



Ground Water Issue

Chemical Enhancements to Pump-and-Treat Remediation

Carl D. Palmer* and William Fish*

Background

Conventional pump-and-treat technologies are among the most widely used systems for the remediation of contaminated ground water. Within recent years it has become recognized that these systems can require protracted periods of time to make significant reductions in the quantity of contaminants associated with both the liquid and solid phases which constitute the subsurface matrix. Evaluating the effectiveness of pump-and-treat remediations at Superfund sites, as well as attempting to improve this effectiveness, are issues identified by the Regional Superfund Ground Water Forum as a concern of Superfund decision makers. The Forum is a group of ground-water scientists and engineers, representing EPA's Regional Superfund Offices, organized to exchange the most recent information related to ground-water remediation at Superfund sites.

Recent research has led to a better understanding of the processes involved in the transport and transformation of contaminants in the subsurface. While some of these processes are not readily amenable to enhanced removal by ground-water extraction, others suggest that there are available techniques to increase the efficiency of these types of remediation systems. The intent of this document is to explore the use of chemical enhancement to improve ground-water remediation efficiencies using pump-and-treat technologies, and point out arenas of contamination where such techniques are not practical.

For further information contact John Matthews, Chief, Applications and Assistance Branch, RSKERL, FTS 743-2408, or Bert Bledsoe, Project Officer, RSKERL, FTS 743-2324. Both may be reached at 405-332-8800.

Summary and Conclusions

Recognition that conventional pump-and-treat remediation often requires lengthy periods of time to achieve clean-up objectives will encourage professionals involved in site remediation to contemplate alternative methods of aquifer

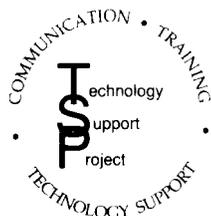
restoration. Some form of chemical enhancement for pump-and-treat will likely be an alternative considered for many waste-site cleanups. Although chemical enhancement of pump-and-treat may be a means of accelerating aquifer remediation, there are many aspects of chemical enhancement that need to be known before these techniques can be successfully implemented.

Not all waste sites are amenable to chemical enhancement methods. In particular, if tailing in the concentration-versus-time curves for the extraction wells is dominated by physical processes, then chemical enhancement methods will have no advantage over conventional pump-and-treat. Knowledge of the relative contributions of chemical and physical processes limiting pump-and-treat are needed during the early stages of site Remedial Investigations to ascertain the general usefulness of chemical enhancement.

Even when it is known that physical processes contribute little to the tailing, specific knowledge is needed about the chemical processes that contribute to tailing at a particular site. Only then can potential chemical agents that are likely to influence these processes be identified. The reactive agents may be chosen to compete with the contaminants for adsorption sites, complex the contaminant, change the redox state of the contaminant, change the solvation properties of the ground water, act as a surfactant, ionize the contaminant, or substitute for the contaminant in a precipitate. If the reactive agents are chosen on the basis of incorrectly-identified limiting processes, there is a risk that the reactive agents will provide no net benefit and may even prolong remediation.

Even when a reactive agent is found that specifically addresses the limiting chemical process, other considerations must be investigated to assure successful implementation. The key areas of concern in any chemical enhancement method are 1) the delivery of the reactive agent to those

*Environmental Science and Engineering, Oregon Graduate Institute of Science and Technology, Beaverton, OR.



Superfund Technology Support Center for
Ground Water

Robert S. Kerr Environmental
Research Laboratory
Ada, Oklahoma

Technology Innovation Office
Office of Solid Waste and Emergency
Response, US EPA, Washington, D.C.

Walter W. Kovalick, Jr., Ph.D.
Director



areas of the aquifer where it is needed, 2) the enhanced removal of the target contaminants by the reactive agent, 3) the removal of the reactive agent from subsurface, 4) the impact of the reactive agent on the treatment of the target contaminant and the volume of sludges to be disposed. Additional site characterization, treatability tests, and design studies must be conducted to address each of these important aspects of a chemical-enhancement program. At some sites, implementation of chemical enhancement will require additional capital expenditures for wells and treatment facilities. The advantages and disadvantages, including the additional costs, of chemical enhancements need to be compared with other methods of remediation, such as conventional pump-and-treat.

While many individual components are associated with the implementation of chemical enhancement to pump-and-treat, they all should be investigated. If one aspect of this process fails, the entire system can fail. While such failure is not necessarily a disaster (conventional pump-and-treat can continue), it is a waste of resources that could be utilized for more beneficial uses. It is believed that these issues must be addressed and a reasonable probability of success demonstrated in all aspects of a chemical enhancement system before it is implemented.

Introduction

The recognition that ground water in many areas of the U.S. is contaminated has brought about demands that the quality of these aquifers be restored. At Superfund sites, the initial cleanup is accomplished in a relatively short time by removing sources of contamination from the surface, removing highly contaminated shallow soil, and in some cases installing a low-permeability cap. In contrast, remediation of the ground water beneath a site is often an inexact process requiring years to complete.

A common method for aquifer remediation is to withdraw the contaminated water from the aquifer and treat it on-site. The treated water may then be returned to the aquifer, discharged to surface water, or transferred to a public water treatment plant. Such "pump-and-treat" technology is widely used for remediating aquifers (Palmer et al., 1988) with about 68% of the Records of Decision identifying it as the method of remediation (Travis and Doty, 1989). However, at many sites pump-and-treat technology will require decades of costly operation to achieve the desired levels of cleanup. Extended periods for remediation are highly undesirable because the operation and maintenance costs associated with the remediation can be large, and, in many cases, otherwise valuable land cannot be used for any economic purpose.

The great costs of cleanup make it essential to investigate technologies that may speed up remediation. One such technology is the injection of chemical constituents, "reactive agents", that improve the rate of removal of contaminants from the subsurface. The applicability of such "chemical enhancement" technology and the specific chemicals that can be used depend on the processes that control the slow "tailing" of contaminant concentrations in the extraction wells. Not all processes leading to lengthy remediations can be corrected by chemical enhancement. However, certain problematic types of contamination maybe amenable to well conceived applications of reactive agents.

The limitations of aquifer remediation by conventional pump-and-treat will encourage engineers, scientists, and regulators to propose various chemical enhancement methods for the remediation of particular sites. While these proposed methods must be evaluated with regard to specific site conditions, there are general concepts applicable to all chemical enhancement methods. This document is intended to 1) outline these general concepts, 2) pose key questions that should be answered before any chemical-enhancement scheme is initiated, 3) stimulate discussion on the merits and limitations of chemical enhancement methods, and 4) focus research on particularly problematic areas of chemical enhancement.

Processes Affecting Pump-and-Treat Remediation

A major concern in pump-and-treat operations is that contaminant concentrations within the extraction wells will decline at a progressively slower rate as pumping continues. When the rate of decline becomes small and the contaminant concentrations are still above the target cleanup levels, an extraction well is said to exhibit "tailing" (Fig. 1). Contaminant concentrations may have dropped several orders of magnitude, but they remain above the target clean-up level despite a considerable period of pumping. A great uncertainty in pump-and-treat operations is the time required for these tailing concentrations to decrease below the target clean-up levels. Reasonable estimates of clean-up times under these conditions require an understanding of the physical and chemical processes that can cause tailing: 1) the differing amounts of time required by contaminated waters to flow along different streamlines from the irregular boundary of the plume to the extraction wells, 2) multiple rates of mass transport within spatially variable sediments, 3) limited mass transfer from reserves of nonaqueous phase liquids and solid phase mineral precipitates, and 4) slow resorption reactions (Keely et al., 1987; Keely, 1989).

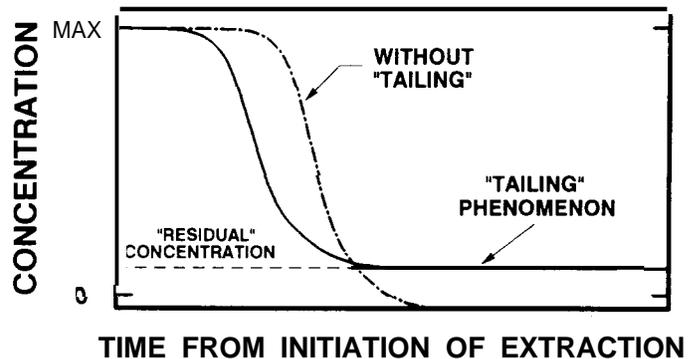


Figure 1. Concentration versus lime curve for an extraction well with continuous pumping (after Keely et al., 1987).

Physical Causes of Tailing

Ground water entering an extraction well is a mixture of waters that have traveled along multiple subsurface pathways between the edge of the contaminant plume and the well. The time required for contaminated ground water to travel along these different flow paths is controlled by 1) placement of the extraction wells relative to the contaminant boundaries, 2) the extraction rate, 3) the aquifer porosity, 4) the magnitude and direction of the natural hydraulic gradient, and 5) the location and types of hydraulic boundaries. As an example, consider a single extraction well in an aquifer with a natural hydraulic gradient of 0.007 towards the east (Fig. 2). If the edge of the contaminant plume is to the west, then only a portion of the plume's edge is captured by the extraction well. The flow paths along the outside of the capture zone for the well have a greater distance to travel and are influenced by lower hydraulic gradients than the flow paths near the center of the capture zone. As a consequence of these variable residence times within each stream tube, the concentration-versus-time curve for the extraction well exhibits substantial tailing even in the absence of chemical reaction (Fig. 3).

In heterogeneous porous media, ground water in higher permeability layers has greater velocities than water within the lower permeability zones. The higher permeability pathways are not necessarily sand or gravel nor are the lower permeability zones necessarily silts or clays; it is sufficient if one region possesses greater hydraulic conductivity relative to the adjacent materials. When the contrast in hydraulic conductivity between these zones is large, the advective component of transport through the lower permeability lenses becomes small. As contaminants are transported through such a heterogeneous aquifer, they are advected along the high permeability layers and diffuse into the lower permeability layers. Such an advection-diffusion process can affect the concentration of contaminants within higher permeability layers (Gillham et al., 1984; Sudicky et al., 1985). If aqueous contaminants have been present over many years, their concentration in the lower permeability layers can equal the concentrations in the higher permeability zones. During pump-and-treat remediation, contaminants in the high permeability layers are removed more quickly than from the lower permeability layers. These variable rates of advective transport create concentration gradients between zones of contrasting permeability and cause the slow diffusion of contaminants from the low permeability zones to the high permeability zones where they can be pumped to the surface (Fig. 4). Thus, the contaminant concentrations in the extracted water are initially high as the more permeable layers are flushed. At later times, the concentration in the extracted water is limited by the rate of diffusion of the contaminants into the high permeability zones (Fig. 5). If pumping is discontinued, the velocities within the high permeability layers decrease and the concentration of contaminants within these zones increase (Fig. 6) because of the greater residence time of a parcel of water within the contaminated portion of the aquifer.

The main point is that, in most cases, lengthy tailing-off of contaminant concentrations in extraction wells is at least partly due to physical attributes of the system that cannot be ameliorated by injections of chemical agents. Thus, chemical enhancement cannot be expected to eliminate all unexpected

delays in pump-and-treat removal. However, when the rates of chemical mass transfer from contaminant reserves in an aquifer are the primary limitations on removal, then the use of reactive agents may substantially enhance remediation.

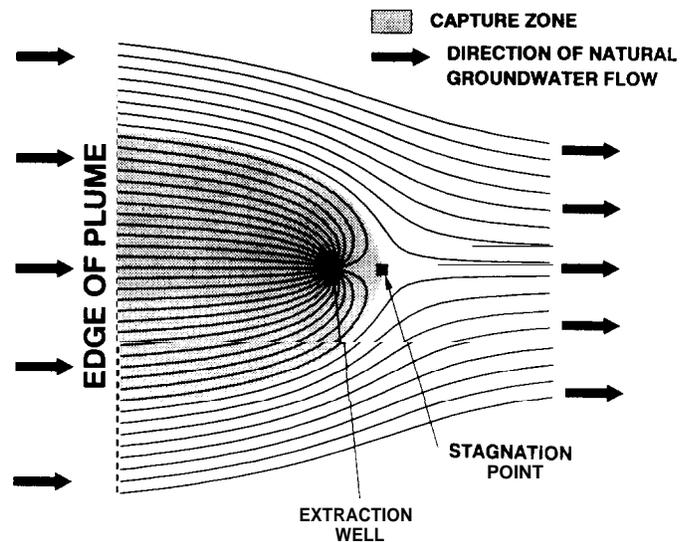


Figure 2. Flow lines from the edge of a contaminant plume toward an extraction well.

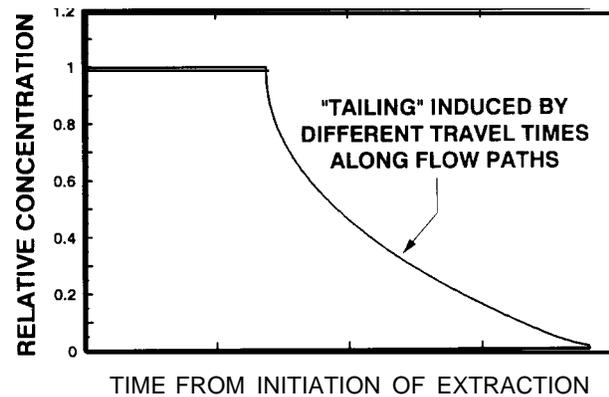


Figure 3. Concentration versus time for the extraction well illustrated in Fig.2. The tailing is caused by the differential travel times along the individual stream lines.

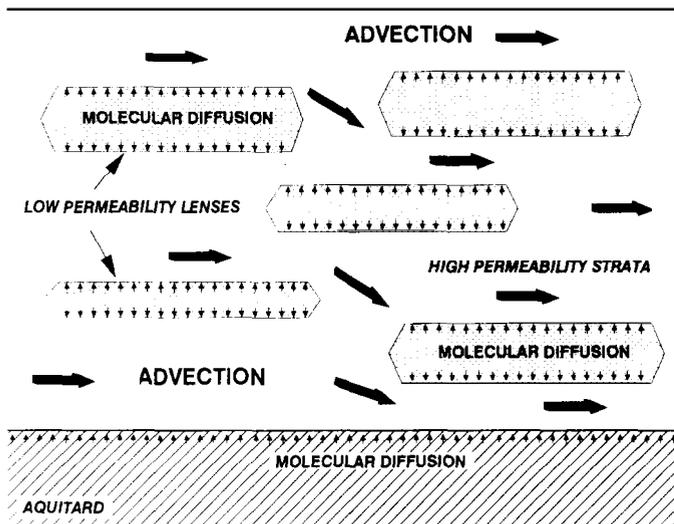


Figure 4. Heterogeneous porous medium with advection through the low permeability zones and mass transfer by molecular diffusion from the lower permeability lenses.

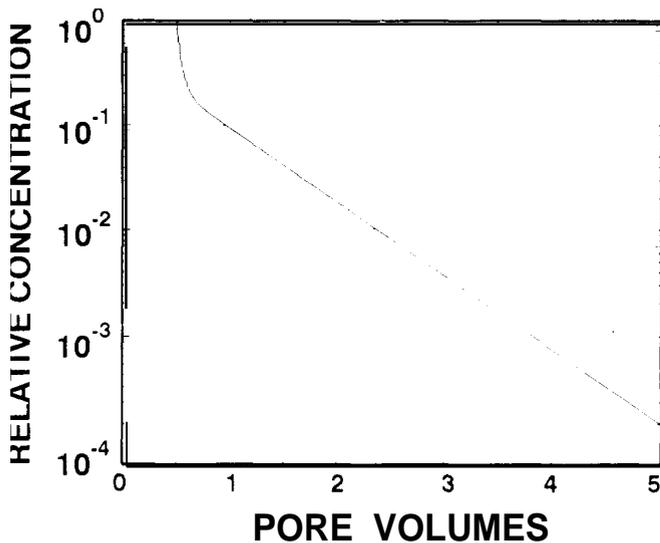


Figure 5. Concentration versus time for removal of contaminants from a ideally layered aquifer. The layers are assumed to be 10 cm thick, the length is 10 m, the retardation factor is unity, and the diffusion coefficient is 10^{-6} cm²/s. Calculated using the equations given by Sudicky and Frind (1962).

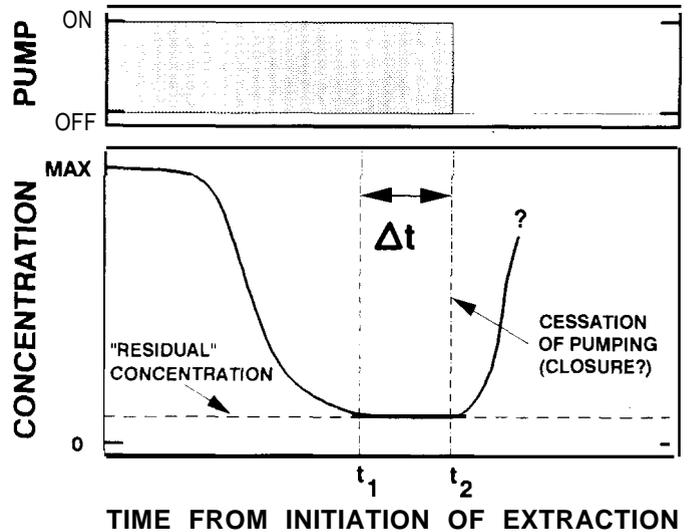


Figure 6. Concentration versus time for an extraction well that is turned off at time t_2 .

Chemical Causes of Tailing

At many sites, some or even most of the contaminant mass will not be dissolved in the ground water but will be present as 1) adsorbed species, 2) precipitates, or 3) nonaqueous phase liquids (NAPLs). These reserves of matrix-associated contaminants and contaminants in the immobile fraction of the NAPLs cannot be directly extracted by pump-and-treat: they must transfer from the solid or NAPL to the ground water before they can be removed. If the equilibrium concentration in the ground water is small relative to the total mass of contaminant in the soil or if the rate of mass transfer is small relative to the ground-water velocity, then large quantities of water must pass through contaminated sections of aquifer before it is remediated.

If reactions between solutes and stationary phases are rapid relative to the flow rate, equilibrium partitioning can be assumed. However, rapid equilibration does not translate to rapid removal rates if the equilibrium concentration in solution is very low. The retention of contaminants by mineral surfaces and microbial cell walls, ion exchange reactions with clays, and the partitioning of organic contaminants between soil organic matter and the ground water can significantly increase the time required for remediation of contaminated aquifers. For hydrophobic, nonpolar organic compounds, resorption can often be represented by linear isotherms (e.g., Chiou et al., 1979). In the absence of free product (NAPL), the number of pore volumes required to remove the organic contaminant from a homogeneous aquifer is approximately equal to the retardation factor, R ,

$$R = 1 + \frac{\rho_b}{n} (f_{oc} k_{oc}) \quad (1)$$

where ρ_b is the dry bulk density of the soil, n is porosity, f_{oc} is the fraction of organic carbon in the soil (mass of carbon/mass of soil), and K_{oc} is the partition coefficient for the contaminant into soil organic carbon (mass per unit mass of carbon/equilibrium concentration in water). A compound with a large K_{oc} value can have a large retardation factor even in a soil with a small to a moderate amount of organic carbon. Thus, many pore volumes of water must be flushed through the soil to remove such hydrophobic organic contaminants.

In some cases equilibrium partitioning may not be applicable. Laboratory tests had shown that weeks are required to achieve equilibrium concentrations in laboratory experiments with sediments (Hamaker and Thompson, 1972; Coates and Elzerman, 1986; Karickhoff, 1980). Resorption of pyrene, hexachlorobenzene, and pentachlorobenzene from river sediments requires days to weeks (Karickhoff and Morris, 1985). If such rates of resorption are slow relative to the rate of ground water flow, then equilibrium concentrations may not be attained during pump-and-treat and tailing in the concentration-versus-time curve can result.

Although the linear adsorption model is adequate for describing the adsorption equilibria of many nonpolar, hydrophobic organic contaminants (Chiou et al., 1979), it does not adequately describe the behavior of organic or inorganic ions over a wide range of pH and adsorbate concentrations. The adsorption of ionic solutes is often represented by an adsorption isotherm. An adsorption isotherm is a plot of the contaminant concentration on the soil versus the equilibrium solution concentration of the contaminant. Adsorption isotherms are defined according to their general shape and mathematical representation. For a Langmuir isotherm, the concentration on the soil increases with increasing concentration in the ground water until a maximum concentration on the soil is reached (Fig. 7). The isotherm can be represented by the equation:

$$S = S_{\max} \left(\frac{KC}{1 + KC} \right) \quad (2)$$

where S (mass/mass) is the concentration on the soil, S_{\max} (mass/mass) is the maximum concentration on the soil, K ((length)³/mass) is the Langmuir adsorption constant, and C (mass/(length)³) is the concentration in the ground water. A Freundlich (or Kuster) isotherm is given by the equation:

$$S = KC^b \quad (3)$$

where K is the Freundlich adsorption constant and b is a positive parameter. The shape of a Freundlich isotherm depends on the value of b . If b is greater than 1.0, the isotherm becomes steeper with increasing concentrations in the ground water. If b is less than 1.0, the isotherm becomes steeper at lower concentrations (Fig. 8). A linear isotherm is a special case of the Freundlich isotherm where the parameter b is equal to unity. At constant pH, cations tend to follow Freundlich isotherms while anions tend to follow Langmuir isotherms (Dzombak, 1986; Dzombak and Morel, 1990).

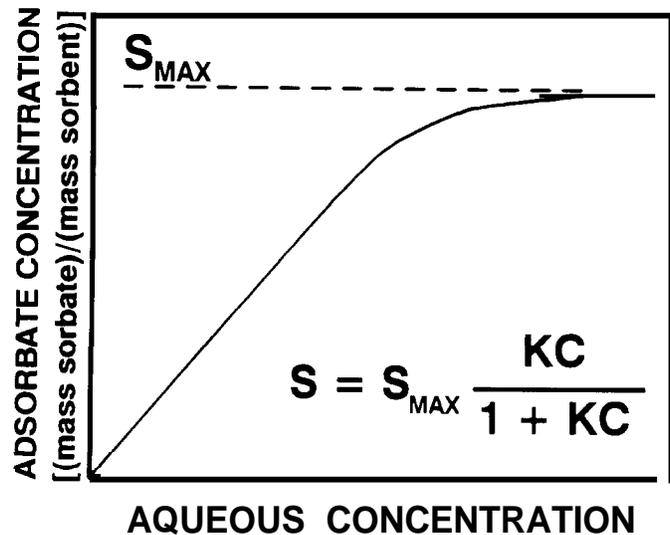


Figure 7. A Langmuir isotherm.

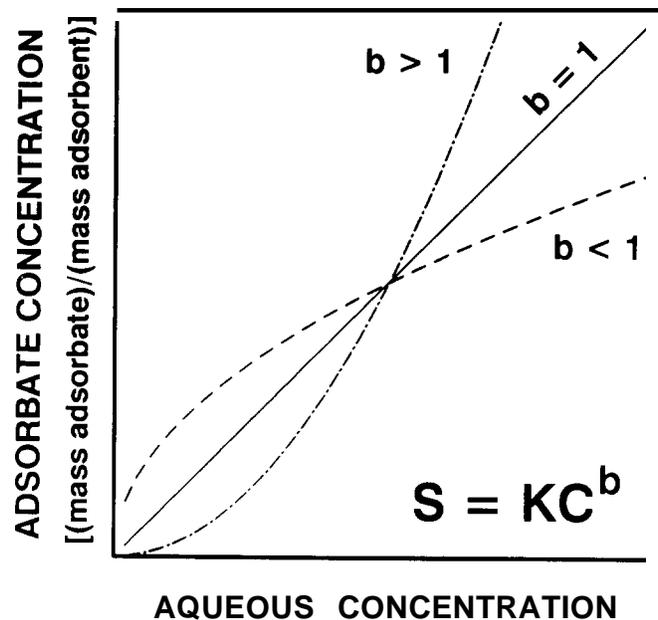


Figure 8. Freundlich isotherms, A linear isotherm is the special case for which the exponent, b , is equal to unity,

Adsorption isotherms are useful for illustrating the dependence of the solid phase concentration of the contaminant on the aqueous phase concentration of the contaminant at a given pH. However, adsorption of inorganic ions is pH-dependent and the form of the isotherm should be known over the entire pH range likely to be found at a site. Sometimes this pH-dependence is presented as the fraction of the contaminant adsorbed versus pH or a "pH-edge" (Fig. 9). For cations, the pH-edge for most minerals show little or no adsorption at low pH. As pH increases, the portion of the contaminant that is adsorbed increases until the fraction is

unity (provided that the mass of contaminant does not exceed the available adsorption sites). The pH-edges for anions are the opposite to those for cations. There is little or no adsorption at higher pH but as pH decreases the fraction of the anion that is adsorbed increases to unity or to the ratio of the mass of sites to the mass of contaminant if the amount of contaminant exceeds the number of available sites. For either cations or anions, the shape and position of the pH-edge depends on the specific mineral surface and ions under consideration.

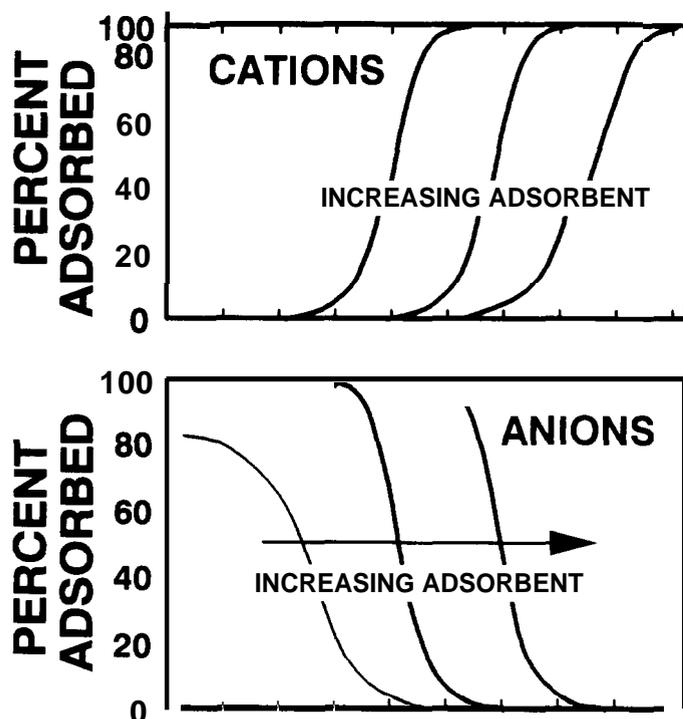


Figure 9. pH adsorption edges for cations and anions. The fraction of contaminant adsorbed will not reach unity if the sites are saturated.

Adsorption processes can also be modeled using surface complexation models (e.g., Stumm et al., 1976; Schindler, 1981; Schindler and Stumm, 1987; Dzombak and Morel, 1990). The key advantage of this type of approach is that it has a foundation in chemical theory allowing the results to be extended beyond the exact test conditions. The dependence of the amount of adsorption on the pH of the solution and the competition between several adsorbates for the adsorption sites are, in principle, accounted for in such a model. The disadvantages of the surface complexation model are the lack of a consistent set of equilibrium constants and the potential lack of linear additivity when multiple adsorbents are present. The first limitation is being overcome through compilations of consistent data sets for oxide surfaces. At this time, there does exist a consistent set of adsorption

constants for adsorption onto hydrous ferric oxide (Dzombak, 1986; Dzombak and Morel, 1990) based on a two-layer surface complexation model. Such data sets need to be derived for other oxide surfaces as well.

The general concepts of ion adsorption can be applied to anticipate some of the behavior of contaminants during pump-and-treat remediation. The rate of removal of ionic contaminants under acidic conditions can be substantially different than under neutral or alkaline conditions. Adsorption of anions, for example, is more likely to be a problem at lower pH than at more neutral or alkaline conditions. Furthermore, there may be changes in the amount of adsorption during remediation as acid or alkaline waters are returned to more neutral pH conditions. In all of these adsorption models, ionic contaminants follow nonlinear isotherms. The partition coefficient equals the slope of the adsorption isotherm. As aqueous contaminant concentrations decrease during remediation, the slope of the isotherm, hence the retardation, changes. In most cases, the retardation will increase with decreasing concentrations making it more difficult to decrease intermediate concentrations below the maximum contaminant level (MCL) than to decrease the initially high concentrations to intermediate levels.

Large reserves of inorganic contaminants may be formed as the result of the precipitation of crystalline and amorphous materials within the soils. For example, one concern is the potential effect of a reserve of solid BaCrO_4 within aquifer systems contaminated with hexavalent chromium (Cr(VI)) (Palmer and Wittbrodt, 1990). As Cr(VI) -laden waters enter the subsurface, natural Ba may react with aqueous chromate (CrO_4^{2-}) to precipitate a reserve of BaCrO_4 . In many cases, the size of the reserve will be limited by the availability of Ba^{2+} in the soil rather than the mass of chromate spilled. During the initial phases of a pump-and-treat remediation, ground water containing high concentrations of Cr(VI) in excess of available Ba^{2+} are removed and the concentrations in the extraction wells quickly decrease (Fig. 10). At some point, BaCrO_4 becomes the principal source of Cr(VI) in the pore water. The Cr(VI) concentration will remain relatively constant for as long as there is BaCrO_4 remaining in the soil. Using equilibrium concepts, Palmer and Wittbrodt (1990) estimated that 25 to 50 pore volumes are required to remove Cr(VI) from soils at a hard chrome plating facility. If equilibrium is not obtained and kinetic processes control the amount of BaCrO_4 dissolved as the ground water passes through the soil, then more pore volumes would be required.

Similar volatility limitations may occur for other inorganic contaminants. The effect of precipitates on efficacy of pump-and-treat remediation depends on the volatility of the mineral phase. The most troublesome mineral precipitates are those with solubilities low enough to create a relatively large contaminant reserve, yet with solubilities large enough to exceed the target clean-up levels. A complicating factor is substitution of contaminants in the crystalline structure of other minerals. The degree of substitution affects the equilibrium concentration of the contaminant. Regardless of whether the contaminant has been precipitated in pure or substituted mineral phases, if the rate of dissolution is slow relative to the velocity of the ground water, then the time required for the removal of the contaminant from the subsurface will be greater than when equilibrium conditions have been achieved.

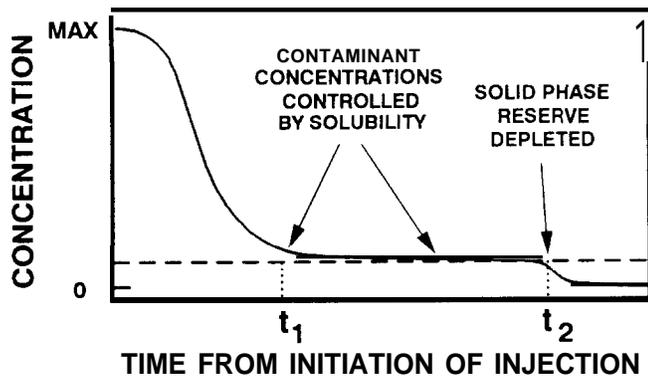


Figure 10. Concentration versus time for an extraction well in a formation that contains a solid phase precipitate.

Nonaqueous-phase liquids can also provide large reserves of contaminants in the subsurface. For example, if a cubic meter of soil with a 35% porosity contains trichloroethylene (TCE) at 20% residual saturation, then approximately 270 pore volumes must pass through the soil and reach equilibrium with the TCE (1100 mg/L) before the solvent is removed from the soil by dissolution. Sandbox experiments with perchloroethylene (Anderson, 1988; Anderson et al., 1992) suggest that this equilibrium is achieved very quickly as the water passes through fingers of residual solvent. Longer periods of time are required to remove solvents when they are present in pools (e.g., Johnson and Pankow, 1992; Anderson et al., 1992). Using the equations given by Hunt et al. (1988) and reasonable choices of transport parameters, it can be shown that only the water that passes very close to the edge of the solvent pool is likely to reach equilibrium concentrations with the solvent while the concentrations further above the pool are limited by the rate of mass transfer from the pool to the bulk aquifer (Fig. 11). The average concentration of the solvent measured in a monitoring well with a two-meter length of screen placed just above the pool will increase across the length of the pool over which the ground water has flowed (Fig. 12). If the 103 kg of TCE used in the previous example is distributed in a 20 cm thick pool below the cubic meter of soil, the average concentration of TCE in the groundwater exiting from the block of soil is 28.6 mg/L and 10,200 pore volumes must pass through the aquifer before the TCE is removed. Thus, it takes approximately 39 times longer to remove solvent from a pool than to remove the same mass of solvent from residual saturation.

When pump-and-treat remediation is predominantly limited by chemical processes that restrict the transfer of mass from these contaminant reserves to the ground water, chemical enhancement to pump-and-treat should be considered. Although the choice of a reactive agent that will greatly enhance contaminant removal is a primary concern, there are several other factors that must be considered before implementation of a chemical-enhancement program.

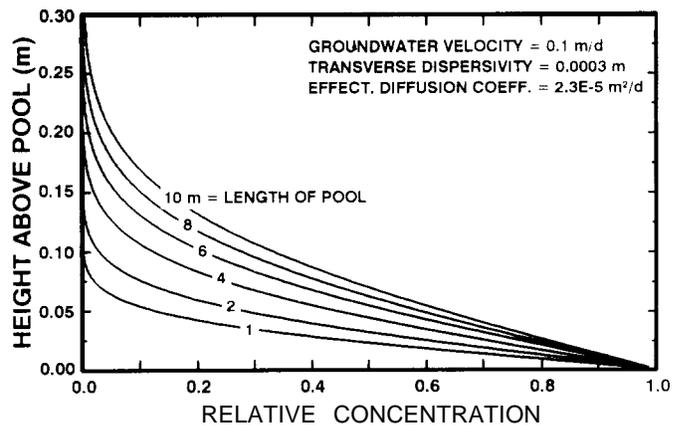


Figure 11. Concentration of a contaminant at different elevations above a DNAPL pool for different pool lengths (after Johnson and Pankow, 1992).

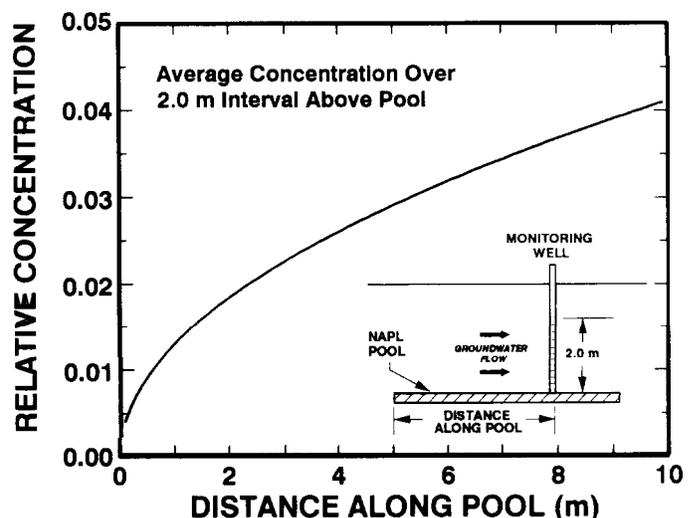


Figure 12. Average concentration of a contaminant over a 2-m interval above a DNAPL pool (after Johnson and Pankow, 1992).

Chemical Enhancements for Pump-and-Treat Remediations

If chemical enhancement of pump-and-treat is to be successful, four key areas must be satisfactorily addressed in the design: 1) delivery of the reactive agent to where it is needed within the aquifer, 2) the interaction between the reactive agent and the contaminant, 3) the removal of the contaminant and the reactive agent from the subsurface, 4) the treatment of the extracted water and disposal of the resulting sludges (Fig. 13).

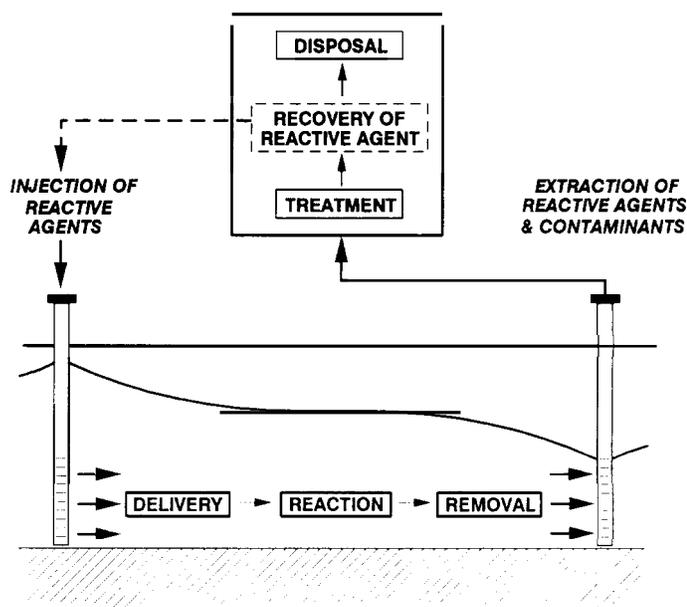


Figure 13. Schematic representation of chemical enhancement of a pump-and-treat operation. Key areas of concern are shown in boxes. In some cases, the reactive agent will be recovered and re-used.

Delivery

Delivery of the reactive agents to the areas within the aquifer where they are needed to enhance the removal of contaminants can be a complex process. Reactive agent solutions must be injected without clogging the aquifer near the injection well with particles and chemical precipitates. The ground water containing the reactive agents must then move in some reasonable period of time to the contaminated portion of the aquifer. The rate, mode, and scheduling of the injection and pumping must be designed such that the reactive agent reaches those areas in a relatively short period of time. Many of these processes are influenced by the heterogeneities within the aquifer.

Clogging of Injection Wells

The clogging of injection wells is a common problem. Clogging can be the result of the physical filtration of suspended particles at the well interface, the formation of inorganic precipitates, or the growth of microorganisms. As more materials are entrapped, precipitated, or grown in the pore space adjacent to the well face, they occupy increasing amounts of the pore space and severely reduce the hydraulic conductivity (Palmer and Cherry, 1984). A plot of the ratio of the new permeability, k , to the original permeability, k_0 , versus the new porosity, θ , to original porosity, θ_0 , using the Carmen-Kozeny model (Carmen, 1937) and the Rumpf - Gupte (1971) model (Fig. 14) illustrates that small changes in porosity can result in order of magnitude reductions in permeability. Because this reduction in permeability is immediately adjacent to the well screen, it is generally manifested as a reduction in well efficiency.

The mechanisms responsible for well clogging dictate the actions to avoid the problem. Additives may be required to prevent precipitation. Problems with particles in the injection water can be overcome by flocculation and removal with filter presses. Microbiological activity can be inhibited by the removal of nutrients or dissolved oxygen. Otherwise, periodic treatment such as surging, jetting, development, and acid treatment of the injection well may be required. These options need to be factored into estimates of capital costs of the remedial design as well as the operation and maintenance costs.

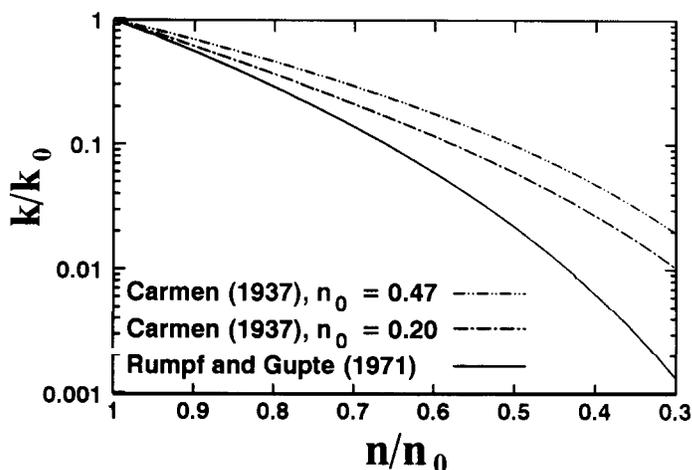


Figure 14. Ratio of permeability to initial permeability versus porosity to initial porosity using several empirical models (after Palmer and Cherry, 1964).

Transport of the Reactive Agent to Contaminated Areas

A fundamental problem with chemical enhancements to pump-and-treat remediation is getting the reactive agent to

the contaminated portions of the aquifer so that it can interact with the contaminants to facilitate their removal. Two major problems should be considered: 1) differential flow paths governed by well hydraulics, and 2) mass transfer between heterogeneities that is governed by molecular diffusion. The paths the injected water follows depend on the hydraulic properties of the medium, the aquifer thickness, the natural hydraulic gradient, the rate of injection, the placement and pumping (injection) rate of other nearby wells, and the location and type of hydraulic boundaries in the vicinity of the site. Some of these effects are illustrated for homogeneous, isotropic aquifers with stream function calculations (Fig. 15).

The two wells in Fig. 15A are 50 feet apart. The up-gradient well injects fluid at a rate of 0.5 gpm while the down-gradient extraction well removes water at the same rate. Not all of the stream lines from the injection well are captured by the extraction well. In this particular case, 20% of the injection fluid continues to be transported through the aquifer. If the wells are placed 25 feet from one another (Fig. 15B), then less of the injected fluid is lost (15%) but a much smaller volume of the aquifer is remediated with the chemical extractant. If the rate of injection is reduced to 0.25 gpm, all of the injected fluid is captured by the extraction well (Fig. 15 C); however, the volume of affected aquifer is diminished even further.

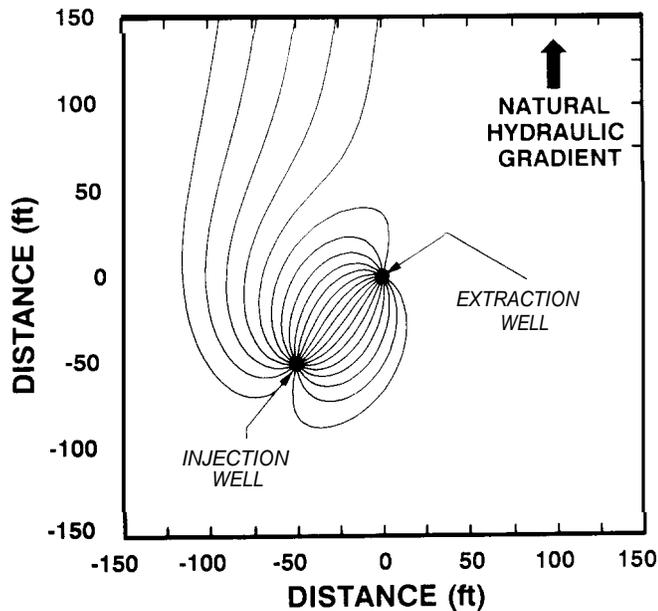


Figure 15a. Flow lines between an injection well and an extraction well located 50 feet apart and with a natural gradient of 0.007 to the north. Extraction rate and injection rate are both 0.5 gpm.

While, in principle, the distribution of wells and the rate of injection and extraction could be optimized, in practice, it may prove to be difficult. Firstly, the factors to be optimized are not universally agreed upon. Possibilities may include minimizing the number of wells, the total cost, or the time for cleanup, or maximizing the mass of contaminant removed per unit time. Secondly, none of the necessary parameters

are known with certainty. For example, concentration isopleths are known only within some range of distance, the variation in the hydraulic parameters have not been measured, and economic factors such as interest rates and costs over the next few years are based on extrapolation of current conditions.

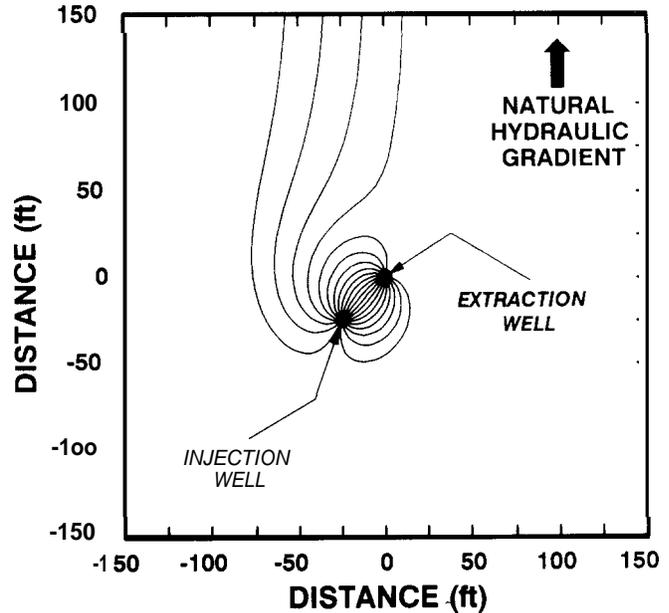


Figure 15b. Flow lines between an injection well and an extraction well located 25 feet apart and with a natural gradient of 0.007 to the north. Extraction rate and injection rate are both 0.5 gpm.

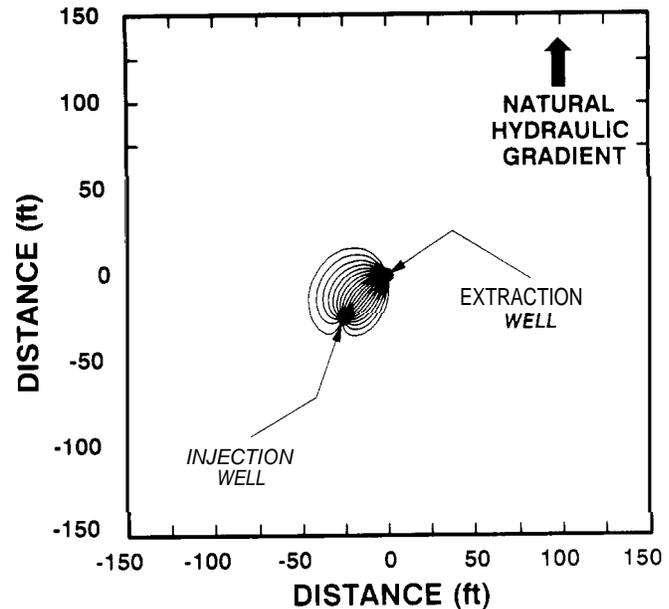


Figure 15c. Flow lines between an injection well and an extraction well located 25 feet apart and with a natural gradient of 0.007 to the north. Extraction rate is 0.5 gpm while the injection rate is 0.25 gpm.

Aquifer heterogeneity is an important factor in the rate of transport of dissolved constituents. As a reactive agent is injected, it is advected along the higher permeability pathways through the aquifer. When the hydraulic conductivity of the low permeability lenses is two or more orders of magnitude less than that of the high permeability zones, transport of the reactive agent into the lower permeability zones is controlled by molecular diffusion. The concentration of the reactive agent in the higher permeability zones should be maintained long enough to permit the diffusion of the reactive agent into the lower permeability lenses. The time it takes the reactive agent to diffuse into the lower permeability lenses depends on the diffusion coefficient, the concentration, and the soil-water interactions of the reactive agent.

The process of diffusion can be complex in a multicomponent system. If a completing agent is used to enhance the pump-and-treat remediation, the complex initially forms in the higher permeability zone, creating a concentration gradient between the higher permeability layers and the lower permeability layers. Thus, not only does the reactive agent diffuse into the lower permeability zones, but so may the complex. The extent to which this affects the time for remediation depends upon the relative rates of diffusion of the solutes into and out of the lower permeability lenses and the relative rates of reaction for the important chemical processes.

Modes of Injection

The above discussion implicitly assumes that the reactive agent is continuously injected into the aquifer, but there are several options for injecting the fluid as well as for adding the reactive agent. The water may be injected continuously, as a series of pulses, or as a slug. With continuous fluid injection the reactive agent may be added to the injection fluid continuously or it may be added in a pulsed or slug mode. For pulsed injection of the fluid, the reactive agent may be injected with each pulse or as a slug into a single pulse of fluid. For a slug injection of fluid, the reactive agent can be added as a single slug. Thus, there are six general combinations of fluid and reactive agent injection modes (Fig. 16). The advantages and disadvantages of these modes of injection (Table 1) were used to determine the suitability of each method for chemical enhancements to pump-and-treat (Fig. 16).

The modes most likely to be useful are continuous fluid injection with either continuous or pulsed addition of the reactive agent. The use of the slug mode for the injection of water is not practical; a relatively small slug of water injected into the aquifer does not affect a large volume of the aquifer. The major concern is the volume of aquifer over which the injected water is transported and how long it takes to accomplish this distribution. While continuous injection may provide the shortest time period over which it takes to distribute the fluid over a given volume of aquifer, there may be inherent economic benefits of using a pulsed mode. If staff must be present during injection, then coordinating the injection pulses with personnel shifts may be advantageous.

A key advantage of continuous addition of the reactive agent during continuous fluid injection is that relatively high

concentrations of the agent can be maintained within the higher permeability zones of the aquifer. This creates a large concentration gradient between the higher permeability lenses and the lower permeability lenses, potentially reducing the time to remove the contaminants from those zones. However, this means that a larger mass of the reactive agent is required. A slug addition of the reactive agent would require less mass; however, the concentrations may decrease with time because of the nonlinear relationship between the adsorbed and aqueous concentrations. Pulsed addition would repeatedly increase the concentration gradients between the higher and lower permeability zones, however, the gradients may be locally reversed between the passing pulses. The system would have to be more carefully designed to ensure that the net direction of diffusion of the reactive agent is into the low permeability zones.

REACTIVE AGENT ADDITION MODE	FLUID INJECTION MODE		
	CONTINUOUS	PULSED	SLUG
CONTINUOUS	good	N.A.	N.A.
PULSED	good	good	N.A.
SLUG	fair	fair	poor

N.A. = not applicable

Figure 16. Relative rating for different combinations of the modes of injection of the fluid and reactive agent.

Timing of Injection of the Reactive Agent

Chemical enhancement can be initiated at any time during the pump-and-treat remediation. Injection of the reactive agent may begin 1) as the extraction program begins, 2) after the concentration-versus-time curve significantly flattens, or 3) at some time intermediate to the first two.

An advantage of initiating injection of the reactive agent at the same time that extraction of the contaminated water begins is that it provides the earliest start to the chemical enhancements. The flow paths over which the reactive agent must travel remain approximately the same and therefore any delay in initiating the injection also delays aquifer cleanup. However, several problems may arise suggesting that this method may not always be the most advantageous. If high concentrations of contaminant are still within the aquifer, then a greater concentration of the reactive agent may be required to remove this material. The cost of the additional reactive chemicals should be compared with the cost of a longer extraction time. Geochemical interactions within the contaminant plume can result in elevated concentrations of solutes other than the contaminant (e.g.,

Table 1. Modes of injection for chemical enhancement to pump-and-treat

FLUID INJECTION MODE	ADVANTAGES	DISADVANTAGES
<i>CONTINUOUS</i>	Fluid distributed over wide area.	Greater potential for clogging of screens.
	Less maintenance of pumping schedules.	Greater pumping costs.
	Less volume of water.	Fluid distributed over very small volume of aquifer.
<i>SLUG</i>	Less potential dogging of wells.	
	Can be developed around working schedules.	Requires more design to insure injection and off periods are balanced relative to natural groundwater flow.
<i>PULSED</i>		
ACTIVE AGENT INJECTION MODE		
<i>CONTINUOUS</i>	Maintain concentration in high permeability zones allowing for diffusion into low permeability zones.	Requires more mass of active agent,
		May not allow sufficient time for diffusion into low permeability lenses.
<i>SLUG</i>	Requires less mass of active agent.	Concentration decreases with time/distance which can reduce effectiveness of the active agent.
		Requires greater maintenance/control.
<i>PULSED</i>	Less total mass of active agent.	Requires more analysis to insure that injection and off periods are of sufficient length.
	Can be planned around work schedules.	
	Allows for sufficient time for diffusion.	

Fe and Mn in anoxic plumes). High concentrations of these solutes may severely impede the effectiveness of the reactive agent, thereby requiring a greater mass of reactive agent to be injected into the aquifer. In some cases, these elevated levels of solutes may result in precipitation of the reactive agent and clogging of the aquifer.

Some of these problems can be avoided by using conventional pump-and-treat until the rate of decline in the concentration of the contaminant is low. As the concentrations of the contaminant decline, the high levels of other solutes present within the contaminated area are also likely to decline toward background levels. At lower concentrations of interfering solutes, the reactive agent interacts more efficiently with that portion of the contaminant that is most difficult to remove by conventional pump-and-treat. However, it may require the removal of several pore volumes over several years to reach these lower concentration levels so added costs for operations and maintenance may be incurred.

The third possibility is to initiate chemical enhancement at some time between the initial start-up of the pump-and-treat system and the time it takes for the concentrations to level off. Deciding the optimal time requires a more sophisticated analysis than either of the previous two choices, however, some simple criteria may serve as guides. For example, if there is concern over the precipitation of a solid phase, the criterion may be the time at which the concentration of the interfering ion decreases below the critical concentration computed from the volatility limit and the concentration of the reactive agent. While this is not necessarily the "optimal" time, it may serve as a practical estimate.

Retardation and the Rate Of Transport of the Reactive Agent

The reactive agent must travel through the aquifer almost as quickly as the water. If the reactive agent is significantly retarded, then it may take longer for the reactive agent to be transported to the target areas of the aquifer than it takes to

remove the contaminant from the subsurface without chemical enhancement. Thus, there is a possible paradox here: the reactive agent must react within the subsurface to enhance the removal of the contaminant, yet it must not be retarded. However, careful consideration of the chemistry of the system may allow this paradox to be resolved so that both objectives are achieved.

If the reactive agent is chosen to compete with the contaminant for adsorption sites, both of these objectives can be realized by controlling the concentration of the reactive agent. For example, if the adsorption of the reactive agent follows a Langmuir-type adsorption isotherm, the amount of retardation is insignificant if the concentrations are high enough to saturate all of the available adsorption sites in the soil. If a competing agent is utilized to enhance the removal of the contaminant, then it should be chosen so that neither the agent nor the complex are significantly retarded. Reactive agents that are reducing or oxidizing agents may be retarded as they react with materials other than the contaminant. Injection may have to simply continue until all of the material between the injection point and the extraction well that reacts faster than the contaminant is titrated from the aquifer. The amount of oxidant or reductant required to titrate the soil can be estimated from the oxidation and reduction capacities of the soil (Barcelona and Helm, 1991). In some cases, if something is known about the reaction rates for these redox reactions, some control can be obtained through control of the ground-water velocities (i.e., by controlling the rates of injection and extraction).

Reactive Agent - Contaminant Interactions

Different reactive agents can be chosen (Table 2) depending upon the processes that control the tailing in the concentration-versus-time curve for the extraction wells. The reactive agent may compete with the contaminant for adsorption sites, complex the contaminant, change the redox state of the contaminant, change the solvation properties of the groundwater, act as a surfactant, ionize the contaminant, or substitute for the contaminant in a precipitate. These possibilities are not necessarily exclusive of one another. For example, a reactive agent may change the redox state of the contaminant and then form a complex with the altered form.

Competition for Adsorption Sites

If the tailing of the concentration-versus-time curves for the extraction wells are controlled by adsorption processes, the reactive agent can be chosen to compete for the adsorption sites. Such competition is most likely to be effective for ionic solutes and least effective in displacing neutral organic molecules partitioned into soil organic matter.

The general concepts of ion adsorption can be applied to anticipate some of the constraints on the use of reactive agents to enhance pump-and-treat remediation. The adsorption of ions onto hydrous ferric oxide may be used as a model for appreciating the qualitative effects. Ultimately, laboratory tests utilizing the site contaminants and geologic materials should be performed. In general, we expect competition to be significant only when the adsorption sites are near saturation. An ionic contaminant can be easily displaced by a reactive agent with similar adsorption

properties if the concentration of the reactive agent is sufficient to saturate the adsorption sites. Ionic contaminants can also be displaced by a reactive agent with a lower adsorption affinity but only if the agent is present in great excess of the total number of adsorption sites in the soil.

Table 2. Reactive agents - contaminant interactions

● Competition for adsorption sites
● Complexation of the contaminant
● Cosolvent effects
● Enhanced mobilization and solubilization by surfactants
● Oxidation
● Reduction
● Precipitation/Dissolution
● Ionization

Complexation

The reactive agent may be effective in forming aqueous complexes with an ionic contaminant. The aqueous complexes are not expected to be adsorbed as readily as the noncomplexed contaminant, therefore they are more mobile and relatively easy to remove by pump-and-treat technology. For example, James and Bartlett (1983) found that citric and diethylenetriaminepentaacetic (DTPA) acids complexed Cr(III) sufficiently to maintain elevated solution concentrations at pH 7.5 and 6.5, respectively. These organic acid anions can also contribute to the removal of chromium by competing with chromate for adsorption sites at oxide surfaces. Citrate may also contribute to the reduction of the Cr(VI) to Cr(III) which can then be complexed by another citrate molecule.

While there are many such potential chelators, those that are environmentally safe enough to be used in aquifers are relatively weak and non-specific in their binding action. Two key consequences of these properties are that 1) the chelator must be present in great excess of the contaminant concentrations and 2) high concentrations of common, nonhazardous soil constituents such as Fe, Mn, and Al may also be removed (e.g., Grove and Ellis, 1980; Norvell, 1984). The presence of these constituents in the waste stream may substantially increase the costs of treatment and disposal over conventional pump-and-treat. Some chelating agents, such as citrate, can be utilized as substrate by bacteria in the subsurface. As the concentrations of contaminants decrease below toxic levels around injection wells, bacterial growth may increase to the level where the increased biomass clogs the aquifer and wells.

In some cases, the adsorption properties of the soil matrix may be altered by the use of chemical extractants. The removal of iron and aluminum oxide surfaces should decrease the adsorption density of the geologic materials. Zachara et al, (1988b); however, found the adsorption of

chromate onto kaolinite increased with treatment with dithionate-citrate-bicarbonate (DCB) or hydroxylamine-hydrochloride (NH₂OH·HCl) solutions. The reasons for this increase in adsorption are not clear.

Treatability studies should be conducted to determine not only the efficacy with which contaminants are removed by such chelators but also to estimate the total load of metals that must be treated and disposed, and the potential increases in biomass. The cost of these additional loads must then be compared with the costs of conventional pump-and-treat remediation.

Cosolvents

The rate of removal of hydrophobic organic contaminants is often limited by their relatively low volatility in water. However, the solubilities of many of these contaminants are much greater in other solvents. Theoretical models suggesting an exponential decrease in the amount of adsorbed organic contaminant with increasing fractions of water miscible solvents (Rao et al., 1985; Woodburn et al., 1986) have been substantiated in laboratory experiments for several organic compounds (Rao et al., 1985; Nkedi-Kizza et al., 1985, 1987; Mahmood and Sims, 1985; Woodburn et al., 1986; Fu and Luthy, 1986a, 1986b; Zachara et al., 1988a). For example, the adsorption coefficient for anthracene in methanol-water mixtures decreased by four orders of magnitude as the fraction of methanol was increased from 0 to 1 (Nkedi-Kizza et al., 1985). The injection of cosolvents may therefore be expected to drastically increase the volatility and decrease the retardation factors for these organic compounds thereby facilitating their removal from the subsurface. Cosolvents that are used as substrate by microbes may have the added advantage of promoting co-metabolism of primary contaminants. Small amounts of biodegradable cosolvent that are difficult to remove from the subsurface will be of less concern because of their eventual transformation. Thus, cosolvents, such as alcohols, are potentially effective reactive agents for chemical enhancement to pump-and-treat of hydrophobic organics. However, some consequences of cosolvent injection may be less desirable.

The order-of-magnitude decreases in adsorbed contaminants are generally achieved with cosolvent concentrations greater than 20%. Fluids containing this amount of cosolvent will have densities and viscosities that differ substantially from the ground water. Thus, the transport behavior of these fluids is more complex and more difficult to predict than for fluids with homogeneous properties. Cosolvent interaction with clays in the aquifer matrix may either increase or decrease the permeability of the soil. Cracks have appeared in soils treated with methanol (Brown and Anderson, 1982). The formation of such high permeability pathways may be particularly troublesome at sites where dense nonaqueous phase liquids (DNAPLs) are present. Cosolvents such as methanol can serve as substrate for subsurface microbes resulting in biofouling of the aquifer. Biotransformation may substantially alter the geochemistry of the aquifer and promote the reductive dissolution of Fe and Mn oxides. These metals can create problems with well clogging and interfere with surface treatment. Also, additional treatment facilities must be constructed for the separation of the

cosolvent from the water. These facilities incur capital expenditures as well as operation and maintenance costs.

Surfactants

A surfactant adsorbs to interfaces and significantly decreases the interfacial tension (Rosen, 1978). This property of surfactants has made these chemicals useful in enhanced oil recovery and several researchers have proposed their use in the remediation of NAPL-contaminated sites (e.g., Ellis et al., 1985). In general, surfactants are composed of a hydrophobic moiety, often a long chain aliphatic (C₁₀ to C₂₀) group, and a hydrophilic moiety (Fig. 17) that can be anionic, cationic, nonionic, or zwitterionic (i.e., possess both positive and negative charges). The orientation of the surfactant molecules at an interface can reduce the interfacial tension and alter the wetting properties of the soil matrix. When the interface is a nonaqueous phase liquid, the lowering of the interfacial tensions decreases the capillary forces keeping the NAPL in place and results in greater mobility of the NAPL.

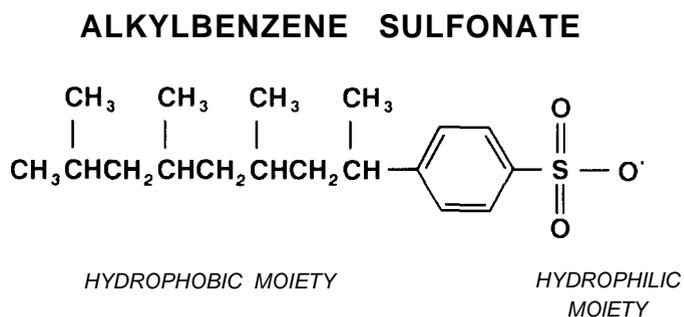


Figure 17. The surfactant alkylbenzene sulfonate.

For enhanced oil recovery, increased mobility of the NAPL allows a greater fraction of the available oil to be pumped to the surface. In the case of NAPLs that have a greater density than water (DNAPLs), increased mobility is not necessarily desirable. Once mobilized, the DNAPL may migrate deeper into the aquifer. If the DNAPL migrates into areas that were previously uncontaminated, additional wells and pumps will be required and the costs of remediation will increase accordingly.

Surfactants can also promote the solubilization of hydrophobic organic contaminants. Above a critical concentration known as the "critical micelle concentration," colloidal-size micelles can form by the aggregation of the monomeric surfactant molecules. In water, the micelles form by the hydrophobic moieties grouping together in the core of the micelle, and the hydrophilic moieties orienting toward the surface of the micelle (Fig. 18). Hydrophobic organic contaminants partition into the hydrophobic core of the micelle thereby increasing the volatility of the organic contaminant.

MICELLE FORMATION

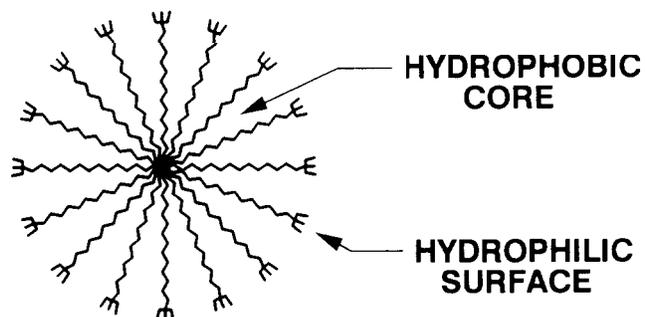


Figure 18. Aggregation of surfactant molecules into a micelle.

Although the successful application of surfactants to enhanced oil recovery has been demonstrated, transfer of this knowledge to aquifer remediation is not direct. Surfactants used for enhanced oil recovery are chosen on the basis of temperatures and salinities that are much higher than those at most hazardous waste sites. To achieve the desired behavior, the surfactant must be chosen for the solvent under the conditions of use (Rosen, 1978). Incorrect surfactant formulations may result in high-viscosity macroemulsions that are difficult to remove. The surfactant can alter the wetting properties of the soil matrix and cause the NAPL to become the wetting phase. The NAPL would then occupy the smaller pores of the soil matrix, thereby exacerbating clean-up efforts. The toxicity and potential biodegradation of surfactants that will remain in the aquifer following NAPL removal is of great concern in shallow aquifers.

The use of surfactants for aquifer remediation looks promising; however, there is little experience in their application. Laboratory experiments have demonstrated enhanced removal of anthracene and biphenyls (Vignion and Rubin, 1989), petroleum hydrocarbons (Ellis et al., 1985), DDT and trichlorobenzene (Kile and Chiou, 1989), automatic transmission fluid (Abdul et al., 1990), and PCBS (Ellis et al., 1985; Abdul and Gibson, 1991). Surfactant mixtures that specifically address the needs for aquifer remediation need to be developed and tested in the field as well as in the laboratory. When DNAPLs are present, mixtures that increase solubilization more than mobilization may be desired.

Oxidants-Reductants

The addition of a reactive agent that changes the oxidation state of a contaminant is potentially useful for 1) decreasing the toxicity of the contaminant, 2) increasing its mobility, or 3) increasing its susceptibility to completing agents. For example, chromium can be reduced from the more toxic

Cr(VI) to the less toxic Cr(III). The oxidation of selenite (Se(IV)) to selenate (Se(VI)) results in a solute that is less toxic and more mobile. However, oxidants and reductants are not specific and must, therefore, be in excess of the amount of contaminant. This will locally alter redox conditions within the aquifer and may result in the precipitation of solid phases that may clog the aquifer and injection/extraction wells or mobilization of other metals that must be handled in the treatment train.

The rate of reaction is an important factor in considering an oxidation or reduction reaction to facilitate the removal of a contaminant from the subsurface. Often the rates are strongly dependent on pH. For example, rate of reduction of Cr(VI) by ferrous iron varies with $\{H^+\}^3$ (Wiberg, 1965).

Precipitation-Dissolution-Ionization

At metal-contaminated sites, it may be possible to add a chemical constituent that will cause the precipitation of the contaminant in a solid phase with very low volatility. For example, the neutralization of acid mine waters by carbonate-buffered solutions will cause the precipitation of metal-oxides, hydroxides, and carbonates. Pb^{2+} can precipitate as a relatively insoluble $PbCO_3$ phase. While this may reduce the risk of contaminant concentrations of exceeding the MCL, it does not remove the metals from the site. The precipitates can continue to act as long-term, low-level sources and the contaminants may still enter the biosphere through plant root systems or erosion. In addition, the precipitation of metal oxyhydroxides and carbonates can cause clogging of the aquifer and severe reduction in well efficiency.

Remediation of contaminated sites by conventional pump-and-treat may often be limited by dissolution of sparingly soluble mineral phases and nonaqueous phase liquids. Reactive agents that increase the volatility of these phases will release the contaminant into solution where it can be removed via an extraction well. For example, many phenolic compounds can be ionized at higher pH (e.g., Palmer and Johnson, 1992). The use of a base as a reactive agent will enhance the volatility of the phenolic phase and decrease the retardation factor of the dissolved compounds. If cadmium is being released into solution from $CdCO_3$, the addition of acid can dissolve the carbonate mineral phase and bring the Cd^{2+} into solution. However, such treatments are not selective and other ions including Fe, Al, and SiO_2 will be added to solution. These ions may interfere with treatment processes and increase the volume of sludge to be disposed. The natural buffering capacity of the aquifer will require that the concentration of injected acid or base be in excess of the amount of contaminant in the subsurface.

At metals-contaminated sites where remediation is limited by the presence of a sparingly soluble mineral phase, it may be possible to release the contaminant more rapidly by the addition of ion that will substitute for the contaminant within the mineral phase. This is most likely to be applicable where the availability of one of the counter ions in the solid phase is limited. By scavenging the counter ion into another solid phase, the contaminant will be released into solution where it can be easily removed. For example, if $BaCrO_4$ limits the remediation of chromium-contaminated sites, the injection of high levels of sulfate would precipitate $BaSO_4$ and increase

the volatility of the BaCrO₄ component, thereby allowing the removal of the Cr(VI) in fewer pore volumes than by conventional pump-and-treat.

Such chemical enhancement methodologies require specific knowledge about the mineral phases limiting aquifer remediation and the geochemistry of the ground waters on site. Detailed geochemical studies will increase the cost of site investigation and feasibility studies but may more than pay for themselves if efficient removal methods can be identified and problems associated with the implementation and operation of the clean-up effort are avoided.

Removal of the Contaminants and Reactive Agents from the Subsurface

The basic concept of chemical enhancement to pump-and-treat is to increase the mobility of the contaminants in the subsurface so they may be more easily removed via extraction wells. Removal of contaminants from the subsurface in a chemical enhancement scheme, therefore, requires decisions about the density, placement, and pumping rates of these extraction wells. Several aspects of such an enhanced extraction system design will be similar to those utilized in conventional pump-and-treat remediations. For example, the contaminants must be contained within the capture zones of the extraction wells. However, key differences between conventional pump-and-treat and chemical-enhancement extraction system designs need to be explored. For example, in conventional pump-and-treat, contaminants are expected to be retarded. Therefore, the density of the well system is typically chosen to shorten travel times and thereby decrease the time for remediation to the extent possible. In chemical-enhancement methods, the reactive agent is used to make the contaminants behave more like a nonreactive tracer. Therefore, it may be possible to utilize a lower density of extraction wells to achieve an effective removal of the mobilized contaminant. Another important consideration in the design of an extraction system for chemical enhancement is the coordination with the injection of the reactive agent. As described above, there can be advantages to initially removing high levels of contaminants by conventional pump-and-treat before initiating the injection of the reactive agent. Also, pumping rates for the extraction wells may be adjusted during the injection to aid in the distribution of the reactive agent within the aquifer.

Use of a reactive agent in a pump-and-treat scheme introduces one or more new chemical constituents into the subsurface. To be effective, reactive agents generally must be added to an aquifer at non-trace concentrations. Even if the reactive agent is harmless to human health, state and federal regulations will often require that concentrations of the reactive agent be lowered to some permissible level. Removal of the agent then involves all of the problems encountered in the removal of the original contaminant and in some cases the agent may even be more difficult to remove. For example, if the reactive agent is a solute that is used to compete with the contaminant for the adsorption sites, then the reactive agent must have a greater affinity for the adsorbent; but this greater affinity also makes it more difficult to remove from the subsurface. There still may be a net benefit if the target clean-up level for the reactive agent is greater than for the contaminant. It can also be argued that

the net risk is reduced because the reactive agent must, by any reasonable choice, be less toxic than the original contaminant.

One complication that may arise during the removal of the reactive agent from the subsurface is clogging of the screen and filterpack as waters are mixed at the extraction wells. This problem is likely to be most acute when the reactive agent changes the redox conditions in the subsurface. As oxidized waters mix with reduced waters that contain iron, precipitates may clog the screen, pipes, and treatment tanks.

Treatment and Disposal

The previous sections have outlined many of the technical considerations that must be addressed to implement an effective chemical enhancement strategy. However, even a chemical enhancement plan that is completely satisfactory in terms of subsurface deployment and removal of solutions may still present technical difficulties in the treatment and handling of the extracted wastes. Three broad categories of post-extraction problems are discussed in this section: the effects of the reactive agent on the treatment of the target contaminants, the removal of the reactive agent from the waste stream before discharge, and the recovery and reuse of the reactive agent.

Removal of the Reactive Agent before Discharge

As described above, the use of a reactive agent in a pump-and-treat scheme introduces one or more new chemical constituents in non-trace levels into the water brought to the surface. Extracted water will, therefore, contain substantial quantities of the reactive agent, probably in excess of the target contaminants. State and federal regulations will often require that concentrations of the reactive agent be lowered to some permitted discharge level. For example, if phosphate is used as an extractant, standards may restrict the permissible concentration in discharges from the treatment facility, even if the treated wastes are routed into a municipal sewage treatment system. Limits on phosphate discharges can be anticipated in localities in which eutrophication is a problem in waters receiving regional waste waters.

If the levels of reactive agent in discharges from the site are regulated, then the treatment plan must explicitly include a means of removing the agent. In many cases, the most efficient system will effect the removal of the reactive agent simultaneously with the treatment of the targeted contaminants. For example, if phosphate were used to enhance chromate removal, then the neutralization step in a treatment process could be modified to induce the precipitation of much of the phosphate. Phosphate and reduced Cr would precipitate in the same step and could be removed collectively in the sludge.

For the specific system mentioned, note that the treatment procedure would need to be modified. Removal of Cr³⁺ alone can be effected by addition of NaOH to achieve a basic pH. The resulting sludge then contains a mixture of Cr hydroxides, probably coprecipitated with by-products of the reductant step. For instance, if bisulfite is the reducing agent, sulfate and bisulfite will constitute part of the sludge.

If phosphate is present in the extracted water, some phosphate is likely to coprecipitate with Cr^{3+} . However, the concentration of phosphate remaining in solution in such a complex system would be difficult to accurately predict and tests would be necessary to find the optimal pH for phosphate precipitation.

It is possible that pH adjustment alone would not precipitate sufficient phosphate. In that case, an additional treatment reagent would be needed; for example, substituting $\text{Ca}(\text{OH})_2$ for some or all of the NaOH in the neutralization step. Calcium phosphates are relatively insoluble and would strip out much of the phosphate. However, pilot studies would be needed to ensure that the sludges produced behaved in the desired fashion. The presence of phosphate might decrease the density of the sludge so that longer settling times are required. Furthermore, the presence of Ca^{2+} could lead to the buildup of scale in unexpected parts of the system. In general, it is wise to bear in mind that the treatment process will be efficient only if it is regarded as a coordinated chemical system in which the alteration of one part can cause dramatic changes in the behavior of another part.

If the reactive agent is successfully coprecipitated with the target contaminants, the total volume of sludge sent to disposal will increase correspondingly. Although the reactive agent may be harmless, once it is commingled with a toxic waste, the entire volume could be classified as hazardous and the cost of disposal assessed accordingly. Thus, while the removal of contaminant and reactive agent in a single step may save operation or capital costs, the increased volume of sludge to be landfilled over the case where no reactive agent is used, will generate costs that will offset some of the savings. The cost of testing and design of the removal system for the reactive agent must also be factored into the economic analysis.

In some cases, it will be desirable or essential to remove the reactive agent in a separate stage of the treatment system. One reason for a separate treatment step is to achieve a better removal of the reactive agent than could be conveniently achieved in a single step. In the example above, it might be desirable to optimize Cr^{3+} precipitation without regard for phosphate and then strip phosphate out of the supernatant with $\text{Ca}(\text{OH})_2$ or alum treatment in a subsequent step. If the Cr^{3+} precipitation step could be designed to minimize phosphate coprecipitation, and if the phosphate sludge were sufficiently free of Cr to be classified as non-hazardous, the two-stage removal would have the added advantage of minimizing the volume of hazardous solids for disposal.

Interference of Reactive Agent with Treatment Processes

Even if regulations do not require the removal of reactive agents, it may be necessary to remove them from the process stream. Some reactive agents may be harmless to humans or to the environment, but they nonetheless may have chemical properties that alter the behavior of the contaminants in the waste stream. For example, many conceivable reactive agents would function by completing the target contaminants and enhancing their volatility. Specifically, citrate or oxalate salts might be used to bind up and mobilize metal ions. The same solubilization of metal

ions that is desirable in the extraction step may become a major headache in the treatment step.

As discussed above, most chelators that are environmentally safe enough to be used in aquifers, such as malonate, succinate, and citrate, will be relatively weak and non-specific in their binding action. A weak affinity for the target metal means that the chelator must be present in great excess and will be found in corresponding excess in the extracted water. The excess chelator may interfere with one or more segments of the treatment process by binding to the target contaminant.

The most obvious interference would be the inhibition of precipitation. The soluble metal-chelator complex will not readily precipitate out of solution. Lowering the pH will dissociate most metal complexes (such as citrate or oxalate), but metal ions will be soluble at the lower pH. Raising the pH will favor precipitation, but the higher pH also favors the binding of most chelators. Very caustic pH levels maybe required to induce precipitation of metals in the presence of excess chelator. An alternative scheme is to remove the chelator from solution before the metal precipitation step. An organic chelator such as citrate could be degraded by biological treatment. An inorganic chelator such as polyphosphate would not biodegrade and would be difficult to remove economically by chemical means. Any process that requires a separate treatment step for the chelator will have greater operation and capital costs than the corresponding process in the absence of that step.

The nonspecificity of chelators used as reactive agents creates another substantial problem for treatment processes. Aquifer materials may contain large amounts of naturally-occurring metals that may be solubilized by the chelator. Iron and manganese will be the most important in many aquifers, but copper, zinc, aluminum, and other metals may be extracted to varying degrees. The solution brought to the surface will contain not only free chelator, but also substantial quantities of chelator bound to non-target metals. In some situations, the amount of chelator actually bound to the target metal(s) may be only a small fraction of the total chelator in the extracted water. The additional metals would not be solubilized in the absence of chelator, so these metals are a specific feature of chemical enhancement.

Large quantities of iron and manganese in the extracted water will require special attention in the treatment process. Precipitation of the target metals will be accompanied by the precipitation of substantial amounts of iron and manganese hydroxides. The sludge volume will be correspondingly increased, with the concomitant elevation of disposal costs. Furthermore, the behavior of iron in particular is apt to be different from that of many target metals. Iron is an especially insoluble metal (under aerobic conditions) and may therefore precipitate out of the waste stream before the target metal precipitates. If this precipitation can be anticipated and controlled, it may simplify the treatment process. However a more likely scenario is that iron precipitation will be somewhat unpredictable and will occur in inopportune sections of the treatment facility, causing plugging or fouling of the equipment and interfere with the treatment process by coprecipitating the contaminants.

Recovery and Re-use of the Reactive Agent

In some cases, it may be beneficial to remove the reactive agent from the waste stream so that it can be re-injected into the aquifer and re-used for additional extraction of the subsurface contaminants. Such re-use may be particularly advantageous when the reactive agent is expensive or when it must be removed because of concerns about interference with treatment or because of regulatory requirements on discharges of the treated water. However, the methods that may be used to extract the reactive agent from the waste stream for re-use may not be the optimal methods for removal for other purposes.

Effects of Rapid and Concentrated Extraction

One of the assumptions underlying the use of chemical enhancement in a pump-and-treat operation is that the rapid extraction of concentrated waste solutions is beneficial to the clean-up operation. Of course, this will be true at many sites because annual operation and maintenance costs are directly reduced by a more rapid removal of contaminants.

Furthermore, more concentrated wastes may be easier to treat than dilute wastes. However, an accurate economic analysis of the various options available in restoring an aquifer should consider all costs associated with chemical enhancement. Besides the above-mentioned increases in research and development and operation and maintenance associated with chemical enhancement, there may be added costs due to the rapid extraction and concentration of wastes.

Careful consideration should be given to the capital costs of designing facilities that can efficiently handle and treat large volumes of a target contaminant in a short time. Injection/extraction wells, settling basins, sludge pumps, metering pumps, and other facilities may need to be greatly expanded to handle the concentrated waste load. Although the system will be operated for a shorter period of time there will be a tradeoff between increased capital costs and lower operation and maintenance costs. It may be cheaper to run a pump-and-treat operation for ten years with a small facility, rather than build a much larger facility that will only need to operate for one or two years.

Furthermore, planning in the pilot stages should give careful attention to the performance of the treatment process at different contaminant concentrations. If the process is especially efficient and reliable at the high concentrations attainable only with chemical enhancement, then the additional costs will be mitigated. If, however, the treatment process becomes more difficult or unreliable when contaminants are very concentrated, then the use of chemical enhancement may be contraindicated. Special care is needed if a biological treatment step is anticipated. Microbes generally thrive at higher substrate concentrations, but if higher contaminant levels lead to toxic levels of the target contaminant or some secondary constituent, then the biological treatment may fail altogether. Many of the problems of high concentration can be circumvented by appropriate dilution, but this is a feature that should be anticipated and incorporated into the design.

Site Characterization for Chemical Enhancements

Rational implementation of a chemically enhanced pump-and-treat remediation will require many of the same characterization and testing methods required for conventional pump-and-treat operations. Physical hydrogeological parameters such as hydraulic conductivity, the potentiometric surface, and porosity (Table 3) can be obtained using the methods outlined by Mercer and Spalding (1992a, b), Palmer and Johnson (1989), Rehm et al. (1985), and Ford et al. (1984). These physical parameters can be used in modelling studies to ascertain the feasibility of getting the reactive agent to the contaminated areas within a reasonable period of time while maintaining a capture zone for the contaminant and the reactive agent. The results of such studies should help identify the optimum injection concentrations, the number of wells, and their location.

If chemical enhancements are to be considered, greater effort must be placed on the chemical characterization of the site. In particular, the key chemical processes that limit pump-and-treat remediation must be identified if the proper type of reactive agent is to be chosen. Important chemical processes and their characterization have been recently addressed by Boulding and Barcelona (1992a,b,c), Palmer and Johnson (1992), and Palmer and Fish (1992).

Table 3. Physical-hydrogeological and chemical parameters that should be identified during site characterization for chemical enhancements to pump-and-treat remediation

Physical-Hydrogeological Parameters

- bulk density
- porosity
- hydraulic conductivity
- storativity
- potentiometric surface
- site boundary conditions
- ground water-surface water interactions
- infiltration rates
- leakage from adjacent aquitards

Chemical Parameters

- pH
 - redox conditions
 - contaminant concentrations and spatial distribution
 - non-contaminant concentrations
 - oxidation capacity of the aquifer
 - reduction capacity of the aquifer
 - organic contaminant partition coefficients
 - ionic adsorption parameters
-

Several approaches must be used to determine the chemical processes limiting pump-and-treat remediation. For ionic solutes, adsorption tests are important for quantifying the fraction of the solute adsorbed onto the surfaces of the soil as a function of pH and the aqueous concentration of the contaminant. The potential for mineral controls can be identified by calculating mineral saturation indices using geochemical models such as MINTeq (Felmy et al., 1984) and may be verified through x-ray diffraction or electron

microscopy. Oxidation and reduction tests (e.g., Barcelona and Helm, 1991) are useful for determining the amounts of oxidant and reductant necessary to alter the redox state of a contaminant in the subsurface. Bench-scale tests to measure the increase in solute concentrations following the addition of proposed reactive agents can provide information about potential compositions of interfering solutes entering the treatment train. Treatment studies using water compositions based on these tests can be used to determine potential problems and test proposed solutions to the treatment process.

For neutral organic contaminants, batch-sorption tests can be conducted to determine the fraction of the contaminant partitioned into the soil organic matter. However, at most sites, the partitioning can be determined from published values of the K_{oc} of the contaminant (e.g. Maybey et al., 1982; Montgomery and Welkom, 1989) and the fraction of organic carbon in the soil. This approach is simpler than batch experiments; however, it does require that the f of the soil be measured. When nonaqueous phase liquid are present, they are the limiting factor in site remediation; pools of NAPLs are more problematic than NAPLs retained at residual saturation in the soil. Again, proposed reactive agents should be tested at the bench scale and the treatability of the extracted water tested before pilot testing and implementation of the chemical enhancement operation.

The tests discussed above are generalizations of a few that can be conducted. The specific tests required at a site depend on the target contaminants and the nature of the soil materials from which they must be extracted. Utilizing the knowledge from laboratory studies and the experience from other hazardous waste sites will be important in directing the type of tests that need to be conducted. Unfortunately, at this time, there have been few field demonstrations of chemical enhancement methods from which to obtain such experience.

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