12-4-94 851

UCRL-ID-115626

Environmental Protection Department
Environmental Restoration Division

Effect of Contaminant Diffusion into and out of Low-Permeability Zones

February 1994

Jacob Bear*
Eric Nichols*
John Ziagos
Adarsh Kulshrestha*

***Weiss Associates, Inc., Emeryville, California**

Lawrence Livermore National Laboratory
University of California Livermore, California 94551

DISSEMINATION OF THIS DOCUMENT IS UNRESTRICTED

Effect of Contaminant Diffusion into and out of Low-Permeability Zones

February 1994

**Jacob Bear*
Eric Nichols*
John Ziagos
Adarsh Kulshrestha***

***Weiss Associates, Inc., Emeryville, California**

Environmental Restoration Division

MASTER

Contents

Abstract	1
1. Background—the LLNL Cleanup Problem	1
1.1. The LLNL Contamination Problem	1
1.2. The LLNL Aquifer	2
1.3. Simulations of Cleanup at LLNL	4
2. Statement of Problem	4
2.1. The Conceptual Model	5
2.2. The Two-Continua Mathematical Model	6
3. Diffusion into and out of the LK Material	8
4. Approximating the Rate of Diffusive Exchange	20
4.1. A Semi-Analytical Approximation	20
5. Impact on Cleanup	22
5.1. Application to a Zero-Dimensional Model	22
5.2. Application to a One-Dimensional Aquifer Model	26
6. Conclusions	27
References	28
List of Main Symbols	29
Acknowledgments	30

Effect of Contaminant Diffusion into and out of Low-Permeability Zones

Abstract

We considered the case of an aquifer in the form of a network of high-permeability (HK) channels imbedded in a very low-permeability (LK) porous medium. Contaminants in the aquifer were adsorbed on the solid matrix in both the LK and HK materials. Contaminants were also diffused into and adsorbed onto the LK material. We also investigated the penetration of a contaminant into the LK material and its subsequent release into the aquifer material during cleanup by pump-and-treat operations.

The model results indicate that the diffusive flux of contaminant into and within the LK zone may significantly reduce the rate of contaminant removal, and, therefore, the progress of remedial actions. We found that the use of a constant transfer coefficient to describe the rate of exchange of contaminant between the two materials was inappropriate for simulating cleanup to low concentrations. Instead, a different method for approximating the effect of diffusive flux into and out of an LK zone was proposed and demonstrated on zero- and one-dimensional models of contaminant transport. The technique was applied to Lawrence Livermore National Laboratory's environmental restoration. The diffusive exchange resulted in a lower concentration of contaminant in the HK material during the initial contamination phase, and a slower rate of concentration decrease during the cleanup phase. The concentrations in the LK material may remain above cleanup goals for prolonged periods.

1. Background—the LLNL Cleanup Problem

1.1. The LLNL Contamination Problem

Lawrence Livermore National Laboratory (LLNL) is a research and development facility owned by the U.S. Department of Energy (DOE) and operated by the University of California. In 1983, volatile organic compounds (VOCs) were detected in ground water in the regional aquifer underlying LLNL. These contaminants pose a potential risk to drinking water wells within 3 mi of the site. Consequently, LLNL was placed on the U.S. Environmental Protection Agency's (EPA's) National Priorities List (NPL) in 1987. The majority of these contaminants originated from past practices that began in the 1940s; thus, contaminants have been present in the subsurface for as long as 50 yr. Therefore, diffusive exchange into low-permeability (LK) materials within the aquifer may have had time to significantly affect restoration efforts.

The approved alternative for ground water remediation involves extracting and treating ground water at a number of initial locations (DOE, 1992). Extraction wells would be strategically installed to control the spread of VOCs from the currently contaminated area in concentrations above Maximum Contaminant Levels (MCLs).

Based on the Remedial Investigation and Feasibility Study analyses, and codified in the Record of Decision (DOE, 1992), the DOE, LLNL, U.S. EPA, California EPA Department of Toxic Substances Control (DTSC), and the California Regional Water Quality Control Board (RWQCB) believe that the preferred alternatives for cleaning the saturated zone fully satisfy the nine EPA evaluation criteria (EPA, 1988). Although more expensive in the short-run, the preferred cleanup alternatives satisfy the State's Applicable or Relevant and Appropriate Requirements (ARARs) for nondegradation of ground water resources, reduce the mobility of the contaminants, provide a permanent solution, utilize alternative treatment technologies to the maximum extent practicable, and will achieve cleanup faster than other alternatives. The hydrogeologic conditions found at LLNL have had and will continue to have influence on the choice of cleanup and operational strategies.

1.2. The LLNL Aquifer

The LLNL study area, covering an area about 1.5 mi by 2.5 mi, is underlain by up to 1000 ft of unconsolidated sediments of late Tertiary to Holocene age, which are subdivided into the Plio-Pleistocene Livermore Formation and undifferentiated late Pleistocene to Holocene alluvium. The Livermore Formation is divided into an upper member composed of interfingered gravel, sand, silt, and clay, and a lower member consisting of more laterally continuous layers of silt and clay with lesser gravel beds. Regional ground water flow is generally westward, locally stratified, and primarily horizontal, but the flow paths deepen gradually westward toward the center of the basin. Contaminants are migrating primarily within the sediments of higher hydraulic conductivity. The upper saturated sediments are separated from a deeper aquifer by a westward-sloping regional confining layer in the upper part of the Lower Member of the Livermore Formation. This confining layer varies in depth from about 60 ft in the eastern part of LLNL to about 400 ft near the western LLNL boundary. Depth to ground water in the LLNL area varies from about 110 ft in the southeast corner of LLNL to 30 ft in the northwest.

According to Carpenter (1984), the interstratified clay, silt, sand, and gravel comprise a sedimentary body of alluvial fan, terrace, and fluvial-plain deposits. The depositional character appears to be that of a braided stream system, where a series of channels crosscuts previously deposited sediments. Typical vertical and horizontal sections are shown in Figure 1.1. Based on this information, the conceptual model developed by the project visualizes the subsurface as a single continuum.

Figure 1.1: Generalized cross section showing distribution of sediments and VOCs in the LLNL subsurface.

1.3. Simulations of Cleanup at LLNL

To evaluate the future migration of contaminants under a variety of cleanup scenarios, and to estimate the corresponding cleanup time, we simulated ground water flow and contaminant transport in the LLNL area using the finite element flow and transport code CFEST (Gupta *et al.*, 1987) as summarized in Tompson *et al.* (1991) and Tompson *et al.* (1993). In these simulations, the aquifer was simulated as a single heterogeneous continuum in the form of a horizontal two-dimensional domain. The heterogeneity took the form of large homogeneous subdomains of different hydraulic conductivity. Contaminant transport was assumed to occur within this single continuum.

The juxtaposition of high-permeability (HK) and LK sediments, and the exchange of contaminants between them, primarily by diffusion, was not represented in the simulations using the CFEST code, although such exchange may play a major role in determining cleanup time. The objective of the research described here is to incorporate this feature in modeling contaminant transport in the considered domain.

As the aquifer considered here is being invaded by a contaminant, the latter will diffuse into the LK zone, in which we assume that water is practically *immobile*. This is reasonable when the ratio of hydraulic conductivities in the two zones is very high, say 10^2 . As the contaminant enters the LK zone, it may adsorb on the very large solid surface area characterizing such material. During the cleanup period, as concentrations in the HK material are gradually reduced, the concentration gradient is reversed and the contaminant is released from the LK material into the aquifer. The LK zone, which, in the period of rising concentrations in the aquifer, acts as a *sink* to the contaminant, now acts as a *source*. It may significantly prolong the required cleanup time, i.e., the time required to reach a desired contaminant concentration.

2. Statement of Problem

The objectives of this paper are to investigate the effect of this sink-source phenomenon, and to suggest a model that accurately quantifies the rate of exchange between the two materials, thus enabling a more realistic estimation of cleanup time.

We consider the problem of contamination in a heterogeneous aquifer, composed of an interconnected network of HK channels imbedded in an LK material, or isolated subdomains of LK material imbedded in an HK aquifer material. Examples are an aquifer composed of a network of sand and gravel channels imbedded in a clay, or silty-clay matrix, and one made of sand and gravel in which lenses of clay are imbedded.

Figure 2.1 shows these two examples. Note that the HK zone is connected in the third dimension.

Figure 2.1: Schematic representation of (a) high-permeability channel network imbedded in a low-permeability material, and (b) low-permeability lenses imbedded in a high-permeability material.

One may visualize these two materials within the framework of a single heterogeneous (say, in permeability) domain. For example, in a numerical model, one way to represent such a domain is to divide it into a very large number of blocks (nodes, elements, finite difference cells), each having its own permeability (and other properties, e.g., molecular diffusivity). Coefficients may be assigned to each block, deterministically or stochastically, on the basis of some distributions derived from data. However, resolution and its associated computational burden make this approach infeasible.

Instead, we undertook a two-media approach, with diffusive exchange between them. This is the approach discussed in this paper.

Within the context of the continuum approach to the description of transport phenomena in porous media (e.g., Bear and Bachmat, 1990), each of the two materials comprising the aquifer may be visualized as a *continuum* that occupies the entire spatial domain of the aquifer: a continuum of HK material and a second one made up of LK material. The two (overlapping) continua may exchange any transported extensive quantity. Here we are interested in the transport of the mass of a contaminant.

Although the discussion is directed at the case of LK materials imbedded in an HK matrix, it is also applicable to the analogous case of HK materials imbedded in an LK matrix.

2.1. The Conceptual Model

The conceptual model of the problem is as follows:

[A.1] The HK and the LK subdomains are considered as continua that occupy the entire aquifer domain.

[A.2] Both the LK and the HK materials are rigid, homogeneous, and isotropic.

- [A.3] A single contaminant (γ) is present in the aquifer.
- [A.4] In the HK continuum, the contaminant may be transported by advection, dispersion, and diffusion. However, we shall assume that transport by diffusion is negligible with respect to that by dispersion.
- [A.5] In the LK subdomain, we usually assume that advection is negligible, and the only mode of contaminant transport is molecular diffusion. However, here we shall assume also that diffusion as a mode of transport is negligible, leaving diffusion only as a mode of exchange between the two continua across their common interface.
- [A.6] The considered contaminant may adsorb on the solid matrix in both zones. We assume that the solute in the liquid and on the solid are under equilibrium, and a *linear isotherm* is used.

2.2. The Two-Continua Mathematical Model

Based on the conceptual model presented above, we describe the transport of the γ -contaminant in the two materials (present in the entire aquifer domain) by the following mathematical model:

Mass balance for γ in the HK material

$$\frac{\partial}{\partial t} [n_h (\phi_h + \rho_{bh} K_{dh}) c_h] = -\nabla \cdot [n_h \phi_h (c_h \mathbf{V} - \mathbf{D}_h \cdot \nabla c_h)] - f_{h \rightarrow l}. \quad (2.1)$$

Mass balance for γ in the LK material

$$\frac{\partial}{\partial t} [n_l (\phi_l + \rho_{bl} K_{dl}) c_l] = \nabla \cdot [n_l \phi_l (\mathcal{D}_l^* \nabla c_l)] - f_{l \rightarrow h}, \quad (2.2)$$

where

n_α	Volumetric fraction of α -continuum within the aquifer, $\alpha = h, l$.
ϕ_α	Volumetric fraction of void space (= porosity) within the α -continuum.
$\rho_{b\alpha}$	Bulk density of a solid matrix within the α -material ($= \rho_s(1 - \phi_\alpha)$).
c_α	Average concentration of the γ -component in the water present in the α -continuum, $\alpha = h, l$.
$\mathbf{V}$	Velocity of water in the HK continuum.
$f_{\alpha \rightarrow \beta}$	Rate of transfer of γ from the α -continuum to the β -continuum, across their common interface, per unit volume of aquifer.
$K_{d\alpha}$	Partitioning coefficient in the α -continuum.
$\mathbf{D}_h$	Coefficient of dispersion in the HK material.
$\mathcal{D}_l^*$	Coefficient of molecular diffusion in the isotropic LK material.

However, in view of assumption [A.5], the first term on the right-hand side of Eq. (2.2) will be deleted.

The coefficient of molecular diffusion in a porous medium, $\mathcal{D}_l^*$, is related to that in a fluid continuum, $\mathcal{D}$, by the *tortuosity* of the porous medium, τ_l^* , in the form $\mathcal{D}_l^* = \tau_l^* \mathcal{D}$. The volumetric fractions obey the relationship

$$n_h + n_l = 1. \quad (2.3)$$

The two mass balance equations may also be rewritten in the form

$$n_h \phi_h R_{dh} \frac{\partial c_h}{\partial t} = -\nabla \cdot n_h \phi_h (c_h \mathbf{V} - \mathbf{D}_h \cdot \nabla c_h) - f_{h \rightarrow l}, \quad (2.4)$$

and

$$n_l \phi_l R_{dl} \frac{\partial c_l}{\partial t} = \nabla \cdot n_l \phi_l (\mathcal{D}_l^* \nabla c_l) - f_{l \rightarrow h}, \quad (2.5)$$

where

$$R_{d\alpha} = 1 + \frac{\rho_{b\alpha} K_{d\alpha}}{\phi_\alpha} \quad (2.6)$$

denotes the *retardation factor* for the α -continuum, $\alpha = h, l$. Again, in view of assumption [A.5], the first term on the right-hand side of Eq. (2.5) will be deleted.

We have here two balance equations in the two variables c_α , $\alpha = h, l$ (assuming that the velocity, $\mathbf{V}$, in the HK material can be determined from the appropriate flow model). However, we need the value of the rate of exchange, $f_{h \rightarrow l}$, appearing in these equations. Our next objective is to discuss this rate of exchange of γ between the LK and the HK materials.

Very often, in a double-continua transport model as considered here, the rate of transfer of γ between the two media is expressed as

$$f_{h \rightarrow l} = \phi_l \alpha^* (c_h - c_l), \quad (2.7)$$

in which α^* is a transfer coefficient, and c_h , and c_l denote the concentrations in the HK and LK materials, respectively (van Genuchten, 1985; Grisak and Pickens, 1980; Tang *et al.*, 1981). Underlying the use of such an expression is the assumption that the transfer coefficient, α^* , is a constant. Its value can be estimated by the ratio of the molecular diffusion coefficient to the length characterizing the distance between the two points at which the two concentrations are assumed to exist, multiplied by the specific area of the interface through which the exchange takes place (equals area of interface times the porosity of the LK zone).

In fact, this is the traditional approach to the description of the exchange of fluid mass between fractures and porous blocks in a fractured porous rock (Barenblatt *et al.*, 1960; Warren and Root, 1963). There, because of the speed at which pressure propagates, we assume that the rate of exchange is proportional to the difference in pressure between the fracture and porous block, with a constant transfer coefficient.

Figure 3.1: Diffusion at the LK-HK interface.

However, solute transport is a much slower process; therefore, the use of a constant transfer coefficient may not be appropriate. We shall examine whether the use of such a constant transfer coefficient is appropriate in the model considered here. This motivated the present study — to find a better way for expressing this exchange term $f_{l \rightarrow h}$ in the balance equation (2.1) in response to changes in the concentration in the HK material.

3. Diffusion into and out of the LK Material

Figure 3.1 shows an element of area of the HK-LK interface. With j denoting the diffusive flux normal to this interface (positive when taking place from the HK zone to the LK one), and Σ_{HK} denoting the specific interface area (equals area per unit volume of aquifer), we can write

$$f_{h \rightarrow l} = j \Sigma_{HK}, \quad (3.1)$$

where, by Fick's law for a porous medium, we express the diffusive flux at the interface (per unit area of porous medium) in terms of the concentration distribution, $c_l \equiv c = c(x, t)$, in the LK material, in the form

$$j \Big|_{x=0} = -\phi_l D_l^* \frac{\partial c}{\partial x} \Big|_{x=0}. \quad (3.2)$$

Thus, the influx or efflux at the interface depends on $c = c(x, t)$. Note that we have used here the coordinate x to denote the (microscopic level) distance normal to the interface, positive in the direction away from the interface in the LK material.

Actually, the double-continua model expressed by Eqs. (2.1) and (2.2) is written at the *megascopic level*. This means that each of the two porous materials (HK and LK) is assumed to occupy the entire aquifer. Each material is regarded as a continuum at the *macroscopic level*, while the term *microscopic level* is employed when we consider a point *within* a phase present in the void space, in either the HK or the LK materials. Since, in what follows, we intend to refer only to the first two levels, we shall simplify

the terminology by referring to them as “macroscopic” and “microscopic,” respectively. Each term in the above two equations represents added mass of γ per unit volume of the aquifer as a whole.

Accordingly, we need a solution for $c = c(x, t)$ as the concentration $c|_{x=0} = c_h(t)$ varies at the boundary. The latter serves as a boundary condition to the diffusion in the LK material. The LK material rises during the contamination period and is gradually reduced during the cleanup operations. The concentration, $c(x, t)$, obeys the mass balance equation, which, when combined with an expression for the diffusive flux, takes the form

$$\frac{\partial \phi_l c}{\partial t} = -\frac{\partial j}{\partial x} = \phi_l \mathcal{D}_l^* \frac{\partial^2 c}{\partial x^2}, \quad (3.3)$$

in which ϕ_l and $\mathcal{D}_l^* = \tau_l^* \mathcal{D}$ are assumed constant in space. Once we solve this problem in the semi-infinite domain, $x \geq 0$, we can determine the total mass accumulated per unit cross-sectional area in the LK material by

$$m(t) = \int_0^\infty \phi_l c(x, t) dx.$$

We can also determine the instantaneous diffusive flux at the HK-LK interface from Eq. (3.2).

Let us consider a number of particular cases.

Case A

The LK material is initially clean, $c(x, 0) = 0$. The HK material is maintained at a constant concentration, c_o .

Initial condition: $x > 0, \quad t = 0, \quad c = 0$

Boundary condition: $x = 0, \quad t > 0, \quad c = c_o$.

The analytical solution of Eq. (3.3) is (Carslaw and Jaeger, 1959, p. 60)

$$\frac{c(x, t)}{c_o} = \operatorname{erfc} \frac{x}{\sqrt{4\mathcal{D}_l^* t}} = \operatorname{erfc} \xi, \quad (3.4)$$

where $\xi = x/\sqrt{4\mathcal{D}_l^* t}$ is a dimensionless variable that incorporates both space and time, and

$$\operatorname{erfc} \xi = \frac{2}{\sqrt{\pi}} \int_\xi^\infty e^{-\mu^2} d\mu = 1 - \operatorname{erf} \xi = 1 - \frac{2}{\sqrt{\pi}} \int_0^\xi e^{-\mu^2} d\mu$$

defines the *error function complement* of ξ .

Figure 3.2 shows Eq. (3.4) in graphical form for $\mathcal{D}_l^* = 31.5 \text{ cm}^2/\text{yr}$. This value is obtained from $\mathcal{D}_l^* = \tau_l^* \mathcal{D}$, in which $\mathcal{D}$ is the coefficient of molecular diffusion, taken as $10^{-5} \text{ cm}^2/\text{s}$, and τ_l^* is the tortuosity of the LK material, taken equal to 0.1 (Bear and Bachmat, 1991).

Figure 3.2: Contaminant distribution within the LK material for Case A.

An interesting conclusion may already be drawn from Figure 3.2. The depth of penetration, say of the point $c/c_o = 0.5$, or even $= 0.1$, is small. In the case shown here for $c/c_o = 0.1$, the depth of penetration is less than 80 cm after 25 yr.

The total mass accumulated within a unit cross section of the LK material is given by

$$\begin{aligned}
 m(t) &= c_o \phi_l \int_0^\infty \left(\frac{2}{\sqrt{\pi}} \int_{\frac{x}{\sqrt{4\mathcal{D}_l^* t}}}^\infty e^{-\mu^2} d\mu \right) dx = 4c_o \phi_l \sqrt{\frac{\mathcal{D}_l^* t}{\pi}} \int_0^\infty \int_\lambda^\infty e^{-\mu^2} d\mu d\lambda \\
 &= 2c_o \phi_l \sqrt{\frac{\mathcal{D}_l^* t}{\pi}}.
 \end{aligned} \tag{3.5}$$

The accumulated mass, $m(t)$, is shown in Figure 3.3. The rate of mass accumulation seems to decrease after about 10 yr of contact.

Finally, let us determine the flux of the contaminant at $x = 0$:

$$\begin{aligned}
 j &= -\phi_l \mathcal{D}_l^* \frac{\partial c}{\partial x} \Big|_{x=0} = -c_o \phi_l \mathcal{D}_l^* \left[\frac{\partial}{\partial x} \left(\frac{2}{\sqrt{\pi}} \int_{\frac{x}{\sqrt{4\mathcal{D}_l^* t}}}^\infty e^{-\mu^2} d\mu \right) \right]_{x=0} \\
 &= c_o \phi_l \sqrt{\frac{\mathcal{D}_l^*}{\pi t}}.
 \end{aligned} \tag{3.6}$$

Figure 3.4 shows how this flux varies in time.

Often, the diffusive flux is estimated as

$$j = \phi \alpha' (c_h - c'), \tag{3.7}$$

Figure 3.3: Contaminant mass accumulated within the LK material in Case A.

Figure 3.4: Contaminant flux into the LK material for Case A.

where c' denotes some representative concentration within the LK material, and α' is a constant transfer coefficient. The α' is the ratio of the molecular diffusion coefficient and the distance between the points at which the representative concentrations c_h and c' occur. To examine the validity of such an estimate, let us assume that $c' = \frac{1}{2}c_o$. Then, let us estimate this diffusive flux by assuming that it is driven by a concentration gradient equal to the difference in concentration between the boundary and the 50% concentration, divided by the distance between the points at which these concentrations occur. Denoting this distance by Δ , we find from Eq. (3.4) that

$$\frac{c}{c_o} = 0.5, \quad \text{at} \quad x = \Delta = 0.477 \times \sqrt{4\mathcal{D}_l^* t},$$

or $\Delta \approx \sqrt{\mathcal{D}_l^* t}$. An estimate of the transfer coefficient α^* is, therefore, $\frac{\mathcal{D}_l^*}{\Delta} = \frac{\mathcal{D}_l^*}{\sqrt{\mathcal{D}_l^* t}}$. Then, using Δ as the characteristic length, we estimate the flux by an expression similar to Eq. (3.7), viz.,

$$j = \phi_l \alpha^* (c_o - \frac{1}{2}c_o) = \phi_l \frac{\mathcal{D}_l^*}{\sqrt{\mathcal{D}_l^* t}} \frac{1}{2}c_o = c_o \phi_l \sqrt{\frac{\mathcal{D}_l^*}{4t}}.$$

This is approximately the expression that was derived for j in Eq. (3.6).

An interesting conclusion at this point is that if we wish to use a flux expression that is based on a transfer coefficient, the latter *is time dependent*, and not a constant. This time-dependence was noted by Dykhuizen (1990). For this reason, in subsequent sections we shall use a different approach to estimate the exchange between the two materials.

Let us consider the same case but with adsorption of the contaminant to the clay particles within the LK zone. The mass balance equation (3.3) now becomes

$$\frac{\partial c}{\partial t} = \frac{\mathcal{D}_l^*}{R_{dl}} \frac{\partial^2 c}{\partial x^2}, \quad (3.8)$$

with

$$R_{dl} = 1 + \frac{\rho_w K_{dl}}{\phi_l}.$$

We note that this is the same equation as Eq. (3.3), except that the coefficient of molecular diffusion in the LK medium, $\mathcal{D}_l^*$, is now reduced by the LK retardation factor, R_{dl} . We can, therefore, modify the results obtained above by replacing $\mathcal{D}_l^*$ by $\mathcal{D}_l^*/R_{dl}$ in Eqs. (3.4) and (3.5). The expression for j in Eq. (3.6) then becomes

$$j = -\phi_l \mathcal{D}_l^* \frac{\partial c}{\partial x} \Big|_{x=0} = c_o \phi_l \sqrt{\frac{\mathcal{D}_l^*}{R_{dl} \pi t}}, \quad (3.9)$$

which means that the effect of adsorption is to reduce j for the same time. This result should not be surprising if we recall that adsorption causes more of the mass to accumulate closer to the interface.

Figure 3.4 shows the effect of adsorption on j . The interfacial flux is reduced by $1/\sqrt{R_d}$.

Before leaving Case A, it may be of interest to note that for the case defined by

$$\begin{aligned} \text{Initial condition:} \quad & x > 0, \quad t = 0, \quad c = c_o, \\ \text{Boundary condition:} \quad & x = 0, \quad t > 0, \quad c = 0, \end{aligned}$$

which corresponds to a contaminated LK zone and a very quick cleanup of the HK zone, we obtain the solution

$$\frac{c(x, t)}{c_o} = \operatorname{erf} \frac{x}{\sqrt{4\mathcal{D}_l^* t}}, \quad j = -c_o \phi_l \sqrt{\frac{\mathcal{D}_l^*}{\pi t}}. \quad (3.10)$$

The flux obtained is the negative of the flux obtained in Eq. (3.6).

Case B

The LK material is initially clean. The HK material is maintained at a constant concentration, c_o , for a period T . Then the concentration at the HK-LK interface is instantaneously reduced to zero. This case represents the best that any pump-and-treat scheme could achieve.

$$\begin{aligned} \text{Initial condition:} \quad & x > 0, \quad t = 0, \quad c = 0, \\ \text{Boundary conditions:} \quad & x = 0, \quad 0 < t \leq T, \quad c = c_o, \\ & x = 0, \quad t > T, \quad c = 0. \end{aligned}$$

The analytical solution is obtained by superposition (Carslaw and Jaeger, 1959, p. 60)

$$\text{for } t \leq T \quad \frac{c(x, t)}{c_o} = \operatorname{erfc} \frac{x}{\sqrt{4\mathcal{D}_l^* t}}, \quad (3.11)$$

$$\text{for } t > T \quad \frac{c(x, t)}{c_o} = \operatorname{erfc} \frac{x}{\sqrt{4\mathcal{D}_l^* t}} - \operatorname{erfc} \frac{x}{\sqrt{4\mathcal{D}_l^* (t - T)}}. \quad (3.12)$$

We can now calculate the diffusive flux into and out of the LK zone at their common interface, $x = 0$.

For $t \leq T$, this flux is the same as in Case A, i.e., expressed by Eq. (3.6). For $t > T$, we obtain

$$\begin{aligned} j &= -\phi_l \mathcal{D}_l^* \frac{\partial c}{\partial x} \Big|_{x=0} = c_o \phi_l \mathcal{D}_l^* \frac{2}{\sqrt{\pi}} \frac{\partial}{\partial x} \left(\int_0^{\frac{x}{\sqrt{4\mathcal{D}_l^* t}}} e^{-\mu^2} d\mu - \int_0^{\frac{x}{\sqrt{4\mathcal{D}_l^* (t-T)}}} e^{-\mu^2} d\mu \right) \Big|_{x=0} \\ &= c_o \phi_l \mathcal{D}_l^* \frac{2}{\sqrt{\pi}} \left(\frac{e^{-\frac{x^2}{4\mathcal{D}_l^* t}}}{\sqrt{4\mathcal{D}_l^* t}} - \frac{e^{-\frac{x^2}{4\mathcal{D}_l^* (t-T)}}}{\sqrt{4\mathcal{D}_l^* (t-T)}} \right) \Big|_{x=0} = c_o \phi_l \sqrt{\frac{\mathcal{D}_l^*}{\pi}} \left(\frac{1}{\sqrt{t}} - \frac{1}{\sqrt{t-T}} \right). \end{aligned} \quad (3.13)$$

Figure 3.5: Contaminant flux into the LK material in Case B, with $T = 40$ yr.

Figure 3.5 shows how j at $x = 0$ varies in time, for 40 yr of $c_h = 1$. Note how the flux *out* of the LK material decreases more rapidly than the flux *in*. This is because, after cleanup has begun, the contaminant continues to diffuse away from the interface in the interior of the LK material, while it also diffuses toward the interface.

We can integrate $c(x, t)$ over the entire domain, $0 < x < \infty$, to obtain the residual mass, $m(t)$, at any instant. This mass is shown in Figure 3.6.

Case C

Let the contaminant concentration in the HK zone, which acts as a boundary to the LK zone, be gradually reduced as a consequence of cleaning operations (say, pump and treat). Let

$$c|_{x=0} = c_o e^{-\beta t} \quad (3.14)$$

describe the change in concentration within the HK zone. This situation corresponds to what happens in a single cell model in which the initial concentration is c_o , and then this concentration is reduced by flushing. The solution is

$$c|_{x=0} = c_o e^{-\frac{Q}{U_v} t}, \quad (3.15)$$

in which Q is the rate of flushing and U_v is the pore volume within the cell. Thus, $\beta = Q/U_v$, with U_v/Q expressing the time required for one flushing (equals mean residence time).

We consider the following conditions:

Figure 3.6: Accumulated contaminant mass in the LK material in Case B.

Initial condition: $x > 0, \quad t = 0, \quad c = 0,$

Boundary condition: $x = 0, \quad t > 0, \quad c = c_0 e^{-\beta t}.$

The solution is (Carslaw and Jaeger, 1959, p. 64)

$$c = \frac{1}{2} c_0 e^{-\beta t} \left[e^{-x \sqrt{\frac{-\beta}{\mathcal{D}_i^*}}} \operatorname{erfc} \left(\frac{x}{\sqrt{4 \mathcal{D}_i^* t}} - \sqrt{-\beta t} \right) + e^{x \sqrt{\frac{-\beta}{\mathcal{D}_i^*}}} \operatorname{erfc} \left(\frac{x}{\sqrt{4 \mathcal{D}_i^* t}} + \sqrt{-\beta t} \right) \right]. \quad (3.16)$$

The diffusive flux into and out of the LK zone at the interface is

$$j = c_0 \phi_i \mathcal{D}_i^* e^{-\beta t} \left[i \sqrt{\frac{\beta}{\mathcal{D}_i^*}} \operatorname{erf} \left(i \sqrt{\beta t} \right) + \frac{e^{\beta t}}{\sqrt{\pi \mathcal{D}_i^* t}} \right]. \quad (3.17)$$

Carslaw and Jaeger (1959) tabulate values of the erfc function for complex arguments.

Case D

Consider the general case described by:

Initial condition: $x > 0, \quad t = 0, \quad c = f(x),$

Boundary condition: $x = 0, \quad t > 0, \quad c = g(t).$

The solution can be obtained as a sum of two solutions, $c = c_1 + c_2$, each satisfying the basic diffusion equation:

$c_1 = c_1(x, t)$, which satisfies:

$$\begin{aligned} \text{Initial condition:} \quad & x > 0, \quad t = 0, \quad c_1 = 0, \\ \text{Boundary condition:} \quad & x = 0, \quad t > 0, \quad c_1 = g(t), \end{aligned}$$

and $c_2 = c_2(x, t)$, which satisfies:

$$\begin{aligned} \text{Initial condition:} \quad & x > 0, \quad t = 0, \quad c_2 = f(x), \\ \text{Boundary condition:} \quad & x = 0, \quad t > 0, \quad c_2 = 0. \end{aligned}$$

Carslaw and Jaeger (1959, pp. 59, 63) present the solutions in the form

$$c_1 = \frac{x}{\sqrt{4\pi\mathcal{D}_l^*t}} \int_0^t g(\lambda) \frac{e^{-\frac{x^2}{4\mathcal{D}_l^*(t-\lambda)}}}{(t-\lambda)^{\frac{3}{2}}} d\lambda, \quad (3.18)$$

and

$$c_2 = \frac{1}{\sqrt{4\pi\mathcal{D}_l^*t}} \int_0^\infty f(x') \left[e^{-\frac{(x-x')^2}{4\mathcal{D}_l^*t}} - e^{-\frac{(x+x')^2}{4\mathcal{D}_l^*t}} \right] dx'. \quad (3.19)$$

Let us now apply this decomposition to the case of an initially contaminated LK zone and a gradual cleanup of the HK zone:

$$\begin{aligned} \text{Initial condition:} \quad & x > 0, \quad t = 0, \quad c = c_o, \\ \text{Boundary conditions:} \quad & x = 0, \quad t > 0, \quad c = g(t) = c_o e^{-\beta t}. \end{aligned}$$

The solution is

$$\begin{aligned} c = & \frac{1}{\sqrt{4\pi\mathcal{D}_l^*t}} \int_0^\infty c_o \left[e^{-\frac{(x-x')^2}{4\mathcal{D}_l^*t}} - e^{-\frac{(x+x')^2}{4\mathcal{D}_l^*t}} \right] dx' \\ & + \frac{x}{\sqrt{4\pi\mathcal{D}_l^*t}} \int_0^t c_o e^{-\beta\lambda} \frac{e^{-\frac{x^2}{4\mathcal{D}_l^*(t-\lambda)}}}{(t-\lambda)^{\frac{3}{2}}} d\lambda. \end{aligned} \quad (3.20)$$

By performing the integrations, we obtain

$$\begin{aligned} \frac{c}{c_o} = & \operatorname{erf} \frac{x}{\sqrt{4\mathcal{D}_l^*t}} \\ & + \frac{1}{2} e^{-\beta t} \left\{ e^{ix\sqrt{\frac{\beta}{\mathcal{D}_l^*}}} \operatorname{erfc} \left[\frac{x}{\sqrt{4\mathcal{D}_l^*t}} + i\sqrt{\beta t} \right] \right. \\ & \left. + e^{-ix\sqrt{\frac{\beta}{\mathcal{D}_l^*}}} \operatorname{erfc} \left[\frac{x}{\sqrt{4\mathcal{D}_l^*t}} - i\sqrt{\beta t} \right] \right\}. \end{aligned} \quad (3.21)$$

The first term on the right-hand side corresponds to the case where the LK zone is initially contaminated at c_o , and a quick cleanup is implemented in the HK material.

Figure 3.7: Contaminant distribution in the LK material for Case D.

Figure 3.7 shows the spatial distribution of residual contamination, at various times after cleanup, for $\beta = 0.2$. If the contaminant is adsorbed on the solid in the LK zone, we have to replace $\mathcal{D}_l^*$ in (3.21) by $\mathcal{D}_l^*/R_{dl}$.

We can also derive the rate at which the contaminant is released into the HK zone

$$\begin{aligned}
 j &= -\phi_l \mathcal{D}_l^* \frac{\partial c}{\partial x} \Big|_{x=0} \\
 &= c_o \phi_l \mathcal{D}_l^* i \sqrt{\frac{\beta}{\mathcal{D}_l^*}} e^{-\beta t} \operatorname{erf} \left[i \sqrt{\beta t} \right].
 \end{aligned} \tag{3.22}$$

The flux as a function of time is shown in Figure 3.8 for $\beta = 0.2$. Note that the interfacial flux reaches a maximum shortly after cleanup begins, then decreases to less than half the maximum rate after about 23 yr.

In the presence of adsorption, we have to replace $\mathcal{D}_l^*$ in Eq. (3.22) by $\mathcal{D}_l^*/R_{dl}$. Again, this result should not be surprising if we recall that, in this case, the total mass accumulating near the interface is R_{dl} times higher.

Case E

We consider the case described by

$$\begin{aligned}
 \text{Initial condition:} \quad & x > 0, \quad t = 0, \quad c = 0, \\
 \text{Boundary conditions:} \quad & x > 0, \quad t \leq T, \quad c = c_o, \\
 & x = 0, \quad t > T, \quad c = c_o e^{-\beta(t-T)}.
 \end{aligned}$$

This means that initially, there is no contaminant in the LK zone. Then, for a period of T , the contamination level in the HK zone is maintained at c_o . After that, cleanup is initiated, and the concentration in the HK zone drops exponentially.

Figure 3.8: Contaminant flux at the HK-LK interface for Case D.

Again, the principle of superposition is applicable. We seek three solutions, with $c = c_1 + c_2 + c_3$, such that:

- For $c_1 = c_1(x, t)$:

Initial condition: $x > 0, \quad t = 0, \quad c_1 = 0,$

Boundary conditions: $x = 0, \quad t > 0, \quad c_1 = c_o.$

- For $c_2 = c_2(x, t)$:

Initial condition: $x > 0, \quad t = 0, \quad c_2 = 0,$

Boundary conditions: $x = 0, \quad 0 < t \leq T, \quad c_2 = 0,$
 $x = 0, \quad t > T, \quad c_2 = -c_o.$

- For $c_3 = c_3(x, t)$:

Initial condition: $x > 0, \quad t = 0, \quad c_3 = 0,$

Boundary conditions: $x = 0, \quad 0 < t \leq T, \quad c_3 = 0,$
 $x = 0, \quad t > T, \quad c_3 = c_o e^{-\beta(t-T)}.$

For $t \leq T$, the solution is the same as Case A.

For $t > T$, the solution is

$$\begin{aligned} \frac{c(x, t)}{c_o} = & \operatorname{erfc} \frac{x}{\sqrt{4\mathcal{D}_l^* t}} - \operatorname{erfc} \frac{x}{\sqrt{4\mathcal{D}_l^* (t - T)}} \\ & + \frac{x}{\sqrt{4\pi\mathcal{D}_l^*}} \int_0^{t-T} \phi'(\lambda) \frac{e^{-\frac{x^2}{4\mathcal{D}_l^* (t-T-\lambda)}}}{(t-T-\lambda)^{\frac{3}{2}}} d\lambda, \end{aligned} \quad (3.23)$$

where $\phi'(\lambda) = e^{-\beta\lambda}$.

We consider the third term on the right-hand side,

$$\frac{x}{\sqrt{4\pi\mathcal{D}_l^*}} \int_0^{t-T} e^{-\beta\lambda} \frac{e^{-\frac{x^2}{4\mathcal{D}_l^*(t-T-\lambda)}}}{(t-T-\lambda)^{\frac{3}{2}}} d\lambda.$$

It can be shown that this integral is equivalent to:

$$\begin{aligned} \frac{1}{2}e^{-\beta(t-T)} & \left[e^{-ix\sqrt{\frac{\beta}{\mathcal{D}_l^*}}} \operatorname{erfc} \left(\frac{x - i(t-T)\sqrt{4\beta\mathcal{D}_l^*}}{\sqrt{4\mathcal{D}_l^*(t-T)}} \right) \right. \\ & \left. + e^{ix\sqrt{\frac{\beta}{\mathcal{D}_l^*}}} \operatorname{erfc} \left(\frac{x + i(t-T)\sqrt{4\beta\mathcal{D}_l^*}}{\sqrt{4\mathcal{D}_l^*(t-T)}} \right) \right]. \end{aligned} \quad (3.24)$$

Combining all the terms in Eq. (3.23), we obtain

$$\begin{aligned} \frac{c}{c_o} &= \operatorname{erfc} \frac{x}{\sqrt{4\mathcal{D}_l^*t}} - \operatorname{erfc} \frac{x}{\sqrt{4\mathcal{D}_l^*(t-T)}} + \frac{1}{2}e^{-\beta(t-T)} \\ & \times \left[e^{-ix\sqrt{\frac{\beta}{\mathcal{D}_l^*}}} \operatorname{erfc} \left(\frac{x - i(t-T)\sqrt{4\beta\mathcal{D}_l^*}}{\sqrt{4\mathcal{D}_l^*(t-T)}} \right) \right. \\ & \left. + e^{ix\sqrt{\frac{\beta}{\mathcal{D}_l^*}}} \operatorname{erfc} \left(\frac{x + i(t-T)\sqrt{4\beta\mathcal{D}_l^*}}{\sqrt{4\mathcal{D}_l^*(t-T)}} \right) \right]. \end{aligned} \quad (3.25)$$

The contaminant flux at the HK-LK interface for $t > T$ is given by

$$\begin{aligned} j &= -\phi_l \mathcal{D}_l^* \frac{\partial c}{\partial x} \Big|_{x=0} \\ &= c_o \phi_l \mathcal{D}_l^* \left[\frac{1}{\sqrt{\pi\mathcal{D}_l^*t}} + i\sqrt{\frac{\beta}{\mathcal{D}_l^*}} e^{-\beta(t-T)} \operatorname{erf} \left(i\sqrt{\beta(t-T)} \right) \right]. \end{aligned} \quad (3.26)$$

The contaminant distribution is shown for selected times in Figure 3.9. Note that even 80 yr after cleanup starts, a considerable mass of contaminants remains in the LK material. This has significant impact on the overall time to cleanup. The maximum concentration in the LK material is still about 20% of the initial value after 80 yr; a typical environmental restoration has a cleanup goal of approximately 0.002 of initial, using U.S. Federal MCLs as the standard. Clearly, this effect has significant negative implications if the LK material is required to be cleaned to low parts-per-billion levels.

In this section, we have derived analytical expressions for the diffusive exchange flux between HK and LK materials for selected boundary conditions. Unfortunately, the kind of boundary conditions for which such solutions can be derived is rather limited. Therefore, the analytical solutions presented above cannot serve as the basis for a generalized expression of diffusive exchange. Another approach, which will lead to a generalized exchange term, is presented in the next section.

Figure 3.9: Contaminant distribution in the LK material for Case E.

4. Approximating the Rate of Diffusive Exchange

The objectives of the above discussion were (a) to gain some insight into the rates of exchange and depth of penetration of a contaminant between the HK and LK zones during the periods of contamination and of cleanup, (b) to examine whether a constant (in time) transfer coefficient can be used to estimate this rate, and (c) to attempt to get an alternative expression for this rate, especially for the case in which the concentration in the HK zone varies in some manner that depends on the progress of the cleanup. The ultimate use of such an expression is in the $f_{h \rightarrow l}$ -term that appears in the balance equation for the contaminant, and especially in a numerical model that would be employed for the solution of this equation for realistic large-scale problems of aquifer contamination. The role of the LK zone, represented through the term of exchange $f_{h \rightarrow l}$, such as in Eq. (2.4), is usually not included in large-scale models.

4.1. A Semi-Analytical Approximation

In general, the cell-by-cell variations of contaminant concentration over time are not simple step-changes, or exponentially declining functions. Therefore, exact analytical expressions for the diffusive flux are not useful within the context of a numerical model. Instead, we seek a generalized cell-by-cell source/sink term that approximates the diffusive flux into and out of the LK zone sufficiently well.

The phenomenon is mathematically analogous to the problem of loss of heat by diffusive (equals conductive) flux into the overburden material that bounds a thermal reservoir. A review of techniques that incorporate this phenomenon into single-continuum numerical models was given by Hansamuit *et al.* (1992). One of the simpler techniques is a semi-analytical approximation of the diffusive heat flux, originally proposed by

Vinsome and Westerveld (1980). Their method uses a flexible function containing two time-varying parameters, calculated in a simple fashion, that solves Eq. (3.3), subject to any boundary and initial conditions. A version of this method was used by Pruess and Wu (1989) to simulate fracture/matrix fluid flow in a dual-continuum flow model.

As above, we start by considering a point on the HK-LK interface. At every instant, the concentration profile in the LK zone, initially at concentration c_o , is approximated by the second-order polynomial

$$c(x, t) - c_o = (\theta_h + px + qx^2)e^{-x/d}, \quad (4.1)$$

where

$$\theta_h = c_h(t)|_{x=0} - c_o, \quad (4.2)$$

$$d = \sqrt{\mathcal{D}_l^* t / 4}, \quad (4.3)$$

$$p = \frac{\frac{\mathcal{D}_l^* \theta_h \Delta t}{d} + I_n - d^3 \frac{\theta_h - \theta_{hn}}{\mathcal{D}_l^* \Delta t}}{3d^2 + \mathcal{D}_l^* \Delta t}, \quad (4.4)$$

$$q = \frac{2pd - \theta_h + d^2 \frac{\theta_h - \theta_{hn}}{\mathcal{D}_l^* \Delta t}}{2d^2}, \quad (4.5)$$

where $c_h(t)|_{x=0}$ is the concentration in the HK material at the interface, and

$$I_n = \theta_{hn} d_n + p_n d_n^2 + 2q_n d_n^3, \quad (4.6)$$

in which subscript n denotes the value of the variable at the previous time step. The effect of adsorption in the LK material can be included by dividing each occurrence of $\mathcal{D}_l^*$ by a retardation factor R_{dl} . From an initial concentration of c at time t in the LK material, new coefficients p and q are calculated after each time step, Δt . Calculation of these coefficients involves the new concentration at the boundary, c_h , and a penetration depth, d , which is calculated as a function of time from the initiation of change at the boundary. The concentration profile from the previous time step affects the updated values of p and q through the intermediate parameter, I .

The function Eq. (4.1) can be used to represent any specified-concentration boundary condition at the LK-HK interface.

The boundary condition at $x = \infty$ must be a constant concentration, typically zero. If p, q , and I are initially zero, the initial condition is one of uniform concentration, which includes the case of $c_o = 0$. However, a nonuniform initial condition can be simulated by starting with values of p, q , and I that replicate the desired concentration profile in the LK material. In practice, this is most easily obtained by conducting a simulation beginning with a uniform (clean) initial concentration distribution and, by history matching, evolving the nonuniform contamination profile up to the desired time-zero.

Figure 4.1: Comparison of analytical solution with polynomial approximation for Case A.

The diffusive flux per unit interfacial area is then obtained from

$$j = -\phi_l \mathcal{D}_l^* \left. \frac{\partial c}{\partial x} \right|_{x=0} = \phi_l \mathcal{D}_l^* \left(\frac{\theta_h}{d} - p \right). \quad (4.7)$$

To validate the proposed approximation, we compared it with some of the analytical solutions discussed in the previous section. Figures 4.1. through 4.1. show comparisons of the fluxes obtained from second-order polynomial approximation to the analytical solutions for Cases A, C, and E. The comparison is quite good, particularly when the concentration at the interface is varying slowly.

5. Impact on Cleanup

5.1. Application to a Zero-Dimensional Model

A simple model of aquifer cleanup assumes that an aquifer is a single, well-mixed domain of volume $\mathcal{U}$, initially at a uniform concentration $c = c_o$. Recharge water at concentration $c = 0$ enters the control volume at a rate Q . Within the control volume, the contaminant can adsorb onto the solids, or degrade in the liquid phase at an assumed first-order transformation rate, λ . Contaminant is extracted from $\mathcal{U}$ at the prevailing concentration, c , by pumping at a rate assumed equal to the rate of recharge, Q . The mass balance equation is

$$\frac{dc}{dt} = -\frac{Q}{\mathcal{U}\phi R_d} c - \frac{\lambda}{R_d} c; R_d = 1 + \frac{\rho_b K_d}{\phi}. \quad (5.1)$$

The problem has an analytical solution of the form

$$c = c_o e^{kt}, \quad (5.2)$$

Figure 4.2: Comparison of analytical solution with polynomial approximation for Case C.

Figure 4.3: Comparison of analytical solution with polynomial approximation for Case E.

where

$$k = -\frac{Q}{U\phi R_d} - \frac{\lambda}{R_d}. \quad (5.3)$$

This analytical model was used by Isherwood *et al.* (1990) to estimate the rate of cleanup of the LLNL Livermore Site ground water plume. It is similar to the batch flushing model proposed by EPA (1988) to estimate ground water cleanup times at CERCLA sites. This zero-dimensional or *lumped parameter* model is a simple and useful tool for estimating the average response of an aquifer as an aid to management and decision making, especially in the early stages of a project, when spatially distributed data are relatively scarce (Bear, 1979).

The preceding single-cell model can be modified to include LK and HK materials and the effects of diffusive transfer across the HK-LK interface at a rate of transfer $f_{h \rightarrow l}$. The mass balance equation is written now for the volume of HK material $U_h = n_h U$ as

$$\frac{dc_h}{dt} = -\frac{Q}{U_h \phi_h R_{dh}} c_h - \frac{\lambda}{R_{dh}} c_h - f_{h \rightarrow l}; \quad R_{dh} = 1 + \frac{\rho_{bh} K_{dh}}{\phi_h}. \quad (5.4)$$

Combining the rate of transfer term defined in Eq. (3.1) and the second-order polynomial approximation of the diffusive flux derived in Eq. (4.7), we obtain

$$\frac{dc_h}{dt} = -\frac{Q}{U_h \phi_h R_{dh}} c_h - \frac{\lambda}{R_{dh}} c_h - \Sigma_{HK} \phi_l \frac{D_l^*}{R_{dl}} \left(\frac{c_h}{d} - p \right). \quad (5.5)$$

This equation can be solved numerically using a finite-difference approximation in time. The concentration in the HK material for the two cases described by Eqs. (5.2) and (5.5) are compared in Figure 5.1, for parameters which are representative of the LLNL contaminant plume. The concentrations are normalized with respect to the maximum predicted concentration in the HK material for the case without diffusive exchange across the HK-LK interface (solid line in Figure 5.1). The dashed line in Fig. 5.1 shows the HK concentration for the case where contaminant mass diffuses across the HK-LK interface. We note that, in the case of diffusive exchange, the HK concentration is slower to increase and *slower to decrease* than the HK concentration in the absence of diffusive exchange.

This figure was produced using a 40-yr contamination period, a value of $\frac{Q}{U\phi R_d}$ equal to 0.042, and assuming a first-order transformation rate with a half-life of 50 yr. The input parameters were determined by Thorpe *et al.* (1990) for application to a zero-dimensional model for cleanup of the regional aquifer underlying LLNL.

There are two important features in Figure 5.1. At short times after the initial contamination of the aquifer, LK diffusion results in lower concentrations in the HK material, since contaminant mass is being lost to the LK material. After cleanup has begun, LK diffusion results in higher concentrations persisting in the HK material, since the LK material now acts as a source of additional contaminant mass. This effect serves

Figure 5.1: A zero-dimensional model for cases with and without diffusive exchange.

to lengthen the cleanup time. If a cleanup goal such as a 5-ppb MCL is the target, which typically requires a ten-fold to thousand-fold reduction in initial concentration, then cleanup will require a much longer pumping duration. However, the incremental cleanup time would depend on the percent reduction in concentration from initial to cleanup levels or, equivalently, on the *cleanup ratio* of the final concentration (say 5-ppb MCL) to the initial concentration.

We demonstrate the effect on cleanup time in Figure 5.2. The incremental cleanup time represents the additional time to cleanup when diffusive exchange is accounted for in the transport model. The estimates on incremental cleanup time are based on aquifer parameters at LLNL. We assume a 50-yr degradation half-life, an HK-LK specific interfacial area of $4 \text{ m}^2/\text{m}^3$, and retardation factors of 1.5 and 3.0 for the HK and LK materials, respectively. For a zero-dimensional model of LLNL ground water, the average initial concentration of total VOCs in ground water is about 81 ppb. The cleanup goal is set to U.S. Federal MCL of 5 ppb. The cleanup ratio of the final to the initial concentration equals 0.06. For LLNL, our simple zero-dimensional model predicts an extra 25 yr to cleanup if diffusive exchange is considered. Likewise, if the initial concentration were 500 ppb, the cleanup ratio would be $5/250 = 0.01$, and the incremental time to cleanup would be 147 yr as shown in Figure 5.2. The zero-dimensional model provides an easy-to-use tool for a preliminary estimate of the additional time to cleanup. The model can be adapted by providing site-specific model parameters in the input.

We note here that if pumping is suspended, the concentration in the HK material may *increase* as a result of the LK-HK diffusion phenomena evaluated in this paper. Observations of this effect have prompted many pump-and-treat cleanup programs to implement intermittent pumping schedules. During the no-pumping period, diffusion into the HK material will continue, thus making the resumed pumping more effective in terms of *mass removal rate* during pumping, if not in terms of *overall time to cleanup*.

Figure 5.2: Incremental cleanup time with diffusive exchange: zero-dimensional model.

This is easily demonstrated with the single-cell model, solved numerically using an on-off pumping pattern.

5.2. Application to a One-Dimensional Aquifer Model

Let us demonstrate the simplified diffusive flux approximation by applying it to a numerical model of one-dimensional horizontal flow in an aquifer. The aquifer consists primarily of HK material, and some LK material of specified HK-LK interfacial area. The aquifer is initially clean ($c = 0$).

At time $t = 0$, contaminated water, at concentration c_o , begins entering the aquifer at velocity V . The contaminant is transported in the HK material by both advection and hydrodynamic dispersion. The contaminant may diffuse everywhere into the LK material across the (microscopic) HK-LK interface. Within each material type, the contaminant may adsorb onto the solids, or degrade in the aqueous phase at an assumed first-order degradation rate of λ . The contaminant continues to enter the aquifer at a constant concentration, c_o , over 40 yr. At the end of 40 yr, the source of contamination is instantaneously removed, and clean water ($c = 0$) starts entering the aquifer at the same rate.

The one-dimensional mass balance equation for the contaminant in the HK material is

$$\phi_h R_{dh} \frac{\partial c_h}{\partial t} = \phi_h \mathbf{D}_h \frac{\partial^2 c}{\partial x^2} - \phi_h V \frac{\partial c}{\partial x} - \phi_h R_{dh} \lambda c - f_{h \rightarrow l}, \quad (5.6)$$

where $\mathbf{D}_h$ represents the dispersion coefficient in the HK material, and we have made use of $\partial V / \partial x = 0$ (which expresses the mass balance of the water).

Figure 5.3: Concentration at $x = 100$ m in a one-dimensional model for cases with and without diffusive exchange.

The exchange term, $f_{h \rightarrow l}$, may be substituted by the polynomial approximation (4.7), combined with Eq. (3.1), to obtain

$$\phi_h R_{dh} \frac{\partial c_h}{\partial t} = \phi_h \mathbf{D}_h \frac{\partial^2 c}{\partial x^2} - \phi_h V \frac{\partial c}{\partial x} - \phi_h R_{dh} \lambda c - \sum_{HK} \phi_l \frac{\mathcal{D}_l^*}{R_{dl}} \left(\frac{c_h}{d} - p \right). \quad (5.7)$$

This equation was solved using a fully implicit finite-difference approximation. Figure 5.3 presents a comparison of the HK concentration with and without ($f_{h \rightarrow l} = 0$) diffusive exchange across the HK-LK interface, at a distance of 100 m downstream of the point where contaminants enter the aquifer. We assumed a ground water velocity of 15 m/yr, dispersion coefficient of 150 m²/yr, a porosity of 0.3 for both the HK and the LK material, and retardation factors of 1.5 and 3 for the HK and the LK materials, respectively. For the case with diffusive exchange across the interface, significantly lower concentrations are observed in the HK material, as some of the contaminant mass diffuses into the LK zone.

More important for cleanup, the mass that diffuses into the LK material will ultimately return to the HK material after cleanup of the HK material begins. In the absence of degradation, this may significantly prolong cleanup.

6. Conclusions

Pump and treat is a favored technology for reducing contaminant concentrations in the saturated subsurface. It is practically the only alternative available for extensive aquifers with relatively low levels of contamination. Experience with pump and treat at Superfund restoration sites such as LLNL has shown that, although concentrations

decrease in the HK material in response to remedial pumping, cleanup often progresses much more slowly than predicted by large-scale, single-continuum models. This paper shows that diffusive exchange of contaminants into and out of LK materials contributes to prolonged cleanups.

Results of this investigation suggest that, depending on the cleanup target, the effects of LK diffusion will persist for many decades, perhaps several times longer than the initial period of contamination, which at LLNL is about 40 yr. In addition, if regulations require that aqueous concentrations in the LK material be reduced to MCL levels, and if no favorable contaminant degradation occurs in the LK material, then cleanup times will be significantly greater than predicted by single-continuum models that ignore the effect of LK diffusion.

References

- Barenblatt, G.I., I.P. Zheltov, and I.N. Kochina (1960), "Basic Concepts in the Theory of Seepage of Homogeneous Fluids in Fissured Rocks," *J. Appl. Math. Mech.*, Engl. Transl., **24**(5), 1286-1303.
- Bear, J. (1979), *Hydraulics of Groundwater*, McGraw-Hill, New York, 569 pp.
- Bear, J., and Y. Bachmat (1991), *Introduction to Modeling of Transport Phenomena in Porous Media*, Kluwer Academic Publishers, Dordrecht, 553 pp.
- Carpenter, D.W. (1984), *Assessment of Contamination in Soils and Groundwater at Lawrence Livermore National Laboratory, Sandia National Laboratories, Livermore, and Adjacent Properties*, Lawrence Livermore National Laboratory, Livermore, Calif. (UCAR-10180).
- Carslaw, J.S., and J.C. Jaeger (1959), *Conduction of Heat in Solids*, 2nd ed., Oxford Univ. Press, London.
- Dykhuizen R.C. (1990), "A New Coupling Term for Dual Porosity Models," *Water Resour. Res.*, **26**(2), 351-356.
- van Genuchten, M.T. (1985), *A General Approach for Modeling Solute Transport in Structured Soils*, in the International Association of Hydrogeologists, Memoirs XVII, Part 2, in Proceedings Hydrogeology of Rocks of Low Permeability, pp. 513-526.
- Grisak G.E., and J.F. Pickens (1980), "Solute Transfer Through Fractured Media, 1: The Effect of Matrix Diffusion," *Water Resour. Res.*, **16**(4), 719-730.
- Gupta, S.K., C.R. Cole, C.T. Kincaid, and A.M. Monti (1987), *Coupled Fluid, Energy, and Solute Transport (CFEST) Model: Formulation and User's Manual*, Report BMI/ONWI-660, Office of Nuclear Waste Isolation, Battelle Memorial Institute, Columbus, Ohio.
- Hansamuit, V., J.H. Abou-Kassem, and S. Farouq Ali (1992), "Heat Loss Calculation in Thermal Simulation," *Transport in Porous Media*, **8**: 149-166.

- Isherwood, W.F., C.H. Hall, and M.D. Dresen, Eds. (1990), *CERCLA Feasibility Study for the LLNL Livermore Site*, Lawrence Livermore National Laboratory, Livermore, Calif. (UCRL-AR-104040).
- Pruess, K.P., and Y.S. Wu (1989), "A New Semi-Analytical Method for Numerical Simulation of Fluid and Heat Flow in Fractured Reservoirs," *Paper SPE-18426*, Soc. of Pet. Eng., Dallas, Tex.
- Tang, D.H., E.O. Frind, and E.A. Sudicky (1981), "Contaminant Transport in Fractured Porous Media: Analytical Solution for a Single Fracture," *Water Resour. Res.*, **17**, 555-564.
- Tompson, A.F.B., E.M. Nichols, P.F. McKereghan, and M.C. Small (1991), *Summary of Preliminary Ground Water Simulations in the Livermore Regional Modeling Study: CFEST Finite Element Code*, Lawrence Livermore National Laboratory, Livermore, Calif. (UCRL-AR-107049).
- Tompson, A.F.B., P.F. McKereghan, and E.M. Nichols, Eds. (1993), *Preliminary Simulations of Contaminant Migration in Ground Water Beneath Lawrence Livermore National Laboratory*, Lawrence Livermore National Laboratory, Livermore, Calif. (in preparation).
- U.S. Department of Energy (DOE) (1992), *Record of Decision for the Lawrence Livermore National Laboratory, Livermore Site*, Lawrence Livermore National Laboratory, Livermore, Calif. (UCRL -AR-109105).
- U.S. Environmental Protection Agency (EPA) (1988), *Guidance for Conducting Remedial Investigations and Feasibility Studies under CERCLA - Interim Final*, EPA/540/G-89/004, OSWER Directive 9355.3-01.
- Vinsome, K., and J. Westerveld (1980), "A Simple Method for Predicting Cap and Base Rock Heat Losses in Thermal Reservoir Simulators," *Canad. Pet. Technol. J.*, 87-90.
- Warren, J.E., and P.J. Root (1963), "The Behavior of Naturally Fractured Reservoirs," *Soc. Pet. Eng. J.*, **3**(5), 245-255.

List of Main Symbols

c_α	Average concentration of the γ -component in the water present in the α -continuum, $\alpha = h, l$.
D_h	Coefficient of dispersion in the HK material.
D_l^*	Coefficient of molecular diffusion in the isotropic LK material.
$f_{\alpha \rightarrow \beta}$	Rate of transfer of γ from the α -continuum to the β -one, across their common interface, per unit volume of aquifer.
j	Diffusive flux normal to the HK-LK interface.
K_α	Hydraulic conductivity of the α -continuum, $\alpha = h, l$.
$K_{d\alpha}$	Partitioning coefficient in the α -continuum, $\alpha = h, l$.
m	The total mass accumulated within the LK material.
n_α	Volumetric fraction of α -continuum within the aquifer, $\alpha = h, l$.

Q	Rate of flushing.
$R_{d\alpha}$	Retardation factor for the α -continuum, $\alpha = h, l$.
t	Time.
T	Time period of contamination event.
U_v	Pore volume within a cell.
V	Velocity of water in the HK continuum.
α^*	Transfer coefficient.
γ	Dissolved contaminant present in the aquifer.
ϕ_α	Volumetric fraction of void space (= porosity) within the α -continuum, $\alpha = h, l$.
$\rho_{b\alpha}$	Bulk density of a solid matrix within the α -material ($= \rho_s(1 - \phi_\alpha)$), $\alpha = h, l$.
Σ_{HK}	Specific interface area (= area per unit volume of aquifer).
τ_α^*	Tortuosity of the α -continuum, $\alpha = h, l$.

Acknowledgments

The authors wish to thank the management of the Environmental Protection Department, Lawrence Livermore National Laboratory, for supporting this work. The first author also wishes to acknowledge the support of the Fund for the Promotion of Research at the Technion-Israel Institute of Technology, Haifa.

**DATE
FILMED**

4/28/94

END