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*Simulations of In Situ Air Stripping
Demonstration at Savannah River*

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SIMULATIONS OF *IN SITU* AIR STRIPPING DEMONSTRATION AT SAVANNAH RIVER

by

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ABSTRACT

This report assesses the performance of the *in situ* air stripping technology demonstrated at the Savannah River Integrated Demonstration (SRID) site. This technology is a combination of air injection below the water table and vacuum extraction in the vadose zone, using a pair of horizontal wells. Our approach is based on the construction of a site-specific numerical model using the FEHM flow and transport code. We use the model as a tool to investigate improvements to performance, to improve the prediction of the performance of this technology over longer periods of time and at different sites, and to compare performance with other remediation technologies.

EXECUTIVE SUMMARY

The Office of Technology Development (OTD) in the Department of Energy's (DOE) Office of Environmental Restoration and Waste Management is investigating new technologies for "better, faster, cheaper, safer" environmental remediation. A program at DOE's Savannah River site was designed to demonstrate innovative technologies for the remediation of nonarid sites contaminated with volatile organic compounds (VOCs) in both the saturated and unsaturated (vadose) zones. The purpose of this report is to assess the performance of the *in situ* air stripping technology demonstrated at the Savannah River Integrated Demonstration (SRID) site. This technology is a combination of air injection below the water table and vacuum extraction in the vadose zone, using a pair of horizontal wells. Our approach is based on the construction of numerical models that simulate the field demonstration (i.e., "history matching").

We successfully simulated removal of one of the main VOCs present at the site (trichloroethylene, TCE) during the 139 day *in situ* air stripping demonstration at Savannah River using the flow and transport code FEHM. Conclusions from this history-matching part of this study are the following:

- The TCE concentration at the extraction well versus time can be simulated very well using a relatively simple model with a dual porosity formulation which assumes a mass transfer limitation between liquid-phase TCE held up in clay lenses and the moving air, which travels mainly in the surrounding sandy zones of higher permeability. More generally speaking, a kinetically controlled process for VOC removal can explain a rapid initial decline in VOC concentration at an extraction well followed by a period of quasi-steady concentrations over long times.
- A relatively large initial inventory of TCE (~16,000 kg) is necessary to match the TCE concentration at the extraction well versus time, if it is assumed that all the contaminant that is eventually extracted is present in the immediate vicinity of the

site. After 139 days, ~15% of this inventory is removed—7.5% of the TCE initially present in the vadose zone and ~7% of the TCE initially present in the saturated zone. If this is not the case, the conclusions of this study are not qualitatively affected provided that the key assumption—that the process is diffusion limited—holds true. In fact, the conclusions of this report should hold true in general for any system with mass transfer limitations.

- Studies of the sensitivity of the TCE concentration at the extraction well versus time curve to various model parameters showed the following. The greater the amount of TCE sorbed onto the sandy material for a given VOC liquid concentration, the flatter the TCE versus time curve. The TCE concentration at the extraction well is sensitive to the assumed TCE air diffusion coefficient in clays, but not highly sensitive to the total amount of clay present or clay saturation level (within reasonable ranges). The curve is sensitive to the value of the equilibrium sorption coefficient for TCE on the clay only at large times.

We used this history-match simulation as a basis to explore ways to optimize the *in situ* air stripping technology. Conclusions from this part of this study are the following:

- Cyclic operation of the system may offer substantial cost savings for only a marginal performance cost. For example, operating the *in situ* air stripping system on a 30-day-on, 30-day-off schedule results in only about a 30-35% decrease in total TCE removed.
- Similarly, operating the system at lower flow rates may offer substantial cost savings for only a marginal performance cost. For example, an increase in flow rate by a factor of four resulted in only a 26% increase in total TCE removal.
- The injection of heated air through the lower well is unlikely to result in increased VOC removal. This is because only a small region is heated at any one time and as soon as air travels from a heated region to one at ambient temperature, any "extra" TCE in the air phase redissolves. Only when the entire path from the injection to the extraction point is heated, will the heating benefit VOC removal.
- Aligning the injection and extraction wells at any particular angle to one another is probably not necessary. Heterogeneities in the medium are likely to be the dominant factor in governing the spreading of air in the saturated zone and for any reasonable configuration, it is very unlikely that VOCs stripped from the saturated zone would not be captured by the extraction well. The injection well should be directly aligned with the major axis of the plume for the greatest likelihood of adequate air sweep through the plume.
- A system consisting of a horizontal air injection well and vertical extraction well(s) in the vadose zone with surface capping may be optimal. In most cases, a single horizontal, vapor extraction well outperforms a single vertical, vapor extraction well (with surface capping) only for a long linear plume. In those cases, the difference can probably be eliminated with additional vertical extraction wells and still be less expensive (Birdsell et al. 1994). By contrast, for the injection well in the saturated zone, there is likely to be a large performance advantage of horizontal wells over vertical wells.

We then used this history-match simulation as a basis to predict long-term performance at the SRID site and performance at other sites. Conclusions from this part of this study are the following:

- Assuming that all the TCE extracted during the field demonstration was initially present in our model of the site (and not from more distant areas, as some of the monitoring data suggest), our modeling shows that 15% of the total TCE present

initially at the site was removed after 139 days. The TCE removal curve is asymptotic. Removing 95% would take about 10 years. Removing 75% would take about 4 years.

- The main characteristic in assessing the performance of this technology at another site is the heterogeneity of the site. For a site with 10 times less heterogeneity (as measured by the average effective clay lens size) than the Savannah River site but otherwise identical, removing 95% of the total TCE present at the SRID site with *in situ* air stripping will take about half the time.

Finally, we used this history-match simulation as a basis to compare *in situ* air stripping with other remediation technologies. Conclusions from this part of this study are the following:

- Changing the lower air injection well into a groundwater pumping well results in almost twice as much TCE being extracted from the groundwater, but the amount of TCE below the water table that is removed in both cases is small (less than 10% in both cases after 150 days).
- Time required to achieve any given removal/destruction percentage is decreased dramatically if *in situ* bioremediation is successfully employed. The diffusion limits for injected materials to reach the TCE within the clays still exist, but once this diffusion takes place, the reaction proceeds rapidly and the TCE is destroyed. The main question with *in situ* bioremediation is whether reactions that are demonstrated in the laboratory can be carried out effectively to destroy VOCs under relatively uncontrolled field conditions.

1. INTRODUCTION

Volatile organic compounds (VOCs) including chlorinated solvents such as trichloroethylene (C_2HCl_3 , TCE) and perchloroethylene (C_2Cl_4 , PCE) are among the most common contaminants in groundwater and soils. A common remediation approach has been to pump the contaminated groundwater to the surface where the water is treated to remove the contaminants. This pump-and-treat approach has been successful in containing contamination and removing much of the contaminant mass at many sites. It has been less successful at remediating sites to the low levels of residual contamination required by regulatory agencies. Moreover, cleanup efforts based on pump-and-treat are often costly and slow, and they do nothing to remediate VOCs in the vadose zone which may be a long term sources of groundwater contamination.

The Office of Technology Development (OTD) in the Department of Energy's (DOE) Office of Environmental Restoration and Waste Management is investigating new technologies for "better, faster, cheaper, safer" environmental remediation. A program at DOE's Savannah River site was designed to demonstrate innovative technologies for the remediation of nonarid sites contaminated with VOCs in both the saturated and unsaturated (vadose) zones.

The purpose of this report is to assess the performance of the *in situ* air stripping technology demonstrated at the SRID site. (See also companion report Birdsell et al. 1994). *In situ* air stripping technology is a combination of air injection below the water table and vacuum extraction in the vadose zone, using a pair of horizontal wells. The system is complex. It involves the flow of air and water and the transport of VOCs in a heterogeneous subsurface environment. Some of the physical processes involved are not entirely understood. Our approach is based on the construction of numerical models that simulate the field demonstration (i.e., history matching). Through this modeling effort, we hope to increase our understanding of the *in situ* air stripping technology. We then use these models as a tool to investigate improvements to performance. (To optimize a system or a process, you have to have a quantitative model of how it works.) We also use these models to improve the prediction of *in situ* air stripping performance over longer periods of time and at different sites (e.g., to extrapolate "lessons learned" from a single field demonstration) and to compare the performance of *in situ* air stripping with other remediation technologies.

We begin with discussion of the SRID site and the *in situ* air stripping demonstration.

2. SAVANNAH RIVER TECHNOLOGY DEMONSTRATION

2.1 Location

DOE's Savannah River facility is located in Aiken South Carolina, near the South Carolina-Georgia border. The SRID site is part of a larger area that was used to process nuclear fuel and target elements for use in reactors. Degreasing operations were included at several stages of the processing. Chlorinated solvents, mainly TCE and PCE, were discharged to a seepage basin (M-Area Settling Basin) via a process sewer pipeline. In the early 1980s, inspections revealed that the process sewer line had extensive cracks, allowing solvents to leak into the subsurface environment. The SRID site is located at one of the areas where this sewer line is known to have leaked. See Fig. 2.1.

2.2 Site Hydrogeology

The Savannah River site is underlain by sediments of the Atlantic Coastal Plain. The upper few hundred feet of these sediments consist of interbedded sands and clays that were deposited in shallow marine, lagoonal and fluvial environments. The local topography is relatively flat with an average surface elevation of ~360 feet above mean sea level.*

The sediments that underlie the site are heterogeneous, varying greatly in thickness and continuity across the site. A generalized description includes a sand unit and four major clay units. These clay units are known as the green clay, the tan clay zone, the 300-ft clay and the 325-ft clay. The 325-ft clay and the green clay are described as clays whereas the tan clay and the 300-ft clay are described as clayey sands, sandy clays and interlayered clays and sands.

The water table lies at an elevation of ~230 ft, about 130 ft below the surface. A thin discontinuous aquitard (spatially undefined) exists at an elevation of ~225 ft separating a water table aquifer from a semi-confined aquifer. This semi-confined aquifer is separated from a confined aquifer by the green clay. See Fig. 2.2 and Eddy et al. (1991) and Eddy Dilek et al. (1993).

2.3 VOC Contamination

Sediments samples show the distribution of VOCs at the site to have been very uneven, generally concentrated in clay zones. The highest values for TCE and PCE in predemonstration sediment samples were 16.3 ppm and 8.75 ppm, respectively. The highest values for TCE and PCE in postdemonstration sediment samples were 6.3 µg/g and 1.6 µg/g, respectively.

The total subsurface inventory of VOCs at the site before the demonstration began is difficult to estimate. Based on sediment sampling data and interpolation calculations, Eddy Dilek et al. (1993) estimate a predemonstration inventory of ~1200 lbs of TCE and PCE for a volume about 300 ft by 250 ft wide centered over the old process sewer line. Monitoring data, however, indicate that over 16,000 lbs of TCE and PCE were removed during the 139 day *in situ* air stripping demonstration. The difference between the pretest inventory and the extracted quantity has been attributed to two causes: (1) contaminant from outside this volume was extracted during the demonstration and (2) initial inventory estimates are too low, because of losses during sampling. Additional details and discussion of the inventories are given in Eddy et al. (1991) and Eddy Dilek et al. (1993).

* Where original data are reported in English units, we have retained these units here.

2.4 Horizontal Wells

Two horizontal wells were used for the *in situ* demonstrations (Looney et al. 1991). One well was installed below the water table and used for air injection. This well is ~300 ft long and at an elevation of ~195 ft. A second well was installed in the vadose zone and used for vacuum extraction. This well is ~175 ft long and at an elevation of ~285 ft. The strike of the extraction well is ~35° to the strike of the injection well. Both wells are screened over most of their lengths and are subhorizontal, dipping toward greater depths at their terminal ends. Fig. 2.2 shows the well locations at the SRID site.

2.5 *In Situ* Air Stripping Demonstration

In situ air stripping combines the techniques of vapor extraction with air injection or air sparging. (For a recent review, see Johnson et al. 1993). Vapor extraction is designed to remediate contamination in the vadose zone. The principle behind vapor extraction is straightforward. Fresh air is drawn by vacuum through a contaminated soil toward an extraction well. This fresh clean air flushes contaminated air from the soil pores. By replacing contaminated air with fresh air, the process causes contaminants in the liquid phase to volatilize to reestablish vapor-liquid equilibrium. These vapor-phase contaminants are then removed by further vapor-phase extraction. The fresh air can be drawn from the ground surface or supplied by an air injection well. Air sparging is the injection of air below the water table. VOCs from the liquid phase move into the air phase and are carried upwards to the vadose zone with the rest of the injected air. In the case of *in situ* air stripping, the air drawn to the vapor extraction well is fresh air from the ground surface and contaminated air from the underlying groundwater. A schematic of the processes involved in this technology is shown in Fig. 2.3.

The *in situ* air stripping demonstration at Savannah River took place over 139 days between July 1990 and December 1990. Details of the field demonstration are given in Looney et al. (1991). The first 15 days of the demonstration consisted of vapor extraction alone at 580 standard cubic feet per minute (scfm). Air injection at a variety of rates—65 scfm, 170 scfm and 270 scfm—was begun on days 16, 28 and 69 of the demonstration, respectively. The air injection portion of the demonstration was completed on day 113. Over the 139 days of the demonstration, ~16,000 lbs of VOCs were removed. Figure 2.4 shows the injection and extraction well rates over the course of the field demonstration and the VOC concentration at the extraction well as a function of time.

3. HISTORY MATCHING SIMULATIONS

3.1 Some Preliminary Observations

Before describing the large number of numerical simulations performed, we make some preliminary observations to place the modeling results in perspective and to provide evidence backing some of the assumptions made in the history matching study.

In Fig. 2.4, (b) shows the concentration of VOCs at the extraction well versus time during the course of the 139 day field demonstration. Note that after an initial high concentration of VOCs, the concentrations fall off rapidly after the first few days to rather steady concentrations for the rest of the demonstration. This suggests that after the most accessible VOCs are removed, breakthrough of fresh air from beyond the contaminated zone takes place to lower the concentrations. However, VOC removal continued at significant levels for many days, suggesting that there is a large source of these VOCs that are relatively difficult to remove but that are somewhat accessible to air. We assume that this behavior is due to a mass transfer limitation between liquid-phase VOCs held up in clay lenses and the moving air, which travels predominantly in the surrounding sandy zones of higher permeability.

Another characteristic of the field results of note is that the addition of air injection at day 16 increased the removal rate of VOCs by only a small amount over the removal rate with vacuum extraction alone. This is especially true for TCE. Note the relatively constant concentration of TCE at the extraction well even after the air injection phase began. Of course it is impossible to know what the extraction curve would have looked like in the absence of air injection. The two possibilities are (1) the extraction was not aided significantly by air injection, and thus the removal rates would have been nearly the same without air stripping; or (2) the constant removal rates until the end of the demonstration were due to a significant contribution from air stripping, without which extraction efficiency would have declined dramatically. Modeling will allow us to distinguish between these two options.

The partitioning of a chemical between the vapor and liquid phases can be described by a relationship known as Henry's Law, which assumes a linear, equilibrium relationship exists between the liquid- and vapor-phase contaminant concentrations. A simple calculation for the saturation, porosity, and other soil parameters typical of the SRID site indicates that TCE partitions about 50% in the air and 50% in the fluid on a mass basis. A volatile contaminant like TCE lends itself nicely to removal by *in situ* air stripping. If for example, flow were homogeneous and there were no transport limitations for TCE to travel between the liquid (including sorbed TCE) and moving air, then the time required to remove the majority of the TCE should be only twice the time required to displace the volume of air within the contaminated zone. The fact that TCE was being withdrawn at nearly a constant rate for much longer times than this suggests that other transport processes in addition to Henry's Law equilibrium are at play.

Initial concentration profiles measured within the soil in both the vadose zone and below the water table show that there is an extremely variable distribution of contaminant as a function of position. VOCs are present at high concentrations at certain depths, while at other depths, the concentrations are below the detection limit. The high concentrations appear to correlate with higher clay content, which in turn are the low permeability regions at the site. Thus, a plausible mechanism for the rate limitations discussed above is slow transport of the contaminant out of the clay lenses via diffusion. Since the clay will tend to sorb VOCs to a much greater extent than the sands, the majority of the initial contaminant inventory probably resides in the clay lenses.

Determining accurate values for the initial TCE inventory (in the air, in the water, and on the soil surface) is very difficult (see Section 2.3). The working assumption for this history matching study is that all of the contaminant that is eventually extracted is present within the model

domain and that the concentration levels are adjustable within reasonable bounds. If this assumption is incorrect and much of the extracted contaminant is from outside the model domain, the conclusions of this study will not be qualitatively affected provided that the key assumption—that the process is diffusion limited—holds true.

3.2 Conceptual Model

Based on the discussion of the previous section, the following conceptual model is used to set up the calculations. Fluid phase transport is governed by solving mass and momentum balance equations for the two phases, air and water, assumed to be isothermal. Heterogeneities are incorporated by assuming a dual porosity representation of the domain. In this formulation, the primary porosity (the sands) provides the long range pathways for air, water, and contaminant. The sands are hydraulically connected to a secondary porosity (the clays), which provides an additional storage capacity for fluids and contaminants. Transfer between the sands and clays occurs by advection, and, for contaminant, molecular diffusion. Thus clays do not themselves represent long-range pathways for flow and transport, but interact only through the sands.

Relative permeability curves (permeability versus liquid saturation) for the sands and clays are modeled using the van Genuchten relationship (van Genuchten 1980), with parameters chosen to be representative of sandy and clayey soils. Qualitatively, when a capillary pressure equilibrium between the sands and clays are established, the saturation level in the sands will be approximately 30% in the sands and 90% in the clays, reflecting the actual case when sands and clays are present together locally at the same horizon. The actual permeability values used in the simulations are of secondary importance, since for contaminant extraction modeling at a given air flow rate the pressure distribution will have only a small impact on the model results.

The initial contaminant distribution is assumed to be a zone of constant liquid concentration extending from the ground surface to the depth of the injection well. Contaminants present at greater depths would not be swept by the injected air. The VOCs partition between the water and air phases in accordance with Henry's Law. In addition, increased levels of contaminants are present in the clays due to sorption. Equilibrium sorption is assumed with a linear sorption isotherm.

When air extraction and injection are established, the primary mode of transport of VOCs over long distances will be via the air phase, with relatively little water movement (although the numerical model does account for water movement as well). Transport from the soil to the liquid and the liquid to the air are instantaneous at any position, given the model assumptions stated above. Transport limitations giving rise to the observed results will thus be limited to diffusion out of the clays, where the bulk of the contaminants is assumed to reside. Thus the characteristic size of a clay lens and the air and water diffusion coefficients (all model parameters that can be varied) will govern the rate of VOC movement out of the clays and, eventually, to the extraction well.

3.3 Numerical Model

The computer code Finite Element Heat and Mass (FEHM) is used in the present study to carry out the history matching simulations (Zyvoloski et al. 1992). FEHM is a three-dimensional finite element heat and mass transport code that solves either one- or two-phase (air-water) fluid flow problems. The two-phase fluid flow solution is obtained by solving Darcy's law and continuity equations for both phases. The solute transport module allows the solution of multiple solutes that interact via chemical reaction models. The solutes may be specified as either liquid, vapor, solid, or Henry's Law species, and may also sorb to the solid surfaces (modeled using a sorption isotherm approach). The nonlinear equations arising from discretizing the fluid flow, heat transfer, or solute transport equations are solved with a Newton-Raphson technique, with the

corresponding linear equations solved using a preconditioned, conjugate gradient method. For details, see Zyvoloski et al. (1992) and Zyvoloski and Dash (1990).

Figure 3.1 shows the model domain and initial and boundary conditions. The two-dimensional, axisymmetric model grid (half-domain of 500 m in the horizontal; 60 m in the vertical) is shown in Fig. 3.2, (a) and (b). The view is along the horizontal wells, assumed to be parallel and thus represented as a point source or sink in the model domain. These points are located at appropriate positions along the axis of symmetry (the boundary on the left side of the domain). The thickness of the domain in the unmodeled direction is 78 m, the approximate distance over which the open-hole sections of the injection and extraction wells overlap. The top boundary is a constant air pressure boundary, while the other three sides are no flow boundaries. (We note that this grid is similar to the one used by Buscheck and Nitao [1992] in their modeling study.) The grid is refined in the area of the extraction well. The size of the element representing the source and sink well is approximately the size of an actual wellbore, thus resulting in as realistic as possible a simulation (given the limitations of two dimensional simulations).

We model only TCE to simplify the calculations. The concentration of TCE in the contaminated zone is assumed to be 1000 ppm by volume in the vapor phase, which corresponds to a liquid-phase concentration of 3.2 ppm. This zone extends out 25 m in the horizontal direction (1/2 of 50 m total extent, since this is an axisymmetric calculation) and down to the water table. Below the water table, the liquid concentration is set to 3.2 ppm as well to a depth of 50 m. Within the clays, the concentrations are the same, but in addition the soil contains sorbed contaminant at a variable concentration (adjusted to achieve a match to the data). Thus the majority of the contaminant resides in the clays. Note that the total inventory of VOCs is an adjustable parameter in these simulations; the air phase VOC concentration is the parameter held constant.

3.4 Simple "Single Porosity" Simulations

Before describing a series of more complex and complete dual porosity simulations of the entire 139 day demonstration, a set of single porosity calculations of the initial extraction phase of the demonstration (the first 16 days) will be presented to elaborate on some of the concepts described in the previous sections. Although none of these simulations are to be considered matches to the data, they are instructive to illustrate the time scales for changes in TCE concentration at the extraction well to take place under the simplest model assumptions.

In the first set of simulations, we examine the concentration of TCE at the extraction well for the case of displacement from the vapor phase only and interchange of TCE from vapor to liquid. Figure 3.3 is an example of a simple displacement process at extraction rates equal to that of the first 16 days of the test, before injection started. Note that for these conditions and the assumed extent of the plume, displacement of all vapor-phase TCE would occur, with extraction concentrations approaching 0. The time scale of the drop-off of concentration with time is similar to the observed values, so we may conclude (tentatively) that the initial drop-off is the result of a contaminant breakthrough process in which fresh, uncontaminated air from beyond the contaminated zone starts to arrive at the extraction well. For this site, extraction at the flow rate selected at the start of the test will result in breakthrough of fresh air within a few days. For the case of Henry's Law equilibrium between TCE in the liquid and vapor phases, the decrease of the concentration is more gradual because, as stated above, there are approximately equal amounts of TCE in the liquid and vapor phases, resulting in an initial inventory that is twice as large. Nonetheless, the curves are qualitatively similar.

Of course, in the field demonstration the concentration of TCE in the extracted air does not drop completely to 0 in a few days as in this initial simulation. We will now consider a rate-limited model in which interphase TCE equilibration is not instantaneous, but is governed by a reversible, first-order reaction rate law. Using FEHM, this is implemented as a chemical reaction

$TCE_l = TCE_v$, assuming a first order reversible reaction with given rate constants for the forward and reverse reactions. The rate constants are set such that when rates are rapid compared to the transport time, Henry's Law behavior is retained. Since the Henry's Law constant is an equilibrium constant, the selection of appropriate rate constants is achieved such that the ratio of the reverse and forward rate constants equals the Henry's Law constant. However, the implementation as a reversible reaction with given rate constants allows us, by varying the magnitudes of the rate constants while keeping the ratio constant, to examine mass transfer effects in the event that Henry's Law is not valid for this system.

Figure 3.4 shows the results of these simulations. As the kinetics become slower, the differences with the Henry's Law behavior show up first at early times, where the reaction cannot occur rapidly enough for local equilibrium to be valid. Therefore, for slower kinetics, the TCE curve begins to look more like the case of no interchange of TCE between vapor and liquid. However, at longer times, equilibrium is closer to reality even for the slower kinetics (i. e., the initial decline is rapid but a plateau is reached whereby the air being drawn to the well spends sufficient time in the contaminated zone to strip some TCE from the liquid even if it cannot reach the Henry's Law equilibrium). A kinetically controlled process such as this can thus be invoked to explain the rapid initial decline followed by a period of quasi-steady extraction well concentration over long times.

Despite the use of this nonequilibrium model here, we are not saying that this particular kinetic process is controlling the behavior of this demonstration, merely that some process such as this explains the data. In fact, it seems that another kinetically controlled mechanism is equally or more likely: namely, mass transfer limitations due to slow diffusion from clay lenses into the more permeable sandy zones. This phenomenon will be simulated in the next section.

The previous simulations neglected the fact that there may be TCE sorbed to the soil surface. To simulate this process with FEHM, we assume that the TCE in the water is in equilibrium with sorbed phase TCE, with the same reversible reaction controlling transport between the liquid and air phases. Figure 3.5 shows the results for simulations with kinetic parameters such that equilibrium is attained between TCE in the fluid and air, but with the addition of sorption on the soil. The system with sorption behaves in a similar way as one without, but the time required for concentrations to decline to a given value is greater. The system with sorption behaves qualitatively as though TCE has a lower Henry's Law constant. For a VOC that sorbs to the soil surface, only the portion of the organic that is present in the liquid will volatilize at any given time. DiGiulio (1992) discusses the effect of sorption on the relative quantities of VOC present in the various phases. The usual Henry's law constant applies for the relative amounts of material in the liquid and vapor phases, with an additional amount of immobile VOC present on the solids. In effect, sorption lowers the effective Henry's law constant by providing another place for the organic to reside (the solid surfaces). Thus, movement of TCE from the clays in the preceding calculations proceeded more slowly than would a nonsorbing organic, and can be conceptualized as a lower effective Henry's law coefficient.

Figure 3.6 shows the effect of varying the sorption coefficient, K_d , for kinetics that are 100 times slower than the Henry's Law case. (Recall that the total inventory of VOCs is not constant, so an increase in K_d corresponds to an increase in total TCE inventory.) The initial breakthrough of fresh air is controlled by the kinetics of the interchange reaction, but the plateau is much flatter for larger values of K_d . There is a much greater supply of TCE when it is sorbed to a greater extent on the rock, but since the height of the plateau is controlled by the rate at which it transports from liquid to vapor, the quasi steady concentration after about 5 days is kinetically controlled. The main difference would be at longer times, where the higher K_d system takes much longer to extract all of the contaminant. This is suggested by the simulations by the flatter plateau of concentration versus time. Measured values of the K_d for the SRID site ranged from less than 0 (clearly an artifact of a measurement problem) to 0.6 ml/g, with most values ranging from 0.1 ml/g to 0.2 ml/g. These values are also highly position dependent, since they are

probably related to the fraction of organic carbon in the soil, which in turn is highly variable (non-detectable to 4000 mg/kg (Eddy Dilek et al. 1993).

3.5 More Complex "Double Porosity" Simulations

The previous simulations established the usefulness of employing a rate-limited mechanism to qualitatively explain the extraction data. Given the nature of the hydrostratigraphy of the site, it is likely that diffusional processes taking place in the low-permeability clays will give rise to the observed rate limitations associated with the long tail of TCE concentration at the extraction well. The FEHM model has a dual porosity feature that requires the following additional input: (1) percentage of primary (sands) and secondary (clays) porosity; and (2) the characteristic length scale of the secondary porosity. The latter may be thought of as the distance over which the fluid and contaminant must travel within the clay lenses. If the clay lenses are irregularly shaped, then this dimension is the smallest dimension of an average clay lens.

The size of a clay lens enters into the rate of diffusion approximately through an order of magnitude calculation of the characteristic diffusion time, which equal Sc^2/D_m , where Sc is the length scale and D_m is the molecular diffusion coefficient. For all SRID simulations, Sc is assumed to be 1 m, and the molecular diffusion coefficient is allowed to vary. This assumption was made to simplify the history matching procedure by reducing the number of adjustable parameters. The diffusion coefficient of interest is the air phase molecular diffusion coefficient of TCE. Typical diffusion coefficients in free air are of order 10^{-6} m²/s, but clay lenses are apt to have quite tortuous air pathways, and in lenses that are about 90% water-filled, the remaining pores will have even more tortuous paths for TCE diffusion. Thus, although the parameter is very uncertain, the molecular diffusion coefficient for TCE in air in the clay lenses could be an order of magnitude lower than the value in free air.

In the first set of dual porosity simulations, we examine the effect of diffusion coefficient on the simulated TCE concentration at the extraction well. Figure 3.7 shows that a diffusion coefficient of 3×10^{-7} m²/s is required to achieve a good match to the initial stages of the test, but for these parameters at later times, the concentration falls off too rapidly. Thus it is assumed that the diffusion limitations are properly accounted for, but the initial inventory of TCE is not large enough to keep the concentrations elevated for the length of the test. The characteristic diffusion time is of the order of 115 days, which could also have been obtained with larger clay lenses and smaller diffusion coefficients (or smaller lenses and larger diffusion coefficients).

Figure 3.8 shows the effect of changing the fraction of the material assumed to be sands (the remainder is clay). This parameter has a relatively minor effect because the inventory of TCE present initially is changed by a relatively small amount, and the rate of diffusion from the clays are unchanged by this parameter. The data still are not adequately matched at long times.

Next, the effect of liquid saturation in the clays on the simulation results was examined by changing the relative permeability parameters of the clays. Figure 3.9 shows that the saturation of the clays also has little effect on the results, all else being equal. Of course, the saturation would probably indirectly change the behavior by changing the diffusion coefficient, but this parameter is a separate input in this model, and was not changed during these runs.

Increasing the sorption coefficient increases the initial amount of TCE present, and thus should impact the simulation results at long times. Figure 3.10 shows that this is indeed the case, with the largest sorption coefficient providing an adequate fit to the data, even at long times. There still appears to be a mild downward trend in the concentration that is not present in the data, but the match is fairly good.

At this point, we will examine the processes occurring below the water table in an effort to assess the impact of air injection on the effectiveness of the process. First, a computation was carried out using the parameter values used in obtaining the match but with the TCE present only below

the water table. Figure 3.11 shows that the air injection is predicted to add relatively little to the effectiveness of the process. However, the slow decline in concentration at long times present in the simulation can be attributed to the depletion of TCE below the water table. Either the sweep of air through the contaminated region of the saturated zone is inadequate to provide a supply of TCE over long times, or else there is somehow more TCE available for extraction in the actual case than was assumed in the model. The next series of calculations will probe this question.

A helium tracer experiment was carried out during the injection phase in which helium was injected as a pulse with the injected air, and the concentration versus time was monitored at the extraction well and at other monitoring wells. We will simulate this test by injecting helium as a vapor-phase tracer at a constant concentration and compare the simulated results to the integrated fractional response curve published in Looney et al. (1991). To examine the effect of anisotropy on the sweep of air through the saturated zone, three simulations were performed: a 1:1, 10:1, and 100:1 permeability ratio, with the larger permeabilities in the horizontal direction. Figure 3.12 shows that as the anisotropy increases, the effective sweep of helium (and air) increases. This is also seen in the two contour plots of liquid saturation shown in Fig. 3.13. Without anisotropy to force air in the horizontal direction, air rises very rapidly, sweeping through only a very small amount of soil.

Also noteworthy in Fig. 3.12 is that even for the highest anisotropy used, the residence times for air to travel from injection to extraction are too short in the simulation. In addition to the volume of soil swept, the vapor saturation also affects the travel times of the tracer. For the relative permeability relationships assumed in this model, air flows through the saturated zone at very low vapor saturations, meaning that there is a very small transit time for air displacement to take place. This factor could be corrected by changing the relative permeability parameters to force air to travel only at higher vapor saturations. Nonetheless, the overall extraction concentration is still reproduced adequately with the present set of parameters.

Thus far, the transport properties of the soil have been assumed to be independent of position. The philosophy behind these simulations has been that the simplest possible model that explains the data adequately is preferable to one that is more complex, even if it is known that the system is highly heterogeneous. To this point, heterogeneities have been accounted for within the context of the dual porosity implementation, which automatically incorporates clay heterogeneities into the model. However, a factor which may add accuracy to the injection phases of the calculations is a proper accounting for the fact that the tan clay zone is swept by the injected air. Thus the assumed value of 30% clays is probably too low for this zone, and the air injection effectiveness may be underestimated for this reason. Figure 3.14 shows the effect on the predicted results of assuming 30%, 55%, and 80% clays in the tan clay zone, assumed to be present from the injection depth to a depth 10 m above the water table. The trends are in the right direction, with the air injection contributing more to the total extraction process. However, the magnitude of the effects are quite small, showing that including this zone in the domain is probably unnecessary.

3.6 Final History Match Simulation

Figure 3.15 shows the output of our final history match simulation and the data from the actual field demonstration.

The basic model domain and boundary and initial conditions are given in Fig. 3.1. In this final simulation, we assume a homogeneous, dual porosity medium that is 70% sand and 30% clay. The sand is anisotropic with a horizontal permeability of $2.5 \times 10^{-10} \text{ m}^2$ and a vertical permeability of $2.5 \times 10^{-12} \text{ m}^2$. The clay permeability is $2.5 \times 10^{-12} \text{ m}^2$ (in a dual porosity formulation, there is only one dimension for flow in the clay). The van Genuchten parameters for the sand and the clay, respectively, are $\alpha(1/\text{m})=0.5$, $\beta=7$, res. liq. sat=30% and $\alpha(1/\text{m})=0.15$, $\beta=1.2$, res. liq. sat=0.01%. The initial saturations are those at hydrodynamic equilibrium—

approximately 34% for the sands and 91% for the clay. The diffusion coefficient for air in the clays is $3 \times 10^{-7} \text{ m}^2/\text{s}$. Henry's law coefficient is $9.9 \times 10^{-3} \text{ atm-m}^3/\text{mol}$. Finally, K_d values are 0 and 6 g/cm^3 for the sand and clay, respectively.

The total initial TCE inventory in the domain for this simulation is 15,700 kg—4,240 kg below the water table and 11,460 kg in the vadose zone. The total TCE extracted from the system over 139 days was 2290 kg (15% of the total)—280 kg from below the water table (~7%) and 2,010 kg (17.5%) from the vadose zone.

The model setup for this simulation will be the base model for the remainder of this report. Keep in mind that the working assumption for this history matching study is that all of the contaminant that is eventually extracted is present within the model domain, but that, the conclusions of this study will not be qualitatively affected provided that the key assumption—that the process is diffusion limited—holds true.

4. TECHNOLOGY OPTIMIZATION

Using the parameter values obtained in the history matching, we may now examine the effect of different operating strategies on the predicted performance of this technology. In this way, modeling may be used to guide the design of future systems .

4.1 Cyclic Operation

The first set of simulations examines the effect of cyclic injection and extraction versus continuous operation. Costs will be lowered if the system can be operated on an intermittent basis. The question is whether the penalty paid in terms of decreased average mass removal rate justifies this decrease in operating costs. To examine the efficiency of the process under this scenario, two simulations were run: one with continuous operation at the injection and extraction flow rates employed during the high-injection rate stage of the demonstration, and the other in which these same flow rates were used on a 30-day-on, 30-day-off schedule. Figure 4.1 shows that there is an increase in the removal rate at the start of each cycle that partially compensates for the shut-in period during which the removal rate is 0. During normal operation, large concentration gradients are set up within the clay lenses due to the diffusion limitations. When the system is shut in, TCE continues to diffuse out of the clays, resulting in higher concentrations when operation is resumed.

For these simulations, the total mass removed for continuous operation was 3196 kg after 180 days, whereas for cyclic operation the mass removed was 2068 kg over the same period. Thus, the average removal rate decreased only 35% despite operating for only half the time. (Note that if there were no benefit to the cycling, the removal rate would decrease by 50%.) This result is valid for the case of air-stripping and vacuum extraction, as well as a vacuum extraction system with no air stripping. Figure 4.2 shows qualitatively similar results when only extraction is employed. In this case, continuous operation yields a total mass removed of 2632 kg, while the cyclic operation resulted in a removal of 1786 kg, or a difference of 33%. The decision of whether to employ air injection does not affect the conclusion that cyclic operation could be a favorable technique for lowering operating costs.

Of course, the system parameters have not been optimized in these simulations, nor will the optimized cyclic conditions be the same for each site. For example, higher flow rates during periods of operation may be preferable to selecting the same rate as would be used during continuous operation. Also, different sites will have different characteristic diffusion times, which will impact the optimal period of the cycles. In general, the shut-in time must be a significant fraction of the diffusional time to allow mass to diffuse out of the low-permeability zones. Nonetheless, this calculation shows that cyclic operation may provide an economically superior operating strategy for remediation using this technology.

4.2 Flow Rates

In this set of simulations, the effect of the extraction flow rate on the mass removal rate of TCE is examined for the case of no air injection (the conclusions are not expected to change with air injection included). Operating costs may be lowered if the system can be operated at lower extraction rates. Figure 4.3 shows the impact on the TCE concentration at the extraction well of varying the flow rate over a range of a factor of four, with the intermediate flow rate equal to that during the field demonstration. The rate of removal is governed primarily by the diffusion rate, so that fresh air drawn more rapidly from beyond the contaminated zone reaches a lower concentration than for the low flow rate cases. Thus, in a system with diffusional limitations governing the mass removal rate, increasing the extraction flow rate results in a lowering of the

outlet concentration with relatively little benefit in the mass removal rate. In fact, the total mass removed for the three cases are 2914 kg for the highest flow rate, 2632 kg for the intermediate rate, and 2162 kg for the lowest rate. Thus, increasing the flow rate by a factor of four results in only a 26% increase in the removal rate. Clearly an optimum exists between the need to remove mass quickly and the operating costs, and it may be that lower extraction flow rates represent an attractive alternative operating strategy. This conclusion is site dependent for the same reasons presented in the section on cyclic operation above.

4.3 Thermally Enhanced Processes

Starting on day 49 of the field demonstration, the injected air was heated to approximately 145°F for the duration of the test. To examine the potential impact of heating of the air on the efficiency of the extraction process, we will carry out an approximate calculation external to the computer simulations. The main questions being asked are (1) how much heat is being deposited in the subsurface due to heating of the injected air; (2) what is the distribution of temperatures in the subsurface; and (3) what possible impact would this have on the transport of TCE? The amount of heat deposited is easily obtained by computing the following expression:

$$\int_0^t \dot{m} c_p \Delta T dt$$

where $\dot{m}$ is the mass flow rate, ΔT is the temperature difference between the injected air and ambient conditions, and c_p is the heat capacity of air. For the conditions of the demonstration, a total of $3.09 \times 10^{10} \text{ J}$ was deposited in the formation. The eventual temperature distribution is governed by the heat transfer processes occurring in the formation. For this calculation, we assume that efficient heat transfer between the air, water, and soil results in a rapid increase in water and soil temperature up to the injection temperature. Thus, a hot temperature wave progresses away from the injection region, and the size of this temperature-perturbed region is given by

$$V_{\text{HX}} = \frac{Q_{\text{HX}}}{[\phi S c_{p,f} + (1-\phi) c_{p,s}] \Delta T}$$

where Q_{HX} is the total heat deposited ($3.09 \times 10^{10} \text{ J}$), and the subscripts "f" and "s" refer to the fluid and soil, respectively. For typical values for the parameters in this expression, the total volume heated to the inlet air temperature is 229 m^3 . This volume is equivalent to a sphere of diameter 7.6 m, so that the thermally perturbed zone probably did not even reach the vadose zone during the test. This calculation points out the difficulty of influencing a large volume of soil using hot air, due to the small heat-carrying capacity of gases compared to the heat capacity of the surrounding medium. Perhaps steam injection, with the large latent heat of vaporization as it flashes, would allow a larger zone to be influenced.

Given that at any time a small region surrounding the injection region is heated to higher than ambient conditions, the remaining issue is how this perturbation affects the extraction of TCE. Assuming Henry's law, it is likely that in the higher temperature zone the concentration of TCE in the air phase will be elevated relative to the case of no heating because of the greater volatility. However, as soon as the air travels into the region that is at ambient temperature, TCE will redissolve into the water at the lower Henry's law constant. While there will be some "conveyer belt" effect gradually moving TCE closer to the extraction well over time, there is no significant enhanced extraction efficiency at the extraction well.

Only when the thermal front has reached the extraction well, and the Henry's law constant becomes elevated at all points along the pathways from injection to extraction, will the heating benefit the extraction efficiency. As shown above, this would take much longer than the duration of the demonstration. This will also generally be the case for most processes of this type (i. e., it will be very difficult to increase the removal rate by heating the injection gases). It should be noted that, in accord with this discussion, there was no discernible increase in the removal rate in the demonstration when heating of the injected air was initiated during the actual field demonstration.

4.4 Placement of Horizontal Wells

The relative placement of horizontal wells is not directly treated in this modeling study, but is discussed here qualitatively. Two considerations are important: (1) the angle the wells make with respect to each other in map view, and (2) the direction of the wells in relation to the plume shape.

Regarding the placement of the wells with respect to each other, at first glance it might seem that an angle of, say, 60° would provide a better sweep of air through the contaminated region than wells directly aligned with one another. However, heterogeneities are likely to force the spreading of air through a large region of soil even for aligned wells. In this sense, heterogeneities aid the air stripping process, though the disadvantages of mass transport limitations probably almost certainly outweigh these gains. Thus, it is not clear that aligning the wells at an angle to one another is advantageous or even necessary.

Regarding the placement of the injection well with respect to the plume, the injection well should be placed enough below the plume to allow the air to spread laterally before reaching the zone of contamination. Unfortunately, there is probably no easy way to determine *a priori* how far below the plume the well should be completed. Its angle should be directly aligned with the major axis of the plume for the greatest likelihood of adequate air sweep through the plume. Since the spreading of air will be controlled by heterogeneities, there will always be some luck involved in well placement for achieving an efficient air stripping process, since obtaining such detailed information on the heterogeneities would be impossible.

The placement of a horizontal vacuum extraction well relative to the contaminant plume is discussed in Birdsell et al. (1994). That study concluded a horizontal vapor extraction well should be placed at the lower edge of the plume and aligned with the plume's major axis (in the horizontal plane), and a vertical well should be placed in the center of the plume. Note that this assumes a system of extraction alone. With the addition of air injection from below, the horizontal well can probably be moved upward to a more highly concentrated region of the plume.

4.5 Mixing Horizontal and Vertical Wells

This history matching study was carried out in two dimensions using horizontal, aligned wellbores. Birdsell et al. (1994) examine the effectiveness of horizontal versus vertical wells for vacuum extraction in the vadose zone. They found that for most cases studied, a single horizontal, vapor extraction well outperforms (i.e., achieves a lower level of residual contamination in a shorter amount of time) a single vertical, vapor extraction well (at a capped site) operating at the same extraction rate only for a long linear plume. "Long" was defined as a plume that extends beyond the radius of influence of the vertical well. They noted, however, that the radius of influence of a vertical well can often be increased so that it "beats" the horizontal well by increasing its extraction rate. They also showed that for cases in which the horizontal well exhibited better performance, the difference could often be eliminated with additional vertical extraction wells.

By contrast, for the injection well, assuming that it is completed in the saturated zone to strip VOCs from below the water table, there is likely to be a large advantage of horizontal wells that will overcome any drilling cost considerations. Because of the buoyant flow of injected air upwards, an extreme short-circuiting of air to the vadose zone is likely with vertical wells. With horizontal wells, although some short-circuiting is inevitable, the lateral coverage of the well will allow for a much broader sweep of air through a contaminated plume. Since alignment of the injection and extraction wells is probably not necessary (see Section 4.4), a system consisting of a horizontal air injection well combined with vertical extraction well(s) in the vadose zone with surface capping would appear to be optimal.

5. PERFORMANCE PREDICTIONS

5.1 Long-Term at the SRID

Given the history match final simulation (Fig. 3.15) as a base model, the next set of calculations is to assess the predicted long-term behavior of the system. Figure 5.1 shows the results out to 5 years for *in situ* air stripping. TCE is predicted to be extracted at significant quantities for many years. The rate-limiting step which is not overcome is the diffusional process of TCE moving out of the clay lenses.

Table 5.1 shows the length of time required to remove a given fraction of the initial TCE inventory and the percent of the initial inventory removed from the vadose zone and the saturated zone respectively. The total fraction of TCE removed is only 50% after 1.8 years, thus pointing out the difficulty of reaching large removal fractions for a heterogeneous system such as this. Also note that the vadose zone is relatively easier to remediate than the saturated zone. Furthermore, each successive increment of TCE removed is more difficult, due to the nature of the diffusional process occurring. We hasten to point out that since the initial quantity of TCE is uncertain, the fractional recovery estimate is very rough, especially since lesser or greater initial TCE masses would yield similar history match results. Nonetheless, the calculations illustrate a fundamental limitation of the technology that will be present whenever contaminant has diffused over long times into soil that is inaccessible to flowing air or water.

Table 5.1. Times Required (yrs) to Achieve Given Percent Removal of TCE at SRID Site Using *In Situ* Air Stripping

Percent removal of TCE:	<u>50%</u>	<u>75%</u>	<u>90%</u>	<u>95%</u>	<u>99%</u>
Years:	1.8	3.7	6.7	10.2	>27
Percent removal of TCE initially present in the vadose zone:	56	81	95	99	
Percent removal of TCE initially present below the water table:	35	58	76	85	

5.2 At Other Sites

Thus far, the focus of our long-term performance predictions and suggestions for technology optimization have been based on the Savannah River Site, or a site with similar characteristics. What can we say with respect to the performance of *in situ* air stripping at other sites? To transfer conclusions from the SRID demonstration to other sites, we will carry out a series of additional simulations.

We believe that the most important characteristic in assessing the potential performance of this technology is the degree of heterogeneity of the site. (We note that the importance of heterogeneity as a critical parameter for assessing processes involving subsurface flow and transport has been suggested by others; see for example Chesnut [1993]. We assume the geologic environment consists of sands and clays. The degree of heterogeneity is parameterized using the average length scale of clay lenses, because diffusion from the clay lenses was shown

to be the rate limiting step for transport. The clay lens size was 1 m for the history match calculation. This parameter is varied in this set of calculations to assess its affect on technology performance.

Table 5.2 shows the times required to achieve a given level of removal of TCE for clay lens sizes ranging from 0.1 to 1 m. For sites with smaller heterogeneities than the Savannah River site, the times required to achieve a given percentage removal are less, especially for the lower percentage removals. Material diffuses much more quickly from the smaller heterogeneities, and mass removal rates are thus much larger at early times. At later times when removal of the remaining few percent of material is being achieved, the behavior is increasingly controlled by larger scale heterogeneities, modeled here as an effective dispersivity of the medium. Thus, if extraction efficiencies of up to, say 75%, are acceptable, reasonable clean-up times can be achieved when the characteristic length scale for diffusion limitations is small enough.

Table 5.2. Times Required (yrs) to Achieve Given Percent Removal of TCE as a Function of Clay Lens Size

clay lens	Percent removal of TCE			
	50%	75%	90%	95%
1 m	1.8	3.7	6.7	10.2
0.3 m	0.64	1.5	3.4	6.0
0.1 m	0.54	1.3	3.2	5.8

The above conclusion can be made more general by considering that a characteristic diffusion time, S^2/D_{eff} , where S is the length scale and D_{eff} is the effective diffusion coefficient from the clay lens, is a more fundamental parameter. Since both S and D_{eff} are largely unknown, the approach in this study was to adjust these parameters within reasonable ranges to obtain the match. The resulting diffusion time for the history match was 155 days, compared to 1.55 days for the 0.1 m clay lens. It is this parameter that is probably a more fundamental measure of the susceptibility of the VOC to be removed by this process.

A practical means for measuring this parameter is through pilot testing. A particularly sensitive technique may be the cyclic testing of the sort modeled above. Figure 5.2 shows that the system will respond much differently to this sort of transient if its characteristic diffusion time is lower. Carrying out this test with accompanying modeling analyses could allow total clean-up times to be estimated more accurately.

At first glance, measurement or estimation of the individual parameters S and D_{eff} might seem to be possible, but in practice, accurate estimates may be difficult to produce. The average length of a clay lens may be determined through examination of drilling logs, but the question of representativeness of a particular site characterization well will always be present. Regarding the diffusion coefficient, the magnitude of this parameter will depend on the free diffusion coefficient of the VOC in air (easily estimated), and the tortuosity of the connected pathways through the air-filled pores in the clays. The latter is probably impossible to obtain from first principles, it being in turn dependent on the tortuosity of the pore space and the vapor saturation. Thus the fallback position is to obtain an estimate of the characteristic diffusion time, a lumped parameter that defines the degree to which diffusional limitations exist.

Another parameter that greatly affects the ability to extract VOCs is the extent to which they are sorbed to the surface of the soils. As pointed out above, the TCE partitions roughly 50% in the water and 50% in the air for the sands, where sorption was assumed to be negligible. However, the VOC subject to Henry's law equilibrium does not include the VOC sorbed to soil surfaces, such as was the case for the clays. The result can be thought of as a lowering of the effective Henry's Law coefficient of the VOC.

6. COMPARISON TO OTHER REMEDIATION TECHNOLOGIES

In this section, we compare *in situ* air stripping, as demonstrated at the SRID site, with other remediation technologies. We consider the performance of *in situ* air stripping as compared to pump-and-treat and *in situ* bioremediation. (For discussion of the role of well geometry, see Section 4.5.)

6.1 Pump-and-Treat

Since pump-and-treat remediates only contamination below the water table, this comparison will be performed using the parameters obtained in the history match, except that the plume will be placed only in the saturated zone. The reason for this assumption is that the interpretation will then depend only on the ability of the technology to remediate VOCs in the saturated zone, discounting any added extraction of vadose zone VOC in the case of *in situ* air stripping. Also, to factor out any effect of wellbore placement relative to the plume geometry, we assume that the well is horizontal for both cases.

Employing these assumptions, the two technologies can be compared directly. (We ignore for the moment that the VOCs removed from the saturated zone by air injection are not really removed from the system, but are merely transferred into the vadose zone). For the pump-and-treat case, the air injection well is converted into a pumping well at a rate of 200 gallons per minute (gpm). For the air injection simulation, the air injection flow rate is assumed constant at the highest air injection rate, and both simulations are carried out to 150 days. The results of comparison can be assessed by comparing the percentage of TCE removed from the subsurface after 150 days.

The air injection resulted in a removal of 4.7% of the TCE from below the water table after 150 days, compared to 8.6% for the pump-and-treat case. In effect, neither technology can effectively remove VOCs from the saturated zone because of the slow diffusion of the TCE from the clays. The pump-and-treat actually exhibits a somewhat more efficient extraction rate despite the slower diffusion in water. This is probably due to a less-than-complete sweep of air through the plume as it moves vertically to the vadose zone. By contrast the horizontal flow established in the pump-and-treat case probably provides better access to the contaminant.

Nonetheless, neither technology provides easy access to the bulk of the contaminant, and there is probably no reason to favor one technology over another on the basis of these simulations, as small changes in flow rates will alter the percent removals slightly. The effectiveness of the air sweep at a given site will probably govern whether air injection will perform better than pump-and-treat technologies (with horizontal or vertical wells), and since performance is similar, relative costs will likely drive decisions on which technology to employ. (Note that small differences in performances may be significant in some cases, particular if groundwater contaminant concentrations are very high.)

6.2 Bioremediation

In principle, a technique that destroys VOCs in the subsurface is superior to one in which the pollutant is extracted and handled above ground. The question typically raised in assessing the applicability of bioremediation technologies is whether biological reactions that are demonstrated in the laboratory can be carried out to effectively destroy a VOC under relatively uncontrolled subsurface conditions. This question can be addressed through field scale demonstrations and accompanying numerical models that incorporate the bioreactions in the mass balance, such as TRAMP (Travis 1993). In the present study, we will examine, using a simplified reaction model meant to simulate a biodegradation reaction, whether bioremediation is likely to be effective for

a system governed by the conceptual model developed here. Note that this highly simplified "bioremediation" model is idealized (e.g., we neglect the real world of nutrient limits on bacterial growth, etc.); it represents an upper limit to possible success.

A simple, first-order degradation model will be assumed for this purpose. It is assumed that a gas with limited solubility is added to the injected air to initiate and sustain the reaction. This gas partitions between the liquid and vapor phases subject to Henry's law, and the following reaction is used to model the degradation

where $\text{S}_{(l)}$ is the portion of the scavenger gas dissolved in the liquid. The kinetics are chosen to be rapid enough that if the two reactants are in contact, the reaction proceeds to completion quickly. Thus, the mass transport limitations controlling the rate of diffusion of the scavenger gas into the matrix (which contains the majority of the TCE) will control the rate of destruction.

To allow direct comparisons with previous simulations, all operating conditions are assumed identical to those used in the long-term predictions for cleanup presented earlier, with injected scavenger gas added at the time air injection began. Table 6.1 shows the results of this calculation. The times required to achieve any given removal/destruction percentage is decreased dramatically if *in situ* bioremediation is employed. Although the diffusion limitations for scavenger to reach TCE within the clays still exist, once this diffusion takes place, the reaction proceeds rapidly and the TCE is destroyed.

Table 6.1. Times Required (yrs) to Achieve Given Percent Removal/Destruction of TCE: *In Situ* Air Stripping vs. Hypothetical *In Situ* Bioremediation

	<u>Percent removal of TCE</u>				
	<u>50%</u>	<u>75%</u>	<u>90%</u>	<u>95%</u>	<u>99%</u>
<i>in situ</i> air stripping	1.8	3.7	6.7	10.2	>27.4
<i>in situ</i> bioremediation	0.73	1.5	3.1	4.5	8.2

This calculation illustrates that if the technical challenges of making a bioremediation reaction proceed *in situ* can be overcome, this technology offers promise for obtaining high-percentage cleanups even in systems with severe mass transport limitations. For modeling studies of the *in situ* bioremediation demonstration conducted at the SRID site, see Travis and Rosenberg (1994).

7. CONCLUSIONS

We successfully simulated removal of one of the main VOCs present at the site (trichloroethylene, TCE) during the 139 day *in situ* air stripping demonstration at Savannah River using the flow and transport code FEHM. Conclusions from this history-matching part of this study are as follows:

- The TCE concentration at the extraction well versus time can be simulated very well using a relatively, simple model with a dual porosity formulation which assumes a mass transfer limitation between liquid-phase TCE held up in clay lenses and the moving air, which travels mainly in the surrounding sandy zones of higher permeability. More generally speaking, a kinetically controlled process for VOC removal can explain a rapid initial decline in VOC concentration at an extraction well followed by a period of quasi-steady concentrations over long times.
- A relatively large initial inventory of TCE (~16,000 kg) is necessary to match the TCE concentration at the extraction well versus time, if it is assumed that all the contaminant that is eventually extracted is present in the immediate vicinity of the site. After 139 days, ~15% of this inventory is removed—17.5% of the TCE initially present in the vadose zone and ~7% of the TCE initially present in the saturated zone. If this is not the case, the conclusions of this study are not qualitatively affected provided that the key assumption—that the process is diffusion limited—holds true. In fact, the conclusions of this report should hold true in general for any system with mass transfer limitations.
- Studies of the sensitivity of the TCE concentration at the extraction well versus time curve to various model parameters showed the following. The greater the amount of TCE sorbed onto the sandy material for a given VOC liquid concentration, the flatter the TCE versus time curve. The TCE concentration at the extraction well is sensitive to the assumed TCE air diffusion coefficient in clays, but not highly sensitive to the total amount of clay present or clay saturation level (within reasonable ranges). The curve is sensitive to the value of the equilibrium sorption coefficient for TCE on the clay only at large times.

We used this history-match simulation as a basis to explore ways to optimize the *in situ* air stripping technology. Conclusions from this part of this study are the following:

- Cyclic operation of the system may offer substantial cost savings for only a marginal performance cost. For example, operating the *in situ* air stripping operation on a 30-day-on, 30-day-off schedule results in only about a 30-35% decrease in total TCE removed.
- Similarly, operating the system at lower flow rates may offer substantial cost savings for only a marginal performance cost. For example, an increase in flow rate by a factor of four resulted in only a 26% increase in total TCE removal.
- The injection of heated air through the lower well is unlikely to result in increased VOC removal. This is because only a small region is heated at any one time and as soon as air travels from a heated region to one at ambient temperature, any "extra" TCE in the air phase redissolves. Only when the entire path from the injection to the extraction point is heated, will the heating benefit VOC removal.
- Aligning the injection and extraction wells at any particular angle to one another is probably not necessary. Heterogeneities in the medium are likely to be the dominant factor in governing the spreading of air in the saturated zone and for any reasonable configuration, it is very unlikely that VOCs stripped from the saturated zone would

not be captured by the extraction well. The injection well should be directly aligned with the major axis of the plume for the greatest likelihood of adequate air sweep through the plume. The horizontal vapor extraction well should ideally be placed at the lower edge of the plume and screened over the entire length of the plume (Birdsell et al. 1994).

- A system consisting of a horizontal air injection well and vertical extraction well(s) in the vadose zone with surface capping may be optimal. In most cases, a single horizontal, vapor extraction well outperforms a single vertical, vapor extraction well (with surface capping) operating at the same extraction rate only for a long linear plume and in those cases, the difference can probably be eliminated with additional vertical extraction wells and still be less expensive (Birdsell et al. 1994). By contrast, for the injection well in the saturated zone, there is likely to be a large performance advantage of horizontal wells over vertical wells.

We then used this history-match simulation as a basis to predict long-term performance at the SRID site and performance at other sites. Conclusions from this part of this study are the following:

- Assuming that all the TCE extracted during the field demonstration was initially present in our model of the site (and not from more distant areas, as some of the monitoring data suggest), our modeling shows that 15% of the total TCE present initially at the site was removed after 139 days. The TCE removal curve is asymptotic. Removing 95% would take about 10 years. Removing 75% would take about 4 years.
- The main characteristic in assessing the performance of this technology at another site is the heterogeneity of the site. For a site with 10 times less heterogeneity (as measured by the average effective clay lens size) than the Savannah River site but otherwise identical, removing 95% of the total TCE present at the SRID site with *in situ* air stripping will take about half the time.

Finally, we used this history-match simulation as a basis to compare *in situ* air stripping with other remediation technologies. Conclusions from this part of this study are the following:

- Changing the lower air injection well into a groundwater pumping well results in almost twice as much TCE being extracted from the groundwater, but the amount of TCE below the water table that is removed in both cases is small (less than 10% in both cases after 150 days).
- Time required to achieve any given removal/destruction percentage is decreased dramatically if *in situ* bioremediation is successfully employed. The diffusion limits for injected materials to reach the TCE within the clays still exist, but once this diffusion takes place, the reaction proceeds rapidly and the TCE is destroyed. The main question with *in situ* bioremediation is whether reactions that are demonstrated in the laboratory can be carried out effectively to destroy VOCs under relatively uncontrolled field conditions.

REFERENCES

- Birdsell, K. H., N. D. Rosenberg and K. M. Edlund (1994), The Performance of Horizontal Versus Vertical Vapor Extraction Wells, *Los Alamos National Laboratory report LA-12783-MS*.
- Buscheck, T. A. and J. J. Nitao (1992), Feasibility of In Situ Stripping of Volatile Organic Compounds at the Savannah River Site: Preliminary Modeling of a Pair of Horizontal Wells, *Lawrence Livermore National Laboratory report, UCRL-LR-104540*.
- Chesnut, D. W., J. Wagoner, J. J. Nitao, S. Boyd, R. J. Shaffer, E. J. Kansa, T. A. Buscheck, K. Preuss and R. W. Falta (1993), Analysis and Evaluation of VOC Removal Technologies Demonstrated at Savannah River, *Lawrence Livermore National Laboratory report, UCRL-ID-111623*.
- DiGiulio, D. C., (1992), Evaluation of Soil Venting Application, *United States Environmental Protection Agency report EPA/540/S-92/004*.
- Eddy, C. A., B. B. Looney, J. M. Dougherty, T. C. Hazen and D. S. Kaback (1991), Characterization of the Geology, Geochemistry, Hydrology and Microbiology of the In Situ Air Stripping Demonstration Site at the Savannah River Site, *Westinghouse Savannah River Company report WSRC-RD-91-21*.
- Eddy Dilek, C. A., B. B. Looney, T. C. Hazen, R. L. Nichols, D. S. Kaback and J. L. Simmons (1993), Post-Test Evaluation of the Geology, Geochemistry, Hydrology and Microbiology of the In Situ Air Stripping Demonstration Site at the Savannah River Site, *Westinghouse Savannah River Company report WSRC-TR-93-369*.
- Johnson, R. O., P. C. Johnson, D. B. McWhorter, R. E. Hinchey and I. Goodman (1993), An Overview of In Situ Air Sparging, *Ground Water Monitoring and Remediation* 13 (4), 127-135.
- Looney, B. B., T. C. Hazen, D. S. Kaback and C. A. Eddy (1991), Full Scale Field Test of the In Situ Air Stripping Process at the Savannah River Integrated Demonstration Test Site, *Westinghouse Savannah River Company report WSRC-RD-91-22*.
- Travis, B. J. (1993), TRAMP (TRACr3D with Microbial Processes): A Numerical Code for In Situ Bioremediation Simulations, *Los Alamos National Laboratory document LA-UR-93-479*.
- Travis, B. J. and N. D. Rosenberg (1994), Numerical Simulations in Support of the In Situ Bioremediation Demonstration at the Savannah River Site, *Los Alamos National Laboratory report LA-12789-MS*.
- van Genuchten, M. Th. (1980), A Closed-Form Equation for Predicting the Hydraulic Conductivity of Unsaturated Soils, *Soil Science Society of America Journal* 44, 892-898.
- Zyvoloski, G. A., and Z. V. Dash (1990), Software Verification Report: FEHMN Version 1.0, *Los Alamos National Laboratory internal report number TWS-EES-5/5-90-3*.
- Zyvoloski, G., Z. Dash and S. Kelkar (1992), FEHMN 1.0: Finite Element Heat and Mass Transfer Code, *Los Alamos National Laboratory document LA-UR-11062-RS, Rev. 1*.

Fig. 2.1 Location of Savannah River facility and Integrated Demonstration site.

Fig. 2.2 Generalized hydrogeology and location of horizontal wells. (a) Map-view. (b) Cross-section view.

Fig. 2.3 Schematic of *in situ* air stripping technology.

(a)

(b)

Fig. 2.4 Field data from in situ air stripping demonstration. (a) Flow rates from injection and extraction wells. (b) VOC concentrations at extraction well.

Fig. 3.1 Model domain, initial and boundary conditions and material properties.

(a)

Fig. 3.2 Numerical grid. (a) Entire mesh. (b) Close-up near well-bore.

Fig. 3.3 TCE concentration at extraction well versus time (preliminary 16-day simulation): comparison of Henry's Law vs. no TCE exchange between liquid and air phase.

Fig. 3.4 TCE concentration at extraction well versus time (preliminary 16-day simulation): effect of rate-limited kinetics of TCE transport from liquid to air.

Fig. 3.5 TCE concentration at extraction well versus time (preliminary 16-day simulation): effect of sorption of TCE on soil, assuming Henry's Law.

Fig. 3.6 TCE concentration at extraction well versus time (preliminary 16-day simulation): effect of sorption of TCE on soil and rate-limited kinetics of TCE transport from liquid to air.

Fig. 3.7 TCE concentration at extraction well versus time (139-day dual porosity simulation): effect of value of D_m , molecular diffusion coefficient of TCE in air.

Fig. 3.8 TCE concentration at extraction well versus time (139-day dual porosity simulation): effect of percent sand and percent clay in medium.

Fig. 3.9 TCE concentration at extraction well versus time (139-day dual porosity simulation): effect of value for water saturation in clays.

Fig. 3.10 TCE concentration at extraction well versus time (139-day dual porosity simulation): effect of value for K_d in clays.

Fig. 3.11 TCE concentration at extraction well versus time (139-day dual porosity simulation): TCE from below the water table vs. TCE from vadose zone.

Fig. 3.12 Helium concentration at extraction well versus time (28-day helium tracer simulation): effect of anisotropy in permeability.

(a)

(b)

Fig. 3.13 Contours of liquid saturation during air injection. (a) Anisotropy ratio in permeability 100 (horizontal: vertical). (b) Isotropic permeability field.

Fig. 3.14 TCE concentration at extraction well versus time (139-day dual porosity simulation): effect of percent sand and percent clay in tan clay zone.

Fig. 3.15 TCE concentration at extraction well versus time (139-day dual porosity simulation): final history match simulation.

Fig. 4.1 TCE concentration at extraction well versus time (180-day dual porosity simulation): cyclic vs. continuous *in situ* air stripping operation.

Fig. 4.2 TCE concentration at extraction well versus time (180-day dual porosity simulation): cyclic vs. continuous operation—extraction only.

Fig. 4.3 TCE concentration at extraction well versus time (180-day dual porosity simulation): effect of extraction rate.

Fig. 5.1 TCE concentration at extraction well versus time (5-year dual porosity simulation): long-term performance prediction.

Fig. 5.2 TCE concentration at extraction well versus time (180-day dual porosity simulation): cyclic operation for various degrees of site heterogeneity.

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