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Soil Cleanup by In-Situ Aeration. XIX. Effects of Spill Age on Soil Vapor Extraction Remediation Rates

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ABSTRACT

A model for soil vapor extraction (SVE) is developed which includes evaporation of nonaqueous phase liquid (NAPL) and mass transport of dissolved volatile organic compounds (VOCs) through low-permeability lumps, lenticular structures, and discontinuous layers of clay by means of a distributed diffusion approach. The configuration modeled is that of a single vertical well screened a short length near its bottom. The model exhibits high off-gas VOC concentrations initially (while NAPL is being evaporated), followed by rapid drop-off to a relatively long period of tailing, the extent of which is highly variable and determined by 1) the thickness of the low-permeability layers from which diffusion is occurring, and 2) the period after the spill which elapsed before SVE was initiated. The results agree with previous models in that they indicate that one cannot predict SVE cleanup times from data taken in short-term pilot-scale experiments removing only 5–25% of the VOC present in the domain of influence of the well. The rebound of soil gas VOC concentration after well shutdown is explored; soil gas VOC levels measured under such static conditions are much more informative than levels measured during well operation.

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INTRODUCTION

Soil vapor extraction (SVE) and its variants are now well-established for the remediation of sites contaminated with volatile organic compounds (VOCs). Some 83 Superfund sites were using or scheduled to use the technique as of October 1992, and it is being used on many other sites involving VOCs. EPA has published a number of reports on SVE (1–4), as well as the proceedings of a symposium on the subject (5). Hutzler and his coworkers (6, 7) and Wilson and Clarke (8) have reviewed the technique in detail. The literature on the subject is quite extensive, and no attempt will be made to provide a complete review of SVE here.

Mathematical modeling for SVE provides support for initial site-specific evaluation, interpretation of lab- and pilot-scale field results, design of pilot- and full-scale field SVE operations, and estimation of costs and cleanup times. Several groups have developed SVE models, including the Vapex group (9–15 and other papers); Johnson, Kemblowski, and their coworkers (16–20 and other papers); Cho (21); the Idaho National Engineering Laboratory (22, 23); and the Eckenfelder–Vanderbilt group (24–26, for example).

The hope that the assumption of local equilibrium with respect to movement of VOC between the advecting soil gas and the stationary phase(s) containing VOC would be an adequate approximation (27, 28) has been dashed at a number of sites. At these, rapid declines in off-gas VOC concentrations after a few days (sometimes only a few hours) of operation and a long-drawn-out period of tailing during the lengthy terminal phase establish that local equilibrium is not being maintained—that diffusion/desorption kinetics are providing a bottleneck which controls the release of VOC to the advecting vapor phase. DiGiulio et al. (29) described possible pilot-scale field experiments to evaluate mass transport limitations, and Lyman and Noonan (3) reported that such limitations are common. DiGiulio (30) commented in some detail on the importance of mass transport limitations in SVE.

Some time ago we described a simple lumped parameter method for including mass transport limitations in SVE models (31–35) which could give removal rates greatly reduced below those from models in which local equilibrium was assumed. This model, however, could not yield with the same parameter set the very rapid initial VOC removal rates and the quite slow removal rates toward the end of the remediation which are observed experimentally. The lumped parameter approach to mass transport was evidently oversimplified.

This difficulty was discussed recently (36), and a lab column model was described which employed a more realistic approach to diffusion transport. This was one of two models investigated. These distributed diffusion models assume that VOC diffuses from water-saturated layers of finite thickness before it reaches the advecting soil gas and is removed. In one approach the nonaqueous phase liquid (NAPL) is present as droplets distributed throughout the water-saturated low-porosity layers; in the other the NAPL is present as a film within the water-saturated lamellae. The two approaches could be made to yield rather similar results on suitable selection of the parameters in the models. The second model requires substantially less than half the computer time required by the first. It also permits use of steady-state approximations which can greatly speed the computations.

In subsequent papers of this series (37, 38) we discussed the extension of the first approach (in which NAPL is present as droplets distributed throughout the low-permeability lenticular domains) and the second approach (in which NAPL is present as a thin layer within the low-permeability lenticular domains from which it must diffuse to the advecting air) to SVE by means of a horizontal slotted pipe well. The models performed well, easily producing the high initial VOC removal rates, the rapid declines in off-gas VOC concentration, and the lengthy plateaus and tailing observed experimentally.

The models seemed somewhat artificial, however. For the first model it was not clear how droplets of NAPL could migrate to or be formed in the interiors of the low-permeability domains. For the second it was difficult to see how the postulated thin layer of NAPL was to be created deep within the low permeability structures in the first place. This left these models of the diffusion process lacking an easily visualized physicochemical basis. They had some meaning in terms of the least dimension of the low-permeability structures, and they produced reasonable results, but they also seemed somewhat contrived.

We avoid these conceptual difficulties if the model permits the NAPL to be present as droplets only in the mobile (air-filled) porosity, and excludes it from the water-saturated low-permeability porous domains. We assume that VOC can migrate into these domains only by diffusion of dissolved VOC through the aqueous phase. We assume that initially (at the time of the spill or sudden leak) the VOC is present only as vapor and NAPL, both in the air-filled porosity, and that subsequently the VOC diffuses into the water-saturated domains. In remediation, we therefore expect to see rapid removal of VOC initially as the NAPL droplets evaporate in the advecting gas stream, followed by a much slower rate of removal as VOC diffuses back out of the water-saturated domains.

We present here the analysis for a single vertical well screened for a short distance along its bottom. This is followed by a section in which results of computations done with this model are presented and discussed. The effects of NAPL droplet size, thickness of the low-permeability domains, and time interval between spill and initiation of remediation will be shown. The rebound of soil gas VOC concentration which occurs when an SVE well is shut down before remediation is complete will also be examined. The paper closes with a short section on conclusions.

ANALYSIS

The configuration of the single vertical SVE well is shown in Fig. 1, along with much of the notation. The model for diffusion transport, together with notation, is shown in Fig. 2. The development of an SVE model breaks down into three major parts: the calculation of the soil gas flow field in the vicinity of the vacuum well, the analysis of the equilibria and mass transport factors governing the release of the VOC being vapor stripped, and the combining of the two to form the model.

A. The Rate of Evaporation of Droplets of NAPL

We first look at evaporation of VOC from a NAPL droplet into the vapor phase. See Fig. 3. The equation for steady-state diffusion from a spherical droplet is

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

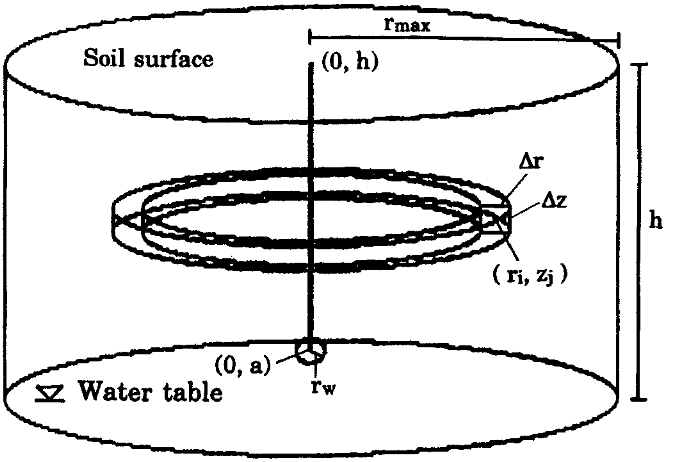

FIG. 1 SVE well, configuration of a vertical pipe screened only near the bottom; geometry and notation.

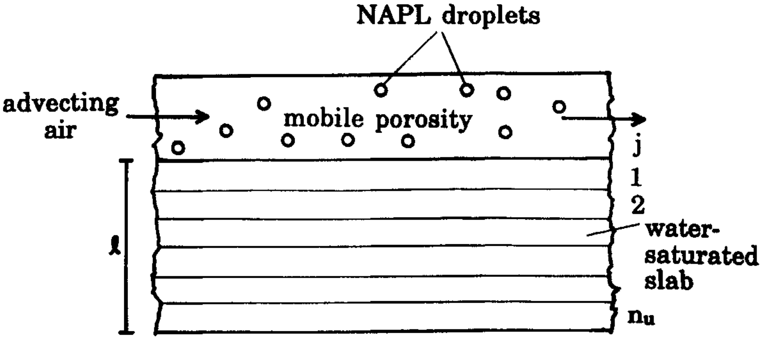

FIG. 2 Model for diffusion transport of dissolved VOC into and from the aqueous phase in a low-permeability porous clay lens which is saturated with water. The slabs used to mathematically represent the lens are shown.

with boundary conditions

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

and

$$C(b) = C^g_0 \tag{3}$$

where C^g_{sat} is the saturation vapor concentration of the VOC and C^g_0 is the VOC concentration at the outer surface ($r = b$) of the boundary layer surrounding the drop. Equation (1) integrates to

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

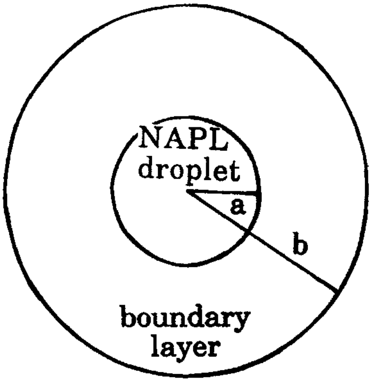

FIG. 3 Evaporation of a single NAPL droplet.

Use of the boundary conditions then gives

$$C(r) = \frac{ab}{b - a}(C^g_{\text{sat}} - C^g_0)/r + c_2 \tag{5}$$

from which

$$\frac{dC}{dr} = -\frac{ab}{b - a}(C^g_{\text{sat}} - C^g_0)/r^2 \tag{6}$$

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

$$\frac{dm}{dt} = -\frac{4\pi D_g a(C^g_{\text{sat}} - C^g_0)}{1 - a/b} \tag{7}$$

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, a_0 is its initial radius, and m and a are values at a later time t. So

$$\frac{dm}{dt} = -\frac{4\pi D_g a_0(C^g_{\text{sat}} - C^g_0)(m/m_d)^{1/3}}{1 - (a_0/b)(m/m_d)^{1/3}} \tag{9}$$

A reasonable value for b, the boundary layer thickness around a droplet, is half the average distance between droplets. This is obtained as follows. Let the number of NAPL droplets in a volume element ΔV_{ij} be given by n. Then

$$n\frac{4\pi a_0^3 \rho_{\text{voc}}}{3} = V_{ij}C^N_0 \tag{10}$$

and

$$n = \frac{3\Delta V_{ij}C^N_0}{4\pi a_0^3 \rho_{\text{voc}}} \tag{11}$$

Let

σ = air-filled porosity
ω = water-filled porosity, assumed to be due only to the saturated clay lenses
ν_{clay} = total porosity (all water-filled) of the clay lenses

Then

$$\omega\Delta V_{ij} = \nu_{\text{clay}} f \Delta V_{ij}$$

where f is the fraction of the domain which consists of clay lenses. So

$$f = \omega/\nu_{\text{clay}} \tag{12}$$

and $1 - f$ is the fraction of the domain which involves air-filled porosity. We therefore have n NAPL droplets distributed in a volume $(1 - f)\Delta V_{ij}$. The volume per droplet is therefore given by

$$(1 - f)\Delta V_{ij}/n = \frac{(1 - f)4\pi a_0^3 \rho_{\text{voc}}}{3C_0^N} \tag{13}$$

The distance between droplets, $2b$, is just the cube root of this, and b, the thickness of the boundary layer, is then given by

$$b = a_0 \left[\frac{(\nu_{\text{clay}} - \omega)\pi\rho_{\text{voc}}}{\nu_{\text{clay}} 6C_0^N}\right]^{1/3} \tag{14}$$

B. Rate of Change of NAPL Mass

Recall that the number of NAPL droplets in a volume element is given by Eq. (11). The initial mass of a droplet, m_d, is

$$m_d = \frac{4\pi a_0^3 \rho_{\text{voc}}}{3} \tag{15}$$

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

$$\frac{dm_{ij}}{dt} = -\frac{3\Delta V_{ij} C_0^N D_g (C_{\text{sat}}^g - C_{ij}^g)(m_{ij}/m_0)^{1/3}}{a_0^2 \rho_{\text{voc}}[1 - (a_0/b)(m_{ij}/m_0)^{1/3}]} \tag{16}$$

C. Gas Flow Field

We assume a porous medium of constant, isotropic permeability, so we may use the method of images from electrostatics (37) for calculating the soil gas pressures near the SVE well. We work in cylindrical coordinates r, z. Let

h = thickness of porous medium (depth to water table), m
r_{max} = radius of domain of interest, m
r_w = radius of gravel packing of the well, m
P_w = wellhead gas pressure (<1 atm), atm
P_a = ambient pressure, atm
$P(r, z)$ = soil gas pressure at the point (r, z), atm
K_D = Darcy's constant, m²/atm·s

a = distance of well above the water table, m
Q = molar gas flow rate to well, mol/s
q = standard volumetric gas flow rate to well, m^3/s
v_r = r-component of superficial velocity, m/s ($m^3/m^2 \cdot s$)
v_z = z-component of superficial velocity, m/s ($m^3/m^2 \cdot s$)
R = gas constant, 8.206×10^{-5} $m^3 \cdot atm/mol \cdot deg$
T = temperature, degrees Kelvin

The pressure of an ideal gas in a porous medium satisfies the equation

$$\nabla^2 P^2 = 0 \tag{17}$$

$$\frac{\partial P^2(r, 0)}{\partial z} = 0 \tag{18}$$

at the water table, and

$$P^2(r, h) = P_a^2 = 1 \text{ atm}^2 \tag{19}$$

at the soil surface. Define a potential function $W(r, z)$ by

$$W(r, z) + P_a^2 = P^2(r, z) \tag{20}$$

so the problem becomes

$$\nabla^2 W = 0 \tag{21}$$

$$\frac{\partial W(r, 0)}{\partial z} = 0 \tag{22}$$

$$W(r, h) = 0 \tag{23}$$

There must also be a sink at (0, a) to represent the vacuum well.

We use the method of images (39) to construct W; it is given by

$$W = A \sum_{n=-\infty}^{\infty} \left[-\frac{1}{\{r^2 + [z - 4nh - a]^2\}^{1/2}} - \frac{1}{\{r^2 + [z - 4nh + a]^2\}^{1/2}} + \frac{1}{\{r^2 + [z - (4n - 2)h - a]^2\}^{1/2}} + \frac{1}{\{r^2 + [z - (4n - 2)h + a]^2\}^{1/2}} \right] \tag{24}$$

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

P_w, the wellhead pressure. Here r_w is the radius of the well gravel packing. This gives

$$W(0, a + r_w) = P_w^2 - P_a^2 \tag{25}$$

or

$$\begin{aligned} P_w^2 - P_a^2 &= A \sum_{n=-\infty}^{\infty} \left[-\frac{1}{|r_w - 4nh|} - \frac{1}{|2a + r_w - 4nh|} \right. \\ &\quad \left. + \frac{1}{|r_w - (4n - 2)h|} + \frac{1}{|2a + r_w - (4n - 2)h|} \right] \\ &= AS \end{aligned} \tag{26}$$

and so

$$A = (P_w^2 - P_a^2)/S \tag{27}$$

where S is the sum appearing on the right-hand side of Eq. (26).

The molar flow rate to the well is given by

$$Q = -\int_0^{2\pi} \int_0^{\pi} c v_\rho \rho^2 \sin\theta \, d\theta \, d\phi \tag{28}$$

where

$$v = -K_D \nabla_\rho P \tag{29}$$

and $c = P/RT$. This can be rearranged to give

$$QRT = q = \int_0^{2\pi} \int_0^{\pi} K_D(1/2)[\nabla_\rho P^2]\rho^2 \sin\theta \, d\theta \, d\phi \tag{30}$$

or

$$q = \int_0^{2\pi} \int_0^{\pi} (1/2)K_D(\nabla_\rho W)\rho^2 \sin\theta \, d\theta \, d\phi \tag{31}$$

When the integration is carried out over the surface of a small sphere containing the screened section of the well, the only term from W which contributes is the first of the four terms, and that only when $n = 0$. In the integral we can therefore write

$$W = -A/\rho \tag{32}$$

so

$$\nabla_\rho W = A/\rho^2 \tag{33}$$

and q is given by

$$q = \frac{K_D A}{2\rho^2} \int_0^{2\pi} \int_0^{\pi} \rho^2 \sin\theta \, d\theta \, d\phi = 2\pi A K_D \tag{34}$$

Then

$$A = q/(2\pi K_D) \tag{35}$$

Setting this result equal to the right-hand side of Eq. (27) and solving for K_D then gives

$$K_D = \frac{qS}{2\pi(P_w^2 - P_a^2)} \tag{36}$$

The superficial velocity of the gas is given by

$$v = -K_D \nabla P \tag{37}$$

where the components of ∇W are $\partial W/\partial r$ and $\partial W/\partial z$, and the velocity components are v_r and v_z.

D. Volume Elements and Surfaces of Volume Elements. Advective Mass Balance

See Fig. 1. The volume of the annular volume element is given by

$$\Delta V_{ij} = (2i - 1)\pi(\Delta r)^2 \Delta z \tag{38}$$

The surfaces of this volume element are as follows:

Inner $\quad S^I_{ij} = 2(i - 1)\pi \Delta r \Delta z \quad$ (39)

Outer $\quad S^O_{ij} = 2i\pi \Delta r \Delta z \quad$ (40)

Top and Bottom $\quad S^T_{ij} = S^B_{ij} = (2i - 1)\pi(\Delta r)^2 \quad$ (41)

The advective mass balance for VOC in this volume element is then

$$\begin{aligned}\sigma \Delta V_{ij} \left[\frac{dC^g_{ij}}{dt}\right]_{\text{adv}} &= S^I_{ij} v^I_{ij} [S(v^I) C^g_{i-1,j} + S(-v^I) C^g_{ij}] \\ &+ S^O_{ij} v^O_{ij} [-S(-v^O) C^g_{i+1,j} - S(v^O) C^g_{ij}] \\ &+ S^B_{ij} v^B_{ij} [S(v^B) C^g_{i,j-1} + S(-v^B) C^g_{ij}] \\ &+ S^T_{ij} v^T_{ij} [-S(-v^T) C^g_{i,j+1} - S(v^T) C^g_{ij}]\end{aligned} \tag{42}$$

where

$$v^I_{ij} = v_r[(i - 1)\Delta r, (j - \tfrac{1}{2})\Delta z] \tag{43}$$

$$v_{ij}^{\mathrm{O}} = v_r[i\Delta r, (j - \tfrac{1}{2})\Delta z] \tag{44}$$

$$v_{ij}^{\mathrm{B}} = v_z[(i - \tfrac{1}{2})\Delta r, (j - 1)\Delta z] \tag{45}$$

$$v_{ij}^{\mathrm{T}} = v_z[(i - \tfrac{1}{2})\Delta r, j\Delta z] \tag{46}$$

and the function $S(v)$ is zero if $v \leq 0$ and one if $v > 0$.

E. Initial Distribution of VOC among the Phases

This question is addressed as follows. The physical picture is that at time zero a spill occurs and that the NAPL rapidly flows through the vadose zone, leaving residual NAPL droplets and vapor phase VOC, but that there is insufficient time for diffusion of VOC into the water-saturated clay lenses to take place to any extent during this period. We may therefore set the initial aqueous VOC concentration $C_0^w = 0$. Let us assume that the initial VOC concentrations in the gas and NAPL phases are constant from volume element to volume element. Then

$$C_{\mathrm{tot}} = \sigma C_0^g + C_0^N \tag{47}$$

where C_0^g and C_0^N are the initial gaseous and NAPL concentrations, respectively. If $C_{\mathrm{tot}} < \sigma C_{\mathrm{sat}}^g$, where C_{sat}^g is the saturation vapor concentration of the VOC, then

$$C_0^g = C_{\mathrm{tot}}/\sigma \tag{48}$$

and

$$C_0^N = 0 \tag{49}$$

If $C_{\mathrm{tot}} > C_{\mathrm{sat}}^g$, then

$$C_0^g = C_{\mathrm{sat}}^g \tag{50}$$

and

$$C_0^N = C_{\mathrm{tot}} - \sigma C_{\mathrm{sat}}^g \tag{51}$$

F. Change in Aqueous VOC Concentration

Let us assume that the clay lenses in which diffusion is taking place are of thickness $2l$, and that they contain the great bulk of the water in the soil. See Fig. 2. Then the volume of water in a volume element can be written as

$$V_w = \omega \Delta V_{ij} = 2lA_{ij}\nu_{\mathrm{clay}} \tag{52}$$

where A_{ij} = total cross-sectional area of saturated clay lenses in the volume element, m^2
ν_{clay} = porosity of the clay

Then

$$A_{ij} = \frac{\omega \Delta V_{ij}}{2l\nu_{\text{clay}}} \tag{53}$$

and the total area of lenses from which VOC may diffuse (counting top halves and bottom halves separately) is

$$2A = \frac{\omega \Delta V_{ij}}{l\nu_{\text{clay}}} \tag{54}$$

This 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 may take place.

A mass balance on the aqueous phase VOC in the kth slab of the ijth volume element then yields

$$\frac{\omega \Delta V_{ij}}{n_u} \frac{dC_{ijk}^{w}}{dt} = \frac{\Delta V_{ij} \omega}{l\nu_{\text{clay}}} \frac{D}{\Delta u} (C_{ijk+1}^{w} - 2C_{ijk}^{w} + C_{ijk-1}^{w}) \tag{55}$$

or

$$\frac{dC_{ijk}^{w}}{dt} = \frac{D}{(\Delta u)^2 \nu_{\text{clay}}} (C_{ijk+1}^{w} - 2C_{ijk}^{w} + C_{ijk-1}^{w}) \tag{56}$$

For the innermost slab ($k = n_u$, on either side of the center plane of the lenses), we have

$$\frac{dC_{ijnu}^{w}}{dt} = \frac{D}{(\Delta u)^2 \nu_{\text{clay}}} (-C_{ijnu}^{w} + C_{ijnu-1}^{w}) \tag{57}$$

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

$$\frac{dC_{ij1}^{w}}{dt} = \frac{D}{(\Delta u)^2 \nu_{\text{clay}}} [C_{ij2}^{w} - C_{ij1}^{w} + 2(C_{ij}^{g}/K_{\text{H}} - C_{ij1}^{w})] \tag{58}$$

G. Completion of Gas-Phase VOC Material Balance. The Model

We return to Eq. (42) for the vapor-phase advection terms, to which we must adjoin a term corresponding to mass transport of VOC by diffusion to or from the outermost aqueous slab and a term corresponding to vaporization of VOC from the NAPL droplets. The first term is given by

$$\sigma\Delta V_{ij}\left[\frac{dC^g_{ij}}{dt}\right]_{\text{diff}} = \frac{\omega\Delta V_{ij}}{l\nu_{\text{clay}}}\frac{D}{(\Delta u/2)}[C^w_{ij1} - C^g_{ij}/K_{\text{H}}] \tag{59}$$

or

$$\left[\frac{dC^g_{ij}}{dt}\right]_{\text{diff}} = \frac{\omega D}{\sigma l\nu_{\text{clay}}(\Delta u/2)}[C^w_{ij1} - C^g_{ij}/K_{\text{H}}] \tag{60}$$

The second term (corresponding to evaporation from NAPL droplets) is

$$\sigma\Delta V_{ij}\left[\frac{dC^g_{ij}}{dt}\right]_{\text{evap}} = -\frac{dm_{ij}}{dt} \tag{61}$$

where dm_{ij}/dt is given by Eq. (16).

The complete equation is therefore given by

$$\begin{aligned}\frac{dC^g_{ij}}{dt} = {} & \frac{S^{\text{I}}_{ij}v^{\text{I}}_{ij}}{\sigma\Delta V_{ij}}[S(v^{\text{I}})C^g_{i-1,j} + S(-v^{\text{I}})C^g_{ij}] \\ & + \frac{S^{\text{O}}_{ij}v^{\text{O}}_{ij}}{\sigma\Delta V_{ij}}[-S(-v^{\text{O}})C^g_{i+1,j} - S(v^{\text{O}})C^g_{ij}] \\ & + \frac{S^{\text{B}}_{ij}v^{\text{B}}_{ij}}{\sigma\Delta V_{ij}}[S(v^{\text{B}})C^g_{i,j-1} + S(-v^{\text{B}})C^g_{ij}] \\ & + \frac{S^{\text{T}}_{ij}v^{\text{T}}_{ij}}{\sigma\Delta V_{ij}}[-S(-v^{\text{T}})C^g_{i,j+1} - S(v^{\text{T}})C^g_{ij}] \\ & + \frac{\omega D}{\sigma l\nu_{\text{clay}}(\Delta u/2)}(C^w_{ij1} - C^g_{ij}/K_{\text{H}}) - (1/\sigma\Delta V_{ij})\frac{dm_{ij}}{dt}\end{aligned} \tag{62}$$

Equations (16), (56), (57), (58), and (62) then constitute the model.

The mass of residual VOC at any time during the course of a simulation is given by

$$M_{\text{tot}} = \sum_{i=1}^{n_r}\sum_{j=1}^{n_z}\left[\Delta V_{ij}\sigma C^g_{ij} + m_{ij} + \sum_{k=1}^{n_u}\frac{\omega\Delta V_{ij}}{n_u}C^w_{ijk}\right] \tag{63}$$

The effluent soil gas concentration is given by

$$C^g_{\text{eff}} = -\frac{M_{\text{tot}}(t + \Delta t) - M_{\text{tot}}(t)}{q(t)\Delta t} \tag{64}$$

An alternative approach to C^g_{eff} is to define it as follows. Let V_{1J} be the volume element containing the well. Then

$$C^g_{\mathrm{eff}} = \frac{S^{\mathrm{T}}_{1J}|v^{\mathrm{T}}_{1J}|C^g_{1,J+1} + S^{\mathrm{O}}_{1J}|v^{\mathrm{O}}_{1J}|C^g_{2J} + S^{\mathrm{B}}_{1J}|v^{\mathrm{B}}_{1J}|C^g_{1,J-1}}{S^{\mathrm{T}}_{1J}|v^{\mathrm{T}}_{1J}| + S^{\mathrm{O}}_{1J}|v^{\mathrm{O}}_{1J}| + S^{\mathrm{B}}_{1J}|v^{\mathrm{B}}_{1J}|} \tag{65}$$

RESULTS

These models were implemented in TurboBASIC on an AlphaSystem 486-DX microcomputer running at 50 MHz. A simple Euler method was used for the integration. Typical runs with the model for SVE with a single vertical well SVE model required about 10–30 minutes, depending on how long an aging period was simulated. The VOC which is simulated is trichloroethylene.

Figure 4 shows the effect of aging period (the period of time which elapses between the occurrence of the spill and the initiation of SVE) on SVE. (The default parameters used with the vertical well model are listed in Table 1.) If cleanup is initiated immediately, 10.75 days are required to achieve 99.5% removal of the VOC. If SVE is started 1 day after the spill, 19.34 days are required for 99.5% removal. For longer aging periods,

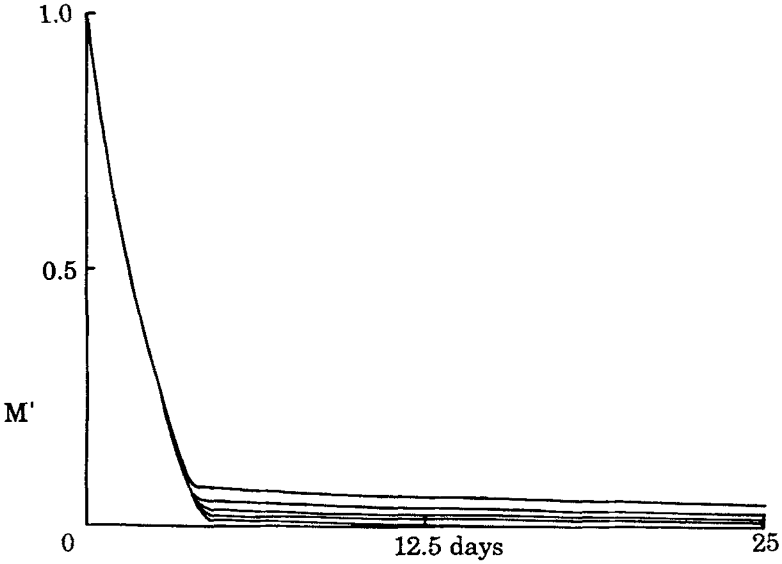

FIG. 4 Plots of M' [$= M_{\mathrm{tot}}(t)/M_{\mathrm{tot}}(0)$] versus time; effect of aging. Aging period = 0, 5, 10, 25, and 50 days, bottom to top. Duration of SVE = 25 days. Other parameters as in Table 1.

TABLE 1
Default Parameters Used with the Vertical Well Model

Radius of domain to be stripped	8 m
Depth of domain to be stripped	5 m
Depth of well	4.5 m
Volumetric gas flow rate of well	50 SCFM (0.0236 m^3/s)
Wellhead pressure	0.85 atm
Diameter of well gravel packing	30 cm
Identity of VOC	Trichloroethylene, TCE
Aqueous solubility of VOC	1100 mg/L
Henry's constant of VOC (dimensionless)	0.2821
Effective diffusion constant of VOC in water (diffusivity × tortuosity/ν_{clay})	2×10^{-10} m^2/s
Effective diffusion constant of VOC in air (diffusivity × tortuosity/ν_{soil})	2×10^{-8} m^2/s
Density of VOC	1.46 g/cm^3
Soil density	1.7 g/cm^3
Soil air-filled porosity	0.2
Soil water-filled porosity	0.2
Porosity of low-permeability clay lenses	0.4
Mean thickness $2l$ of porous clay lenses	5.0 cm
Initial NAPL droplet diameter	0.1 cm
n_r	8
n_z	5
n_u	5
Total VOC concentration in the soil	1000 mg/kg
Initial total mass of VOC	1704 kg
Δt	100 seconds
Duration of simulated SVE run	25 days (Figs. 4–7) 15 days (Figs. 8–16)
Calculated Darcy's constant	0.1136 $m^2/atm{\cdot}s$

99.5% removal is not achieved during the 25-day period of SVE. For an aging period of 50 days, 25 days of SVE leaves about 4.5% of the VOC in the soil; this run is shown in Fig. 5. The run shows quite rapid removal of VOC during the first 4 days (while the NAPL droplets are evaporating), followed by very slow removal as dissolved VOC diffuses out of the clay lenses (5 cm thick in this run). We note that the model parameters will be highly site-specific, so our results should be regarded as showing semi-quantitative trends only. Still, the calculations make it very clear that one can expect to pay a heavy price for delays in SVE remediation if the soil contains low-permeability lenses.

The effects of the thickness of the low-permeability lenses are shown in Fig. 6. In these runs the same fraction of the medium is low-permeability

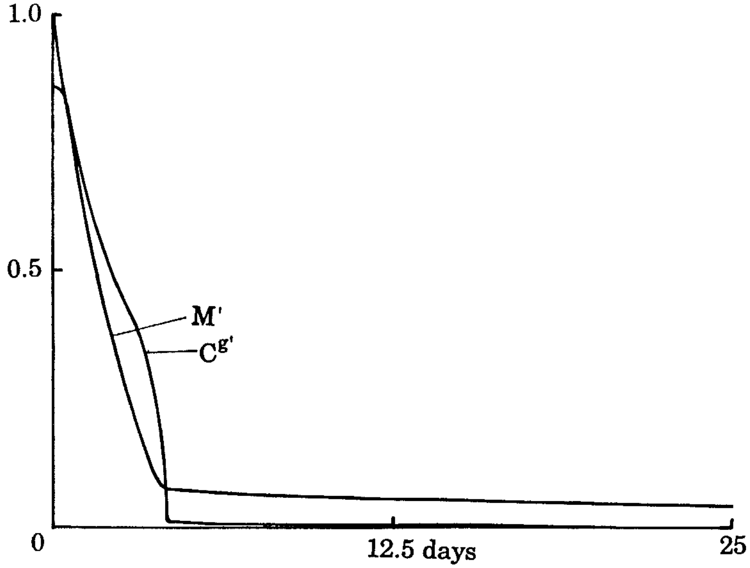

FIG. 5 Plots of M' and $C^{g'}$ [$= C^g(t)/C^g_{sat}$] versus time. Aging period = 50 days. Other parameters as in Table 1.

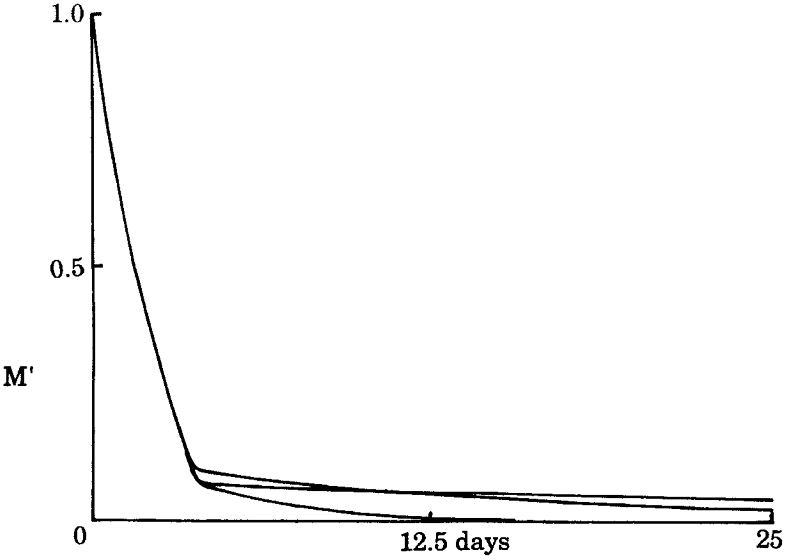

FIG. 6 Plots of M' versus time; effect of thickness of the low-permeability lenses, l. l = 1.25, 2.5, and 5.0 cm, bottom to top, right-hand side. Aging period = 50 days. Other parameters as in Table 1.

clay (50%); the lens thicknesses $2l$ are 1.25, 2.5, and 5.0 cm; the aging period is 50 days. In all cases the initial rapid evaporation of NAPL is followed by much slower removal rates as the dissolved VOC diffuses from the lenses. As expected, the thinner the lenses, the more rapid is this diffusion process. For a lens thickness of 1.25 cm, 99.5% cleanup required 14.45 days; systems having thicker lenses were not cleaned up to the 99.5% level during the 25-day period of SVE. The crossing of the curves for the runs having lens thicknesses of 2.5 and 5.0 cm is not unexpected. Since the volume of clay is the same in these runs, the cross-sectional area of clay lens available for diffusion transport decreases with increasing lens thickness. During the aging period, therefore, diffusion of VOC into the thicker lens occurs to a lesser extent than it occurs into the thinner lens, so the mass of dissolved VOC is smaller in the former case at the beginning of SVE. However, during SVE the rate of diffusion of dissolved VOC from the thicker lens is slower than it is from the thinner, resulting in the observed crossing of the curves plotting residual mass of VOC.

The effect of the size of the NAPL droplets is shown in Fig. 7. In these runs a 10-day aging period was followed by 25 days of SVE. As one would

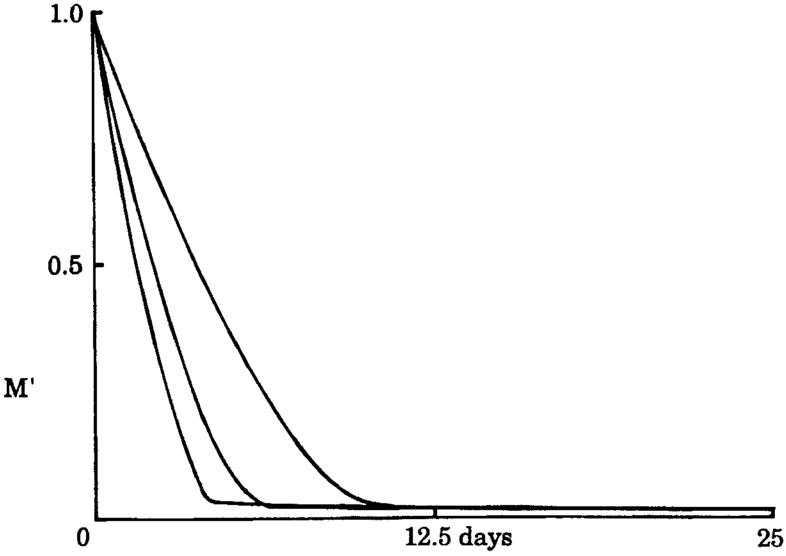

FIG. 7 Plots of M' versus time; effect of NAPL droplet diameter, $2a_0$. Droplet diameter = 0.1, 0.3, and 0.5 cm, left to right. Aging period = 10 days. Other parameters as in Table 1.

expect, the principal effect is on the rapid rate of removal of VOC during the period in which NAPL is evaporating; the larger the droplets, the slower the rate of evaporation. This is expected, since the total NAPL–air interface decreases with increasing droplet size for these runs in which the initial total mass of VOC is held constant. Even in the run for which the droplet diameter is 0.5 cm, an unrealistically large value, the VOC removal rate is sufficiently fast that one would not be concerned about it. Evidently droplet size is not a significant parameter in determining SVE cleanup times. In all of the runs we see prolonged tailing after the NAPL has been removed, and diffusion of dissolved VOC becomes the limiting factor in the cleanup.

In SVE it is common practice to rely rather heavily on soil gas analyses to follow the progress of the remediation, since these are quicker and cheaper than analyzing actual soil samples. As was seen in Fig. 5, the effluent soil gas VOC concentrations become quite low after the NAPL has evaporated, even though substantial quantities of dissolved VOC remain in the soil. DiGiulio (30) noted the importance of taking soil gas samples under static conditions; i.e., when the well has been turned off and the soil gas VOC has had sufficient time to come to equilibrium with the dissolved and adsorbed VOC in the soil, and we examined this "rebound" phenomenon in the context of other models (35, 38). Figures 8–11 show plots of total residual VOC mass and effluent soil gas VOC concentration for runs in which the sites have had aging periods of 1, 10, 25, and 50 days (not shown in the plots). After aging, they were subjected to SVE for 15 days, after which the well was turned off and the soil gas allowed to approach equilibrium with the soil for a period of 10 days.

In all four runs the effluent soil gas VOC concentration becomes extremely small after the NAPL has been removed by evaporation. In all four runs, however, the plots of total mass residual VOC indicate that cleanup is not complete after 15 days of SVE, and in all four runs a rebound of the soil gas VOC concentration is observed after the well is shut down. The extent of this rebound increases as the length of the aging period increases, as expected, since the longer the aging period, the larger the quantity of VOC present in aqueous solution in the soil available for partitioning into the gas phase during equilibration.

Figures 12–16 simulate systems having different thicknesses of the low-permeability lenses; these are 1, 2, 3, 4 and 5 cm, respectively. In all cases the aging period was 25 days (not shown), the period of SVE was 15 days, and the equilibration period was 10 days. The run shown in Fig. 12 (lens thickness of 1 cm) shows no rebound because cleanup is complete after 15 days of SVE. For the other four runs extensive rebound is observed, with the initial rate greatest for the lens of 2 cm thickness and least for

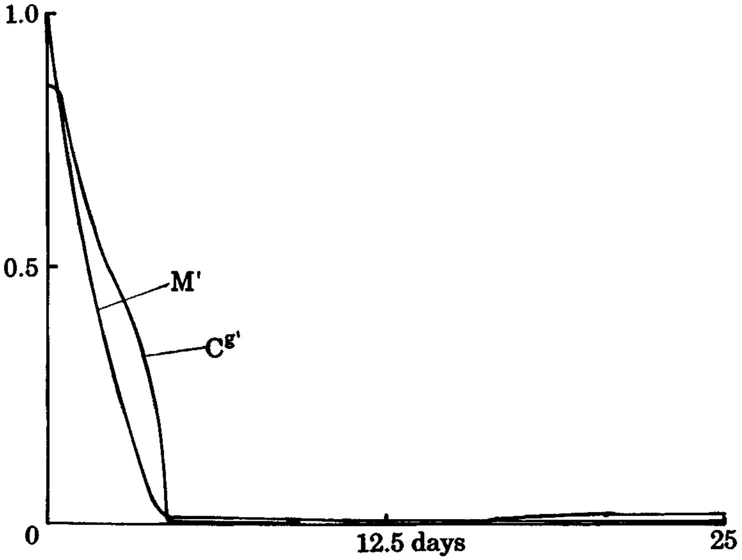

FIG. 8 Plots of M' and $C^{g'}$ versus time; Figs. 8–11 show the effects of aging on the rebound of the soil gas VOC concentration. The aging period here is 1 day, the duration of SVE is 15 days, and the equilibration period is 10 days.

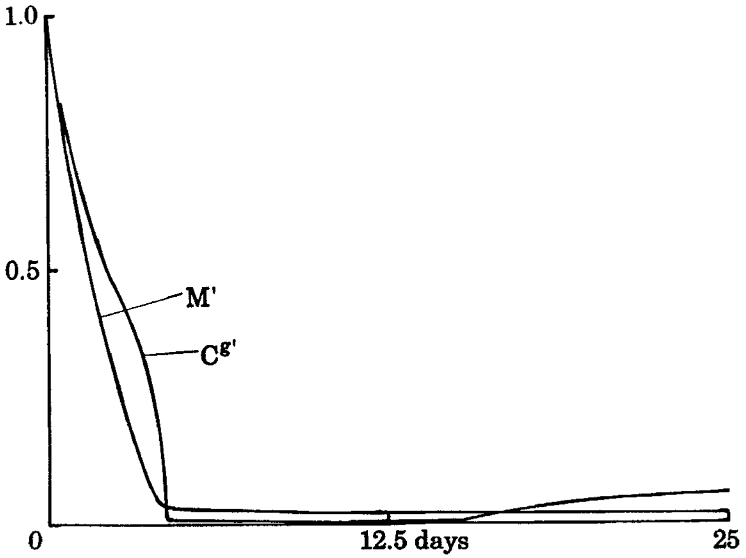

FIG. 9 Plots of M' and $C^{g'}$ versus time. The aging period here is 10 days, the duration of SVE is 15 days, and the equilibration period is 10 days.

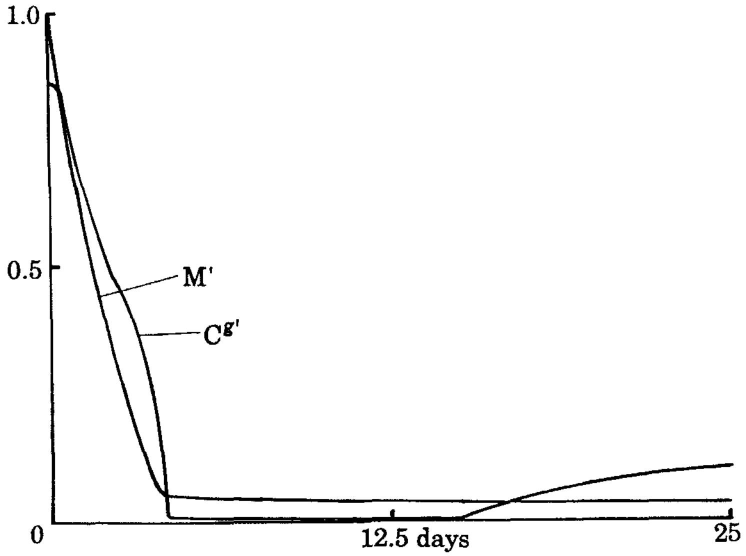

FIG. 10 Plots of M' and $C^{g'}$ versus time. The aging period here is 25 days, the duration of SVE is 15 days, and the equilibration period is 10 days.

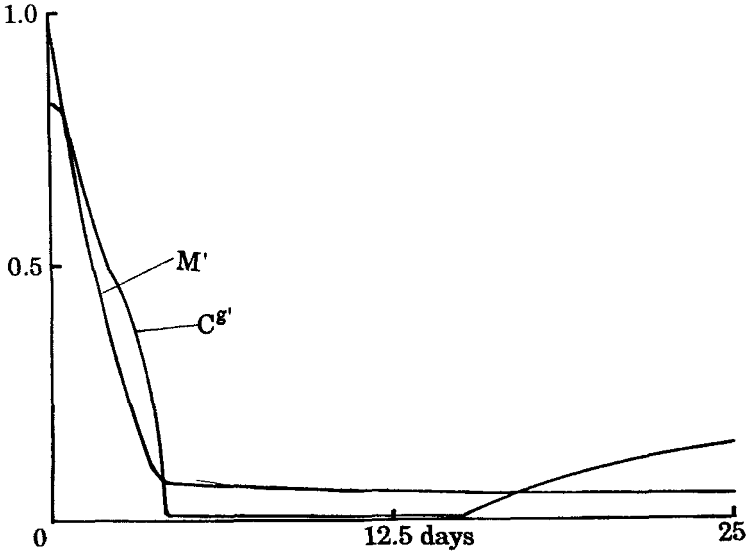

FIG. 11 Plots of M' and $C^{g'}$ versus time. The aging period here is 50 days, the duration of SVE is 15 days, and the equilibration period is 10 days.

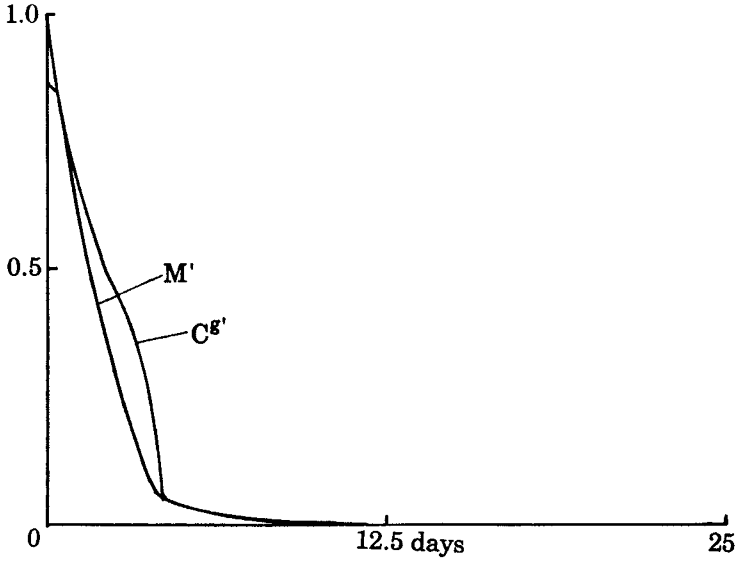

FIG. 12 Plots of M' and $C^{g'}$ versus time; Figs. 12–16 show the effect of the thickness of the clay layers on the rebound of the soil gas concentration. The aging period in the runs shown in these figures is 25 days, the duration of SVE is 15 days, and the equilibration period is 10 days. In Fig. 12 the thickness of the clay layers is 1 cm. Other parameters as in Table 1.

the lens of 5 cm thickness. The 10-day equilibration period was not long enough to achieve equilibrium for these systems. The fraction of the original VOC remaining in the soil after treatment was 2.4% (2 cm), 3.6% (3 cm), 4.2% (4 cm), and 4.2% (5 cm). One expects this to go through a maximum for a finite aging period, since the total cross-sectional area of the lenses available for diffusion transport decreases with increasing thickness of the lenses because the volume of clay is being held constant.

CONCLUSIONS

A model for the operation of a soil vapor extraction (SVE) well (single vertical well configuration) has been constructed which includes the rates of NAPL droplet evaporation and the diffusion of VOC through water-saturated clay lenses. NAPL droplet evaporation is sufficiently rapid that it presents no problem in SVE cleanups. Diffusion of SVE through water-saturated layers, on the other hand, can result in severe "tailing" of cleanups (i.e., a very prolonged terminal phase of the cleanup during which

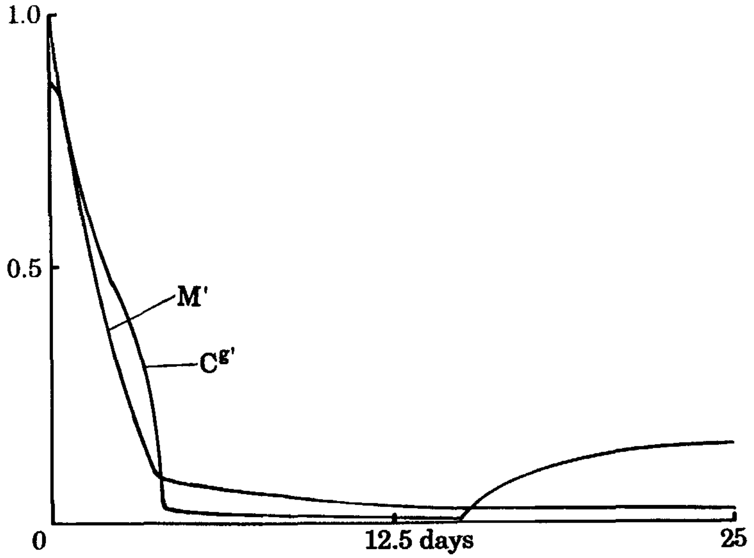

FIG. 13 Plots of M' and $C^{g'}$ versus time. The thickness of the clay layers is 2 cm, the aging period is 25 days, the duration of SVE is 15 days, and the equilibration period is 10 days. Other parameters as in Table 1.

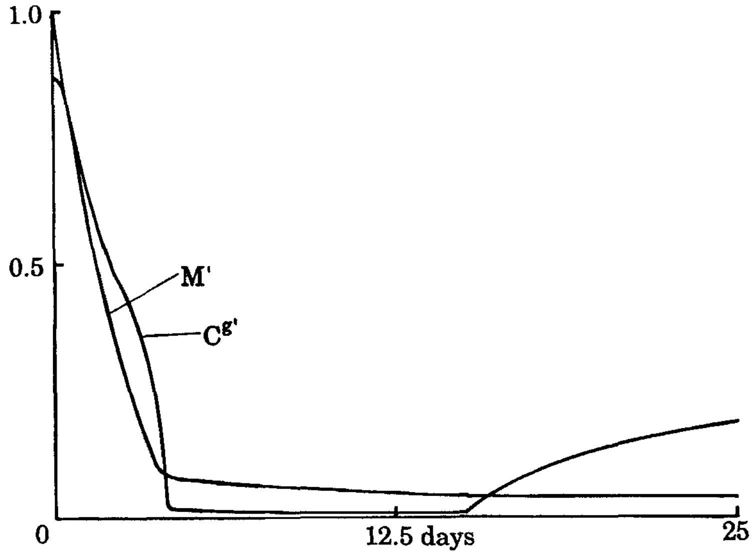

FIG. 14 Plots of M' and $C^{g'}$ versus time. The thickness of the clay layers is 3 cm, the aging period is 25 days, the duration of SVE is 15 days, and the equilibration period is 10 days. Other parameters as in Table 1.

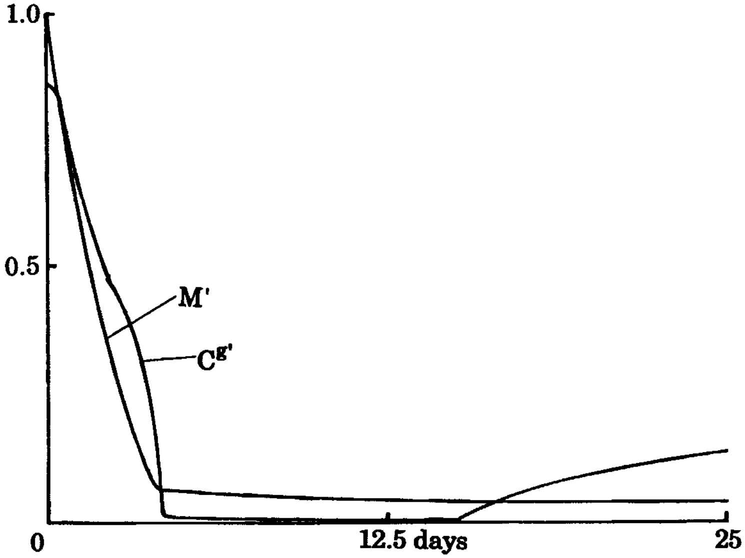

FIG. 15 Plots of M' and $C^{g'}$ versus time. The thickness of the clay layers is 4 cm, the aging period is 25 days, the duration of SVE is 15 days, and the equilibration period is 10 days. Other parameters as in Table 1.

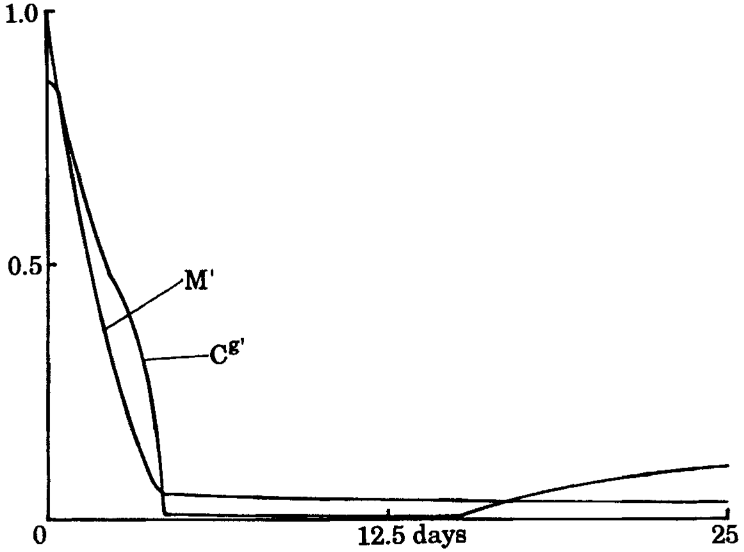

FIG. 16 Plots of M' and $C^{g'}$ versus time. The thickness of the clay layers is 5 cm, the aging period is 25 days, the duration of SVE is 15 days, and the equilibration period is 10 days. Other parameters as in Table 1.

effluent soil gas VOC concentrations are very low and SVE is quite inefficient).

VOC removal rates during the period in which NAPL is evaporating (the first few days of operation) give no indication of the behavior to be expected of an SVE cleanup during the period in which dissolved VOC is diffusing into the advecting soil gas. Removal rates during this latter period may be very slow if diffusion kinetics limitations are unfavorable.

The aging period (the interval between the occurrence of a spill and the initiation of SVE) is shown to have a major impact on SVE cleanups; the longer the aging period, the more severe the tailing of the remediation.

The thicker the low-permeability lenses, the more severe the tailing of the remediation.

The extent of the rebound of soil gas VOC concentrations under static conditions (after the well has been shut down) provides a useful method for assessing the completeness of SVE cleanups. Measurements of effluent soil gas VOC concentrations during well operation typically give results which do not reflect the true VOC content of the soil.

One can use the soil gas rebound data to adjust the gas flow rate during the terminal phases of the remediation. There is little point in using gas flow rates which yield effluent soil gas VOC concentrations an order of magnitude or more smaller than the rebound soil gas concentration after a period of static equilibration. An alternative approach is to use pulsed gas flow, with a down period (no gas flow) equal to the time required for the soil gas VOC concentration to rebound to half of its maximum value, and an up period (well in operation) long enough to reduce the effluent soil gas VOC concentration to a tenth or a twentieth of this maximum value. In either case, one will be drastically reducing the volume of soil gas requiring treatment and will increase the cleanup time only marginally. This point was explored in more detail in connection with an earlier model (40).

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