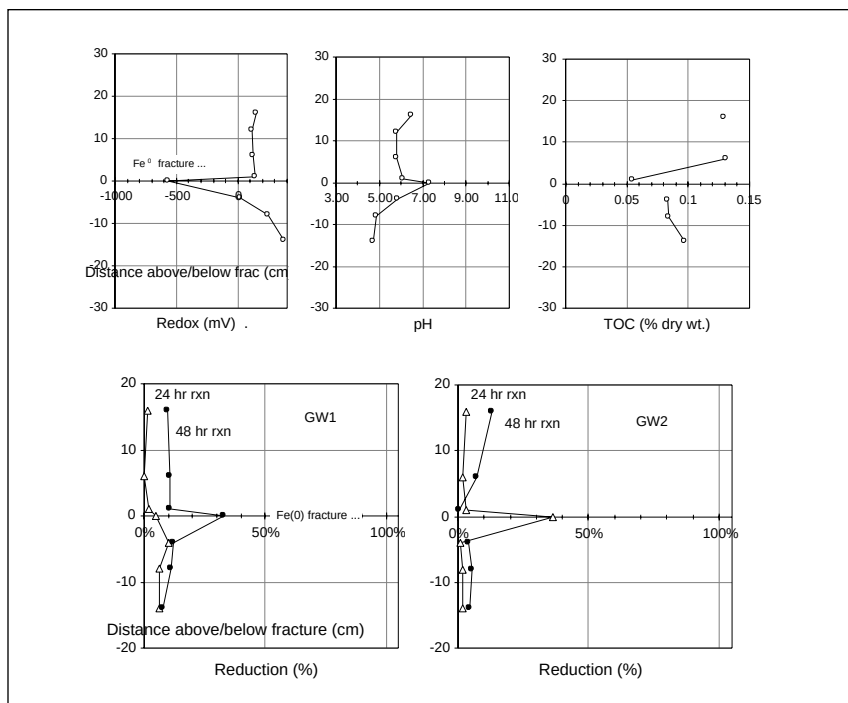


Figure 3. Geochemical properties and TCE-degradation potential of Fe⁰ metal fracture zones 10 months after emplacement in a silty clay deposit (Siegrist *et al.* 1999). Note: TCE degradation measured using 5 g of media in 40 mL of GW1 (initial TCE = 477.0 mg/L) or GW2 (initial TCE = 53.7 mg/L)

months dropped to 70 percent, as the TCE load exceeded the oxidant capacity remaining. These efficiencies and rates are consistent with oxidation stoichiometry and previously determined half-lives of less than 2 minutes for permanganate oxidation of TCE. There were no marked effects in both test cells on the chemistry or contamination levels in the groundwater beneath the cells (Siegrist *et al.* 1999).

Results of laboratory work revealed that the OPM had a TCE degradation rate that was equal to or greater than that of permanganate alone. The rate of oxidative destruction of TCE was 2nd-order with respect to TCE and MnO_4^- , yielding a reaction rate constant is in the range of 0.6 to 0.9 L mol⁻¹s⁻¹ (at 20° C without appreciable natural organic matter [NOM]). Lower temperatures reduced the rate of organic chemical destruction, as will the presence of other oxidant-demanding substances in the system (such as NOM). Diffusive transport of potassium permanganate from a 5 g-KMnO₄/L source zone through the silty clay soil was studied in the lab. In uncontaminated cores, diffusing permanganate did oxidize some, but not all of the

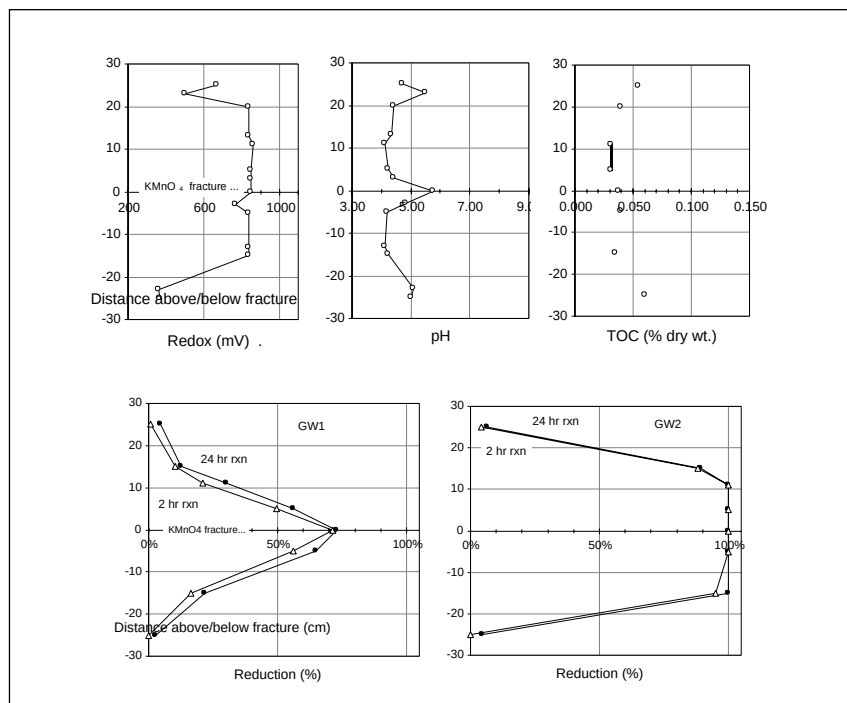


Figure 4. Geochemical properties and TCE degradation potential of permanganate fracture zones 10 months after emplacement in a silty clay deposit (Siegrist *et al.* 1999). Note: TCE degradation measured using 5 grams of media in 40 mL of GW1 (initial TCE = 490.5 mg/L) or GW2 (initial TCE = 50.5 mg/L).

NOM in the soil (approximately 10 to 30 percent destruction), and did yield MnO_2 deposits, but they did not alter system tortuosity. In contaminated cores (approximately 100 to 1,000 mg/kg TCE), permanganate transport was retarded due to reaction with the TCE. Oxidation of residual TCE in the silty clay soil was almost complete, but tortuosity appeared to be increased, possibly due to more focused and intense MnO_4^- oxidation of residual TCE. With a MnO_4^- concentration of 40 g/L in a fracture upon emplacement, the enveloping reactive zone was modeled and predicted to have extended to 60 cm in total width after 6 months of emplacement (Struse 1999). These experimental and modeling results compared well with the observations made during the field trial noted below.

DISCUSSION

The feasibility of *in situ* remediation of TCE and other organic compounds in low-permeability vadose zones was demonstrated at the X-231A site. However, general

application of this technology requires consideration of the horizontal continuity, degradation capacity, and longevity of the treatment agents. During the field trial described, both types of reactive media were handled and emplaced by conventional hydraulic fracturing equipment and methods. Handling of the permanganate was more problematic in some respects, although modifications to fracturing equipment or development of encapsulation methods should resolve this issue. In general, the geometry of the reactive media fractures was similar to that of conventional sand-filled fractures emplaced at the same site. The Fe^0 -filled fractures are discrete layers and appear to have limited effect on the soil deposit beyond the fracture boundaries. Thus, any *in situ* degradation of TCE or related compounds must rely on contaminants being mobilized to a fracture and then reacting with the Fe^0 within the fracture. The degradation rates observed in this study were consistent with previous studies suggesting a half-life on the order of 1 to 2 hours for TCE degradation in Fe^0 -filled fractures. While slow, this is still rapid enough for high treatment efficiencies to be achieved during a day or less of contact that is achievable for most LPM deposits. For example, if ground water percolation through the fracture is controlled by a surrounding LPM that has a K_{sat} of 10^{-6} cm/s and a hydraulic gradient of unity, then the retention time in an Fe^0 -filled fracture of 5 mm thickness would be on the order of 1 to 5 days, depending on the effective porosity. As a treatment zone that relies dominantly on diffusive transport of contaminants to the iron, the reactivity of the Fe^0 surface would need to exist for an extended period (for example, years). Field investigations of iron-filled zones placed in groundwater as permeable treatment walls have revealed reactivity for up to five years (Gavaskar *et al.* 1997). However, such information is lacking for iron metal emplaced in fractures in a vadose zone without high advection through or across the iron surface. Analysis of the micromorphology of iron particles retrieved from the fractures made in this study revealed some corrosion of the iron surface after residing in the subsurface for nearly 11 months. The effect was limited to a fraction of the available iron surface, however, and it had no apparent effect on TCE degradation (Siegrist *et al.* 1999).

Fractures filled with a KMnO_4 OPM yield MnO_4^- ions that migrate away from their original location, predominantly by diffusion in an LPM deposit, but possibly aided by advection driven by capillary gradients as well. This behavior will produce a zone at least several dm wide where resident TCE will be rapidly degraded, and it could also provide a barrier that would degrade mobile TCE. As a result, the gaps between offset fracture lobes or discontinuities between neighboring fractures might be "healed" by the migration of permanganate ions. The field results suggest that TCE degradation is fast and extensive, which is consistent with companion laboratory studies carried out with KMnO_4 crystals and OPM. These lab studies revealed nearly 100% destruction of TCE following pseudo first-order kinetics with degradation half-lives of less than 2.4 minutes for TCE concentrations up to 800 mg/L (Case 1997). The permanganate degradation of TCE appears to proceed stoichiometrically, which can be used to roughly estimate the active life of a permanganate-filled fracture. A

5-mm thick permanganate-filled fracture contains about 0.4 g KMnO_4 per cm^2 of fracture horizontal area. Based on complete oxidation and a stoichiometric TCE demand of 2.5 wt./wt., each cm^2 of fracture can treat about 0.16 grams of TCE. This oxidant loading is sufficient to degrade an initial TCE concentration of 1,000 mg/kg within a zone of LPM that is 90 cm thick. Alternatively, it is sufficient to treat 16 L of water with a concentration of 10 mg/L of TCE, which is equivalent to a 50-year life at a deep percolation flux of 1 cm/d. Realistically though, it is anticipated that the oxidant demand of natural organic matter or the advective loss of oxidant out of the treatment region could markedly diminish this life. Based on direct observation in this study, the oxidation capacity within and around the permanganate fractures was striking, even 15 months after emplacement.

The total estimated costs of the horizontal treatment zone systems are similar to the costs for SVE systems. For the 2.2-hectare X-231A site contaminated to 5-m depth, the costs for implementing horizontal treatment zones were estimated to be in the range of \$25 to \$35/ m^3 for iron and permanganate zones, respectively. This cost was based on 6-meter diameter fractured zones with 1-meter overlap and fractures installed at depths of 1.7 and 3.5 m. Assuming no bulk media discounts, this yields an estimated materials cost of \$2,700K for the iron metal and \$3,800K for the permanganate. The installation time was estimated at 140 days for a 3-person crew and equipment, yielding a labor cost, including travel and per diem, of \$450,000, plus a mobilization/demobilization cost of \$50,000.

CONCLUSIONS

Hydraulic fracturing equipment and methods were used to create reactive zones of Fe^0 metal or KMnO_4 OPM in horizontally oriented layers within a silty clay vadose zone at depths up to 5 meters. The Fe^0 -filled fractures produced a reactive seam with limited effect on the surrounding LPM, while the KMnO_4 -filled fractures yielded a broad zone of reactivity within the LPM. With both types of fracture zones, degradation potential for high levels of TCE was sustained after 10 months of emplacement in the subsurface. Both types of horizontal treatment zones may reduce risks associated with exposure to TCE from a contaminated site. Although the system using iron-filled fractures may leave immobile contaminants in the ground untreated, data from this study suggest that it is capable of degrading mobile TCE, and thus may reduce the risks by effectively eliminating TCE release from a low permeability unit to the atmosphere or an underlying aquifer. The system using permanganate-filled fractures, where MnO_4^- ions are diffusively distributed through a broad region, offers the possibility to both curtail TCE release to the atmosphere, or an underlying aquifer, as well as destroy TCE throughout a low permeability formation. However, diffusive transport is slow, and the rate and extent are highly dependent on the physical and chemical properties of the formation. This approach for remediating low permeability formations using fracture emplaced reactive solids is encouraging. While

TCE has been the target contaminant in studies to date, other organic compounds, and also redox sensitive metals, might be amenable to such an *in situ* remediation strategy. While the results to date are promising, this *in situ* remediation approach is still early in its development and further work is necessary and appropriate to provide needed design, implementation, and performance data for a range of site and contamination conditions.

ACKNOWLEDGMENTS

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CASE HISTORY OF REACTIVE BARRIERS OF POROUS CERAMICS USED TO ENHANCE BIODEGRADATION OF PETROLEUM HYDROCARBONS

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The Denver Federal Center (DFC) in Lakewood, Colorado was originally the location of a Remington Arms Plant during World War II. In 1993, soil contaminated with an oily substance was found during construction near Building 56 at the DFC. A site assessment conducted in 1994 by the U. S. Public Health Service (PHS) found petroleum hydrocarbons typical of cutting oils. Total Petroleum Hydrocarbon (TPH) concentrations in soils from this location exceeded the levels allowed under Colorado Department of Public Health and U.S. Environmental Protection Agency (USEPA) guidelines.

The TPH contaminants were found in both the saturated and unsaturated zones. Petroleum hydrocarbons are normally biodegradable. However, little biodegradation had taken place during the past 50 years. Clearly, intrinsic biodegradation of the cutting oil contamination was not taking place, or was taking place at a very slow rate. This was due in part to the fact that the sediments beneath the site are composed of low-permeability shale and clay, which restrict most bioremediation and other conventional treatment methods.

A pilot test was designed to evaluate the feasibility of using reactive barriers created of porous ceramic granules to enhance the biodegradation of the TPH. Hydraulic fracturing techniques were used to emplace the ceramic granules. The reactive barriers were designed to enhance the biochemical conditions and speed the biodegradation of the hydrocarbon contaminants. Laboratory testing showed that the total background heterotrophic and autotrophic population counts were extremely low. Accordingly, a specialized treatment population for the site was developed through bioaugmentation of indigenous microorganisms.

The objectives of the project were to demonstrate that:

1. Hydraulic fracturing of soils with a guar gum and water mixture can be accomplished in shale and clay, typical of sediments underlying the Denver area.
2. The horizontal extent of fractures can be monitored and controlled within design parameters.
3. An inoculated porous ceramic material (Isolite®) can be used as a fracture proppant.

4. Accelerated oil degradation will take place at and near the inoculated Isolite-filled fractures.
5. A surfactant will assist in emulsifying oil to enhance degradation by microorganisms and in transporting oil to the Isolite-filled fractures.
6. Post-fracture-installation injection of microorganisms, nutrients, surfactants, and oxygen is feasible to recharge the system.

Sponsors and participants in the project were Foremost Solutions, Inc., the U.S. Environmental Protection Agency, Sumitomo Corporation of America, Pintail Systems, FRx, the U.S. Bureau of Reclamation, and the U.S. General Services Administration.

SETTING

The Denver Formation underlies the site and consists of nearly horizontal interbedded mudstone, shale, siltstone and sandstone. Depth to weathered bedrock ranges from 7.5 to 15 feet. Ground water (possibly perched) was encountered at a depth of 9 feet. The site assessment showed TPH concentrations in the soil to be approximately 2,400 mg/kg prior to remediation.

REMEDIATION

Reactive barriers were created to enhance and stimulate the growth and degradation capacity of microbes. The barriers were created by injecting Isolite into flat-lying hydraulic fractures. Isolite is a highly porous, silica-based ceramic material formed into mm-sized granules. The Isolite was inoculated with indigenous microbes that were selected because they could effectively degrade contaminants found at the site. Isolite is particularly well-suited for inoculation because each granule has an extremely large surface area and is chemically inert. Moreover, a layer of Isolite granules is highly permeable and can be readily accessed by injected fluids. Injecting Isolite into a hydraulic fracture forms a biologically reactive layer roughly 1 cm thick and 30 to 40 feet in maximum dimension. The term "BioLuxing" is often used to describe a remediation technology using inoculated Isolite injected into hydraulic fractures. This term has now been accepted by the state of Colorado as standard terminology for this process.

Two sets of reactive barriers were installed at the site during June 1995 (Figures 2, 3, 4). One set of barriers, Location 1, was centered 38 feet south of Building 56 and contained fractures filled with inoculated Isolite at depths of 8.8, 11.5, 13.0, and 15.1 feet below ground surface (bgs), whereas the other set, Location 2, was centered 94 feet south of Building 56 and contained fractures at 15.3 and 17.2 feet bgs.

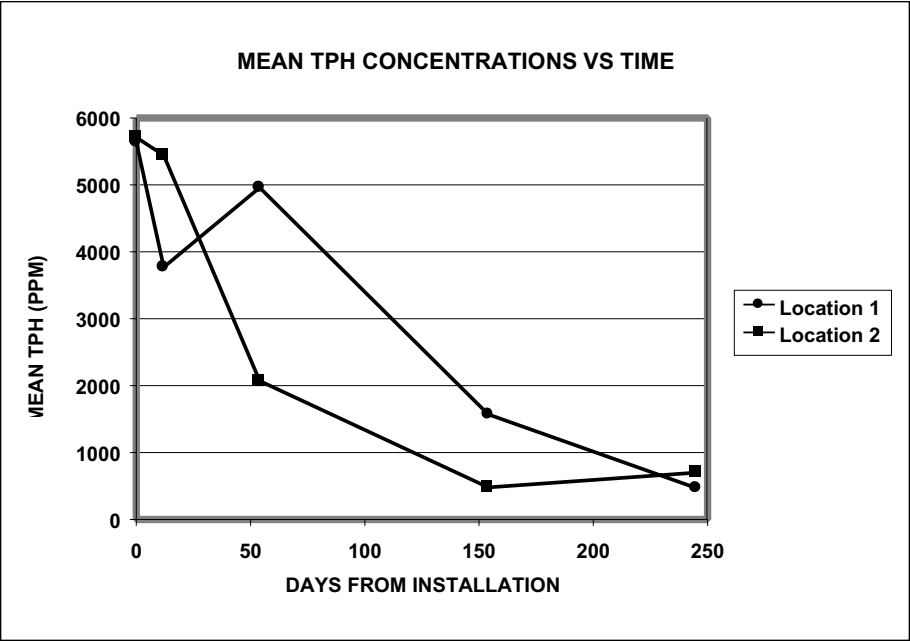


Figure 1. Mean TPH Concentration vs. Time.

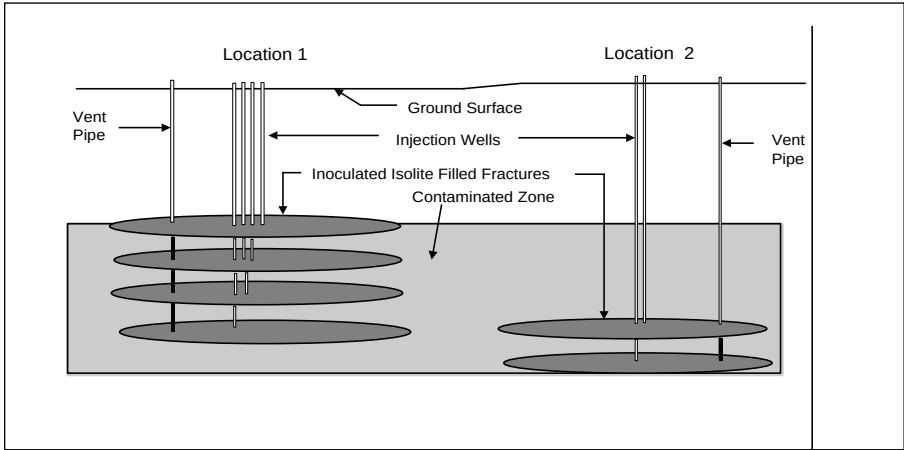


Figure 2. Installation diagram.

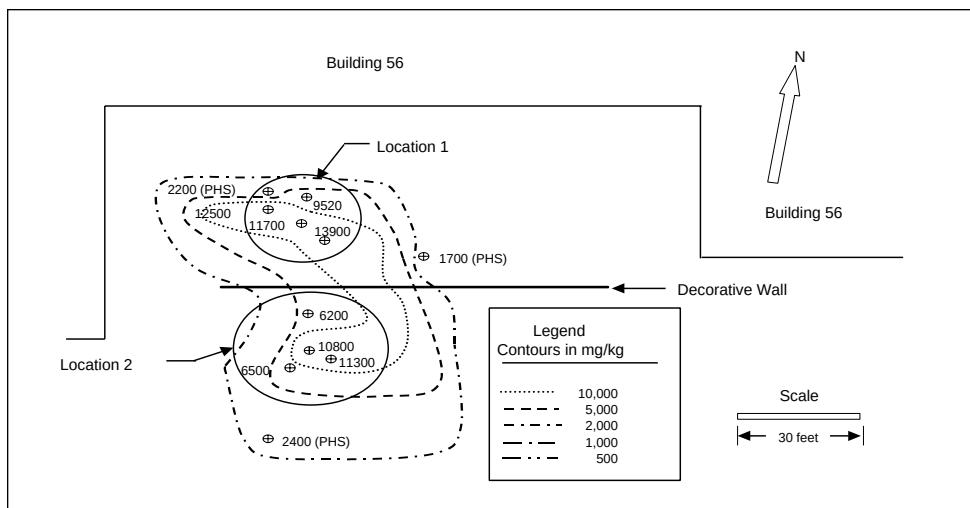


Figure 3. Maximum total petroleum hydrocarbon concentrations in mg/kg.

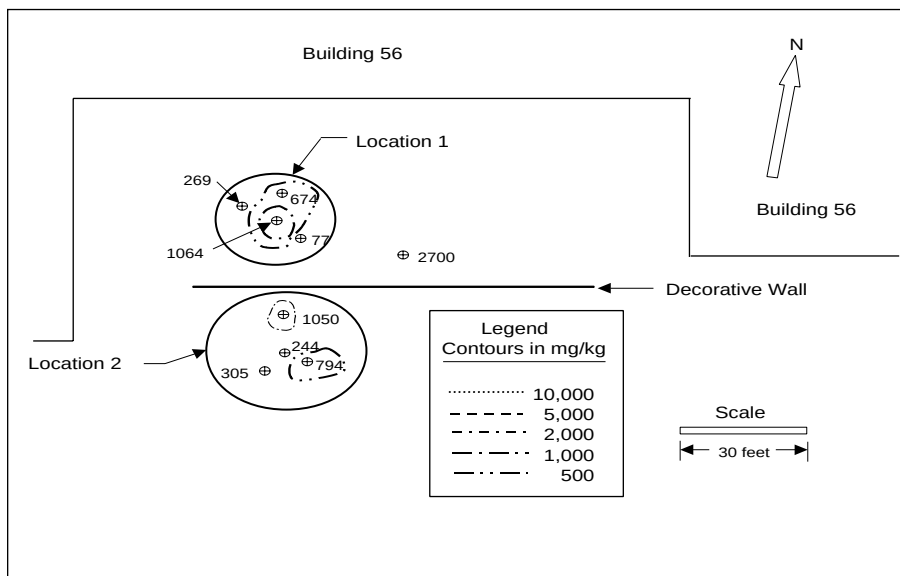


Figure 4. Final total petroleum hydrocarbon concentrations in mg/kg.

Hydraulic fracturing with the Isolite slurry produced flat-lying layers roughly one-half-inch thick and 30 to 40 feet in maximum dimension.

One week after the creation of the Isolite layers, a mixture of microorganisms, nutrients, and a surfactant was injected into the fractures at depths of 8.8, 11.5, and 15.1 feet at Location 1. Location 2 received no such injections. One slotted PVC pipe was installed at each of the sampling locations to provide aeration. Air was injected into Location 1 between the 154-day and 245-day sampling events described below. Aeration was performed daily on Isolite layers at Location 1 with a small portable air compressor over a six-week period (mid-November 1995 to late December 1995). The air compressor was operated on a two-hour on/two-hour off cycle to force air into the boreholes used to create the fractures. An air pressure of between 8 and 15 psi was sufficient to sustain air movement through the fractures. The Isolite layers were found to be connected, since air injected at the 14.7-foot depth was observed escaping from the three vent pipes at Location 1. Active aeration was not performed at Location 2, but vent pipes were installed to provide passive aeration to the contaminated zone.

RESULTS

Soil samples were taken at four locations between the Isolite-filled fractures at Locations 1 and 2. Samples were collected immediately prior to installation and at 12, 54, 154, and 245 days after installation. In addition, control samples were taken outside the demonstration area at points that coincided with sampling locations of the initial site assessment. All soil samples, except those taken during the fourth sampling event at 154 days, were collected using a rotary auger rig with heavy duty 8 inch diameter, five-foot length hollow stem augers and a continuous sample tube system (split-spoon). The samples obtained on day 154 were taken using a Geoprobe® with a macro-core sampler (with liner). The EPA project officer took all samples to the EPA Region 8 Laboratory within 24 hours of sample collection. Initial (baseline) performance verification samples were obtained in each fracture borehole before fractures were installed. Additional samples were collected between the Isolite-filled layers at three lateral locations. The three locations were on lines of equal uplift, where 50% of the maximum uplift had occurred during fracturing, approximately midway between the fracture center and zero edge. The same sample locations were resampled (within 1 foot laterally and 3 inches vertically) during each performance-verification sampling event, in an effort to collect comparative samples. Isolite-filled fractures were observed in the sample cores (at the 50% uplift locations) at depths indicating horizontal fracture propagation. The thickness of fractures averaged 2.5 centimeters at these locations. Control samples were taken within 2 feet laterally and 6 inches vertically at two of the original sample locations documented by the U.S. Public Health Service. The results of analyses of soil samples taken from both locations are shown in Table 1.

TABLE 1

Partial list of HFBR characterization technologies evaluated *(continued)*
 (Adapted from EPA 1997.)

Sample Location/Depth (feet) *	TPH Initial Samples (mg/kg)	TPH 12 Day Samples (mg/kg)	TPH 54 Day Samples (mg/kg)	TPH 154 Day Samples (mg/kg)	TPH 245 Day Samples (mg/kg)	Percent Reduction Initial to Last Sample
Location 1						
Center/10.5	3,730 & 489	2,820	5,470	875	488	86.9
SE 4.9/10.0		5,720	1,210	1,640	145	
N 9.8/10.7	1,120	4,580	769	275		75.4
NW 9.8/10.5	9,750	1,490	3,970	806		91.7
Center/12.0	1,240	11,700	2,840	11,200	1,064	14.2
SE 4.9/11.4	8,440	760	13,900	669	77	99.1
N 9.8/12.7	9,520 & 7,250	1,590	2,240	674		92.9
NW 9.8/12.4	12,500	1,610	8,560	269		97.8
Center/13.8	560	2,870	1,990	202		63.9
SE 4.9/13.9	5,380	3,820	7,320	486		91.0
N 9.8/13.5	7,620	6,020 & 3,480	7,610	1,510	593	92.2
NW 9.8/13.7	4,960	3,490	3,610	189		96.2
MEAN	5,581	3,677	4,757	1,566	473	91.5
Location 2						
Center/17.0	2,050 & 1,720	10,800	2,090	178	244	88.1
N 14.7/16.5	6,220	3,060	2,220		1,050	83.1
SW 9.8/16.0	6,550	1,580	1,070	305		95.3
SE 4.8/16.8	11,300 & 5,100	6,320	2,880		794	93.0
MEAN	5,490	5,440	2,065	242	696	87.3

* Location in compass directions & feet from site center
 Depth in feet (below ground surface)

Analyses of the final samples at Location 1 show that the mean TPH concentration was reduced by 92 percent (from 5,580 mg/kg to 473 mg/kg) (Figure 1), and that the maximum concentrations were reduced between 90 percent (from 10,700 mg/kg to 1,060 mg/kg) and 99 percent (from 13,900 mg/kg to 77 mg/kg). The results of analyses at Location 2 show that the mean TPH concentration was reduced by 87 percent (from 5,490 mg/kg to 696 mg/kg) (Figure 1), and that the maximum concentrations were reduced between 83 percent (from 6,220 mg/kg to 1,050 mg/kg) and 99 percent (10,800 mg/kg vs. 244 mg/kg).

The maximum concentrations at Location 1 were found between Isolite-filled fractures at a depth of approximately 12.2 feet bgs and ranged between 9,520 mg/kg and 13,900 mg/kg (Figure 3). At Location 2, the highest concentrations were found between fractures at a depth of 16.2 feet and ranged between 6,200 mg/kg and 11,300 mg/kg (Figure 3). The final TPH concentrations at Location 1 ranged between 77 mg/kg and 1,074 mg/kg and at Location 2 ranged between 244 mg/kg and 1,050 mg/kg (Figure 4).

The TPH concentration of the control sample taken 18 feet laterally from the edge of the Location 1 fractures, and within the contaminated zone at 12.1 feet bgs, was 2,700 mg/kg in 1996 compared to 1,700 mg/kg in 1994. The TPH concentration at 16 feet bgs at this same location was 3,140 mg/kg in 1996 compared to 2,300 mg/kg in 1994. The degradation observed at Locations 1 and 2 was not reflected in these control samples, and provides further evidence that observed reductions in TPH concentrations at Location 1 are related to the activities performed during this demonstration. The TPH concentration of an additional background control sample taken more than 98 feet south of Location 2, at 16.4 feet bgs, was 30 mg/kg in 1996 compared to 210 mg/kg in 1994.

The cost of the project was approximately \$70,000. Much of this cost was in development and mobilization, and we estimate that the size of the project could have been doubled to include another two locations for an additional \$20,000. Costs for other sites will depend on conditions and cleanup objectives.

CONCLUSIONS

Over a nine-month period, the reductions in mean TPH concentrations at Locations 1 and 2 were 92% and 87%, respectively. The final mean TPH concentration at Location 1 was below the Colorado Remedial Action Category III limit of 500 mg/kg for this site.

The TPH concentration may have been reduced due to: (1) transport of contaminant to fractures; (2) migration of bacteria away from fractures; or (3) a combination of (1) and (2). Some amount of degradation may have resulted from volatilization during drilling and fracture creation. However, contaminant reduction would be

expected to be minimal due to volatilization because of limited drilling activity, the asphalt cover, and the low volatility of cutting oil. Significant degradation of petroleum hydrocarbons, present since the 1940's, was observed over a nine-month time period within the contaminated zone at this site, and can most likely be attributed to the fracturing and *in situ* bioremediation activities performed.

This project showed that hydraulic fractures filled with inoculated Isolite could form reactive zones that enhanced the degradation of hydrocarbons with minimal operation and maintenance. Air was briefly injected at one location, but otherwise only natural processes occurred after the reactive zones were created. The process reduced TPH concentrations to below regulatory limits within a 9-month period.

The project resulted in the following conclusions:

1. Clay and silty soils were easily fractured with this technique.
2. Six BioLuxes were created as designed.
3. The inoculated Isolite, which had been suspended in water-filled incubation columns in the laboratory, was easily transported through the fracturing equipment and into the subsurface.
4. The cutting oil was successfully degraded during a nine-month period.
5. The effect of the surfactant in emulsifying and transporting the oil to inoculated Isolite fractures is unclear. An increase in TPH concentrations in the 54-day sampling event and subsequent reduction in the 154 and 245-day samples may indicate contaminant transport by the surfactant.
6. Post-fracture-installation injection of microorganisms, nutrients, surfactants, and oxygen was also successfully accomplished.

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CASE HISTORY OF MIXED-REGION VAPOR STRIPPING IN A SILTY CLAY VADOSE ZONE

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Fine-grained soils contaminated by organic compounds present a significant environmental restoration challenge. While conventional soil vacuum extraction (SVE) can function at sites with moderate-to-high permeability (for example, $K_{sat} > 10^{-3}$ cm/s), SVE is normally ineffective in silty and clay soils and sediments. A potential approach to rapid *in situ* treatment within low-permeability media involves the use of soil mixing coupled with various physical or chemical treatment processes. In concept, soil mixing creates continuously mixed subsurface soil reactors where various treatment processes can be implemented (Figure 1). Mixed-region vapor stripping (MRVS) is a treatment technology that couples soil mixing with high pressure aeration, and is potentially applicable at sites where contaminants are relatively volatile (West *et al.* 1995a; Siegrist *et al.* 1995a; Gierke *et al.* 1995; DOE 1996). Columns of contaminated soil are mixed and air-stripped by a rotating, hollow auger that also serves as a delivery system for high-pressure ambient or heated air. By applying a slight vacuum within the shroud set on top of the treatment column (Figure 1b), contaminant-laden offgases are collected and channeled through a gas treatment process train and subsequently released into the atmosphere. MRVS is very similar to SVE, in that treatment occurs through the volatilization of organic contaminants into a moving air phase. However, in contrast to SVE, mixed-region vapor stripping is potentially feasible in low-permeability soils. Higher air flow rates can be used during treatment since mixing increases the *in situ* conductivity of the soil. In addition, soil disaggregation which results from the mixing (that is, a block of dense soil is broken up into smaller aggregates) improves the mass transfer of the organic compounds from the soil into the stripping air stream (West *et al.* 1995a; Gierke *et al.* 1995). A full-scale field demonstration of MRVS was conducted at an inactive land disposal site at the Department of Energy (DOE) Portsmouth Gaseous Diffusion Plant in Piketon, OH. This field demonstration was conducted by Oak Ridge National Laboratory (ORNL) with support from the DOE's Environmental Restoration Program. Based on the results of the field demonstration, the entire site was remediated using MRVS. This case study focuses on the results of the field test for which intensive process monitoring and pre- and post-treatment characterization were conducted.

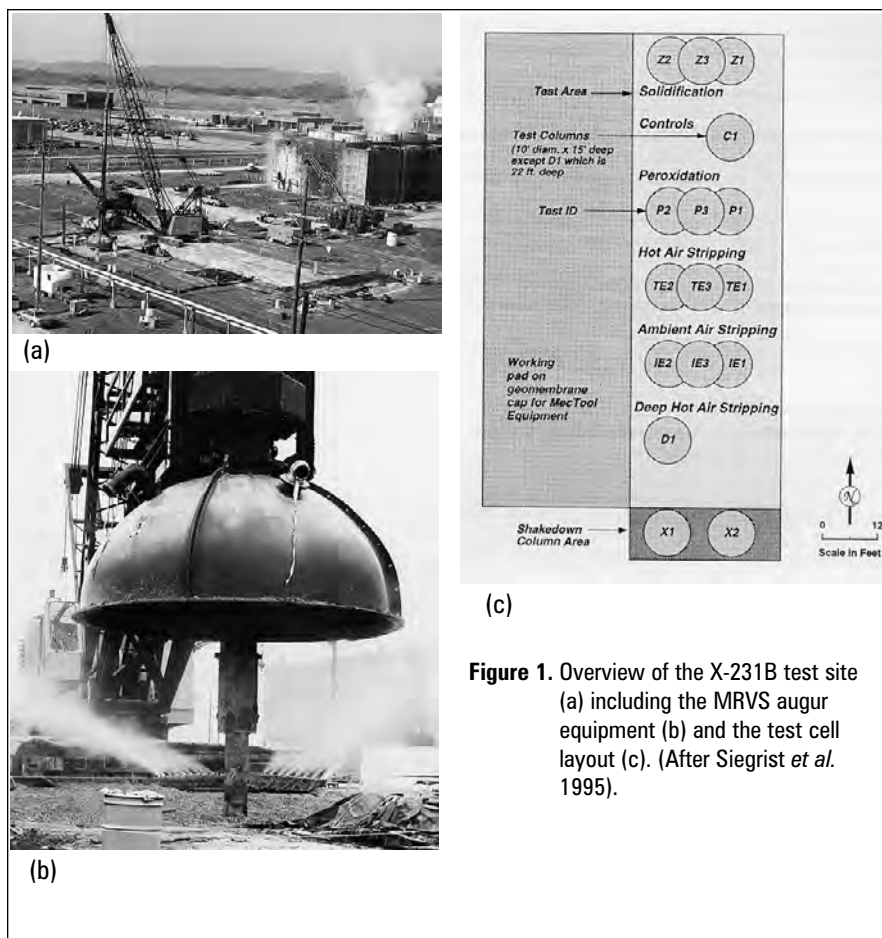


Figure 1. Overview of the X-231B test site (a) including the MRVS augur equipment (b) and the test cell layout (c). (After Siegrist *et al.* 1995).

SETTING

The field test was conducted at the X-231B unit, a former land treatment facility that was used from 1976 to 1983 for the disposal of waste oils and solvents. The site is underlain by 6 to 8 meters of low-permeability clays and silts ($K_{sat} < 10^{-6}$ cm/s) known as the Minford member. Underlying the Minford is a moderately permeable layer known as the Gallia member, which consists of pebbles and gravel in a fine-grained silty-sand matrix that is 1 to 2.5 meters thick. Extensive sampling of the Minford layer showed contamination from trichloroethene (TCE) 1,1,1-trichloroethane (TCA), and other VOCs at concentrations typically less than 20 mg/kg, but up to 100 mg/kg or more (West *et al.* 1995b; Siegrist *et al.* 1995a). Low

levels of uranium and technetium were also present (Table 1). The remediation goal at X-231B was to significantly reduce residual VOCs in the Minford, because the latter was believed to be a persistent source for contamination in the underlying Gallia formation.

REMEDIATION APPROACH

After technology screening and subsequent laboratory testing, a field test was completed to comparatively evaluate mixed region processes including vapor stripping, chemical oxidation, and grout stabilization under full-scale conditions (West *et al.* 1995a,b; Siegrist *et al.* 1995a,b; Gierke *et al.* 1995). This case study describes the MRVS field tests; information on the other technologies are described elsewhere (Siegrist *et al.* 1995a,b).

TABLE 1

Representative characteristics of the subsurface within the test site.

Note: Total VOCs is the summation of the predominant organics observed at the site, including trichloroethene; 1,1,1-trichloroethane; trans-1,2-dichloroethene; cis-1,2-dichloroethene; 1,1-dichloroethene; 1,1-dichloroethane; and methylene chloride.

Characteristic	Representative Range of Properties in 0 to 5.4 m Depth Interval
Grain size distribution	
Clay: <0.002 mm (wt.%)	12 - 25
Silt: 0.002-0.05 mm (wt.%)	39 - 67
Sand: 0.05-2.0 mm (wt.%)	17 - 46
Moist Bulk Density (g cm ⁻¹)	1.8 - 2.0
Water Content (dry wt.%)	16 - 24
pH	5.3 - 7.4
Total Organic Carbon (mg kg ⁻¹)	200 - 1,200
Trichloroethene (ug kg ⁻¹)	0 - 20,000
1,1,1-Trichloroethane (ug kg ⁻¹)	0 - 4,200
1,1-Dichloroethene (ug kg ⁻¹)	1 - 14,000
Methylene chloride (ug kg ⁻¹)	2 - 40,000
Total VOCs - Range (ug kg ⁻¹)	9 - 64,000
Total VOCs - Average; Std.Dev. (ug kg ⁻¹)	5,640; 15,730
Total alpha (nCi kg ⁻¹)	nd - 150
Total beta (nCi kg ⁻¹)	nd - 200
Total Uranium (mg kg ⁻¹)	1 - 150

The auguring equipment used for the field test (MecTool®, Millgard Environmental Corporation, Livonia, MI) consisted of a track-mounted crane with a hollow, kelly bar attached to a drilling tool with two 1.5-meter long blades, yielding an effective mixing diameter of approximately 3 meters (Figure 1). Compressed air is forced through the hollow kelly bar, and injected into the mixing region through 0.5 to 1.25-cm orifices located on manifolds attached to the mixing blades. During the field test, the augers were used to mix columns of soil 3 meters in diameter by 4.6 or 6.7 meters deep, while compressed air (at 1,240 kPa) at either ambient (15-25°C) or elevated temperature (120-130° C) was simultaneously injected at flow rates ranging from 0.47 to 0.66 m³/s (Table 2). The ground surface above the mixed region was covered by a hood maintained under low vacuum (approximately 1 kPa) to capture air emissions for treatment by high efficiency particulate filtration and activated carbon adsorption.

Ambient air MRVS was conducted in a total of 3 columns (4.6 meters deep), with one column overlapping the other two (with an overlap volume of 39 percent). Columns IE1 and IE2 were mixed first, followed by column IE3 (Figure 1c). MRVS using heated air was similarly conducted in a total of 3 columns, TE1, TE2, and TE3, with TE3 being the overlapping soil column (Figure 1c). To test the efficacy of MRVS

TABLE 2

Process operating conditions during full-scale field testing of in situ MRVS.
See Figure 1 for column locations within the test site.

Operating parameters	Units	Ambient air	Heated air	Heated air
Soil regions treated	-	3 (IE1 - IE3)	3 (TE1 - TE3)	1 (D1)
Mixed region diameter	m	3.0	3.0	3.0
Mixed region depth	m	4.5	4.5	6.6
Mixed region volume	m ³	33	33	49
Auger rotation speed	rev min ⁻¹	5 to 10	5 to 10	5 to 10
Auger vertical movement rate	m min ⁻¹	0.3	0.3	0.3
Air delivery rate	m ³ s ⁻¹	0.47 - 0.66	0.47 - 0.66	0.47 - 0.66
Air exchange in soil column	min	0.8 - 1.2	0.8 - 1.2	0.6 - 0.8
Air temperature at the source	°C	15 - 25	120 - 130	120 - 130
Air pressure at the source	kPa	1,240	1,240	1,240
Shroud vacuum	kPa	1.2	1.2	1.2
Mixing treatment cycles for:				
0- to 2.1-m depth interval	down/up	8	8	8
2.1- to 4.5-m depth interval	down/up	4	4	4
Treatment time per column	min	225	225	225

to depths below the water table, one 6.7-meter column (D1) was treated with heated air (Figure 1c). At the time of the field tests, the depth to saturation and free water was approximately 4.1 meters. At the beginning of the tests, the soil temperature was approximately 18° C near the ground surface and approximately 14° C at the 4.6 meter depth.

At the beginning of each test, a section of an existing temporary geomembrane was peeled back and the soil surface was exposed, after which the 3-meter diameter auger was positioned over the center of a treatment column (Figure 1) and the hood was placed on the ground surface. Auger rotation was initiated at approximately 5 revolutions per minute (rpm), and after penetration to a depth of approximately 0.6-meters, air injection was started. Then the auger was moved continuously down and up at a rate of approximately 0.3 meters per minute. The upper 2.1-meter-depth zone was treated during the initial 60 minutes of operation (Stage 1), after which penetration was continued to a depth of 4.6 meters and auger rotation was increased to approximately 10 rpm. Mixing and treatment of the 0.6- to 4.6-meter-depth zone (or the 6.6-meter-depth interval for cell D1) then followed for another 165 minutes (Stage 2). After a total of approximately 225 minutes of operation, treatment was terminated and the auger was removed from the subsurface.

Auger depth, offgas air flow rate and VOC content, soil vapor pressure and temperature were monitored by sensors and recorded by a computerized data acquisition system (DAS) at intervals of approximately 0.5 to 3 minutes. In addition to the DAS sensor data (Figure 2), soil matrix and soil gas samples were collected before and after *in situ* treatment for analyses of physical, chemical, and biological properties. Relevant aspects of offgas monitoring, pre- and post-treatment soil characterization follow, while details regarding the other process parameters monitored during the field test may be found elsewhere (Siegrist *et al.* 1995a). The treatment performance achieved as a result of 225 minutes of MRVS operation to a depth of 4.6 meters was computed using the results of soil matrix VOC analyses before and after MRVS (Siegrist *et al.* 1995a). The estimated reduction in soil concentrations for TCE and the summation of the seven target VOCs were computed for four depth intervals (0-0.9, 0.9-1.8, 1.8-3.0, and 3.0-4.6 meters) using the average concentration of VOCs measured at the sample depths of 0.3-0.6, 1.2-1.5, 2.4-2.7, and 3.9-4.2 meters, respectively. The pre- and post-treatment data were analyzed using statistical procedures employing classical descriptive statistics, as well as stochastic simulation methods developed in another facet of the overall project (West *et al.* 1993 and 1995).

RESULTS

GC/ECD analysis of the offgas samples showed that TCE, 1,1,1-TCA, and 1,1-DCE were predominant in the offgas, accounting for an average of 53, 25, and 18 percent

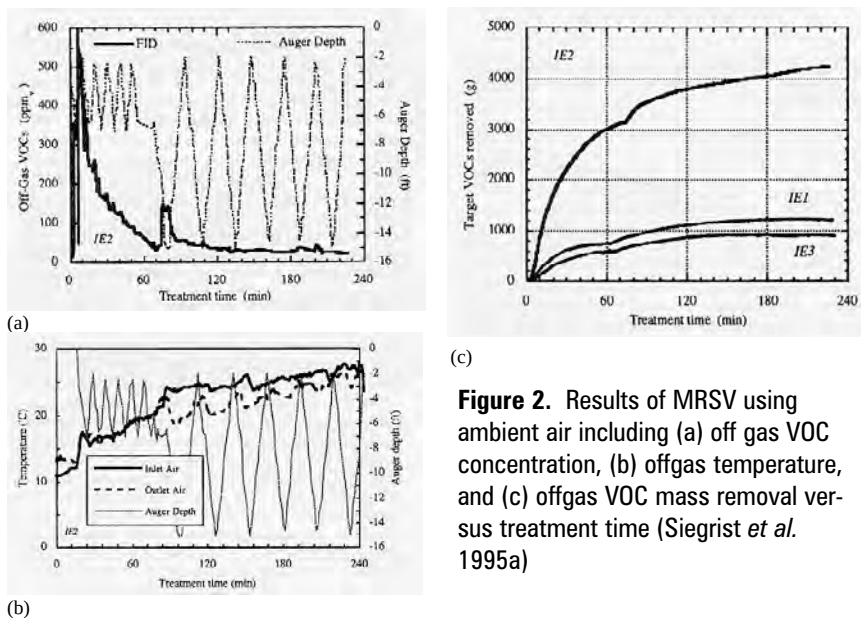


Figure 2. Results of MRSV using ambient air including (a) off gas VOC concentration, (b) offgas temperature, and (c) offgas VOC mass removal versus treatment time (Siegrist *et al.* 1995a)

of the offgas VOC ppmv content, respectively. This is consistent with the mass fraction of total VOCs as measured in the soil matrix throughout the MRVS test area (Siegrist *et al.* 1995a; West *et al.* 1995b). On average, the offgas VOC concentration measured by the FID was approximately 110 percent of the summation of target VOCs as determined by the GC. Some discrepancies between the FID response and the GC analysis of a discrete sample can likely be explained by a steeply rising or falling FID response at the time of discrete sample collection which normally took 1 minute or more. Based on these offgas data, the FID measurements were used to assess the removal of target VOCs during MRVS.

Inlet air temperature rose from 10° C to 25° C during ambient air MRVS, probably due to equipment heating during operations. Outlet air temperature also increased, following the same range and trend as the inlet air temperature (Figure 2b). During ambient air MRVS in the upper 2.1-m depth zone (Stage 1), the concentrations of VOCs in the offgas increased immediately upon air injection and then gradually declined (Figure 2a). Upon penetration to a depth of 4.6 meters (Stage 2), the VOC concentrations exhibited a similar response, although typically lower in magnitude. During MRVS, intermittent spikes in the offgas VOC concentrations were observed. These spikes appeared to be correlated with passage of the injection auger through certain depth intervals (see Figure 2). Removal of VOCs continued throughout the

entire treatment period, but at a gradually decreasing rate. The mass of VOCs in the offgas from each of the soil columns was estimated from the FID response curve and injected air flow rate for each column. Based on the total mass removed in the off-gas from the 4.6-meter deep columns, VOC removal efficiencies of approximately 50% were achieved during the initial 90 minutes of treatment, while ~85 percent was achieved after 140-180 minutes of operation. Based on the analysis of pre- and post-treatment soil matrix samples, the average VOC concentrations were reduced by approximately 92 percent due to ambient air MRVS (Siegrist *et al.* 1995a). Post-treatment soil samples collected from three locations within soil in the berm created over each column treated revealed negligible concentrations of VOCs.

During heated air MRVS, inlet air temperatures were maintained at approximately 130° C throughout the treatment process, while outlet air temperatures rose from 20 to 25° C. Concentrations of VOCs in the offgas rose immediately after heated air injection was initiated, but slowly declined during continued treatment of the upper 2.1-meter zone. Upon penetration to a depth of 4.6 meters and initiation of Stage 2 treatment, the VOC concentrations exhibited a similar response, but typically lower in magnitude. During upward/downward motion of the injection blade, intermittent spikes in the offgas VOC concentrations were observed. These appeared to correlate with passage of the injection blade through certain depth intervals. This was also observed for the ambient air MRVS columns. Removal of VOCs from the soil columns continued throughout the entire treatment interval, although the rate of removal declined with increasing treatment time. In the columns treated to a depth of 4.6 meters, VOC removal efficiencies were approximately 50 percent after the initial 90 minutes of operation and approximately 85 percent after approximately 120 to 150 min of operation. Analysis of the pre- and post-treatment soil VOC data indicated that the removal efficiency for a 4.6-meter-deep column treated by heated air MRVS was approximately 98 percent (Siegrist *et al.* 1995a).

During heated air MRVS to a depth of 6.7 meters in column D1, treatment operation was similar to that for the 4.6-meter-deep columns TE1 to TE3 (Table 2). However, with the estimated depth of water saturation at 4.1 meters, treatment within D1 included approximately 2.6 meters of saturated soil. VOC removal efficiency during heated air MRVS to a depth of 6.7 meters appeared to be approximately 88 percent lower than that achieved during treatment of the 4.6-meter-deep columns. This lower efficiency is speculated to be due to several factors, including reduced treatment time per volume of soil in the mixed region and treatment being done in saturated soil (that is, 2.6 meters of the 6.7 meter depth).

DISCUSSION

In the MRVS process, the air flow rate required (and the resulting pore volume throughput rate) is controlled by both the need for auger cutting fluid as well as for

stripping and advective removal of VOCs. Ideally, air flow rate should be established at the minimum required for auguring while providing adequate flow for removal of VOCs. Reducing the air flow rate from the 40 m³/min used in the field tests, to the 8.5 m³/min rate used in companion laboratory studies (West *et al.* 1995a) may not have adversely affected VOC removal rates. However, a lower air flow rate was not possible in the field due to the need for higher air flow rates to enable auger mixing under full-scale field conditions. During all of the MRVS tests, the concentrations of VOCs in the offgas gradually declined with increasing treatment time. However, there were intermittent spikes in concentration that appeared to be correlated with passage of the injection auger through specific depth intervals. Presumably, these depth intervals were contaminated at higher concentrations, and the passage of the injection blade through this zone resulted in higher advective removal rates. Removal of VOCs generally continued throughout the entire treatment period, but at a gradually decreasing rate. These results suggested that volatilization and advective VOC removal were principally occurring from zones proximal to the auger and the injected air source, while diffusive transport (for example, from intra-aggregate pores of the fine-grained matrix) may have been dominant in regions distal from the auger. Moreover, this suggested that with increasing percent removal of the mass of VOCs initially present, continuing removal became increasingly mass-transfer limited. This effect is consistent with prior observations concerning matrix diffusion and mass-transfer limitations in fine-grained soils.

In this study, the pre- and post-treatment concentrations of VOCs were estimated by collection and analysis of 28 and 32 soil samples, respectively, from each set of treatment columns or approximately 1 sample per 0.3 m³ of treated soil. Based on these data, the average VOC removal efficiency for MRVS to a 4.6-meter depth was approximately 92 percent for ambient air and approximately 98 percent for heated air while MRVS to 6.7-meter depth with heated air was lower at approximately 88 percent. These estimates are based on statistical analysis of the pre- and post-treatment soil matrix samples, where results for IE1-IE3, TE1-TE3, and D1 were combined, respectively. Given the similar behavior in offgas VOC removal, this treatment of the data was judged appropriate. Efforts to complete material balances for the VOCs within each of the individual treated columns (that is, comparison of the estimated mass in the offgas to that lost from the soil) was not possible. This is due to the limited number of pre- and post-treatment soil samples collected and analyzed from each individual soil column.

MRVS represents an aggressive approach to *in situ* treatment of contamination in fine-grained deposits. Mixing of the subsurface while simultaneously injecting high volumetric flow rates of air provides intimate contact between the stripping gas and the volatile contaminants within the media. In fine-grained media characterized by preferential pathways (such as fractures) and VOCs diffused into matrix blocks, this approach may prove to be the only way to rapidly and extensively treat high percentages of contaminants from the subsurface. While MRVS works well with

volatile contaminants like TCE, it may be feasible to reduce treatment time and/or increase removal efficiency of less volatile compounds as well. For example, treatment agents could be introduced into the mixed region in combination or following MRVS to enhance treatment of other non-volatile contaminants. Particles containing slow-release nutrients and electron acceptors could be dispersed to facilitate secondary bioremediation. Particles or fluids could also be introduced to oxidize (such as hydrogen peroxide or permanganate) and/or reduce (such as zero valence metals) TCE as well as other organics and metals.

While high VOC removal efficiencies were measured in these MRVS trials and meet performance expectations for the MRVS in the field test, the residual VOC concentrations were still typically above 1 mg/kg. The impact of these high, but incomplete, VOC removal efficiencies on associated groundwater contamination remains unanswered. This is a critical but complex issue that is increasingly being confronted as the performance of various *in situ* treatment processes are being assessed, and their performance and costs are being weighed against the benefits gained in risk reduction.

CONCLUSIONS

Based on the results of these full-scale field experiments, MRVS appears to be a viable process for *in situ* stripping of TCE and similar VOCs from fine-grained media. *In situ* mixing of dense silty clay soil was accomplished with auger rotation rate and vertical movement controlled, while simultaneously injecting air at a desired rate, pressure, and temperature, and capturing and treating the resulting offgases. Compared to ambient air (at approximately 15-25° C), the use of heated air (at approximately 120-130° C) appears to offer modest improvement in removal efficiency, likely due to a limited increased energy input that may heat soil surfaces at the injected air/soil aggregate contact point, and thereby enhance volatilization rates. The magnitude of this thermal enhancement will be likely be controlled by the properties of the target VOCs and soil matrix. VOC removal following active MRVS may occur as a result of the disruption of the subsurface and the resulting increased permeabilities, as well as the potentially elevated matrix temperatures that persist. This may enhance volatilization as well as degradation processes for some contaminants.

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PHYTOREMEDIATION OF PETROLEUM CONTAMINATED SOIL

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INTRODUCTION

Phytoremediation of soil contaminated with petroleum hydrocarbons has received considerable attention in the laboratory and in the field. Several field studies have been reported with similar results (Qiu *et al.* 1997; Banks *et al.* 1997a, b, and c; Kulakow *et al.* 1998). Flathman and Lanza (1998) have reviewed some of these studies. The objectives in the field studies have been to investigate the effectiveness of phytoremediation and the fate of petroleum hydrocarbons especially polynuclear aromatic hydrocarbons. Qiu *et al.* (1997) carried out their field study at the Union Carbide Seadrift Plant in Texas in cooperation with faculty and students at Utah State University. Banks and coworkers have carried out several field studies including East Coast sites, a Gulf Coast site, and West Coast sites. In addition to faculty and students at Kansas State University, professionals from major oil companies have assisted with the projects.

SETTINGS

The investigation by Qiu *et al.* (1997) was in a clay soil (51-61 percent clay) at the olefins production area. Banks and coworkers have addressed a crude oil pipeline spill in an agricultural field in Texas, contaminated soil at an oil refinery in California, and a sandy loam soil at a U.S. Navy fuel terminal near Norfolk, Virginia. The hydrogeologic characteristics of the sites varied from near-wetland conditions to sites where irrigation was needed. In the work of Qiu *et al.* (1997), polynuclear aromatic hydrocarbons (PAHs) ranged from 0.1 to 5 mg/kg soil. At the fuel terminal, Banks *et al.* reported initial total petroleum hydrocarbons (TPH) ranging from 3,036 mg/kg to 7,923 mg/kg soil. At the California refinery site, initial TPH values ranged from 2,211 mg/kg to 13,564 mg/kg soil. In many of these case studies, there was great variation of contaminant concentration with position.

REMEDIATION

The methods were similar in each of these studies, in that vegetated plots were established, and the growth of the vegetation and associated contaminant degradation was followed as a function of time. Generally, an unvegetated plot was included to provide data on natural bioremediation without the benefit of vegetation. Qiu *et al.* (1997) used a 2X7X2 nested design with three sources of variation and ten

replicates. The factors of depth, time since planting, and control versus planted plots provided the variation. Prairie buffalograss was used in the vegetated plots. The field samples were extracted by Soxhlet extraction and analyzed for PAHs using gas chromatography/mass spectrometry (GC/MS). In another study, 12 different warm-season plant species were compared.

At the Gulf Coast site, Banks and coworkers used sorghum, legume/St. Augustine grass, rye, and Pensacola Bahia grasses, and an unvegetated plot. In California, they used tall fescue, an erosion control mixture of cool-season grasses, a mixture of perennial native grasses, and an unvegetated plot. At the Navy site, white clover, tall fescue, bermudagrass, and an unvegetated control were investigated. In some investigations, only TPH results were obtained, while in other cases, PAH compounds were also measured using GC/MS.

Qiu and coworkers sampled at two different depths. Because of the great variation with position 10 replicates were used so that each mean value is the average from 10 samples. The variations among field samples is the most significant source of variation in all of these studies.

RESULTS

With buffalograss, Qiu and coworkers found that the unvegetated plots performed as well as the vegetated plots. When the 12 different plant species were compared at the end of a three year study, Verde kleingrass was found to be far superior compared to the other plant species and the unvegetated control. The measured concentrations of PAHs for the plots of Verde kleingrass were either nondetectable or approximately one or two orders of magnitude lower than the unvegetated control and the other grass species (Qiu *et al.* 1997). The kleingrass developed dense roots which were healthier and deeper than the other grasses. This study shows that plant species selection can be very important. Qiu and coworkers examined the shoots and roots for bioconcentration of PAHs and did not find any evidence of increased concentration.

For the Gulf Coast crude oil spill, Banks *et al.* (1997a) found that it was necessary to replant some plots because of flooding and climatic events. In September, one month after the initial seeding, the legume plot was reseeded with sweet clover, and the Pensacola Bahia grass plot was overseeded with ryegrass. Seven months later, in April, the legume plot was planted with St. Augustine grass. The final results, after 21 months, are given in Table 1. Based on these results, the responsible party seeded the entire bioremediation area in annual ryegrass in May 1996.

For the California site, results are shown in Table 2 for TPH, after 29 months, and benz(a)pyrene, after 15 months. The percentage degradation for benz(a)pyrene was greater in the vegetated plots. Total petroleum hydrocarbon degradation percent-

TABLE 1

Percent reduction of total petroleum hydrocarbon concentration after 21 months at the Gulf Coast site where crude oil was spilled. Data of Banks *et al.* (1997a).

Sorghum	34
Legume/St. Augustine grass	43
Grasses	46
Unplanted	17

TABLE 2

Percent reduction of total petroleum hydrocarbon and benz(a)pyrene concentrations at the California refinery site. TPH results are after 29 months, while benz(a)pyrene results are after 15 months. Data from Kulakow *et al.* (1998).

Native grasses	37	53
Erosion control mixture	55	56
Fescue	31-62	55
Unvegetated	44	42

ages were influenced more by spatial variation in initial TPH concentration than vegetation type. All plots showed decreasing hydrocarbon concentrations, and the vegetated treatments were not statistically differentiated from the unvegetated treatment.

The results for the U.S. Navy fuel terminal are similar. After 23 months, TPH concentrations were reduced by 50 percent in the clover plots, compared to 31 percent in the unvegetated plots.

Risk reduction is achieved with phytoremediation. In these studies, the PAH compounds do not move up into the plant leaves and shoots to any significant extent. Furthermore, the organic matter added to the soil acts as sorption sites for the contaminants. The cost of phytoremediation is of the order of \$10 to \$20 per ton of soil. The cost depends more on monitoring costs than on the cost to establish and maintain the vegetation. Vegetation can be established for about \$100 per acre on large plots where irrigation is not required.

DISCUSSION

In these studies, the biodegradation process appears to have been continuing when the experiment was terminated because of the length of time allowed for the study.

Only in the case of Qiu *et al.* (1997), with Verde kleingrass, was the experiment carried to the nondetectable level. From these studies, it is clear that phytoremediation requires several years to achieve the desired reductions in many applications. A positive feature of phytoremediation is that the planted vegetation may act to contain the contaminants within the region where they are found by evapotranspiring any precipitation which infiltrates the soil. Vegetation also reduces soil erosion associated with surface water flows.

CONCLUSIONS

Phytoremediation has been demonstrated to be a valuable technology that can be applied where biodegradable contaminants are present in soil. Several years are required for biodegradation of many petroleum compounds, especially PAHs. Phytoremediation is inexpensive and worthy of further investigation. The best plant species for many contaminants and the fate of many compounds remain to be investigated.

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8

Remediation of Inorganic Contamination in the Vadose Zone

Eric Lindgren and Jim Phelan

INTRODUCTION AND GENERAL BACKGROUND

In situ remediation of inorganic contaminants is the focus of this chapter. Inorganic contaminants primarily include heavy metals (such as chromium, lead, and mercury), radionuclides (such as uranium, plutonium, and strontium), and a few problematic others (such as nitrate and perchlorate). The *in situ* remediation of inorganic contamination in vadose zone soil is a difficult task, but, in general, three types of remedial actions are possible: removal, stabilization, or natural attenuation. Examples of these actions appear in Table 8-1. Note that physical and chemical barriers may provide a viable option for inorganic contamination, but are not discussed here. For a detailed discussion on barriers and containment methods, see Chapter 9.

The vadose zone basically consists of porous soil (solid phase) in which the pores are filled with either air or water (vapor and liquid phases). Capillary action ensures that the smallest pores are filled with water first, while the larger pores are initially filled with vapor (see Chapter 3). As the moisture content of vadose zone soils increases, water resides in larger and larger pores, which explains the strong

TABLE 8-1 Examples of *in situ* remedial options for inorganic contaminant remediation.
(Adapted from EPA 1997.)

<i>In Situ</i> Remedial Action	Examples	Status	Issues
Enhanced removal	<i>In situ</i> flushing	Field-tested	Capture efficiency
	Electrokinetics	Field demo	Cost
	Phytoextraction	Field demo	Removal rate
	Biodegradation	Varies	Limited applicability
Stabilization	<i>In situ</i> vitrification	Commercial	Cost/performance
	Deep soil mixing	Commercial	Adequate mixing/ coverage
	Jet grout	Field-tested	Coverage
	Gaseous reduction	Field-tested	Treatment uniformity
	Phytostabilization	Lab testing	Long-term maintenance
Natural attenuation	Radioactive decay	Well-established	Time period
	Metals sequestering	Under evaluation	Bioavailability/ monitoring costs

dependence of unsaturated hydraulic conductivity on moisture content. The hydraulic conductivity of low-moisture content soils is very low because the water is restricted to moving through the smallest pores. At moisture contents below 10 percent by weight, the hydraulic conductivity of a sandy permeable soil is like that of a saturated clay, and movement in the vapor phase is less restricted than is movement in the liquid phase.

While many organic contaminants are found in either the air- or water-filled pores, inorganic contaminants are found in the water-filled pores or strongly associated with the soil surfaces. Because the vapor pressure of most inorganic compounds is nil at ambient temperatures (with the notable exception of metallic mercury), the vapor phase cannot be used as a vehicle for their removal. Additionally, most inorganic contaminants (for example, heavy metals and radionuclides) cannot be destroyed. In general, the most useful methods for *in situ* remediation of

organic contaminants, destruction (biodegradation) and vapor phase extraction, are not useful for inorganic contaminants. Accordingly, *in situ* remediation of inorganic contamination must rely either on the slow movement of the contaminant through the vadose zone soil liquid phase or on conversion and incorporation of the contaminant into a stable solid phase (thereby reducing risk of exposure or inherent toxicity).

TECHNICAL CHALLENGES

All *in situ* remediation technologies, whether implemented above or below the water table, must deal with the great physical uncertainty resulting from the heterogeneity of subsurface soils. Heterogeneity results in preferential flow paths through the more permeable portions of the soil and the potential bypass of large volumes of lower permeable soil. Any technology that relies on the pressure-driven fluid flow of liquid or vapor to remove contaminants or to deliver reagents can be plagued by this problem. The result is an initial rapid response, followed by slow, drawn-out tailing as slow flow and diffusion into or out of small pores dominates.

A related challenge common to *in situ* remediation technologies involves the spatial and temporal scaling of the method. Many innovative, emerging technologies work well and in a predictable manner for short periods of time under laboratory conditions. However, long-term operation effects are difficult to study at the bench scale. Operation under field conditions for longer time periods sometimes results in diminished efficiency and predictability. The scale of the field deployment relative to the scale of the site heterogeneity is an important consideration and often points to the need for field-scale testing. Only after field testing can a knowledge base for required site characterization be developed.

Chemical uncertainty in the subsurface is another challenge confronting most *in situ* remediation technologies. Geochemical reactions can retard or prevent contaminant movement. Under such conditions, removal will require mobilizing agents. Geochemical reactions can also result in the reversal of existing *in situ* stabilization schemes. Careful consideration of the geochemical character of a given site is vital when considering remedial options. Important questions to consider are as follows:

- If a mobilizing agent is required, is the risk posed by the sequestered contaminant truly great enough to warrant remobiliz-

ing it for removal? (In other words, what is the bioavailability and toxicity of the contaminant in the sequestered state?)

- If *in situ* stabilization is an objective, will the geochemistry support the stabilized form now and in the future? And if so, are there any natural geochemical reactions that would lead to the same end-point without engineered intervention?

Another challenge occurs when organic and inorganic contamination are co-located. The treatment of organic contamination can affect the mobility and treatability of inorganic contamination. For example, there are situations where the contamination problem is primarily with organic contamination with lesser amounts of inorganic contamination. Bioremediation of the organic portion of a contamination problem can result in a redox change of a heavy metal contaminant and thus increase or decrease the mobility or leachability of the heavy metal. Situations where treatment of organic contamination could exasperate an inorganic contamination problem must be fully understood. At the same time, opportunities to achieve remediation of inorganic contaminants along with the remediation of organic co-contaminants, such as the sequestering of a heavy metal or consumption of nitrate, should not be missed.

ENHANCED REMOVAL

Complete removal of heavy metal and radionuclide contamination from the subsurface is highly desirable because it eliminates the possibility that the contaminants may remobilize in the future. However, for many of the reasons discussed earlier, removal of heavy metal and radionuclide contamination from vadose zone soil is a difficult task. Many metals precipitate, strongly adsorb, or are otherwise sequestered in the solid phase of the soil and require a mobilization step to bring the contaminants into the liquid phase. And even then, the low unsaturated hydraulic conductivity of vadose zone soils thwarts efforts to hydraulically move out dissolved contaminants. Nonetheless, several technologies for enhancing the removal of contaminants from vadose zone soils are under development:

- Physical/chemical methods: Soil flushing essentially washes contaminants from the vadose zone into the groundwater, where it is removed by pump-and-treat technologies.

- Electrochemical methods use electrical gradients, rather than hydraulic gradients, to remove contaminants through the liquid phase of vadose zone soils.
- Biological methods: Phytoremediation uses plants to extract contaminants from the vadose zone through root systems, accumulating the metals in the biomass of growth. Biodegradation is another biological process that can destroy non-metallic inorganic contaminants such as nitrate or perchlorate.

Each of these technologies is addressed in more detail in the following sections.

PHYSICAL/CHEMICAL METHODS

In Situ Soil Flushing

Soil flushing is the injection or infiltration of aqueous mobilizing solutions into the contaminated soil (saturated or unsaturated) followed by the downgradient collection of the mobilized contaminant and excess mobilizing agent in the groundwater (as shown in Figure 8-1). Water-soluble, inorganic contaminants like chromate, nitrate, or perchlorate might be removed from vadose zone soils with water flushing alone. For less soluble metals, aggressive chemical flushing agents (or lixiviants) may be required. More aggressive solutions include acids or bases that alter the soil pH, chelating agents that make the contaminant more soluble, reducing or oxidizing agents that convert the chemical form of the metal to a more soluble form, or ionic solutions that displace the toxic ion with a nontoxic ion. In most instances, collection techniques rely on standard pump-and-treat systems in underlying aquifers. The pump-and-treat system is an extremely important component in an *in situ* flushing system because it can ensure that mobilized contaminants (and the mobilizing agent) are completely captured. However, if complete capture cannot be achieved by hydraulic control alone, physical containment (for example, sheet pile or slurry walls) may be required at considerable expense.

In situ flushing has generally been applied below the water table and can usually be considered an enhancement to pump-and-treat methods. The overall process usually includes aboveground treatment of the col-

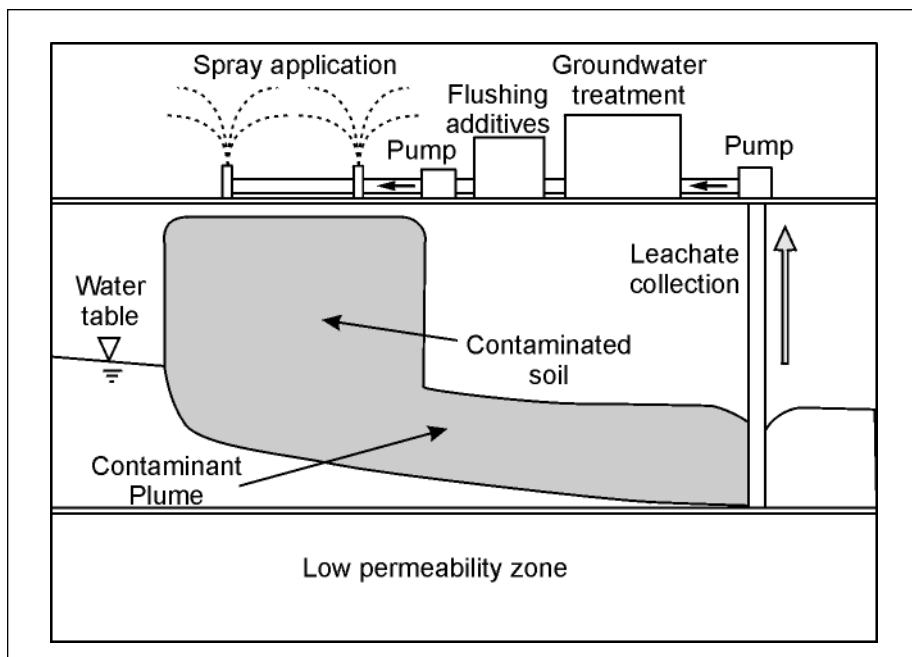


Figure 8-1. Schematic of soil flushing for thin vadose soils.

lected solutions to remove the contaminant and to recycle the mobilizing solution. For metals, the treatment system may include precipitation/flocculation systems, ultrafiltration, or electrochemical or ion exchange systems. The reuse of the extracted solution (provided state regulations allow it) is important to reduce disposal costs. Even when reinjection is permitted, in order to maintain efficient hydraulic control, the amount of solution extracted must always exceed the amount injected. This means that some provision must always be made for disposal of extracted solution.

Project success can be monitored by measuring the contaminant removal as a function of the pore volumes of flushing agent applied and removed. Overall performance can be verified through analysis of soil core samples before and after flushing. Once the recovery system has been shut down, it may be necessary to cap the site to prevent residual contaminant migration by controlling infiltration (EPA 1997).

Only a few field projects for metals treatment have taken place. The majority of these included water flushes and were limited to flushing saturated soils. While the two examples discussed below are for saturated soils, they illustrate the scales involved (both spatial and temporal) and highlight some issues with *in situ* flushing of metal contamination.

An arsenic remediation project is thought to be the first full-scale project in the United States in which a flushing additive (non-nutrient) was used to enhance contaminant recovery. The site, owned by Gulf Power in Lynn Haven, Florida, has a shallow aquifer (5 to 25 feet below ground surface) contaminated with an arsenic-based herbicide. *In situ* flushing of the aquifer began in November 1994 using 14 wells for either extraction or injection. The wells were pumped at 10 gpm, and the water was treated, supplemented with additives, and re-injected. Citric acid was originally used as the flushing additive but was replaced by a proprietary compound. Using the flushing additive, contaminant removal appeared to be twice as efficient as an unenhanced pump-and-treat method. Assurances had to be made to the regulatory agency that the proprietary additives used were benign. Details can be found in an Electric Power Research Institute (EPRI) report by Redwine *et al.* (1997).

Another, apparently successful, full-scale implementation of soil flushing for metals occurred (and is ongoing) at the United Chrome Products Superfund site in Corvallis, Oregon, where the EPA began remediation in 1985. At this 8-acre site, surface water, soil, and groundwater were contaminated by hexavalent chromium. Two water-bearing zones, separated by a clay aquitard, lie under the site. High concentrations of chromium (VI) are found in the upper zone (up to 19,000 ppm), in the aquitard, and in the lower aquifer (up to 223 ppm). The lower aquifer consists of sand and gravel and supplies water for commercial and residential use. Over time, a flushing system has been established, consisting of 2 infiltration basins, 1 infiltration trench, 23 groundwater extraction wells in the upper aquifer, injection and extraction wells in the lower aquifer, and an onsite treatment system for the chromate-laden waste stream (Roote 1998).

Groundwater is extracted from the upper aquifer, treated to remove the chromate contamination, and injected into the lower aquifer. This procedure produces an upward hydraulic gradient that flushes the contamination from the lower aquifer into the upper aquifer through the aquitard. Between 1988 and 1996, 58 million gallons of groundwater

were extracted, and 31,200 pounds of chromium (VI) were removed (EPA 1997). While the approach is working to remediate the site, the results are highly variable and depend on the well location. Because of highly variable yields of the extraction wells, some areas are flushed more rapidly and completely than others (Roote 1998).

***In Situ* Flushing and Vadose Zone Soils**

When vadose zone soils are considered for treatment, they are usually adjacent to and actively impacting an aquifer. It is reasonable to assume that flushing contaminants through previously uncontaminated vadose zone soils and into a previously uncontaminated aquifer for recovery would meet with unfavorable scrutiny. For *in situ* flushing to be conducted entirely in the vadose zone, a suction lysimeter extraction system would be required. While the technology for such systems theoretically exists, no one has demonstrated the high degree of extraction efficiency required to completely capture contaminants and additives. Without physical barriers, the thickness of vadose zone soils that can be treated by *in situ* flushing is limited because of uncertainties in predicting flow paths. It is difficult to determine with certainty where the flushing solution will enter the aquifer, so the thickness of vadose zone soil treated must be small compared to the dimensions of the aquifer area under hydraulic control. This ratio limits application of *in situ* flushing to the vadose zone soils immediately above the water table. For thick vadose zones, soils just above an aquifer can be flushed using vertical or horizontal injection wells or by raising the water table around the point of solution injection with injected solution. For thin vadose zones, treatment may extend to the ground surface (as shown in Figure 8-1) and the flushing solution can be applied using surface flooding, sprinklers, leach fields, and trench or basin infiltration systems. Furthermore, heterogeneity and flow instability in the vadose zone complicates the likelihood of uniform soil treatment. Thus, special consideration must be given to the issue of contacting the flushing fluid with the contaminated soil.

A soil flushing approach is under consideration (through the Innovative Treatment Remediation Demonstration (ITRD) program for strontium-90 remediation in the aquifer and vadose zone at the 100N Area of Hanford. Strontium-90 is a fuel processing fission product with

ficient is 15 to 20). The aquifer and vadose zone soils about 10 meters above the aquifer are being considered for *in situ* flushing using a proprietary, non-toxic, lixiviant mixture to mobilize the strontium. A number of lixiviant systems have been considered in bench-scale testing using uncontaminated soil samples from the area. A lixiviant system has been identified that reduces the partitioning coefficient for Sr to much less than one and is somewhat selective for strontium over calcium. The nature of the lixiviant system has been disclosed to the appropriate regulators, who are apparently willing to consider its use for strontium-90 removal at this site.

Technical Issues with Soil Flushing

There is some reluctance to use additives in the flushing solution because of concern over the solution's toxicity and capture efficiency. The unstable behavior of unsaturated flow and the heterogeneous nature of vadose zone soils and aquifers make it very difficult to achieve complete capture and containment of the mobilized contamination, and there is considerable concern about unknowingly exacerbating the problem. Selection of a mobilizing agent is extremely site- and contaminant-specific. Additives that effectively mobilize a contaminant and work well in one soil may chemically attack another soil and lead to remediation failure. In a column study using ethylenediaminetetraacetic acid (EDTA) to enhance lead removal from carbonate-rich soil, the formation of preferential flow channels severely limited the contaminant removal efficiency (Garcia-Delgado *et al.* 1998). It might be expected that this effect would be more severe in a 3-D field system. Bench-scale testing using actual contaminated soil samples is required to screen additives with confidence.

In addition, it is not always possible to re-inject treated groundwater because of regulatory concerns and constraints. The cost of required containment systems and disposal of treated groundwater can make *in situ* flushing economically impractical. The development of acceptable additives with low toxicity may alleviate many of these concerns.

ELECTROCHEMICAL METHODS

Electrochemical methods offer techniques to remove ionic contamination from soil (saturated or unsaturated) and avoid the problems

associated with soil flushing. Here we will focus on electrochemically-induced transport, and not on electrochemical destruction (which finds application in *ex situ* treatment technologies). Electrochemical contaminant transport uses an electrical gradient rather than a hydraulic gradient. The rate of transport is a function of the soil's electrical conductivity rather than hydraulic conductivity. Unsaturated hydraulic conductivity is a strong, nonlinear function of the pore-size and water distribution in the soil and can vary by many orders of magnitude in a given remediation region. This variation is the root of the heterogeneity problem that plagues other *in situ* remediation processes. In contrast, electrical conductivity is a function of moisture content and the concentration of ions in the system, and does not depend on the soil pore-size distribution. While the electrical conductivity of soil varies, it is generally within a single order of magnitude.

To perform electrochemical remediation, anode and cathode electrodes are placed in the soil, and direct current is applied between the electrodes, as illustrated in Figure 8-2. The important phenomena that occur are depicted in Figure 8-3. The electrolysis of water produces acid at the anode and base at the cathode. The applied current transports

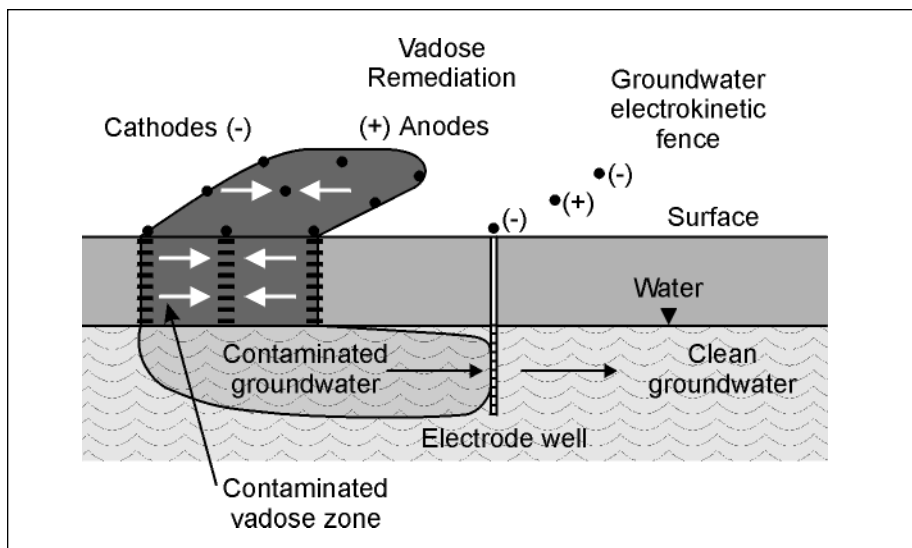


Figure 8-2. Schematic of electrokinetic implementation.

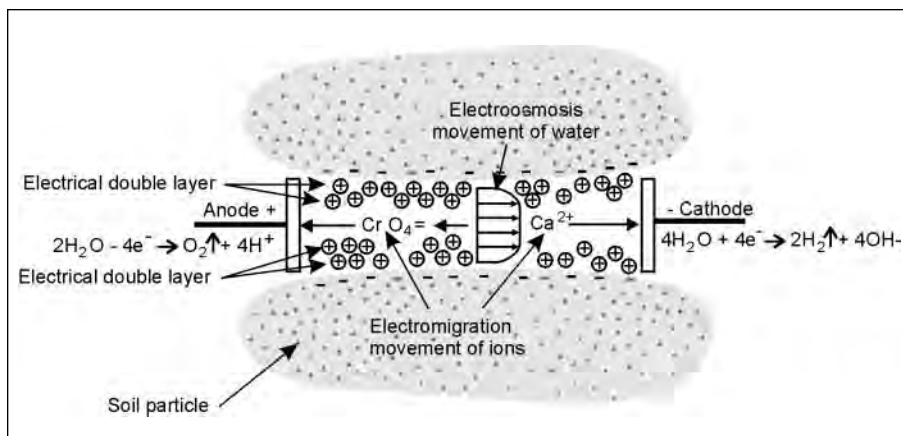


Figure 8-3. Electrokinetic phenomena.

dissolved ions towards the appropriate electrode in a phenomenon called electromigration. The soil water also moves in response to the electric field, in a process called electroosmosis. Typically, soil water is transported towards the cathode because of the high density of cations attracted to the negative surface of the soil. The net movement of ions near the pore surface toward the cathode imparts momentum to the water and leads to all the water in the pore moving towards the cathode at the same velocity. Note that both electromigration and electroosmosis operate independent of pore size.

Electromigration and electroosmosis, as the principal electrokinetic transport mechanisms exploited by electrochemical remediation methods, are often referred to as electrokinetic remediation. Typically, electromigration velocities are an order of magnitude faster than electroosmotic velocities, and horizontal electroosmotic velocities can be an order of magnitude greater than vertical unsaturated hydraulic velocities. Figure 8-4 illustrates the relative magnitude of flow rates of an anionic dye: the measured electromigration and electroosmosis flow rates, and the calculated, vertical unsaturated flow rate based on hydraulic characterization data. Once contaminant ions reach an electrode, they can be captured (by methods such as electroplating, ion exchange, or adsorption) or extracted to the soil surface for further treatment and disposal.

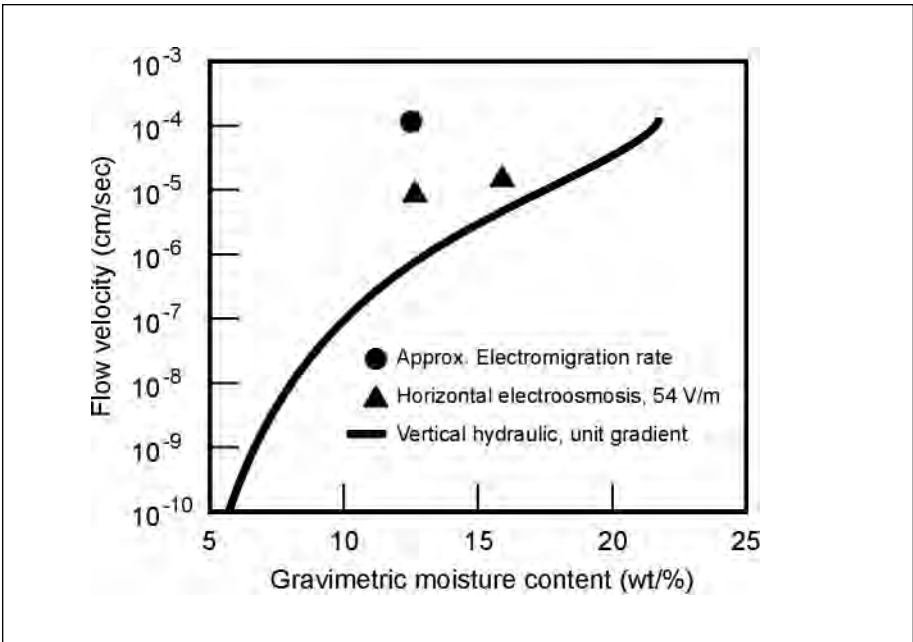


Figure 8-4. Relative migration rates of electromigration, electroosmosis, and unsaturated hydraulic flow.

History of Electrokinetics

Electrokinetic phenomena have been studied for a long time (Reuss 1806). A review of the evolution of electrokinetic remediation indicates a focus on fine-grained saturated soils (that is, saturated clay-like soils). Electrokinetic techniques have been used extensively to stabilize soft soils (Casagrande 1949, Nikolaev 1962) and to achieve other dewatering operations (Sprute and Kelsh 1980 and 1982; Lockhart 1983a,b, c and 1986; Sunderland 1987). Sprute and Kelsh (1980, 1982) describe electroosmosis scenarios to dewater mine tailings. Lockhart (1983a,b,c) studied the dewatering of kaolinite clay. The notion that electrokinetic phenomena may be applicable to hazardous waste remediation appears to stem from the work of Segall *et al.* (1980), who found that dewatering dredging sludges electrokinetically led to extracted water rich in heavy metals. Ironically, they considered this to be an inhibition to the

use of electrokinetics in the field, since it produced a toxic liquid waste that required further treatment.

By the mid-1980s, numerous researchers, apparently simultaneously, realized that separations of heavy metals from soils posed a potential contamination solution rather than a potential contamination problem. Mitchell (1986) and Renaud and Probst (1987) described the possibility for removing contaminants by electroosmosis from fine-grained saturated soils. Shapiro *et al.* (1989) described removing small organic contaminants from columns of saturated clays in the laboratory. In similar bench-scale experiments, Acar *et al.* (1989) and Hamed *et al.* (1991) describe the removal of heavy metals from clays. In each of these experiments, the concept has been to convect contaminants with water using electroosmosis as the separation mechanism.

Electrokinetic Remediation in the Vadose Zone

The initial emphasis on fine-grained saturated or nearly saturated soils led to a misconception that electrokinetics was not applicable to unsaturated sandy soils, even though experimental work (albeit limited) has documented its feasibility. Runnells and Larson (1986), as well as Dahab *et al.* (1992), demonstrated electrokinetic transport of copper to the cathode electrode in unsaturated sands, without, however, considering whether electromigration or electroosmosis was the transport mechanism. Lindgren *et al.* (1994) demonstrated the electromigration of anionic food dye and chromate through unsaturated fine-grained sand to the anode electrode and Mattson and Lindgren (1995) experimentally demonstrated chromate migration and removal from unsaturated sandy soil at the laboratory scale. Using the same experimental set-up, Booher *et al.* (1997) demonstrated the electrokinetic extraction of uranium from unsaturated soils using citrate as a complexing agent. The citrate was introduced at the cathode by buffering the base formation with citric acid, and the uranium was removed at the anode as an anionic complex. In control experiments using acetate (which does not form anionic complexes with uranium), essentially no extraction of uranium was observed. Electrokinetic extraction of uranium was slower and less efficient than the electrokinetic extraction of chromate.

Controlling the rate of water addition at the anode is critical for the success of electrokinetic remediation in vadose zone soils. In unsatu-

rated sandy soils, electroosmotic water transport causes an accumulation of water near the cathode and a depletion of water in the vicinity of the anode. The soil water at the anode must be replenished to maintain the electrokinetic process for long periods of time. Slotted well casings used in saturated soils are not suitable for use as anode casings in unsaturated sandy soils. Slotted electrode casings lose water to the soil by hydraulic flow, forming a saturated wetted bulb beneath the casing similar to that formed during vadose zone permeability measurements. After a saturated bulb is established, a steady flow of water will leave the ceramic casing. The rate of outflow depends on soil texture, well diameter, and height of water in the casing (Amoozegar and Warrick, 1986). In sandy unsaturated soils, and in situations where the ratio of the height of water to the radius of the well is large, the water outflow rate can be significant enough to hydraulically wash soluble contaminants deeper into the subsurface, which worsens the problem.

The method used by Mattson and Lindgren (1995) is the only electrokinetic method specifically designed to operate continuously in vadose zone soils. This method uses porous ceramic electrode casings, filled with solution held under tension by a vacuum. The electrode casings are essentially large suction lysimeters, providing engineered control of water movement between the solution in the electrode casing and the soil pore water. In the only field demonstration specifically targeting contaminated vadose soils, the method was successfully used to extract chromate ions (Lindgren and Mattson, 1998). The method is described in the case study cited below. The soil moisture content was on the order of 10 percent by weight (but spatially varied, ranging from 2 to 16 percent by weight) and the addition of significant amounts of water was not required. This method targets important soluble anionic species such as chromate, (CrO_4^{2-}), molybdenate (MoO_4^{2-}), selenate (SeO_4^{2-}), perchlorate (ClO_4^-), and radionuclides such as iodide ($^{129}\text{I}^-$) and pertechnetate, ($^{99}\text{TcO}_4^-$).

The case study "Electrokinetic Demonstration at the Unlined Chromic Acid Pit," by Eric Lindgren and Earl Mattson, summarizes recent chromate extraction efforts from vadose zone soils. See page 1279.



Technical Issues and Challenges

Some electrokinetic methods described in the literature are similar in that they target cationic heavy metals and rely on the acid generated at the anode to reduce the soil pH, and thus mobilize the contaminants (Lageman *et al.* 1989, Lageman 1993, Acar *et al.* 1989, Hamed *et al.* 1989, and Shapiro *et al.* 1989). The cationic metals are then collected at the cathode. Care must be taken to neutralize the base formed at the cathode (by the controlled addition of acid) so that the metals do not re-precipitate before the cathode is reached. This method suffers from a number of shortfalls. First, natural soils are usually highly buffered, and it takes a lot of acid to lower the soil pH. The amount of acid produced by the process is directly related to the amount of current applied to the electrodes. Accordingly, producing a large amount of acid requires the expense of a large amount of electricity. Second, the liberation of ions from the dissolution of precipitated solid phases in response to attempts to acidify soil has detrimental effects on the electrokinetic process. While this is also the mechanism by which many heavy metal contaminant ions are solubilized, an even larger amount of other, non-contaminant ions are also usually solubilized. This significantly increases the electrical conductivity of the pore water and thus decreases the current efficiency of the process. Third, the hydrogen ion is the most conductive ion in solution by a factor of five. This means that under acidic conditions, a significant part of the current will be carried by H^+ ions and not by the targeted heavy-metal ion. In other words, the current efficiency suffers even more.

Generally, the electrokinetic extraction of soluble, anionic contaminants is more efficient and predictable than that of cationic contaminants that require solubilization. The solubilization step adds a great deal of uncertainty to the overall process because it is highly dependent on the geochemistry of the site. It can also add significantly to the remediation time and expense of the process and require site-specific testing for optimization.

The economic viability of electrokinetic remediation has not been demonstrated for vadose zone extraction. As discussed in the case study cited above, electrokinetic extraction of chromate from vadose zone soils has been successfully demonstrated. However, attempts to increase the rate of extraction have been severely limited by soil heating. The only way to alleviate soil-heating problems is to reduce the current,

which slows down the remediation. The active nature of the vadose electrokinetic extraction process, with vacuum controls, water level controls, pH controls, among others, is not conducive to unattended operation over long periods of time (~1 year). A new and greatly simplified second-generation electrokinetic approach for chromate (CrO_4^{2-}) removal (described in Lindgren and Mattson 1999) is discussed in the next section. This method uses solid-state, contaminant-adsorbing anodes that allow passive, low-cost, unattended operation for long periods of time.

Improved, Passive Electrokinetic Method

In the new method, chromate is attracted into the anode where it is either reduced or adsorbed using commercially-available activated carbon. This approach exploits a number of unique properties of activated carbon. Activated carbon, a porous form of nearly pure carbon with extremely high surface area (500 to 2500 m^2/g), has the resistivity of a semi-conductive material. This moderate conductivity is vitally important because electrical current is conducted both as the flow of electrons through the carbon matrix and as the movement of ions in the carbon matrix pore fluid, which allows penetration and reaction of the contaminant ions throughout the carbon bed. Activated carbon is well-known for its ability to remove organic compounds from water. In the past 10 years, the removal of ions from solution has also been studied, with particular attention given to chromate (Alaerts *et al.* 1989; Bautista-Toledo *et al.* 1994; Moreno-Castilla *et al.* 1995; Perez-Candela *et al.* 1995). Recently, the chromate adsorption capacity of some activated carbons have been shown to be as high as 3.5 g Cr/g carbon at a pH of 1 (Perez-Candela *et al.* 1995).

In laboratory evaluations, soil spiked with chromium (VI) was cleaned from an initial level of 200 mg/kg to less than 0.3 mg/kg. The total chromium concentration detected in the activated carbon, as determined by x-ray fluorescence, was ~6000 mg/kg. This accounted for over 90 percent of the chromium (Lindgren and Mattson 1999). Per technetate is also known to be adsorbed by activated carbon at low pH, but has not been as extensively studied as chromate (Westrich *et al.* 1998; Gu *et al.* 1996; Yamagishi and Kubota 1989, 1993).

The anode design is similar to commercial-scale cathodic protection anodes. Cathodic protection anodes are often constructed by hanging a string of metallic anodes in an open borehole and filling it with petroleum coke, which is an inexpensive source of powdered carbon (Schrieber 1994). Cathodic protection anodes are widely used for preventing corrosion in structures such as bridges and pipelines. The purpose of the petroleum coke in cathodic protection applications is twofold. First, it distributes the electrical current to the soil with less contact resistance and lower current density. The moderately conductive nature of carbon allows efficient transition between electron conduction at the drive electrode surface and ionic conduction in the soil pore water. Second, it moves the electron transfer reactions away from the drive electrode and prevents accelerated deactivation by preventing oxygen gas formation on the electrode surface. Such installations are designed to passively operate for 20 years at the same electrode current densities and voltages as those used in electrokinetic remediation.

The anodes for the electrokinetic remediation can be installed in the same manner as cathodic protection anodes, except that activated carbon is used as a backfill. The activated carbon functions like the petroleum coke, but also adsorbs, concentrates, and reduces the contaminant ions. The acid generated at the anode lowers the pH and increases the adsorption capacity of the activated carbon for chromate (and pertechnetate as well). The cathodes for this method are bare, metallic rods (such as iron rebar or pipe) pneumatically driven into the ground. The cost for installing each cathode is very low. A large array of these simple cathodes is affordable. They can therefore be used in sufficient numbers to create an even distribution of current and minimize soil-heating problems. The low cost also makes it possible to install additional cathodes closer to the anodes as the remediation proceeds, which, in effect, “herds” the contaminants to the collection anodes. As the cathodes are moved closer to the anodes, the power efficiency of the process increases.

An additional application of the passive electrokinetic approach is as an electrokinetic fence for vadose zone soils. Unsaturated hydraulic flow transports the contaminant through an electric field that deflects the targeted contaminant ion to the collection electrode. This application may be useful for capturing the pertechnetate plume beneath the leaking Hanford tanks. Various concepts for pertechnetate plume capture under a leaking Hanford tank are shown in Figures 8-5 and 8-6.

Figure 8-5[a] shows the simplest-to-install electrode configuration. As in a typical remediation application, the electrodes are installed vertically in rows of anodes and cathodes. The idea is to place electrodes deeply enough below the tank and to impose an electrical gradient just large enough to ensure that the horizontal velocity of pertechnetate, due to the electric field, is 5 to 10 times greater than the vertical velocity due to hydraulic gradients. It is expected that only low level current will be required and that far fewer boreholes will be required than would be needed to place a reactive barrier under the tank (Westrich *et al.* 1998). With this configuration, however, the maximum travel distance can be large for the larger tanks.

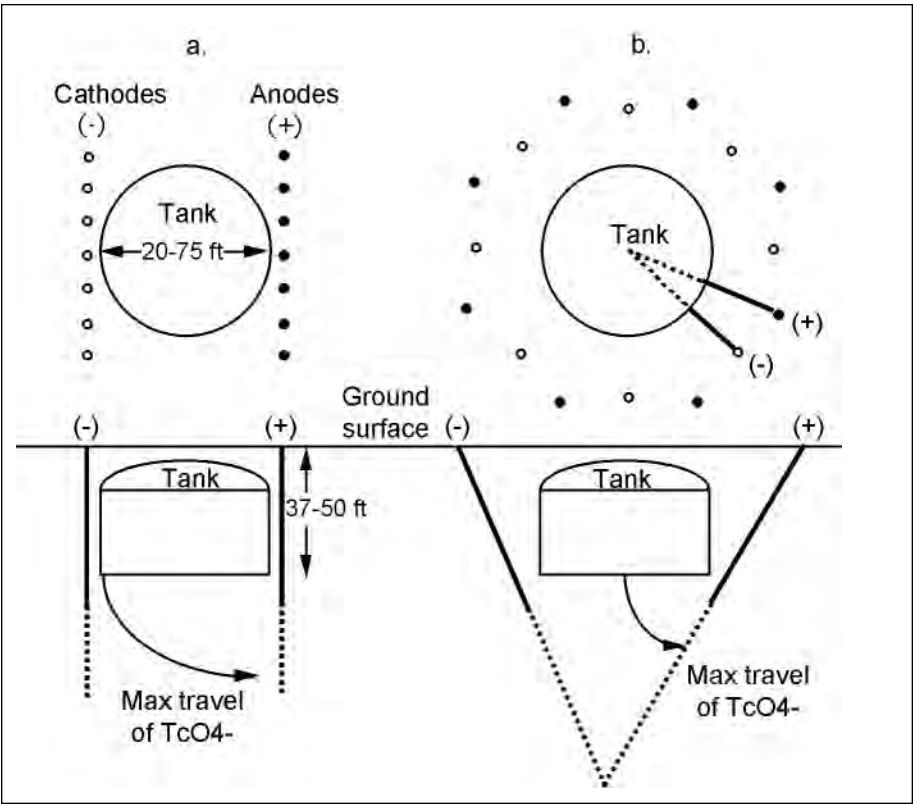


Figure 8-5. Electrode configuration schematics for the capture of pertechnetate leakage into vadose zone soils. (a) vertical electrodes (b) slant electrodes.

The horizontal boreholes are the most expensive to drill, however, and the installation of the anodes is the most complicated of all the methods.

BIOLOGICAL METHODS

“Phytoremediation” is the term for using plants to remediate soils contaminated with hazardous waste. Phytoremediation technology can be developed for a wide range of cleanup applications. The basic scheme is illustrated in Figure 8-7. For heavy-metal and radionuclide remediation of vadose zone soils, there are two types of phytoremediation: “phytoextraction” and “phytostabilization.” Phytostabilization is discussed in more detail in the stabilization section of this chapter. We will concentrate here on phytoextraction.

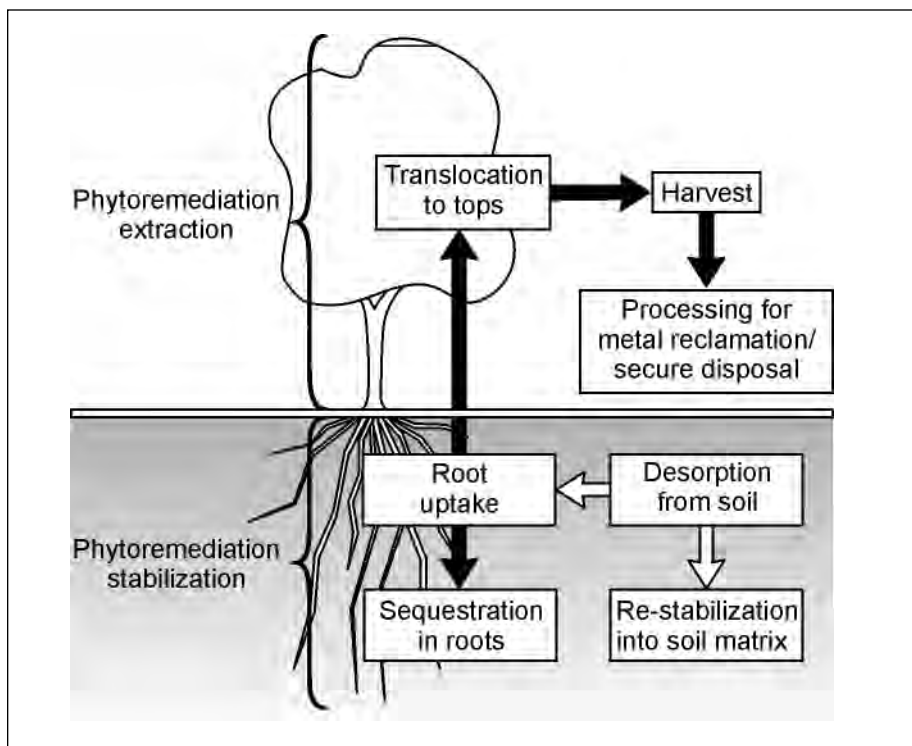


Figure 8-7. Schematic of phytoremediation (figure based on Cunningham and Berti, 1993)

In the process of phytoextraction, plants extract ionic contaminants from the soil through their root systems and store them in their above-ground biomass, which is periodically harvested and treated to reduce volume. The harvested biomass treatment can be microbial (composting), thermal (ashing or combustion), or chemical (extraction), and the value of reclaimed metals may provide an additional incentive for remediation (Cunningham and Ow 1996).

The root system of a plant can develop enormous surface area in contact with soil that adsorbs and accumulates moisture and essential nutrients. Plants excrete a variety of compounds through the roots that affect the root-soil environment by serving as nutrients for soil microorganisms and by forming stable metal-chelates. Through complex metabolic processes, plants selectively extract and absorb contaminant ions from the soil. Plants (and animals) require trace amounts of many metals such as iron, zinc, manganese, copper, nickel, chromium, and molybdenum. Many of these required micronutrients are toxic at higher concentrations, so the cellular concentration in a plant must be regulated. Some plants have genetically adapted to grow in soils containing toxic levels of metals. Most metal-tolerant plants successfully exclude the uptake of toxic metals, but some take up large amounts of toxic metals that accumulate in the plant biomass (Raskin *et al.* 1994). Depending on the degree of accumulation, these plants are referred to as accumulators (when the level of accumulation is about 10 times higher than normal) and hyperaccumulators (when the level of accumulation is 100 times greater than normal). However, most known hyperaccumulators do not produce large amounts of biomass.

The best opportunities for the application of phytoremediation are situations when the surface soil (top 30 cm) is contaminated with low levels of metals and radionuclides over large areas. In this respect, phytoextraction complements other remediation methods that target smaller areas of higher contaminant concentration.

The potential for phytoextraction can be assessed by comparing the mass of the toxic element present in the soil to be treated with the mass of the toxic element that the plant can accumulate in a single growing season. For remediation to be effective, the volume of biomass produced must be less than the volume of soil treated, which necessarily means that the concentration of contaminant in the biomass must be greater than the concentration in the soil. In other words, the accumulation

factor must be greater than 1, and the larger the better. Furthermore, biomass productivity must be sufficient for remediation to occur over a reasonable number of harvests.

Indian mustard (*Brassica juncea*), for example, has been shown to produce 18,000 kg dry weight per hectare and to accumulate lead, at least 2 percent by weight, in the aboveground biomass (on a dry weight basis) under ideal conditions (Kumar *et al.* 1995). At a site with 500 mg lead per kilogram of soil in the top 30 cm of soil, which amounts to 2000 kg of lead per hectare (or 10,000 m²) of soil, this translates to a potential for removing 360 kg of lead each year, with complete remediation in fewer than 6 years. The case study, "Field Demonstrations of Phytoremediation of Lead Contaminated Soils," provides further details.

The case study "Field Demonstrations of Phytoremediation of Lead Contaminated Soils," by Robert Taylor, illustrates the use of Indian mustard plants, with EDTA as a soil amendment, for phytoremediation of lead. See page 1287.



Technical Issues and Challenges

A fundamental limitation of phytoremediation is the rooting depth of the plant. The zone of influence of the method is restricted to rooting zone, or rhizosphere. This zone typically extends from the surface to a depth of 20 to 100 cm, depending on the type of plant and soil conditions. The use of poplar trees can extend the root zone to several meters. Additional limitations include the maximum concentration of toxic metals that can be accumulated in the plant's biomass and the amount of biomass produced. There is an obvious tradeoff between the concentration of the toxic element accumulated and the amount of biomass produced (DOE 1994).

The use of soil amendments will likely be required to approach optimal conditions in the field, which could be an issue with some regulators. Chelating agents form metal-chelate complexes that prevent precipitation and sorption of metals, and thereby maintain their availability for plant uptake. Soil pH is another important factor controlling the solubility of metals in soil. Lowering the soil pH will decrease the adsorption of heavy metals and thereby increase their concentration in the soil solution. Therefore, lowering the soil pH and amending the soil with metal chelates are effective ways to increase some metal species'

solubility and optimize plant uptake (Salt *et al.* 1995). However, these measures can also allow the heavy metal to migrate deeper into the vadose zone below the root zone, especially if excessive water is applied. Measures should be taken to insure this does not occur.

OTHER BIOLOGICAL METHODS

Recent studies suggest that bioremediation technology might be applicable to some types of metal contamination. Novel species of bacteria capable of mobilization and immobilization of metal ions have been discovered (Stephen and Macnaughton 1999). In addition, microbes might be used to remediate metal contamination by enzymatically changing the redox state to solubilize the metal. Changing the redox state may lead to the sequestering of the metal in the soil through biosorption or precipitation. Bioremediation of metals is still primarily a research problem, with little large-scale application (Lovley and Coates 1997), and thus will not be discussed in detail in this chapter.

The techniques for biodegradation and bioremediation of organic contaminants are discussed in detail in Chapter 7. In contrast to organic compounds, most inorganic contaminants cannot be degraded. Exceptions include a limited number of problematic, non-metallic, anionic contaminants that are amenable to biological destruction (Alguacil and Merino 1998). The most notable are nitrate and perchlorate, both of which pose serious health risks when present in drinking water. Nitrate can serve as a nitrogen source for many bioremediation processes and can be co-metabolized with many organic contaminants, such as carbon tetrachloride or trichloroethylene (Chu and Alvarezcohen 1996). Perchlorate has only recently been identified as a serious water contaminant. Presently, biological reduction appears to hold the most promise for large-scale treatment of drinking water (Ubansky and Schock 1999). While this process presently targets *ex situ* treatment of drinking water, eventual extension of this technology to *in situ* bioremediation of groundwater and vadose soils is possible.

STABILIZATION

Because heavy metal contamination can be so difficult to remove from vadose zone soils, considerable attention has been given to *in situ* contaminant stabilization techniques. The term “contaminant stabiliza-

tion” refers to any technique that changes the physical characteristics of the contaminated soil to limit the mobility of the contaminant. Containment is the treatment of uncontaminated soil in the proximity of contaminated soil in order to prevent further transport of the contaminant. Containment is discussed in Chapter 9.

Contaminant stabilization can be a physical alteration, such as *in situ* vitrification and grouting, or it can be a chemical alteration through redox state manipulation to cause precipitation. The approach can be abiotic, and reagents are usually added in the gaseous or solid phase. Gas-phase manipulation takes advantage of the vadose zone soil vapor pore space. Solid-phase mixing is accomplished by mixing soil with large augers or high-pressure jets. Redox manipulation can also be accomplished biologically, by fixing the contaminant in a plant root system (phytostabilization) or by bioaccumulation in bacteria. A more detailed discussion of these techniques follows.

***IN SITU* VITRIFICATION (ISV)**

In situ vitrification (ISV) is a thermal-based method that relies on high-density electrical energy to melt soil and waste into a glassy monolith from which only small amounts of leaching is expected over long time periods. ISV has been under development by the DOE since 1980. Initially, the technology was developed as a “top-down” approach (Figure 8-8[a]). Contaminated soil is treated *in situ* by passing large electrical currents between graphite electrodes and melting it via Joule heating. A highly conductive starter path is placed between the electrodes to allow melting to begin. As electricity flows through the starter path, the path heats up and causes the surrounding soil to melt. Once the soil is molten, it becomes electrically conductive allowing the process to continue as long as electrical power is applied. The melt starts at or near the surface and proceeds downward until the desired depth—to a limit of approximately 6 meters—is reached. The process is stopped by simply terminating the electrical power and allowing the 1,500°C melt to cool (which can take up to a year). The molten rock temperatures destroy any organic compounds and combustible material with certainty. This pyrolysis causes offgasing, which is mitigated with a large vacuum hood (and associated offgas scrubbers and treatment systems) placed on the surface over the treatment region (EPA 1997).

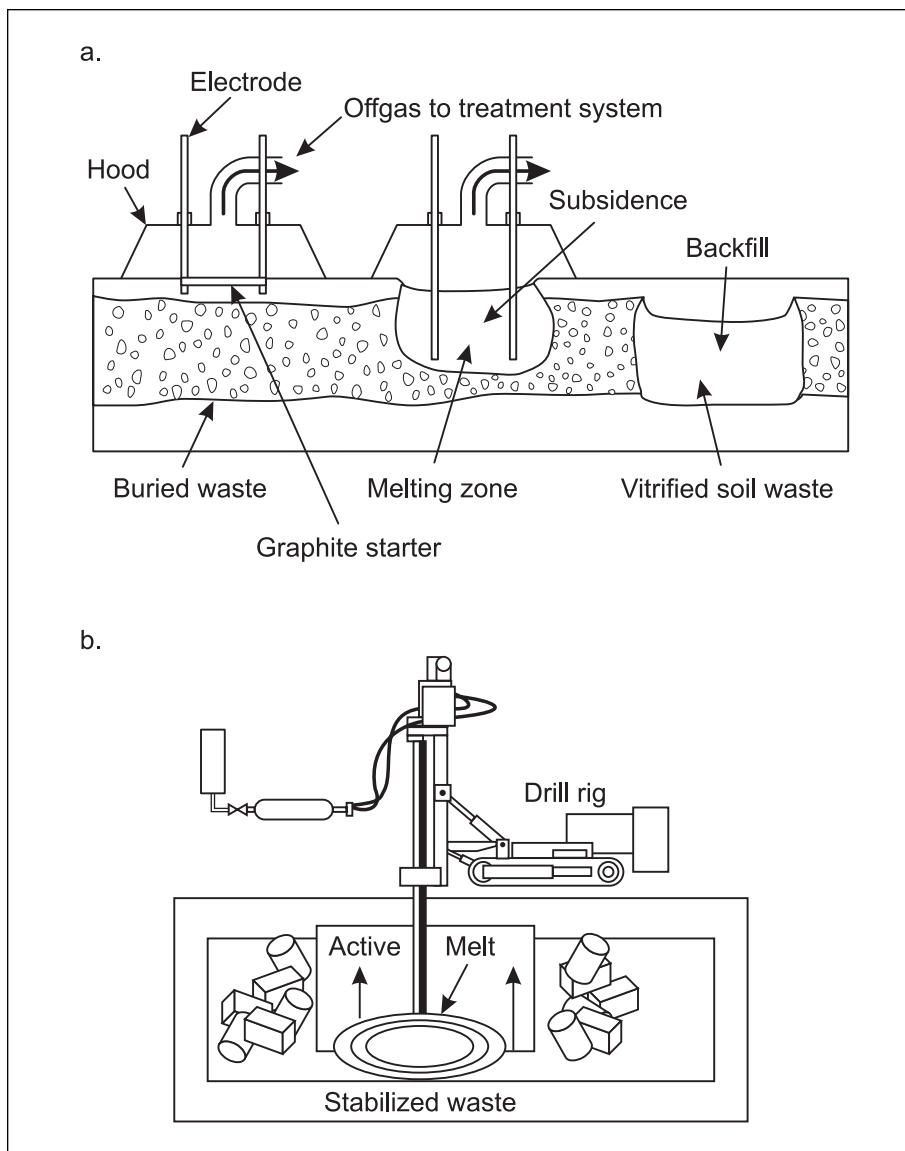


Figure 8-8. Schematic of *in situ* vitrification (a) top down (b) bottoms up.

A number of field demonstrations of the top-down ISV approach have been conducted. The first full-scale application of ISV treatment at an EPA Superfund site was conducted at the Parsons Chemical/ETM Enterprises Superfund Site in Grand Ledge, Michigan, between May 1993 and May 1994. Eight melt cells, each measuring 7.9 m by 7.9 m (26 ft by 26 ft) and 4.9 m (16 ft) deep, were used to vitrify approximately 2,450 m³ of soil contaminated with pesticides, dioxins, and mercury. Each melt ranged in duration from 10 to 20 days and consumed 560,000 to 1.1 million kWh of electricity. Mercury concentrations in the treated waste were reduced by more than 98 percent when compared to the untreated soil, and the waste form passed the toxicity characteristic leach procedure (TCLP) test (EPA 1995).

The vendor estimates the cost for the vitrification operation to be \$375 to \$425/ton of treated soil, \$300,000 to \$400,000 for mobilization and demobilization, and \$50,000 to \$150,000 for treatability/pilot testing. The process is quite energy-intensive, and special accommodations are required to equip the site with ample electrical power. The major factors affecting the cost of implementing ISV are the scale of the operation, the moisture content of the soil, the combustible waste content, the depth of treatment zone, and the cost of electricity (EPA 1997).

Technical Issues and Challenges

Serious—even catastrophic—complications have occurred in ISV implementations. Rapid volatilization of water or organics has caused the eruptions of gases and expulsion of molten rock. At a field demonstration of ISV of radioactive waste contaminated with ¹³⁷Cs at Oak Ridge National Laboratories in Oak Ridge, Tennessee, a melt expulsion event occurred. This expulsion, which sprayed radioactive glass around the treatment site and damaged the offgas collection hood, highlighted the problems with ISV. A number of recent technological developments have resulted in improvements that should minimize the occurrence of eruptions and expulsions; however, none have yet been fully demonstrated at a field scale. These developments are discussed, briefly, below.

One development allows the starter path to be injected in a horizontal plane between the electrodes in the subsurface, thus allowing the melt process to be initiated at any depth. The melt then proceeds down-

ward for a maximum of 6 meters from the depth of initiation. This technique allows overburden to be left in place, preventing eruption of gases and expulsion of molten rock, and allows the vitrification of columns much greater than 6 meters tall by sequential application of the process to 6 meter tall portions of the contaminated soil. The controlled injection of the starter path has also led to a new planar method for performing *in situ* vitrification. Rather than injecting the starter path in a horizontal plane between electrodes, it is injected in a vertical plane between two electrodes, thus allowing the initiation of tall, thin melts. These planar melts can be focused sideways for treating buried waste and underground tanks. Planar melting is better for treating wastes that might generate high volumes of gas, because the method allows gases to escape to the surface through the adjacent soil or untreated waste rather than the melt (Geosafe Corp. 1998).

A “bottoms up” approach is also under development. The melt is started at a desired depth using a high-temperature arc melter deployed through a pipe in a cased borehole (Figure 8-8[b]). A much greater degree of control is possible with this approach, and depth limitations are not an issue. Oxygen can be metered to the combustion melt zone to ensure complete *in situ* oxidation of organic waste components. Offgas formed during the process is removed through the annulus surrounding the arc melter pipe and the borehole casing. The process is controlled through online monitoring of the offgas using conventional stack gas measurement instrumentation. The melt then proceeds upward by slowly withdrawing the arc melter. Because the most rapid heating is occurring at the top, gases can escape through the soil or untreated waste, rather than the melt, making eruptions much less likely (DOE 1999).

SOIL-MIXING WITH CHEMICAL REAGENTS

Deep-soil mixing is a commercially available technology for introducing reagents into the subsurface that solidify and/or stabilize the hazardous contaminants in place in the soil matrix. Deep-soil mixing is a well-established technology. Cement footers and grout curtains and slurry walls have been installed, using standard construction techniques and materials, for many years. Reagents for solidification include Portland cement and other ordinary pozzolanic materials.

Depending on the required properties of the final waste form and the characteristics of the contaminated soil or waste, various additives can be used, including bentonite, silicates, or any of a number of proprietary agents. Bentonite improves the pumping of the reagent mixture (Bruce 1996) and helps to decrease the permeability of the treated waste. Reagents for stabilization usually react with the targeted contaminant to form an insoluble solid phase. Silicates form insoluble chemical complexes with many metals, with lower solubility than the corresponding hydroxide, carbonate, or sulfate complexes. Lead-contaminated soil can be treated with trisodium phosphate to form highly insoluble lead phosphate. Reduced iron can be added as ferrous ions, or as zero valent iron filings, to form a highly insoluble hydroxide solid, with chrome reduced from the highly toxic +6 valence to the +3 valence state. Combining solidification and stabilization methods offers the advantage of providing both chemical and physical encapsulation of the contaminants and results in *in situ* treatment with better long-term performance (Al-Tabbaa and Evans 1996).

The reagents are mixed into the soil using a large auger drill rig and specially designed augers incorporating numerous injection ports (Figure 8-9). Some vendors can inject two or more reagents simultaneously. The diameter of the auger generally depends on the depth of drilling, as well as the hardness and porosity of the soil. Augers with diameters between 4 feet and 12 feet are usually used to depths of 40 feet. From 40 feet to a maximum of 100 feet, 2.5-foot to 4-foot diameter augers are used. Smaller diameter augers generally mix the soil more thoroughly.

The keys to successful deep-soil mixing are thorough mixing of the contaminated soil with the reagents and producing overlapping columns of treated soil.

Usually, to achieve the desired contaminant immobilization and final waste form permeability and compressive strength, a reagent formulation must be developed for the specific soil and contaminants present at a given site. This is typically done in the laboratory. Confirmation sampling of pilot- or field-scale tests is used to determine whether the treated materials are meeting performance requirements. Failure to meet the performance requirements in the field can occur if the reagent formulations are inconsistent or if injection ports become clogged during

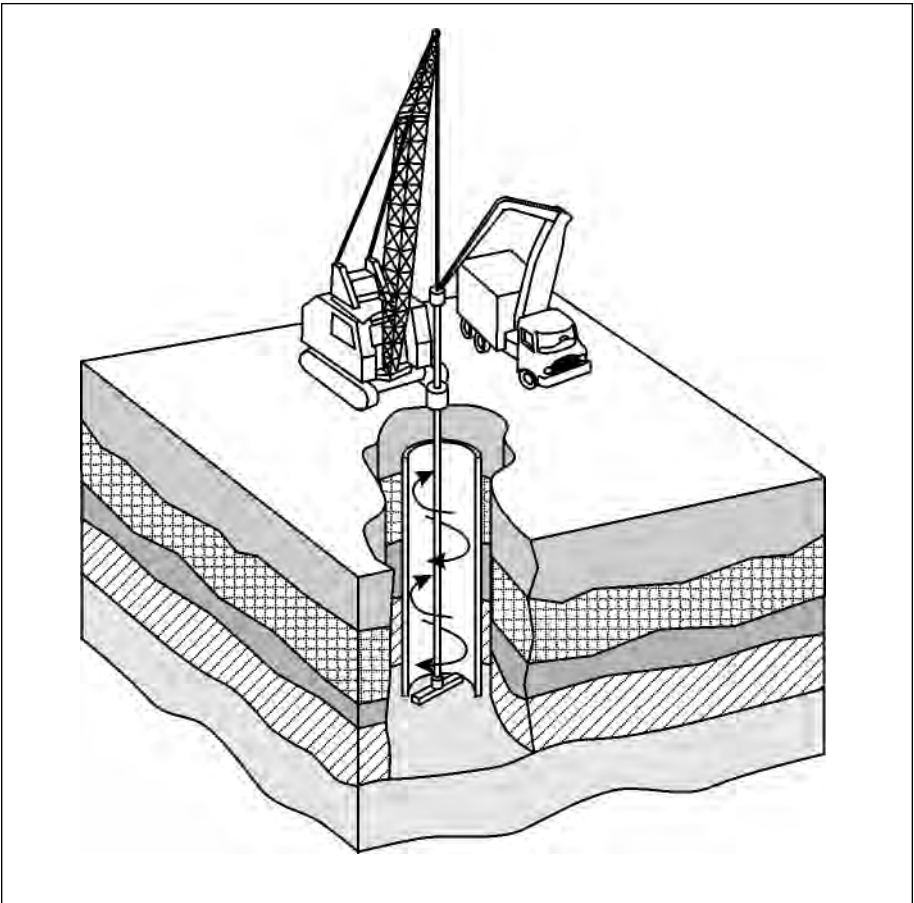


Figure 8-9. Schematic of deep soil mixing.

mixing. Clogged ports result in non-uniform spray patterns and incomplete mixing, which are difficult to identify in the field.

Technical Issues and Challenges

Large augers require very large, expensive drill rigs, for which site access may be an issue. If the site is not level, a level drilling pad and appropriate access must be constructed at additional cost. The size of the required equipment also significantly increases the cost of mobilization

and demobilization. Because of these costs, soil mixing is usually considered only for large sites.

JET GROUTING

Jet grouting is another method for mixing reagents with contaminated soil. With jet grouting, the grout is injected under high pressures (5,000 to 10,000 psi), into the soil in standard boreholes. This procedure mixes the grout with the soil, breaks up brittle debris, and surrounds and encapsulates nonbrittle debris. The boreholes are placed so that the grouted columns overlap and an *in situ* monolith is formed when the grout cures. Jet grouting offers the advantages of requiring less capital-intensive equipment, simpler installation, and better overlap (Dwyer *et al.* 1999). The grout pumps and drill rigs required for jet grouting are much smaller than the equipment required for soil mixing, so mobilization and demobilization costs, as well as site access and preparation costs, are much less of an issue. This makes jet grouting of small sites more economically feasible. Other advantages of jet grouting over soil mixing include essentially no depth limitation and compatibility with directional drilling technology, so that it is possible to treat under-structure environments.

The case study "Demonstration of *In Situ* Stabilization of Buried Waste at Pit G-11 at the Brookhaven National Laboratory Glass Pits Disposal Site," by Brian Dwyer, J. Heiser, and J. Gilbert, describes how jet grouting has been successfully used to encapsulate contaminated debris. See page 1291.



GASEOUS REDOX MANIPULATION

For some inorganic contaminants, it may be possible to effect *in situ* stabilization by manipulating the redox state of the contaminant and causing precipitation. The manipulation may be as simple as ventilating the soil with air, but usually more aggressive gaseous reagents are injected into the ground. This approach requires that the contaminant have at least two stable oxidation states, with one being much less soluble than the other. Chromate (CrO_4^{2-}) is an ideal example, as it is highly

toxic and mobile in the +6 valence, and much less toxic and insoluble in the +3 state. Furthermore, since atmospheric oxygen will not re-oxidize the precipitated form, it tends to remain fixed in environments low in Mn(IV). Other candidates for redox manipulation include: most toxic metals forming an oxyanionic species (such as molybdenate, selenate, and perchlorate ($[\text{MoO}_4^-]$, $[\text{SeO}_4^{2-}]$); some radionuclides, like pertechnetate ($[\text{TcO}_4^-]$); and anionic forms of uranium, such as uranyl carbonate ($[\text{UO}_2(\text{CO}_3)_2^{2-}]$). Each of these species is highly soluble in its highest oxidation state and will form a much less soluble form if the oxidation state is reduced.

As described in the case study, “*In-Situ* Gaseous Reduction,” hydrogen sulfide has been demonstrated for chromate gaseous reduction. Hydrogen sulfide (H_2S) reacts very readily with chromate, but soil permeability can limit the uniformity of treatment. Because H_2S is poisonous at high concentrations and objectionable at low concentrations, monitoring systems and interlocked control systems may be required for safe operation. This method may be contraindicated if houses or other occupied structures are nearby. The principle issue is the uniformity of treatment due to variations in soil permeability.

The case study “*In Situ* Gaseous Reduction,” by E.C. Thornton, discusses the gas-injection method of treating chromate contaminated soils. See page 1302.



Technical Issues and Challenges

A critical issue with gaseous reduction is the long-term stability of the stabilized precipitates. For example, although Cr(III) is commonly stable, the potential for oxidation back to the toxic and mobile Cr(IV), through reactions with Mn(IV), need careful consideration. Since Mn(IV) oxides are common in many soils and sediments, the stability of Cr(III) cannot be assumed. Research is needed on the potential for gaseous reduction of Mn(IV) to Mn(II). If a significant amount of the naturally present Mn(IV) can be reduced with the same treatment, the long-term stability of Cr(III) is more assured. Follow-up monitoring at sites treated with H_2S , for evidence of Cr(III) reoxidation back to Cr(IV), is also needed to provide assurance of the long-term stability of the method.

PHYTOSTABILIZATION

Phytostabilization uses plants to chemically fix contaminants in the soil by stimulating processes of sorption, precipitation, complexation, or reduction of metal valence. Some researchers consider phytostabilization to be an interim method to be used until phytoextraction becomes better developed. It is important to use plants for phytostabilization that exhibit low levels of accumulation in the above-ground biomass, so that no special treatment or disposal is needed.

Heavy-metal contaminated soils usually lack vegetative cover because of the toxic effects of the metals. Such soils are prone to erosion and leaching that spreads pollution into the surrounding environment. Some plants have adapted genetically to grow in soils containing toxic levels of metals. Most of these metal-tolerant plants successfully exclude the uptake of toxic metals by stabilizing them in the roots and soil. Thus, additional general benefits associated with establishing such vegetation over contaminated soil include physical stabilization of the contaminated soils to reduce or prevent erosion and, due to plant evapotranspiration, the reduction of net seepage from the vadose zone into groundwaters.

Re-vegetation of mine wastes using local metal-tolerant plant species has been successful in the United Kingdom. Based on this success, three cultivars of metal-tolerant grasses are now commercially available: *Festuca rubra*, "Merlin," for calcareous lead/zinc wastes; *Agrostis tenuis*, "Goginan," for acidic lead/zinc wastes; and *Agrostis tenuis*, "Parys," for copper wastes (Salt *et al.* 1995). An issue with phytostabilization is that the established vegetative cover may require maintenance indefinitely to keep the metal contamination sequestered.

NATURAL ATTENUATION

There is a growing realization that complete cleanup to precontamination background conditions at many of the nation's contaminated sites, while highly desirable, is economically and technically unattainable in the near term. Billions of dollars have been spent, with few complete remediations. In many instances, the actual risk of the contamination is low and becomes lower naturally over time. Allowing a site to self-cleanse by natural processes has been termed "natural attenuation." The idea of combining long-term monitoring with natural

attenuation has been termed “monitored natural attenuation” (MNA) and is a recently-developed concept (Brady *et al.* 1998).

Natural attenuation of organic contaminants relies on the activity of indigenous microorganisms to biodegrade (or in effect, destroy) contaminants. The concept is well-accepted, and both direct and indirect methods are available to monitor progress. The situation for natural attenuation of metals is different because, unlike organics, metals cannot be destroyed.

Many metals exhibit a propensity to reduce, precipitate, or adsorb to various mineral phases in soil. Once sorbed to a mineral surface, the metal ion can migrate into dead-end pores or can be chemically or physically incorporated into the mineral matrix (Brady *et al.* 1998). These events effectively isolate the metal from the environment. In other words, they drastically reduce the bioavailability of the contaminant. It is often observed that removal of aged metal contamination from soil is much more difficult than removal from freshly-spiked soil. Often, an aged, contaminated soil requires complete soil dissolution to extract all the metal contaminant. If contaminants in ingested soil are not leached in the human digestive tract, then the soil poses a much lower risk to human health. For radionuclides with relatively short half-lives, such as strontium-90, radioactive decay eventually eliminates all risk. Nevertheless, it is difficult to sell the idea that even though the contaminant is still there, it is not a threat.

The first step of MNA as described in the book *Natural Attenuation* by Brady, Brady and Borns (1998), is to remove or isolate the source term. Removal, stabilization, or containment can be through *ex situ* means (for example, after excavation), *in situ*, or by any of the methods described above. The steps of MNA can be summarized as follows:

1. Develop a conceptual model for the site that combines likely transport pathways with likely natural attenuation mechanisms (biotransformation, chemical or nuclear transformations, adsorption, or dispersion).
2. Design a long-term monitoring network and program that can test the conceptual model. This includes defining a “Point of Compliance.”
3. Monitor the site. Use monitoring data to support or refine conceptual model (perhaps refining the monitoring network as well).

4. Determine if natural attenuation is working as expected; if yes, continue monitoring at a reduced schedule; if no, design remedial action.

The objective is to remove, stabilize, or contain the contamination as much as possible, then monitor the movement of the remaining contamination to validate predictive conceptual models. As long as the conceptual models remain valid and predict minimal risk, there will be confidence that no additional remedial action is required, and the expensive components of the monitoring program (such as groundwater sampling) can be scaled back. Long-term monitoring shows that actual performance is consistent with the predicted performance relative to the risk of the remaining contaminants.

Technical Issues and Challenges

A significant issue with MNA (and all other nonclean-closure remedial options) is the potential cost of long-term monitoring. On first consideration, it would seem that MNA is a very low-cost option. However, since long-term monitoring will continue for 10 to 100 years, the overall cost is very high, and could easily exceed the initial characterization and restoration costs if current technologies are used. The most commonly used monitoring technique today is groundwater sampling.

Groundwater sampling and analysis is expensive and requires crews to go out to each monitoring well, purge the well, and collect the sample. This procedure generates considerable amounts of purge water that often must be handled and disposed of as hazardous waste. The collected samples are usually sent offsite for analysis using contract laboratories and EPA procedures. This is also quite expensive, with each analysis costing between \$100 and \$1,000. At large sites—such as the DOE Savannah River Site in South Carolina, where there are 1,400 monitoring wells that require 40,000 groundwater samples per year—the cost can be staggering. Efforts to reduce the cost of long-term monitoring, as discussed in Chapter 4, are expected to significantly reduce the lifecycle cost of MNA.

SUMMARY OF METHODS

We have examined a number of methods for remediating vadose zone soils contaminated with inorganic contaminants, especially heavy metals and radionuclides. These methods can be categorized, generally, as: (1) contaminant removal technologies, where the contaminants are removed or destroyed or (2) contaminant solidification/stabilization technologies, where the contaminants are immobilized and left in place. Some methods are best used for shallow, widespread, low concentration contamination (for example, phytoremediation) while other methods are best directed at deeper, higher contaminant concentration “hot spots”. In short, all methods have strengths and weaknesses, and none are perfect for all situations.

Of the source-term removal technologies, *in situ* soil flushing is best-suited if metal contamination in vadose zone soils is actively impacting an aquifer, and a pump-and-treat system is already in place or anticipated for use as a capture system. In this case, accelerating the leaching into the groundwater may be acceptable if the flushing solution is not toxic and the capture system can be shown to be effective. In cases where the contamination in the vadose zone soils is not yet impacting an aquifer, *in situ* flushing of the contamination into the groundwater will not likely be acceptable.

If the contaminant is water-soluble, electrokinetic technologies can be considered. Electrokinetic extraction of chromate from low-moisture-content soils has been field-demonstrated, but the active process may be costly. Many water-soluble heavy metals are adsorbed by activated carbon. A simpler, passive electrokinetic approach using activated-carbon anodes is under development that may be much more efficient and cost-effective. However, the passive approach has not yet been field-tested.

If the metal contamination is not water-soluble, the question should be raised as to whether or not it presents a risk. Surface contamination must be considered a risk and phytoremediation is suggested. Phytoextraction can be used to stabilize the surface soil while removing the contamination. With phytoextraction, key issues are the range of metals for which the process is applicable and the rate at which the metals can be removed. The advantage of contaminant removal through any

combination of these technologies is the possibility of clean closure with no further liability or requirement for long-term monitoring.

When extraction of the metal contamination is not technically or economically possible, or if the hazards are so great that excavation is dangerous, *in situ* solidification or stabilization of the contaminants can be an alternative for remediation. *In situ* vitrification uses electrical energy to melt soil and incorporate the contaminants into a very stable waste form. Catastrophic events during past field-demonstrations have led to improvements that are still undergoing evaluation. This is an expensive option, however, and is probably best suited for high-risk contaminants, such as long-lived radionuclides.

Deep soil mixing and jet grouting are alternative methods for producing solidified, monolithic waste forms or for delivering reagents to stabilize contaminants. These two methods rely on standard, commercially-available, large-scale construction technologies. One disadvantage of all solidification/stabilization technologies, however, is that the contaminants are left in place and eventually could be remobilized. For this reason, long-term monitoring may be required at sites using this remediation approach.

Lastly, there is MNA. This approach is, perhaps, the first that should be considered. The concept behind monitored natural attenuation is that many contamination problems pose a low risk and will attenuate to no risk if left alone, especially after the source term is first removed or stabilized. A conceptual model is developed for contaminant movement and sequestering under the specific hydrogeologic conditions of the site. A long-term monitoring plan is also developed and implemented. If the monitoring data support the conceptual model, the monitoring frequency is reduced and monitoring is eventually eliminated. However, if the conceptual model is not supported, adjustments are made to the model and the monitoring plan and additional remedial action may be required.

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C A S E S T U D I E S



ELECTROKINETIC DEMONSTRATION AT THE UNLINED CHROMIC ACID PIT

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PROBLEM

Heavy-metal contamination of soils and groundwater is a widespread problem at Environmental Protection Agency (EPA) Superfund sites, Department of Energy (DOE)-operated sites, and privately-owned facilities throughout the nation. Currently, the only viable method for remediating heavy-metal contaminated soil is by excavation followed by soil washing or relocation. One possible technique for *in situ* removal of such contaminants is electrokinetic remediation, in which electrodes are implanted into the ground and a direct current is imposed between the electrodes. Metal ions migrate in pore water toward either an anode or a cathode where they can be removed. Contaminants arriving at the electrodes may be removed from the soil in several ways, including electroplating or adsorption onto the electrode, precipitation or co-precipitation at the electrode, pumping water near the electrode, or complexing with ion-exchange resins.

CHALLENGES OF MOISTURE CONTROL

The electrokinetic remediation program at Sandia National Laboratories (SNL) has focused on applications for chromate removal from unsaturated soils. Unlike groundwater in saturated soil, pore water in the unsaturated zone is held under tension in the soil pores. (Soil tension can describe the moisture content of the soil: the greater the soil tension, the dryer the soil.) This soil tension prevents the pore water in the unsaturated zone from entering simple groundwater extraction wells like it does in the saturated zone. Conversely, if a simple groundwater extraction well were used in unsaturated soil and filled with water, the soil around the well would become saturated. Thus, one serious problem in applying electrokinetic technology in unsaturated soils using existing electrode wells is the potential for washing the contaminants out of the remediation area. As a result, in unsaturated soils, an effluent extraction system at an electrode must be specifically designed to overcome the soil tension problems.

The SNL research has led to a patented electrode design to remove the contaminants from the soil without the addition of significant amounts of water that could spread the contamination (Lindgren and Mattson 1995). This electrode design extracts contaminants by moving them into water held under tension (that is, under partial vacuum) inside a ceramic casing that surrounds the electrode—becoming, in effect, a large suction lysimeter. Previous research at the laboratory scale had

proven the concept of transporting and extracting chromium from unsaturated soils using this suction lysimeter electrode (Mattson and Lindgren 1995). In 1996, a field demonstration of the Sandia electrode design was conducted in a chromium plume that resides in the unsaturated vadose zone beneath the Unlined Chromic Acid Pit (UCAP) in the Chemical Waste Landfill (CWL) at SNL. The purpose of the demonstration was to show that chromate could be extracted from vadose soils on a field scale without the addition of significant amounts of water. A detailed description of the demonstration can be found in the final report (Lindgren *et al.* 1998).

FACILITY AND SITE DESCRIPTION

SNL is located southeast of Albuquerque, New Mexico, in Bernalillo County. SNL facilities are located within the boundaries of Kirtland Air Force Base (KAFB). The CWL is located in Technical Area III, which is approximately four miles south of the nearest drinking water supply well and at least three miles from any natural groundwater discharge point.

Climate

The climate of the region is semi-arid. Average annual precipitation is approximately 8 inches (20 centimeters). Most of the precipitation occurs as thunderstorms during late summer to early fall. There is also a limited amount of snow. Average daytime summer temperatures are around 90°F (32°C), while average daily winter temperatures are about 50°F (10°C). At the CWL, the water table is located approximately 485 feet below the land surface and did not play a role in this electrokinetic remediation demonstration.

Geology

The near-surface geology at the CWL consists of alluvial fan deposits with some eolian deposits. The individual beds range from coarse-grained material to caliche-cemented sediments. Laterally, they are not extensively continuous. Little organic matter (0 to 0.2 percent) was measured in samples taken in TA III from the top 9 meters of the soil profile (Persaud and Wierenga 1982).

Chromium Species

The chromium disposed of in the UCAP was in the form of chromic sulfuric acids. Within the pH and Eh range of soils, chromium can exist as two oxidation states: (1) Cr(III) as precipitated $\text{Cr}(\text{OH})_3$ solids or (2) as Cr(VI) either as CrO_4^{2-} or $\text{Cr}_2\text{O}_7^{2-}$, both anions. The anionic chromate form exhibits little to no adsorption to soils (Persaud and Wierenga 1982). It is to be expected that in and immediately below the UCAP, some of the chromate would be reduced to its trivalent form and precipitated in the soil. However, due to the alkaline nature of the soil and the lack of organic matter at

depth (that is, a few feet from the bottom of the pit), much of the chromium in the soil was in its hexavalent form in the soil water.

OVERVIEW OF FIELD DESIGN

LAYOUT

The layout of the field demonstration is shown in Figure 1. The demonstration targeted the most-contaminated soils immediately below the floor of the former pit, at a horizon 8 to 14 feet below the surface. Three rows of electrodes were placed in a 12-foot by 12-foot area. The center row consisted of five anodes and the outer two rows each contained five cathodes. The electrokinetic remediation system designed for this demonstration included the extraction electrode and four main operational units: a vacuum control system, a liquid control system, a power application system, and a monitoring system. A 6-ft portion of the electrode casing was constructed of porous ceramic that acted as the lysimeter. The upper portion of the electrode was constructed of an impermeable, non-conducting PVC material. The fluid between the electrode and the ceramic casing was continuously recirculated to remove contaminants that entered the electrode and to clear the electrode of gas bubbles formed by water electrolysis. A pH control system was used to neutralize hydrolysis reactions. Chromate rich solution extracted from the electrode lysimeter was collected at the surface for hazardous waste disposal.

ELECTRODE DESIGN

The success of the demonstration is attributed to the patented electrokinetic extraction electrodes (Lindgren and Mattson 1995). These electrodes allow the transfer of contaminant ions from water contained in the soil pores to liquid contained in the electrode casing. The electrode system is constructed of a porous-ceramic outer casing and an inner iridium-coated titanium electrode. A vacuum applied to the interior of the electrode allows liquid to circulate freely within the electrode casing without being transferred to the surrounding soil. A voltage potential is applied between electrodes, resulting in a current that provides the transport mechanism for the contaminant ions through the soil and into the electrode casing. Over time, the contaminant concentrations will build up in the electrode casing liquid, where they are removed by pumping the electrode liquid to the ground surface for subsequent treatment or disposal.

RESULTS AND DISCUSSION

CHROMATE REMOVAL

The SNL electrokinetic remediation demonstration successfully removed chromate contamination from unsaturated soil at the field scale without significantly changing

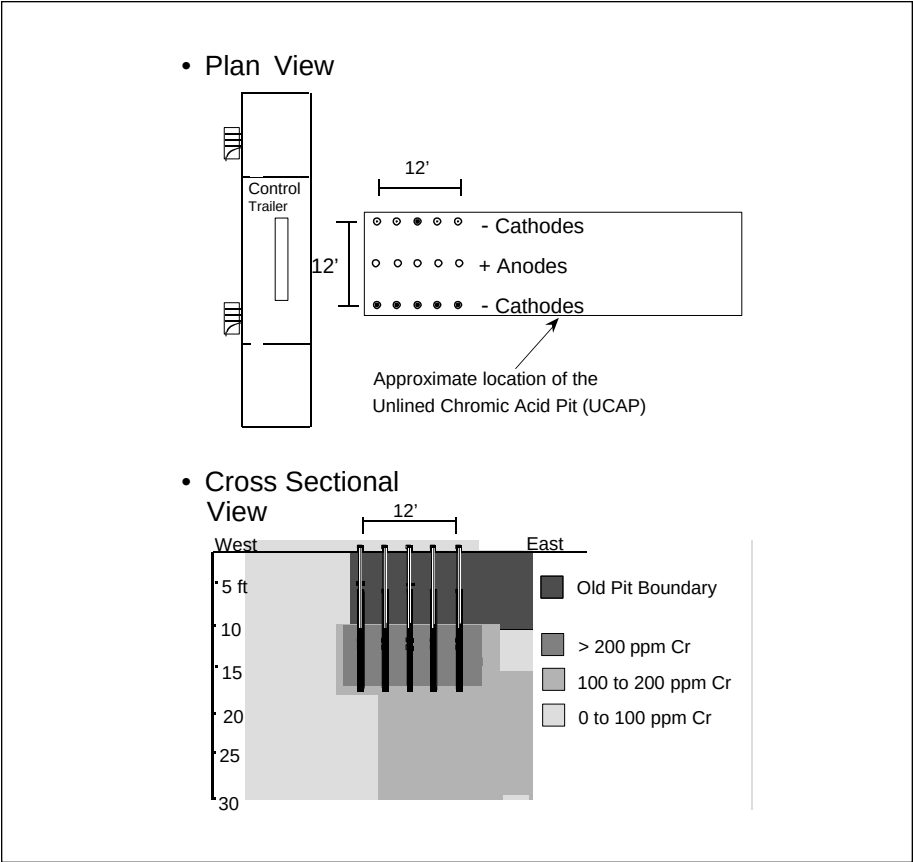


Figure 1. Layout of field demonstration.

the soil moisture content. After 2,700 hours of operation, 600 grams of chromium(VI) were extracted from the soil beneath the SNL CWL. The contaminant was removed from soil that had moisture contents ranging from 2 to 12 percent by weight. This demonstration was the first electrokinetic field trial to successfully remove contaminant ions from arid soil at the field scale.

The electrokinetic demonstration was terminated prior to complete cleanup of the soil beneath the UCAP site. During the demonstration, chromium extraction efficiencies [as measured in grams Cr(VI) removed per amp hour] did not deteriorate, indicating that the electrokinetic process is stable over long periods of time (see Figure 2). Note that the operation of anode A2 was terminated early in the demonstration because of low extraction efficiency.

Post-test soil sample chemical results in the remediation zone indicate a cleaning of the soil near the cathodes and an accumulation of chromate in the area near the

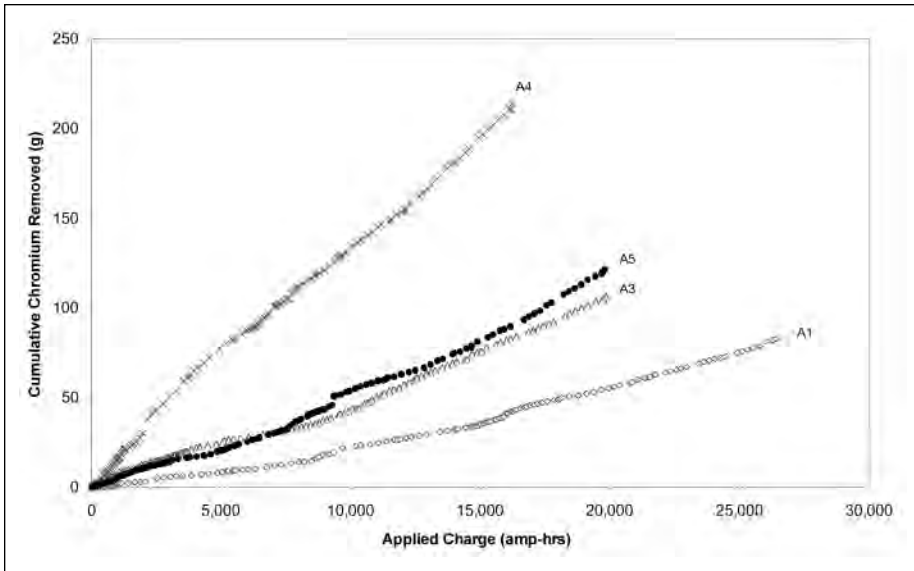


Figure 2. Cumulative chromium removal as a function of applied charge per anode.

anodes. No significant changes in chromium concentrations were noted outside of the remediation zone. Soil samples adjacent to the cathodes would pass the Toxicity Characteristic Leach Procedure (TCLP) criteria, indicating that soil in this area would not be considered hazardous waste if excavated and removed to the surface. Soil samples taken in the area of the cathodes had TCLP extract chromium concentrations as high as 28 ppm prior to conducting the demonstration. It is expected that all of the soil in the remediation area could have passed TCLP criteria if the demonstration had run to completion.

MOISTURE CONTROL

A special feature of the patented electrode system is its ability to control the amount of water added to the soil in the electrokinetic demonstration. The anode casings were treated prior to placement in the ground with a coating which mitigated the water loss to the soil by electroosmosis, as was noted in previous field testing of the electrode system (Mattson and Lindgren 1994). Water mass-balance calculations indicate that only a net of approximately 20 gallons of water were added to the soil during the electrokinetic demonstration (see Table 1). However, three times that amount of water was transported in the soil-water system from the anodes to the cathodes due to electroosmosis. No significant changes in the soil moisture content profiles were noted when compared to the pre-demonstration values. In addition, no

TABLE 1 Summary of water balance calculations

Item	Cathodes (gal)	Anodes (gal)	Total (gal)
Make-up Water to Electrodes	661	1404	2065
Acid Additions	74	—	74
Base Additions	—	134	134
Water Injections	25	25	50
Chiller Water Additions	5	30	35 (+/-10)
Total Additions	765	1593	2358
Effluent Water Extractions	(831)	(1506)	(2337)
Total	(66)	87	21 (+/-10)

significant changes in electrical conductivity, and only minor changes in soil pH, were noted during the electrokinetic demonstration.

TRANSFERENCE NUMBERS

Transference numbers compare the fraction of the current carried by the contaminant ions to the total amount of current applied. Calculating contaminant transference numbers from soil samples collected prior to conducting electrokinetic remediation can be used to estimate the extraction performance. Transference numbers calculated from pretest soil samples closely correlated with electrokinetic extraction efficiencies (see Table 2). Using these numbers, an estimate of the amount of chromium removed per applied charge can be made for individual electrodes. If the total mass of contaminant is known in the remediation zone, the amount of electricity needed to remediate the site can also be estimated.

IMPORTANT LESSONS

Electrical Power

The application of increased power to the electrokinetic remediation zone has a two-fold effect on electrokinetic remediation. First, although the soil can be remediated in less time by increasing the applied electrical power, the electrical cost per mass of contaminant removed will increase. Increasing the electrical power increases the driving force of electromigration, thereby hastening the time to remediate the soil. For active processes that require frequent operator attention, less time spent remediating a site will result in an overall remediation cost savings. However, increased power density to the soil also results in more electrical energy being expended to

TABLE 2**Transference numbers calculated by conductivity-based and current-based methods**

Anode	Pretest Soil Extract- Conductivity-Based Transference Numbers (%)	Initial Anode Effluent- Current-Based Transference Numbers (%)	Long-Term Anode Effluent- Current-Based Transference Numbers (%)
A1	0.42	0.28	0.28
A2	0.05	0.07	—
A3	1.16	0.30	0.52
A4	1.20	1.02	1.39
A5	1.90	0.53	0.57

remove a certain mass of contaminant. The time savings by increasing the electrical power would have to be weighed against the higher energy costs of contaminant extraction. For passive processes that do not require frequent operator attention, operating at lower power over a longer period of time would be the most cost-effective approach.

Soil Heating

The application of more power leads to increased heating of the soil. Attempts to speed chromate extraction by increasing the power density during this demonstration led to soil heating problems. Although some benefits are realized by limited soil heating, overall, excess soil heating is likely to be detrimental to the electrokinetic process. Electrical currents may concentrate in certain areas of the soil profile, bypassing other contaminated soil zones. Soil pore water could be diminished by thermally-induced gradients or be evaporated from soil zones, effectively stopping the electrokinetic process. Indigenous biological organisms may be killed. Concentrations of VOCs in the soil gas may be significantly increased by an increase in organic vapor pressures. Although the electrokinetic demonstration did not exhibit all of these effects, it is reasonable to assume that they were taking place to some extent. Operation at lower power density alleviates soil-heating problems

Metal Objects

Any metal in the electrokinetic remediation area should be avoided. Metal is much more electrically-conductive than soil, and, therefore, can create a current "short circuit" through the soil. When applied to soil that contains significant amounts of metallic objects, electrical current could effectively bypass zones of contaminated soil. In addition, metallic objects would be oxidized to the extent that they would contribute to dissolved ions in the soil water. Proposed electrokinetic remediation

under buildings that contain structural steel, metallic pipes, and other electrically conductive materials deserves special consideration.

RECOMMENDATIONS

Although the newly-patented electrode system was successful in removing an anionic contaminant (chromate) from unsaturated sandy soil, the electrode system was a prototype that has not been specifically engineered for commercial use.

The system uses a solid matrix chromate capture system, thus eliminating the need for a liquid control system and a vacuum system. In addition, the new electrodes can be planar in design to better transfer the electrical power to the soil. Electrical costs can be reduced by operating the system at a lower power, thereby avoiding the expense of actively cooling the electrokinetic electrode system. A redesign of the electrode system is suggested for future electrokinetic field trials. Additional funding is being sought to further develop the system using a passive, low-power approach.

CONCLUSION

A field demonstration of electrokinetic extraction of chromate from vadose soils has shown that chromate can be extracted from vadose soils without the need to increase the soil moisture content. The extraction efficiency of each anode remained stable over the operation of the demonstration. It has also been demonstrated that a simple water extraction test can be used as a predictor of the electrode performance. Attempts to increase the chromate extraction rate by increasing the power density can lead to soil heating problems, and create an overall inefficient mode of operation. A passive approach is currently under development that would allow long-term, efficient operation at low power densities.

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FIELD DEMONSTRATIONS OF PHYTOREMEDIATION OF LEAD CONTAMINATED SOILS

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INTRODUCTION

Phytoremediation is a new technology that uses specially-selected metal-accumulating plants to remediate soil contaminated with heavy metals and radionuclides. Phytoremediation offers an attractive and economical alternative to currently-practiced soil removal and burial methods. The integration of specially-selected metal-accumulating crop plants (for example, *Brassica juncea*) with innovative soil amendments allows plants to achieve high biomass and metal accumulation rates from soils.

Two field demonstrations of phytoremediation were recently conducted at sites in the United States to demonstrate the technical feasibility of phytoremediation for remediating lead-contaminated soils. At both sites, total soil lead levels were significantly reduced during a single growing season. This paper will detail the results of these field demonstrations. A brief description of each site is given below.

BAYONNE, NEW JERSEY

The first site is an industrial site in Bayonne, New Jersey contaminated with various heavy metals, predominantly high levels of lead. Due to the shallow water table and potential for site flooding, an elevated, plastic-lined lysimeter of approximately 1,000 sq. ft in area and 3.5 ft deep was constructed and filled with lead-contaminated soil from the site for the purposes of the field trial. A sump was created at one end of the lysimeter to collect any excess drainage water. The source of metal contamination at this site has been attributed to cable manufacturing operations.

DORCHESTER, MASSACHUSETTS

The second site is located in a heavily-populated, urban residential area in Dorchester, Massachusetts. The site is a backyard to young children who have been treated twice for lead poisoning. A 1,081 sq. ft. area was selected for the field trial. The source of lead at the site is unknown but is believed to be from paint and aerial deposition. The plot has been used as a home garden for a number of years.

METHODS

INITIAL SAMPLING

A field trial was planned and conducted at each site. An initial sampling of each site, to obtain baseline soil data, was conducted by sampling on a 3 m (10 ft) grid at three depths (0-15 cm, 15-30 cm, and 30-45 cm). The soil samples were collected using a hand-operated, 5 cm diameter, stainless-steel bucket auger. Duplicate samples were collected from 20 percent of the soil cores. Each extracted soil core was mixed in a polyethylene bucket and transferred to a polyethylene bag. Soil samples were collected again at the end of the growing season on the same grid as the initial sampling to determine metal removal efficiency and monitor changes in Pb concentration in the surface (0-15 cm) and subsurface soil (15-45 cm).

SITE PREPARATION AND CULTIVATION

The sites were fertilized according to the soil fertility test results and roto-tilled to a depth of 10-15 cm before seeding with *Brassica juncea* (cv. 426308). Tensiometers were installed at two depths (30 and 45 cm) to monitor soil water content. Irrigation was conducted using overhead impact sprinklers. Soil amendments containing EDTA were applied at a rate of 2 mmol/kg through the irrigation system to enhance metal uptake. The crop was harvested after 6 weeks of growth. Plant samples were collected randomly for metal analysis from 1 m² blocks, rinsed with water, and placed in paper bags for drying. The remaining biomass was harvested by mowing and removed from the plot for appropriate disposal. Roots were not collected and were left in the soil to decompose. After harvest the plot was roto-tilled to 10 cm depth and replanted within one week of the harvest. A total of three crops were grown and harvested at each site during 1996.

RESULTS AND DISCUSSION

BAYONNE

The excavated soil in the lysimeter at the Bayonne site varied in pH from 7.3 to 8.7. Because surface soil (0-15 cm) was used to fill the lysimeter, the Pb contamination was distributed throughout the 3.5 feet deep profile. Initially, the surface (0-15 cm) samples ranged in lead concentration from 1,000 to 6,500 mg/kg, with an average of 2,055 mg/kg. Average soil Pb concentrations of the subsurface samples were similar (± 800 mg/kg) to those of the surface soil samples, ranging from 780 to 2,100 at the 15-30 cm depth and 280 to 8,800 at the 30-45 cm depth. After three crops, the lead contamination in the surface soil ranged from 420 to 2,300 mg/kg, with an average concentration of 960 mg/kg. The average lead concentration in the 15-30 cm depth decreased slightly to 992 mg/kg (from 1,280 mg/kg, initially), while concentrations in the 30-45 cm depth remained relatively unchanged.

DORCHESTER

Initial total lead concentrations in the surface soil at the Dorchester site were lower than at the Bayonne site and ranged from 640 to 1,900 mg/kg, with an average of 984 mg/kg. The subsurface soil exhibited lower total Pb levels than the surface, averaging 538 mg/kg at the 15-30 cm depth and 371 mg/kg at the 30-45 cm depth. The Dorchester site exhibited a slightly narrower pH range than the Bayonne site, but was much more acidic, with a pH range of 5.1 to 5.9. After three phytoremediation crops, the average concentration in the surface soil decreased from 984 mg/kg to 644 mg/kg, while the 15-30 cm depth samples increased slightly to 671 mg/kg and the 30-45 cm depth decreased slightly to 339 mg/kg.

The change in lead concentrations in specific areas of the plot can be evaluated through the surface contour maps created by krigging the data. This allows interpretation of the data based on sample locations and the spatial variability that exists. It also allows one to calculate areas associated with particular Pb concentrations, and, by comparing the initial and final contour maps, to evaluate an increase or reduction in concentration in particular areas. Areas in the plots where the soil exceeded defined Pb concentrations (such as 400, 600, 800 or 1,000 mg/kg), were calculated based on the initial sampling. The process was then repeated after the final sampling.

Through the process of phytoremediation, the area at the Bayonne site with lead concentrations exceeding 1,000 mg/kg was reduced from 73 percent to 32 percent of the total plot area. A reduction in area where total soil Pb concentration exceeded the 600, 800, 1,200, 1,500, and 1,700 mg/kg levels was also observed, and is quantified in Table 1. The greatest reductions were observed in the areas contaminated at the 1,000, 1,200, and 1,500 mg/kg levels.

TABLE 1	Effect of phytoremediation on the area of surface soil (0-15 cm) Pb contamination at the Bayonne site. Values given are the percentage of the plot area that exceed the given total soil Pb concentrations before and after one season of phytoremediation (3 harvests).		
	Soil Pb Concentration	Initial	After 3 rd harvest
	mg/kg	% of Plot Area	
	> 600	100	87
	> 800	80	66
	> 1000	73	32
	> 1200	67	20
	> 1500	49	10
	> 1700	24	6

The implementation of phytoremediation technology at the Dorchester site was also successful in reducing the area of lead-contaminated soil. At the time of the initial sampling, 68 percent of the plot was above 800 mg/kg and about 25 percent of the plot exceeded 1,000 mg/kg (Table 2). After three crops, none of the treated area exceeded 800 mg/kg.

These results provide an important first step in establishing phytoremediation as a method to reduce soil Pb levels in the field. Phytoremediation, as implemented at these sites, is projected to be comparable in cost to non-permanent remediation systems such as capping, while eliminating the liability concerns and requirements for long-term monitoring. In addition, phytoremediation provides an environmentally-compatible means of removing the contaminant. Although phytoremediation may not be applicable to all contaminated soils (that is, it will work best in sites with shallow vadose zones within the root zone), it is particularly effective for those sites where the average lead contamination is less than 1,500 mg/kg. Phytoremediation has the potential to treat many of the federal, urban, and industrial sites containing metal concentrations above the required action limits. The substantial cost savings will enable remediation at many more sites than would otherwise be economically possible.

TABLE 2

Effect of phytoremediation on the area of surface soil (0-15 cm) Pb contamination at the Dorchester site. Values given are the percentage of the plot area that exceed the given total soil Pb concentrations before and after one season of phytoremediation (3 harvests).

Soil Lead	Initial	After 3 rd harvest
mg/kg	% of Treated Area	
> 500	100	100
> 600	100	100
> 800	68	0
> 1000	25	0

For more detailed information on this study, contact the author, Michael J. Blaylock, Phytotech, Inc., 1 Deer Park Drive, Suite I, Monmouth Junction, NJ 08810. Phone: (732) 438-0900, Fax: (732) 438-1209.

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DEMONSTRATION OF *IN SITU* STABILIZATION OF BURIED WASTE AT PIT G-11 AT THE BROOKHAVEN NATIONAL LABORATORY GLASS PITS DISPOSAL SITE

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ABSTRACT

In 1989, Brookhaven National Laboratory (BNL) was added to the National Priorities List of the Environmental Protection Agency (EPA). The site is divided into seven operable units (OU), the first of which includes the former landfill area. The field task site is noted as the "AOC 2C Glass Holes" location. Beginning in the 1960's and continuing into the 1980's, BNL disposed of laboratory waste (glassware, chemicals, and animal carcasses) in numerous shallow pits.

The specific site chosen for this demonstration was pit G-11. The requirements that led to choosing this pit were that it be well-characterized and relatively isolated, so that construction operations would not impact on adjacent pits. The glass holes area, including pit G-11, was comprehensively surveyed using a suite of geophysical techniques (for example, EM-31, EM-61, GPR). Prior to stabilizing the waste form, a subsurface barrier was constructed to contain the entire waste pit. The pit contents were then stabilized using a cement grout applied via jet grouting. The stabilization was performed to make removal of the waste from the pit easier and safer in terms of worker exposure. The grouting process would mix and masticate the waste and grout and form a single monolithic waste form. This large monolith would then be subdivided into smaller 4 foot by 4 foot by 10 to 12 foot block using a demolition grout. The smaller blocks would then be easily removed from the site and disposed of in a Comprehensive Environmental Response Compensation and Liability Act of 1980 (CERCLA) waste site.

During the summer of 1997, the Glass Pits Disposal area remediation was completed. The stabilized waste in pit G-11 was removed, and inspection, coring and testing were performed. This paper will discuss the construction, inspection, performance, and adequacy of the stabilization process, as well as subsequent subdivision and removal efforts. Data is also provided on the Toxicity Characteristic Leaching Procedure (TCLP) result of the stabilized monolith.

ACKNOWLEDGMENTS

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INTRODUCTION

Contaminated soils and buried waste, both treated and untreated, pose a threat through contaminant transport to groundwater or back to the surface. Many hazardous waste sites contain buried waste constituents that, if left untreated, may eventually become mobile in the environment. In many instances, this may result in unacceptable human health and environment exposures. One of the options for controlling contaminant migration from such buried waste sites is *in situ* stabilization of the waste. In addition to preventing the spread of contamination (and the resulting clean-up costs), *in situ* treatment can result in large cost savings and reduced worker exposure when compared to conventional restoration technologies (such as excavation, re-treatment and re-disposal of the waste).

In 1989, BNL was added to the EPA's National Priorities List. The site is divided into seven operable units (OU). OU-I includes the former landfill area. The field task site is noted as the AOC 2C Glass Holes location. Beginning in the 1960's and continuing into the 1980's, BNL disposed of laboratory waste (glassware, chemicals, and animal carcasses) in numerous shallow pits. In the glass holes area, historical records indicated that there were 10 glass pits excavated, but further investigation revealed the presence of 17 glass pits. The glass pits were typically excavated with a clam-shell. Individual pits were approximately 3.0 to 4.6 m (10 to 15 feet) in diameter and 3.0 to 4.6 m (10 to 15 feet) deep. Waste materials and backfill were placed into the individual unlined pits in lifts with final backfill to grade. Record keeping on the number of pits, location and contents were poor by today's standards. This makes it difficult to fully assess the problem and to develop a remediation plan. The drivers for remediating the pits are: historical records that indicate hazardous materials may have been disposed of in the pits; the fact that ground water contamination is possible down-gradient from the pits; the results of a test excavation of one of the glass holes, which unearthed laboratory glass bottles that still contained unidentified liquids; and the fact that BNL is located on top of an EPA designated sole-source aquifer.

The remediation plan called for the excavation and removal of waste from the pits. At this time, interest in *in situ* treatment of buried waste was sufficient to allow a demonstration at one of the pits. The final remediation would still be removal. The demonstration would not interfere with, and might enhance, the removal by reducing worker exposure and facilitating removal as a monolithic waste form rather than

as unconsolidated waste. An isolated pit was chosen for the demonstration. Many of the glass bottles in the pit contained liquids, and there was concern that should the stabilization not fully mix the grout and waste, materials might seep into the aquifer. Therefore, the pit was first isolated from the environment by a containment barrier—as part of demonstration of a close-coupled subsurface barrier technology—to prevent contamination spread to the shallow aquifer approximately 3 m below the bottom of the pit. The barrier was designed to capture any leakage of hazardous materials should they be mobilized by the solidification efforts. Stabilization of the pit contents proceeded after verifying the integrity of the barrier.

SITE

Brookhaven National Laboratory is located in Upton, Long Island, New York, near the geographical center of Suffolk County. Suffolk County contains approximately 1.32 million people. Originally constructed and used by the U.S. Army during World Wars I and II and used by the Civilian Conservation Corps between the wars, the site was known as Camp Upton. In 1947, ownership of the property was transferred to the Atomic Energy Commission for research on atomic energy and materials. In 1975, the site was transferred to the Energy Research and Development Administration, and finally to the DOE in 1977. The site is presently a multi-disciplinary scientific research center operated by Associated Universities Inc.

Long Island's hydrogeologic system consists of three major aquifers: the Lloyd Sand Member of the Raritan, the Mongothly Formation, and the upper Pleistocene Glacial deposits separated by two confining units (the Raritan Clay between the Lloyd and the Mongothly aquifers, and the Gardiners Clay unit between the Mongothly and the upper glacial aquifer). Taken together, these aquifers and confining layers have been designated by the EPA as a Sole Source Aquifer System. The Mongothly aquifer is the principle public water supply aquifer beneath Long Island. The Upper Pleistocene Glacial Aquifer is an important aquifer for private and public water supplies.

The specific site chosen for this demonstration was pit G-11 of the glass holes (AOC-2C). The requirements that led to choosing this pit were that it was a well-characterized pit that was relatively isolated, so that our construction operations would not impact on adjacent pits. The glass holes area, including pit G-11, was comprehensively surveyed using a suite of geophysical techniques (such as EM-31, EM-61, GPR). Pit G-11 was originally believed to be a doublet pit consisting of two nearly-connected pits. Just prior to this demonstration (but after the pit selection process) the data was re-evaluated using better analysis methods, resulting in the pit being re-defined as a single pit. The layout for grouting the pit was re-set accordingly and the pit outline was staked out by personnel of the BNL-Office of Environmental Restoration based on this evaluation. In the area of concern, the water table is approximately 13 m (42 feet) from the ground surface with a gradient from the north/northwest to the south/southeast. There is also a 0.3 m (1 foot) thick

cobble layer located approximately 1.5 m (5 feet) below grade, consisting of 2 to 8 cm (1 to 3 in.) of quartz stones. Groundwater sampling in the OU-I area has shown the presence of volatile organics, heavy metal(s), and fission product(s). There is some uncertainty as to the exact origin of contaminants within OU-I; (for example, whether a specific contaminant is from AOC 2A or the former landfill).

***IN SITU* STABILIZATION OF THE PIT CONTENTS**

The pit contents were stabilized with a cement grout via jet grouting. Jet grouting is performed by injecting a grout through a pipe into the subsurface. The pipe has a drill tip on it which is used to drill the initial borehole. The pipe is then rotated 360°, while injecting the grout, and slowly withdrawn from the ground. The high velocity jet masticates and mixes the soil and grout, which results in a column approximately 1 meter in diameter that resembles a pancake stack. The technique requires a pumpable grout that can be injected at pressures greater than 300 bars (5,000 psi) through a small orifice (typically 2 mm). The small orifice limits any aggregate additions to fine particle sizes. Most often, the jet grouting uses a low viscosity grout (approximately 5 cps), and incorporates only the existing soils for aggregate.

A Casa Grande C-6 jet grouting unit (Figure 1) was mobilized from Hanford to Brookhaven National Laboratory during the last week of May 1996. This included a diesel/hydraulic crawler-mounted injector and a diesel high-pressure, triplex slurry



Figure 1. Casa Grande jet grouting unit used for *in situ* stabilization of pit G-11 at Brookhaven National Laboratory.

pump. On arrival at the glass pit location, all systems were configured for operation, interfaced, and tested for performance before initiation of the containment barrier and *in situ* stabilization demonstration activities.

Using plastic sheet piling, a large cell was constructed around the waste pit, internal to the containment barrier, forming a vertical rectangular wall around the pit contents. This wall served as a “mold” for the *in situ* stabilization, keeping the outer edges of the monolith uniform and preventing the stabilization grout from adhering to the barrier walls. The panels were placed by trenching around the pit to a depth of 2 m. Plastic sheet pile sections were assembled in the trench and the trench was then backfilled. The internal area bounded by the sheet piling, and containing the waste, was then solidified.

In situ stabilization was performed in June 1996 by Applied Geotechnical Engineering and Construction, Inc (AGEC). Grouting took place over a two-day period. The initial parameters were based on the Hanford installation. The grout was a standard Portland type I cement mix ($w/c=1$, by weight) specified by Sandia National Laboratories (SNL), which provided the engineering aspects of this project. The cement was supplied by a local ready-mix vendor and trucked to the site in a cement mixer, from which it was delivered to a 210 liter (55 gallon) surge tank fitted with a screen to remove coarse particulates that may have been in the ready-mix truck. From the surge tank the cement was transferred via a trash pump to the high pressure pump. The tractor-mounted drilling unit was positioned at the first hole, the drilling angle set at 90° to the horizon, and the drill stem driven into the ground to the desired depth. The orifice was set at 2.2 mm. There were two openings on opposite sides of the drill tip. The cement stream was activated and grouting proceeded as follows. While delivering the grout at 400 bars (6,000 psi), the drill stem was slowly revolved and withdrawn from the ground. The withdrawal was performed in discrete 5 cm steps at a rate of 4.25 seconds per step. Rotation occurred at two revolutions per step. The step rate was adjusted in the field to minimize spoils return. Spoils production was slightly higher than observed at an earlier cold test at Hanford, WA, but still at an acceptable level. This sequence was repeated for each of the odd number holes in the first line of columns and then repeated on the even number holes.

Allowing the first column to cure slightly and using alternating holes eliminated cross-communication between columns. If the second column injection were to be performed immediately adjacent to the first, the high velocity grout could break through to the first grouted area. Any grout injected could have penetrated into the first hole and been pumped via the drill hole to the surface as spoils rather than completing the second column.

Columns were 0.66 to 0.76 m (26 to 30 inches) in diameter and spaced 0.5 m (21 inches) on centers to allow for sufficient overlap of adjoining columns and assured complete coverage. Spiral-wound tubing was inserted vertically through the

entire height of the grouted monolith such that the array of tubes outlined 1.3 m by 1.3 m (4 foot by 4 foot) cells. The tubes were sealed at the bottom and simply pushed into the drill hole following completion of a column. In plan view, the tubing was placed every foot in the east-to-west direction and every two feet north-to-south. Figure 2 shows the pit stabilization scheme in cross-sectional view. Retrieval picking eyes were also placed in each stabilization cell before the materials cured. Upon complete curing of all cells, the solidified monoliths containing the stabilized contaminant materials could be retrieved by cranes using the picking eyes in each cell. Each cell monolith could then be containerized, transported and stored, or disposed to other facilities, or other actions could be taken in accordance with BNL closure plans.

The monolith was allowed to cure for several months. On September 4, 1996, personnel from AGEC returned to BNL to apply the Bristar demolition grout. This is a fast-curing, expansive grout that is commonly used to fracture rock and concrete structures. Representatives from Bristar accompanied AGEC, mixed the grout, and placed it in the spiral-wound tubes. The grout was mixed in a 19 liter (5 gallon) bucket and poured into the tubes. The 0.3 meter (1 foot) spacing break lines were treated first, and after all these tubes were filled the grout was allowed to cure and expand for 24 hours. The grout sets rapidly, with high heat generation. As the grout cures, it expands greatly, putting pressure on the tubes. The tubes, being spiral-wound, tend to "un-wind," exerting tensile loads on the cement monolith. This

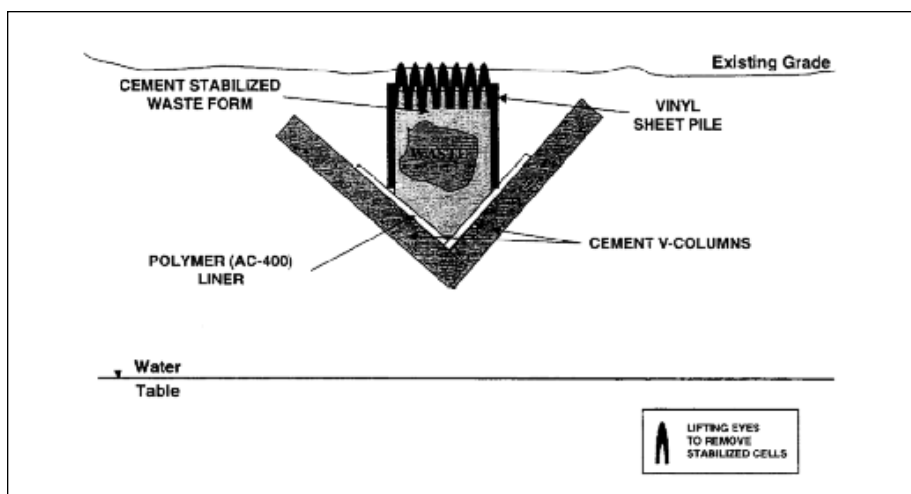


Figure 2. Cross-sectional view of *in situ* stabilization of waste pit.

pressure is designed to cause the monolith to crack preferentially along the line of spiral tubes. At the end of 24 hours the destructive nature of the demolition grout was evidenced by cracks in the ground along the tubing line. Demolition grout was then applied to the 0.6 m (2 foot) spacing tubes. It was predicted that after another 24 hours, the slabs would be divided into 1.3 m by 1.3 m (4 foot by 4 foot) cells.

EXCAVATION OF THE WASTE FORM

The monolithic cells were left in place until the summer of 1997, when the Glass Pits remediation project was initiated. The remediation consisted of excavating the pit waste and disposing of it off-site. The pit contents of G-11 were removed at this time. In the initial attempt to remove the monoliths, a backhoe was used to unearth the top of the monoliths and to remove the dirt from the inside of the south portion of the barrier (adjacent to the monolith). At this time no cracking of the cement waste form was noticeable. A chain was attached to the four picking eyes of one of the 1.3 m square monoliths and a tractor was used to pull the monolith away from the waste pit area. However, the tractor did not succeed in separating the monolith from the large waste form. In fact, the pulling eventually led to failure of the re-bar picking eye. The Bristar demolition grout and spiral tubing had failed to crack the cement monolith as predicted and observed at other installations. It is possible that the waste acted as an aggregate or reinforcing fiber, or that the glass pieces prevalent in the waste form stopped the crack propagation process initiated by the Bristar grout. Regardless, the demolition process had no noticeable effect on the cement matrix and is, therefore, not recommended for future use in waste-form resizing.

After the failure of the monolith to separate, a backhoe was used to physically break the cement waste form into smaller pieces. The pieces obtained in this manner were irregular in size and shape and more difficult to handle due to lack of lifting eyes (or balanced lifting) and non-conformity to one another. Figure 3 shows typical cement columns and pieces broken from the larger monolith. Several of these pieces were separated for coring and testing to determine homogeneity and stabilization effectiveness. The monolith was slowly broken into many smaller pieces as the excavation continued.

POST EXCAVATION EXAMINATION OF THE WASTE FORM

After the excavation was completed, ten large pieces from the monolith were set aside for further inspection. These pieces were from 0.5 to 2 m³ each. MSE-TA, Inc was tasked by the DOE to perform the visual inspection, coring, and cross-sectioning of the monoliths. The ten waste forms were moved to a safe work area where they were inspected and photographed. Due to health and safety concerns related to the material being sampled, Class-B-personnel protective clothing was required for all work. BNL health and safety officers provided coverage (such as air sampling

and radiation monitoring) during all aspects of the sampling. Cross-sectioning of the large pieces was performed using a CASE excavator with a chisel hammer.

For the most part, the bottles and glassware in the pit were broken up by the energy of the jet (Figures 3 and 4). However, in many cases the bottles (but no laboratory glassware) appear to be relatively intact. The degree of consolidation was very good, as the cement grout kept the waste together for easier removal. Small pieces of waste such as syringes were encapsulated by the grout. There were no major voids observed (greater than fist sized), and later coring would prove there were very few small voids (1 to 10 cm). Overall, the degree of mixing was very good, and the encapsulation efficiency was extremely good.

It was apparent that plastic bottles and apparatus fared much better than the brittle glass. The high pressure grout jet appears to have been capable of breaking up most of the glassware and encapsulating parts. In a few cases, plastic bottles merely collapsed and were encased in the cement.

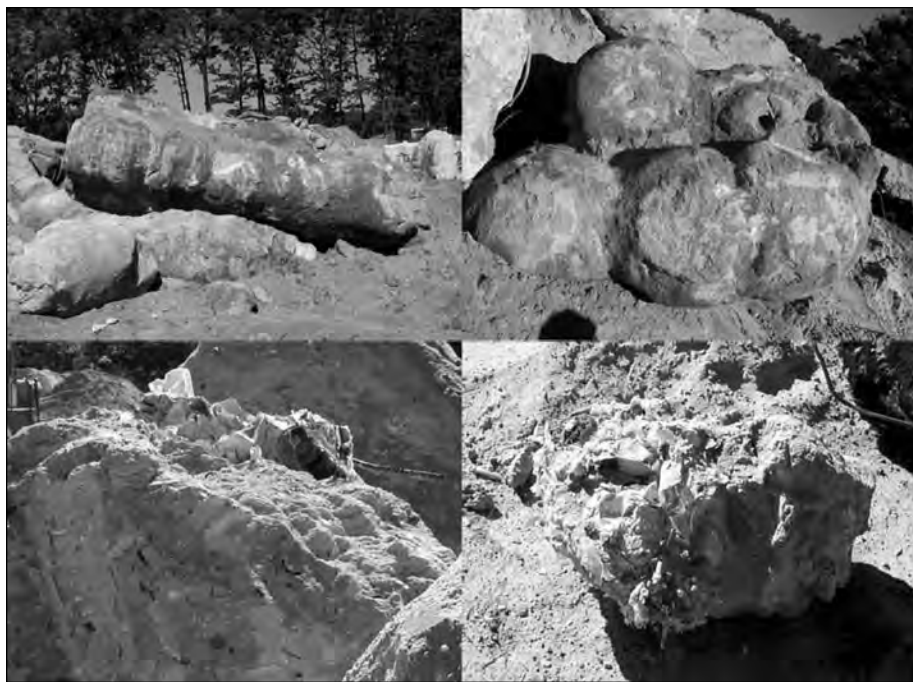


Figure 3. Excavated pieces of the *in situ* stabilized waste form from pit G-11 at Brookhaven National Laboratory.

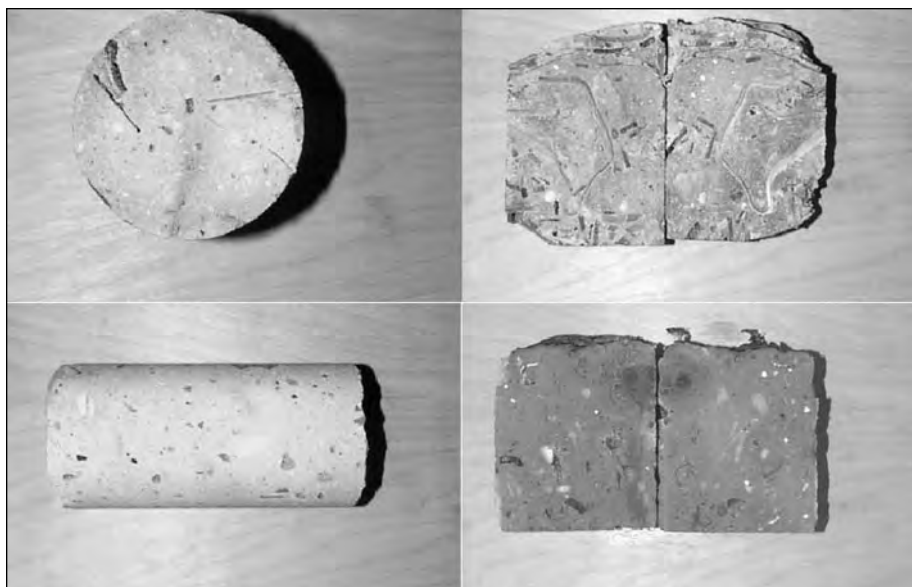


Figure 4. Core sections taken from the *in situ* stabilized waste form from pit G-11 at Brookhaven National Laboratory.

Some types of waste, such as plastic sheet, plastic tubing, copper tubing, stainless steel tubing, coated wire and similar materials, had poor adhesion to the cement grout. The pieces were fully encapsulated; however, wherever the cross-sectioning encountered such debris, the pieces would shear along the contact faces of this material.

Core samples were taken from the monolith remnants to gain a better picture of the success of the stabilization. Coring was accomplished using a Milwaukee 4035 electric core drill and a 10 cm (4 inch), diamond-tipped core barrel. The core barrel was lubricated and cooled by water supplied from a truck-mounted tank. Three cores were taken from each of the ten waste pieces, varying in length from 10 cm to 25 cm. The cores were returned to the laboratory and trimmed square. Density measurements were then taken, and one core sample from each large piece was stored for future testing. Densities are given in Table 1. Subsamples from each of the ten pieces were composited and sent out for RCRA metals analysis following the EPA Toxicity Characteristic Leach Procedure. The results were below the EPA limits for all RCRA metals. One core sample from each of the ten sets was cross-sectioned along the long axis using a wet diamond saw. Inspection of these sections showed good homogeneity, a well mixed product, and most importantly, virtually no voids.

TABLE 1 **Densities of core samples from the Pit G-11 stabilization.**

Core sample ID	Density (g/cm ³)	Core sample ID	Density (g/cm ³)
1A	1.78	6A	1.77
1B	1.63	6B	1.88
2A	2.06	6C	1.67
2B	1.98	7A	1.85
2C	2.02	7C	1.76
3A	1.80	8A	1.78
3B	2.11	8B	1.84
3C	1.92	8C	1.85
4A	2.00	9A	1.80
4B	1.94	9C	1.64
4C	1.87	10A	1.99
5A	1.92	10B	2.01
5B	1.85	10C	1.98
5C	1.90		

Average density = 1.87 ± 0.12 Median density = 1.86 ± 0.10

Only a few small (less than 1 cm) voids were seen in the ten cores. Typical core and cross-sections are shown in Figure 4.

Four cement/soil samples, 4.4 cm (1.75 inches) in diameter and lengths ranging from 3.5 to 4.0 cm were measured for hydraulic conductivity. These samples, taken from the containment barrier wall, where there was no observable waste, provided a baseline hydraulic conductivity for the cement/soil composite that encapsulates the waste. The hydraulic conductivities were measured using a flexible wall perimeter following ASTM D-5084 [3]. Conductivities ranged from 1.1 x 10⁻⁶ cm/sec [1.1 x 10⁻⁸ m/s] to 1.6 x 10⁻⁸ cm/sec [1.6 x 10⁻¹⁰ M/sec], averaging 3.4 x 10⁻⁷ cm/sec [3.4 x 10⁻⁹ m/sec].

CONCLUSIONS

In situ stabilization appears to have produced a reasonably well-homogenized waste form. Smaller components such as bottles, glassware, syringes, and other materials were either broken up by the jet energy or were fully encased in grout. Larger components such as 55 gallon drums and pressure cylinders were left intact by the jet and were simply macroencapsulated.

The large monolithic waste form constructed from the pit contents using cement-based jet grouting had to be resized for removal and disposal. Bristar demolition grout had no noticeable effect on the cement matrix and is not recommended for future use in waste-form resizing.

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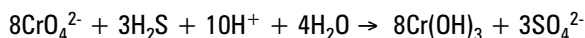


IN SITU GASEOUS REDUCTION

E. C. Thornton, PNNL

INTRODUCTION

Laboratory investigations conducted over the last several years by the U.S. Department of Energy (DOE) indicate that chromate-contaminated soils can potentially be remediated by treatment with a diluted hydrogen sulfide mixture. Results of these tests suggest that 90 percent or better reduction and immobilization of hexavalent chromium can be achieved by the gas treatment approach (Thornton and Jackson 1994). The primary chemical reaction of this approach involves the reduction of Cr(VI) to Cr(III), with subsequent precipitation as an oxyhydroxide solid phase. The reduction and immobilization of Cr(VI) may be represented by the following generalized reaction:



where Cr(VI) is represented by the chromate anion. Note that the products of this reaction include minor amounts of sulfate, which is generally not regarded as a contaminant of concern, and Cr(III)(OH)₃, an insoluble and essentially nontoxic solid.

Application of diluted H₂S to reduction of hexavalent chromium can be undertaken through the injection of the gas mixture into waste site soils in a central borehole (Figure 1). The gas mixture is then drawn by the vacuum applied at extraction boreholes located at the site boundary. Monitoring of H₂S breakthrough at the extraction wells thus provides a basis for assessing treatment progress. Verification of treatment effectiveness can subsequently be accomplished through comparison of Cr(VI) distribution through site soils before and after treatment.

A challenge facing this technology is the toxic nature of H₂S. However, the gas is relatively safe to work with when diluted to concentrations below 500 ppm_v. In addition, engineering controls can be utilized to ensure that essentially no H₂S is released to the environment so that workers are not exposed to H₂S during remediation operations, and (Thornton *et al.* 1999).

SELECTION AND CHARACTERIZATION OF FIELD TEST SITE

In order to test the effectiveness of the *in situ* gaseous reduction approach and verify that it can be applied in a safe and environmentally acceptable manner, a search was initiated to locate a waste site for undertaking a small-scale field demonstration. A Cr(VI)-contaminated site was subsequently identified at the U.S. Department of Defense's (DOD's) White Sands Missile Range that appeared to be a good candidate for initial testing efforts. A joint collaboration was subsequently developed

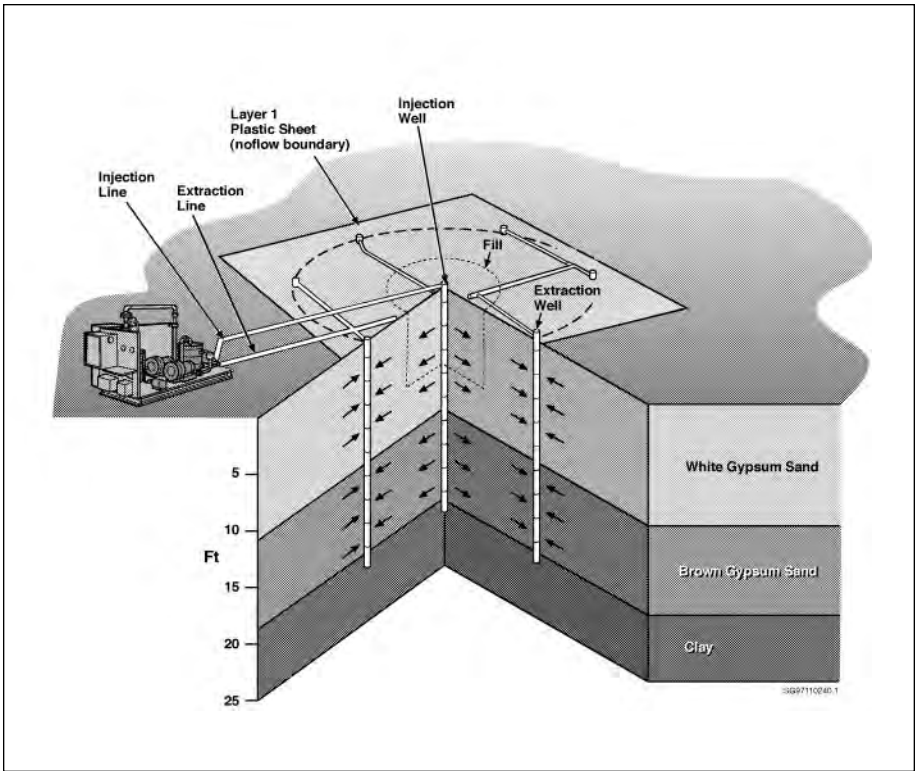


Figure 1. Gas-treatment system and cross section of well-field network.

between the U.S. DOE and DoD to undertake a field demonstration at this site (Thornton *et al.* 1999). During the demonstration, Pacific Northwest National Laboratories (PNNL) and Sandia National Laboratory (SNL) collaborated in the field work, aided by DoD staff at White Sands Missile Range.

The chromate-contaminated waste site designated as Solid Waste Management 143 resulted from the spillage of corrosion inhibitor in the early 1980s. The contamination was discovered in January 1990 when preparations were underway to pave the area. Greenish-yellow soil was sampled and analyzed and found to contain Cr(VI). Approximately 17 55-gallon drums of contaminated soil were excavated in 1990. Clean closure could not be obtained, however, and the expensive excavation effort was delayed until a better cleanup method could be implemented. Additional site investigations were conducted in 1992 and 1993 by several companies contracted by the U.S. Department of the Army. These investigations provided additional information regarding extent of Cr(VI) contamination at the site. Analysis of

groundwater samples also indicated that chromium contamination in nearby monitoring wells exceeded the federal and state maximum contaminant levels and state groundwater-protection standards.

Results of these investigations and recent DOE characterization efforts indicate that the upper 18 feet of the site is composed of gypsum sand, as illustrated in Figure 1. The upper part of this interval is a relatively clean, eolian deposit of gypsum sand ("white" sand) and the lower interval is a brownish gypsum sand with a higher clay content ("brown" sand). A dense brownish clay is present at a depth of about 18 feet. Soil samples were also collected from boreholes drilled by SNL staff and analyzed for Cr(VI) by contract laboratories. This data provided a detailed model of subsurface contamination levels and the vertical and lateral extent of contamination. It was determined that the contamination was located in the gypsum sand and did not penetrate into the clay. It is inferred that Cr(VI) reached groundwater by moving laterally through the gypsum sand and then vertically downwards as the clay pinches out.

The soil Cr(VI) analytical data was used to position the injection borehole at the center of the waste site. Soil gas points were also emplaced at various depths and locations and a plastic sheet placed over the site as a cover. A vacuum test was then performed by pulling air from the central borehole and measuring the resulting vacuum at the soil gas points. This information was utilized to obtain gas flow rates and a radius of influence estimate.

A laboratory treatability test was also conducted with contaminated soil from the site. In these tests, Cr(VI) was reduced by 98 percent by treatment with 100-ppm_v H₂S after application of a ratio of 0.00004 lb of H₂S/pound of soil. The characterization and treatability test data were utilized to design the well-field network and provided a basis for estimating the treatment time required. The well-field was completed by installing the extraction wells at the edge of the contaminated region. The radial distance from the central injection borehole to each of the six extraction boreholes was 15 feet.

PERFORMANCE OF DEMONSTRATION

The primary objectives of the field demonstration were to obtain information needed to complete a technical performance assessment of the technology, verify that the technology can be applied in a safe and environmentally acceptable manner, and obtain sufficient cost information to support a cost analysis (Thornton *et al.* 1999).

Following installation of the well-field network, a tracer test was conducted in 1997. In this test a 400 ppm_v mixture of sulfur hexafluoride (SF₆, a nonreactive and non-toxic gas tracer) was injected via a skid-mounted gas-treatment system. Test results provided gas-flow rates and indicated good gas-capture characteristics. Satisfactory operation of the system was also verified during the tracer test.

Additional activities conducted prior to initiating the injection phase of the demonstration included preparation of work and safety plans, completion of field site preparation activities, and determination of site operating requirements and state operating and permitting requirements. A significant outcome of these activities was the development of monitoring and alarm systems for notification of treatment gas emissions, as described in the project safety plan.

The gas-treatment-injection test was performed between mid-April through June 1998. During the test, a 200 ppm_v mixture of H₂S in air was injected into the site at flow rates ranging from 20 to 56 cfm. The extraction wells were monitored for breakthrough of H₂S, which signaled completion of treatment. This residual H₂S was subsequently removed from the air stream by a gas scrubber before release of the air back to the site atmosphere. All systems performed in a satisfactory manner, and no significant releases of H₂S to the atmosphere occurred. Collection of post-treatment soil-characterization samples was also accomplished during July 1998.

SUMMARY OF DEMONSTRATION RESULTS

A performance assessment of the technology has been completed based on the analysis of the post-treatment characterization samples for Cr(VI) and comparison of these results to the pre-treatment data (Thornton *et al.* 1999). This information indicates that 70 percent of the Cr(VI) was reduced. In particular, the zone of highest Cr(VI) concentration, located at a depth of 4 to 10 feet, was nearly completely treated, with Cr(VI) concentrations of soil samples decreasing from an average of 8.1 mg/kg before treatment to 1.14 mg/kg after treatment. This corresponds to the white sand interval, which appears to have a moderate to high permeability (Figure 2). However, a zone of lower contamination (corresponding to the lower-permeability brown sand interval from 10 to 16 feet) was largely unaffected. Thus, geologic heterogeneity was found to limit treatment effectiveness during the demonstration. Selective treatment is not surprising, however, since the injection and extraction boreholes were slotted over the entire interval from 3 to 18 feet. Additional gas treatment of the remaining contaminated soil in the brown sand interval can be undertaken, if necessary, by limiting the slotted interval to that zone.

No significant releases of treatment gas were identified during the demonstration. Thus, it was shown that the *in situ* gaseous reduction approach can be undertaken in a safe and environmentally-acceptable manner.

A life-cycle cost model has been developed for the technology based on information collected during the demonstration (Hogan 1998). In a typical example examined by the model, a unit cost of \$43/yd³ was obtained for *in situ* gaseous reduction versus \$214/yd³ for excavation. The *in situ* gaseous reduction approach becomes more

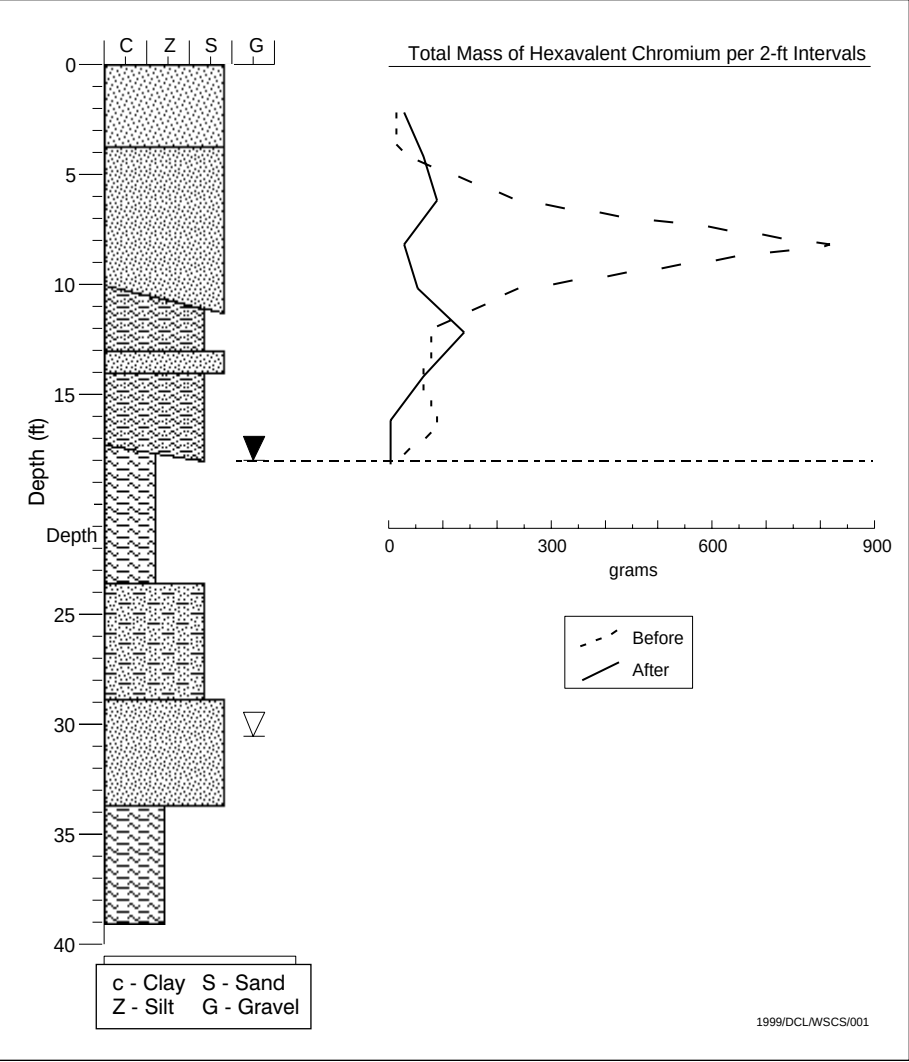


Figure 2. Site stratigraphy and comparison of Cr(VI) mass before and after gas treatment of site soils

cost effective when contamination exists at depths of greater than 15 feet. Estimated costs can vary significantly, however, depending on the specific inputs. Therefore, it is recommended that the user perform the analysis for the combination of model inputs associated with a particular site.

CONCLUSIONS

Treatment of Cr (VI) contamination by gas injection is an effective approach, although potentially limited by geologic heterogeneity. Treatment of lower permeability zones can probably be accomplished, if necessary, through injection of gas into the zone through a borehole specifically screened or slotted over these intervals.

No significant releases of H_2S occurred during the demonstration, indicating that *in situ* gaseous reduction technology can be applied in a safe and environmentally-acceptable manner. A safety plan was developed in support of the demonstration that can be utilized as a guide that defines monitoring operations and appropriate response actions for applying this technology to other sites.

Results of the demonstration also suggest that the technology is cost-effective. In particular, the technology is likely to cost less than excavation when hexavalent contamination exists at depths of greater than 15 feet.

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9

Barriers and Containment Methods

D. E. Daniel

INTRODUCTION

This chapter summarizes current knowledge concerning surface and subsurface barriers used for containment of contaminants in the vadose zone. “Barrier” refers to any natural or man-made layer, material, boundary, or system designed to slow, stop, or control the movement of fluids (which may include either gases or liquids or both).

Containment can be accomplished in two ways: (1) physical containment provided by either an impermeable barrier designed to block fluid movement or by a permeable chemical barrier designed to adsorb or degrade contaminants, or (2) hydraulic containment achieved by control of the hydraulic gradient. Physical containment may be achieved by using naturally occurring soil or rock (such as a low-permeability stratum beneath the contaminated zone) to stop or limit downward migration of waste constituents, or by using man-made barriers (such as vertical cut-off walls). Hydraulic containment is usually accomplished by installing groundwater or soil vapor extraction (SVE) wells in the area of heaviest contamination and pumping from those wells, creating flow toward the extraction wells and a zone of capture.

This chapter focuses on the current state of knowledge for barriers and containment methods used in the vadose zone. It does not dwell on technologies that are intended primarily for the saturated zone, for example, vertical barrier walls constructed with slurry trenching techniques, but instead focuses on technologies that are specifically targeted for the vadose zone. Knowledge gaps that limit the effectiveness of barriers and containment methods are discussed at the end of the chapter.

TYPES OF PHYSICAL BARRIERS

There are three types of physical barriers (Figure 9-1): (1) final cover systems (“caps” or “covers”), (2) vertical barriers (“cutoff walls”), and (3) bottom barriers (“floors”). Barrier walls can also be constructed at an angle to form a combined wall/floor system (Figure 9-2).

Final Cover Systems (CAPS)

Final cover systems for contaminated zones and landfills may serve a variety of purposes, depending on the type of project, remediation objectives, and regulatory agency requirements. However, nearly all caps have two primary objectives: (1) to provide physical separation of

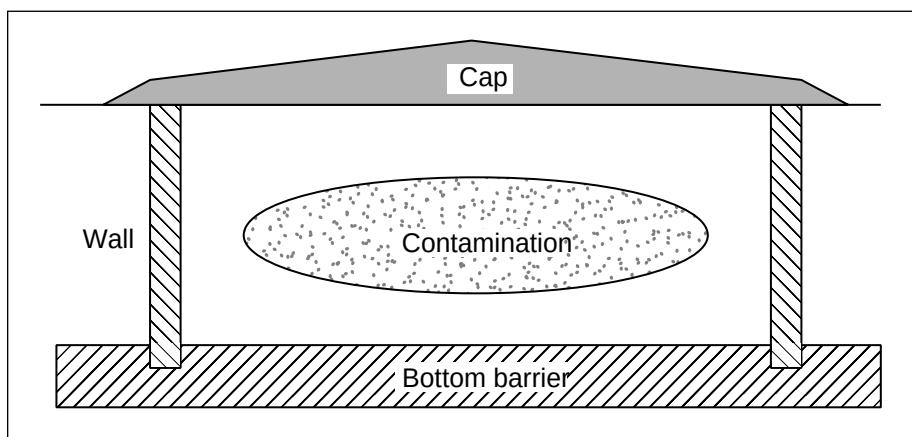


Figure 9-1. Three types of barriers: final cover system (cap), vertical barrier (wall), and bottom barrier (floor).

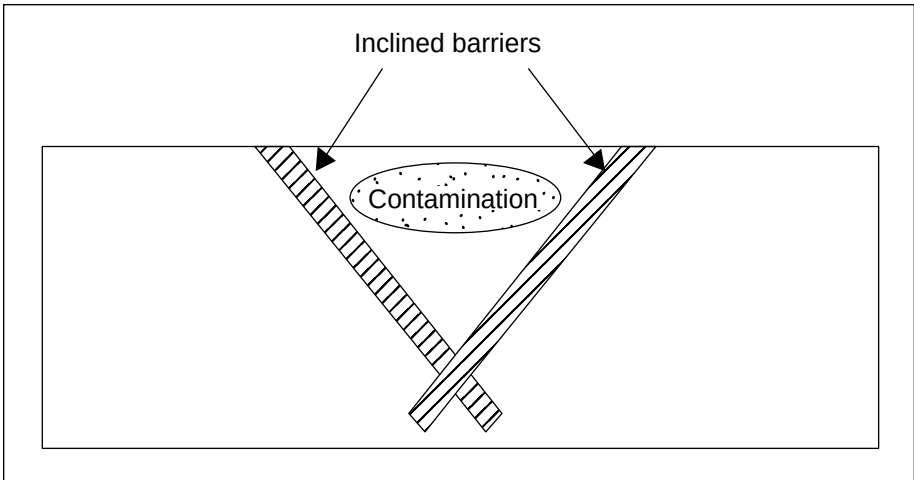


Figure 9-2. Inclined barriers forming a wall and floor.

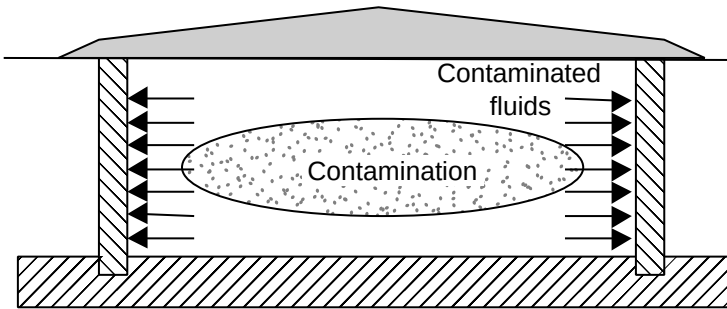
the underlying contaminants from the surface environment, and (2) to minimize percolation of water into the underlying contaminated zone.

Although virtually all caps are placed above the water table, and therefore function as vadose zone barriers, the construction approach can vary depending on the local climate. For example, most caps constructed in humid climates use clay soils to resist water infiltration, but in arid or semi-arid climates, clays tend to crack as a result of desiccation. In humid regions, sheet and rill erosion due to running water causes the most concerns; in arid or semi-arid regions, wind erosion may be more significant. While this chapter discusses the full range of capping technology, because of the book's focus on the vadose zone, the author will pay particular attention to problems and technology that are unique to arid and semi-arid climates.

Vertical Barriers (Walls)

Vertical barriers are the most common type of man-made subsurface barrier used for waste containment. In some situations, vertical barriers are designed to contain contaminants (Figure 9-3[a]); in other situations, they are intended to keep clean fluids out of an area undergoing source removal (Figure 9-3[b]).

- a. Vertical barrier contains contaminants or limits outward migration of contaminants.



- b. Vertical barrier contains or limits inward migration of uncontaminated fluids.

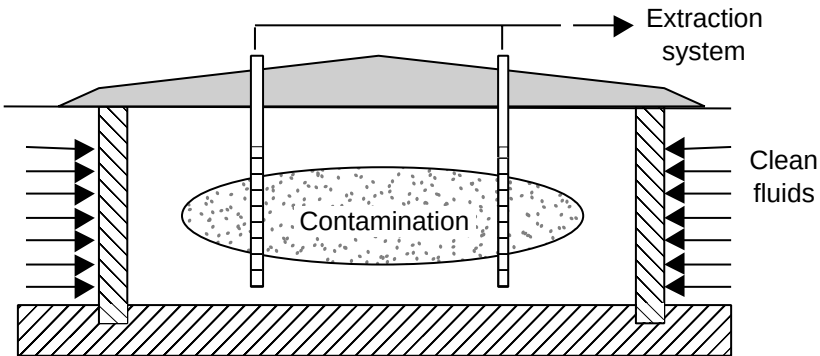


Figure 9-3. Vertical barriers.

At sites with relatively shallow groundwater, a vertical barrier normally extends through the vadose zone and into the groundwater, providing containment in both the saturated and vadose zones. Usually in such cases, the vertical barrier is designed primarily for groundwater containment. However, there are unique challenges associated with waste containment in the vadose zone, and these are emphasized in this chapter.

By design, the key characteristics of vertical barriers are impermeability to gas or water, or both, and durability (for example, resistance to deterioration or degradation from the chemicals to be contained). Vertical barriers can be designed to be permeable to water or gas but relatively impermeable to chemicals. Permeable reactive barriers are typically used for groundwater treatment but can also be used in the vadose zone (Gavaskar *et al.* 1998; and U.S. EPA 1998a).

Bottom Barriers (Floors)

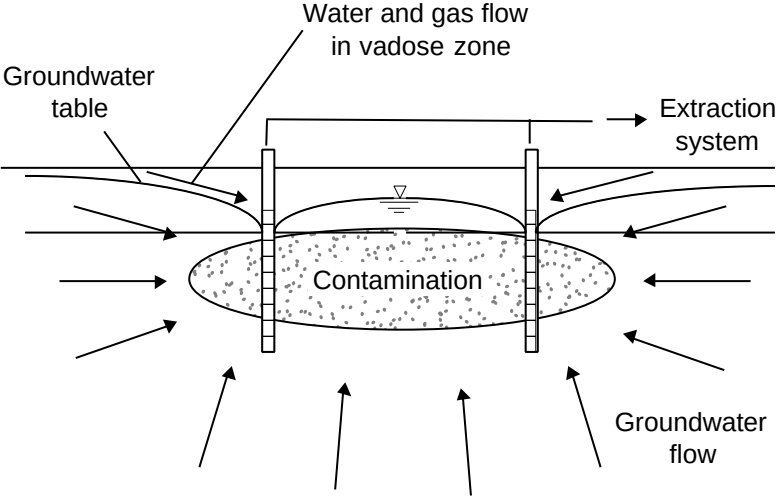
Bottom barriers can either be naturally occurring formations of low-permeability soil or rock, or can be man-made. However, while several prototype bottom barriers have been constructed, to the author's knowledge, no full-scale, man-made bottom barrier has ever been constructed at an actual waste disposal site. Instead, vertical barriers are typically extended to depths that are sufficient to penetrate, or key into, low-permeability strata.

HYDRAULIC CONTAINMENT

Hydraulic containment refers to creation of a hydraulic gradient that draws fluids and contaminants toward a contaminant removal zone. Two types of systems are typically used for the vadose zone (Figure 9-4). As illustrated in Figure 9-4[a], hydraulic containment may be achieved in the vadose zone as a by-product of groundwater containment. Hydraulic containment of groundwater almost always produces a gradient in soil water potential in the vadose zone that directs the soil water from the vadose zone toward the groundwater capture zone. In addition, a gradient in gas pressure may be created by withdrawing gases from the vadose zone either in separate SVE wells, or with dual pumping of water and gas from the same well (Figure 9-4[a]).

Figure 9-4[b] shows how an SVE system pumps air from the subsurface to draw soil gas and contaminated vapors and contain them within the radius of influence of the SVE wells. The vacuum created by SVE pumping forms a vacuum, or pressure, gradient that also draws vadose zone water toward the SVE extraction wells, although the dominant mass transfer mechanism is through the vapor phase.

a. Hydraulic containment of groundwater below water table and containment of soil water and gas in the vadose zone.



b. Hydraulic containment of gas in the vadose zone.

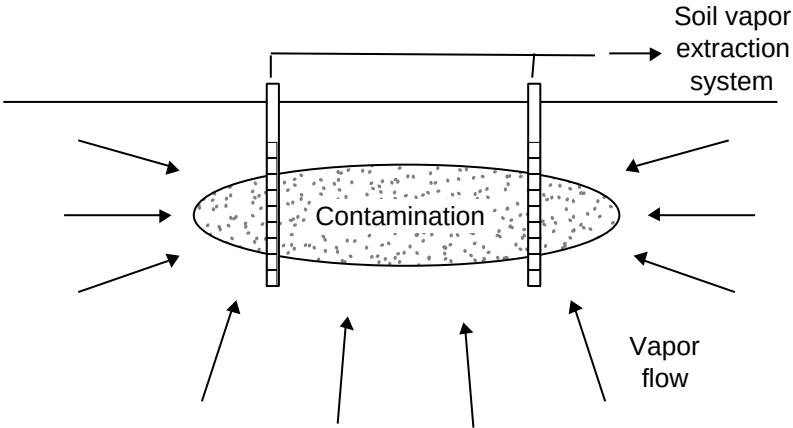


Figure 9-4. Hydraulic containment in the vadose zone.

COMPARISON OF CONTAINMENT IN THE VADOSE ZONE WITH CONTAINMENT IN THE SATURATED ZONE

Several differences exist between barriers and containment technologies in the vadose zone and in the saturated zone. The following factors make containment in the vadose zone more challenging than in the saturated zone:

1. Contaminant transport in the vadose zone, can occur in three phases (water, nonaqueous-phase liquids [NAPLs], and gas) while flow in saturated materials takes place in only two phases (water and NAPLs, if present).
2. Vadose zone soils are drier than saturated zone soils, which compromises the integrity of clay soils. Because clays tend to dry and crack in the vadose zone, engineers are challenged to find or develop materials that will resist desiccation .
3. Contaminant transport in the vadose zone is more difficult to characterize and to analyze than in the saturated zone, complicating the assessment of barrier performance. Gravitational and capillary forces control the direction of contaminant migration in the vadose zone. In many cases, penetration, or vertical flow components, dominate vadose transport. The complexity of vadose zone transport mechanisms influences the design parameters for, and potential usefulness of, different barrier types (e.g., caps versus walls versus floors).
4. While groundwater monitoring procedures for the saturated zone are well established, monitoring methods for subsurface barriers in the vadose zone are not.
5. There is much less experience in constructing subsurface barriers in the vadose zone—for example, most of the experience with vertical barrier walls deals with containment of groundwater in the saturated zone.
6. Many regulatory agency guidelines, such as those for caps, were intended for sites with relatively humid climates, and not for arid or semi-arid sites, or sites with deep groundwater tables.

When examining barriers in the vadose zone, the following issues must be considered:

- Wet clays are not effective, and alternative materials must be developed.
- Experience with barriers in the vadose zone is very limited.
- Regulatory hurdles may exist simply due to lack of focus on the vadose zone in regulatory agency guidance documents.

On the positive side, there is a tremendous opportunity for engineers and scientists who understand the vadose zone to take advantage of its characteristics. For example, SVE systems tend to be relatively simple and economical, and can provide not only source reduction but also effective containment and enhanced biodegradation of some contaminants. Containment schemes often are just one component of a larger contaminant control system.

CAPS

Background information on landfill caps is available in several documents. The U.S. EPA's technical guidance document for caps (U.S. EPA 1989) is perhaps the most significant document because it is widely used and cited. However, this document currently is undergoing revision, in part because it does not address alternative caps and vadose zone issues very well. Other useful EPA documents include reports that deal with radioactive waste (U.S. EPA 1978), hazardous waste (U.S. EPA 1982a, 1985a, and 1987), closure of hazardous waste impoundments (U.S. EPA 1982b), vegetation of cover systems (U.S. EPA 1983), and subsidence of caps (U.S. EPA 1985b). The U.S. Army Engineer Waterways Experiment Station (1991) published three volumes containing recommendations for cover system designs for uranium mill tailings sites. Chapter 5 of Rumer and Ryan (1995) summarizes design issues for caps, and Chapter 6 of Rumer and Mitchell (1995) provides updated information and several case histories. Daniel and Koerner (1996) discuss construction quality assurance of waste containment facilities. Koerner and Daniel (1997) provide a comprehensive treatment of design issues for caps. Benson (1997) summarizes alternative landfill cover demonstrations, and a conference proceedings edited by Reynolds and Morris

(1997) contains papers on landfill capping in the semi-arid west. General information on materials and design approaches may be found in Daniel (1994a), and on regulatory aspects in Richardson (1997). Long-term issues are discussed by Johnson and Urie (1985).

SIX BASIC COMPONENTS OF CAPS

The six basic components of a traditional cap are illustrated schematically in Figure 9-5. From top to bottom, the layers are as follows: surface layer, protection layer, drainage layer, hydraulic barrier layer, gas collection layer, and foundation layer. The surface layer and protection layer may be combined into a single cover soil layer.

Not all components are necessary for all caps. For example, a gas collection layer is unnecessary if the underlying waste generates no vapors that require collection or control. Also, as discussed below, alternative caps for relatively arid sites may have a significantly different cross-section than that shown in Figure 9-5.

Each component in a final cover serves a specific purpose. The components should be designed to work together as a system. For example, the gas collection layer works properly only if one of the overlying layers (typically the hydraulic barrier layer) serves as a barrier to gas migration, allowing the gases to accumulate in the gas collection layer where they can be collected and removed.

Surface Layer

The surface layer is the uppermost layer in a multi-layered cap. The primary function of the surface layer is to resist erosion and, for caps with a vegetative cover, to promote the growth of healthy vegetation which aids in removing water from cover soils by evapotranspiration.

Vulnerability to erosion depends upon the slope of the cap. As illustrated in Figure 9-6, landfill caps often have a relatively flat section on top and steeper slopes on the sides. Typically, the cross-sections of the flat and steep areas will be different. For example, a cap at Hanford, Washington, utilizes a gravel-soil admix in relatively flat areas and basalt rip-rap on the steep edges of the cap (Wing and Gee 1994b).

One disadvantage of armoring the surface layer with rip-rap is the adverse impact on water infiltration. Precipitation that falls on the sur-

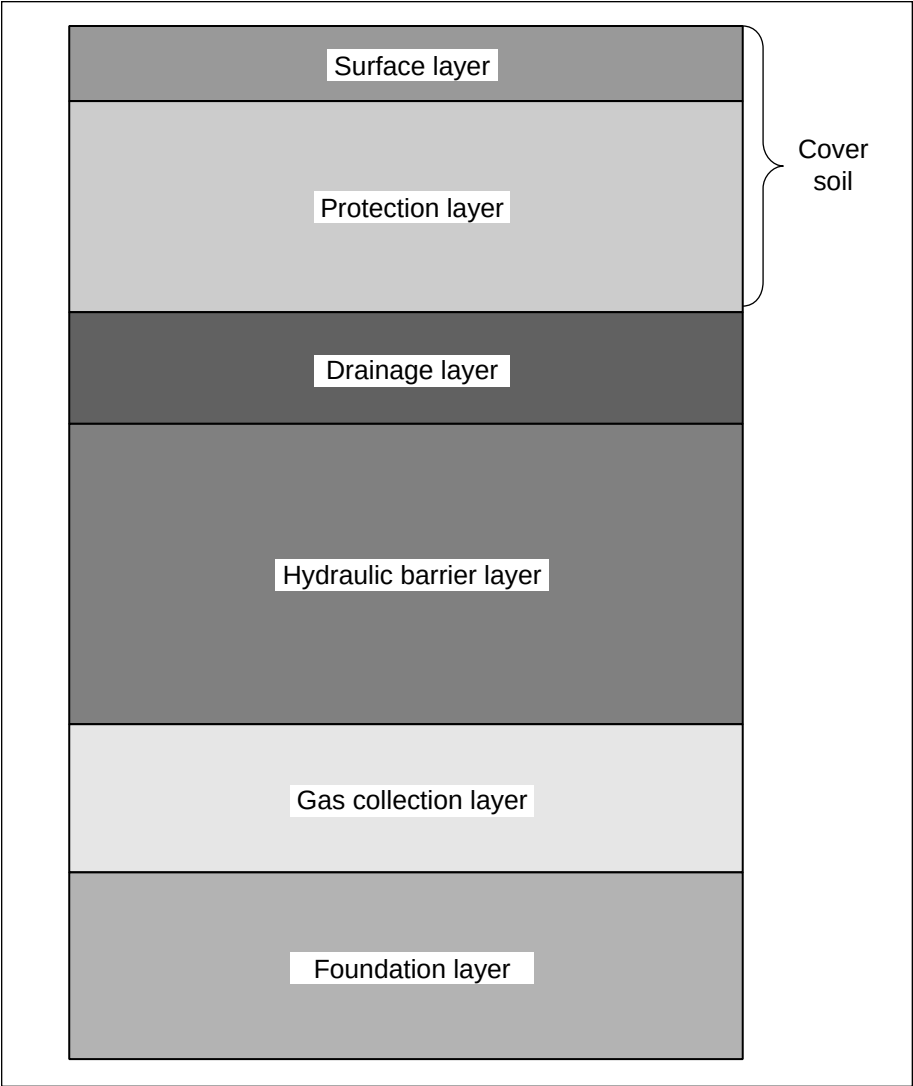


Figure 9-5. Six basic components of a traditional cap.

face of the cover percolates downward through the rip-rap, but because plants do not normally grow on the rip-rap, there is little transpiration. Plants assist in water infiltration by removing water from the subsoil and transpiring it back to the atmosphere. The rip-rap serves as a “one-way window” for moisture, allowing water to percolate downward into the underlying materials but contributing little to upward water migration.

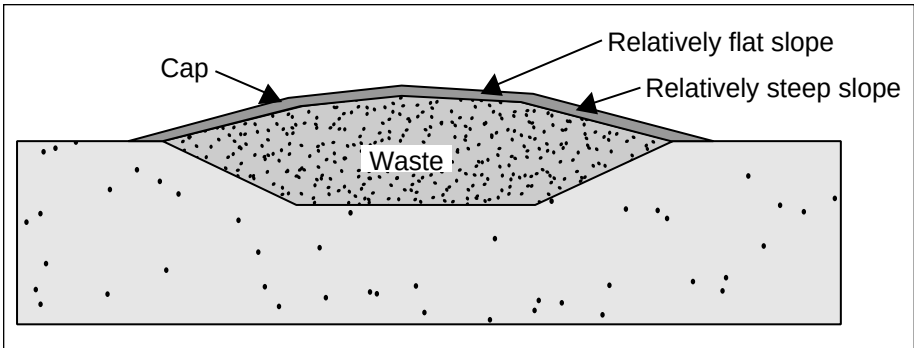


Figure 9-6. Typical cross section of a landfill cap with relatively flat and steep slopes in different areas.

Field experiments at Hanford, Washington, demonstrated that a layer of gravel at the surface of a silty soil allowed approximately half of the annual 150 mm of rainfall to percolate through the upper 2 m of soil (Gee *et al.* 1992). In contrast, when silt (even unvegetated silt) was exposed at the surface and not covered with gravel, there was zero percolation through the 2-m-thick soil profile. This behavior of granular material is utilized by gardeners when they apply mulch to bare soil. The mulch allows water to percolate down to the underlying soil but shields the soil from evaporative loss of moisture (Kemper *et al.* 1994).

A mixture of gravel and soil has been used at Hanford (Ligotke and Klopfer 1990; Wing and Gee 1994a), and on uranium mill tailings caps (Waugh and Richardson 1997). The gravel-soil admix includes a fine-grained soil component to retain moisture and support growth of plants. As wind erodes the soil component, the gravel is left behind, forming a thin “desert pavement” layer, which resists erosion and suppresses surface evaporation. The gravel is underlaid just a few millimeters below the surface by the soil-bearing material, which can support growth of plants.

There are instances in which it may be desirable to promote a relatively large amount of infiltration. One such instance concerns caps constructed above radioactive wastes that emit radon gas. One way to control surface emissions of radon is to cover the waste with a thick, wet layer of soil (Waugh and Richardson 1997). Wet, clayey soils are practically impermeable to gas. Maintaining a high water content of the soil in such instances is desirable, and a layer of rip-rap at the surface can help to keep the underlying soil wet.

If the surface layer is composed of topsoil, the topsoil should be selected and designed to support the growth of vegetation that is well adapted to a particular region. Plants are often essential in providing the desired protection from erosion, particularly in areas that receive large amounts of rainfall. Maintaining viable vegetation on a cap in an arid or semi-arid climate is obviously much more difficult than in a humid climate, and for this reason, the cap is often designed to resist erosion even without vegetation, for example, by using the gravel-soil admix mentioned previously. Procedures for analyzing erosion rates are discussed by U.S. EPA (1989) and, with emphasis on problems in relatively arid climates, by Anderson and Stormont (1997).

Plants withdraw water from the soil and return it to the atmosphere via evapotranspiration, which is an essential function in most cap systems (Anderson *et al.* 1990; Andraski 1997). Plant selection is usually based upon range of root depths. It is desirable for the roots to tap into a large range of soil depth for purposes of extracting soil water over the full depth of the cover soil. However, if rooting depths are too great, penetrating roots can plug a drainage layer, break through and damage a barrier layer, or in some cases, penetrate into the waste itself, bringing waste constituents to the surface. In solid waste landfills, grasses are normally planted on the surface and mowed to keep undesirable plants with deeper roots off the cap. However, because long-term maintenance may not be dependable, especially with remediation projects, it may be advisable to ensure that the components of the cap are designed to accommodate local vegetation, which may include deep-rooted plants.

It is important that the topsoil contains adequate organic matter and nutrients to support plant growth. If it doesn't, supplements such as fertilizers may have to be added. An increasingly common practice at municipal solid waste landfills is to supplement topsoil with organic matter such as wastewater treatment sludge or fibrous waste from production of paper. This organic matter, which would otherwise constitute a waste material, helps to promote growth of vegetation and results in productive use of a material that would otherwise have to be disposed. However, in arid and semi-arid regions, and for sites where long-term maintenance is not desirable, soil supplements may not maintain long-term soil conditions, leading to short-term development of a vegetative cover that may not be representative of the plants that will grow on the cap in the long term.

Asphaltic concrete, a mixture of aggregate (usually sand and gravel) and asphalt, can also be used as a surface layer. Heated asphalt is mixed with aggregate, spread in a thin layer (typically 50 to 100 mm thick), and compacted with heavy steel drum compactors using essentially the same technology that is used to construct roadways. Asphaltic concrete can be very permeable unless special attention is given to minimizing air voids during mixing and application (Repa *et al.* 1987). To achieve low hydraulic conductivity 1.5 to 2 times more asphalt is used than for roadway pavements. This type of asphaltic concrete is referred to as “low permeability asphaltic concrete.” However, a permanent, low-permeability asphaltic concrete barrier usually is not recommended for use as the surface layer of a cap because the asphalt will degrade due to exposure to ultraviolet radiation and oxygen. If asphalt is used as a permanent hydraulic barrier, it should be buried beneath a protection layer, not exposed at the surface. If asphalt is used as a surface layer, it typically is viewed as an erosion-resistant layer (for example, for a parking lot), and not the primary hydraulic barrier layer.

It is advisable to implement a regular monitoring and maintenance program for the surface layer, at least in the initial years after construction. Periodic inspection of the surface layer for erosion, health of vegetative cover, growth of undesirable plants, burrow holes, stability of slopes, and general integrity is recommended.

Protection Layer

The protection layer lies directly beneath the surface layer and in some cases can be combined with the surface layer to form the cover soil layer (as shown in Figure 9-5). The protection layer serves both to protect the underlying components and to store water that has percolated through the surface layer. The underlying layers may need to be protected against exposure caused by erosion, excessive wetting/drying, freezing, penetration by plant roots, penetration by burrowing animals, and accidental human intrusion. In addition, the protection layer may serve to attenuate radon gas emissions from uranium mill tailings.

Soils

The protection layer may be constructed from locally available soil. Medium-textured soils such as loams have the best overall characteris-

tics for development of plant root systems. Fine-textured soils such as clays have excellent water-holding capability but are vulnerable to cracking when desiccated. Sandy soils may create problems because of their low water retention capacity and high hydraulic conductivity.

Filters

If the protection layer is placed above a drainage layer, or if the protection layer includes a layer of gravel or cobbles, filter criteria must be considered. In general, filter criteria should be satisfied between all adjacent layers in the cap. If filter criteria are not met between adjacent layers, then a separate geosynthetic or soil filter should be provided. Filter criteria are discussed in numerous books and documents, such as U.S. EPA (1989).

Prevention of Desiccation

The protection layer is often designed to prevent desiccation of underlying layers. The hydraulic integrity of a compacted clay liner (CCL) or a radon attenuation layer may be compromised if it is allowed to desiccate and crack. The degree of desiccation protection required for a wet soil depends upon whether the soil is covered with a geomembrane or other relatively impermeable membrane such as asphalt. If a geomembrane or similar membrane material is placed over the CCL, the membrane will protect the compacted clay from desiccation. If no geomembrane is used in the hydraulic barrier layer, the problem of protecting the CCL from desiccation is particularly challenging. Experience has shown that severe desiccation can occur to depths of up to 1 m, and probably deeper (Corser *et al.* 1992; Melchior *et al.* 1994). The information that is available on desiccation is based on a field observation period of approximately 5 years. The problem of protecting underlying soils from desiccation for longer periods is even more difficult. The thickness of the protection layer required to prevent desiccation of an underlying compacted clay layer not covered with a geomembrane is not known, but it is clearly greater than 1 m. Further, the required thickness no doubt would vary from one site to another. Because of this lack of information, a conservative approach is recommended. It appears that in most situations, in the absence of a geomembrane, the protection layer would have to be at least 2 m thick, and perhaps as much as 5 m thick,

to protect underlying layers from seasonal desiccation. If it is desired to protect a compacted clay or other type of barrier layer from desiccation (and it almost always is desirable to do so), the best approach is to place a geomembrane or other water/vapor barrier over the layer, and then cover the geomembrane or barrier with soil.

Freeze Protection

The protection layer is generally designed to prevent underlying layers from freezing. The most vulnerable material to freeze-thaw damage is compacted clay (Othman *et al.* 1994), which should normally be placed below the maximum depth of frost penetration. It is advisable to prevent the drainage layer (if one is present) from freezing, particularly on relatively steep side slopes. The primary purpose of a drainage layer in many final cover systems is to dissipate pore water pressures and thereby promote slope stability. If the drainage layer freezes, its drainage function is destroyed for part of the year. During the thaw period, it is particularly important that the drainage layer drain from the outlet at the top of the slope, and that the protection layer be sufficiently thick to provide protection from freezing. Several techniques are available for estimating depth of frost penetration, including: frost penetration maps, such as the one in U.S. EPA (1989); local experience; and computer simulations.

Rooting Depth

The total depth of soil required to support the growth of vegetation depends on numerous site-specific factors. Most grasses are thought to have effective rooting depths of about 150 mm to 450 mm. Over time, deeper-rooted plants may become established and displace the grasses that were planted initially. Suter *et al.* (1993) provide examples of problems with plant roots. In landfill caps, the combined thickness of the topsoil and protection layer is typically 450 mm to 600 mm to accommodate plant roots. However, for caps with very long design lives and minimal maintenance requirements, thicker protection layers (on the order of 1 m or more) are more routine. Smith *et al.* (1997) recommend that this thickness be at least 3 m when long-term containment is essential and plant roots cannot be allowed to penetrate the protection layer. However, as a general rule, roots will not penetrate into dry soils. In soil

profiles containing a fine-textured soil overlying a coarse-textured soil, roots will remain in the relatively moist, fine-textured soil and will not penetrate into the coarse-textured soil so long as it remains dry. Thus, in relatively dry climates, a system with a relatively shallow (nearly equal to 1 m thick) cover soil underlain by a layer of gravel or cobbles (separated with suitable filter layers) should prevent root penetration.

DePoorter (1982) found that a 900-mm layer of cobbles, or 150 mm of gravel over 750 mm of cobbles, is effective in stopping root penetration of deep-rooted plants. Care should be taken to provide adequate filter layers above and below the cobbles to prevent overlying and underlying soil particles from migrating into the cobbles.

Burrowing Animals

Research by Cline *et al.* (1982) and Hokanson (1986) found that a layer of cobbles will stop further penetration by burrowing animals. Barriers to burrowing animals typically consist of a layer of cobbles approximately 0.5 to 1 m thick. The maximum particle size should be determined based on the types of burrowing animals. Typically, maximum particle size is on the order of 100 mm.

A geomembrane may also act as a barrier to burrowing animals. Available information indicates that burrowing animals cannot penetrate through geomembranes like those made from high density polyethylene (Steiniger 1968, cited by Koerner 1998).

Accidental Human Intrusion

When accidental human intrusion is considered, the principal concern is with exposure, such as excavation to lay a buried pipeline or excavation for a basement of a home. The cover can be thicker, up to approximately 5 m or more, to account for these types of routine excavations. No amount of thickness can prevent all types of intrusion, for example, drilling a boring or digging a deep utility excavation, or performing intentional intrusion.

Drainage Layer

Water that permeates through the surface and protection layers can be removed from the cover system by using a drainage layer. The drainage

layer consists of a highly permeable material that conveys water down-slope to a discharge point at the edge of the cover system.

A drainage layer serves the following three principal functions:

- To reduce the head of liquid on the underlying barrier layer, thereby minimizing the amount of water that percolates into underlying layers, waste, or contaminated soil
- To drain water from the overlying soil, allowing the overlying soil to absorb and retain additional water
- To reduce pore water pressures within the cover system, which enhances the stability of slopes

A potentially serious problem with drainage layers is long-term clogging associated with the migration of soil particles from adjacent layers into the drainage layer (Boschuk 1991). Excessive clogging can be prevented by ensuring that overlying and underlying materials meet filter criteria. Filters prevent migration of soil particles between layers, yet have sufficiently high saturated hydraulic conductivity to maintain capability for draining free water. Filter criteria can be met by: (1) ensuring that adjacent layers meet specific quantitative parameters, for example, as described by Koerner and Daniel (1997); or (2) constructing or installing a soil or geosynthetic fabric filter between adjacent materials. Earthen filters typically have an intermediate particle size. For example, if a silt soil overlies gravel, there is a risk that the loam particles may migrate into the gravel. A properly designed filter, such as one comprised of coarse sand and some gravel and placed between the silt and gravel, should not tend to migrate into the underlying gravel, and should prevent the overlying silt from migrating into the filter.

In arid locations, when considering whether or not a drainage layer is needed, and if so, how it should be designed, decisions should be based on the frequency and intensity of precipitation, and the capacity of the cover system components to absorb and retain water. It may be possible to construct a surface layer and protection layer that will absorb most, if not all, of the precipitation that infiltrates those layers, thereby eliminating the need for a drainage layer. Additional details on drainage layer design are provided by Koerner and Daniel (1997).

Hydraulic Barrier Layer

The primary purpose of the hydraulic barrier layer is to minimize the infiltration of water into the underlying waste mass. The hydraulic barrier layer is intended to provide high impedance to water flow due to its very low hydraulic conductivity. For wastes that generate gases, such as municipal solid waste, another function of the barrier layer is to prevent such gases from escaping into the atmosphere.

Three types of materials are typically used for hydraulic barrier layers:

- Geomembranes
- CCLs
- Geosynthetic clay liners (GCLs)

These materials can be used by themselves as single barrier materials, or in composite form. Choices in the composite category typically are geomembrane/GCL or geomembrane/CCL. In addition, asphaltic concrete and sprayed-on asphalt membranes can be used as hydraulic barrier layers.

Geomembranes have the following advantages: (1) extremely low rates of water and gas permeation through intact geomembranes; (2) the ability to stretch and deform without tearing; (3) the ability to protect underlying clay materials from desiccation and root penetration. Disadvantages of geomembranes include leakage through occasional imperfections in the material or field seams, and the potential for slippage along interfaces between geomembranes and adjacent materials. Koerner (1998) discusses all aspects of geomembrane performance and design.

CCLs are constructed from common materials that are mineralogically stable. CCLs also offer the advantage of a much greater thickness than other hydraulic barrier materials, which makes them comparatively invulnerable to accidental puncture. CCLs have been the most commonly used hydraulic barrier material in landfill covers for the past several decades. However, several studies indicate that CCLs may be severely damaged by desiccation if they are not covered with a geomembrane and adequate cover soil for the site-specific conditions (Montgomery and Parsons 1989; Corser *et al.* 1992; Suter *et al.* 1993; Melchior *et al.* 1994; Maine Bureau of Remediation and Waste Management 1997). Another significant limitation of CCLs is their tendency

to crack as a result of differential settlement of the underlying waste. Tension cracks penetrating entirely through the CCL can render it nearly useless as a barrier to water infiltration or gas release. Persoff *et al.* (1997b) discuss methods for repairing cracks in CCLs. General information and references on design and construction of CCLs used in caps are provided by Koerner and Daniel (1997).

GCLs are the newest type of material used in landfill final covers. They offer the advantages of extremely low hydraulic conductivity (lower than CCLs) and excellent self-healing capabilities (Koerner 1998). Research has demonstrated that GCLs can withstand considerable differential settlement (Koerner *et al.* 1996; Lagatta *et al.* 1997) and freeze-thaw cycles (Erickson *et al.* 1994; and Hewitt and Daniel 1997). The disadvantages of GCLs are the low shear strength of the bentonite (Stark and Eid 1997), potentially low interface shear strength (Daniel *et al.* 1998), and potential for alterations in hydraulic conductivity caused by ion exchange (James *et al.* 1997).

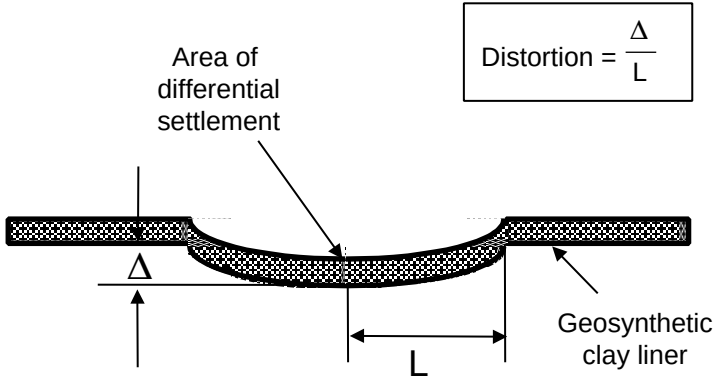
Asphalt offers the following advantages: (1) essentially unlimited service life if protected from exposure to ultraviolet light; (2) an extremely low permeability to water and gases if the asphalt or asphaltic concrete is free of excessive air voids; and (3) the ability to flow and self-heal. Wing and Gee (1994a) describe a compacted asphalt barrier overlaid by a sprayed-on asphalt membrane as an alternative to a geomembrane/CCL composite liner. Glade and Nixon (1997) compare asphaltic concrete to compacted clay.

Each type of barrier layer has advantages and disadvantages. No one type should be viewed as optimal for all caps. The appropriate material(s) should be selected based upon the specific objectives of a particular project and expected conditions in the landfill final cover system. Koerner and Daniel (1997) provide details on alternative materials and criteria for design. Critical parameters are discussed below.

Differential Settlement

Differential settlement is usually quantified in terms of the magnitude of differential settlement (Δ) that occurs over a horizontal distance (L), yielding distortion (Δ/L) as shown in the Figure 9-7[a]. Distortion causes materials to stretch, placing them in tension. If stretched too much, materials fail in tension, causing tensile cracks to form. The theoretical relationship between distortion and tensile strain is shown in Figure 9-7[b].

a. Definition of distortion.



b. Relationship between distortion and tensile strength.

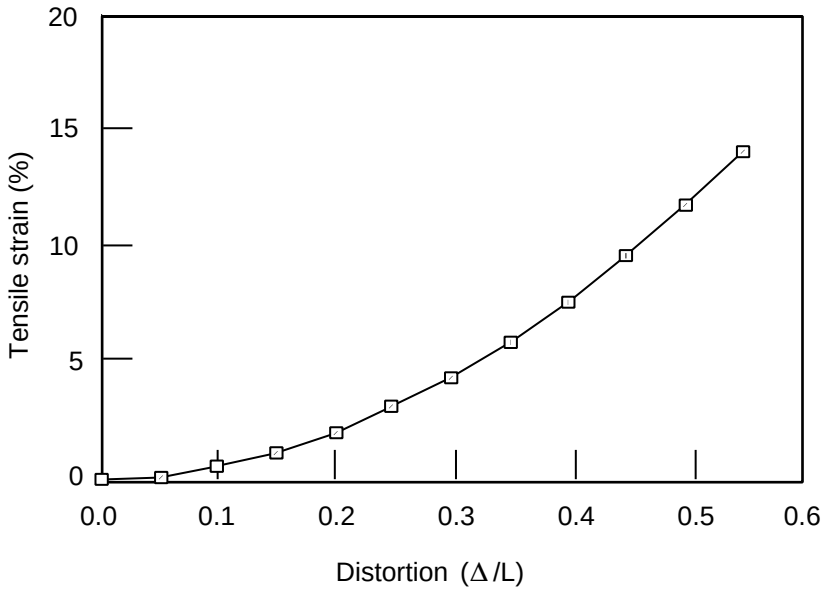


Figure 9-7. Differential settlement in terms of distortion.

Procedures for estimating differential settlement are not well developed for landfills. Designs estimates of Δ/L are frequently based more on experience and observations than on calculations. The magnitude of Δ/L is highly site-dependent and is a function of variables such as type of waste, age of landfill, and details of waste emplacement.

LaGatta *et al.* (1997) present data on the capability of geomembranes, compacted clay, and GCLs to withstand differential settlement. The maximum tensile strain that geomembranes can withstand without rupture depends on the type of geomembrane, but is typically 20 to 100-plus percent. Research indicates that GCLs can withstand 5 to 20 percent tensile strain. Compacted clay is the material most vulnerable to cracking from tension and typically fails at a tensile strain of 1 percent.

Design Percolation Rate

The selection of the hydraulic barrier layer, to some extent, depends upon the allowable rate of water percolation through the final cover system. In most instances, the final cover is intended to allow very little percolation of water, and the hydraulic barrier layer is essential to achieving low percolation rates. In other instances, particularly those involving risk-based corrective actions, larger amounts of percolation may be permissible.

It is recommended that the percolation objective for the final cover be defined prior to design. Appropriate decisions about the types of materials to be used for the hydraulic barrier layer, and the characteristics of those materials, can only be made if there is an understanding of the degree to which percolation through the final cover system must be minimized.

Need for Gas Containment

Some wastes produce gases, while others do not. Thus, whether or not there is a need for gas containment depends upon the type of waste. Geomembranes generally make excellent barriers to gas. Wet clays also make excellent barriers to gas; however, it is difficult to ensure that clay will remain wet, particularly in relatively arid regions.

Cyclic Wetting and Drying

Cyclic wetting and drying can have a major impact on clay soils, and the impact on CCLs can be particularly significant. CCLs buried

beneath 150 mm to 450 mm of soil, without a covering geomembrane, can be severely damaged within a few years (Montgomery and Parsons 1989; Melchior *et al.* 1994; Maine Bureau of Remediation and Waste Management 1997). GCLs appear to be much less vulnerable to permanent damage from desiccation, probably due to the swelling and self-healing capabilities of bentonite (Boardman and Daniel 1996). However, even GCLs can be damaged if unprotected or subjected to chemical alterations (James *et al.* 1997; Melchior 1997). The potential for wet-dry cycles to affect the integrity of CCLs and, to a lesser extent, GCLs, should be considered. If there is judged to be a risk of damage to CCLs or GCLs, the normal solution is to use a composite geomembrane/CCL or geomembrane/GCL hydraulic barrier layer. The geomembrane appears to protect the clay from desiccation damage (Corser *et al.* 1992; Melchior *et al.* 1994).

Freeze-Thaw

The potential for freeze-thaw damage to a CCL or GCL should be considered. Available information indicates that CCLs will not maintain a hydraulic conductivity of 1×10^{-7} cm/sec or less if subjected to freeze-thaw at the level of overburden stress normally encountered in landfill final cover systems (Othman *et al.* 1994). Soil-bentonite CCLs (Wong and Haug 1991; Zimmie *et al.* 1997) and GCLs (Hewitt and Daniel 1997) appear to be unaffected by freeze-thaw. If the hydraulic barrier is below the maximum depth of frost penetration, then the layer is usually assumed to be adequately protected from long-term frost damage. If the hydraulic barrier layer is within the zone of frost penetration, then the impacts of frost upon those materials should be considered. Frost is generally assumed to have no effect on geomembranes, and little or no effect on GCLs. Concern over frost action is focused principally on CCLs.

Service Life

The anticipated service lifetime of the barrier material is an important consideration. Research is ongoing for geomembranes using time-temperature superposition procedures followed by Arrhenius modeling (Koerner 1998). Available data indicate that the useful service life of high-density polyethylene geomembranes is hundreds of years or longer

(Koerner 1998). Service life for CCLs and GCLs is more difficult to assess, not based on the soil or bentonite particles themselves, but on their association with water. If the CCL desiccates or suffers freeze-thaw cycling, its hydraulic conductivity will be compromised.

Protection (Cushion) Layer

Protection layers are often installed between angular gravel or crushed rock materials and an underlying geomembrane. A protective geotextile used in this way is sometimes referred to as a “cushion.” The cushion layer protects the geomembrane from puncture by the overlying stones. In final cover systems, the overburden stresses produced by cover soils, as compared to angular stone, are normally not very large, which makes the design of a geotextile cushion relatively simple. When a geomembrane is overlaid with angular gravel or rock materials, it is subjected to high compressive stresses. Design procedures are provided by Koerner (1998).

Gas Collection Layer

A gas collection layer is often the most effective means for collecting and controlling vapors and gases. Municipal waste landfill gases generally contain a mixture of methane and carbon dioxide, as well as smaller volumes of other gases. Methane typically constitutes 50 percent to 70 percent of the landfill gas (Barlaz and Ham 1993). The methane can occur in concentrations that are toxic, flammable, or even explosive. Because of these potential dangers, great care must be taken in handling landfill gases. In addition, condensate usually forms as gases are collected because the temperature at the surface is often lower than the temperature of the gas. Gas collection systems typically include condensate traps and piping that directs condensate back into the landfill. Volatile organic liquids partition to the gas phase, and vapor transport can be a significant mechanism of mass transfer. Some radioactive elements emit potentially harmful gases, for example, radon gas.

The gas collection layer usually consists of a layer, typically about 300 mm thick, of sand, gravel, or an equivalent geosynthetic material. Pipes often tap into the gas collection layer, and the collected gases may be discharged under the natural pressure gradient created, or they may be collected with the assistance of vacuum pumps. A soil or geotextile

filter may be required to prevent migration of fine soil particles from adjacent layers into the gas collection layer.

Foundation Layer

The foundation layer is the layer upon which the cap will be constructed. The soil of the foundation layer is usually compacted directly. However, even a large compactor cannot compact soil or waste layers more than about 1 m deep. Therefore, soils and wastes are typically spread in relatively thin layers and compacted layer by layer.

Deep dynamic compaction has been used to compact waste at greater depths. A large weight (usually a concrete block) is lifted by a crane and dropped from a height approximately 10 meters (or more), thereby delivering a tremendous energy to the zone directly below. The impact of the weight leaves a crater the size of the weight, and about a meter or so deep. The resulting craters are eventually filled and the surface is proof-rolled with compaction equipment. The material is compacted to a depth approximately equal to the width of the dropped mass.

TYPICAL CAP DESIGNS

Certain cap designs tend to be used frequently. Perhaps the most common cap design is illustrated schematically in Figure 9-8. The cross section in Figure 9-8 is adapted from Figure 1 of EPA's technical guidance document for hazardous waste closures (U.S. EPA 1989), and is commonly called a RCRA Subtitle C cap (The Resource Conservation and Recovery Act ([RCRA]) is the federal legislation authorizing EPA to regulate hazardous waste disposal under Subtitle C). The upper 600 mm of this typical cap consists of cover soil, which is intended to support growth of vegetation and provide for water storage. A drainage layer provides a means for reducing the head of water on the underlying hydraulic barrier layer, and for maintaining the stability of slopes. The hydraulic barrier consists of a composite geomembrane/CCL. No gas collection layer is included in this design, because gases are rarely an issue for disposal of treated hazardous waste.

A common alternative to the RCRA Subtitle C cap is illustrated in Figure 9-9. This design uses a geosynthetic drainage layer (usually geonet) rather than a sand or gravel drainage material, and a GCL rather

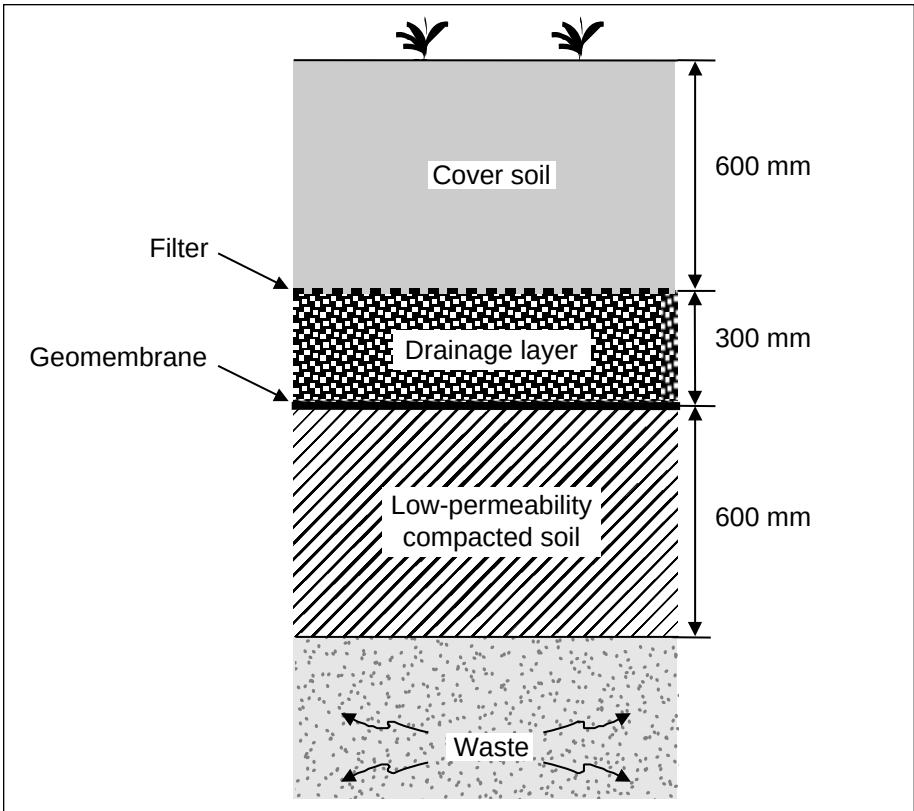


Figure 9-8. Typical RCRA Subtitle C cap recommended by EPA for hazardous waste closures (U.S. EPA 1989).

than compacted clay. The advantages of this cap include a thinner cross-section and, in many cases, lower cost. Its performance characteristics, such as its ability to withstand larger differential settlement and freeze-thaw cycles, offer advantages over compacted clay.

The U.S. EPA regulates municipal solid waste through RCRA Subtitle D. A typical cap that complies with EPA Subtitle D criteria is illustrated in Figure 9-10. This cap consists of a 150-mm-thick layer of topsoil underlain by a single hydraulic barrier layer of 450 mm of compacted soil with a hydraulic conductivity of 1×10^{-5} cm/sec or less. This design has been criticized because of the thinness of the top soil layer and lack of infiltration control provided by a material with a relatively high hydraulic conductivity of 1×10^{-5} cm/sec.

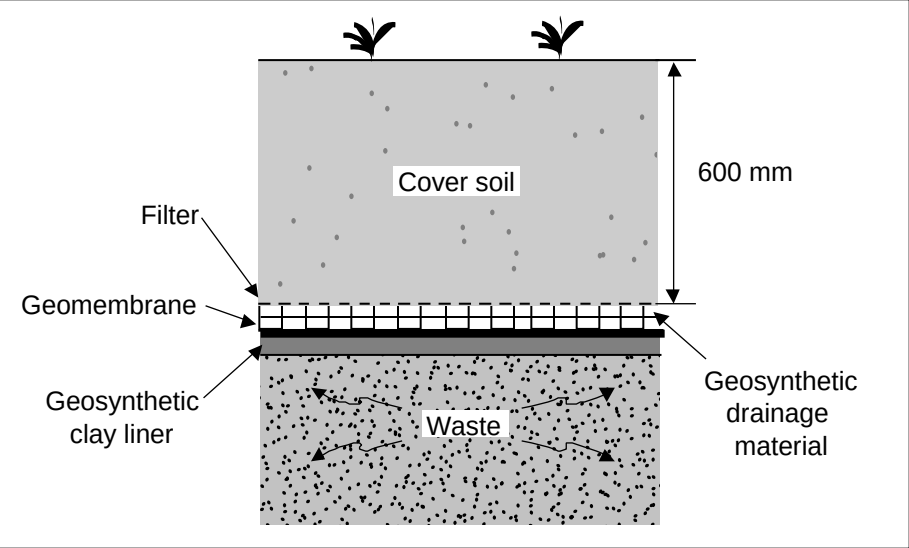


Figure 9-9. Typical cap similar to RCRA Subtitle C cap but including a geosynthetic drainage layer and geosynthetic clay liner.

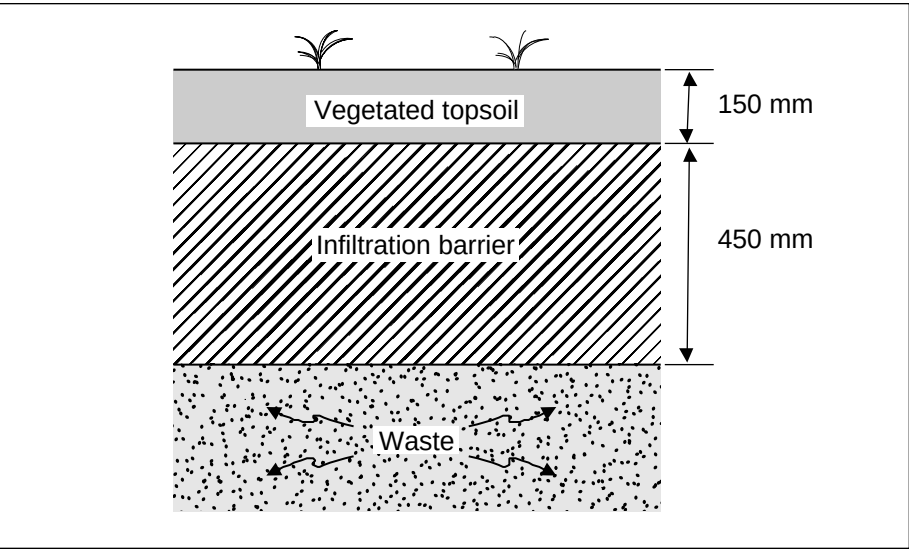


Figure 9-10. Typical cap used for municipal solid waste (RCRA Subtitle D cap).

When the typical RCRA Subtitle C cap design is applied to arid or semi-arid sites, the top soil is often replaced with gravel or cobbles to provide protection from wind erosion, and a design similar to that illustrated in Figure 9-11 may be employed. A GCL is preferable to compacted clay in arid climates because of compacted clay's vulnerability to desiccation cracking.

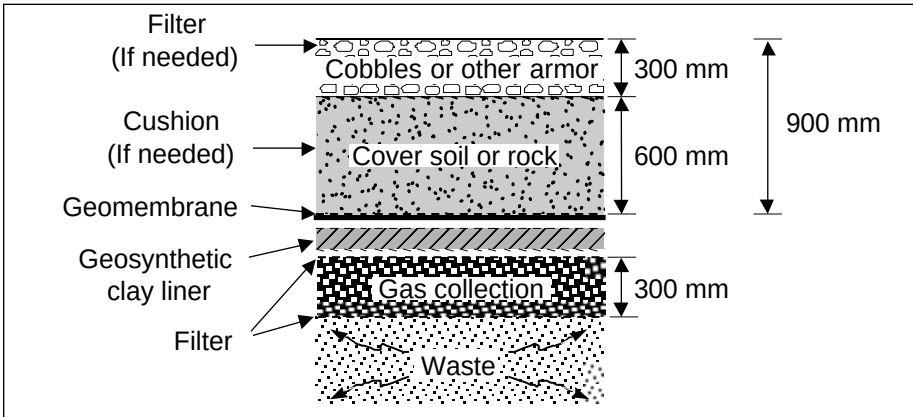


Figure 9-11. Typical cap similar to RCRA Subtitle C cap but designed for arid or semi-arid site.

ALTERNATIVE CAP DESIGNS

Numerous alternatives to the typical cap designs presented in the preceding section have been developed, some of which have been implemented in the field. Some variations make use of alternative materials such as paper mill waste (Moo-Young and Zimmie 1997), self-sealing materials (McGregor and Stegemann 1997), asphalt (Glade and Nixon 1997), or spray-on membranes (Miller *et al.* 1997). However, the alternative cap designs that have generated the broadest interest have involved designs that are intended to function in arid or semi-arid climates, taking advantages of the physics of moisture movement in the vadose zone.

Evapotranspiration Cap

The evapotranspiration (ET) cap usually consists of a relatively thick single layer of soil that stores water and promotes water extraction by plant roots. This layer consists of fine-textured, low-permeability soil, which promotes water storage and very slow infiltration. The key advantage of the ET cap is low cost—a single layer of soil approximately 1 m thick usually comprises the ET cap. The ET cap undoubtedly will work extremely well in arid and semi-arid climates most of the time. The critical challenge for the ET cap occurs during and following periods of unusually heavy precipitation, when storage and evapotranspiration capacity may not be sufficient to prevent deep percolation.

The limitations of an ET (only) cap can be mitigated by incorporation of additional design elements to help control and buffer moisture. One example would be combining an ET cap with the capillary barrier discussed in the next section. As previously implied, the potential success of ET in reducing infiltration is strongly dependent upon the local climatic conditions. The ET cap performs best in warm, arid climates with limited potential for periods of intense precipitation. Conversely, the ET cap provides little or no benefit in cold, wet climates. As discussed in Chapter 1, regions where potential evapotranspiration greatly exceeds precipitation are the best candidates for the technology. To broaden the possible applicability of evapotranspiration in cap systems, research to quantify performance as a function of the various climatic factors is necessary. Such research will allow better technical estimates of the robustness of the process (that is, the ability to meet infiltration criteria, and the probable frequency and significance of failure). Such research will also support engineers who wish to better incorporate ET into combination barriers.

Capillary Barrier Cap

An alternative cover receiving a great deal of attention is the capillary barrier. As illustrated schematically in Figure 9-12[a], a capillary barrier consists of a fine-textured soil overlying a coarse-textured soil. In the vadose zone, the soil moisture potential (or soil suction) is the same in the two soils at equilibrium, as indicated in Figure 9-12[b]. Because the fine-textured soil can retain more moisture than the coarse-textured soil at a given soil suction, the volumetric water content (θ) of the fine-

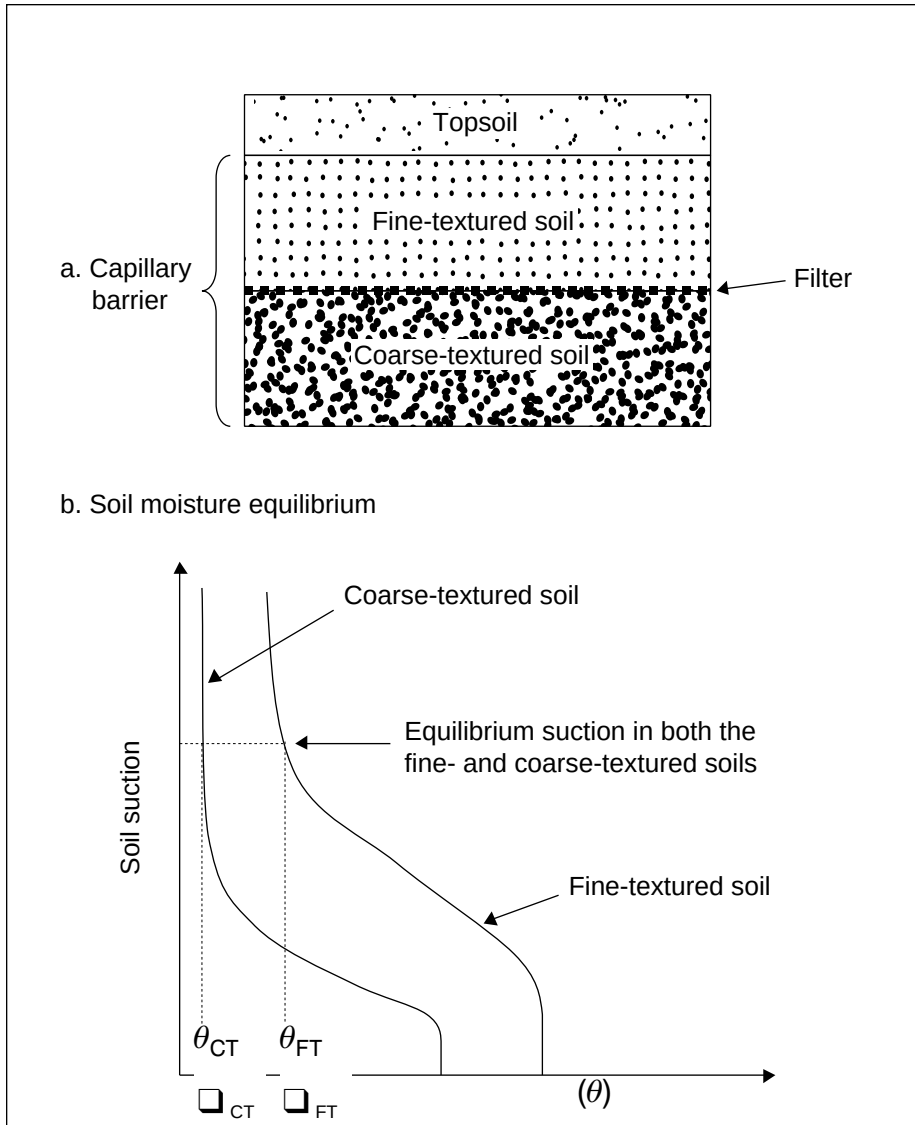


Figure 9-12. Capillary barrier and soil moisture equilibrium.

textured soil is greater than that of the coarse-textured soil ($\theta_{FT} > \theta_{CT}$). Because coarse-textured soil is far drier than fine-textured soil, the coarse-textured soil has a much lower hydraulic conductivity (Figure 9-13), which serves to impede flow. Dry gravel or cobbles make an ideal barrier to liquid water movement in the vadose zone, only allowing moisture transmission in the vapor phase. The dry, coarse-textured soil helps the overlying fine-textured soil retain water. The water stored in the fine-textured soil is eventually returned to the atmosphere via evapotranspiration. Useful information on moisture movement in a capillary barrier, based on numerical modeling, is provided by Oldenburg and Pruess (1993).

Particles of the fine-textured soil cannot be allowed to migrate into the underlying coarse-textured material because, should particle migration occur, the underlying layer would retain water and cease to function

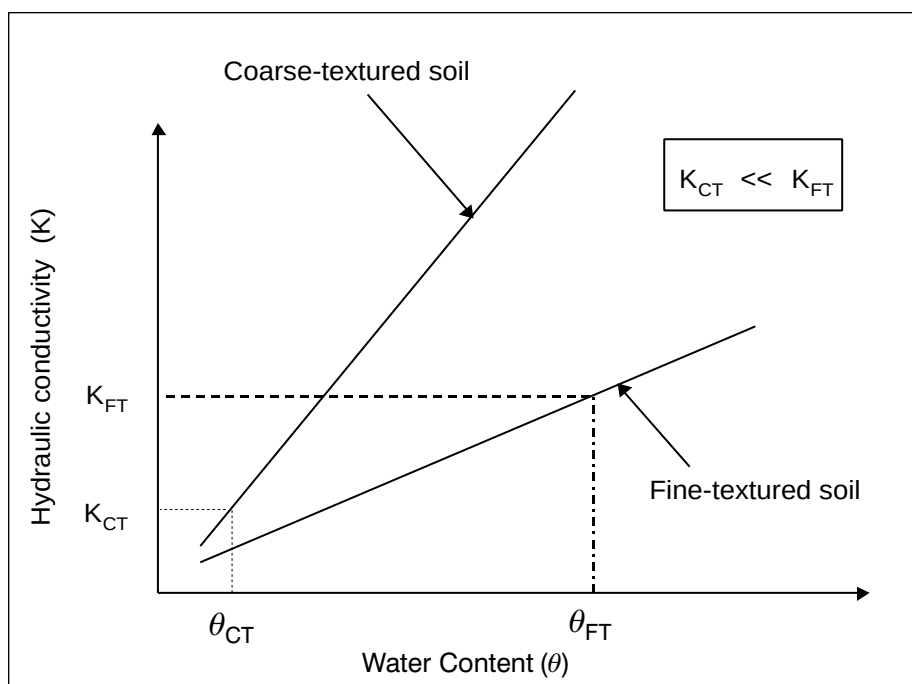


Figure 9-13. Relationship between hydraulic conductivity and water content, illustrating how the relatively dry, coarse-textured soil maintains a low hydraulic conductivity in a capillary barrier.

as a capillary barrier. Filter criteria must be met between the fine- and coarse-textured soil components. The filter can consist of soil or geotextile materials. For extremely long service lifetimes, fiberglass geotextiles (both woven and nonwoven) are often considered for this application.

The main issue with capillary barriers is often whether the fine-textured soil will have enough moisture storage capacity to function properly even in unusually wet periods, when the storage and evapotranspiration capacity can be exceeded by infiltration. When this occurs, significant percolation into and through the coarse-textured soil will take place. The capillary barrier is a more viable alternative barrier in arid or semi-arid climates than in regions of comparatively high precipitation.

Although capillary barriers have been used for approximately 2 decades, the initial applications were restricted to radioactive waste disposal sites in arid areas where 1000-plus year design lives are required. Under such circumstances, it was desirable to rely principally on natural materials and processes. In recent years, capillary barriers have been considered for a broader range of waste disposal situations. The appeal of such systems is their ability to impede moisture percolation without using physical barriers such as geomembranes or compacted clay. Experience with capillary barriers is limited, but field data are discussed later in this chapter.

Wicking Layers

A variant on the capillary barrier used alone is the capillary barrier combined with a layer that is designed to wick water via unsaturated flow. The wicking layer serves a similar function to a lateral drainage layer, but does so under conditions of incomplete saturation (Goode 1986). Sometimes the drainage is called “wick drainage.” An underlying coarse-textured soil provides a capillary barrier, and an overlying fine-textured soil provides the layer that retains water and drains by gravity to a low point. The interface between the coarse- and fine-grained soil must be sloped fairly steeply in order for gravity to drive drainage, and the fine-textured soil must be close to field capacity in order for significant water movement to occur. Although the concept has been tested in the laboratory and in field test plots (Nyhan *et al.* 1990), no full-scale applications are known to the author.

Other Alternatives

A variety of alternative materials have been used for final covers, including mixtures of combustion ashes and bentonite, waste materials such as sludge, and recycled materials such as tires. Most of these alternative materials are used in the types of conceptual designs discussed earlier.

A rather unique alternative design involves pumping ambient air through a layer of gravel buried at the base of a cap (Stormont *et al.* 1994). The ambient air (which is relatively dry in arid and semi-arid regions during much of the year) maintains a dry capillary break.

Analysis of Water Transport in Unsaturated Caps

A critical component to alternative cap design is consideration of moisture movement in the unsaturated cap, thereby accounting for precipitation, runoff, evapotranspiration, storage, and fluid transport. Several computer programs are available for analyzing moisture movement in caps; the most commonly used one is clearly the program Hydrologic Evaluation of Landfill Performance (HELP) developed by the U.S. EPA (Schroeder *et al.* 1994). HELP was developed for use primarily at humid sites, and it is widely recognized that it may not be realistic for arid or semi-arid sites (Fayer and Gee 1997; Khire *et al.* 1997a). The latest version of HELP may work better than earlier versions for analyzing performance at arid sites (Aschough *et al.* 1997). The computer code UNSAT-H (Fayer and Jones 1990), and to a lesser extent TOUGH2 (Pruess 1991), is often used for modeling water movement in caps located in arid and semi-arid regions. However, all of the available computer models have shortcomings, such as failing to account rigorously for snow melt (Khire *et al.* 1997a). Also, accurate soil hydraulic properties are difficult to obtain. The performance and use of various vadose zone models and uncertainties are discussed in Chapter 5.

CASE HISTORIES

Numerous case histories of the performance of prototype caps and test plots have been described in the literature. Table 9-1 summarizes the most significant cases that are known to the author. Selected case histories are summarized below to illustrate key points concerning performance of caps.

TABLE 9-1 Summary of case histories of cap performance.

Reference	Type of Cap	Design Profile	Period of Monitoring (Years)	Key Findings
Montgomery and Parsons (1989)	Test Plots on Omega Hills Municipal Solid Waste Landfill, Milwaukee, Wisconsin	Three test plots: (1) 150 mm topsoil over CCL (2) 450 mm topsoil over CCL (3) Topsoil over CCL over capillary barrier over CCL	3	• CCL was damaged by desiccation • 450 mm of cover soil protected underlying CCL no better than 150 mm of cover soil • Capillary barrier layer worked as lateral drainage layer and did not prevent desiccation of upper CCL
Anderson <i>et al.</i> (1990)	Idaho National Engineering Laboratory Cap Study	Ten test sections, each with native clayey silt loess to depth of 2.4 m, but with different vegetative treatments	5	• Section with crested wheatgrass removed the most moisture while bare (unvegetated) test sections removed the least moisture
Nyhan <i>et al.</i> (1990)	Integrated Test Plot Experiment, Los Alamos National	Two test plots: (1) Conventional design with 200 mm of sandy loam over 1.1 m of crushed tuff (angular silty sand) (2) Improved design with 710 mm sandy loam over 460 mm gravel over 910 mm cobbles over 380 mm crushed tuff	3	• Improved design produced significantly less percolation of water through the cap

TABLE 9-1 Summary of case histories of cap performance *(continued)*

Reference	Type of Cap	Design Profile	Period of Monitoring (Years)	Key Findings
Limbach <i>et al.</i> (1994)	Idaho National Engineering Laboratory Protective Cap Bio-Barrier Experiment	Twelve test plots with three replicates (varying vegetation and irrigation) of four designs: (1) RCRA design with 900 mm clay loam loess over GM/CCL (600 mm thick) composite hydraulic barrier (2) Monolayer design (ET cap) with 2 m clay loam loess (3) Capillary barrier with 500 mm clay loam loess over 300 mm cobbles over 1.5 m clay loam loess (4) Thicker capillary barrier with 1 m clay loam loess over 300 mm cobbles over 1.5 m clay loam loess	0	• No data presented; only the testing concept described
O'Donnell <i>et al.</i> (1994) and Schultz <i>et al.</i> (1995)	Test Plots at Beltsville, Maryland	Five test plots: (1) Monolayer with 4 m native soil vegetated with grass (2) Earthen resistive barrier with rip-rap surface; with 150 mm cobbles over 300 mm gravel over 450 to 600 mm of CCL compacted clay	5 years	• The monolayer yielded by far the greatest percolation (10 to 30 percent of precipitation), while the others yielded essentially no percolation • Bioengineered barrier with juniper to remove soil moisture was considered to be highly effective

TABLE 9-1 Summary of case histories of cap performance. *(continued)*

Reference	Type of Cap	Design Profile	Period of Monitoring (Years)	Key Findings
		(3) Earthen resistive barrier with vegetated topsoil; with 200 mm topsoil over 300 mm gravel over 450 to 600 mm CCL of compacted clay (4) Capillary barrier with 200 mm vegetated topsoil over 300 mm gravel over 450 to 600 mm compacted clayCCL over 200 mm diatomaceous earth over 200 mm gravel (5) Bioengineered cover with panels of fiberglass sheet panels over 4 m of native soil		
Hakonson <i>et al.</i> (1994) and Warren <i>et al.</i> (1997)	Alternative Cover Study, Hill AFB, Utah	Four test plots in flat area: (1) Monolayer (ET covercap) with 900 mm sand loam (2) RCRA cover with 1.2 m loam topsoil over 300 mm sand drainage material over 600 mm CCL (soil-bentonite mixture)	4	RCRA cap provided the least amount of water percolation through barrier, probably because of water absorption by soil-bentonite CCL layer (layer was not yet saturated at end of period of observation reported)

TABLE 9-1

Summary of case histories of cap performance. (continued)

Reference	Type of Cap	Design Profile	Period of Monitoring (Years)	Key Findings
		(3) Capillary barrier with grass:, with 1.5 mm sandy loam topsoil over 300 mm gravel (4) Capillary barrier with grass and brush, with same profile as other capillary barrier(3)		• Monolayer (ET cap) allowed the greatest amount of percolation
Melchior <i>et al.</i> (1994) and Melchior (1997)	Test Plots on Municipal Solid Waste Landfill, Hamburg, Germany	Four Five test plots: (1) 750 mm topsoil over DL over CCL over DL (2) 750 mm topsoil over DL over GM/CCL composite barrier over DL (3) 750 mm topsoil over DL over CCL over capillary barrier over DL (4) 300 mm topsoil over 150 mm DL over GCL composite layer (5) 300 mm topsoil over 150 mm DL over GCL composite layer 300 mm topsoil over 150 mm DL over GM/GCL composite layer	4	• CCL that was not covered with geomembrane was damaged by desiccation • Capillary barrier layer worked more as lateral drainage layer than a capillary break and did not prevent desiccation of upper CCL • GCL was damaged from possible desiccation and/or calcium replacement of sodium in bentonite

TABLE 9-1 Summary of case histories of cap performance. *(continued)*

Reference	Type of Cap	Design Profile	Period of Monitoring (Years)	Key Findings
Stormont (1995)	Capillary Barrier Study, Kirtland AFB, New Mexico	Two capillary barrier test plots with constant simulated precipitation of 5 mm/day: (1) 900 mm fine-grained soil over 250 mm gravel (capillary break) (2) 900 mm alternating fine-grained soil and sand over 250 mm gravel	100	Layered surface layer with alternating fine-grained soil and sand was much more effective in limiting percolation —sand layers drained laterally
Viebricher Associates (1996), described by Benson (1997)	Grede Foundries Alternative Cover Study, Wisconsin	Five test sections: (1) Permitted cap with 150 mm topsoil over 600 mm conventional CCL (2) New required cap with 150 mm topsoil over 900 mm soil protection layer over 600 mm conventional CCL (3) Alternative design with 150 mm topsoil over 900 mm waste foundry sand (90 percent sand, 10 percent bentonite) protection layer (90 percent sand, 10 percent bentonite) over 600 mm conventional CCL (4) Alternative design with 150 mm topsoil over 900 mm waste foundry sand protection layer over 900 mm compacted foundry sand (5) Alternative design with 150 mm topsoil over 2.4 m waste foundry sand protection layer over 1.5 m compacted foundry sand	4	- The permitted cap allowed by far the greatest amount of annual percolation, followed closely by the new required cap - The three alternative caps all allowed about two orders of magnitude lower percolation than the permitted cap or new permitted cap - Excavation of test sections showed that CCLs in permitted cap and new permitted cap were extensively cracked due to desiccation and possibly frost action - Bentonite in foundry sand may have made it much more water absorbent and resistant to desiccation cracking or freeze-thaw damage

TABLE 9-1 Summary of case histories of cap performance. *(continued)*

Reference	Type of Cap	Design Profile	Period of Monitoring (Years)	Key Findings
Andraski (1997)	Amargosa Desert near Beatty, Nevada	Four test sites, all with native soils and variable vegetation treatment	4	Under non-vegetated conditions, precipitation can accumulate and penetrate downward, thereby increasing potential for water percolation
Dwyer (1997)	Alternative Landfill Cover Demonstration (ALCD), Kirtland AFB, New Mexico	Six test plots: (1) RCRA Subtitle D cap:, 150 mm top-soil over 450 mm of soil with $K \approx 1 \times 10^{-5}$ cm/s (2) RCRA Subtitle C cap:, 600 mm top-soil over 300 mm drainage sand DL over GM/CCL (600 mm) composite barrier (3) RCRA Subtitle C cap: same as (2) above, but with GCL rather than CCL, and 8 1 cm² holes in GM (4) Capillary barrier with 300 mm top-soil over 80 mm sand filter over 220 mm pea gravel (capillary break) over 450 mm compacted soil over 300 mm sand (5) Anisotropic capillary barrier with 150 mm of topsoil/gravel mix over 600 mm soil over 150 mm fine sand filter over 150 mm pea gravel (6) ET cover with 150900 mm of soil over 750 mm compacted soil	1	All caps performed well after the first year, but the RCRA Subtitle D cap permitted significantly more percolation through the cap than the other test plots

TABLE 9-1 Summary of case histories of cap performance. *(continued)*

Reference	Type of Cap	Design Profile	Period of Monitoring (Years)	Key Findings
Gee <i>et al.</i> (1997) and Wing and Gee (1994b)	Hanford Surface Barrier, Richland, Washington	Cap over waste crib with following profile: 1 m silt loam/gravel admix surface layer over 1 m silt loam over 150 mm sand filter over 300 mm gravel filter over 1.5 m basalt rip-rap (animal intrusion barrier and capillary break) over 300 mm gravel cushion/drain layer over 150 mm asphaltic concrete coated with fluid-applied asphalt membrane over foundation soils Edges of cap constructed with rip-rap berms for slope stability	2	• Excellent performance; no percolation of water into drainage layers
Khire <i>et al.</i> (1997)	Greater Wenatchee Regional Landfill, East Wenatchee, Washington	Two test caps: (1) Resistive barrier (RCRA Subtitle D cap) with 150 mm topsoil over 450 mm CCL (2) Capillary barrier with 150 mm topsoil over 750 mm sand	3	• Significant percolation through the capillary barrier occurred in winter of 1993 when record snow fall occurred • Percolation through resistive barrier increased significantly in fall of 1995, after summer desiccation apparently caused cracking in CCL

TABLE 9-1 Summary of case histories of cap performance. (continued)

Reference	Type of Cap	Design Profile	Period of Monitoring (Years)	Key Findings
Maine Bureau of Remediation and Waste Management (1997)	Actual MSW Landfill Covers in Main	(1) GM/Cumberland Landfill: 150 mm topsoil over 450 mm silty clay (2) Vassalboro Landfill: 150 mm sludge-amended topsoil over 450 mm CCL (3) Yarmouth Landfill: 150 mm sludge-amended topsoil over 450 mm CCL (4) Waldoboro Landfill: 150 mm sludge-amended topsoil over 450 mm CCL	5	• Comparison of hydraulic conductivities measured in the laboratory and in the field (with sealed double ring infiltrometer) showed a trend for of increasing hydraulic conductivity (typically one to two orders of magnitude) with time • Indications are that the compacted clay liners CCLs were damaged as a result of desiccation and/or freeze-thaw
Nyhan <i>et al.</i> (1977)	Los Alamos National Laboratory, Los Alamos, New Mexico	Four test caps, each constructed on slopes of 5, 10, 15, and 25 percent: (1) Conventional design with 150 mm loam topsoil over 760 mm crushed tuff (angular, silty sand) over 300 mm gravel (2) EPA design with 610 mm loam topsoil over a geotextile separator/filter over 300 mm drainage sand over 610 mm sand-bentonite CCL (however, no GM was included over CCL)	4	• EPA design has worked well because of water storage in the soil-bentonite CCL • Note that in EPA design there was not a GM over the CCL • Conventional design has allowed the greatest amount of percolation • For all plots, increasing the surface slope decreased percolation through the caps

TABLE 9-1 Summary of case histories of cap performance. *(continued)*

Reference	Type of Cap	Design Profile	Period of Monitoring (Years)	Key Findings
Nyhan <i>et al.</i> (1977) <i>(continued)</i>		(3) Loam capillary barrier with 610 mm of loam topsoil over 760 mm fine sand (capillary break) (4) Clay loam capillary barrier with 610 mm clay loam topsoil over 760 mm fine sand (capillary break)		

Legend:
 CCL = Compacted Clay Liner
 DL = Drainage Layer
 ET = Evapotranspiration
 GCL = Geosynthetic Clay Liner
 GM = Geomembrane
 MSW = Municipal Solid Waste

Test Sections at Omega Hills

Montgomery and Parsons (1989) presented the first detailed information on the performance of CCLs in landfill covers. The study involved the construction of three large test pads on the top of the Omega Hills landfill, a closed municipal solid waste landfill located approximately 30 km northwest of Milwaukee, Wisconsin. The test plots were constructed to evaluate the performance of alternative final cover designs.

The cross-sections of the three test plots are shown in Figure 9-14. Test Plot 1 represented the existing final cover system design at the time that the study was initiated. It consisted of 150 mm of topsoil (uncompacted clay loam to silty clay loam) seeded with a mixture of grasses, overlying 1.2 m of CCL that was designed to have a hydraulic conductivity less than or equal to 1×10^{-7} cm/sec. Test Plot 2 had a CCL of the same thickness, but a thicker topsoil layer that was intended to promote better vegetative growth, and thereby enhance evapotranspiration. Test Plot 3 used a layer of coarse-grained soil (sand) sandwiched between two CCLs to take advantage of the capillary barrier effect and promote retention of water in the upper CCL, where the water could be returned to the atmosphere via evapotranspiration. All test plots were constructed on the 33 percent side slopes of the actual landfill surface.

The key measurements were: precipitation (via an on-site weather station), runoff, percolation through the test plots, and temperature. Soil

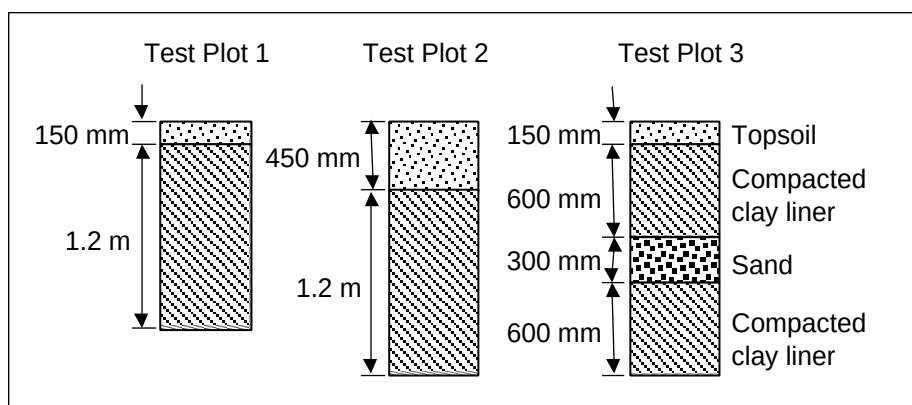


Figure 9-14. Three test plots at the Omega Hills Landfill (after Montgomery and Parsons 1989).

moisture content was monitored with neutron access probes. A typical cross-section is illustrated in Figure 9-15. The percolation/collection lysimeter consisted of (from top to bottom) a geotextile filter, a geo-composite drainage layer, and a geomembrane.

The 12-month period of September 1986 through August 1987 was near normal. The 12-month period of September 1987 through August 1988 was dominated by a severe drought in the summer of 1988, which was characterized by substantially below-average rainfall and temperatures that averaged 6°C above normal. The drought reduced the cover vegetation to a dry, dormant state, and cracking of the surface of the cover soils was obvious. The third and final year of data collection saw a return to normal conditions.

At the end of 3 years, test pits were excavated in each test plot, outside the area of the lysimeters. A summary of data collected is presented in Table 9-2. The key parameter is the quantity of percolation, that is, the rate of water flow into the lysimeter. In Test Plots 1 and 2, the percolation in the first year was 2 to 7 mm/year (6×10^{-9} to 2×10^{-8} cm/sec, respectively). However, by the third year, these values had increased to a range of 56 to 98 mm/year (2×10^{-7} and 3×10^{-7} cm/sec, respectively).

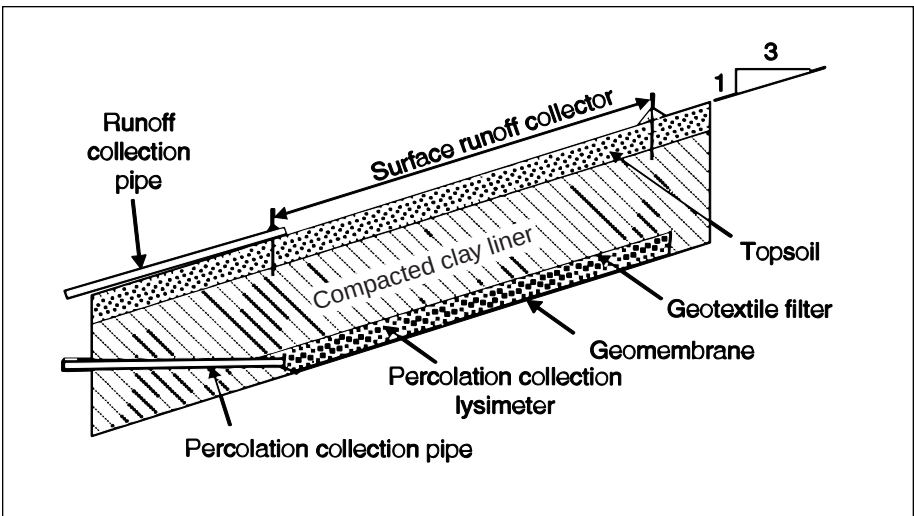


Figure 9-15. Cross section of Test Plot 1 at Omega Hills Landfill, showing surface runoff collection system and lysimeter to measure percolation (after Montgomery and Parsons 1989).

TABLE 9-2 Summary of information concerning performance of field test plots at Omega Hills landfill (data from Montgomery and Parsons 1989).

Test Plot	Year	Precipitation (mm)	Runoff (mm)	Percolation (mm)
1	1986–87	896	180	2
	1987–88	579	38	5
	1988–89	823	56	56
2	1986–87	896	109	7
	1987–88	579	38	30
	1988–89	823	51	98
3	1986–87	896	97	40
	1987–88	579	38	22
	1988–89	823	66	41

As detailed below, the test pits showed that the CCLs in Test Plots 1 and 2 were in a similar condition after 3 years:

- The upper 200 to 250 mm of the CCLs were weathered and blocky (probably from desiccation and/or freeze-thaw)
- Cracks 6 to 12 mm wide extended 0.9 to 1 m into the CCLs
- Roots penetrated 200 to 250 mm into the CCLs in a continuous mat, and some roots extended into crack planes as deep as 750 mm

The drought conditions during the summer of 1988 apparently caused severe desiccation of the CCL, which led to significantly increased hydraulic conductivity in subsequent years. The CCL initially may have had a hydraulic conductivity of 1×10^{-7} cm/sec or less. After 3 years, desiccation damage raised the CCLs' level of hydraulic conductivity.

Test Plot 3 was designed with the intention of maintaining moisture in the upper CCL with an underlying capillary barrier. The percolation rate through Test Plot 3 was more consistent, and ranged from 22 to 41 mm/year (7×10^{-8} to 1.3×10^{-7} cm/sec). At the end of the 3-year study period, the upper 200 to 250 mm of the uppermost CCL was weathered and blocky, and cracks extended through the entire thickness of the uppermost CCL. This cracking allowed significant amounts of water to enter the sand drainage layer. Discharge of water from the sand layer

occurred within hours of the start of precipitation, suggesting rapid transmission of water through cracks in the upper CCL. In fact, the sand may have functioned more as a lateral drainage layer than a capillary barrier. Moisture in the sand drainage layer probably helped to protect the underlying CCL from damage. The multi-component cap in Test Plot 3 did not function as anticipated. It was expected that the sand drainage layer would help the overlying CCL retain moisture, but the uppermost CCL dried and cracked. Most likely, cracking was intensified by the 1988 summer drought.

The principal lesson learned from the Omega Hills study was that in a fairly short period of time (3 years), CCLs overlain by 150 to 450 mm of topsoil may be subject to major desiccation, cracking, and increases in hydraulic conductivity. The CCL could not maintain a hydraulic conductivity of 1×10^{-7} cm/sec or less under these conditions.

Test Plots in Hamburg, Germany

Melchior *et al.* (1994) describe what may be the most extensive test plot program involving CCLs performed to date. Three test plots were constructed, as shown in Figure 9-16. Results are summarized in Table 9-3. All test plots were constructed on top of an existing municipal solid waste landfill in Hamburg, Germany. There were two sections for each test plot. The upper section was located on the relatively flat portion near the top of the landfill, with a 4 percent slope. The lower half sloped more steeply at an inclination of 20 percent. The test plots were underlaid with a percolation collection lysimeter. Test Plots 1 and 2 are similar to the RCRA Subtitle C cap, except that Test Plot 1 did not contain a geomembrane. Test Plot 3 employed a sand layer beneath the CCL to serve as a capillary break and to keep the CCL moist, similar to what was attempted unsuccessfully at Omega Hills.

Test Plots 1 and 3, which did not have a geomembrane overlying the CCL, experienced a very large increase in leakage in 1992. The summer of 1992 was extremely dry in Hamburg, and the subsequent fall season was very wet. Excavations made in 1993 confirmed that the clay liner was cracked. Barely visible fissures were observed between soil aggregates (around 50 mm in diameter). Plant roots were observed to have reached the upper parts of the CCLs. A CCL with a hydraulic conductivity of 1×10^{-7} cm/sec and a unit hydraulic gradient, has a percolation

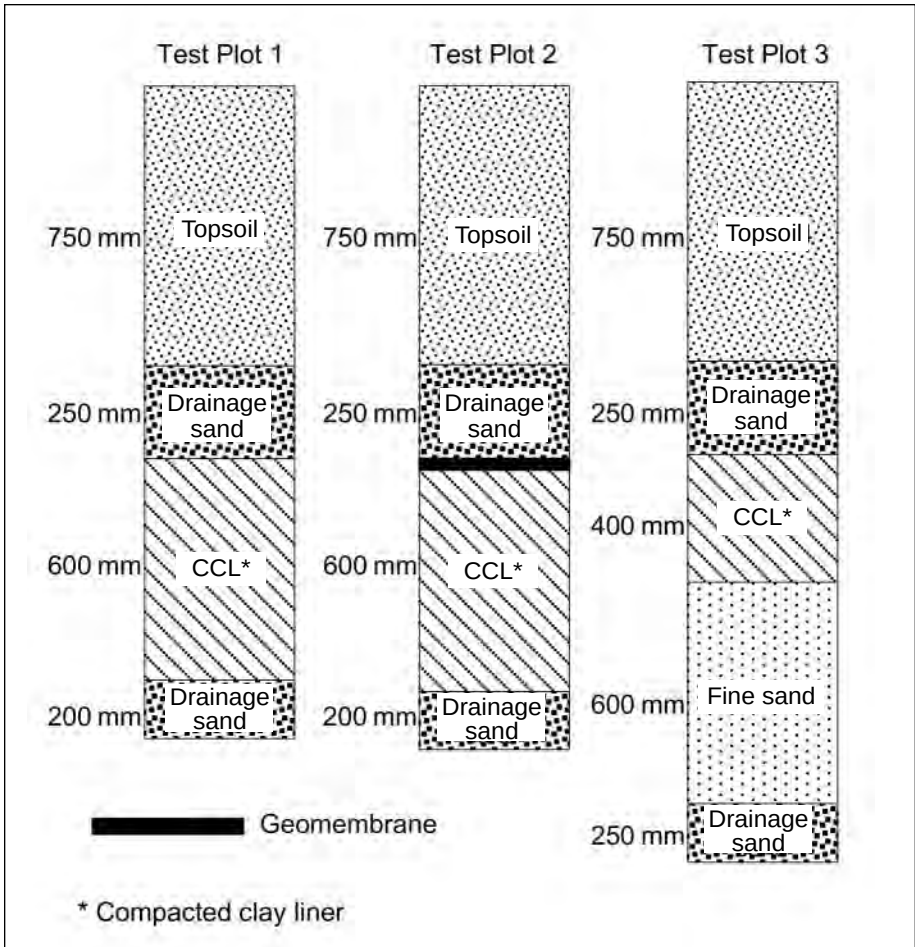


Figure 9-16. Cross sections of test plots at Hamburg, Germany (after Melchior *et al.* 1994).

rate of approximately 30 mm/year. The actual leakage rates through the CCLs at Test Plots 1 and 3 exceeded 30 mm/year in 1992 (Figure 9-17). The apparent problem was the gradual deterioration of the CCL caused by desiccation during a particularly dry summer. Test Plot 2, which did have a geomembrane overlying the CCL, maintained a very low leakage rate (Figure 9-17), because the geomembrane impeded percolation and protected the CCL from desiccation. The capillary barrier layer did not protect the overlying CCL from desiccation and drained water following

TABLE 9-3

Summary of information concerning performance of field test plots at Hamburg, Germany (data from Melchior *et al.* 1994).

Test Plot	Year	Drainage (mm)	CCL Leakage (mm)	Leakage/Drainage %
1	1988	371	7	2
	1989	181	8	4
	1990	291	18	5
	1991	184	9	5
	1992	225	103	31
2	1988	296	3	1
	1989	155	0.6	0.4
	1990	269	0.4	0.1
	1991	164	0.5	0.3
	1992	311	0.8	0.3
3	1988	390	8	2
	1989	233	14	6
	1990	321	31	10
	1991	198	32	16
	1992	278	116	42

heavy precipitation, just as found at Omega Hills. The findings at both the Omega Hills site and the Hamburg site, that desiccation and eventual failure of compacted clay occurs in caps not protected with a geomembrane, are consistent with the analysis of Suter *et al.* (1993), who indicate that compacted clay barriers are likely to fail even in the short term.

Melchior (1997) describes subsequent work performed at the Hamburg site in which two additional test covers were constructed and monitored. The two additional test covers each consisted of 300 mm of topsoil underlaid by 150 mm of drainage sand, which in turn was underlaid by a GCL. Two different geotextile-encased, needle-punched GCLs were used for the two test plots. As with the Test Pilot 2 test cover, the two additional covers with GCLs were underlaid by drainage sand and a geomembrane to collect any water that percolated through the test cover. Both GCLs performed well for about a year, with almost no liquid appearing in the drainage layers beneath the test covers. However, in the fall of 1992, about a year after construction (and following a dry

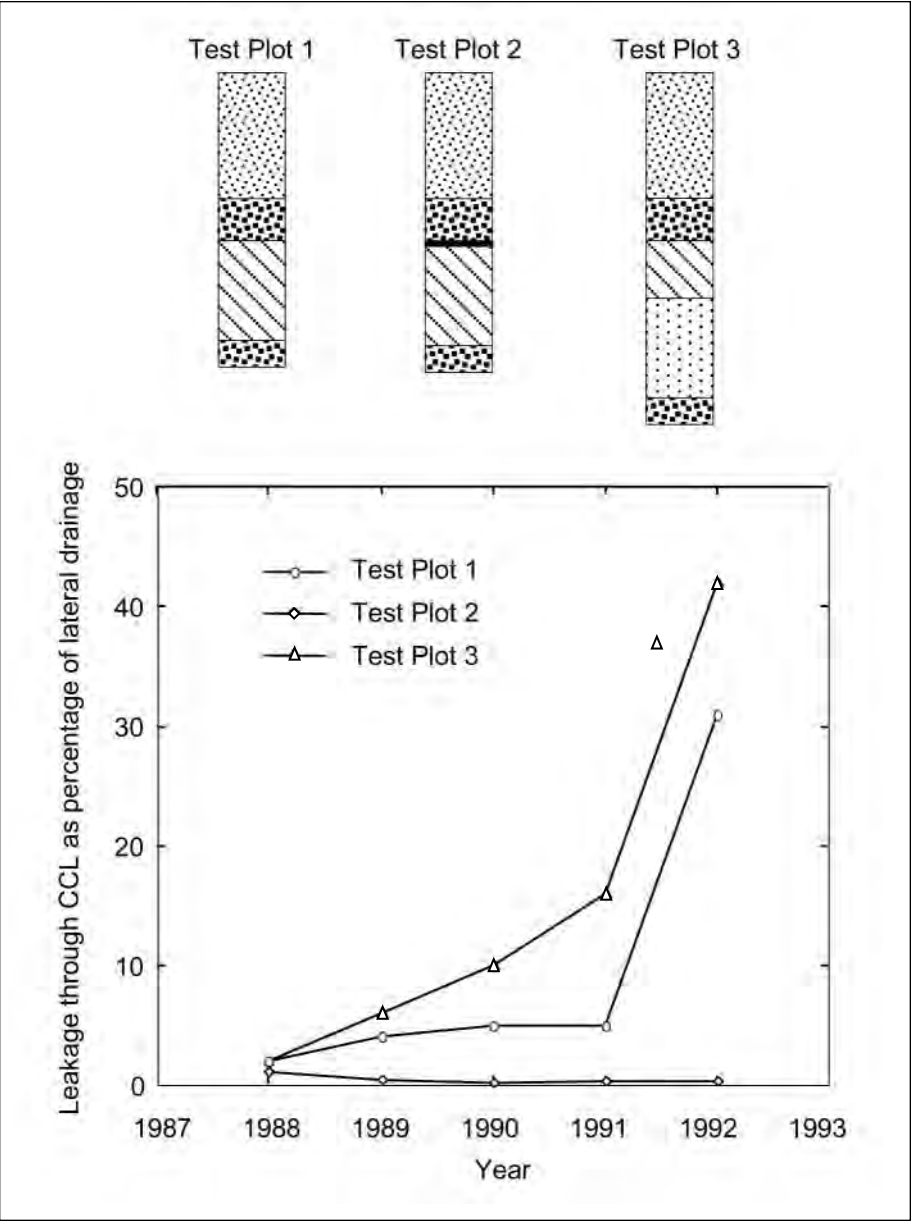


Figure 9-17. Results of percolation measurements through test plots at Hamburg, Germany (after Melchior *et al.* 1994).

summer), percolation began to occur, closely linked with rainfall events. Peak percolation rates were on the order of 0.4 mm per hour (about 1×10^{-5} cm/sec). Melchior (1997) states that research into the causes of a high percolation rate is ongoing, but indications are that the increase in hydraulic conductivity of the GCLs may have been related to the following: (1) penetration of the GCL by plant roots; (2) desiccation of the GCL, leading to high initial seepage rates following major rainfall events; (3) ion exchange (calcium was apparently leached from cover soils; when sodium in the bentonite is replaced with calcium, an increase in hydraulic conductivity can be expected).

Alternative Landfill Cover Demonstration

A major field demonstration project, initiated in the mid-1990s, is underway at Sandia National Laboratories and, although only preliminary data were available at the time of preparation of this book, the project bears mentioning here. The Alternative Landfill Cover Demonstration project is a large-scale field test conducted at Sandia National Laboratories, on Kirtland Air Force Base in Albuquerque, New Mexico, a semi-arid site. The goal of the project is to field test, compare, and document the performance of alternative landfill cover technologies and their various complexities and costs, with emphasis on arid and semi-arid environments (Dwyer 1997). A major objective of the study is to provide information on cost, construction, and performance, so that design engineers and regulatory agency officials will have data on conventional cover design alternatives.

Each test plot is 13 m wide by 100 m long. All cover layers are constructed with a 5 percent slope, with slope lengths of 50 m. The test covers are crowned at the middle half of the length. The western slopes are maintained and monitored under natural conditions, while a sprinkler system installed on the eastern slopes facilitates stress testing of the covers. There are six test covers, including two conventional covers and four alternative covers, with cross-sections as follows:

1. Baseline Test Cover 1 is a RCRA Subtitle D conventional cover, consisting of 150 mm of topsoil underlaid by 450 mm of compacted “barrier layer soil” with a maximum hydraulic conductivity of 1×10^{-5} cm/sec. (Actual hydraulic conductivity measured on laboratory samples recovered from the constructed barrier layer

were in the range of 5×10^{-7} cm/sec to 6×10^{-6} cm/sec. An *in situ* hydraulic conductivity test yielded a hydraulic conductivity of 5×10^{-7} cm/sec.)

2. Baseline Test Cover 2 is a RCRA Subtitle C conventional cover, consisting of (from top to bottom): 600 mm of topsoil, a geotextile separator/filter, 300 mm of sand drainage material, a 1-mm-thick linear low-density polyethylene geomembrane, and 600 mm of compacted clay with a design hydraulic conductivity less than or equal to 1×10^{-7} cm/sec (an *in situ* hydraulic conductivity test indicated a hydraulic conductivity of 8×10^{-7} cm/sec, with the comparatively large hydraulic conductivity thought to have been caused by desiccation cracking during construction).
3. Alternative Test Cover 1 is essentially identical to the RCRA Subtitle C cover, except that it incorporates a GCL rather than CCL and, (very significantly), the geomembrane component was punctured with eight holes, each measuring 1 cm^2 , to simulate defects in the geomembrane.
4. Alternative Test Cover 2 contains a capillary barrier, which makes use of a clean, granular layer below a topsoil layer to provide a capillary break between the topsoil and underlying soils, thus promoting moisture retention in the topsoil layer. So long as the granular layer beneath the topsoil remains relatively dry, the downward movement of moisture should be minimal. The capillary barrier test cover consists of (from top to bottom): 300 mm of topsoil, an upper lateral drainage layer of 80 mm of sand underlain by 220 mm of clean pea gravel (the sand serves as a filter that prevents the overlying topsoil from migrating downward into the gravel), a barrier layer of 450 mm of compacted soil, and a lower drainage layer of 300 mm of sand. The barrier layer was compacted dry of optimum water content and was not intended to have a hydraulic conductivity comparable to a traditional CCL.
5. Alternative Test Cover 3 is referred to as the anisotropic barrier. A layering of capillary barriers was used in an attempt to limit downward movement of water. The various layers were enhanced by varying soil properties and techniques that comprise the cover's anisotropic properties. The anisotropic barrier consists of

(from top to bottom): 150 mm of a topsoil/pea gravel mix (a mixture of 75 percent topsoil and 25 percent pea gravel, by weight), 600 mm of native soil to allow for water storage, a 150-mm-thick interface layer consisting of fine sand to serve as a filter between the overlying native soil and underlying gravel, and 150 mm of pea gravel. The fine sand layer was intended to create one capillary break, and the gravel layer was intended to create a second capillary break.

6. Alternative Test Cover 4 is referred to as the ET cover. The ET cover consists of a single, 900-mm-thick layer of native soil. The bottom 750 mm of soil was placed in lifts and compacted, while the top 150 mm was not compacted. The cover material was seeded with native species that contained a mix of cool- and warm-weather plants (primarily native grasses).

Preliminary results indicate that all six test covers are performing well, although there are significant differences in percolation rates. Table 9-4 shows a personal communication summary of the first year of percolation and the cost data. The program promises to provide valuable insights into conventional and alternative cover designs as more data are developed and analyzed in the future.

TABLE 9-4

Summary of preliminary data from Alternative Landfill Cap Demonstration Project (source: Dwyer, personal communication, 1999).

Test Cover	Construction Cost (\$/m²)	Percolation (L) after One Year
RCRA Subtitle D cover	51	6724
RCRA Subtitle C cover	158	46
Alternative RCRA Subtitle C cover with GCL (Geomembrane with eight defects)	90	572
Capillary barrier	93	804
Anisotropic barrier	75	63
Evapotranspiration cover	74	80

Test Covers in East Wenatchee, Washington

Khire *et al.* (1997b) describe a project at the Greater Wenatchee Regional Landfill in East Wenatchee, Washington (a semi-arid region), in which two test covers were constructed and monitored. The test covers measured 30 m by 30 m and were constructed on a 37 percent slope. Instruments were installed to measure runoff and percolation, as well as to monitor moisture conditions within their various layers.

Test Cover 1, referred to as a “resistive barrier,” was an RCRA Subtitle D type cap. The cover consisted of 150 mm of topsoil underlaid by a 450-mm-thick barrier layer constructed from low-plasticity, silty clay compacted to achieve a hydraulic conductivity of 2×10^{-7} cm/sec. The low-permeability barrier layer was intended to provide resistance to water infiltration; (thus the use of the term resistive barrier). Test Cover 2 was a capillary barrier consisting of 150 mm of vegetated silt topsoil, underlaid by a 750-mm-thick layer of medium, uniformly graded sand that served as the capillary break layer.

Performance of the test covers was documented over a 3-year period (Khire *et al.* 1997a). For the first 3 years, Test Cover 1 allowed 33 mm of water (equal to 5.1 percent of precipitation) to percolate through the cover, while Test Cover 2 allowed only 5 mm of water percolation (equal to 0.8 percent of precipitation). Significant percolation through the capillary barrier occurred only during the winter of 1993, due to record snow fall. If the surface layer of the capillary barrier cover had been increased, it is conjectured that percolation through the capillary barrier would have been nearly zero. In the resistive barrier cap, percolation occurred only when the wetting front reached the base of the low-permeability barrier layer. Percolation increased significantly in 1995. The primary reason for this increase appeared to be preferential flow through vertical cracks in the barrier layer, which apparently formed from desiccation during the previous summer. Animal burrows, found during field reconnaissance in the spring of 1995, may also have contributed to the increase in percolation.

Test Covers at Los Alamos National Laboratory

Nyhan *et al.* (1997) describe the performance of four test covers constructed at Los Alamos National Laboratory for the Protective Barrier Landfill Cover Demonstration. The four test plots were each constructed

on slopes of 5, 10, 15, and 25 percent, making a total of 16 test plots. None of the plots were vegetated, apparently to simulate extreme conditions in which plants provided no evapotranspiration. Precipitation, runoff, drainage, and percolation were measured for each plot, and the moisture content of the soils was also monitored. Performance for the first 4 years is documented by Nyhan *et al.* (1997).

The four test plots contained the following cross sections:

1. Test Cover 1 was termed the “Los Alamos conventional design” and consisted of 150 mm of loam topsoil underlaid by 760 mm of crushed Los Alamos tuff (an angular, silty sand), underlaid by 300 mm of gravel.
2. Test Cover 2 was termed the “EPA design” and consisted (from top to bottom) of 610 mm of loam topsoil, a geotextile separator/filter, 300 mm of sand drainage material, and 610 mm of low-permeability clay-sand material. The geomembrane component that usually overlies compacted clay in EPA designs was intentionally omitted because, in the late 1980s, when the design was conceived, it was thought that the geomembrane would not have a sufficiently long service life for radioactive waste disposal units.
3. Test Cover 3 was termed the “loam capillary barrier design” and consisted of 610 mm of loam topsoil underlaid by 760 mm of fine sand, which served as the capillary break.
4. Test Cover 4 was termed the “clay loam capillary barrier design” and consisted of 610 mm of clay loam topsoil underlaid by 760 mm of fine sand.

Performance data showed that 86 to 91 percent of all precipitation that fell on the covers evaporated from the unvegetated test covers, which was not unexpected in the semi-arid climate of Los Alamos. Of the four test covers, the EPA design provided the least amount of percolation through the test plots (zero percolation on all four test plots employing the EPA design). The barrier layer, consisting of bentonite mixed with sand, apparently helped with the water balance at this semi-arid site by absorbing moisture. Test Cover 1 (Los Alamos conventional design) allowed the greatest amount of seepage, varying from 174 mm of percolation for the 5 percent slope to 31 mm for the 25 percent slope over a 4.5 year period. Test Cover 3 (loam capillary barrier design)

allowed 76 mm of percolation for the 5 percent slope, 36 mm of percolation for the 10 percent slope, and no percolation for the 15 percent and 25 percent slopes over the same 4.5 year period. Test Cover 4 (clay loam capillary barrier design) allowed 48 mm of percolation for the 5 percent slope, and no percolation for test plots with steeper slopes for the 4.5-year observation period.

The Los Alamos test plots appear to be the only documented cases in which compacted clay, placed in a test cover, without a protective geomembrane, worked well over a period of several years of observation. However, it appears that the clay worked more as a water absorbing layer than as a low-permeability barrier.

UMTRA Experience

Waugh and Richardson (1997) summarize experience of covers constructed for uranium mill tailings remedial action (UMTRA) projects. The accepted remedial action for large volumes of tailings is to place an engineered cap with a design life of 200 to 1,000 years over the tailings. Engineered covers for tailings repositories typically consist of compacted soil layers, sand drains, and rock rip-rap intended to limit radon releases and provide long-term protection from erosion and water infiltration. Several years of performance observation indicate that biological disturbances threaten the integrity of covers at many sites.

Waugh and Richardson (1997) review design and performance objectives for a cap at the Monticello facility. The cap consists of 200 mm of soil-gravel admixture, underlaid by 1.5 m of protection soil (which includes a 300-mm layer of cobbles to impede animal intrusion), underlaid by a 300-mm capillary break, underlaid by a geomembrane and 600 mm of compacted soil that serves as a barrier to the release of radon gas. The design was intended to meet typical RCRA performance objectives and allow revegetation of the landfill cap in the gravel-soil admix.

Hanford Prototype Barrier

A team of researchers has worked over a period of about 15 years on development of the fundamental science and engineering necessary to design effective caps in the semi-arid climate of the Hanford facility near Richland, Washington. Wing and Gee (1994a 1994b) describe the overall

program, and Gee *et al.* (1997) provide monitoring results for an actual cap constructed over a contaminated crib area. Gee (1997) summarizes the research that supported development of design concepts. Further information is contained in the case study 9CS22, “Hanford Site Surface Barrier Technology,” by Anderson L. Ward and Glendon W. Gee.

The case study, “Hanford Site Surface Barrier Technology,” by Anderson L. Ward and Glendon W. Gee, describes the development and testing of a prototype surface barrier at the DOE Hanford Site in Washington State. *See page 1414.*



The barrier that evolved from the Hanford research is illustrated schematically in Figure 9-18. The gravel-silt admix at the surface is intended to provide a fine-grained soil matrix to support plant growth, while leaving the gravel as a stable “desert pavement” surface as wind erodes the silt component. The underlying silt provides a rooting medium for plants. A layer of fractured basalt rip-rap in the cap serves as a barrier to burrowing animals and also provides a capillary break to promote water retention in the overlying silt soils. Graded filters ensure that fine particles of soil will not penetrate the rip-rap. A composite barrier of asphaltic concrete overlaid with fluid-applied asphalt provides a barrier that is functionally equivalent to a conventional geomembrane/compacted clay barrier, but able to withstand the dry Hanford climate without desiccation, and with an anticipated service life stretching into thousands of years. Although expensive, the cap design provides the best that vadose zone technology can offer and is supported by numerous field experiments and numerical simulations. The most significant challenge at Hanford may be determining how more economical caps can be constructed at sites that do not require such a high level of protection.

VERTICAL BARRIERS

Vertical barrier walls are used widely to control lateral spreading of contaminants in groundwater. For large masses of buried waste, such as uncontrolled hazardous waste dumps, containment with vertical barriers, coupled with source reduction via extraction wells, is often the only technically and economically viable remediation alternative. Although

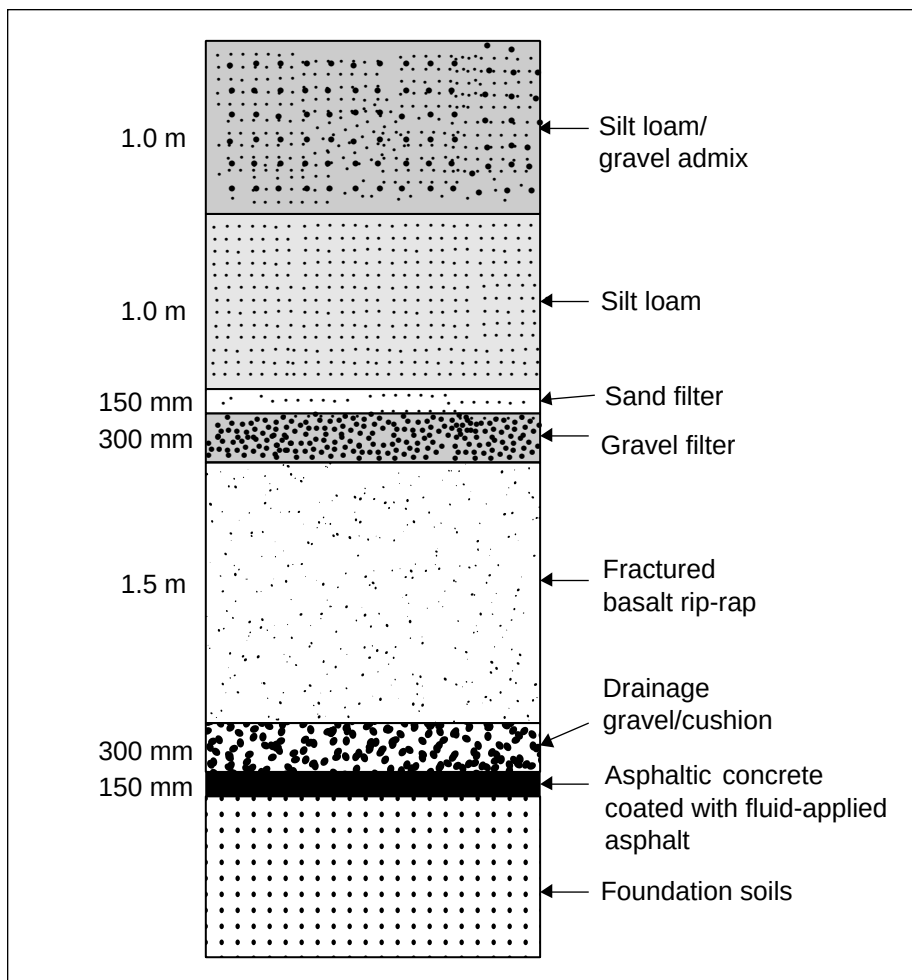


Figure 9-18. Cross section of cap used at the Hanford, Washington, facility (after Wing and Gee 1994b).

vertical barriers have often been used for groundwater control, information on their field performance is lacking, methods for quality control are not well developed, and vadose zone applications are limited. Nevertheless, reliable vertical barriers are needed for the vadose zone. Current knowledge concerning vertical barrier technology is summarized below.

TYPES OF WALLS

The following types of walls and other vertical construction techniques are described in this subsection:

- Walls constructed with slurry methods
- Deep soil mixed walls
- Grouted walls
- Sheet pile walls
- Geomembrane walls
- Ground freezing

Walls Constructed with Slurry Methods

Walls constructed with slurry methods are built by excavating a trench with a backhoe or clamshell (Xanthakos 1979). The trench is filled with a water-clay mixture, usually water and sodium bentonite, although other clays, such as attapulgite, have occasionally been used. The slurry level is maintained near the top of the trench and always at least a meter or more above the water table. The slurry seeps from the trench into the surrounding soil. As this seepage occurs, the bentonite in the slurry forms a thin film (called “filter cake”) on the walls of the trench. This filter cake serves like an impermeable membrane. The hydrostatic pressures from the slurry press against the filter cake and maintain stable walls of the trench, even for trenches excavated into saturated sand.

Typical properties of the slurry are described by Xanthakos (1979) and in an EPA guidance document on slurry walls (U.S. EPA 1984). Koeling *et al.* (1997) describe a typical project. The minimum viscosity of the slurry was 40 seconds (Marsh funnel method), and the minimum unit weight was 10.06 kN/m³. Numerous research papers dealing with a variety of construction, backfill, and long-term performance issues are contained in the conference proceedings edited by Paul *et al.* (1992).

Walls constructed with slurry methods are routinely excavated through the vadose zone and into groundwater. These types of walls are used primarily as barriers to lateral movement of groundwater below the vadose zone. In the vadose zone, wet backfill placed in the slurry-filled

trench may eventually desiccate and crack. For this reason, slurry trenching is not considered an ideal technology for vadose zone containment but is mentioned here because it is the dominant method for constructing vertical barrier walls.

Soil-Bentonite Backfill

Once the slurry trench is excavated, a relatively impermeable material must be placed in the trench. In the United States, the most commonly used material is soil-bentonite backfill. In most cases, the soil excavated from the trench is mixed with bentonite-water slurry and augmented if necessary, with additional dry powdered bentonite. The mixture is placed in the trench, where it flows readily, displacing the slurry and filling the trench (Figure 9-19). Examples of soil-bentonite back-filled slurry trenches are described by Barvenik and Ayres (1987) and Deming (1997).

The literature contains several papers that describe the fundamental variables that influence the hydraulic conductivity of the backfill, including D'Appolonia (1980), Millet and Perez (1981), Ryan (1985), and

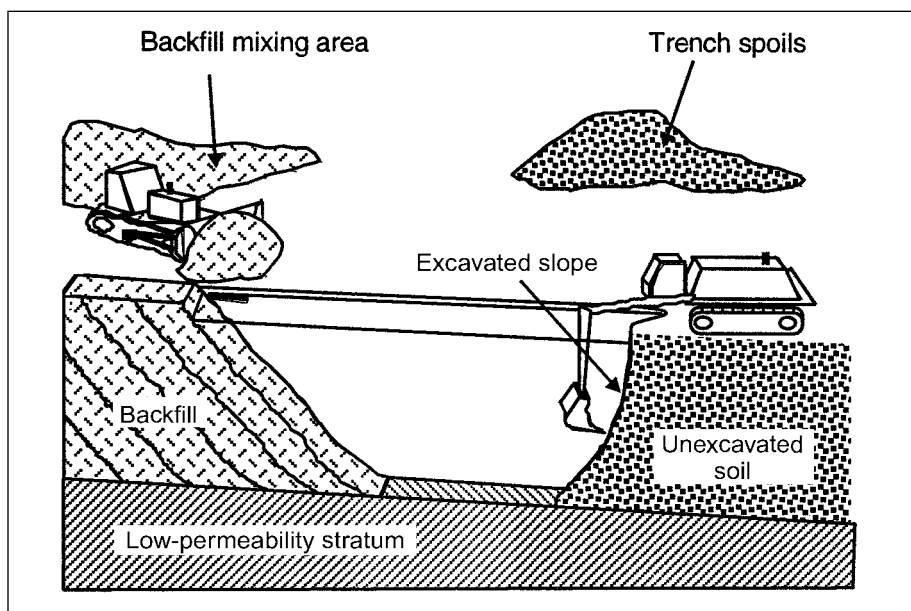


Figure 9-19. Construction of a soil-bentonite-backfilled slurry trench.

Evans (1994). One of the potential problems with bentonitic backfills is that they are vulnerable to large increases in hydraulic conductivity from certain chemicals, such as concentrated organic liquids (Anderson *et al.* 1985), and certain inorganic liquids (Alther *et al.* 1985). Methods of evaluating compatibility are discussed by Day (1994). Another problem is consolidation, which leads to vertical stresses in the backfill that can be considerably lower than calculated geostatic stresses (Evans *et al.* 1995) because some of the weight of the wall is supported by shearing stresses along the vertical walls of the barrier.

Freeze-thaw cycles evidently do not degrade soil-bentonite backfill (Zimmie *et al.* 1997), but wet-dry cycles can significantly damage wet soil-bentonite backfill. The potential for desiccation cracking is so large that soil-bentonite backfill normally would not be considered for containment in the vadose zone, except for relatively moist soils located just above the water table.

Construction quality assurance is discussed by Tamaro and Poletto (1992), Rumer and Mitchell (1995), Daniel and Koerner (1996), and Poletta and Good (1997). The construction contractor typically monitors the density, viscosity, the characteristics of the backfill, and, (sometimes), sand content of the slurry during excavation. Koeling *et al.* (1997) describe a soil-bentonite barrier for which the following backfill properties were specified: hydraulic conductivity less than or equal to 1×10^{-7} cm/sec, fines content greater than or equal to 20 percent, unit weight at least 2.36 kN/m³ greater than the unit weight of the trench slurry, and slump (which is a measure of the ability of the backfill to flow) of at least 76 to 178 mm. The hydraulic conductivity was determined by ASTM D-5084, but the effective confining stress was not specified. Hydraulic conductivity decreases with increasing confining stress, and the decrease can be significant in porous, compressible materials such as soil-bentonite backfill. Because the *in situ* stresses tend to be significantly less than calculated geostatic stresses, it is easy to consolidate the test specimen to too large an effective confining stress and thereby to measure a hydraulic conductivity that is too low. Without specifying the effective confining stress to which the specimens were to be subjected, the method leaves a great deal of latitude in measuring the actual hydraulic conductivity. Methods for determining the hydraulic conductivity of soil-bentonite and other types of barriers are discussed later in this chapter.

The current practice of construction quality assurance (CQA) in the United States is often driven primarily by the contractor's quality control process, sometimes with superficial oversight from an independent engineer. Monitoring of the depth of trenching and key-in to an "impermeable" stratum are often the major components of CQA. Figure 9-20 illustrates some of the defects ("windows") that can occur in soil-bentonite backfilled slurry trenches. Tachavises and Benson (1997) discuss the effect of hydraulic imperfections in a vertical barrier wall and conclude that the hydraulic conductivity of the defect is a key factor. The overall hydraulic conductivity of a barrier wall can be orders of magnitude higher than design specifications when the wall contains small permeable defects (for example, less than 2 percent of the wall's area). Comprehensive guidance for good CQA is lacking for the commonly-used soil-bentonite backfilled slurry trench, and is essentially non-

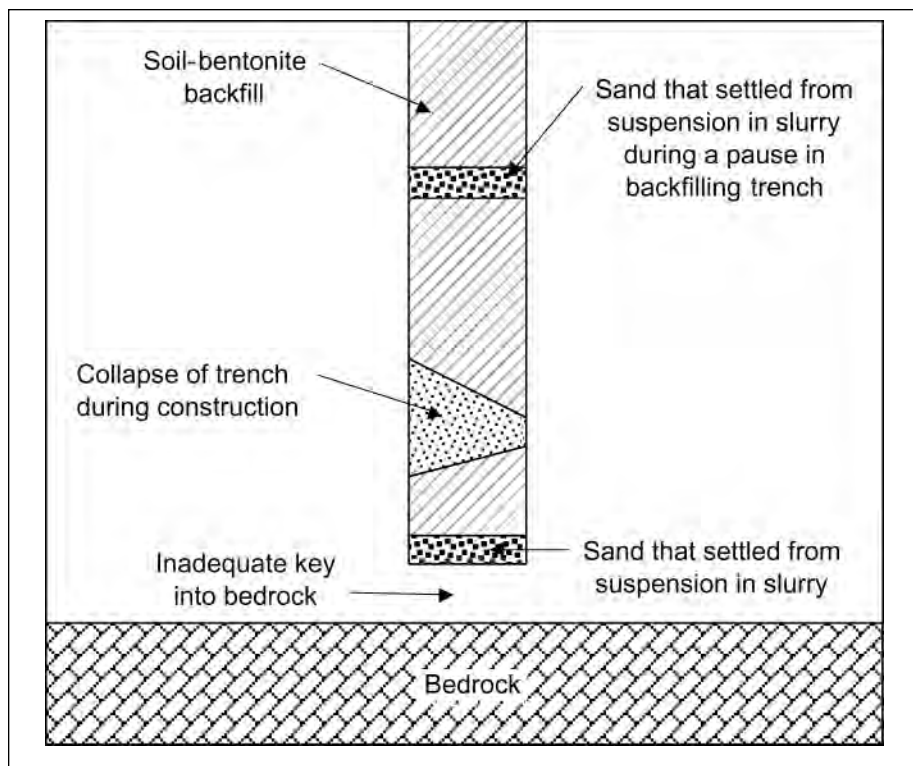


Figure 9-20. Potential defects in a soil-bentonite-backfilled slurry trench.

existent for other types of vertical barriers. An example of a high level of CQA on a project is described by Barvenik and Ayres (1987).

The performance of soil-bentonite backfilled slurry trenches for groundwater control has been reviewed by the U.S. EPA (1998b). Data were assembled from groundwater monitoring wells at 38 sites (most of which contained soil-bentonite backfilled walls), and the data were examined in light of remedial performance objectives. These objectives varied among the sites, from maintenance of a specific hydraulic head differential to achievement of a specific groundwater quality standard downgradient. The performance of the barriers could not be compared to a specific absolute standard. The evidence showed that of the 38 sites, 8 had met and 17 may have met the performance objectives established by the owner or regulatory agency for that system. Seven sites may not have met performance objectives, and 6 had insufficient evidence to determine if objectives had been met. Barrier failures were due primarily to underflow near the key-in. However, information is limited, and despite the large number of soil-bentonite barrier walls that have been constructed for groundwater control at waste disposal sites, one is hard pressed to develop a convincing case (based on field performance data) that the walls have the properties and performance characteristics intended in the original design. This is partly due to lack of comprehensive CQA data, partly to the inability to measure the properties of the completed wall, and partly to the fact that soil-bentonite walls are typically part of a complex containment and source removal system that makes verification of any one component of the system difficult. For instance, if the wall contains defects or windows, the consequence simply may be a greater rate of fresh groundwater flow into the zone of source removal. This may allow the overall remedial objectives to be met, but does not necessarily indicate that the vertical barrier had the intended properties and performance characteristics.

Cement-Bentonite Backfill

Cement-bentonite cutoff walls are constructed using a slurry that usually contains water, bentonite, and Portland cement (Jefferis 1981 and 1997). Blast furnace slag significantly lowers the hydraulic conductivity of cement-bentonite mixtures, as illustrated in Figure 9-21 (Jefferis 1997). Tallard (1997) describes an example of an alternative cement-bentonite material containing attapulgite clay and blast furnace slag.

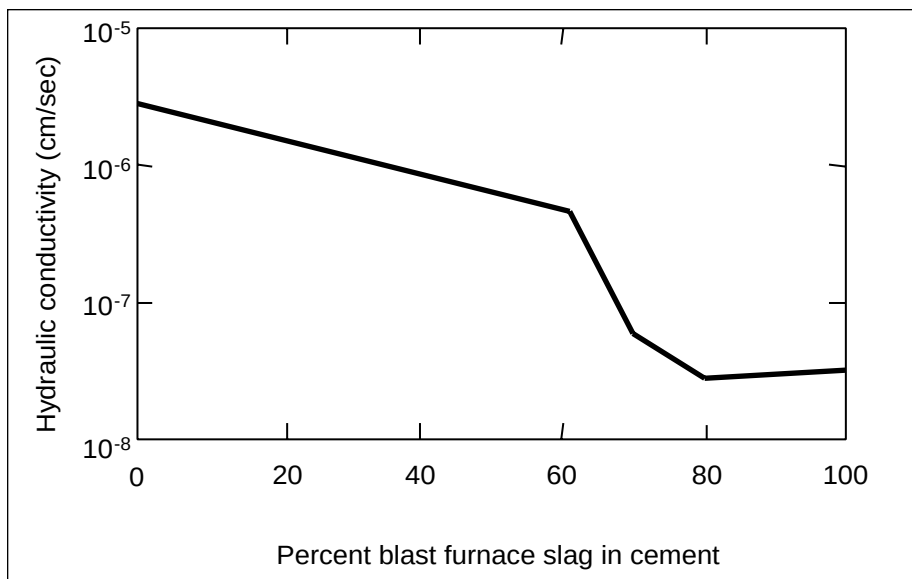


Figure 9-21. Effect of blast furnace slag on the hydraulic conductivity of cement-bentonite backfill (Jefferis 1997).

The cement bentonite slurry maintains stable trench walls during excavation and later hardens into a relatively low-permeability mass. The excavation can either be an open trench excavation (as illustrated in Figure 9-19) or the wall can be constructed in panels, sometimes referred to as the “diaphragm wall” method (as shown in Figure 9-22). One advantage of cement-bentonite cutoff walls is that there is no need to mix soil with bentonite, which makes construction more convenient when space for mixing is very limited. On the negative side, because it is relatively porous, cement-bentonite backfill tends to have a higher hydraulic conductivity than soil-bentonite backfill, and the cement-bentonite gradually attains its relatively low hydraulic conductivity over a period of many months as the cement cures (Manassero *et al.* 1995; and Jefferis 1997). Evans and Dawson (1999) contrast the cement-bentonite and soil-bentonite backfilling methods and note that in the United Kingdom, cement-bentonite is mixed with slag to lower hydraulic conductivity significantly.

Cement-bentonite hardens to a stiff material, not a concrete-like material. Because the primary component of cement-bentonite is water

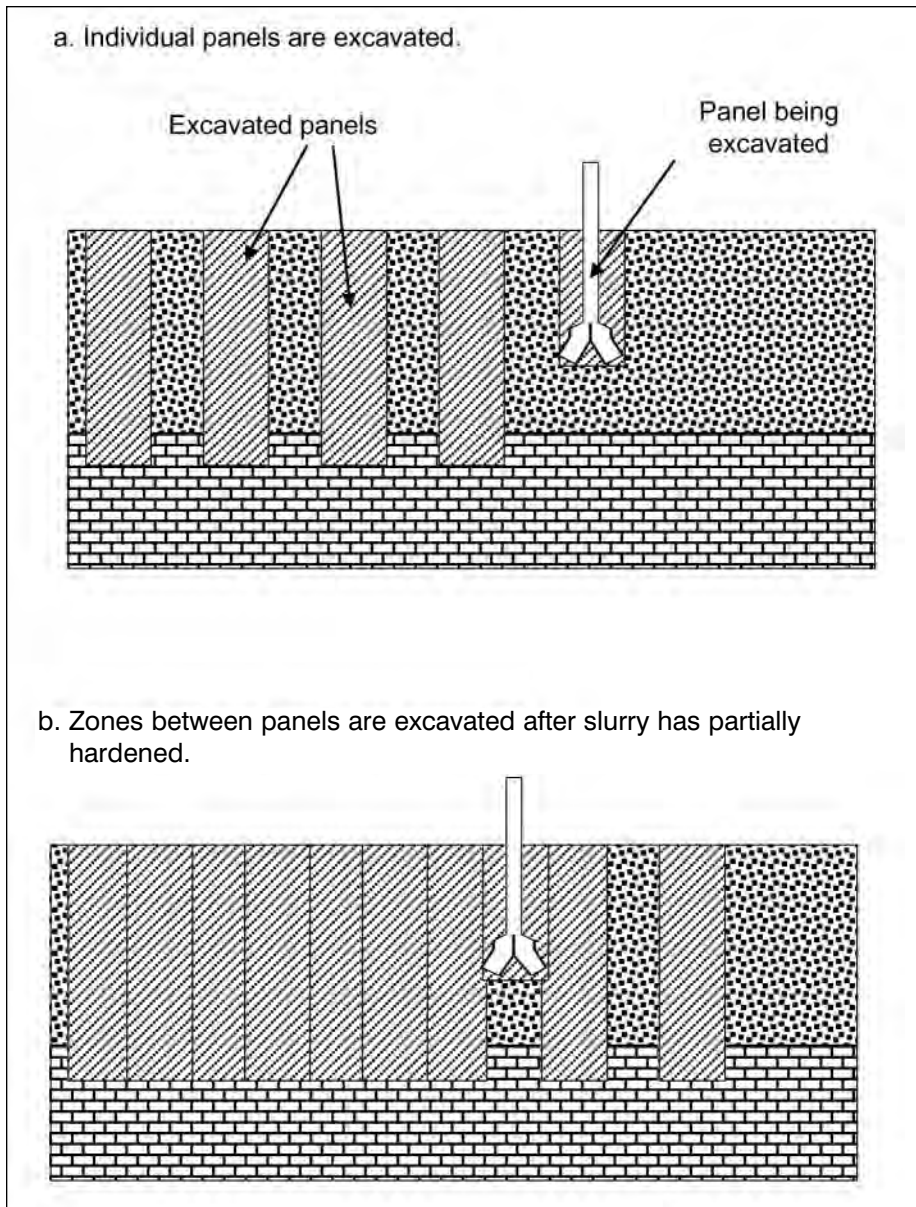


Figure 9-22. Construction of a cement-bentonite slurry trench using the diaphragm wall method.

(approximately 60 percent to 70 percent by volume), cement-bentonite is highly vulnerable to desiccation cracking in the vadose zone. It may be possible to design a more desiccation-resistant cement-bentonite mixture that is suitable for the vadose zone, but no research on this subject was located in the literature. Clearly, development of desiccation-resistant cement-bentonite backfill for the vadose zone is a research need.

Plastic-Concrete Backfill

“Plastic concrete” is a relatively fluid material composed of a mixture of aggregate, cement, bentonite, and water (Evans *et al.* 1987). In the construction procedure, which is similar to that used to build reinforced concrete diaphragm walls (Xanthakos 1979), slurry trenches are usually excavated in panels that are filled from the bottom up with plastic concrete. The zones between the plastic concrete panels are excavated after the panels have hardened and are capable of structurally supporting themselves when adjacent soil is removed.

Plastic concrete may be less vulnerable to damage from desiccation than cement-bentonite due to its higher mineral content and lower porosity. However, no information on the use of plastic concrete as a desiccation-resistant material for vadose zone applications was found in the literature.

Other Backfills

Slurry trenches can be backfilled with numerous other materials. For example, soil-bentonite-cement is a fairly common backfill. Cement added to soil-bentonite provides greater strength, less compressibility, and more resistance to desiccation cracking. Materials may be added to improve the capability of the backfill to sorb chemical constituents; for example, adding carbon enhances sorption capacity for organic contaminants (Bergstrom and Gray 1989; Mott and Weber 1989). Brandl (1997) investigated the use of several additives to improve the chemical sorption characteristics of vertical barrier walls: organophilic bentonite, zeolite, fly ash, and water treatment sludge. Brandl found that the sorbents reacted favorably with either a heavy metal or organic compound. Evans *et al.* (1997) and Evans and Prince (1997) describe studies that showed attapulgite, calcium chabazite, and additional bentonite all attenuated

cesium migration, but that attapulgite was the most effective additive to traditional soil-bentonite backfill for enhanced chemical adsorption. The possibilities for backfill seem to be nearly endless, and possible advantages of additional admixtures may be undiscovered.

Deep Soil Mixed Walls

One of the fundamental problems of using slurry trenching to construct a vertical barrier wall in the vadose zone is desiccation of the wet backfill that is placed in the trench. Desiccation can lead to cracking, and, although the design engineer can specify ways to minimize desiccation cracking, it may be worthwhile to examine other methods of constructing vertical barrier walls to avoid this problem. One such alternative method is the deep soil-mixed wall.

Deep soil-mixed walls are constructed by drilling several overlapping holes into the ground simultaneously, using rotating augers. The augers do not remove the soil, they just mix the soil with permeability-reducing liquids that are injected during the mixing. After mixing, the materials are left to react or cure. The equipment is moved a meter or two and the next section of the deep soil-mixed wall is constructed, overlapping with the previously constructed section. The injected liquid is normally a bentonite-cement mixture, but a variety of sealants or grouts can be used. The process is described by Yang *et al.* (1993). Shallow and deep soil mixing are contrasted by Nicholson *et al.* (1997).

Deep soil mixing offers several advantages over conventional cutoff wall methods (Mutch *et al.* 1997). First, the soil does not have to be fully excavated, which reduces costs for soil disposal if the soils are contaminated, and minimizes risk of chemical exposure to workers. Because the walls are constructed in short sections and the soil is not excavated, there is minimal risk of wall collapse. The method is also well suited to construction in confined areas.

One of the potential problems with deep soil mixed walls is verification of hydraulic conductivity, as discussed by Yang *et al.* (1993) and Daniel and Choi (1999). With deep soil mixed walls, it may be difficult to obtain a representative sample for laboratory testing. Normally, samples are taken from the surface of the barrier, which may not be a representative location, and then prepared in the laboratory, producing a specimen that may be different from the *in situ* material. Further, the

wall is usually formed from cementitious materials added to native soil, and the material must be allowed time to cure. Often, hydraulic conductivity of barrier wall materials containing Portland cement declines significantly for many months as the cementitious material cures and other reactions occur. It is difficult to take undisturbed samples of backfill without damaging it (for example, creating microcracks in weakly cemented backfill), and although *in situ* tests are possible, questions remain about the performance of such tests (Daniel and Choi 1999). Verification of the properties of the completed wall is one of the areas in which further research and development are needed.

Grouted Walls

“Grout” refers to any material that is injected into soil to strengthen or lower the hydraulic conductivity of the soil. Hundreds of grouts have been used in soil, although Portland cement-based grouts have been the most common. Numerous books (Bowen 1975; Karol 1990) and conference proceedings focus on grouting issues (Baker, 1982). Rumer and Mitchell (1995) discuss specific applications to waste containment problems.

Grouts can be divided into two categories: particulate grouts and chemical grouts (Karol 1990). Particulate grouts are composed of particles suspended in water, such as Portland cement or bentonite. Chemical grouts consist of chemicals dissolved in water. A fundamental limitation of particulate grouts is that if the grout is injected into the soil, the suspended particles tend to be filtered out of the soil and may not penetrate very far. Very coarse materials, such as gravel or cobbles, are easily grouted with particulate grouts; but fine soils, such as fine sands or silts, cannot be grouted with particulate grouts. Grouts have been used extensively for grouting fractured rock in the construction of dams, and the technology is easily transferred to sealing fractured rock in waste containment systems (McCloskey *et al.* 1997). However, major questions persist about the grout’s effectiveness because verification of sealing is extremely difficult. A critical advantage of chemical grouts is that they can penetrate fine soils much farther than particulate grouts. One way to improve the penetration capability of particulate grouts is to grind the solid material very finely, for example, “micro-fine cement.”

The actual design of a grout can be very complex because the properties of the fluid grout, as well as those of the cured soil-grout mixture, must be considered. Often, changing a characteristic to benefit one parameter, such as lowering the viscosity of the injection fluid to maximize grout penetration, can negatively affect another parameter, such as increasing hydraulic conductivity of the cured material. The flow behavior of the liquid grout is critical since it determines the ability to mix, pump, and place the grout (Rumer and Mitchell 1995). Viscosity, which influences penetration of the grout, can be controlled by adjusting the water-cement ratio and through chemical additives. The water-cement ratio is the most significant parameter controlling the strength and hydraulic conductivity of hardened cementitious grouts. Reducing the water-cement ratio decreases hydraulic conductivity, but may require the use of superplasticizers to lower the viscosity of the fluid grout sufficiently to achieve the desired penetration into the soil. Gel strength, which is often defined as the unconfined compressive strength after curing, is a widely used indicator of grout effectiveness.

There is significant concern regarding the durability of grouts. For example, some grouts can be degraded by sulfates in groundwater. In the vadose zone, shrinkage and subsequent cracking are often a major cause for concern. Crack resistance is enhanced with low water-cement ratios.

Several investigations have been conducted recently to develop and evaluate the durability of chemical grouts. Voss *et al.* (1994) describe studies of natural wax and sodium silicate, both of which were found to be promising. Heiser *et al.* (1994) studied the durability of polymer grouts, including methacrylates, polyester styrene, vinylester styrene, furfuryl alcohol, and sulfur polymer cement. All polymer grouts showed good resistance to freeze-thaw, wet-dry, and chemical exposure. Persoff *et al.* (1994 and 1997a) studied injectable colloidal silica grouts for barrier construction at Hanford, Washington, but discovered problems with uncontrolled and rapid gelling due to reactions between the grout and soil. Several methods for slowing the gelling reaction were evaluated.

Jet Grouting

Jet grouting originated in Japan in the mid-1970s (Kauschinger *et al.* 1992). The idea behind jet grouting is to inject grout horizontally from the end of a drill stem that is rotated and moved vertically. The grout penetrates the soil, mixes the soil with grout, and leaves a pile-like soil

column with a diameter of approximately 1 to 2 m in place when completed. Grout is allowed to flow back to the surface so that excessive pressure cannot build up in the subsurface. The drill holes are closely spaced to provide a continuous barrier. This system is referred to as a “single fluid system.”

The double fluid jet grouting system employs compressed air in addition to high-pressure grout injection at the tip of the drill bit. The introduction of compressed air increases the penetration depth of the grout, often doubling the size of the treated soil column (Kauschinger *et al.* 1992). A major drawback of the double fluid system is the high air content of the treated soil, which can lead to high hydraulic conductivity or air permeability.

The three fluid jet grouting system injects water, air, and grout simultaneously. The water’s cutting action causes removal of significant quantities of soil, facilitating the mixing and replacement of the soil.

The advantages of jet grouting are its applicability to a wide range of soils (Mutch *et al.* 1997), good grout penetration (because of the mixing action of the jets), and the ability to direct the mixing action to the desired depth range. Drill holes can be vertical or angled to create an inclined wall. Jet grouting can also be used to construct a horizontal barrier, as discussed below.

Jet grouting is thought to be a viable technology for use in the vadose zone. However, construction does involve wet slurry systems, and the vulnerability of the grouted material to desiccation cracking is an unresolved issue. No information was found in the literature on the long-term performance or impermeability of jet grouted materials in relatively dry soils.

Fracture Creation/Grouting

A method for creating a vertical fracture into which grout can be injected involves insertion of a beam or plate into the ground to create a physical void that then can be grouted. This is the idea behind the “vibrated beam” (Leonards *et al.* 1985). The process is initiated by inserting a steel H-pile into the soil to the desired depth (typically with the help of vibration). The H-pile is equipped with grout injection nozzles at its tip. A gap equal to the size of the pile remains as the soil is removed but is immediately grouted as the H-pile is withdrawn, leaving

a thin grouted barrier in place. Guides provide alignment so that the pile insertions overlap slightly, providing continuity to the segmental wall.

The integrity of a barrier constructed with a vibrating beam is subject to question (Rumer and Ryan 1995). First, the barrier is thin, making it vulnerable to “windows” or other imperfections that could compromise its integrity and continuity. Second, the location of the beam’s tip is uncertain; stones or cobbles in the ground can deflect the beam to unknown locations, even if the alignment at the surface is perfectly controlled.

Another method of fracture creation is hydraulic fracturing, in which the injection pressure of a grout exceeds the soil stresses in the ground, thus creating a hydraulic fracture. Injected grout flows rapidly into the fracture, expanding the fracture as the grout fills it. The injected grout can be a low-permeability material (Carter 1997), or a permeable, reactive material (Murdoch *et al.* 1997). Jet nozzles can initiate fractures along the eventual plane of the barrier wall. No studies of the behavior of a thin, grouted barrier in vadose zone soils were located in the literature.

Permeation Grouting

Permeation grouting involves injection of grout under pressure, allowing time for the grout to penetrate into the soil, and then allowing the grout to set or harden. Grout holes are closely spaced to overlap and create a continuous or nearly continuous barrier. The grout injection can occur over a controlled range of depth. Particulate grouts can be injected into soils with hydraulic conductivities as low as about 0.1 cm/sec, and chemical grouts can be injected into soils with conductivities as low as about 1×10^{-3} cm/sec (Karol 1990). Table 9-5 indicates approximate relationships between hydraulic conductivity and groutability.

“Viscous barrier” is a term used to describe a barrier constructed with a special type of grout developed by researchers at the Lawrence Berkeley National Laboratory (Moridis *et al.* 1997). The viscous barrier technology employs barrier liquids which, after being injected into the subsurface, produce chemically benign, low-permeability barriers through a very large increase in viscosity which occurs after injection. The initially low-viscosity liquids are injected by permeation grouting and gel over time. The grout that is employed is colloidal silica (Persoff *et al.* 1994).

TABLE 9-5	Approximate relationships between hydraulic conductivity and groutability (after Karol 1990).
Hydraulic Conductivity (cm/sec)	Groutability (Ability of the Soil to Receive Grout)
Less than or equal to 10^{-6}	UngROUTable
10^{-5} to 10^{-6}	Groutable, with difficulty, by grouts with viscosity less than 5 cp and ungroutable with grouts having a viscosity greater than 5 cp
10^{-3} to 10^{-5}	Groutable with low viscosity grouts, but difficult with grouts with a viscosity greater than 10 cp
10^{-1} to 10^{-3}	Groutable with all commonly used chemical grouts
Greater than or equal to 10^{-1}	Requires suspension grouts or chemical grouts containing a filler material

The main concerns with grouting to achieve low hydraulic conductivity are the complete filling of void spaces with grout and control over the extent of grout penetration (Rumer and Ryan 1995). Grout has a tendency to penetrate the most permeable zones and not penetrate the least permeable zones, leading to uneven grout penetration in non-homogeneous soils. Although models are available to predict injection patterns (Finsterle *et al.* 1997), such models are highly dependent upon knowledge of subtle variations in hydraulic conductivity, which are nearly impossible to ascertain.

Further work on grouts that can be injected into soil, including examining the range of variables, is needed. Key variables are viscosity during injection, hydraulic conductivity after curing, and most important, long-term durability. However, in the end, the uncertainties of whether, where, and how the grout penetrates must be resolved if grouted barriers are to be used routinely for effective containment in the vadose zone.

Sheet Pile Walls

Steel sheet piles have been used to shore temporary excavations for decades. They have also been used occasionally as a seepage control mechanism for dams (Sherard *et al.* 1963), although experience has shown that these systems tend to leak due to lack of interlock sealing.

A major advance occurred recently with the development of thick, cold-formed sheet pile walls with far larger interlocks than conventional steel sheet piling. This permits the interlocks to be grouted for a positive seal. The Waterloo Barrier™ (Smyth and Cherry 1997) consists of 7.5-mm-thick steel sheet piling with sealable interlocks (Figure 9-23) that can be driven to depths up to 20 m. Different interlock sealants can be used, depending upon sealant and contaminant compatibility requirements. The types of sealants available include clay-based grouts, such as bentonite and attapulgite; cement-based grouts; epoxy polymers; urethane polymers; and miscellaneous sealants such as vinyl esters, polysulfides, swelling gaskets, and bituminous grouts (Smyth and Cherry 1997).

Advantages of the Waterloo Barrier™ system include installation without removing any soil (which avoids health and safety issues as well as disposal costs for contaminated soils), flexibility in installation to desired depths and geometries, and minimal problems with desiccation

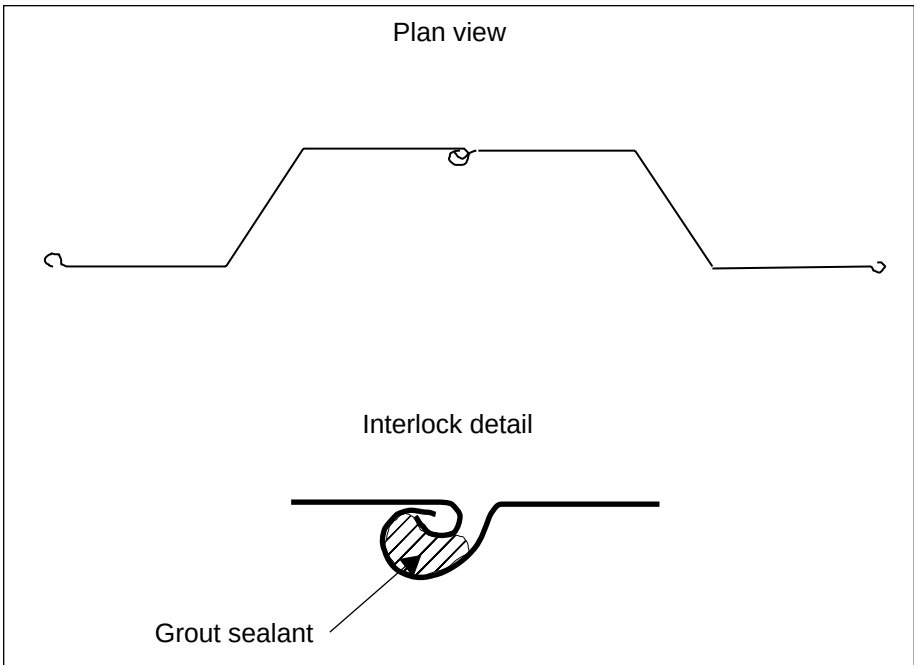


Figure 9-23. Waterloo Barrier™ interlocking steel sheet piling (after Smyth and Cherry 1997).

or freeze-thaw impacts on the barrier. Steel barriers are well suited to the vadose zone because they are not vulnerable to desiccation, damage by plant roots, or the other mechanisms that threaten the integrity of soil materials used for waste containment in the vadose zone. However, the longevity of the interlock sealants is open to question. Other potential drawbacks include depth limitations, difficulty in keying the barrier into bedrock, difficulty of installation through cobbles and boulders, and vibration and noise associated with installation.

Smyth *et al.* (1997) describe case histories in which sheet pile barriers have been used. A 5,500 m² barrier was constructed in three enclosures around contaminated zones in Washington. The barrier was driven to depths ranging from 8 m to 18 m in soils that included fill materials, sand, silt, and clay with some gravel. The installation was disrupted by the occurrence of buried wooden pilings. Holes were predrilled through the wooden pilings to allow the sheet piles to be inserted without damage. An attapulgitic-cement grout was used to seal the interlock cavities. In another project, a 250-m-long, 7.5-m-deep barrier was installed in soils that were favorable for sheet-pile installation. On yet another project, a 3,125 m² barrier was installed around a landfill to depths of 4.5 m to 9.5 m, into fine sands and silts, to control migration of landfill gases.

Geomembrane Walls

A comprehensive discussion of geomembranes used in vertical barrier walls is presented in Chapter 5 of Rumer and Mitchell (1995).

Table 9-6 summarizes typical installation methods for geomembrane vertical barrier walls. The most common type of geomembrane wall construction involves insertion of vertical panels of high-density polyethylene (used because of its strength, excellent chemical resistance, and durability) with special interlocking joints into either a slurry-filled trench or directly into the subsurface with a steel insertion plate.

For shallow walls, a rolled geomembrane material is often used. The roll can be lowered down a hole and unrolled horizontally. Geomembrane interlocks are sealed with a material that expands when hydrated with water (“hydrophilic gasket”).

Rumer and Mitchell (1995) discuss construction quality assurance issues, provide information on costs, and cite examples of use. To date,

TABLE 9-6**Installation methods for geomembrane vertical barrier walls (after Rumer and Mitchell 1995).**

Method Number	Method or Technique	Geomembrane Configurations	Trench Support	Typical Trench Width (mm)	Typical Trench Depth (m)	Typical Backfill Type
1	Trenching machine	Continuous	None	300 to 600	1.5 to 4.5	Sand or native soil
2	Vibrated insertion plate	Panels	None	100 to 150	1.5 to 6.0	Native soil
3	Slurry supported	Panels	Slurry	600 to 900	No limit	Soil-bentonite backfill, cement-bentonite backfill
4	Segmented trench box	Panels or continuous	None	900 to 1200	3.0 to 9.0	Sand or native soil
5	Vibrating beam	Panels	Slurry	150 to 220	No limit	Cement-bentonite

documented uses of steel barriers have been primarily for containment of liquids in the saturated zone.

Bocchino and Burson (1997) discuss the “one pass” deep trenching method, a technique for installing high-density polyethylene geomembranes in a vertical wall. The trencher digs the trench and immediately inserts a geomembrane panel. Although panel widths exceeding 2.4 m can be installed, narrower panels are more convenient to accommodate changed conditions encountered during excavation.

Rawl (1997) describes the “Polywall” technique, also a one-step operation, in which a 400-mm-wide trench is excavated with the cutters oriented vertically. A continuous high-density polyethylene geomembrane barrier is housed in an installation box that is pulled through the ground behind the cutter assembly. The geomembrane is unrolled vertically from fabricated rolls that are equipped with male-female joints on the beginnings and ends of the rolls. The maximum depth of the barrier wall is limited to approximately 10 m.

Burke *et al.* (1997) briefly describe several case histories involving geomembranes employed as vertical barriers. At a site in Oxnard, California, a 4.5-m-deep high-density polyethylene geomembrane was unrolled in a trench to construct a shallow wall to stop methane gas movement from an adjacent landfill. At a petroleum refinery in Denver, Colorado, a biodegradable slurry was used to excavate a trench into which drainage material and a high-density polyethylene geomembrane were inserted to provide both drainage and containment. A similar system was installed to a depth of 4.5 to 17.5 m adjacent to an ash landfill in Morgantown, Maryland, for control of contaminated groundwater, and to a depth of up to 12 m at a landfill site in Massachusetts.

Schindler and Maltese (1997) describe a project in which a 640-m-long high-density polyethylene wall was installed next to a river to eliminate offsite migration of a nonaqueous-phase liquid. The geomembrane wall was constructed by excavating a trench to a depth of 4.5 to 7.5 m, employing a slurry to maintain stable side walls, and then inserting geomembrane panels into the slurry using a frame to support the panels. Each panel was 12.2 m wide and as deep as required for each section of the wall. The geomembrane itself was 2 mm thick. Interlocking joints and hydrophilic, high-swelling gaskets were used to join panels. One construction challenge was high winds, which tended to blow the geomembrane housed in the support frame out of alignment.

Guglielmetti and Gutler (1997) describe a project at a Superfund site in Delaware in which a geomembrane was placed in a shallow trench to provide containment adjacent to a structural steel sheet pile wall.

One of the obvious advantages of geomembrane walls in the vadose zone is their invulnerability to damage by desiccation. High-density polyethylene is a relatively stable polymer with a useful design life on the order of hundreds of years or more (Koerner 1998). Durability of joint sealants is less well understood. The backfill in a slurry-filled trench (such as cement-bentonite) provides added protection from contaminant migration and redundancy of containment.

Ground Freezing

Ground freezing is a widely used technique for constructing tunnels or other underground excavations below the water table in highly permeable soils. Barriers to fluid transport can be constructed by freezing

saturated soil using refrigeration pipes inserted in the subsurface at the desired barrier location. Ground freezing was used in a demonstration project at Oak Ridge, Tennessee (Peters 1994). Inclined boreholes were drilled at a field demonstration location to create a combined wall/floor barrier (like that in Figure 9-2) with two layers of barrier. Ground freezing has been considered at arid sites such as Hanford, Washington (Grant and Iskandar 1997), but one problem is that water must be injected to saturate the soil so that the frozen ground will provide a barrier to fluid movement. Technical information on frozen barriers constructed with and without additional water is provided by Dash *et al.* (1997).

Ground freezing is a more obvious choice for containment in saturated soils than for the vadose zone because of the need to saturate a portion of the soil in order to create an impermeable frozen barrier. However, there may be unique applications for which frozen barriers in the vadose zone are attractive, such as projects where temporary containment is needed and other construction techniques are unusually difficult, for example, because of cobbles in the subsurface.

HYDRAULIC CONDUCTIVITY

Vertical barrier walls constructed from porous materials (for example, grouted barriers or deep soil mixed walls) will only function as barriers if their hydraulic conductivity is extremely low. Determination and verification of the hydraulic conductivity are critical. Even for barriers in the vadose zone, the hydraulic conductivity of the material when saturated is the design parameter usually considered. A common requirement is that the conductivity not exceed 1×10^{-7} cm/sec.

Daniel and Choi (1999) review methods for determining hydraulic conductivity of vertical barriers. The methods fall into the following three basic categories:

- Laboratory tests on reconstituted samples (often called “wet samples”) recovered from the barrier at the time of construction and cured in the laboratory
- Laboratory hydraulic conductivity tests on relatively “undisturbed” samples (of course, no sample is truly undisturbed) taken from the constructed barrier
- *In situ* tests on the constructed barrier

Table 9-7 summarizes the relative advantages and disadvantages of each type of test. Daniel (1994b) reviews laboratory-testing methods for low-permeability materials. The most reliable method of testing involves a flexible-wall permeameter and ASTM Method D-5084. *In situ* slug tests or air permeability tests, like those shown in Figure 9-24, are a very attractive testing possibility but are currently plagued by several significant, unresolved technical issues (Daniel and Choi 1999). One of these issues is that the actual location of the screened section of the test well is uncertain if the well is not perfectly centered in the wall, if the wall is not perfectly vertical, or if the well is not perfectly vertical (Figure 9-25). Inert gases can be injected on one side of a barrier and monitored on the other side, but point injection/monitoring tests a relatively small area of a wall.

Developing reliable methods for verifying the low hydraulic conductivity of vertical barriers is an area of much-needed research.

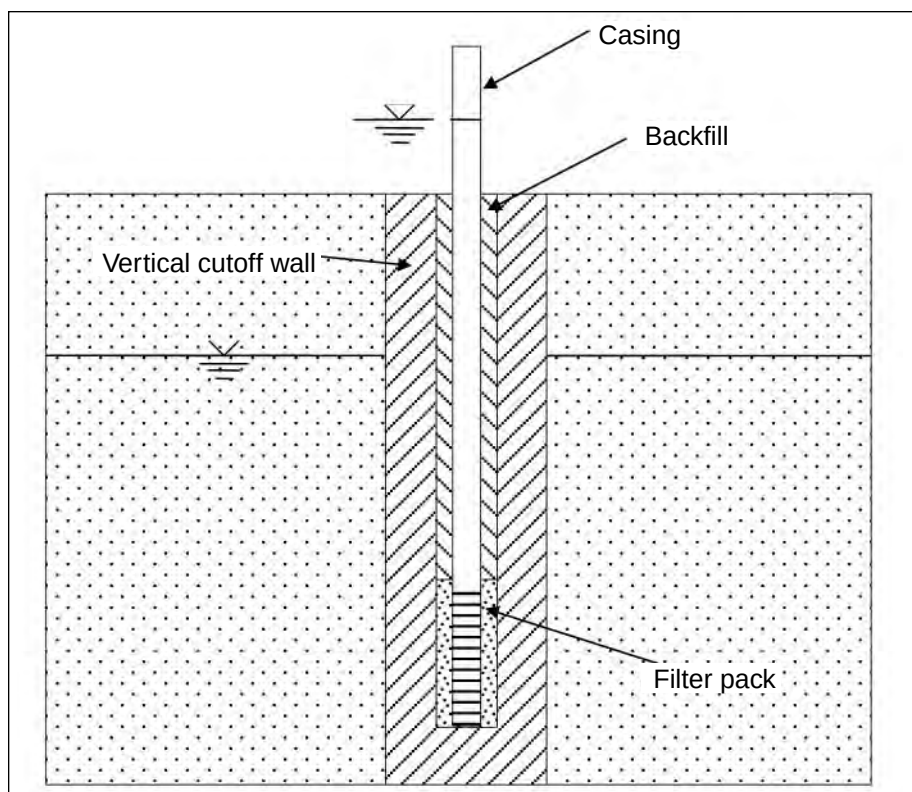


Figure 9-24. Well used in a vertical barrier to measure hydraulic conductivity *in situ*.

TABLE 9-7**Advantages and disadvantages of hydraulic conductivity testing methods for vertical barriers (Daniel and Choi 1999).**

Category	Method	Advantage	Disadvantages
Laboratory tests on reconstituted samples	Test in fluid loss apparatus	• Inexpensive • Minimal sample handling issues	• Void ratios of test material highly variable • No control over stresses or saturation • Reconstituted sample may not be representative of barrier material constructed in field
	Consolidation-cell test	• Compressive stress controlled • Easy to form a test specimen by consolidating test material from a loose or nearly fluid state • Convenient for permeation with contaminated liquids	• Equipment relatively complex and expensive • No control over saturation • Reconstituted sample may not be representative of barrier material constructed in field
	Flexible-wall permeameter	• Flexible-wall permeameter is industry standard method of testing low permeability materials • Full control over stresses • Sample completely saturated	• Difficult to form a test specimen for a very soft material • Equipment relatively complex and expensive • Reconstituted sample may not be representative of barrier material constructed in field
Laboratory tests on "Undisturbed Samples"	Test in sampling tube	• Low cost	• Potential sidewall leakage • Lack of control over stresses • Lack of control over saturation

continued

TABLE 9-7	Advantages and disadvantages of hydraulic conductivity testing methods for vertical barriers (Daniel and Choi 1999). (continued)		
Category	Method	Advantage	Disadvantages
Laboratory tests on "Undisturbed Samples" (continued)			• Lack of flexibility over direction of fluid flow (vert. or horiz.) • Sample almost certain to be disturbed to some extent
Laboratory tests on "Undisturbed Samples"	Flexible-wall permeameter	• Flexible-wall permeameter is industry standard method of testing low permeability soil • Full control over stresses • Sample completely saturated • No restriction on size of sample • Can trim sample to permeate in any direction	• Soft sample may be difficult to handle • Difficult to test at very low effective stress • Sample almost certain to be disturbed to some extent
<i>In situ</i> tests	Pizeocone	• Additional information besides hydraulic conductivity is collected • <i>In situ</i> barrier material is tested	• Permeated volume very small • Experience very limited
	Single well ("slug") test	• Large volume of material tested • <i>In situ</i> barrier material is permeated	• Borehole may be smeared • Proximity of well screen to edge of barrier unknown • Methods for calculating hydraulic conductivity not well developed for thin, compressible vertical barriers

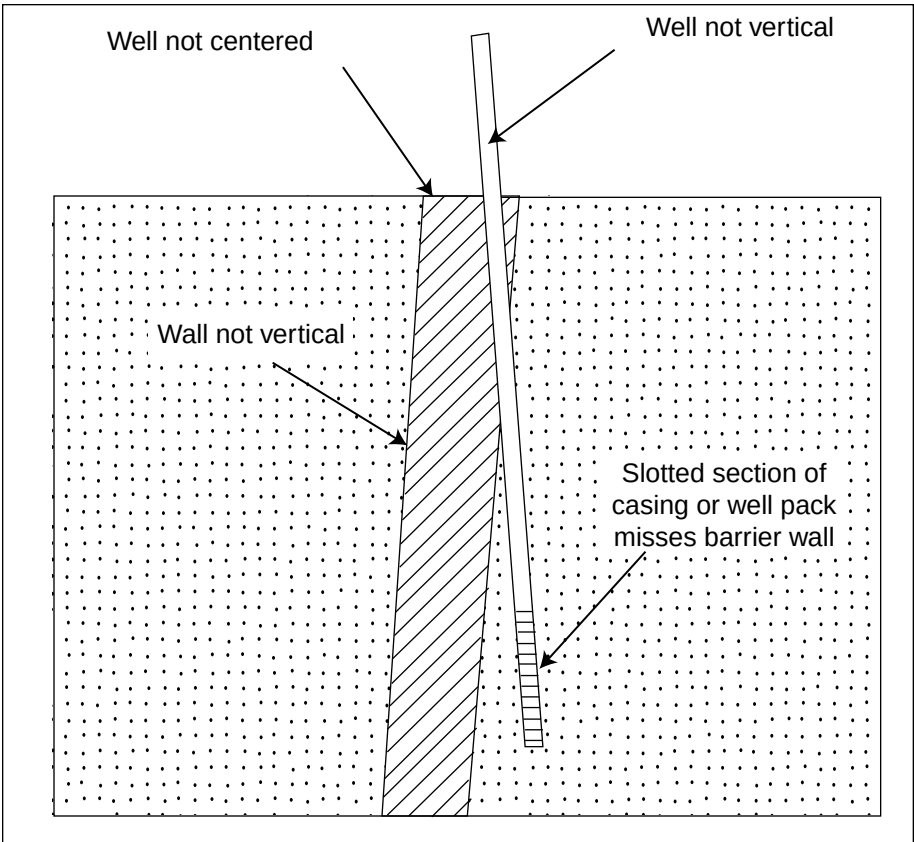


Figure 9-25. Potential problems with well location in a vertical barrier wall.

FLOORS

Chapter 4 of Rumer and Ryan (1995) and Chapter 8 of Rumer and Mitchell (1995) contain detailed discussions of possible methods for constructing bottom barriers beneath contaminated zones. These methods are not necessarily targeted for the vadose zone, although all or nearly all of the floors could be constructed in the vadose zone almost as easily as in the saturated zone. Natural barriers that form a floor beneath a contaminated zone are discussed in Chapter 7 of Rumer and Mitchell (1995) and the references therein.

NATURAL BOTTOM BARRIERS

A natural bottom barrier consists of layers of relatively low-permeability soil or rock. To make use of a natural barrier, one must first determine the presence of the natural barrier. However, this can pose problems for two reasons: (1) the continuity of the barrier may be difficult to verify in some geologic settings without extensive investigation, and (2) drilling of boreholes through the barrier can create problems unless the boreholes are properly sealed. There is an obvious tradeoff between the need to drill borings, in order to confirm the presence and thickness of the barrier, and the need to make as few penetrations through the barrier as possible.

Once the continuity of the barrier is reasonably well assured, the next challenge is to determine the properties (particularly hydraulic conductivity and air permeability) of the natural barrier. *In situ* tests are essential for making reliable assessments. Often, small samples recovered for laboratory tests fail to capture large-scale flow patterns and, therefore, hydraulic conductivity (or air permeability) is underestimated. Pumping tests coupled with monitoring wells on the opposite side of the barrier provide an excellent means of confirming the integrity of the barrier.

GROUTED BARRIERS

Permeation grouting (discussed earlier for vertical barriers) can be used to emplace a horizontal barrier beneath a contaminated zone (Rumer and Ryan 1995; Kretzschmar and Lakatos 1997). The risk that some zones will go ungrouted makes this alternative less desirable than those that provide a greater degree of control over the location of the grouted zone. Several other grouting procedures (particularly jet grouting), are possible and have been considered.

An alternative to grout injection is creation of a horizontal fracture zone that is filled with grout. Fractures can be created by a technique called "hydrofracturing." If the pressure in the grout exceeds the weight per unit area of the soil above the injection depth, the grout will lift the soil and spread it laterally along a fracture. Ideally, the soil is "notched" beforehand to initiate a fracture, and then the grout is injected under pressures that cause hydrofracturing. The fracture or crack expands and spreads, and grout flows into the fracture to form what should eventually become a thin, low-permeability barrier. An example of this type of

fracture grouting is the construction of a bottom barrier at a field demonstration described by Brunsing *et al.* (1983). In this field demonstration, grouted vertical barriers were created by notching the soil in closely spaced vertical boreholes. Then a grouted bottom barrier was created at the desired depth, with relatively closely spaced boreholes and horizontal notching of the soil. An entire block of soil was lifted upward when grout filled the horizontal notches with pressure sufficient to hydrofracture the soil. The hydrofracturing can also be done with directionally drilled holes at any desired angle.

Dwyer (1994) describes a Sandia National Laboratory field demonstration of grout injection into a silty sand with layers of cobbles. The silty sands had a hydraulic conductivity of 10^{-3} to 10^{-6} cm/sec, which made these materials marginally groutable (see Table 9-5). Three grouts were injected: microfine cement, mineral wax-bentonite, and glyoxal-modified sodium silicate grout. All three grouts were able to penetrate the silty sand, but only for small distances (less than 1 m). The silty sand was apparently too fine-grained to permit substantial penetration distances.

Carter (1997) describes the TECT™ buoyant lift process, which is designed to cut a horizontal slot in the ground mechanically with a cable saw and then grout the slot with a relatively impermeable material. Because the slot is cut mechanically, there is no need for high-pressure fracture grouting. This method provides a potentially higher degree of quality control and facilitates locating and overlapping the grouted sections with a degree of reliability and control.

Moridis *et al.* (1997) describe an application of the viscous barrier at Basin 281-3H at the Savannah River Site. Injection tubes (three at a time) were planned for sequential grouting of a bottom barrier. Grouting occurred over a depth of at least 1 m, proceeding from top to bottom of the grout zone in order to limit downward movement of the grout during injection. Computer simulations provided estimates of grout penetration patterns.

Dwyer *et al.* (1997) describe a project in which a cone-shaped side/bottom barrier was constructed as a demonstration at a clean site at Hanford, Washington. Soils consisted of sands and gravels located several meters above the water table. Jet grouting was used to install slanted columns as the exterior barrier. Next, a low viscosity polymer was injected inside the jet-grouted barrier to form a second, interior barrier.

Shibazaki and Yoshida (1997) discuss jet grouting technology that was developed and tested in Japan for construction of bottom barriers. They note that conventional jet grouting usually produces a column of grouted soil about 2 m in diameter, but for bottom barrier construction, a larger diameter (nearly equal to 5 m) is needed. A system with varied pressure and flow rates and modified jetting tools was developed, and examples of grout injections are described.

Furth and Deutsch (1997) describe a project in which a jet-grouted barrier was constructed at the Philadelphia, Pennsylvania, airport. Because of the presence of compressible materials, the grout needed to be flexible as well as low in hydraulic conductivity. The mixture was a combination of Portland cement, blast furnace slag, and bentonite.

Sass *et al.* (1997) describe the combination of horizontal directional drilling with high pressure grout injection for construction of bottom barriers. Conceptual design issues and configurations are discussed.

TUNNELS

Another method of constructing a bottom barrier, developed in Germany, involves excavation of deep construction trenches on opposite sides of the area requiring a bottom barrier (Rumer and Ryan 1995). Tunnels are constructed from one trench to another, under the contaminated area, and filled with virtually any low-permeability material. The advantages of this method are a very thick bottom barrier and absolute verification of the continuity of the bottom barrier. Obstacles are cost and safety issues.

Although several methods for constructing bottom barriers have been proposed and, in some cases, evaluated with field trials, much work remains to develop practical, reliable, and verifiable methods.

HYDRAULIC CONTAINMENT

SOIL VAPOR EXTRACTION

SVE is a widely used method for removing volatile organics from the vadose zone. Wells are installed and hooked up to vacuum pumps, which draw soil gases and vapors from the subsurface. This process creates a negative pressure, drawing all mobile gases toward the wells. The vac-

uum provides a form of hydraulic containment for gases in the vadose zone.

To the author's knowledge, SVE has never been used explicitly and solely as a form of containment. However, while SVE is considered to be a method of contaminant removal from the vadose zone, it can provide containment in the treatment area.

RELATIVE HUMIDITY CONTROL

One vadose zone containment method is maintenance of a relatively dry barrier. Dry soils are essentially impermeable to water movement. Layers of gravel or cobbles in a cap constructed in arid or semi-arid regions create a barrier to water infiltration and act as a capillary barrier, as discussed earlier in this chapter. However, if the layer of gravel or cobbles becomes saturated, the material becomes highly conductive (rather than resistive) to water flow. The material must remain dry to function as a barrier.

Morris *et al.* (1997) describe a dry barrier that is created by circulating ambient air through a layer of coarse-grained material in the vadose zone. The blower and vacuum wells can be directionally drilled to create a horizontal, dry barrier beneath a disposal facility. As illustrated by Morris *et al.* (1997), ambient air is sufficiently dry in summer months, at a site in Albuquerque, New Mexico, to permit operation of the air circulation system for at least a portion of the year. Theoretically, sufficient moisture can be removed to maintain a dry barrier year round. Successful application of a dry barrier depends on climatic conditions conducive to water evaporation from the soil during a significant part of the year, and site characteristics that are conducive to maintaining a dry barrier system (such as the presence of a thick layer of coarse-textured material that can be maintained in a dry state). The major cost associated with a dry barrier is that of drilling the air injection and extraction wells.

PERFORMANCE MODELING

Modeling of contaminant transport in the vadose zone is discussed in Chapter 5. Performance modeling is an essential component in the engineering design of barrier systems. Although many aspects have been discussed earlier, it is useful to summarize critical issues here.

CAPS

The most commonly used method for predicting moisture movement in a cap is the computer program HELP developed by the U.S. EPA (Schroeder *et al.* 1994). HELP is easy to use and contains a wealth of default data on weather and soil conditions. However, while providing convenience to the user, the default information is also an open invitation for misuse because the user does not need to know much about a cap or its properties in order to utilize the program to perform an analysis.

Also, HELP was developed for use primarily at humid sites and may not be accurate for arid or semi-arid sites (Fayer and Gee 1997; Khire *et al.* 1997a). The computer code UNSAT-H (Fayer and Jones 1990) is often used for modeling water movement in caps located in arid and semi-arid regions because of its more rigorous and, presumably, more accurate simulation of moisture transport in unsaturated soil. Further work on verification of the models for arid climates and further refinement of the models to account for extreme events (such as years of unusually high snow fall) are needed.

WALLS AND FLOORS

Contaminant transport models for walls and floors tend to be comparatively straight-forward in that analysis can often be performed in one dimension, considering flow perpendicular to the wall or floor. Discussions of analysis methods are provided by Rumer and Ryan (1995), Rumer and Mitchell (1995), and Khandelwal *et al.* (1997). The main limitation of performance models is that the predicted transport flux is directly proportional to the assumed hydraulic conductivity or air permeability of the barrier. At present, no reliable method exists to verify the integrity of the wall (Heiser 1994) or to determine hydraulic conductivity (Daniel and Choi 1999). Although improvements are clearly needed in performance prediction methodology (particularly for coupled water and vapor transport), all models are ultimately limited by uncertainties in input parameters, and the hydraulic conductivity is such a dominant uncertainty that it is the fundamental limiting parameter in the accuracy of performance predictions, particularly when potential changes over time are considered.

PERFORMANCE MONITORING

Performance monitoring in the vadose zone is discussed in Chapter 4, but special considerations for barriers are mentioned here.

Of the various types of barriers, surface barriers are by far the easiest to monitor, as sensors can be located precisely and even replaced if necessary. The keys to effective performance are management of moisture (for control of water infiltration) and, if gas is to be contained, impermeability to gas. Moisture in the cap is relatively easy to monitor with technologies such as neutron probes and time-domain reflectometry. Gas sensors can be used to confirm containment of gases. Visual observations can provide a significant means for further verification of the cap's integrity.

Monitoring the performance of a subsurface barrier is a far more challenging task. The ideal goal would be to confirm that no small defects (like cracks) exist or have developed in the subsurface barrier. The problem of locating a very small defect in a large barrier located remotely from the ground surface is fundamental and difficult to overcome. Geophysical techniques can be used to detect defects or anomalies, but there are significant limitations on the sizes of defects that can be located. Injection of inert gases on one side of a barrier, and monitoring for those gases on the other side, allows verification of barrier integrity. However, because the gases are typically injected at a point via a well, the area being tested is relatively small. Perhaps the greatest challenge is to develop new ways of performance verification. If materials that would aid in verification could be included in the barrier itself, or if better ways of delivering tracer gases over the full area of the wall were developed (perhaps by incorporating an injection layer on one side of the barrier and a monitoring layer on the other side), significant advances in performance monitoring might be possible. Performance monitoring of subsurface barriers is an area that clearly needs more work and, perhaps, some very different approaches than attempted in the past.

COSTS

Very little reliable information has been published concerning the costs of various barrier materials. The following is offered simply to provide a first-order approximation of some of the relative costs of various materials.

The primary components of caps are earth and geosynthetics. Earthen materials available on or near a project site, that do not require extensive processing, typically cost on the order of \$1 to \$2 per cubic meter. For compacted clay, the cost can typically range from \$2 to \$5 per cubic yard. For earthen materials that must be heavily processed, such as soils that must be screened and then blended with bentonite, the cost can be on the order of \$25 to \$50 (or even more) per cubic meter. For granular materials such as stone, the cost is highly dependent upon the hauling distance, but might be on the order of \$10 to \$20 per cubic meter. The final, installed cost of a cap is often on the order of \$100,000 per hectare for a soil-only cap, ranging up to \$500,000 per hectare for a complex, multi-component cap. Some specialty caps, such as the Hanford protective barrier, can cost far more.

The cost of soil-bentonite backfilled vertical barrier walls is typically in the range of \$50 to \$100 per square meter of wall (assuming a thickness of 0.5 to 1 m). Geomembrane panels inserted into cement-bentonite backfill might cost roughly \$100 to \$200 per square meter, although, since applications have been limited, these cost figures may not be typical. Other methods of construction are difficult to price because they are so sensitive to particular site conditions.

No information is available on the costs of bottom barriers because no such barriers have been constructed to full scale.

SUMMARY OF KNOWLEDGE GAPS AND RESEARCH NEEDS

Throughout this chapter, an attempt has been made to summarize existing knowledge about barriers for waste containment in the vadose zone, using references to case histories to illustrate the current level of application of various technologies. Critical areas have been mentioned, and research needs have been identified. These needs are summarized in this section.

Perhaps the greatest need for subsurface barriers is development of verification technologies. Heiser (1994) evaluated available techniques for subsurface barriers and concluded that there is no suitable methodology available to validate the containment integrity of an emplaced barrier. Unless the integrity of a barrier can be verified, great uncertainty remains concerning its effectiveness. Also, there is the risk that a great deal of money will be wasted to construct barriers that ultimately prove

ineffective. Tens (probably hundreds) of kilometers of soil-bentonite-backfilled slurry trenches have been constructed for groundwater containment around abandoned chemical dumps and landfills, and yet we know very little about the continuity, *in situ* hydraulic conductivity, and general performance of these vertical barriers. The lack of information is largely because these types of barriers are used in conjunction with groundwater pumping/treatment systems, so even if the wall is relatively ineffective, the ineffectiveness of the wall may not be known until many years later when the source removal systems are shut off and the barrier is left to contain the residual contaminants. In many cases, it appears that the responsible parties really do not want to know if a barrier is not fully effective, due to the potential costs and liability associated with correcting the problem. If we continue to take the same approach to containment problems in the vadose zone, we are likely to be at the same stage in 20 years as we are now: not really knowing how well or poorly our subsurface barriers met their design objectives, and, therefore, repeating past mistakes by constructing barriers that are not as effective as hoped.

The major research needs are summarized as follows:

- For surface barriers (caps)
 - The most significant disappointment in existing caps has been compacted clay, which has repeatedly been shown to desiccate and crack. More work is needed on alternative materials, such as GCLs and asphaltic concrete, that might serve the same function as compacted clay but be a much more durable alternative.
 - Existing caps are rarely designed for a specific water percolation goal. Unless design objectives are quantified, designs will be arbitrary and empirical. How much water reasonably can be allowed to percolate through a cover? Are we willing to accept zero percolation through a cap for most years but small, occasional percolation in extraordinarily wet years (a critical issue for capillary barriers)? How much water percolation (if any) should be allowed in occasional wet seasons? No information or guidance is published to aid these types of decisions, and yet these issues are fundamental and essential if we are to build better vadose zone caps.

- Further refinement of performance models is needed, particularly in dealing with extreme events such as an unusually wet year or high snowfall in an otherwise arid region.
 - More research is needed on graded caps. Performance objectives, redundancy, and cost must be linked to develop cap systems that will deliver performance value to the facility owner. Current cap designs range from single-layer caps less than a meter thick to caps with a dozen or more layers and a thickness of 5 m or more. There is little guidance or scientific justification regarding how to link the design and cost with performance objectives. Without further work to define better approaches and performance objectives, many caps are likely to lack sophistication and fail to meet performance objectives, and others are likely to be over-designed and wasteful in meeting objectives.
 - More field performance data must be collected. We have only in the past 10 years begun to collect field performance data on actual caps or prototype caps. These data have been incredibly useful in understanding field performance. For example, we have learned that compacted clay will often be damaged by desiccation and fail, and that capillary barriers work well in dry years, but not during years with extreme precipitation.
 - We must monitor existing caps and prototypes, and construct new caps for performance observation (for example, using graded caps with different levels of sophistication and redundancy) if we are to advance our knowledge.
 - We need to develop better edge details. A number of landfill caps have failed due to slope failures. Problems to be addressed include water drainage at the edge of the cap, overhang beyond the contaminated zone, and materials for use near the edges.
- For vertical barriers (walls)
 - The single most important factor in vertical barrier walls is proper construction to minimize the risk of defects in the barrier. There is no comprehensive, detailed guidance for construction quality control of vertical barriers, even for the commonly used slurry trench. Verification will remain difficult until engineers have better mechanisms for verifying construction quality.

Long-term performance monitoring makes no sense without short-term confirmation of barrier integrity during construction. Detailed guidance, standard test methods, procedures for taking samples and testing materials, and documentation of the CQA process are needed.

- Most of the commonly used methods for constructing vertical barriers employ wet materials (either slurries, wet backfills, or wet grouts). Any wet material left in the vadose zone as a barrier will tend to desiccate. Virtually no research has examined how these materials so commonly used for groundwater containment hold up in the vadose zone. Work is needed in this area, as well as research regarding how these materials might be modified or their design mixes altered to make them more resistant to desiccation cracking.
- The most promising vertical barriers for vadose zone containment arguably are: (1) deep soil mixed walls (because the mixing action of augers allows relatively dry emplacement of permeability-reducing agents); (2) geomembrane walls (because the geomembrane should last for hundreds of years in the vadose zone); and (3) sheet pile walls (because of their invulnerability to desiccation). Because all three are fairly new technologies, little information has been published, and details are relatively few. A comprehensive data collection of existing case histories of deep soil mixed walls, geomembrane walls, and steel sheet pile walls would be helpful. Most vertical barriers constructed in the vadose zone over the next 10 years will be likely to use one of these promising new technologies; we should, therefore, make greater efforts to understand practical lessons from previous installations.
- More research is needed on methods to verify the hydraulic conductivity of vertical barriers. The deep soil mixed wall is an example of a vertical barrier wall technology that is very promising for the vadose zone; however, there is considerable controversy over measurement of hydraulic conductivity (Daniel and Choi 1999). The accuracy of performance predictions hinges on the hydraulic conductivity of the barrier material, and yet the community has a very poor understanding of how to reli-

ably measure hydraulic conductivity of vertical barriers. Research is needed to develop methods of determining hydraulic conductivity of deep soil mixed walls and other vertical barriers.

- More research is needed on the hydraulic conductivity, desiccation, and long-term durability of grouts and hydrophilic gaskets used to seal joints in geomembrane and sheet pile walls. The impermeability of geomembrane and sheet pile walls – both of which appear to be very promising technologies for use in the vadose zone – may ultimately hinge on joint sealant performance. Practically no information has been published on these sealants, and much more work is needed to understand their characteristics in vertical barriers.
- More work is needed to develop methods to monitor performance and to confirm integrity of vertical barriers after construction. New methods should be sought that can facilitate location of occasional, small defects over large areas. These might include adding elements to the barrier to make them easier to monitor (for example, adding electrical monitoring devices to deep soil-mixed walls) or developing new techniques to verify the integrity of sealants in panel joints (for example, installing continuous layers adjacent to the barrier into which tracer gases might be injected over the full area or in a segment of the barrier).
- For bottom barriers (floors)
 - Bottom barriers are the most poorly developed of the various containment schemes. More research is needed in just about all aspects of this technology. However, the reality remains that most bottom barriers are natural strata of soil or rock, and the verification of low hydraulic conductivity is the key to effective use of such barriers. More research is needed on methods of *in situ* testing, for example, determining low hydraulic conductivity over relatively large volumes of *in situ* material.
 - More research and small-scale demonstrations of potential emplacement methods are clearly needed. Because of the very high cost of such demonstrations, and the relatively infrequent use of man-made bottom barriers, it seems logical to target

demonstrations to specific site locations where the barriers are needed, such as the Hanford site.

- The most common method of bottom barrier construction is some form of grouting, such as jet grouting or hydrofracturing/grouting from directionally drilled holes. The long-term integrity of wet grouts pumped into dry soils is cause for concern due to the potential for desiccation cracking. More research is needed on grouts, with attention focused on grouting to achieve extremely low hydraulic conductivity (less than 1×10^{-7} cm/sec) and maintaining low hydraulic conductivity over long time periods in the vadose zone. This work would be applicable not only to bottom barriers but also to walls.

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C A S E S T U D Y



HANFORD SITE SURFACE BARRIER TECHNOLOGY

Anderson L. Ward and Glendon W. Gee

ABSTRACT

At the DOE Hanford Site in Washington State, a field-scale prototype surface barrier was constructed in 1994 over an existing waste site, as a part of a Comprehensive Environmental Response Compensation and Liability Act (CERCLA) treatability test. The above-grade barrier consists of a 2-m thick fine soil (silt loam) layer over coarse layers of sand, gravel, basalt rock (riprap), and a low permeability asphalt layer. Two side-slope configurations, a clean-fill gravel on a 10 percent slope and a basalt riprap on a 50 percent slope, were part of the overall design and testing. Design considerations included: constructability, drainage and water balance monitoring, wind and water erosion control and monitoring, surface revegetation and biotic intrusion, subsidence and side-slope stability, and durability of the asphalt layer. The barrier was monitored for four years to study specific questions related to stability and long-term performance. Tests were designed to "stress" the prototype to predict long-term performance. One-half of the barrier was not irrigated. One-half of the barrier was irrigated for three years such that the total water applied, including natural precipitation, was 480 mm/yr, or three times the long-term annual average. An extreme precipitation event (71 mm in 8 hr) representing a 1,000 year return storm for Hanford was applied in late March of the first three years, when soil water storage was at a maximum. In response to the irrigation treatment, the protective side slopes drained significant amounts of water.

Over the four-year testing period, both side slope configurations drained less than expected, based on tests of configurations with similar materials at an adjacent lysimeter site. The basalt riprap configuration drained less than the gravel side slope configuration. One plot on the soil cover drained a minute quantity (less than 0.2 mm) after three years of testing. Soil drainage was attributed to lateral flow from water diverted off an adjacent road surface. After the first year of testing, there was no measurable wind erosion. Runoff occurred only twice, when there was frozen ground and rapid snowmelt conditions. The minimal erosion rates are attributed to extensive revegetation of the soil surface. The side slopes and soil cover have remained stable. The riprap side slopes remain barren while there has been a slow, but persistent, increase in vegetation on the gravel side slopes. Performance data from the surface barrier will be useful to DOE in evaluating site-closure decisions at Hanford.

INTRODUCTION

The U. S. Department of Energy (DOE) has been actively pursuing surface-cover design technology at the Hanford Site for nearly two decades (Wing and Gee 1994). A multi-year barrier development program was started at Hanford in 1985 to develop, test, and evaluate the effectiveness of various barrier designs (Wing 1993). A series of reports, totaling over 120, document the progress of the barrier development work (e.g., Gee *et al.* 1996). These reports detail field tests, natural analog studies, and modeling of surface barrier performance, and provide information on water balance, wind and water erosion, and biotic intrusions studies supporting surface barrier development at the Hanford Site. This paper details a barrier development program designed specifically for 1,000 year performance, and describes current research activities at a prototype surface barrier, located at the Hanford Site, that could be used at waste sites in arid climates.

SURFACE BARRIER DESIGN

Figure 1 shows the scope of work, leading toward a final barrier design undertaken during the past 10 years. As part of the overall development effort, a prototype barrier, incorporating all essential elements of a long-term surface barrier, was constructed at the Hanford Site in 1994.

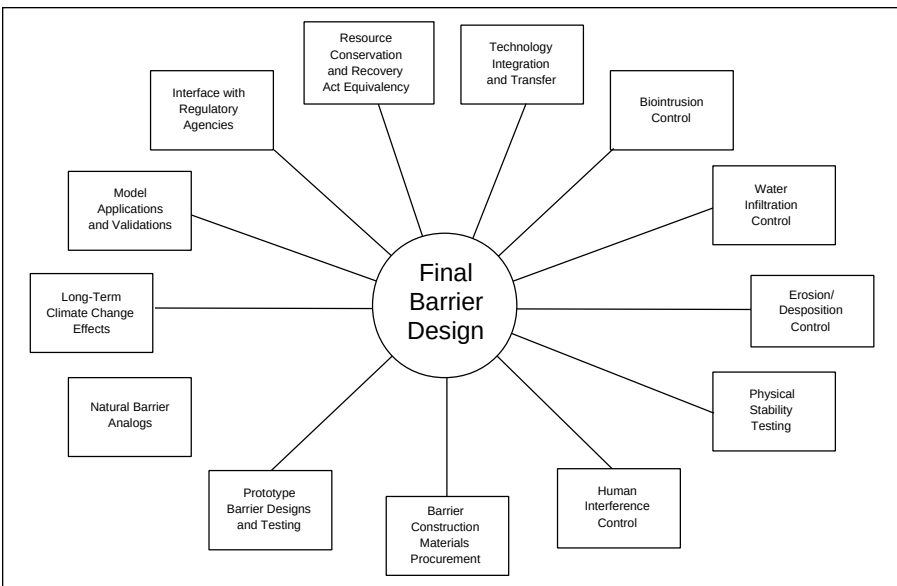


Figure 1. Hanford Barrier development tasks.

Because of the demand for a barrier that could perform for at least 1,000 years without maintenance, natural construction materials (for example, fine soil, sand, gravel, cobble, basalt riprap, asphalt) were selected to optimize barrier performance and longevity. Most of these natural construction materials are available in large quantities on the Hanford Site and are known to have existed in place for thousands of years. The prototype barrier consists of a fine-soil layer overlying other layers of coarser materials such as sands, gravels, and basalt riprap (Figure 2).

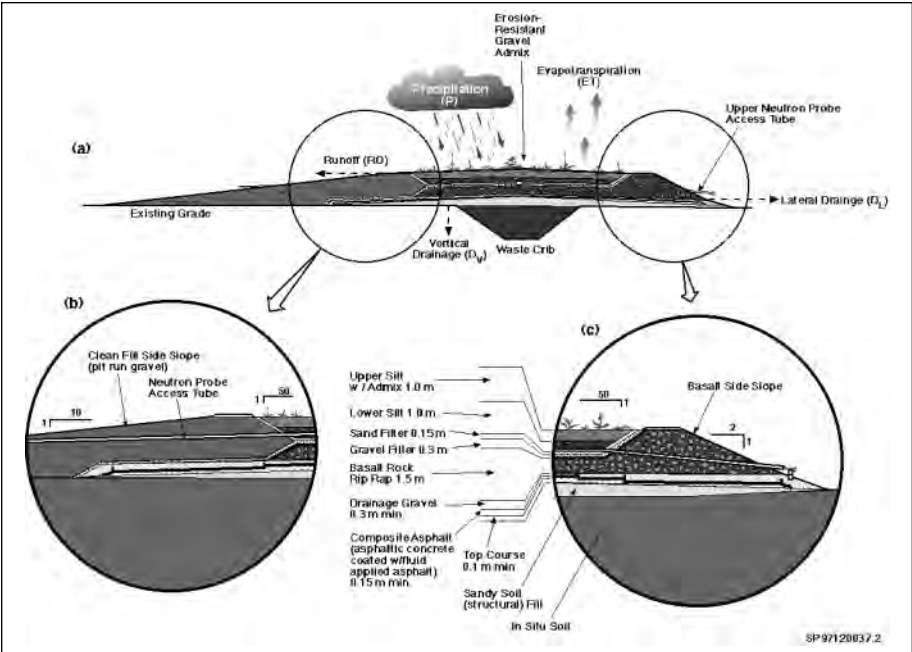


Figure 2. Cross-sections of Hanford Prototype Barrier showing (a) Interactive water balance processes, (b) Gravel side slope, and (c) Basalt riprap side slope.

Each layer serves a distinct purpose. The fine-soil layer acts as a medium in which moisture is stored until the processes of evaporation and transpiration recycle any excess water back to the atmosphere. The fine-soil layer also provides the medium for establishing plant growth, which is necessary for transpiration to take place. The coarser materials placed directly below the fine-soil layer create a capillary break, which inhibits the downward percolation of water through the barrier. By placing the fine soil layer directly over coarser materials, the design promotes a favorable environment for plants and animals while limiting their intrusion into the lower layers.

The coarser materials also help to deter human intruders from inadvertently digging deeper into the barrier profile. Low-permeability layers, placed below the capillary break, are used to: (1) divert away from the waste zone any percolating water that crosses the capillary break and (2) limit the upward movement of noxious gases from the waste zone. The coarse materials located above the low-permeability layers also serve as a drainage medium to channel any percolating water to the edges of the barrier.

In addition to testing the performance of a capillary barrier design, the prototype is being used to test two different side slope designs: (1) a relatively flat (10 percent slope) apron of pit-run gravel (commonly called a clean-fill dike) and (2) a relatively steep (50 percent slope) embankment of fractured basalt riprap (Gee *et al.* 1993b; Ward and Gee 1997). Figure 2 also shows details of the two side slope configurations used in the prototype barrier. A shrub and grass cover was established on the soil surfaces of the prototype in November 1994. Shrubs were planted at a density of 2 plants/m² with four sagebrush (*Artemisia tridentata*) plants to every rabbitbrush (*Chrysothamnus nauseosus*) plant.

Designing a maintenance-free barrier requires an understanding how natural processes affect barrier performance. A series of tests was designed to provide a better understanding of these processes and enable the design of a barrier that passively meets performance objectives.

RESULTS OF FIELD TESTS

From November 1994 through October 1997, soil (capillary barrier) plots on the northern half of the prototype barrier were subjected to an irrigation regime of three times (3X) the long-term average annual precipitation. This treatment included: (1) application of sufficient irrigation water on one day, during the last week of March for three years (1995 through 1997), to mimic a 1,000 year storm event (70 mm of water) and (2) periodic applications that each water year (November 1–October 31) achieved a precipitation target each year of 480 mm/yr.

Survival rates of the transplanted shrubs have been remarkably high, 97% for sagebrush and 57% for rabbitbrush (Gee *et al.* 1996). Heavy invasions of tumbleweed (*Salsola kali*) occurred in 1995 but were virtually absent in 1996. Grass cover, consisting of 12 varieties of annuals and perennials (including cheatgrass, several bluegrasses, and bunch grasses), dominated the surfaces, particularly those that were irrigated. Approximately 75% of the total surface area was covered by vegetation, a cover value typical of shrub-steppe plant communities. In all respects, the vegetated cover appeared to be healthy and normal. There was a surface response to irrigation, with nearly twice as much grass cover on the irrigated surfaces compared to the non-irrigated surfaces (Gee *et al.* 1996).

Figure 3 compares temporal changes in mean soil water storage on the irrigated and nonirrigated treatments at the prototype barrier through September 1998. All irrigation and natural precipitation plus all available stored soil water was removed via evapotranspiration (ET) during the first year of surface barrier operation. Water was removed from the entire soil profile so that by the late summer of each year, soil water content in both irrigated and non-irrigated plots reached a relatively uniform lower limit of 5–8 percent by volume throughout the soil profile. Correspondingly, water storage was reduced to levels of 100–150 mm for both the irrigated and non-irrigated soil surfaces. This is about one-fifth the amount of water required for drainage. Based on these observations, and considering the extreme irrigation treatments, the soil cover would not be expected to drain, even under the wettest Hanford climate conditions.

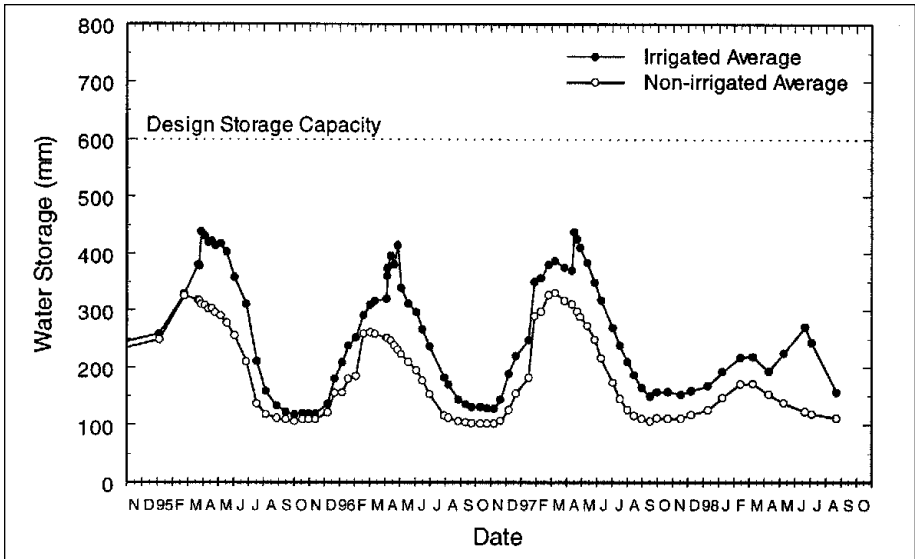


Figure 3. Temporal variation in mean soil water storage at the prototype site between November 1994 and September 1998.

Figure 3 also shows that following each simulated 1,000 year storm, all of the water was removed from the soil profile. Since no drainage occurred, the change in storage must be attributed to water loss by evapotranspiration, thus demonstrating the continued positive benefits of having vegetation on the barrier surface. Evapotranspiration for the irrigated plots was nearly double that for the non-irrigated (ambient) plots suggesting that vegetation is capable of adapting to extreme water applications (Table 1). It is apparent that the capacity of vegetation for water

TABLE 1 Water Balance Summary for the Hanford Prototype Barrier

Treatment	Water Year (WY) ^(a)	W _L (mm)	W ₂ (mm)	ΔW (mm)	P (mm)	I (mm)	R (mm)	D (mm)	ET (mm)
Irrigated	1995	238.48	119.29	-119.19	287.27	350.60	1.78	1.84×10 ⁻⁵	755.52
	1996	119.29	127.80	-8.52	224.28	247.35	0.00	9.37×10 ⁻³	463.61
	1997	127.80	152.57	24.77	289.81	224.92	36.30	9.06×10 ⁻²	453.57
	1998	152.57	156.90	4.33	146.81	200.00	0.00	1.28×10 ⁻³	342.48
	1995–1998	238.48	156.90	-81.58	948.43	1022.87	38.08	1.12×10 ⁻¹	2014.69
Non- Irrigated	1995	227.64	109.24	-118.40	287.27	150.00	0.00	1.05×10 ⁻²	555.65
	1996	109.24	102.37	-6.87	224.28	0.00	0.00	3.38×10 ⁻²	231.12
	1997	102.37	110.92	-8.55	289.81	0.00	0.00	1.70×10 ⁻⁴	281.26
	1998	110.92	111.60	0.68	146.81	0.00	0.00	1.30×10 ⁻³	146.13
	1995–1998	227.64	111.60	-116.04	948.43	150.00	0.00	4.54×10 ⁻²	1214.42

Start and end dates for the WY used in these calculations were determined by the start and end dates for water storage measurements, W₁ and W₂, respectively. In WY 1995, W₁ and W₂ were September 30, 1994 through October 24, 1995; in WY 1996, W₁ and W₂ were October 24, 1997 through October 23, 1996; in WY 1997, W₁ and W₂ were October 23, 1996 through October 25, 1997; in WY 1998 W₁ and W₂ were October 25, 1997 through September 24, 1998.

Legend:

WY = Water year

W₁ = Water year 1

W₂ = Water year 2

ΔW = Change in water constant

P = Precipitation

I = Irrigation

R = Runoff

D = Drainage

ET = Evapotranspiration

consumption was not exceeded even at the 3X precipitation rates, applied after the second year of testing. This further supports the hypothesis that the combination of vegetation and soil storage capacity were more than sufficient to remove all applied water under the imposed test conditions.

Drainage did not occur from the soil-covered part of the prototype barrier until the third year, and then only in minute amounts (less than 0.2 mm) for one of the soil plots subjected to the 3X irrigation treatment. The drainage was attributed to lateral flow from water diverted off an adjacent roadway. These observations from the prototype barrier agree with the results of extensive lysimeter testing of capillary barriers designs (Campbell *et al.* 1990; Gee *et al.* 1993a) and suggest that the water storage capacity of soil is well in excess of 3X (480 mm) precipitation. In contrast, both sideslope configurations drained, although the amount of drainage was significantly less than predicted based on the lysimeter testing that has been done with coarse materials (Gee *et al.* 1993a).

Sideslope drainage was expected since the surfaces are coarse and bare, with no vegetation growing on the basalt riprap and only a sparse (less than 10%) cover growing on the clean-fill gravel (Gee *et al.* 1993a; Sackshewsky *et al.* 1995). Figure 4 compares cumulative drainage from the gravel and riprap slopes through 10/31/96. On the nonirrigated surfaces, the total amount of drainage from the clean-fill sideslope was greater than that from the basalt riprap side slopes. A similar trend was observed on the irrigated slopes up until November 1995. While irrigation of the soil surfaces started in February 1995, irrigation of the side slopes did not start until November 1995. A closer look at these results show a relationship between season and drainage. While drainage from the clean-fill gravel side slope was continuous, there was essentially no drainage from the riprap in the summer. In the winter, both side slope configurations drained at similar rates. It is our hypothesis that advective drying similar to that described by Stormont *et al.* (1994) and Rose and Guo (1995) may be partly responsible for the lower drainage on the riprap side slopes, and may also have an effect on water storage in the fine-soil cover. Additional testing and numerical modeling will be used to test this hypothesis.

The rapid establishment of vegetation on the soil surface was thought to be responsible for at least three positive benefits to surface barrier performance:

- First, the vegetation was the dominant factor in the water removal process from the soil surfaces.
- Second, the surface was stabilized against water erosion and runoff. Runoff from the 1,000-year storm in 1995 was 1.8 mm (about 2% of the 70 mm applied). There was no runoff in 1996. The improvement was attributed to vegetative growth. Thermally-induced pedoturbation and root growth caused changes in soil bulk density and an increase in soil organic matter content near the surface, which may have enhanced permeability.

- Finally, vegetation had a positive benefit in controlling wind erosion. After plant establishment in November 1994, there were no measurable losses of soil from the surface of the prototype by wind erosion. This is attributed to the vegetation and lack of surface disturbance since establishment of the vegetative cover.

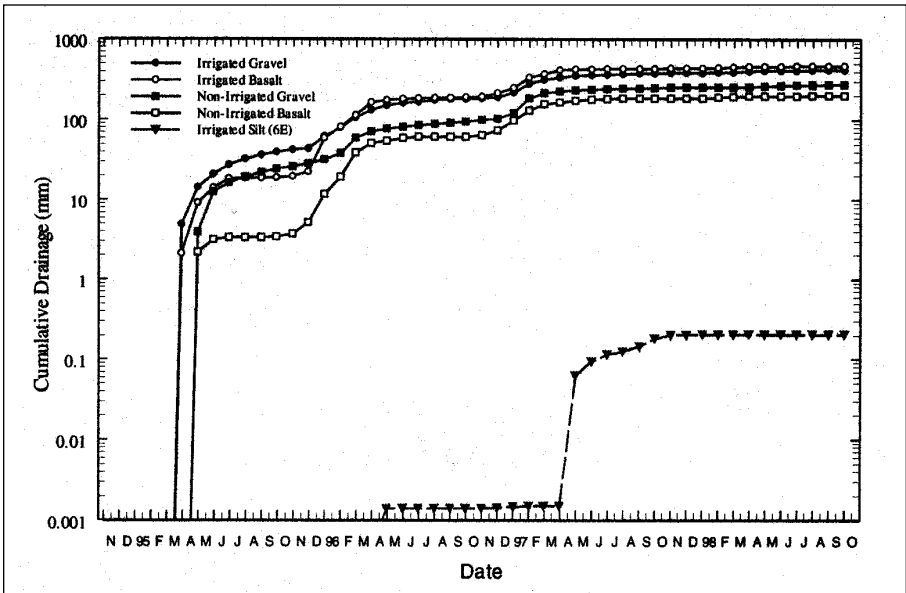


Figure 4. Cumulative drainage from four side slope plots and one soil plot from November 1994 through September 1998.

Four years of testing provide important, but limited, information for long-term barrier performance estimates. Long-term monitoring of the prototype barrier is desirable because a succession of vegetation types, full development of root profiles, and natural colonization of the barrier surface by burrowing animals can be expected to occur over a longer time period. Long-term monitoring would also provide valuable data for hydrologic model validation studies and would aid in the assessment of the long-term performance of cover systems at Hanford.

CONCLUSIONS

The study of surface barriers at the Hanford Site has evolved into an integrated demonstration of key features of barriers designed to minimize water intrusion, ero-

sion, and biointrusion. The results of field tests, experiments, and lysimeter studies provide baseline information upon which future barrier designs can be based. Test results show that for the Hanford Site's arid climate, a well-designed capillary barrier limits drainage to near-zero amounts. A subsurface asphalt layer provides redundancy. Data collected under extreme conditions (excess precipitation) provides confidence that the barrier has the ability to meet its performance objectives for the 1,000-year design life. Data from the prototype surface barrier, tested under elevated precipitation conditions, confirm earlier observations with lysimeters and field plots, showing that virtually all applied water can be removed from the soil surfaces by evapotranspiration. Side slopes, in contrast, drain because they are barren. Side slope drainage was less than predicted because of advective heating and wind action. Still, side slope drainage must be accommodated in the final design. Asphalt sub-layers can be successful in extending areas of surface protection and can divert drainage water away from underlying wastes but the durability of the asphalt must be evaluated.

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INTRODUCTION

WHY ARE WE HERE?

The nation is faced with minimizing the risk posed by the large quantities of contaminants that currently reside in the vadose zone. The vadose zone regulates the movement of contaminants to the groundwater. The natural processes that govern this movement are complex and not always well understood. Moreover, the current regulatory climate does not provide an agreed-upon framework for characterizing and remediating problems in the vadose zone before they reach the groundwater. Considering all of these factors, it is clear that those with responsibility for managing and performing vadose zone cleanup programs are in a very difficult position. The profile of potential risk, complex and interrelated processes, and the need for decisions in the face of scientific uncertainties and limited resources is similar to other major environmental challenges of our time—global climate change, equitable resource management, and the like.

The first nine chapters of this book provide a ready reference to help readers understand these complex problems in a practical way—pre-

senting both the state of science and the state of practice. Each of these chapters also identifies uncertainties and challenges for future research. This final chapter provides a prioritized summary of the gaps in vadose zone knowledge that still exist and that will require future investment. As the knowledge of vadose processes grows, the quality of the remediation efforts will improve and the cost should decrease.

WHAT DID WE LEARN?

A Large Group of Diverse Experts is Needed for this Broad Challenge

The basic data for this book were obtained through a series of three workshops with a diverse group of key experts from across the country, representing the fields of agriculture, mathematics, chemistry, geology, hydrology, biology, social science, and management practice. These respected managers, scientists, and engineers, from universities, national labs, federal agencies, and industry gathered to share their experiences and ideas. The workshop format, while challenging to organize, provided many benefits that were not predictable at the beginning of the process.

The topics for various breakout sessions were selected to encourage interaction among the participants. For example, in one breakout session we encouraged scientists, including microbiologists, geochemists, hydrogeologists, and others, to identify, compare, and contrast various complications that impact transport. In another parallel session, mathematicians discussed numerical modeling of vadose zone processes. The two groups were combined in a joint session that provided the opportunity for each group to offer suggestions on how to improve vadose zone predictions. This format encouraged lively discussion of hard questions across disciplines and facilitated identification of potential solutions. In this particular case, the participants discussed the importance of theoretical work at the small (for example, pore) scale and the need for upscaling, and developed specific approaches for upscaling. A detailed record of each of the breakout sessions was produced and this information was used to generate and annotate the scientific and technical issues outlined below.

In the final two workshops, we supplemented the detailed meeting record with a resource allocation exercise. Each participant was provided \$100 in “vadose bucks” that they were asked to invest in a

portfolio representing the data gaps and solutions that they felt had the highest potential return. The investments were then tallied and discussed. The results of the resource allocation exercises and the subsequent discussions helped to crystallize key issues. While not a rigorous scientific survey, the exercise did in fact highlight the most important gaps and future research needs. It also proved to be interesting and stimulating, facilitating broad input and providing maximum benefit from the assemblage of distinguished attendees. As a final item of interest, anonymous demographic data (such as discipline, employment category, and geographical region) were collected on each participant. The issues that attracted the most investment were examined to determine differences based on these factors.



The case study “The Vadose Zone Resource Allocation Challenge” by Michelle Silbernagel and Joann Hafera provides additional details on the procedures and outcomes of the resource allocation exercises implemented at the Las Vegas and Seattle workshops. *See page 1444.*

The Complexity of the Vadose Remediation Problems Tends to Foil Conventional Approaches

Problems in the vadose zone span the range from the limited scientific understanding of the fate and transport of contaminants to the ultimate risk to the local stakeholders. Since there is no currently agreed-upon regulatory framework, each case must be dealt with on an individual basis. In the process of developing this book, through a series of workshops, it became apparent that new approaches would be needed to achieve successful long-term solutions to vadose problems:

- Program managers in the field must be open to adopting new approaches and techniques to achieve successful remediation solutions.
- Multidisciplinary teams, including a broad range of scientific specialists as well as representatives from the social sciences, may be required to provide appropriate information to decision-makers.

- These teams of managers and scientists must learn to effectively communicate with both the regulator and stakeholder communities.

WHERE DO WE GO FROM HERE?

A substantial investment must be made in vadose zone science and technology. This process has begun at a few sites and will need to be expanded to ensure that all types of climatic and geologic settings are considered. Inclusion and coordination of the very best technical resources, wherever they may exist, is crucial to the success of future vadose science and technology efforts.

The knowledge gaps identified in this book will help to map the path forward for new research initiatives and to identify the resources that will be required to support them.

WHAT ARE THE CHALLENGES?

In the technology development business, making the difficult transition from new concepts to viable market products is often referred to as “crossing the valley of death.” This transition normally requires a significant infusion of capital and always requires a steadfastness of purpose. New products often die in this valley from lack of one or both of these key drivers. Vadose zone science and cleanup face similar challenges. However, we see the challenge of developing and implementing vadose zone solutions more as crossing a “technology desert.” A desert is difficult to cross, but with planning, resources, and sustained effort, one can successfully reach the other side. A roadmap is important to expedite the crossing and to avoid getting stalled. Further, various technologies and solutions are at various stages in the process and resources must be prioritized to support the overall goal of responsible clean-up and risk reduction.

In science and technology development programs for the vadose zone, there are actually two deserts that must be crossed: 1) the transition from basic science to applied science (many of the items identified herein are in basic science arena), and 2) the transition from applied science to application in the field (see Figure 10-1). Therefore, generating products that are usable in the field will require that vadose zone science and technology development programs cross both deserts. Crossing the

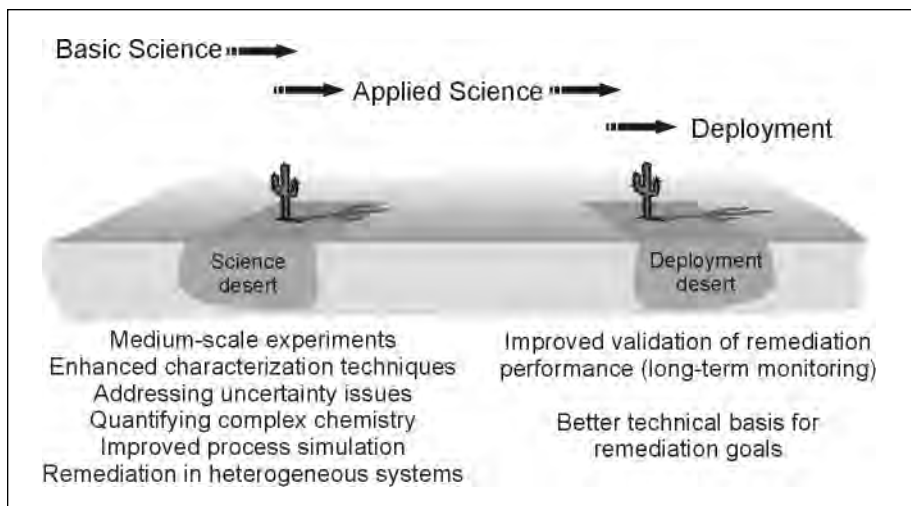


Figure 10-1. Conceptual diagram showing high-priority vadose zone science and technology needs. There are “deserts” between the development of basic and applied science and between applied science and the practical deployment of new technologies in the field.

first will require long-term funding and a thoughtful maturation process. Crossing the second will require a focus on targeted deployment investment and the early involvement of end users and stakeholders.

Various federal agencies provide funding for vadose zone research. Traditionally, such efforts have been delineated as basic science, applied science, or deployment. More attention to the transition between these traditionally disparate efforts would facilitate maturation of the technologies that are at various stages in the process. The entire effort will depend on a long-range vision and a consistency of purpose to yield truly meaningful results.

WHAT ARE THE RECOMMENDED RESPONSES FOR ADDRESSING THE MAJOR KNOWLEDGE GAPS?

This book has attempted to present as complete a representation as possible of the breadth of existing knowledge and to help identify the major gaps in the understanding of vadose zone science and technology. Various technologies and solutions are at various stages in the process

and resources must be prioritized to support the overall goal of responsible clean-up and risk reduction. The eight most significant areas recommended for further investment and investigation to enhance understanding of processes in the vadose zone are listed below and described in detail later in this chapter.

- Perform detailed and integrated medium-scale field experiments.
- Develop enhanced characterization techniques and technologies.
- Address issues of uncertainty in vadose zone flow and transport modeling.
- Develop improved validation and performance monitoring for vadose zone remediation activities.
- Develop a better technical basis for taking action and setting goals at contaminated sites.
- Develop a better understanding of complex biological and chemical influences on migration.
- Improve process simulation capabilities for vadose zone chemical fate, transport, and remediation.
- Develop remediation methods for strongly heterogeneous systems, and for complex mixed wastes.

KEY RESEARCH ACTIVITIES AND DEVELOPMENT AREAS

PERFORM DETAILED AND INTEGRATED MEDIUM-SCALE FIELD EXPERIMENTS

Research and development activities related to vadose zone characterization and remediation have typically been performed on the laboratory-bench scale, followed in many cases by field testing on a large scale. Laboratory-scale experiments are almost always the first step in understanding a new measurement or remediation process, and they provide valuable data for validating mathematical models and for designing larger scale systems. Laboratory experiments, however, do not necessarily represent realistic vadose zone field conditions, where larger scale effects, such as subsurface heterogeneity, may dominate. Mathematical simulation models that are only validated using laboratory-scale data are reliable only for modeling processes at that scale.

Large-scale field-testing is certainly an important component in the development of any new technology or method. Unfortunately, limited

research budgets usually do not allow for a fine spatial and temporal resolution of the process or properties of the system at this scale. Therefore, while large-scale applications are the desired technology endpoints, they often do not provide data at sufficient resolution to fully understand the field system or process. While mathematical models can sometimes be calibrated to reproduce the field results, these calibrations inherently are not unique due to the scale of data collection. When new remediation methods are applied at the full field scale, the assessment of remediation performance can be unreliable due to uncertainties in the initial and final site characterization.

Intermediate-scale field experiments, conducted at scales of a few meters up to a few tens of meters, could address these shortcomings. While they are by no means inexpensive, intermediate scale tests can provide realistic vadose zone conditions, with high degrees of spatial and temporal data resolution, at a reasonable cost. Whenever possible, such experiments should involve close integration of subsurface characterization, predictive modeling, remediation method testing, and remediation method performance assessment.

These tests would have the most value when performed at contaminated sites under consideration for cleanup. Interdisciplinary teams would design and test chemical and hydrogeological characterization methods. These would be used to design the remediation system at the site, to constrain mathematical models of the site, and to assess the performance of the remediation system. Modeling would serve several purposes. Initial model simulations would help to design sampling and characterization tests, and in the initial design of the remediation system. Process modeling, using the detailed characterization results, would serve to validate the models, identifying any weaknesses or inconsistencies. The validated models of the experiment would, in turn, provide a more thorough understanding of the physical and chemical processes, and could be used to explore the sensitivity, of the system. The remediation performance assessment would use the detailed initial and final site characterizations to provide reliable estimates of the full field-scale performance. More integrated medium-scale experiments can be expected to lead to useful developments in remediation technology, performance assessment, chemical and hydrogeological characterization, and predictive modeling.

DEVELOP ENHANCED CHARACTERIZATION TECHNIQUES AND TECHNOLOGIES

Enhanced characterization, in terms of type, quality and quantity of data, was identified as a crucial need for the vadose zone. Importantly, the identified gaps and potential solutions did not lead directly to larger, more expensive characterization efforts, but rather to an approach based on developing and incrementally improving a conceptual model. Each characterization activity is selected to provide specific information needed to refine the conceptual model and/or to support selection of potential cleanup methods. The resulting “toolbox” approach has been suggested at various times in the literature, but has not been routinely implemented at real field sites—especially for the vadose zone, with its incumbent sample collection/representativeness challenges. This general approach encourages creativity, as well as benefits the sampling location site, where later phases are optimized based on earlier results. The toolbox approach also encourages appropriate use of data quality objectives and similar approaches to realize maximum benefit from each borehole, monitoring station, or geophysical study. As with modeling and cleanup, the amount and type of data collected should be consistent with the degree of contamination and potential risk. Based on the three workshops, we developed a consensus regarding key characterization challenges. The participating vadose zone scientists and engineers also identified potential solutions and classes of solutions to overcome those challenges. In priority order, the primary characterization needs (topic areas in which previous vadose zone characterization efforts have failed) that were identified are:

1. Techniques that define and describe heterogeneity so that it can be incorporated into models/predictions.
2. Techniques that provide more discrete data to describe contamination and controlling geology (both vertical and horizontal distribution).
3. Improved samplers—in particular, instruments that improve the sample/data quality, reduce costs, and/or simplify logistics.

Each of these characterization needs can be described in terms of scale. Vadose zone characterization programs must collect data at the scales necessary to support understanding and planning. Many examples of multiple-scale needs were discussed. Two example cases were:

1) methods for delineation of fine scale (for example, sub-meter or centimeter) layering that provides a pathway for contaminant through a confining layer, and 2) volumetric averaging methods for estimating total contaminant mass. These examples show that the scale and measurement tools selected should be related to the purpose and intended use of the data.

The most promising classes of characterization solutions suggested by the participants included improved geophysics and tracer tests, improved core collection and analysis tools, improved instrumentation, and improved geostatistics and imaging methods. The participants felt that low-cost field screening methods, where appropriate, should be encouraged. Obtaining a larger number of samples would allow improved understanding of critically important heterogeneity and uncertainty in the system. (The traditional regulatory focus of allocating resources to reduce uncertainty in each individual sample results in a small number of samples.) Geophysical tools provide various opportunities for delineation of controlling geological features, contaminant locations, and contaminant media interactions. As with tracer tests, geophysical tests can provide data on various scales, depending on technology/design.

A variety of tools for interpreting data and planning characterization have been used and are under development. Such tools, often based on traditional geostatistics, must be improved and expanded. New mathematical methods, such as fractals and chaos theory, and enhanced imaging methods have the potential to improve scientific interpretation and communication of results.

A number of scientists and engineers who participated in the workshops recommended that the scientific community follow a twofold approach to standardization: 1) reaching consensus on, and where possible, using standard methods, such as ASTM, and 2) committing to incorporating newly developed methods into such standard formats as they are developed. This would encourage wider use of the methods and acceptance of the results.

ADDRESS ISSUES OF UNCERTAINTY IN VADOSE ZONE FLOW AND TRANSPORT MODELING

Vadose zone flow and transport processes can be grouped into two categories: those that have diffusive characteristics, and those that have

advective or convective characteristics. Diffusive processes are governed by elliptical or parabolic partial differential equations, which are often linear or almost linear. In general, their solutions are smooth and show only a moderate sensitivity to geological heterogeneity. For these reasons, they usually can be reliably modeled. Examples of such processes relevant to vadose zone flow and transport include heat conduction, single-phase gas flow, water flows dominated by capillary effects, and gas phase chemical diffusion.

Advective processes consist of the transport of chemicals and components with flowing fluid phases. The transporting fluid phase can flow in a stable, or unstable manner in the vadose zone, depending on the phase density, viscosity, wettability, saturation, and capillary pressure relative to the other phases. Advective processes are governed by hyperbolic partial differential equations that are highly nonlinear in the case of multiphase flow. These solutions usually contain sharp fronts, and they can be extremely sensitive to geological heterogeneity at various scales. This is especially true when the transporting fluid flow is unstable, such as the case of liquid water or nonaqueous phase liquid (NAPL) moving downward by gravity through a fractured or heterogeneous vadose zone. While these processes can be modeled in some cases, a detailed knowledge of the site geology, and a fine numerical grid are normally required. This type of geological knowledge and computational capability is not available at the large three-dimensional field scale, and as a result, there can be a great deal of uncertainty associated with model results.

Methods are needed that can quantify the uncertainties associated with these processes. Since many of the significant flows occur at a small scale, or in response to small-scale features, there is a need for mathematical methods that can simulate the important characteristics of these flows at a scale smaller than that of a numerical gridblock (that is, at the subgridblock scale). Similarly, because the numerical gridblocks are large, due to computational constraints, there is a need for improved techniques to upscale flow parameters such as permeability, capillary pressures, and relative permeabilities. These properties are usually measured at a small scale, in cores; yet, measurements made at these scales may not be relevant at the scale of the numerical gridblocks used in field-scale simulations. Instead, the approach used at the gridblock scale must somehow incorporate the heterogeneous distribution of these

local properties. Current dual-media approaches used in fractured porous media are a step in this direction. This topic is also an active area of research in petroleum engineering.

A similar upscaling problem exists with respect to modeling chemical reactions in the vadose zone. Most chemical reactions are sensitive to the small-scale distribution of reagents. When chemical concentrations are averaged over large volumes in gridblocks, the nature of the reactions change, sometimes severely. It would seem likely that mathematical approaches that are developed for the flow-upscaling problem could also be adapted to this chemical reaction-upscaling problem.

DEVELOP IMPROVED VALIDATION AND PERFORMANCE MONITORING FOR VADOSE ZONE REMEDIATION ACTIVITIES

Many who attended the workshops advocated development of a reasonable approach to verify the performance of vadose cleanup and containment systems. Long-term monitoring, in particular, was identified as a critical research thrust that should be emphasized over the next three to five years. As with the other types of need-based activities (for example, characterization and modeling), monitoring parameters and design must derive from project goals that are carefully developed and clearly described. This area of study is most mature in the area of barriers. In this application, goals for leakage rate and specific maximum amount of moisture movement allowed through the contaminated volume (based on exposure or concentration criteria) are set. These goals, in turn, define the sensitivity and accuracy of the monitoring technologies selected from a variety of protocols. The clarity and simplicity of the project goals encourages creativity and simplicity in design of the monitoring systems. Short-term and long-term tracer techniques have been used for qualitative and quantitative measurement of leaks or leakage. Field instruments such as moisture sensors and data loggers, geophysical studies such as electrical resistance tomography, and similar methods, are the current baseline and remain viable for performance monitoring of barriers. Importantly, the participating scientists felt that innovations were possible and necessary, even for barriers. Areas for research include the increased use of remote sensing data (for example, use of overflight or of increasingly available and low cost satellite data),

improved geophysics, biological/microbial markers, and other strategies to reduce costs.

Methods to verify remediation based on destruction and removal technologies (nonbarrier methods) in a cost-effective manner clearly require advances and improvements in technology and implementation approaches. Collection of analytical data, in the form of high cost-per-sample snapshot information, at individual locations is the current baseline. Such an approach is both expensive and ineffective in providing robust performance information. The participants recommended that new technology for monitoring physical and chemical removal/destruction should learn from, and evolve from, the approaches developed over the past decade for barrier monitoring. Thus, participants proposed setting clear quantitative vadose zone goals in terms of concentration, flux, and other factors. Goals that relate to the underlying groundwater encourage implementation of insensitive and indirect monitoring systems that provide little information about the release and migration of contaminants in the vadose zone. Updated approaches are needed that are similar to the advanced tensiometer and vadose zone sampling systems being installed at a few sites. As with barrier monitoring, the scientists felt that technology innovations in geophysics, tracer testing, measurements of biological/microbial markers, and similar methods are promising and necessary to develop a rational strategy that can provide the required data at a reasonable cost. Unique to the nonbarrier technologies is the potential to measure specific chemical or biological performance-related parameters. In the case of a chemical destruction process, such as free radical based oxidation, the parameters to be measured might include reagents like peroxide, elevated temperature, high levels of oxygen, or indirect effects such as the precipitation of minerals. For bioremediation, performance monitoring might include measures such as monitoring the numbers and types of organisms. Interestingly, experience suggests that the best monitoring methods for bioremediation projects might be broader measures of performance. In the vadose zone, examples of these broad measures range from the low-cost analysis of carbon dioxide and oxygen (which are often directly related to contaminant destruction) to the low-cost (but high technology) measurement of the presence and expression of the necessary genes for contaminant destruction using RNA and DNA probes.

Do vadose zone cleanup and barrier systems work as we expect them to? Do they provide information for responsible management of contaminated sites? Is the public protected? Can we assure the public that they are safe? Do we have the money and desire to monitor performance for the necessary period of time? These are the questions that require answers and form the gauntlet that innovations in performance monitoring must pass through to be useful.

DEVELOP A BETTER TECHNICAL BASIS FOR TAKING ACTION AND SETTING GOALS AT CONTAMINATED SITES

Virtually every scientist and engineer at the three workshops supported the need for developing improved remediation goals. In terms of resource allocation, however, this topic was viewed as important but not a top priority. Interestingly, this topic had a high standard deviation: some people invested heavily and others did not. Based on subsequent discussion, these relative priorities may be too low. Most workshop participants believed that setting clear and rational goals is extremely important in developing a successful vadose zone monitoring and cleanup program. They did not necessarily believe, however, that increased investments in vadose zone science and technology would translate into improved goal setting.

A variety of technical approaches for improving and clarifying remediation goals were identified. Importantly, these approaches require significant input from stakeholders (the public and regulators). Defining the “end-state” (the goal or “where we are going”) must be a shared effort among stakeholders, facility owners, and technical support organizations. Following the definition of the end-state, each site must develop a site-specific prioritization of technical challenges and a roadmap for doing so. To be successful, all of these steps must be performed in cooperation with the stakeholders. Setting up a “social science” system to successfully support this project approach was identified as an overall, and challenging, need.

A number of questions related to science and technology investments were discussed at the workshops, including:

- What is the value of removing 90 percent of the contaminant from source areas of residual chlorinated organic solvent? The remain-

ing 10 percent will often contaminate soil and groundwater above agreed regulatory limits for hundreds of years.

- Do we need an alternative measure of progress or a different type of long-term land use plan for such sites?
- How do we develop protective and reasonable ecological and human health standards for natural elements? Current methods often generate calculated standards at or near background levels.

Also discussed was the question: “Can we develop methods to properly evaluate lifecycle costs and impacts, including collateral damage associated with the clean up activities?” Participants invoked the medical analogy that the cure must not be worse than the disease; in other words, “first, do no harm!”

In terms of science and technology investments, the participants identified a few key areas: 1) improve scientific estimates of human and ecological impacts; 2) integrate tools for prioritizing and estimating impacts all the way from the source through the receptor; 3) increase the use of scoping evaluations to prioritize later phases of modeling and risk assessment; 4) acknowledge uncertainty as part of responsible management and communication; 5) develop tools to maximize the use of historical data at sites; and 6) develop and document an improved technical management paradigm. The participants advocated improved and increased use of biomarkers such as sensitive species, ecosystem health indices, and related methods, to improve impact evaluation. They also advocated development and use of improved data presentation methods such as three-dimensional visualization, and uncertainty presentation methods that support clear communication and help to develop site-specific priorities.

DEVELOP A BETTER UNDERSTANDING OF COMPLEX BIOLOGICAL AND CHEMICAL INFLUENCES ON MIGRATION

Improved understanding and parameterization of complex biogeochemistry was identified as being an important data gap and an area where investment would significantly improve models and environmental management decisions. The workshop participants noted and discussed the tremendous progress in this area during the last part of the

20th century. Unfortunately, this progress has not been routinely incorporated into vadose zone (or even saturated zone) transport models. Several reasons were cited for this lack of implementation, notably the challenges presented by scale, nonequilibrium processes, unstable processes, and complex waste mixtures. Overcoming these challenges forms the basis of future solutions.

Chemists and biologists studying transport processes typically work at a very small scale. It is not unusual to find research at the grain-size or pore-throat scale, or smaller. Studies and descriptions at the size of a typical modeling grid block are rare and may not be particularly informative about mechanism or process. Thus, the first challenge is to develop approaches to convert the high quality information obtained in current and future basic science studies into forms that can be used in models. These approaches might include new mathematical formulations, modifications to earlier numerical methods (for example, dual-media methods), and reintroduction and increased use of analytical solutions and transfer functions for transport. Importantly, the biogeochemists asserted that the latest chemical and biological knowledge should be incorporated as early as possible to improve models. An incremental approach to improvement was advocated for biogeochemistry: moving from the state of practice (models in current use), to state-of-the art (for example, models that are possible today but which are still highly simplified), with a long-term goal of creating comprehensive, fully descriptive models. As an example, using the analogy of solid/liquid partitioning, these steps would be K_D , conditional K_D /partitioning, and mechanistic surface and solution molecular-scale parameterizations, respectively. As they did for physical heterogeneity in vadose zone hydrology, the participants expressed agreement that a fully comprehensive model probably will never be obtained, but also agreed that maintaining such a stretch goal would encourage bold changes in the science.

Nonequilibrium processes and unstable processes pose challenges similar to those of scale. Most models do not account for chemical kinetics. This may not be a problem because the system may exhibit relatively predictable pseudo-steady-state or equilibrium behaviors. This issue does contribute varying degrees of error, however, and stepwise improvement in models was recommended. Unstable processes are an even more complex and difficult challenge. Examples of unstable

processes include colloidal formation and movement and liquid/multi-phase phase-penetration problems such as a dense phase overlying lighter phases. These problems are often characterized by fingering (formation of small channels within the overall system) and by chaotic behavior. Researchers often observe a pulse of colloidal migration followed by long periods of low colloid concentration. Unstable process problems are shared between the modelers and biogeochemists and the solutions generated must be developed jointly. In addition to the scale solutions outlined above (notably multiple-domain models), chaos theory and stochastic methods may be useful in addressing these issues.

The processes discussed above operate throughout the flow and transport domain—in both the vadose and saturated zones. Thus, in terms of the waste they can be viewed as applicable in both the “near field” and the “far field.” Complex wastes are a chemical challenge that occurs primarily in the “near field” (adjacent to waste and waste accumulation areas). Much research, primarily basic science, has been performed in this area. The results of this work have not been routinely incorporated into modeling (a single K_D is often used throughout the model domain, even if there are gross chemical differences in the near field conditions!). The participants recommended rapidly incorporating current research results into models and making the stepwise model improvements, as discussed above, to improve performance and credibility.

IMPROVE PROCESS SIMULATION CAPABILITIES FOR VADOSE ZONE CHEMICAL FATE, TRANSPORT, AND REMEDIATION

Current process simulation capabilities are sophisticated, and there are a variety of numerical simulation codes that can model the three-dimensional, nonisothermal multiphase flow and transport of certain classes of chemicals. Typically, these codes simulate either organic compounds, inorganic compounds, metals, or radionuclides. These numerical simulators may also include various biological and chemical reactions of the chemical species. Other codes simulate the coupled fluid flow, heat transfer, and rock mechanics that occur in the vadose zone.

While existing process simulation capabilities are considered strong, there are some clear gaps. There is currently no single numerical model capable of simultaneously simulating the nonisothermal biologically

and chemically reactive multiphase flow and transport of a comprehensive mixture of organic, inorganic, radioactive, and metallic compounds. Similarly, there is no single code capable of simultaneously modeling the fully coupled problem of multiphase fluid flow, heat transfer, reactive multicomponent chemical transport, and rock mechanics.

These gaps are due, in part, to current computational constraints: a truly comprehensive simulator modeling three-dimensional field problems may require so much processing time that it is impractical. The simulation capability gaps are also due to the relatively recent interest in such fully coupled problems. Moreover, they are due in part to the tremendous complexity and range of the possible interacting phenomena. Nonetheless, the development of such capabilities would improve vadose zone remediation and waste isolation efforts, and continuing improvements in computational power should make these simulations practical in the future.

An important and often overlooked aspect of code development is the issue of usability, including ease of training. As mentioned above, there are currently several three-dimensional nonisothermal multiphase flow and transport codes available. In fact, versions of many of these codes have been available for a decade or more. Yet, despite the availability of the codes, they are rarely used outside of a research environment. This under-utilization is because the codes are difficult and time-consuming to run, and most engineers, geologists, and scientists are not trained in their use.

If an effort is made to develop a new generation of comprehensive numerical simulators, as described above, it will also be critical to make conscious efforts to make them as easy as possible to use, for example, through graphical user interfaces and complete pre- and post-processors. Such codes should be modular to simplify maintenance and upgrades or modifications. Finally, code development efforts should be accompanied by significant efforts to educate and train potential users in government agencies, industry, and academia.

DEVELOP REMEDIATION METHODS FOR STRONGLY HETEROGENEOUS SYSTEMS, AND FOR COMPLEX MIXED WASTES

It is generally agreed that the remediation of heterogeneous or fractured sites, and of sites contaminated with mixtures of radionuclides and

organic chemicals, are among the most difficult vadose zone problems. While we insist that it is unrealistic to expect that these problems will ever be solved by one single technique, (the “silver bullet”), it is possible that new approaches and combinations of techniques could be applicable at some sites.

Contaminated sites that are strongly heterogeneous or fractured are difficult to clean up because it is hard to contact the contaminants efficiently with a flowing fluid (gas or aqueous) phase. Because most current remediation methods rely on the advective transport of extracting or reacting liquids or gases, or on the convective transport of heat, these attempts are invariably subject to severe mass transfer limitations, as the mobile remediation fluids bypass much of the contamination. This situation is compounded by the large degree of uncertainty associated with the characterization of heterogeneous or fractured systems, making it difficult even to assess the degree of success of a remedial action based on advective or convective flows.

It may be a productive strategy to focus on the development of new remediation methods which depend less on advective and convective transport, or in which the advective or convective transport is somehow stabilized in the heterogeneous/fractured system. As an example, gaseous diffusion and thermal and electrical conduction processes are relatively insensitive to heterogeneities. While these diffusive transport processes are usually slower than advection and convection, mass and heat flows resulting from these processes tend to be much more uniform and predictable.

A different approach would involve the development of improved isolation and stabilization techniques and improved reactive barriers for these systems. One of the major challenges of this approach is the issue of long-term performance assessment.

The remediation of mixed waste sites is complicated by the widely varying physiochemical properties of radionuclides and organic chemicals, as well as by complex interactions between these classes of compounds. It seems unlikely that a single remediation technique could simultaneously address both classes of compounds. However, there are undoubtedly combinations of techniques that could be performed sequentially. Efforts could be directed to identifying and testing complementary technologies for these mixed sites. We would recommend a phased approach, beginning with bench-scale laboratory experiments

and numerical modeling, and proceeding to the detailed, intermediate-scale field experiments. As discussed above, improved isolation, stabilization, and reactive barrier methods for containing mixed wastes should be pursued. Future research should also address the problem of long-term performance assessment of mixed waste sites.

SUMMARY

As we've said before, the vadose zone is both complex and fascinating. It is not only a potential source of large-scale contamination, but is also a great opportunity for developing highly creative, innovative, and useful advances in the art and science of remediation. To meet the challenges presented by the vadose zone, not only must our nation be willing to commit considerable money and other resources, but it must resolve that these challenges *can* and *will* be met. Those of us whose careers and interests have led us to confront the challenges of vadose zone remediation find ourselves intimately involved in trying to communicate the scope and complexity of the problems we face as well as trying to solve them.

In this book, we've discussed, often in great detail, theories, techniques, and processes. Clearly, the technical skill and scientific expertise exist to develop the new solutions that will be required. But even the best science and the most noble intentions can be rendered ineffective by failure to engage all stakeholders in the defining of common goals and objectives, or by the failure to maintain clear lines of communication among regulators, managers, researchers, implementers, and consumers. Can we, and will we, live up to the title of this book by making the commitment of resources, energy, and spirit necessary to turn vadose zone science into vadose zone solutions? The tools are there, the will exists, and the future awaits.

C A S E S T U D Y



THE VADOSE ZONE RESOURCE ALLOCATION CHALLENGE

Michelle Silbernagel and Joann Hafera

INTRODUCTION AND BACKGROUND

The effort to develop a book that documents the state of vadose zone science was initiated at the request of the DOE's Office of Science and Technology in May 1998. Assembling the prevailing knowledge of this vast system was achieved through a series of three workshops, each of which focused on different aspects of vadose zone science. Preeminent scientists and technical experts representing industry, government, and academia attended the three workshops. During the workshops' general and topical breakout sessions, the experts engaged in discussions that provided the technical basis for the book. The workshop participants also identified numerous field case studies that provide a contextual sampling of the wide range of vadose zone scientific experience that has been achieved to date, and demonstrate how the science has been applied in the field.

THE WORKSHOPS

The task of documenting the state of vadose zone science extends beyond reporting current achievements and knowledge. A major component of the effort includes identifying the areas in need of continued and future research—the gaps. The free-flowing and thoughtful discussions of the first workshop, at Lawrence Berkeley National Laboratory in July 1998, provided an abundance of additional research issues and data needs. However, a clear consensus of the most immediate needs and priorities in vadose zone science did not readily emerge.

The rich diversity of expert opinion represented at the workshop and the uncertainty associated with the vadose zone itself made it difficult to arrive at a consensus on the most urgent needs. The dynamic nature of the discussions also made it difficult to capture and then provide a real-time synthesis of the priority issues. The core book team and workshop organizers determined that a technique was needed to prioritize key technology needs.

THE MODEL

The challenge of documenting and prioritizing information about a complex natural system fraught with scientific uncertainty was faced recently by the Carnegie



WORKSHOPS

Workshop #1, July 1998

- Conceptual foundations of vadose zone science
- Characterization

Workshop #2, September 1998

- Fate and transport of contaminants in the vadose zone
- Modeling and performance

Workshop #3, January 1999

- Contaminant remediation and containment
- Performance validation

Mellon University (CMU) Global Climate Change Integrated Assessment Program (Morgan and Keith 1995). The CMU team was confronted with the need to prioritize a range of dramatically different expert opinions about underlying physical climate processes. Drawing upon an expert elicitation method widely used in applied Bayesian decision analysis (DeGroot 1970), the CMU team implemented a process that formalized and quantified the probabilistic judgments of individual experts. Using this process as a loose model, the core book team developed a similar prioritization technique that provided a semi-quantitative, cumulative ranking of the key issues and research needs as perceived by the participating experts.

THE TECHNIQUE

The final outcome of the vadose zone workshop prioritization process was an ordered list of key research, data, and development needs organized by issue. This ranking was achieved by inviting the participants to indicate their preferences for continued research and development from among listed issues.¹ The prioritization process that was implemented at the second and the third vadose zone book workshops was called the *Vadose Zone Resource Allocation Challenge*. At the work-

¹The Las Vegas workshop participants worked with a list of 17 issues and the Seattle workshop participants worked with a list of 18 issues.

shops, each participant was given \$100 in *vadose zone bucks* (two \$20s, four \$10s, three \$5s, and five \$1s). Participants were then asked to vote for their favorite issues by distributing their vadose bucks into the appropriate marked box.

The identification of the key issues was an iterative and collaborative process. Prior to the Las Vegas and Seattle workshops, the registered participants were surveyed to see what they considered to be the key challenges to vadose zone science with respect to the specific focus of the workshop (that is, fate and transport or containment and remediation). The survey results provided a framework, which was further developed at the workshops. During the workshop breakout sessions, participants engaged in a comprehensive brainstorming session in which they were again asked to note their key issues or challenges. Participants wrote these issues on individual index cards, which were collected, shared with all of the session participants, and then collaboratively categorized by subject matter on flip charts. Participants then engaged in a free-flowing technical discussion of the issues, which resulted in the clarification of concepts and definitions, identification of data and/or technology needs, and most importantly, led to the identification of the interactions and interdependencies of certain issues, needs, technologies, and systems. As each issue was discussed, the experts described their own related scientific challenges and successes, identified potential applications for various methods and models, and provided examples from their work, representing the current state of the science. At the end of the session, the participants further refined the list of issues and data gaps by selecting their top three preferences for continued research and development. The results of these brainstorming sessions were the two workshop-specific lists of important issues. These lists were the ultimate source of categories among which the participants allocated their vadose bucks.

"The resource allocation challenge provided an effective and real time method to crystallize the issues and approaches for solutions that had been generated throughout the proceedings by some of the top experts in the world."

—Dr. Brian B. Looney, Savannah River Technology Center, co-editor



The actual allocation process took place at the end of each workshop. Each voting participant received a set of vadose bucks and a demographic data sheet to fill out. Each set of vadose bucks was pre-coded with an identification number, which the participants noted on their demographic data forms. These forms maintained the anonymity of the participants, while providing a method to gather general information about the experts who participated in the exercise. Among other things, the data sheets asked the participants to classify themselves according to research focus, organizational affiliation, and discipline. When the voting was complete, the vadose bucks were quickly tallied for each issue. The result was a cumulative and semi-quantitative prioritized ranking of the top issues. There are two immediate

benefits of this technique: 1) it ensures that the full array of important issues is represented, and 2) it indicates the relative importance of the issues. Another advantage of the technique is that it allows one to see if different types of participants allocated their resources differently among the top issues. In this application, such comparisons are not statistically significant, because of the small sample size. However, the results of the demographic analysis are reported here to provide an example of the sorts of analyses that are possible in future applications of this prioritization method. For example, a multivariate analysis of the demographic variables in relation to resource allocation might provide additional insight regarding issue preferences among the experts.

The overall findings from each of the two resource allocation exercises are reported separately because of the workshops' distinct subject matter and associated research issues. In spite of the difference in subject matter, the resource allocation process revealed some noteworthy patterns. For example, both showed slightly different priority preferences between the applied scientists and basic scientists. Priority preferences also varied slightly by organizational affiliation.

THE RESULTS

WORKSHOP #2 LAS VEGAS—FATE AND TRANSPORT

Participant Profile

Forty-four people participated in the Resource Allocation Challenge on fate and transport issues. The majority of participants, nearly 80 percent, represented a government organization (for example, DOE, a government national laboratory, other agencies such as USGS, U.S. Corps of Engineers, USDA; see Figure 1). Sixteen percent of the participants came from academia and the remaining participants represented industry or non-profit organizations. As shown in Figure 2, the majority of the participants (63 percent) indicated a research focus in applied science. About a quarter of the participants indicated their primary emphasis as basic science. Some participants indicated other areas of practice, such as planning, decision-making, and engineering.

A wide array of expertise was represented among the participants. Twenty-three percent of the participants were hydrogeologists, twenty-one percent were engineers, and sixteen percent were field experimentalists. A number of chemists, geochemists, earth scientists, and modelers also were present.

The vast majority of the participants had either a doctorate (68 percent) or a master's degree (21 percent). While a large proportion (41 percent) of the participants were from the northwest part of the country, the southeastern and southwestern regions were also well represented (23 percent and 25 percent, respectively). Several participants were from the midwestern and northeastern parts of the country.

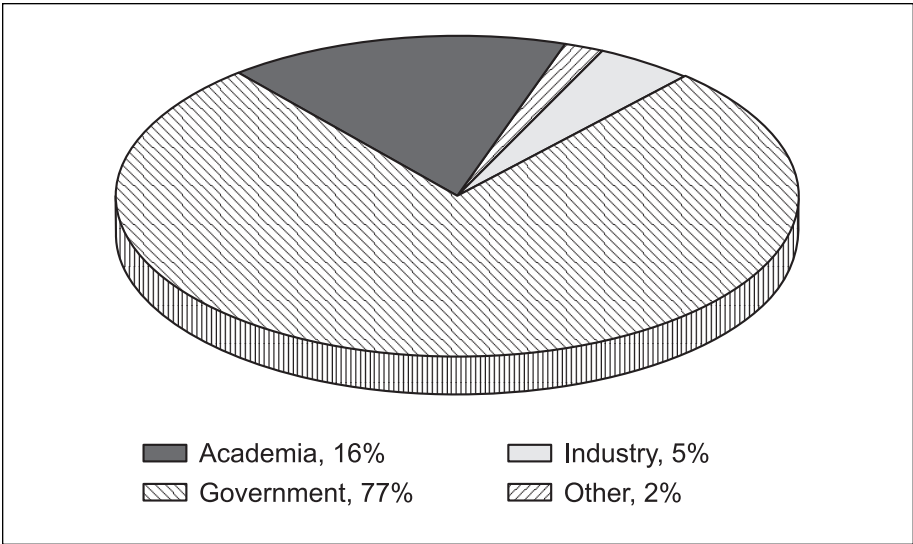


Figure 1. Las Vegas Workshop Resource Allocation Participants—Organizational Affiliation

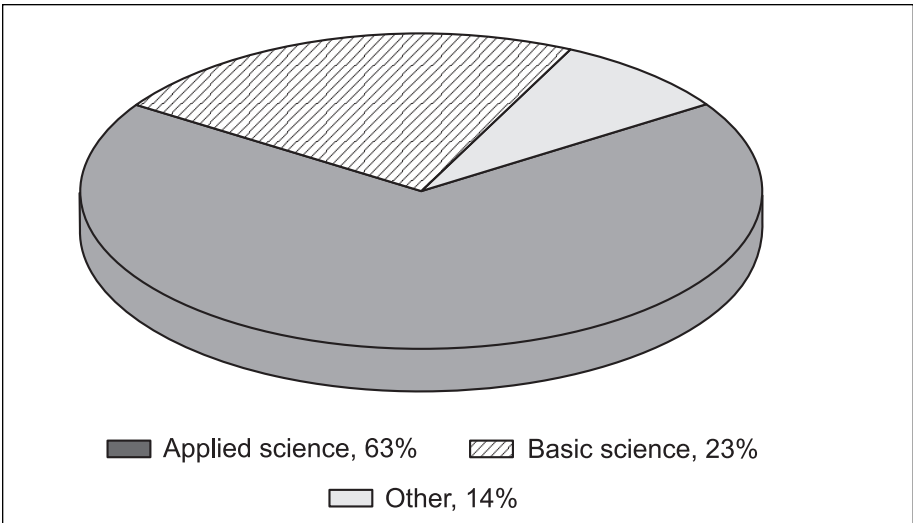


Figure 2. Las Vegas Workshop Resource Allocation Participants—Research Focus

General Findings

A total of \$4,377² vadose zone bucks was allocated among 17 allocation options suggested during the workshop sessions.

Participants' allocations ranged between \$1 and \$55 vadose bucks for any one issue, with an average allocation of \$25 per issue. Participants allocated their resources among an average of 8 issues, with some voting for as few as three issues or as many as thirteen.

The top five fate and transport research issues (out of a total of seventeen) were:

1. Intermediate Scale Experiments
2. Transport Upscaling
3. Couple Flow and Transport
4. Initial/Boundary Conditions
5. Representing Heterogeneity

Thirty-eight percent of all resources were allocated among these five issues (Figure 3). Intermediate-scale experiments received the largest proportion of vadose bucks.

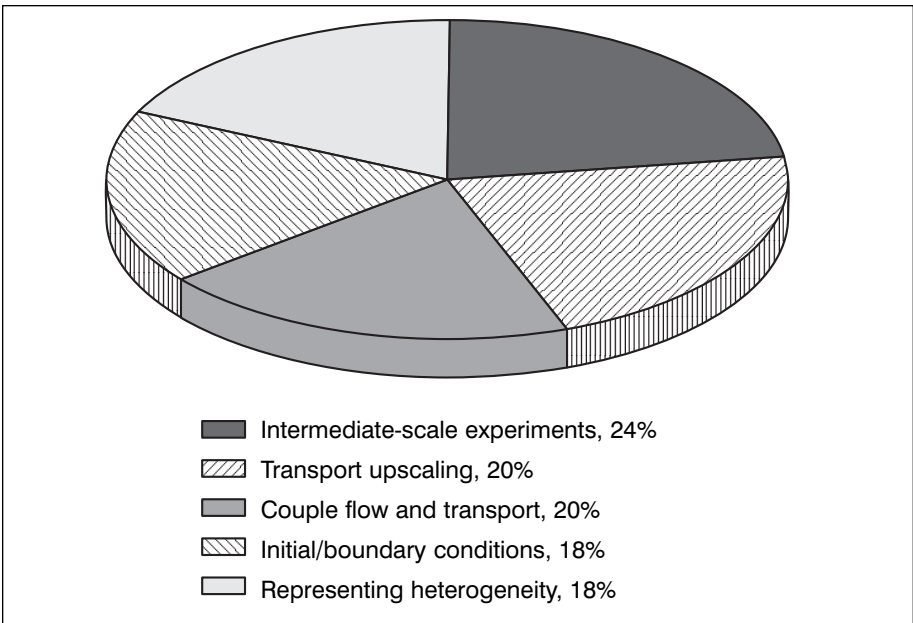


Figure 3. Las Vegas Workshop Top Five Issues

²Three participants did not allocate all of their vadose bucks.

This prioritization generally holds true regardless of the participants' research focus, organizational affiliation, or discipline. However, a more in-depth analysis of the allocation by these specific categories (research focus, discipline, and organizational affiliation) revealed some finer distinctions among the allocation preferences of the experts. For example, the basic scientists allocated a greater proportion of their resources to the coupled flow and transport issue than did the other participants (Figure 4). The applied scientists and other experts allocated a greater share of their resources to the issue of initial boundary conditions than did the basic scientists.

In terms of research discipline, there appears to be a clear preference for intermediate-scale experiments among field experimentalists, based on the proportion of resources allocated to the issue (Figure 5). Experts who classified themselves as engineers also rated intermediate-scale experiments a high priority. However, among hydrogeologists and geochemists, the largest proportion of resources was allocated to the issue of representing heterogeneity.

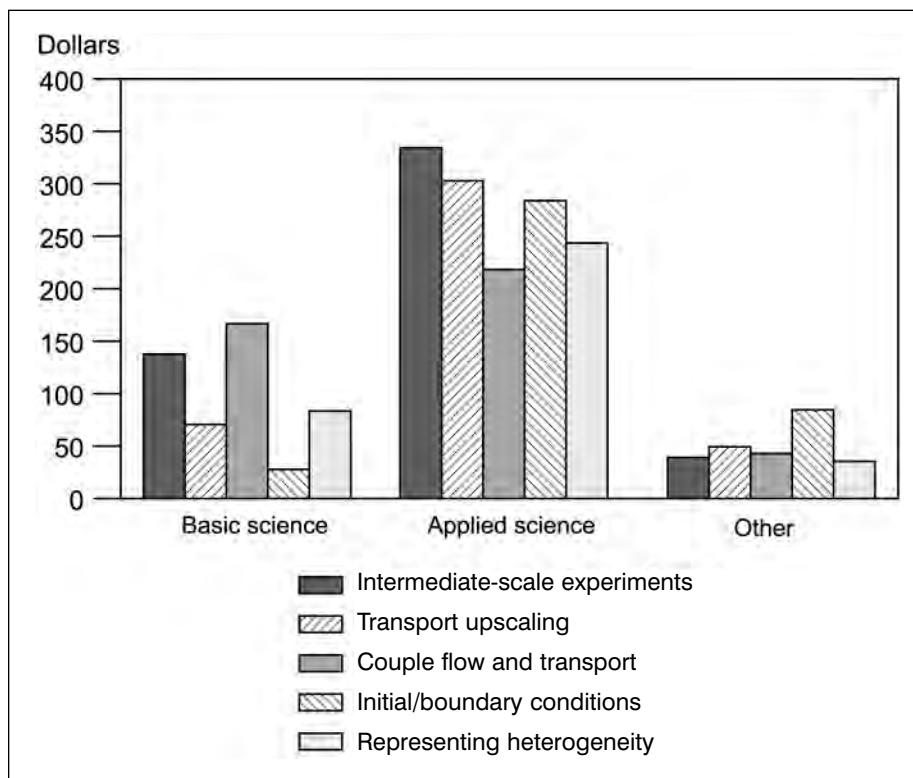


Figure 4. Las Vegas Workshop—Issues by Research Focus

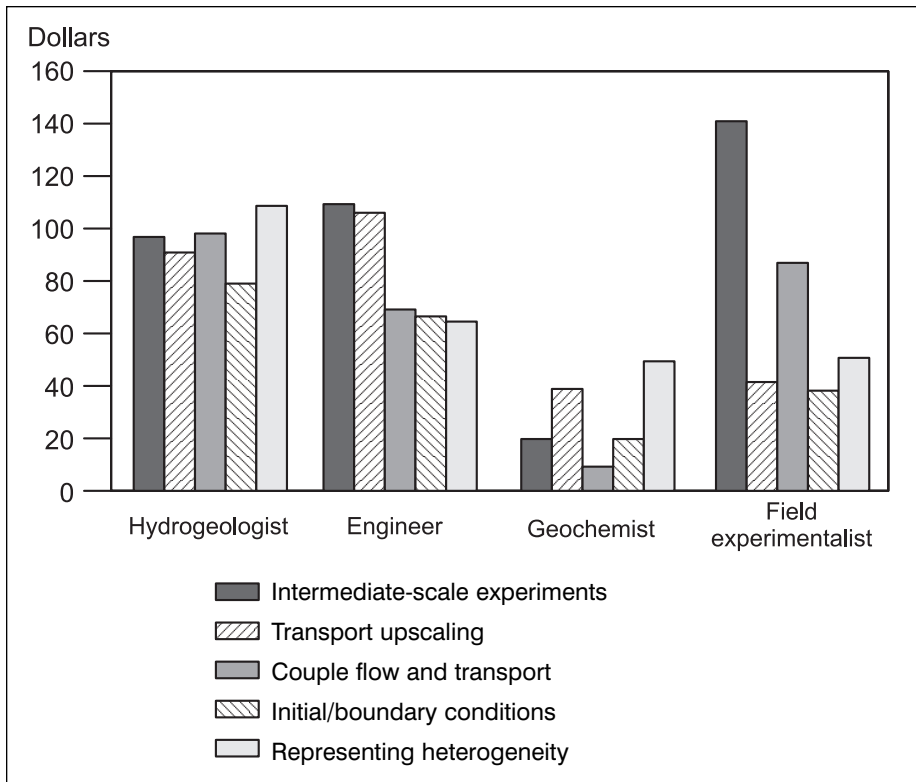


Figure 5. Las Vegas Workshop—Issues by Discipline

When viewing issue priorities in terms of the organizational affiliation of the experts, the exercise indicates that the participants representing academia allocated more of their resources to the issue of representing heterogeneity than to other issues (Figure 6).

WORKSHOP #3 SEATTLE—CONTAMINANT REMEDIATION AND CONTAINMENT

Participant Profile

Forty-one people participated in the Resource Allocation Challenge at the final workshop in Seattle. The organizational representation among the Seattle participants was much more balanced than at the Las Vegas workshop, which had fewer industry representatives. About half of the participants (52 percent) indicated affiliation with a government agency. About a quarter of the participants represented industry, and twenty-two percent reported an academic affiliation (Figure 7).

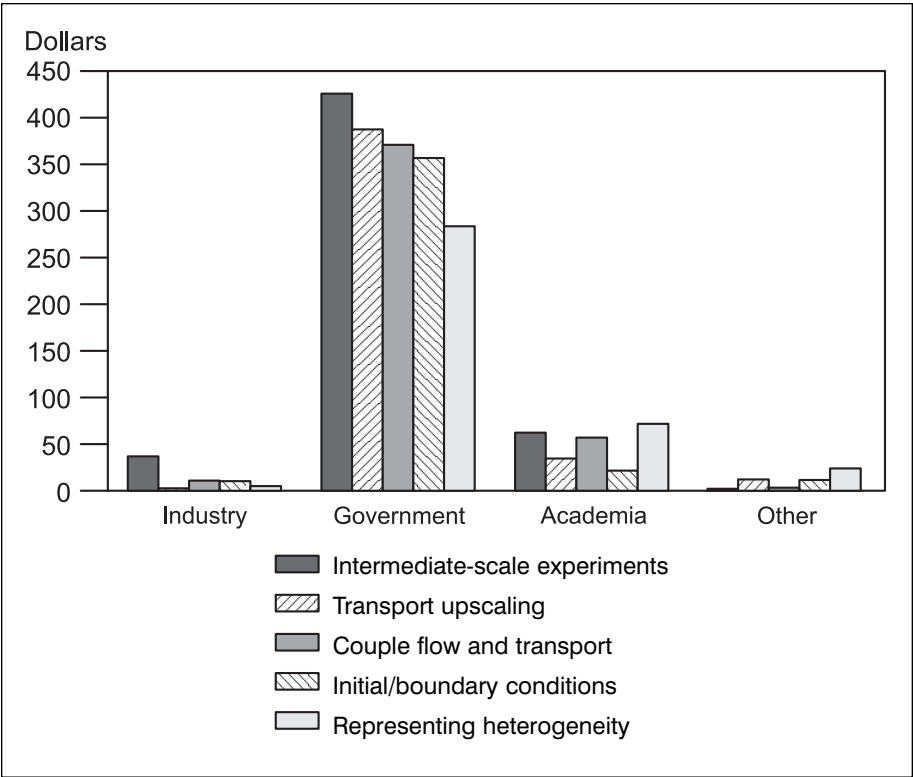


Figure 6. Las Vegas Workshop—Issues by Affiliation

Like the Las Vegas participants, most of the Seattle participants (62 percent) indicated that they have an applied-science focus. Twenty-seven percent indicated a basic-science focus. Regulators, project managers, and consultants were also represented (Figure 8). The expertise of the participants encompassed a range of disciplines. Hydrogeologists, engineers, geochemists, and chemists were the most commonly represented professions. About half of the participants had doctorate degrees, and nearly as many had master's degrees. Like the Las Vegas workshop participants, a large proportion of the Seattle participants were from the western part of the United States. A third of the Seattle participants were from the northwest part of the country and another third were from the southwest region. Seventeen percent indicated that they were from the Southeast, ten percent from the Midwest, and the remaining participants were from the Northeast and other regions of the country.

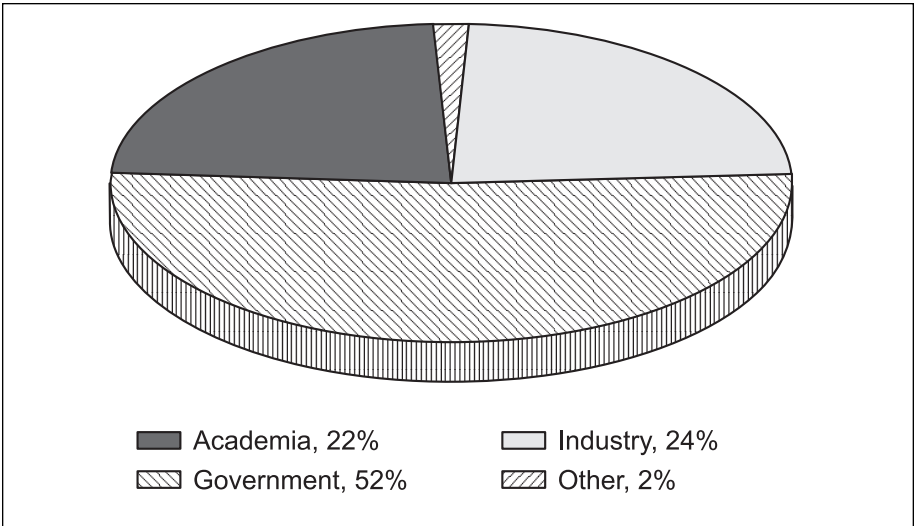


Figure 7. Seattle Workshop Resource Allocation Participants—Organizational Affiliation

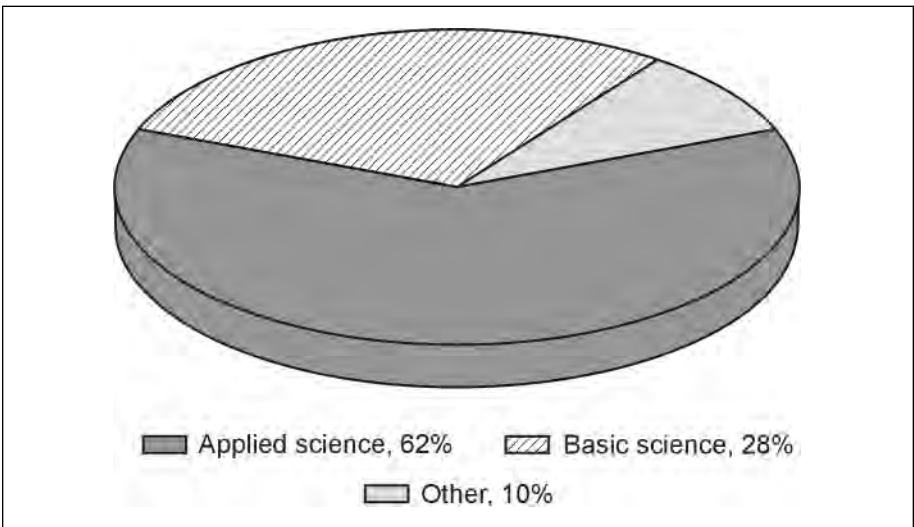


Figure 8. Seattle Workshop Resource Allocation Participants—Research Focus

General Findings

A total of \$4,100 was allocated among 18 allocation options suggested during the workshop sessions. Allocations by participants ranged between \$7 and \$33 vadose bucks for any one issue, with an average allocation of \$18 per issue. The average number of issues among which the participants allocated their resources was 7, with at least one participant selecting as few as 1 or as many as 13 issues.

The top five (two issues were tied for fourth) contaminant remediation and containment issues, out of a total of 18 possible issues (in order of allocation) were:

- 1. Modeling and Performance Prediction
- 2. Medium-Scale Technology Demonstrations
- 3. Characterization and Monitoring
- 4. Risk Assessment/Remediation Goals *and* Overcoming Heterogeneity (these two issues tied)
- 5. Containment/Stabilization

Notably, nearly 60 percent of all resources were allocated among these six issues (Figure 9). In terms of the total resource allocation, modeling and performance

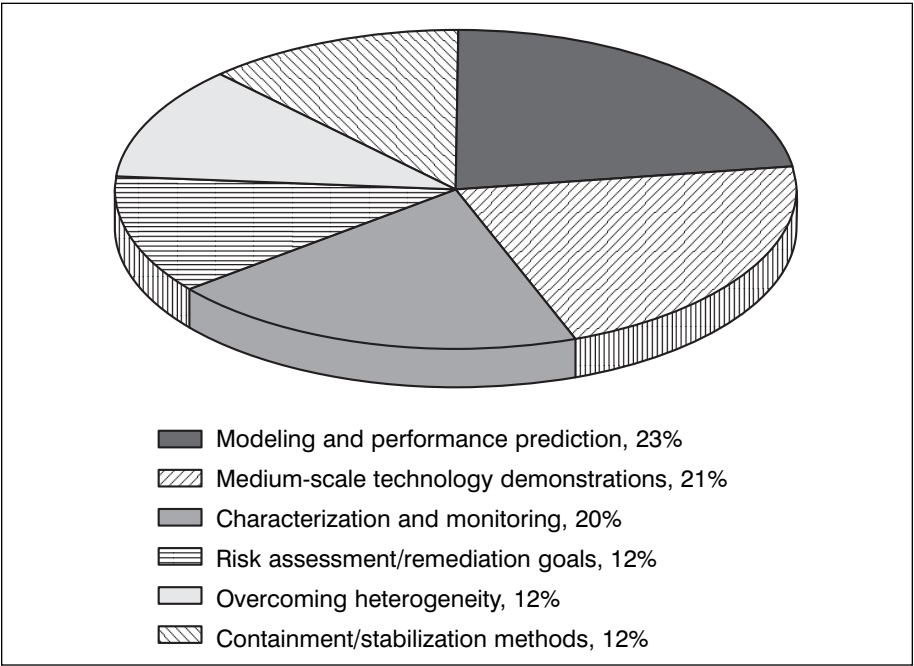


Figure 9. Seattle Workshop Top Five Issues

prediction and medium-scale technology demonstrations were the top two priority issues. The prioritization of these two issues generally holds true when examining the allocation of resources by participant research focus, discipline, and organizational affiliation. However, as shown in Figure 10, the applied scientists allocated more of their resources to risk assessment/remediation goals than did the basic scientists, who allocated a greater proportion of their resources to overcoming heterogeneity.

In-depth analysis of the proportional allocation of the top six issues by the participants' area of discipline indicated that experts who classified themselves as geochemists ranked overcoming heterogeneity above modeling and performance prediction, which along with characterization and monitoring, was a top priority issue for the other disciplines (Figure 11).

An analysis by organizational affiliation revealed that both the academic participants and industry representatives allocated slightly more of their total resources to the

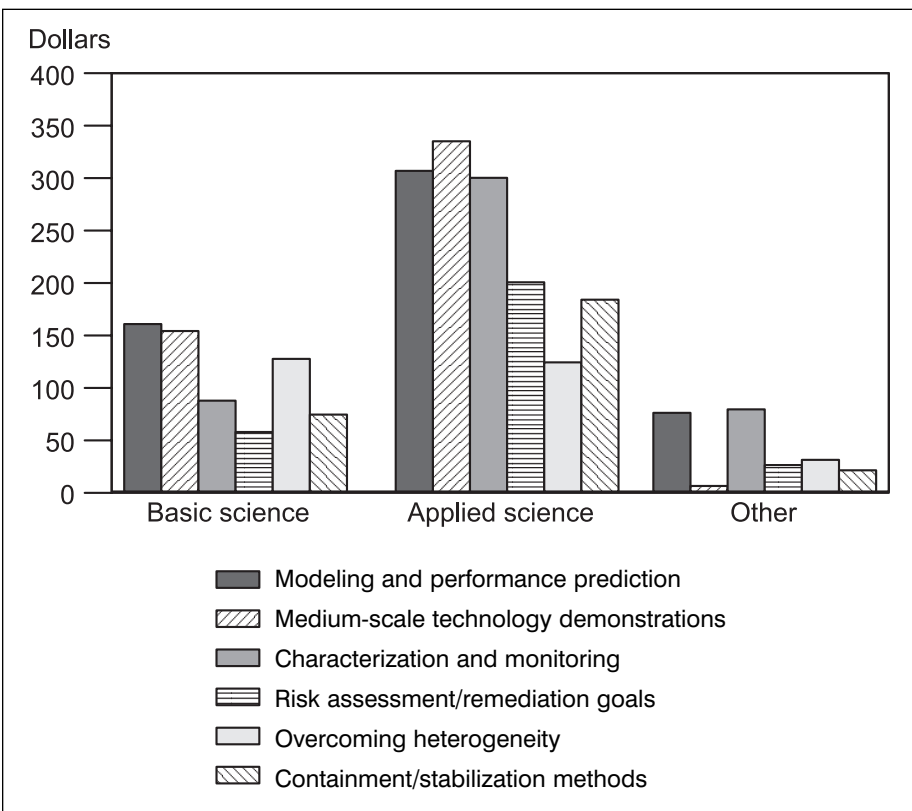


Figure 10. Seattle Workshop—Issues by Research Focus

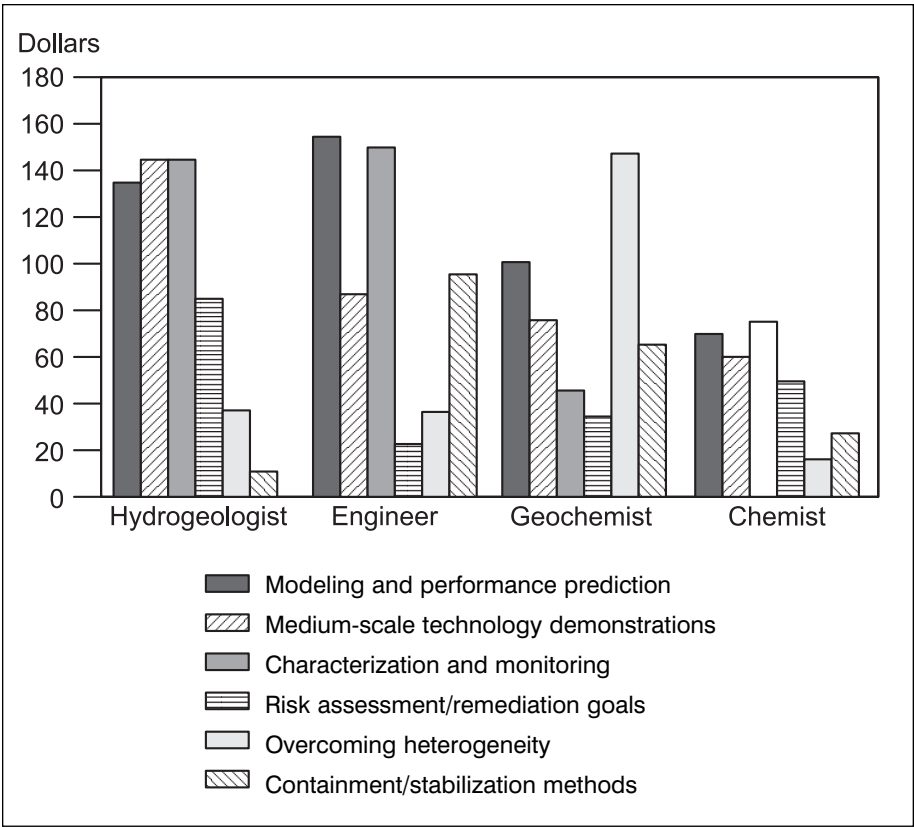


Figure 11. Seattle Workshops—Issues by Discipline

issue of medium-scale technology demonstrations. The government-affiliated participants, many of whom work at national laboratories, allocated the largest proportion of their resources to modeling and performance and characterization and monitoring issues (Figure 12).

CONCLUSION

The resource allocation exercise provides a mechanism to ascertain in a relatively easy and immediate manner the priority issues of the participating experts. It allows for both a high-level summary of the main issues and gaps, as well as the opportunity for a slightly more detailed assessment of the priority issues by more specific areas of interest (such as research focus, discipline, or organizational affiliation). For example, with regard to contaminant fate and transport issues, the number one

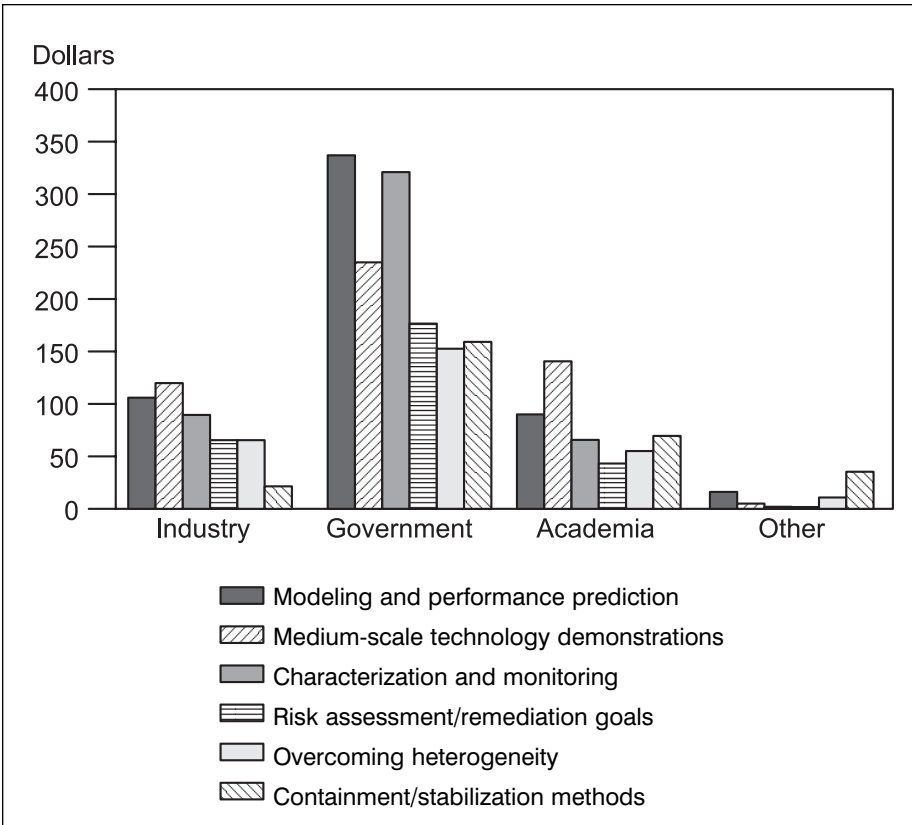


Figure 12. Seattle Workshops—Issues by Affiliation

issue was intermediate scale experiments. However, the exercise indicated that the prioritization shifts slightly according to participants' research focus. For basic scientists at the Las Vegas workshop, couple flow and transport appeared to be the higher priority issue. At the Seattle workshop on contaminant remediation, containment and performance measures, basic scientists and applied scientists generally agreed that modeling and performance prediction was a priority concern. However, the basic scientists allocated a larger share of their resources to overcoming heterogeneity than did the applied scientists. Due to the small sample sizes of both exercises, these findings cannot be viewed as statistically significant, but they may be indicative of the preferences that exist among different experts.

While these findings are not generalizable, the resource allocation challenge process itself addresses the matter of issue representation—the iterative process of identi-

fying issue categories ensures that the full spectrum of pertinent issues is represented. The resource allocation technique has been recognized and well-received by independent peers, such as the National Academy of Sciences. However, most important to the development of the vadose zone book, the resource allocation challenge helped to identify the priority research issues and data gaps that are the basis for the summary discussion in Chapter 10.

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Appendix

Additional Case Studies on Accompanying CD

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