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Soil Cleanup by in-situ Aeration. XVI. Solution and Diffusion in Mass-Transport-Limited Operation and Calculation of Darcy's Constants

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Soil Cleanup by in-situ Aeration. XVI. Solution and Diffusion in Mass-Transport-Limited Operation and Calculation of Darcy's Constants

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ABSTRACT

A model for soil vapor extraction (SVE) in laboratory columns is developed which includes mass transport kinetics of volatile organic compounds (VOCs) between nonaqueous phase liquid (NAPL) droplets and the aqueous phase, and between the aqueous and vapor phases. The model provides a detailed treatment of diffusion of VOCs through a stagnant aqueous boundary layer or low-permeability lamellar domain, and permits time-dependent gas flow rates in the vapor extraction column. Runs made with the model exhibit high initial effluent soil gas VOC concentrations typically followed by a fairly rapid decrease in concentration which in turn is followed by a prolonged tailing region in which the effluent soil gas VOC concentrations decrease quite slowly until nearly all of the VOC has been stripped from the column. The model suggests the futility of trying to predict SVE cleanup times on the basis of pilot-scale experiments carried out for only a few days. These give no idea as to the rate of VOC removal late in the remediation. The model permits the gas flow to be varied with time; shutting off the gas flow after partial cleanup results in rebounds in the soil gas VOC concentrations which can be quite large, particularly if some NAPL is still present. A comparison is made between Darcy's constants calculated by commonly used approximate formulas and more exact formulas based on the method of images. Configurations examined are 1)

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a well with a gravel packing of length roughly equal to its diameter, and 2) a well with a gravel packing long compared to its diameter. Appreciable discrepancies between the approximate and exact formulas are found for the second configuration.

INTRODUCTION

The use of soil vapor extraction (SVE, soil venting, soil vapor stripping, in-situ vapor stripping, soil vacuum extraction) is now quite common in the remediation of sites at which there is vadose zone contamination with volatile organic compounds (VOCs). The U.S. EPA has published a guide (1) and a reference handbook (2) discussing the technique, both of which include an extensive list of references. Hutzler and his coworkers published a detailed review (3), and this was updated in a subsequent paper from our group (4). The literature on soil vapor extraction is now extensive and the technology is fairly mature.

The nature of the technique is such that assessing its feasibility and designing a SVE system in any particular application are rather site-specific. These depend on the site geology (depth to water table, pneumatic permeability of vadose zone soils, presence of overlying impermeable structures such as floors or parking lots, heterogeneity of soil, moisture content, presence of natural or other nonvolatile organics) and on contaminant properties (vapor pressure, water solubility, partition coefficient on organic carbon, and Henry's constant, all at ambient soil temperature).

Because of this, there has been considerable interest in the mathematical modeling of SVE for feasibility studies, data interpretation, and system design. Johnson, Kemblowski, Colthart, and their associates published a number of papers on this (5–7). Hoag, Marley, Cliff, and their associates at Vapex (8–10) were among the first to use mathematical modeling techniques in SVE. Cho carried out a quite detailed study in which modeling work was supported by extensive experimental verification (11). Our group published several papers on the mathematical modeling of SVE under a variety of conditions (Refs. 12–14 and other papers in this series).

One of the more troublesome of the site-specific aspects of SVE is the extent to which the kinetics of diffusion and/or desorption may limit the rate at which VOCs can be removed, particularly in the latter stages of a cleanup. If one has a site with a highly homogeneous sandy soil containing very little clay and natural organic material and relatively little moisture, one may reasonably hope to find that diffusion/desorption rates present no problem and that a local equilibrium treatment of the process is adequate. If, however, the porous medium has a highly heterogeneous permeability, if it contains significant amounts of clay or humic organic material, or if it contains substantial amounts of water, the kinetics of diffusion and/or desorption may be serious bottlenecks in the removal of VOCs by SVE.

DiGiulio et al. (15) discussed this problem and described experiments which could be done during SVE pilot studies to determine the extent to which these mass transport processes may slow down the remediation. Such kinetic processes have plagued pump-and-treat remediations to an extreme degree, and we have developed microcomputer models for the modeling of diffusion kinetics in that connection (16, 17). Kinetically limited processes can also be presumed to be operative in air sparging operations (18). In SVE we developed mathematical models which include diffusion and solution kinetics, and we discussed the use of models in designing and interpreting experiments to estimate the time constants of these mass transport processes (Refs. 19–21, for example).

Our approach to diffusion kinetics, however, has been by means of a lumped parameter method in which a single time constant is used to approximate the time dependence of the diffusion process. By suitably selecting the time constant, one can produce model results which show the sort of tailing near the end of the remediation which is often observed. However, when this is done, the initial rate of VOC removal is greatly reduced, too. Therefore, if one carries out a short (i.e., less than a week) pilot SVE test and sees, as is generally the case, quite rapid VOC removal, one calculates a lumped parameter diffusion rate constant which is much too large. The model, when used with a rate constant predicted in this way, predicts cleanup times that are far too short. In effect, the diffusion rate constant decreases quite markedly during the course of the remediation.

When the lumped parameter method is used, the pilot-scale tests must be carried out until remediation of the soil being treated is nearly complete if a lumped parameter diffusion rate constant is to be obtained which is applicable to the remediation of the site as VOC removal approaches completion. The pilot-scale tests must also employ some isolation procedure such as was described by DiGiulio et al. (15) to prevent the confounding of the diffusion kinetics with the very slow advective transport of VOCs from soil at long distances from the well.

In short, local equilibrium SVE models, which ignore diffusion/desorption kinetics altogether, are very likely to predict cleanup times which are far too short, thereby causing trouble and recriminations. Similarly, lumped parameter models, if fitted to data taken during a SVE pilot run lasting only a few days, are very likely to predict cleanup times which are far too short. Successful use of such lumped parameter models requires properly designed pilot tests of considerable duration which include post-SVE monitoring of soil gas VOC concentrations to assess the extent and rate of concentration rebound.

The more lengthy and elaborate testing needed to assess the extent to which diffusion/desorption kinetics may control the rate of remediation is obviously more costly in terms of money and time than cheap, quick tests which only demonstrate that in the initial stages of the cleanup, SVE is indeed able to move product. Clients should understand that such shortcut testing will not allow any more than estimation of an extremely optimistic lower bound to the cleanup time. This is true both for local equilibrium modeling and lumped parameter modeling.

In the following sections we first propose and transcribe into equations a fairly realistic physical model for the kinetics of the removal of both dissolved VOC and NAPL from the vadose zone during SVE in a laboratory column. The results of a number of runs made with the model are then examined; we shall see that the type of behavior observed at kinetically limited sites is easily produced with the model. Finally, the section closes with consideration of the implications of these results with regard to pilot-scale SVE tests.

The last portion of the paper deals with the errors involved in the use of two simple approximate formulas commonly used in calculating Darcy's constants from vacuum well wellhead pressures and gas flow rates. The results of the approximate formulas are compared with more nearly exact results obtained by the method of images.

MODEL AND ANALYSIS

Notation

Let us consider a laboratory column partitioned for mathematical analysis as indicated in Fig. 1. The column is divided into n_x disk-shaped volume elements, each of thickness Δx. The water layers or water-saturated lamellae present in each of these volume elements are further divided into n_y slabs, each of thickness Δy; the first is in contact with the advecting air, and the last is bordered by the solid soil surface. These water-saturated domains model thin porous strata and lenses of low permeability which are saturated or nearly saturated with water. These can lose VOC only by diffusion transport through the aqueous phase. The model thus permits the representation of small-scale heterogeneities in the medium by means of an approximation which permits treatment of the gas flow field as if the medium were homogeneous over the individual volume elements.

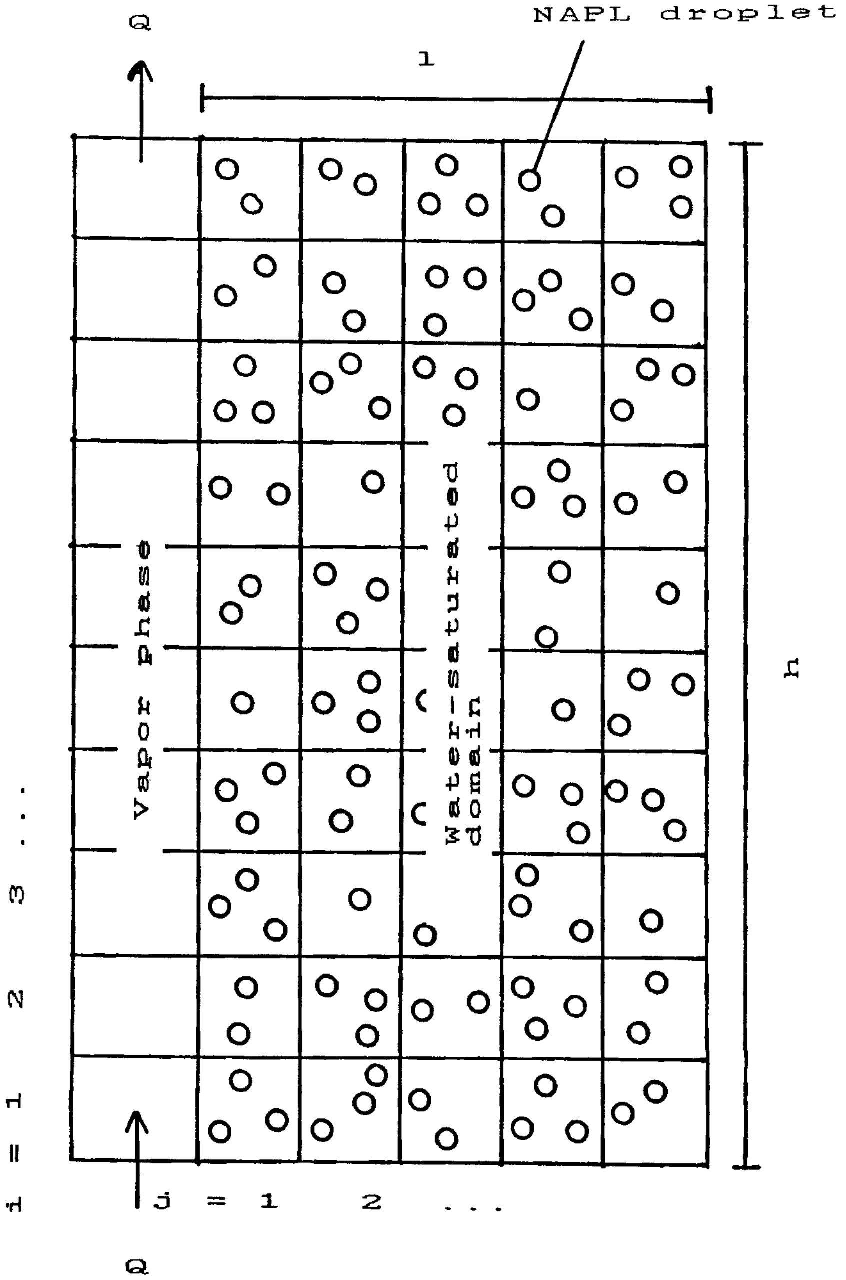

FIG. 1 Geometry, notation, and mathematical partitioning of an SVE laboratory column.

Let

h = height of column, cm
r_c = radius of column, cm
A = cross-sectional area of column, cm^2
Δx = h/n_x
$A\Delta x$ = volume of a volume element, cm^3
Q = gas flow rate through column, mL/s
ω = water-filled porosity of soil
σ = air-filled porosity of soil
l = average thickness of (stationary) soil water layer, cm
n_y = number of slabs into which the soil water layer is divided
Δy = l/n_y, the thickness of one of the slabs into which the soil water layer is divided, cm
a_0 = average initial NAPL droplet size, cm
D = diffusivity of the VOC in soil water, cm^2/s
C_{sat} = solubility of VOC in water, g/cm^3
ρ_{voc} = density of NAPL VOC, g/cm^3
ρ_{soil} = density of bulk soil, g/cm^3
K_H = Henry's constant of VOC, dimensionless
m_{ij} = mass of NAPL in the jth slab of the ith volume element, g
C_{ij}^w = dissolved VOC concentration in the jth slab of the ith volume element, g/cm^3
C_i^g = VOC concentration in the gas phase in the ith volume element, g/cm^3

Rate of NAPL Droplet Solution

We first examine the rate of dissolution of VOC from a NAPL droplet into the aqueous phase. The equation for steady-state diffusion from a spherical droplet is

$$0 = \frac{1}{r^2}\frac{d}{dr}\left[r^2\frac{dC}{dr}\right] \tag{1}$$

with boundary conditions

$$C(a) = C_{\text{sat}} \tag{2}$$

and

$$C(b) = C_0 \tag{3}$$

where C_0 is the VOC concentration at the outer surface of the aqueous boundary layer surrounding the drop. Equation (1) integrates to give

$$C(r) = c_1/r + c_2 \tag{4}$$

where c_1 and c_2 are integration constants. Use of the boundary conditions then yields

$$C(r) = \frac{ab}{b - a}(C_{\text{sat}} - C_0)/r + c_2 \tag{5}$$

and

$$\frac{dC}{dr} = -\frac{ab}{b - a}(C_{\text{sat}} - C_0)/r^2 \tag{6}$$

Fick's first law and Eq. (6) then give for the mass m of the droplet

$$\frac{dm}{dt} = -\frac{4Da(C_{\text{sat}} - C_0)}{1 - a/b} \tag{7}$$

It is easily shown that

$$a = a_0(m/m_d)^{1/3} \tag{8}$$

where m_d is the initial mass of the droplet, so the rate of change of mass of the droplet is

$$\frac{dm}{dt} = -\frac{4\pi Da_0(C_{\text{sat}} - C_0)(m/m_d)^{1/3}}{1 - (a_0/b)(m/m_d)^{1/3}} \tag{9}$$

A reasonable value for b, the boundary layer thickness around a droplet, is half the distance between droplets. This is obtained as follows. The number of NAPL droplets in a volume element, $A\,\Delta x$, is given by n, where

$$n\frac{4\pi a_0^3\rho_{\text{voc}}}{3} = A\,\Delta x C_0^N \tag{10}$$

and so

$$n = \frac{3A\,\Delta x C_0^N}{4\pi a_0^3\rho_{\text{voc}}} \tag{11}$$

These are contained in a volume of water equal to $\omega A\,\Delta x$, so the volume of water per droplet is given by

$$V' = \frac{4\pi\omega\rho_{\text{voc}}a_0^3}{3C_0^N} \tag{12}$$

Then the distance between droplets is given by

$$2b = a_0\left[\frac{4\pi\omega\rho_{\text{voc}}}{3C_0^N}\right]^{1/3} \tag{13}$$

and finally

$$b = a_0 \left[\frac{\pi \omega \rho_{\text{VOC}}}{6 C_0^N} \right]^{1/3} \tag{14}$$

[A reasonable alternative assumption is to place the droplets at the center of spheres of aqueous phase; this yields

$$b = a_0 \left[\frac{\omega \rho_{\text{VOC}}}{C_0^N} \right]^{1/3} \tag{15}$$

for the thickness of the boundary layer.]

Physically, the thickness of the slabs into which the domains of diffusion are partitioned (Δy) should be larger than b, the distance between the droplets, if the model is to be an accurate representation of the solution/diffusion process. One hopes that when this criterion is not satisfied, one still has a reasonably good approximation.

Initial Distribution of VOC among the Phases

The initial amounts present in the vapor, aqueous, and NAPL phases are calculated as follows. We assume the initial concentrations in the gas, aqueous, and NAPL phases are constant from volume element to volume element, and that the aqueous and NAPL phase concentrations are constant from slab to slab within a volume element. Then

$$C_{\text{tot}} = \sigma C_0^g + \omega C_0^w + C_0^N \tag{16}$$

where C_0^g, C_0^w, and C_0^N are the initial gaseous, aqueous, and NAPL concentrations, respectively. Assume that $C_0^N = 0$ and that the aqueous and gaseous phases are at equilibrium with each other with respect to VOC transport. Then, on using Henry's law, it is easily shown that

$$C_0^w = \frac{C_{\text{tot}}}{\sigma K_{\text{H}} + \omega} \tag{17}$$

and

$$C_0^g = K_{\text{H}} C_0^w \tag{18}$$

If $C_0^w > C_{\text{sat}}$, however, set $C_0^w = C_{\text{sat}}$, $C_0^g = K_{\text{H}} C_{\text{sat}}$, and calculate C_0^N from

$$C_0^N = C_{\text{tot}} - (\sigma K_{\text{H}} + \omega) C_{\text{sat}} \tag{19}$$

Rate of Change of NAPL Mass

Recall that the number of NAPL droplets in a volume element is given by

$$n = \frac{3A\,\Delta x C_0^N}{4\pi a_0^3 \rho_{\text{voc}}} \tag{11}$$

The number of NAPL droplets in a single slab in a volume element is then given by

$$n_s = \frac{n}{n_y} = \frac{3A\,\Delta x C_0^N}{4\pi a_0^3 \rho_{\text{voc}} n_y} \tag{20}$$

The initial NAPL mass in a single slab is

$$m_0 = A\,\Delta x C_0^N / n_y \tag{21}$$

The initial mass of a droplet m_d is

$$m_d = 4\pi a_0^3 \rho_{\text{voc}}/3 \tag{22}$$

Finally, on using Eq. (9), we find that the mass of NAPL in the jth slab of the ith volume element is governed by

$$\frac{dm_{ij}}{dt} = -\frac{3A\,\Delta x C_0^N D(C_{\text{sat}} - C_{ij}^w)(m_{ij}/m_0)^{1/3}}{a_0^2 \rho_{\text{voc}} n_y [1 - (a_0/b)(m_{ij}/m_0)^{1/3}]} \tag{23}$$

Change in Aqueous VOC Concentration

The volume of water in a single volume element is given by

$$V_w = \omega A\,\Delta x \tag{24}$$

This water is assumed to be spread in a layer of thickness l. The areal extent of this volume of water is therefore given by

$$S_w = \omega A\,\Delta x / l \tag{25}$$

which is also the area of the interface between any two adjacent slabs within the volume element into which the aqueous phase is partitioned and between which diffusion transport of VOC takes place.

A mass balance on the aqueous phase VOC in the jth slab of the ith volume element then yields

$$\frac{\omega A\,\Delta x}{n_y}\frac{dC_{ij}^w}{dt} = \frac{S_w D}{\Delta y}(C_{ij-1}^w - 2C_{ij}^w + C_{ij+1}^w) - \frac{dm_{ij}}{dt}$$

$$(j = 2, 3, \ldots, n_y - 1) \tag{26}$$

or

$$\frac{dC^w_{ij}}{dt} = \frac{n_y}{\omega A \Delta x}\left[\frac{S_w D}{\Delta y}(C^w_{i,j-1} - 2C^w_{i,j} + C^w_{i,j+1}) - \frac{dm_{ij}}{dt}\right]$$

$$(j = 2, 3, \ldots, n_y - 1) \quad (27)$$

The first group of terms on the right-hand side of Eq. (26) represents diffusion of dissolved VOC from slab to slab [the coefficient of the terms in the C^w's simplifies to $D/(\Delta y)^2$, as expected]; the last term represents mass transport to the aqueous phase from the dissolving NAPL droplets. For the slab adjacent to the solid medium we have

$$\frac{dC^w_{i,n_y}}{dt} = \frac{n_y}{\omega A \Delta x}\left[\frac{S_w D}{\Delta y}(-C^w_{i,n_y} + C^w_{i,n_y-1}) - \frac{dm_{i,n_y}}{dt}\right] \quad (28)$$

For the slab adjacent to the advecting gas phase we assume that the aqueous VOC concentration at the air–water interface is given by Henry's law, so

$$\frac{dC^w_{i1}}{dt} = \frac{n_y}{\omega A \Delta x}\left[\frac{S_w D}{\Delta y}(C^w_{i2} - C^w_{i1}) + \frac{2S_w D}{\Delta y}(C^g_i/K_{\mathrm{H}} - C^w_{i1}) - \frac{dm_{i1}}{dt}\right]$$

$$(29)$$

A mass balance on the gas phase VOC in the ith volume element yields

$$\frac{dC^g_i}{dt} = \frac{Q}{A \Delta x \sigma}(C^g_{i-1} - C^g_i) - \frac{2S_w D}{A\sigma \Delta x \Delta y}(C^g_i/K_{\mathrm{H}} - C^w_{i1}) \quad (30)$$

Computations

The model then consists of Eqs. (23) and (27)–(30), together with the prescription for calculating the initial values of the vapor, aqueous, and NAPL phase VOC concentrations. The model parameters and concentrations are initialized, and the differential equations are integrated forward in time to model a run. The model was implemented in TurboBASIC, and most of the computations were done on a 16 MHz MMG 386 SX microcomputer with a math coprocessor. Typical runs took approximately half an hour. It is estimated that a two-dimensional model (needed to simulate simple vertical SVE wells or SVE by means of a buried horizontal pipe) would require some 5–6 hours of time per run with such a computer following this approach. Some runs were made on a 50 MHz 486 machine; these typically took about 2–3 minutes, so one would expect that two-dimensional models of this type could be run on such a machine in about 30–45 minutes.

RESULTS

Default parameters for the runs are given in Table 1. Parameter values not equal to the values given in Table 1 are listed in the captions to the figures. In these runs the VOC is trichloroethylene.

Total residual VOC mass and effluent soil gas VOC concentration are plotted in Figs. 2–5 on a normalized basis—that is, these variables are divided by their values at the beginning of the run. The run durations are 50 days. The initial NAPL concentrations are 0.00312 g/cm^3, initial aqueous VOC concentrations are 0.00110 g/cm^3 (saturated), and the initial VOC vapor concentrations are 0.00031 g/cm^3 (saturated vapor). The initial total VOC concentration in the soil is 2000 mg/kg, so this soil is highly contaminated. For Figs. 2–5 the initial NAPL droplet diameters are 0.01, 0.025, 0.05, and 0.1 cm, respectively.

The plots of effluent soil gas VOC concentration indicate initial saturation, followed quickly by a rapid fall-off through a transition region lasting

TABLE 1
Default Parameters for Laboratory Column Simulations

Column length	50 cm
Column diameter	10 cm
Soil air-filled porosity	0.2
Soil water-filled porosity	0.2
Soil density	1.7 g/cm^3
Water layer thickness	1 cm
VOC being simulated	Trichloroethylene
Henry's constant of VOC	0.2821 (dimensionless)
Aqueous solubility of VOC	1100 mg/L
Density of NAPL VOC	1.46 g/cm^3
Diffusion constant of VOC in water-saturated porous medium	2×10^{-6} cm^2/s
Initial NAPL droplet diameter	0.1 cm
Air flow rate	0.1 mL/s
Total VOC concentration in soil	2000 mg/kg
Number of volume elements into which column is partitioned	10
Number of slabs into which each volume element is partitioned	10
Δt	900 seconds
Duration of run	4,320,000 seconds (50 days)

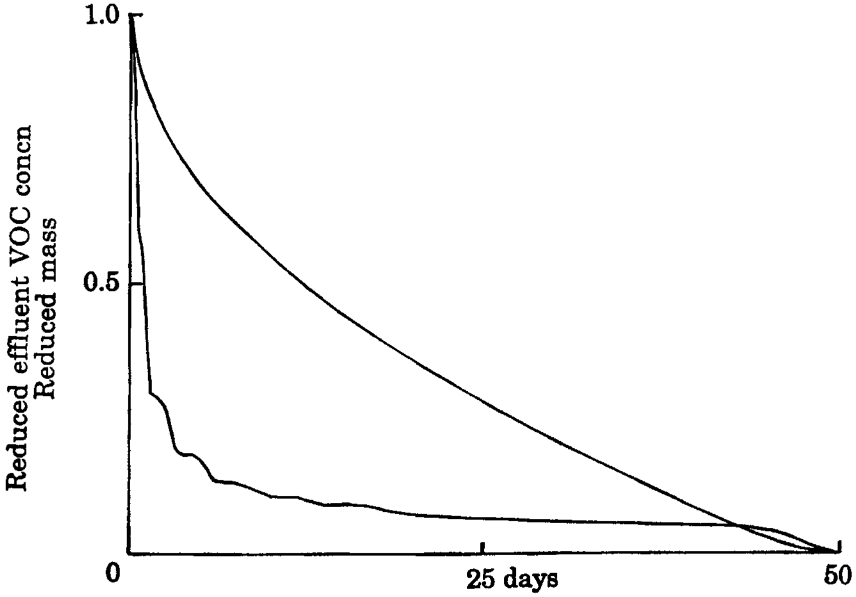

FIG. 2 Plots of normalized residual mass of VOC and normalized effluent soil gas concentration versus time. In this run the initial NAPL droplet diameter is 0.01 cm. Other parameters as in Table 1. The initial NAPL concentration is 0.00312 g/cm^3, the initial aqueous VOC concentration is 0.00110 g/cm^3, the initial gaseous VOC concentration is 0.00031 g/cm^3.

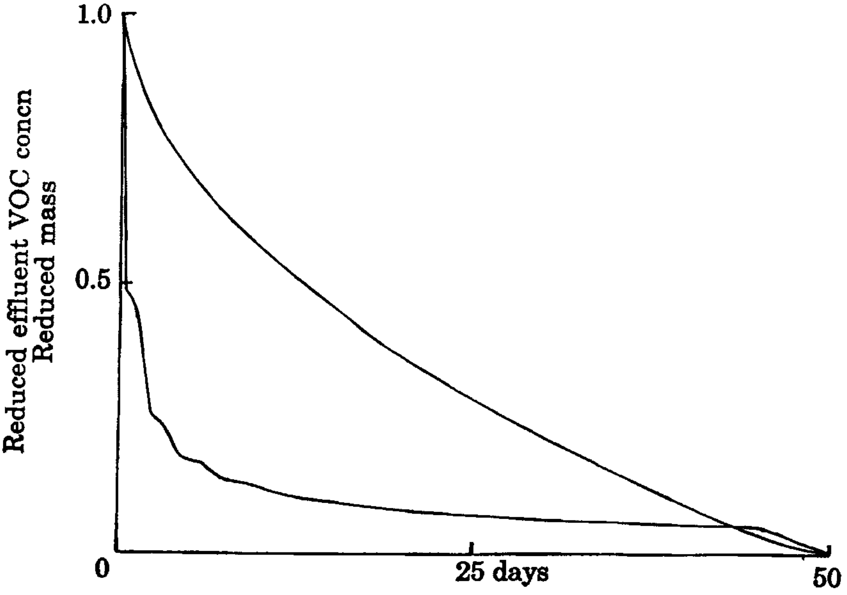

FIG. 3 Plots of normalized residual mass of VOC and normalized effluent soil gas concentration versus time. In this run the initial NAPL droplet diameter is 0.025 cm. Other parameters as in Table 1 and Fig. 2.

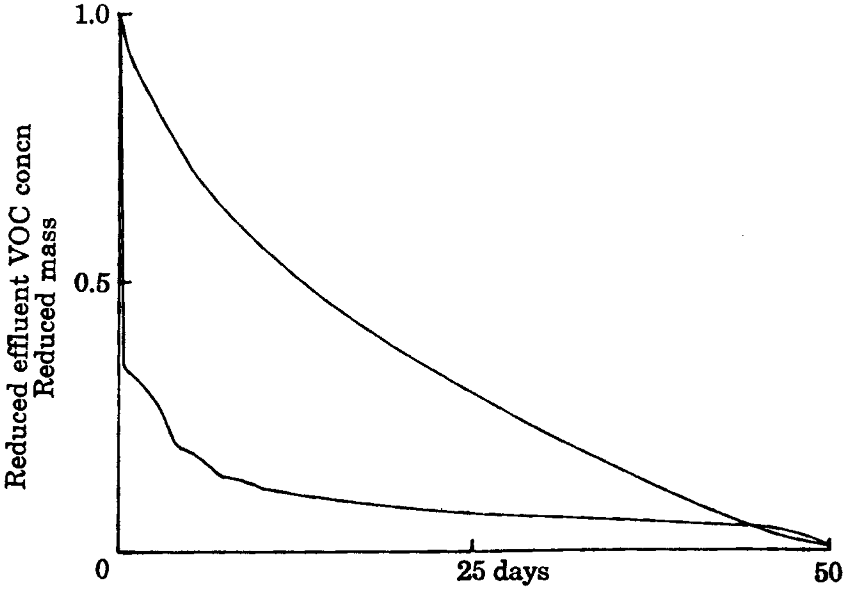

FIG. 4 Plots of normalized residual mass of VOC and normalized effluent soil gas concentration versus time. In this run the initial NAPL droplet diameter is 0.05 cm. Other parameters as in Table 1 and Fig. 2.

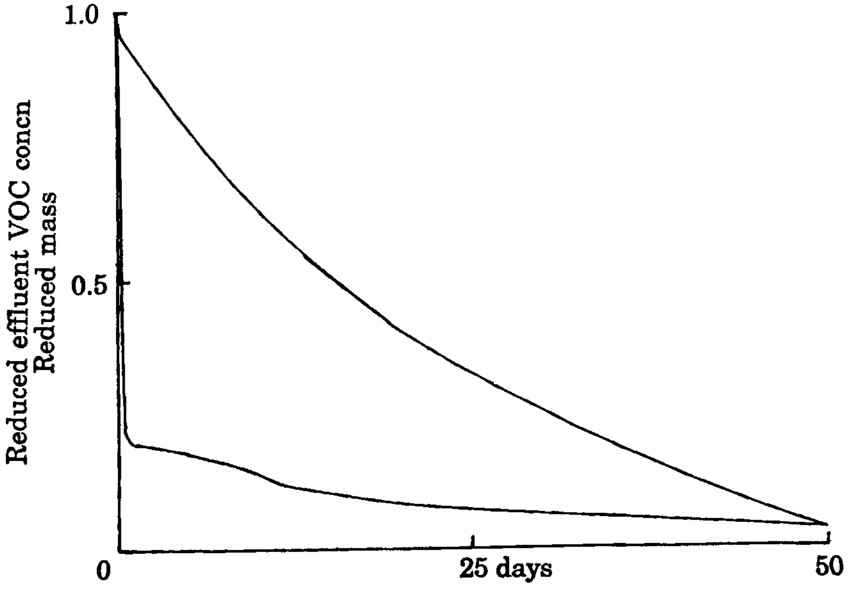

FIG. 5 Plots of normalized residual mass of VOC and normalized effluent soil gas concentration versus time. In this run the initial NAPL droplet diameter is 0.1 cm. Other parameters as in Table 1 and Fig. 2.

only a few days which, in turn, leads into a prolonged region of tailing before, rather abruptly, the soil gas VOC concentrations decrease fairly rapidly to zero as remediation becomes complete. Note that, despite the rather low gas flow rate through the column (6 mL/min), the effluent VOC concentrations are far below saturation even when the bulk of the residual VOC in the column is present as NAPL. Obviously, attempts to fit exponential curves to the effluent soil gas concentrations would be futile. Examination of the soil gas curves in the initial phases of the remediation would lead to cleanup time estimations which would be ridiculously optimistic. Similarly, examination of the rather flat regions between roughly days 20 and 45 might lead one to conclude that the tailing period was going to last for perhaps hundreds of days. In fact, as we can tell from the total mass curves, cleanup is proceeding in rather good order, with all cleanup times being roughly 50 days. It is evident, however, that the systems with larger NAPL droplet sizes are cleaning up somewhat more slowly than the systems in which the droplet sizes are smaller. This is as expected, because the total NAPL–water interfacial area is smaller for the systems with larger droplets.

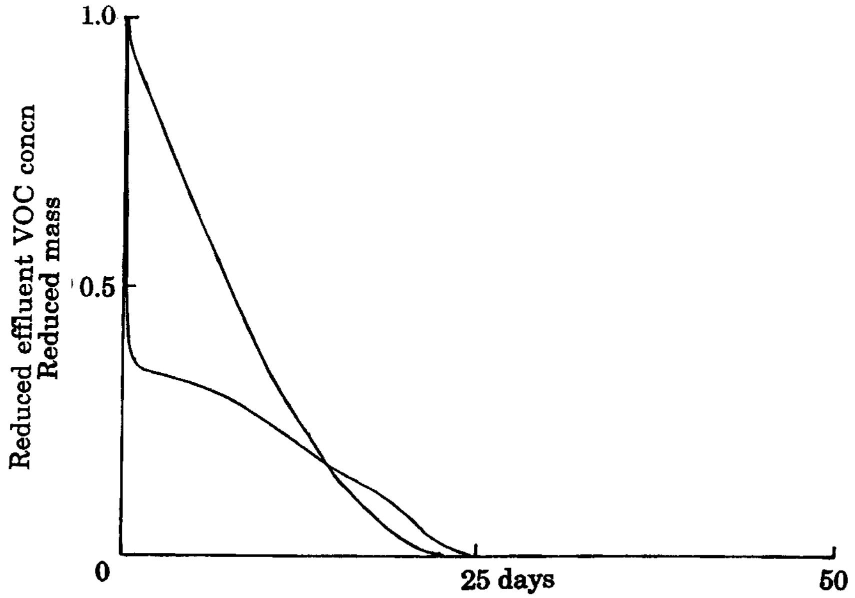

FIG. 6 Plots of normalized residual mass of VOC and normalized effluent soil gas concentration versus time. In this run the initial NAPL droplet diameter is 0.1 cm and the aqueous diffusion layer has a thickness of 0.5 cm. Other parameters as in Table 1.

The effluent soil gas concentration curves show some quite short-term fine structure which is a mathematical artifact of the finite difference scheme used to represent the physical system; we therefore shall not attempt to further interpret this fine structure. This is particularly apparent in Fig. 2.

In Figs. 6 and 7 the thickness of the stagnant water layer has been reduced to 0.5 cm. The initial NAPL droplet diameter is 0.1 cm in Fig. 6 and 0.2 cm in Fig. 7. Comparison of Fig. 6 with Fig. 5 shows the very substantial accelerating effect on the VOC removal rate of decreasing the thickness of the aqueous layer through which VOC must diffuse to reach the advecting soil gas. In Fig. 7, however, the larger NAPL droplet size makes solution of NAPL the rate-limiting step, and we see a slow rate of remediation (about 50 days) despite the relatively thin (0.5 cm) aqueous layer. As before, the initial rate of VOC removal is quite large, but this decreases dramatically as solution of NAPL (principally) and diffusion through the aqueous layer become rate limiting.

Figure 8 shows the effect on cleanup rate of the thickness of the water layer in which the VOC is dissolved. Here the initial VOC concentration

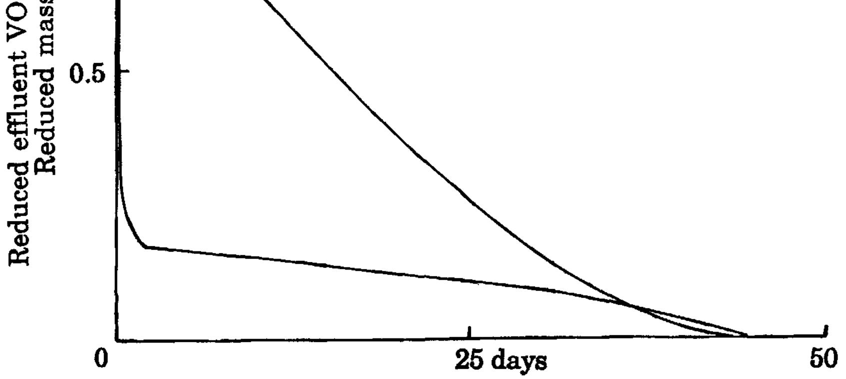

FIG. 7 Plots of normalized residual mass of VOC and normalized effluent soil gas concentration versus time. In this run the initial NAPL droplet diameter is 0.2 cm and the aqueous diffusion layer has a thickness of 0.5 cm. Other parameters as in Table 1.

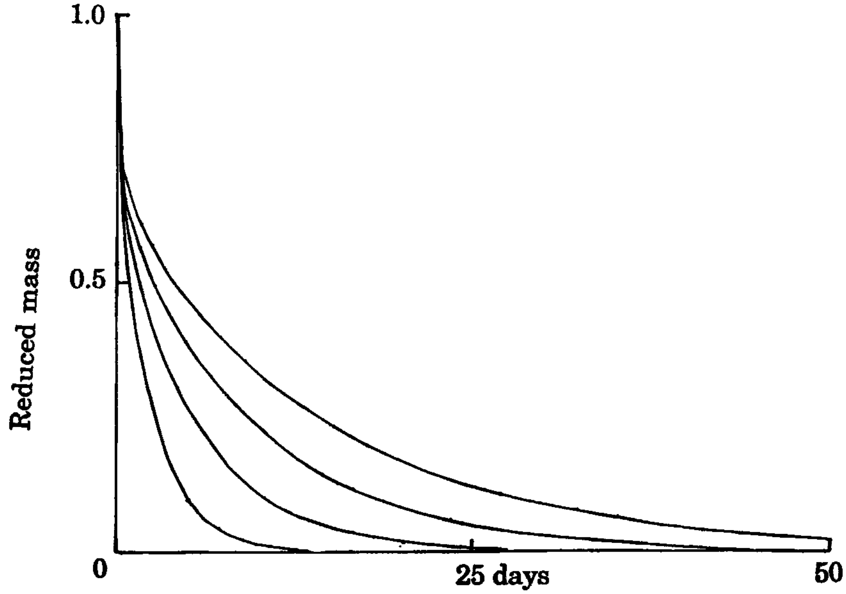

FIG. 8 Plots of normalized residual mass of VOC versus time; effects of diffusion layer thickness. In these runs the initial total VOC concentration is 100 mg/kg and the aqueous diffusion layer has thicknesses of 1.0, 1.5, 2.0, and 2.5 cm, as indicated. No NAPL is present. The initial aqueous phase VOC concentration is 0.000663 g/cm^3; the initial vapor phase VOC concentration is 0.000187 g/cm^3. Other parameters as in Table 1.

is only 100 mg/kg, so that no NAPL phase is present even at the beginning of the runs. The gas flow rate in these runs is 0.02 mL/s (1.2 mL/min). In these systems diffusion transport is the only rate-limiting factor in the remediation. It is evident that thick aqueous layers result in slow remediation.

If the system is in a diffusion or solution rate-limiting regime, increasing the gas flow rate permits one to spend more money on blowers and off-gas treatment but does not result in any significant decrease in the cleanup time. In the runs plotted in Fig. 9 the air flow rate Q is varied tenfold, but the impact on the time required for complete cleanup is very small. The volume of effluent soil gas which must be treated is therefore essentially proportional to the gas flow rate in this regime. As noted by Gómez-Lahoz et al. (21) and by Rodríguez-Maroto et al. (22), substantial savings can result if one employs SVE air flow rates small enough so that one is not operating in the diffusion-controlled limit. In these runs the initial VOC

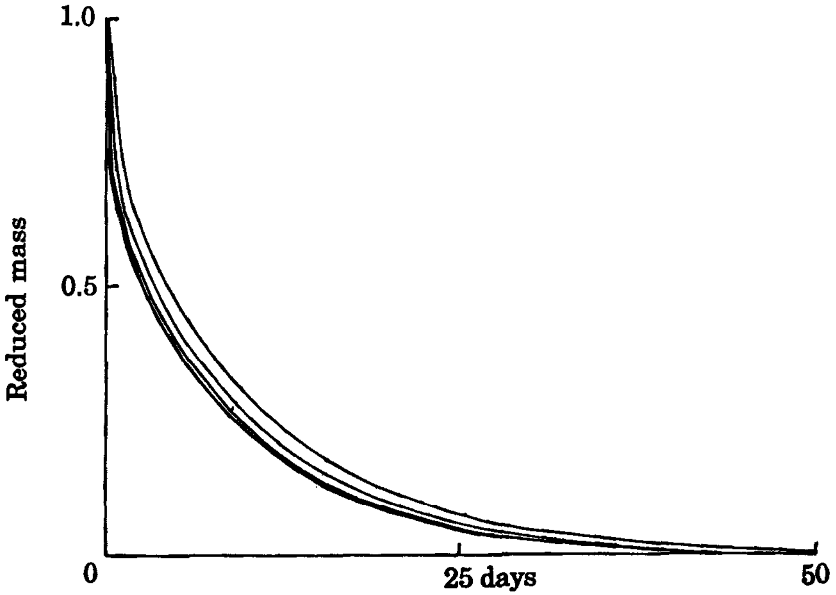

FIG. 9 Plots of normalized residual mass of VOC versus time; effects of air flow rate. In these runs the initial total VOC concentration is 100 mg/kg and the aqueous diffusion layer has a thickness of 2.0 cm. No NAPL is present. The air flow rate is 0.1, 0.05, 0.02, and 0.01 mL/s as indicated. Other parameters as in Table 1 and Fig. 8.

concentration is small (100 mg/kg) and no NAPL is present; in other runs (not shown) in which the bulk of the VOC is present as NAPL, the same results occur.

The effect of the initial total VOC concentration on the effluent soil gas VOC concentration is shown in Fig. 10; the reduced residual VOC masses for these runs are shown in Fig. 11. In these runs the water-saturated diffusion layer is 1 cm thick; the NAPL droplet diameter is 0.1 cm; the initial total VOC concentrations are 100, 250, 500, 1000, and 2000 mg/kg; and the gas flow rate is 0.02 mL/s. The other parameters are given in Table 1. We see that the cleanup times increase quite substantially with increasing initial VOC concentration. In all runs in which NAPL is present (the run with 100 mg/kg initial VOC has no NAPL present) after the initial rapid drop-off, there is extensive tailing. However, cleanup is complete within 50 days for all runs except that with 2000 mg/kg initial VOC, which required 75 days for cleanup.

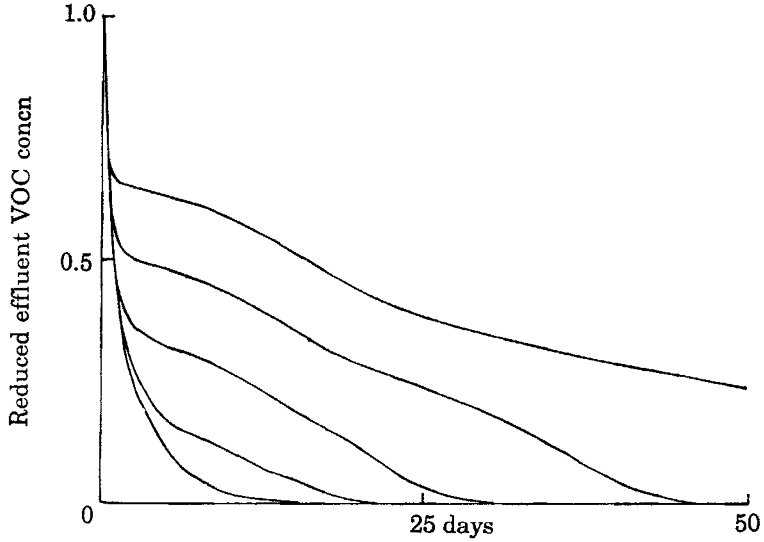

FIG. 10 Plots of normalized effluent soil gas VOC concentration versus time. Effects of initial total VOC concentration. In these runs the initial total VOC concentrations are 100, 250, 500, 1000, and 2000 mg/kg. The aqueous diffusion layer thickness is 1.0 cm and the NAPL droplet size is 0.1 cm. (No NAPL is present in the run with an initial total VOC concentration of 100 mg/kg.) Gas flow rate is 0.02 mL/s, Δt = 1800 seconds. Other parameters are as in Table 1.

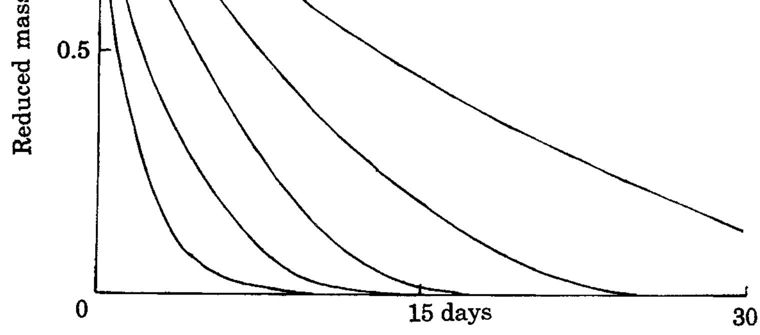

FIG. 11 Plots of normalized residual VOC mass versus time; effects of initial total VOC concentration. These plots are for the same runs as shown in Fig. 10.

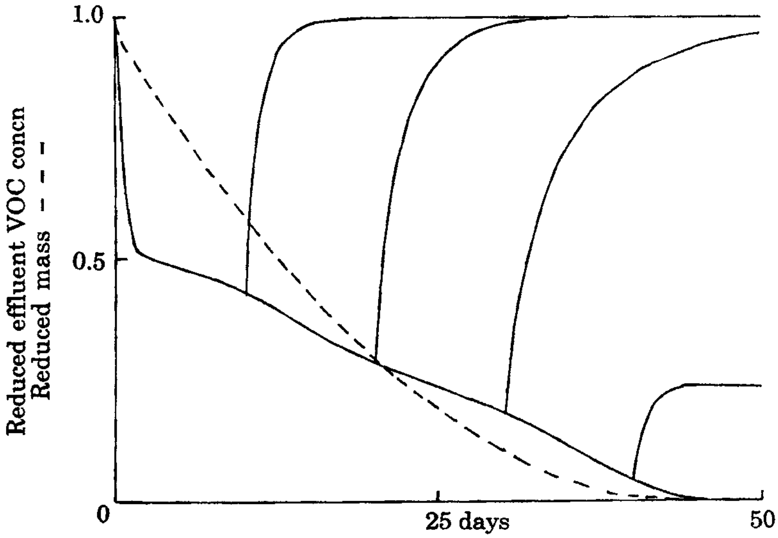

FIG. 12 Plots of normalized residual VOC mass and normalized effluent soil gas VOC concentration; effect of shutting off the gas flow to the column after 10, 20, 30, 40, and 50 days. Initial total VOC concentration = 1000 mg/kg, water diffusion layer thickness = 1.0 cm, initial NAPL droplet diameter = 0.1 cm, gas flow rate = 0.02 mL/s, Δt = 1800 seconds. Other parameters are as in Table 1. The normalized residual VOC masses remain constant after the gas flow is shut off; the resulting horizontal lines have been omitted from the figure.

Figure 12 shows effluent soil gas VOC concentration plots for runs which were shut down after 10, 20, 30, 40, and 50 days. Cleanup is complete after about 45 days if the run is not interrupted earlier. The effluent soil gas VOC concentration curves exhibit rebound after the gas flow is turned off; the vapor concentration rebounds to the saturation vapor pressure concentration if NAPL is still present. The rate of equilibration between the VOC in the vapor phase and the VOC in the condensed phase(s) decreases the longer the duration of the run before shutdown, indicating the inadvisability of using a single lumped parameter diffusion rate constant obtained from measurements made fairly near the beginning of a run. By the time 40 days has elapsed, all of the NAPL has dissolved, so the rebound in soil gas VOC concentration is to a value determined by Henry's law and the final aqueous VOC concentration, rather than to the

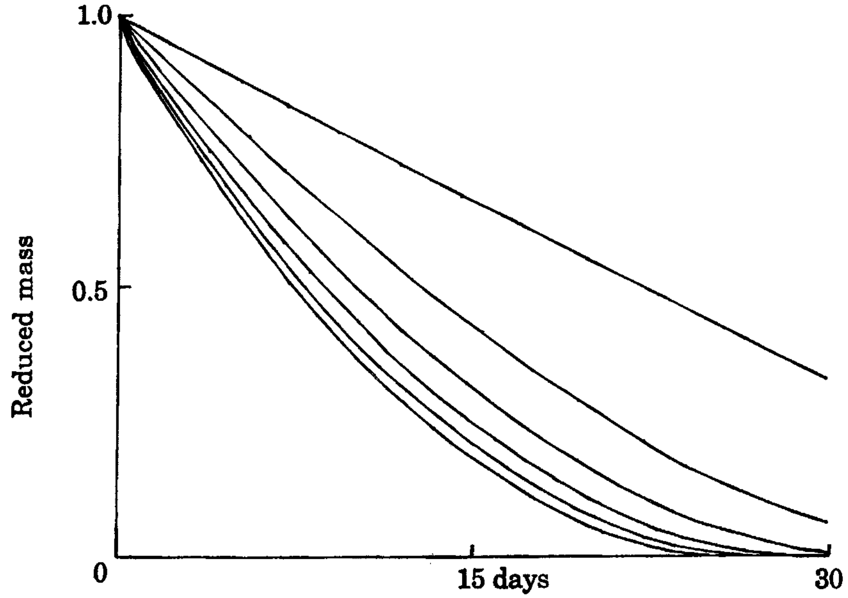

FIG. 13 Plots of normalized residual VOC mass versus time; effect of Henry's constant. K_H = 0.05, 0.1, 0.15, 0.2, 0.25, and 0.3 from top to bottom. Air flow rate = 0.02 mL/s, water layer thickness = 1.0 cm, initial NAPL droplet diameter = 0.1 cm; other parameters as in Table 1.

saturation concentration. Notice that there is substantial rebound even after 40 days of SVE, by which time only about 2% of the original amount of VOC is still present in the column. Evidently it would be difficult, if not impossible, to correlate the extent of cleanup with the effluent soil gas VOC concentration during operation of the well or with the final equilibrium value of the rebound soil gas VOC concentration.

The effect of varying Henry's constant is shown in Fig. 13 in which reduced residual VOC mass is plotted against time. As expected, increasing K_H increases the removal rate, but the removal rate is not proportional to K_H since diffusion kinetics are significant.

CONCLUSIONS

The results of these calculations modeling the effects of diffusion and dissolution kinetics lead to some useful conclusions regarding the design of pilot-scale SVE tests and the interpretation of the resulting data.

The first is that short pilot-scale tests in which only 5 to 20% of the VOC is removed from the domain of interest are not useful, as a general rule, for predicting the progress of the later stages of SVE remediation. These can be relied on only if post-SVE rebound of the soil gas VOC concentration is clearly demonstrated not to occur, in which case the system can be modeled by a local equilibrium model.

The second conclusion is that the varied transit times of the gas flow paths to SVE wells and the interaction between NAPL solution kinetics and VOC diffusion in aqueous solution lead to considerable complexity. This complexity is such that it seems unlikely that any theoretical method will permit accurate estimation of the entire course of an SVE remediation at a site from pilot-scale effluent soil gas VOC data which do not extend over virtually the entire cleanup—i.e., to essentially 100% removal of the VOCs.

The third is that proper treatment of the diffusion of VOC through an aqueous boundary layer yields not one time constant but a spectrum of time constants which vary over a rather wide range. This makes use of the lumped parameter approach for modeling diffusion/desorption kinetics fraught with some peril unless the lumped parameter diffusion rate constant is fitted against data taken near the end of the remediation of the pilot-scale domain.

The fourth is that it is probably impossible to reliably correlate the extent of cleanup (the percent of the VOC which has been removed) with either effluent soil gas VOC concentration during SVE operation or with soil gas VOC concentration after the well has been shut down and rebound to equilibrium has occurred. About the only reliable conclusion one can come to from the modeling exercises is that effluent soil gas concentrations are zero and there is no rebound when remediation is complete, which is not terribly helpful.

The fifth and last conclusion is that one may very well realize significant reduction in operating costs by operating SVE wells at flow rates sufficiently low that the effluent soil gas VOC concentration is maintained at an appreciable fraction (say 20% or so) of the soil gas VOC concentration which is achieved when the well is shut down and the soil gas is allowed to come to equilibrium with the contaminated soil. This will result in reduced volumes of gas to be treated, higher concentrations of VOCs in the effluent gas, and quite minor increases in cleanup times.

We note with some regret that the computing time required for modeling wells (rather than laboratory columns) with the approach described here would be excessively long when implemented on many microcomputers, since one must work in two dimensions. Such models should be feasible on 486 computers running at 50 MHz or faster, however. We hope to develop models of this type for SVE wells which make use of the steady-state approximation in order to decrease the computing time to an acceptable level for a model of this type for wells and horizontal slotted pipes.

ESTIMATION OF DARCY'S CONSTANTS FROM VACUUM WELLHEAD PRESSURES AND GAS FLOW RATES

One of the parameters determined in the course of site investigations assessing the feasibility of SVE is the pneumatic permeability or Darcy's constant. Two approximate formulas are commonly used for this, depending on the configuration of the well. One is used if the screened section of the well is a horizontal slotted pipe or a rather long vertical section; the other, if the length of the screened section is roughly comparable to the diameter of the gravel packing of the well. The method of images from electrostatics can be used to obtain more exact formulas involving infinite series which can readily be evaluated on a microcomputer. In this section we develop the approximate and exact equations for Darcy's constant for the two well configurations. Some numerical results are then presented to give an idea of the accuracies of the approximate equations. We note that this analysis presupposes the validity of Darcy's law over the entire domain of interest; if the well vacuum is sufficiently high, this is incorrect, and the wellhead vacuum becomes a quadratic, rather than a linear, function of the flow rate (23).

A Single Vertical Well with a Short Screened Section

We first develop the approximate equation. For a porous medium of constant isotropic permeability the soil gas pressure in the vicinity of a vacuum well having a short screened section is governed by Laplace's equation in cylindrical coordinates,

$$\frac{1\partial}{r\partial r}\left[r\frac{\partial P^2}{\partial r}\right] + \frac{\partial^2 P^2}{\partial z^2} = 0 \tag{31}$$

with boundary conditions

$$P(h, r) = 1 \text{ atm} \tag{32}$$

at the surface of the soil,

$$\frac{\partial P(0, r)}{\partial z} = 0 \tag{33}$$

at the water table, and a sink representing the vacuum well at (0, a). The superficial gas velocity is given by

$$v = -K_D \nabla P \tag{34}$$

Symbols are defined as follows:

z = distance above the water table, m
h = height of the soil surface above the water table, m
a = distance of the screened section of the well above the water table, m
r = radial distance from the axis of the well, m
$P(r, z)$ = soil gas pressure at (r, z), atm
$c(r, z)$ = molar gas concentration at (r, z), mol/m^3
P_w = wellhead pressure, atm
P_a = ambient pressure at the soil surface, atm
Q = molar gas flow rate to the well, mol/s
q = volumetric gas flow rate to the well, m^3/s at 1 atm
= RTQ
K_D = Darcy's constant, m^2/atm·s

For an approximate calculation of Darcy's constant for this system we choose

$$P^2 = F + G/\rho \tag{35}$$

where ρ is the radial coordinate in spherical coordinates centered at the well. The constants F and G are calculated by fitting this function to the pressures at $\rho = r_w$ and at $z = h$, $r = 0$, for which $\rho = h - a$. The value of G is given by

$$G = -\frac{(P_a^2 - P_w^2) r_w (h - a)}{h - a - r_w} \tag{36}$$

and the value of F will not be needed. Equation (35) fits the boundary condition, Eq. (32), only approximately, and does not fit the boundary condition at the water table, Eq. (33), so we expect that our approximate result will show substantial departures from the exact result when the well is screened near the water table. The molar flow rate to the well is given by

$$Q = -\int_0^{\pi} \int_0^{2\pi} cv\rho^2 \sin(\theta) d\theta \, d\phi \tag{37}$$

where

$$v = -K_D \nabla_\rho P \tag{38}$$

Equations (36) and (37) and the definition of c then permit us to write

$$QRT = q = \int_0^{\pi} \int_0^{2\pi} K_D(1/2)[\nabla_\rho P^2]\rho^2 \sin d\theta \, d\phi \tag{39}$$

and to obtain

$$q = \frac{2\pi K_D(P_a^2 - P_w^2)r_w(h - a)}{h - a - r_w} \tag{40}$$

from which finally

$$K_D = \frac{q(h - a - r_w)}{2\pi(P_a^2 - P_w^2)r_w(h - a)} \tag{41}$$

which is our approximate formula for calculating Darcy's constant for a single vertical well screened only along a distance comparable to the diameter of the well packing. We next turn to the calculation of a more exact formula which satisfies the boundary conditions. Define

$$P^2(r, z) = P_a^2 + W \tag{42}$$

where W, obtained by use of the method of images and symmetry arguments, is given by

$$\begin{aligned} W = A \sum_{n=-\infty}^{\infty} \Bigg[&- \frac{1}{\{r^2 + [z - 4nh - a]^2\}^{1/2}} - \frac{1}{\{r^2 + [z - 4nh + a]^2\}^{1/2}} \\ &+ \frac{1}{\{r^2 + [z - (4n - 2)h - a]^2\}^{1/2}} \\ &+ \frac{1}{\{r^2 + [z - (4n - 2)h + a]^2\}^{1/2}} \Bigg] \end{aligned} \tag{43}$$

The constant A is evaluated by the requirement that at $(0, a + r_w)$, $P = P_w$; this gives

$$W(0, a + r_w) = P_w^2 - P_a^2 \tag{44}$$

or

$$\begin{aligned} P_w^2 - P_a^2 = A \sum_{n=-\infty}^{\infty} \Bigg[&- \frac{1}{| r_w - 4nh |} - \frac{1}{| 2a + r_w - 4nh |} \\ &+ \frac{1}{| r_w - (4n - 2)h |} + \frac{1}{| 2a + r_w - (4n - 2)h |} \Bigg] \\ = AS & \end{aligned} \tag{45}$$

and

$$A = (P_w^2 - P_a^2)/S \tag{46}$$

where S is the sum on the right-hand side of Eq. (45). Evaluation of the volumetric flow rate is done by using $P^2 = P_a^2 + W$ in Eq. (38), and W is given by Eq. (43). When the integration over a small sphere containing the screened section of the well is carried out, the only term which contributes is the first of the four terms, and that only when $n = 0$. W can therefore be written as

$$W = -A/\rho \tag{47}$$

so

$$\nabla_\rho W = A(1/\rho^2) \tag{48}$$

Then q is given by

$$q = \frac{K_D A}{2\rho^2} \int_0^\pi \int_0^{2\pi} \rho^2 \sin\theta \, d\theta \, d\phi = 2\pi A K_D \tag{49}$$

and

$$A = q/(2\pi K_D) \tag{50}$$

Equating the two expressions for A (Eqs. 46 and 50) and solving the result for K_D then gives as an exact result for Darcy's constant:

$$K_D = \frac{qS}{2\pi(P_w^2 - P_a^2)} \tag{51}$$

where S is the sum on the right-hand side of Eq. (45). Note that the sums of the first, second, third, and fourth terms diverge if calculated separately; it is necessary to calculate the combined sum in order to obtain convergence.

A Single Long Horizontal Slotted Pipe Well

Again we first develop the approximate equation for Darcy's constant. We assume that the well is long enough so that end effects can be neglected in order to obtain a problem in two dimensions. For a porous medium of constant isotropic permeability, the soil gas pressure in the vicinity of a vacuum well having a long horizontal screened section is governed by Laplace's equation in Cartesian coordinates,

$$\frac{\partial^2 P^2}{\partial x^2} + \frac{\partial^2 P^2}{\partial y^2} = 0 \tag{52}$$

with boundary conditions

$$P(h, x) = 1 \text{ atm} \tag{53}$$

at the surface of the soil,

$$\frac{\partial P(0, x)}{\partial y} = 0 \tag{54}$$

at the water table, and a sink representing the vacuum well at $(0, a)$. The superficial gas velocity is given by

$$v = -K_D \nabla P \tag{34'}$$

New symbols are defined as follows:

L = length of horizontal slotted pipe, m
x = horizontal Cartesian coordinate at right angles to the pipe, measured from the pipe, m
y = vertical Cartesian coordinate, measured from the water table, m
r = radial distance from the horizontal slotted pipe, m

We choose as a solution to Laplace's equation

$$P^2(r) = F + G \log_e r \tag{55}$$

and choose F and G so that

$$P_w^2 = F + G \log_e r_w \tag{56}$$

and

$$P_a^2 = F + G \log_e(h - a) \tag{57}$$

As before, this satisfies the boundary condition at the surface of the soil only approximately, and does not satisfy the no-flow condition at the water table. Solution of Eqs. (56) and (57) for G (F will not be needed) gives

$$G = \frac{P_a^2 - P_w^2}{\log_e[(h - a)/r_w]} \tag{58}$$

From Eqs. (55) and (58) we have

$$\nabla_r P^2 = 2P\nabla_r P = \frac{P_a^2 - P_w^2}{\log_e[(h - a)/r_w]r} \tag{59}$$

The molar gas flux to the well is then given by

$$Q = LK_D \int_0^{2\pi} c(\nabla_r P) r \, d\theta \tag{60}$$

which gives

$$q = QRT = \frac{2\pi K_D (P_a^2 - P_w^2) L}{\log_e[(h - a)/r_w]} \tag{61}$$

From this we see that

$$K_D = \frac{q \log_e[(h - a)/r_w]}{2\pi L (P_a^2 - P_w^2)} \tag{62}$$

gives the approximate value for Darcy's constant for a well which is a long horizontal slotted pipe. The exact result for the horizontal slotted pipe is obtained as follows. As before, we define a potential function W, given by

$$P_a^2 + W = P^2(x, y)$$

as

$$\begin{aligned} W = B \sum_{n=-\infty}^{\infty} [&\log_e\{x^2 + [y - 4nh - a]^2\} + \log_e\{x^2 + [y - 4nh + a]^2\} \\ &- \log_e\{x^2 + [y - (4n - 2)h - a]^2\} \\ &- \log_e\{x^2 + [y - (4n - 2)h + a]^2\}] \end{aligned} \tag{63}$$

which satisfies Laplace's equation and allows the pressure to satisfy the boundary conditions at the water table and at the soil surface. Since the wellhead pressure is P_w, evaluating Eq. (63) at (r_w, a) must give

$$\begin{aligned} P_a^2 - P_w^2 = -B \sum_{n=-\infty}^{\infty} [&\log_e\{r_w^2 + [a - 4nh - a]^2\} \\ &+ \log_e\{r_w^2 + [a - 4nh + a]^2\} \\ &- \log_e\{r_w^2 + [a - (4n - 2)h - a]^2\} \\ &- \log_e\{r_w^2 + [a - (4n - 2)h + a]^2\}] \end{aligned} \tag{64}$$

$$= -BU \tag{65}$$

where U is the sum on the right-hand side of Eq. (64). B is therefore given by

$$B = -(P_a^2 - P_w^2)/U \tag{66}$$

As before, the molar flow rate is given by

$$Q = LK_{\mathrm{D}} \int_0^{2\pi} (P/RT)(\nabla_r P) r \, d\theta \tag{67}$$

From Eq. (64) we have

$$W = B \log_e r^2 + \text{terms regular as } r \to 0 \tag{68}$$

The regular terms contribute nothing to the integral, so we obtain

$$RTQ = q = 2\pi LK_{\mathrm{D}}B \tag{69}$$

So

$$B = q/2\pi LK_{\mathrm{D}} \tag{70}$$

Setting Eqs. (66) and (70) equal and solving for K_{D} then gives

$$K_{\mathrm{D}} = \frac{qU}{2\pi L(P_w^2 - P_a^2)} \tag{71}$$

as the exact expression for Darcy's constant in terms of measurements made on a long horizontal slotted pipe well.

RESULTS

Values of Darcy's constant were calculated using both the approximate and the exact equations for the two well configurations. The parameters for the calculations for a vertical well with spherical gravel packing were as follows:

Radius of well gravel packing = 0.15 m

Wellhead pressure = 0.90 atm

Gas flow rate = 25 SCFM (0.01180 m^3/s)

For the horizontal slotted pipe the parameters were:

Radius of well gravel packing = 0.15 m

Length of horizontal slotted pipe = 10 m

Wellhead pressure = 0.90 atm

Gas flow rate = 200 SCFM (0.09439 m^3/s)

Darcy's constant values obtained for the vertical well with a spherical gravel packing are given in Table 2. Values obtained for the horizontal slotted pipe are given in Table 3.

TABLE 2
Exact and Approximate Values of K_D (m^2/atm·s) for Various Depths to the Water Table and for Various Well Depths (m), Vertical Well with Spherical Gravel Packing

Water table depth	Well depth	K_D(approx)	K_D(exact)
5	4.5	0.063679	0.071703
7.5	4.5	0.063679	0.065411
10	4.5	0.063679	0.064978
15	4.5	0.063679	0.064815
20	4.5	0.063679	0.064781
20	5	0.063898	0.064900
20	10	0.064886	0.065525
20	15	0.065216	0.066132
20	17.5	0.065310	0.067101
20	19	0.065354	0.069784

The results indicate that both approximations improve as the distance between the well and the water table increases. The approximate formula for calculating Darcy's constants from data taken with a vertical well with spherical gravel packing is rather good over the entire range of parameters examined. The approximate formula for calculating Darcy's constant from horizontal slotted pipe data shows substantially larger discrepancies when the distance between the well and the water table is small, and its results converge toward the results of the exact formula rather slowly as the distance between the well and the water table increases.

TABLE 3
Exact and Approximate Values of K_D (m^2/atm·s) for Various Depths to the Water Table and for Various Well Depths (m), Horizontal Slotted Pipe

Water table depth	Well depth	K_D(approx)	K_D(exact)
5	4.5	0.053784	0.088411
7.5	4.5	0.053784	0.070951
10	4.5	0.053784	0.067981
15	4.5	0.053784	0.066248
20	4.5	0.053784	0.065703
20	5	0.055450	0.067530
20	10	0.066411	0.081429
20	15	0.072822	0.095323
20	17.5	0.075260	0.106898
20	19	0.076561	0.121511

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