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Removal of Semivolatiles from Soils by Steam Stripping. II. Effects of Diffusion Kinetics

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ABSTRACT

The validity of steady-state models for steam stripping of volatile and semivolatile organic compounds (VOCs and SVOCs) is explored within the framework of a simple one-compartment approach. The steady-state approximation appears to be valid after a relatively short warming phase. A mathematical model for the in-situ steam or hot-air stripping of volatile and semivolatile compounds from vadose zone soils at hazardous waste sites is presented. The model assumes that the pneumatic permeability of the soil is constant and isotropic, and that the adsorption isotherm of the contaminant on the soil is linear. Diffusion kinetics are included in the model; it is assumed that the contaminant is adsorbed in porous low-permeability lenses of clay, till, or silt, and must diffuse to the surfaces of these structures in order to be removed by the advecting vapor phase. The dependence of results on model parameters is explored.

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I. INTRODUCTION

The techniques of soil vapor extraction (SVE) and in-situ air sparging (ISAS) are proving quite useful for the remediation of vadose zone soils and of aquifers contaminated with volatile organic compounds (VOCs). Their application, however, is limited to contaminants having sufficiently high vapor pressures at ambient temperature to permit cleanup at an acceptably rapid rate. These technologies become marginal when the contaminant vapor pressure is about 0.5 torr (1), so are ineffective for use with fuel oils, diesel fuel, kerosene, PCBs, polynuclear aromatic hydrocarbons, etc. Since the vapor pressures of organic compounds generally increase by a factor of roughly 4 for each 10°C rise in temperature, the use of steam for the removal of these compounds of low volatility has been explored, and is regarded by EPA as a developing technology (2). Ghassemi (3) and Houthoofd et al. (4) published reviews a few years ago on several thermal remediation technologies.

These reviews have been updated the last couple of years. Truong and Parmele (5) reviewed several treatment technologies (SVE, steam stripping, diffused aeration, aboveground biological treatment, and ultraviolet-catalyzed oxidation using H_2O_2 and O_3) for the removal of methyl-*t*-butyl ether, methanol, benzene, toluene, and xylene from polluted groundwater. They include an analysis of treatment costs for the removal of methyl-*t*-butyl ether and methanol.

Just and Stockwell (6) prepared an extensive review on the applicability of a number of treatment techniques to soil remediation. Both older and emerging technologies were considered, including low-temperature thermal treatment, r.f. heating, steam stripping, soil vapor extraction, aeration, in-situ bioremediation, and soil flushing/washing. The feasibility, advantages and disadvantages, limitations, and performance of the treatment methods are assessed, and the cleanup levels achieved by the various techniques are discussed. The review emphasizes the treatment of soils contaminated with solvents such as trichloroethylene (TCE).

Noonan, Glynn, and Miller (7) reviewed two of the enhancements of SVE, steam stripping and in-situ air sparging. They noted that the effectiveness of a combination of the two techniques for the cleanup of soils contaminated with gasoline and chlorinated hydrocarbons had been demonstrated at a number of sites. Martin (8), discussing waste treatment technology demonstrations under the SITE program, notes that some 20 demonstration projects had been completed at the time the report was written. Those completed within 1990 included microfiltration, waste excavation and emissions control, integrated SVE and steam vacuum stripping, solidification of contaminated soil, and flame reactor recovery of lead.

The pioneering work of Lord and his associates at Drexel University (9–15) was discussed in our earlier paper (16); the references are included here for convenience. These workers presented a mathematical model (11, 15) for steam stripping which they used in interpreting their experimental results and in estimating what could be expected in scaled up steam stripping operation. Our steam stripping model (16) is built on their foundation, but eliminates some of the approximations which they made.

Toxic Treatment (USA), Inc., conducted a SITE demonstration of their in-situ steam/hot-air stripping technology in the fall of 1989 at a site in San Pedro, California; this was described by Jackson (17). A chemical storage and transfer facility was contaminated with various solvents as a result of spills and a fire; contamination extended into the salt water table. Some 85% of the VOCs and 50% of the SVOCs (semivolatile organic compounds) were removed from the soil by steam/hot-air stripping. Fugitive air emissions were quite low, and lateral and downward migration of contaminants during the treatment were minimal. It was concluded that the process is cost-effective.

Heglie et al. (18) described a steam injection/vacuum extraction project being planned by CH2M/Hill. The USAF is planning a pilot test of the steam injection/SVE remediation technology at McClellan AFB. The approach combines in-situ steam injection into the soil in both the vadose and saturated zones with SVE of VOSs and SVOCs from the soil. Dioxins, dibenzofurans, petroleum hydrocarbons, volatile and semivolatile organics, and PCBs are present in the waste fill material. Treatability testing indicates that 1) low concentrations of dioxins and dibenzofurans were mobilized by the steam condensate, 2) high concentrations of hydrocarbons were reduced by one order-of-magnitude by the steam, and 3) dioxins and dibenzofurans appear to be dissolved mainly in the hydrocarbon NAPL phase.

Dablow (19) described the use of steam injection to enhance the removal of diesel fuel from contaminated soil and groundwater; he discussed laboratory-scale experimental studies, pilot-scale plants, and full-scale application.

Hadim, Shah, and Korfiatis (20) presented the results of a bench-scale laboratory study of the steam stripping of light nonaqueous phase liquid (LNAPL)-contaminated soils. Increased steam pressures resulted in faster removal rates and reduced steam requirements for remediation. Fine-grained soils were cleaned more slowly than coarse-grained soils, and retained a larger final concentration of residual LNAPL. Experiments with jet fuel and No. 2 heating oil showed no significant variation in steam front propagation, temperature profile, and maximum LNAPL removal. LNAPL residuals after treatment were essentially independent of the initial LNAPL concentrations.

Smith, Adams, and Basile (21) recently presented an evaluation of DNAPL removal from a low-permeability porous medium by means of a combination of steam injection with groundwater and vapor extraction at an industrial facility contaminated with trichloroethylene and 1,1,1-trichloroethane. A dramatic reduction was observed in DNAPL concentrations near suspected source areas; removal was achieved at temperatures well below the boiling points of the compounds.

Our initial in-situ steam-stripping model (16) utilized the local equilibrium assumption—the assumption that the vapor phase and the stationary phase(s) with which it is in contact are at local equilibrium with respect to mass transport of the VOCs and/or SVOCs which are being removed. In SVE operations, however, it has become evident that the assumption of local equilibrium is an approximation that is often not warranted, and that diffusion/desorption kinetics must be taken into account if one is to construct a model which can be applied to most sites (22, 23, for example). We therefore developed mathematical models for SVE which include the kinetics of diffusion of the VOC from porous structures of low permeability (lumps or lenses of clay, silt, or till) (24–26, for example), and found that these models were able to describe both the very rapid initial VOC removal rates and the very prolonged tailing of the remediations which are often observed.

There seems no reason why the same mass transport constraints which appear in SVE should be absent from steam stripping. The only differences between the two techniques in terms of modeling are 1) the temperature at which the separation is being carried out, 2) the sign of the pressure gradient of the advecting gas, and 3) the existence of a preliminary transient period in steam stripping during which the soil is being heated up to temperature. One expects the same types of diffusion and desorption kinetic considerations to be operative in both techniques, so that the demonstration of mass transport bottlenecks in SVE removal rates strongly suggests that similar bottlenecks exist in steam stripping.

In the first of the following sections we explore the domains of applicability of steady-state models such as the one considered here. A simple lumped parameter approach is used to estimate the time periods required to heat the contaminated soil up to 100°C, to dry it, and then to heat it up to a temperature somewhat below the temperature of the injected steam.

We then turn to the development of the model. In this second portion of the paper we first present an analytical section which includes a physical description of the model and a formulation of this description in mathematical terms. The analysis breaks down into three components. The first of these is the calculation of the gas flow field. The second, analysis of

the local behavior of the SVOC—its adsorption isotherm and its diffusion transport in such low-permeability porous structures as clay or silt lenses. The last component is the joining together of the first two to form the steam stripping model.

The analytical section is followed by a section on results. The dependence of the course of a steam stripping operation on the various parameters of the model is explored by means of plots of $M_{\text{residual}}(t)/M_{\text{residual}}(0)$ versus time t , where $M_{\text{residual}}(t)$ is the mass of residual contaminant after a time period t of steam stripping. A brief section on conclusions then closes the paper.

II. ESTIMATION OF THE DURATION OF TRANSIENTS IN STEAM STRIPPING

The objective here is to obtain an approximate estimate of the time during which the behavior of a steam stripping operation will exhibit transient behavior—i.e., the time during which soil temperatures will be changing and/or water will be evaporating or condensing, thereby changing the soil permeability. Existing models for steam stripping make the assumption that this transient period is sufficiently short compared to the time required to remove the semivolatile organic compounds that it can be neglected. We have had some doubts as to the validity of this assumption, and it seems advisable to explore the validity of this approximation in more detail.

In the following approach we use a one-compartment model to estimate approximately 1) the time required to heat 1 m³ of moist soil from an initial temperature T_{soil}^0 to a final temperature of 100°C by the injection of steam at a temperature of T_{steam} ; 2) the additional time required to evaporate all of the soil water (water initially present plus condensate from the first phase of the heating); and finally 3) the additional time to heat the dry soil from 100°C to a temperature somewhat below the temperature of the entering steam.

Let

T_{soil}^0 = initial soil temperature, °C

T_{steam} = influent steam temperature, °C

$T(t)$ = soil temperature at time t

C_{soil} = specific heat of dry soil, J/kg·deg

C_{water} = specific heat of liquid water, J/kg·deg

C_{steam} = specific heat of steam, J/kg·deg

ρ_{soil} = density of dry soil, kg/m³

ρ_w = density of liquid water, kg/m³

ω = initial volumetric moisture content of soil

λ = latent heat of vaporization of water, J/kg

q = rate of steam flow, kg/s

M_s = mass of dry soil, = $\rho_{\text{soil}} \cdot 1 \text{ m}^3$

M_w^0 = initial mass of water in the system, = $\rho_w \cdot \omega \cdot 1 \text{ m}^3$

M_w = mass of water in the system at time t

A. First Phase

Let the soil temperature be $< 100^\circ\text{C}$, so that the steam condenses. A heat balance on the system gives

$$(C_{\text{soil}}M_s + C_{\text{water}}M_w) \frac{dT}{dt} = q[C_{\text{steam}}(T_{\text{steam}} - 100) + \lambda + C_{\text{water}}(100 - T)] \quad (1)$$

Since all the steam condenses,

$$dM_w/dt = q \quad (2)$$

so

$$M_w(t) = M_w^0 + qt \quad (3)$$

gives the mass of water in the system at time t . Substitution of Eq. (3) in Eq. (1) and rearrangement then gives

$$\frac{dT}{dt} = \frac{q[C_{\text{steam}}(T_{\text{steam}} - 100) + \lambda + C_{\text{water}}(100 - T)]}{C_{\text{soil}}M_s + C_{\text{water}}M_w^0 + C_{\text{water}}qt} \quad (4)$$

Separate the variables to obtain

$$\frac{dT}{C_{\text{steam}}(T_{\text{steam}} - 100) + \lambda + C_{\text{water}} \cdot 100 - C_{\text{water}}T} = \frac{qdt}{C_{\text{soil}}M_s + C_{\text{water}}M_w^0 + C_{\text{water}}qt} \quad (5)$$

Rearrange to get

$$\frac{dT}{\frac{C_{\text{steam}}(T_{\text{steam}} - 100) + \lambda}{C_{\text{water}}} + \frac{100 - T}{C_{\text{water}}}} = \frac{dt}{\frac{C_{\text{soil}}M_s}{qC_{\text{water}}} + \frac{M_w^0}{q} + t} \quad (6)$$

Integrate between the limits (lower limits T_{soil}^0 and 0; upper limits $T(t)$ and

t) to get

$$\log_e \left[\frac{\frac{C_{\text{steam}}}{C_{\text{water}}}(T_{\text{steam}} - 100) + \frac{\lambda}{C_{\text{water}}} + 100 - T_{\text{soil}}^0}{\frac{C_{\text{steam}}}{C_{\text{water}}}(T_{\text{steam}} - 100) + \frac{\lambda}{C_{\text{water}}} + 100 - T(t)} \right] = \log_e \left[\frac{\frac{C_{\text{soil}}M_s}{qC_{\text{water}}} + \frac{M_w^0}{q} + t}{\frac{C_{\text{soil}}M_s}{qC_{\text{water}}} + \frac{M_w^0}{q}} \right] \quad (7)$$

We are interested in the time required to heat the soil to 100°C, t_{100} ; $T(t_{100}) = 100^\circ\text{C}$. For this, Eq. (7) gives

$$\left[\frac{\frac{C_{\text{steam}}}{C_{\text{water}}}(T_{\text{steam}} - 100) + \frac{\lambda}{C_{\text{water}}} + 100 - T_{\text{soil}}^0}{\frac{C_{\text{steam}}}{C_{\text{water}}}(T_{\text{steam}} - 100) + \frac{\lambda}{C_{\text{water}}}} \right] = \left[\frac{\frac{C_{\text{soil}}M_s}{qC_{\text{water}}} + \frac{M_w^0}{q} + t_{100}}{\frac{C_{\text{soil}}M_s}{qC_{\text{water}}} + \frac{M_w^0}{q}} \right] \quad (8)$$

Solving Eq. (8) for t_{100} then yields

$$t_{100} = [C_{\text{soil}}M_s + C_{\text{water}}M_w^0] \frac{(100 - T_{\text{soil}})}{[C_{\text{steam}}(T_{\text{steam}} - 100) + \lambda]q} \quad (9)$$

The mass of water in the system at this point is

$$M_w(t_{100}) = M_w^0 + qt_{100} \quad (10)$$

B. Second Phase

The soil temperature has been raised to 100°C during the first phase. We now wish to determine the time t_{dry} that will be required to evaporate $M_w^0 + qt_{100}$ kg of water with the same steam as used in the first phase.

A heat balance gives

$$t_{\text{dry}} q C_{\text{steam}} (T_{\text{steam}} - 100) = \lambda (M_w^0 + q t_{100}) \quad (11)$$

Solution of Eq. (11) for t_{dry} yields

$$t_{\text{dry}} = \frac{\lambda (M_w^0 + q t_{100})}{q C_{\text{steam}} (T_{\text{steam}} - 100)} \quad (12)$$

Recall

$$t_{100} = [C_{\text{soil}} M_s + C_{\text{water}} M_w^0] \frac{(100 - T_{\text{soil}})}{[C_{\text{steam}} (T_{\text{steam}} - 100) + \lambda] q} \quad (9')$$

Substitution of this result into Eq. (12) then gives

$$t_{\text{dry}} = \frac{\lambda \left[M_w^0 + (C_{\text{soil}} M_s + C_{\text{water}} M_w^0) \frac{(100 - T_{\text{soil}})}{C_{\text{steam}} (T_{\text{steam}} - 100) + \lambda} \right]}{q C_{\text{steam}} (T_{\text{steam}} - 100)} \quad (13)$$

C. Third Phase

In the third phase a mass M_s of dry soil is being heated by the passage of dry steam at an inlet temperature of T_{steam} . The heat balance is

$$C_{\text{soil}} M_s \frac{dT}{dt} = q C_{\text{steam}} (T_{\text{steam}} - T) \quad (14)$$

This rearranges to

$$\frac{dT}{dt} + \frac{q C_{\text{steam}}}{C_{\text{soil}} M_s} T = \frac{q C_{\text{steam}} T_{\text{steam}}}{C_{\text{soil}} M_s} \quad (15)$$

which integrates to give

$$T(t) = T_{\text{steam}} - (T_{\text{steam}} - 100) \exp \left[-\frac{q C_{\text{steam}}}{C_{\text{soil}} M_s} t \right] \quad (16)$$

Let us define

$$t_{\text{III}} = (C_{\text{soil}} M_s) / (q C_{\text{steam}}) \quad (17)$$

which is the time required for the soil temperature to come within $(T_{\text{steam}} - 100)/e$ degrees of its final value, T_{steam} . Then the estimated duration of the total transient period for the steam stripping operation is given by

$$t_{\text{total}} = t_{100} + t_{\text{dry}} + t_{\text{III}} \quad (18)$$

D. Conclusions, Lumped Parameter Model

We note that very little SVOC removal is likely to occur during the first phase, in which the wet soil is heated to 100°C; the duration of the phase is short and one can expect vapor pressures to be low. During the second phase, SVOC is removed by what is essentially steam distillation. The process is isothermal and SVOC is being removed by steam distillation at 100°C; steady-state models for steam stripping by a mechanism similar to steam distillation are applicable to this second phase. During the third phase, SVOC is removed by the passage of hot, dry gas. This third phase marks a second point at which steady-state models for steam stripping, by means of thermal desorption by superheated dry steam, become at least approximately applicable. As we shall see, however, there are some serious disadvantages to operation in this third phase, and it is not likely to be used in practice.

We next examine some results obtained by this one-compartment approach. Recall that the volume of soil being treated is 1 m³. Default parameters for these calculations are given in Table 1.

Table 2 shows the effects of the rate of steam flow on t_{100} , t_{dry} , and t_{III} . As expected, we see that these times are inversely proportional to the steam flow rate. The times are also directly proportional to the volume of soil being treated. These facts permit one to use the following results in scaling calculations to other volumes of soil and other steam flow rates. We see that the time required for drying the soil is by far the largest of these transient periods.

The effect of soil moisture is indicated in Table 3. The values of t_{100} and t_{dry} (the times required to heat the soil to 100°C and to vaporize all

TABLE I
Default Parameters Used in Examining Transient Phenomena with
the 1-Compartment Model

Volume of soil treated	1 m ³
Water-filled porosity	0.2
Initial soil temperature	15°C
Influent steam temperature	170°C
Steam flow	1 kg/h
Soil density	1700 kg/m ³
Water density	1000 kg/m ³
Latent head of vaporization of water	2.259×10^6 J/kg
Specific heat of steam	1860 J/kg-deg
Specific heat of liquid water	4183 J/kg-deg
Specific heat of soil	800 J/kg-deg

TABLE 2
Effect of Steam Flow Rate on t_{100} , t_{dry} , and t_{III}

Steam flow rate (kg/h)	Days		
	t_{100}	t_{dry}	t_{III}
0.5	6.51	402.16	60.93
1.0	3.26	201.08	30.47
1.5	2.17	134.05	20.31
2.0	1.63	100.54	15.23

TABLE 3
Effect of Soil Moisture Content on t_{100} , t_{dry} , and t_{III}

Soil moisture content	Days		
	t_{100}	t_{dry}	t_{III}
0.10	2.64	118.03	30.47
0.15	2.95	159.55	30.47
0.20	3.26	201.08	30.47
0.25	3.57	242.61	30.47
0.30	3.88	284.13	30.47
0.35	4.19	325.66	30.47
0.40	4.50	367.18	30.47

the water) increase markedly with increasing initial soil moisture content, indicating that one should dewater the soil as much as is feasible before initiating steam stripping to reduce both remediation time and energy costs.

The effect of influent steam temperature is given in Table 4. The value of t_{dry} , the time required to dry the soil after it has been heated to 100°C, is essentially inversely proportional to $(T_{steam} - 100)$, as one would expect. The same type of behavior was shown by another set of runs for which the initial volumetric soil moisture content was 0.1. Evidently, if drying is necessary, one should operate steam stripping facilities at the highest steam temperature practical to reduce the time required for drying and, with this, energy costs as well. On the other hand, we see that the time required to heat the soil to 100°C is affected only slightly by the temperature of the steam.

The quantity of steam required to heat 1 m³ of soil to 100°C and to dry it is readily calculated from the above results; it is given by M_{steam} (kg/m³ of soil) = $q(t_{100} + t_{dry})$. For soil with a volumetric moisture content of 0.2 and steam at temperatures of 140, 170, and 200°C, we find from the

TABLE 4
Effect of Influent Steam Temperature on t_{100} , t_{dry} , and t_{III}

Steam temperature (°C)	Days		
	t_{100}	t_{dry}	t_{III}
110	3.42	1426.94	30.47
120	3.39	711.79	30.47
130	3.36	473.42	30.47
140	3.33	354.26	30.47
150	3.31	282.76	30.47
160	3.28	235.11	30.47
170	3.26	201.08	30.47
180	3.23	175.56	30.47
190	3.21	155.72	30.47
200	3.18	139.85	30.47

results in Table 5 that $M_{\text{steam}} = 8582$, 4904, and 3433 kg/m³ of soil. Evidently the steam stripping of organics which require that temperatures above 100°C be achieved will be an extremely lengthy, energy-intensive, and costly process. We note that the the energy cost for the vaporization

TABLE 5
Default Values of the Parameters Used in the Steam-Stripping
Model Calculations

Depth to water table	10 m
Depth of well	8 m
Soil density	1.7 g/cm ³
Soil permeability	0.1 m ² /atm·s
Soil porosity	0.4
Fraction of soil which is low permeability lenses	0.25
Thickness of low permeability lenses	4 cm
Porosity of low permeability clay	0.4
Temperature	100°C
Adsorption isotherm parameter K_L of SVOC	0.01
Diffusion constant of SVOC in the clay lenses	1×10^{-7} m ² /s
Steam flow rate	5 kg/h
Contaminant concentration	100 mg/kg of soil
Radius of contaminated zone	8 m
Depth of contaminated zone	4 m
Initial total contaminant mass	136.7 kg
Domain radius	15 m
I_r	15
I_z	10
n_u	6
Δt	50 seconds
Duration of run	10 days

of soil water must be paid by low-temperature thermal treatment and by incineration, too.

The quantities of steam required merely to raise the temperature of the soil to 100°C are very much less. For a volumetric soil moisture content of 0.2 and steam temperatures of 110, 140, 170, and 200°C, $M_{\text{steam}} = 82.1, 79.9, 78.2$, and 76.3 kg/m^3 . If the SVOCs have vapor pressures at 100°C such that they can be removed by a process analogous to steam distillation, steam stripping becomes much more feasible in terms of time and energy requirements. In addition, in such operation the use of low-temperature, low-pressure steam reduces the cleanup rate only slightly, permitting the use of low-cost steam boilers or, if available, low-pressure waste steam.

III. STEAM STRIPPING MODEL WITH DIFFUSION KINETICS

A. Analytical

We assume that the gas flow field resulting from the steam injection is at a steady state, and that the porous medium is homogeneous and isotropic, at least at a scale of approximately a meter. Later we shall introduce small-scale heterogeneities—the clay or silt lenses mentioned above—but we assume that these are sufficiently small that they do not affect the large-scale flow pattern of the steam. Note that the model does not apply to the conditions at the beginning of a steam stripping run, during which condensation of steam is occurring, a steam front is advancing through the soil, and the temperature of the soil at any point in the vicinity of the steam injection well is changing rapidly. We make the assumption that relatively little SVOC is removed during this transient period while the soil is being heated up, and we start our time from the point at which the domain of interest has reached or very nearly reached a constant, uniform temperature. In general, we are concerned with the second phase of the process, during which the soil is at a temperature of 100°C and SVOCs are being removed by a process analogous to steam distillation.

The adsorption isotherm of the SVOC on the soil is assumed to be linear. More complex alternative isotherms can readily be handled within the framework of the model, but generally the data base available for a site does not provide sufficient information to permit one to calculate the parameters needed by these more complex equations.

The contaminant SVOC is presumed to be present in the sorbed state mainly within clay or till lenses of sufficiently low permeability that the SVOC must diffuse to the surface of the lens in order to reach advecting

steam which only then can remove it from the soil. This diffusion process is assumed to be governed by Fick's law.

1. The Gas Flow Field

The superficial gas velocities in the flow field here are calculated by the method of images from electrostatics (27). The calculation is described in detail in our first paper (16), so we will give only the results here. It is assumed that the porous medium is of constant and isotropic permeability to the steam.

The steam injection well and the surrounding soil are illustrated schematically in Fig. 1. We work in cylindrical coordinates (r, z) , since our system is axially symmetrical. A representative volume element and notation are shown in Fig. 2. Let

- h = height of the surface of the soil above the water table, m
- a = height of the point of steam injection above the water table, m
- P_0 = ambient pressure at the surface of the soil, atm
- P_w = wellhead pressure, atm
- $P(r, z)$ = pressure at the point (r, z) , atm
- K_D = Darcy's constant of the soil, $\text{m}^2/\text{atm}\cdot\text{s}$
- r_w = radius of well gravel packing
- R = gas constant, $8.206 \times 10^{-5} \text{ atm}\cdot\text{m}^3/\text{mol}\cdot\text{deg}$
- T = temperature, $^{\circ}\text{K}$
- Q = molar steam flow rate, mol/s
- q = volumetric steam flow rate, standard m^3/s

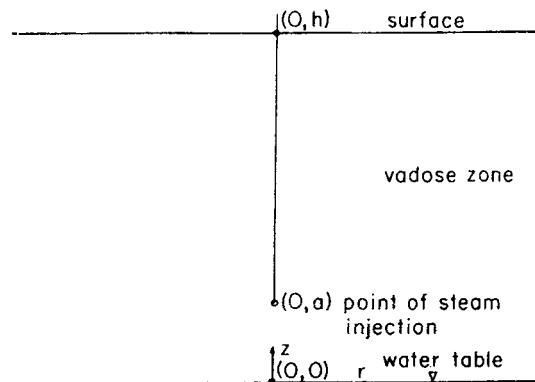


FIG. 1 Schematic of the geometrical setup for a steam or hot air stripping well.

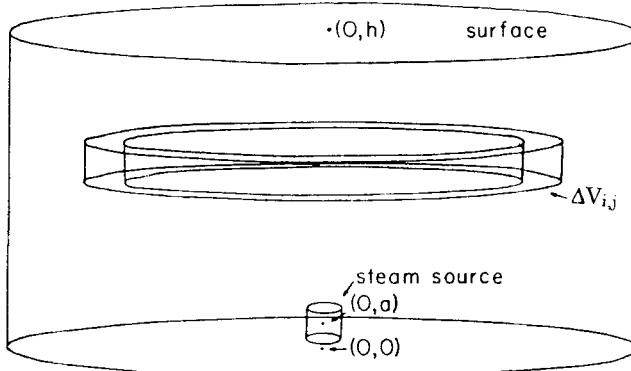


FIG. 2 A representative volume element in the steam-stripping model.

v_r = r -component of the superficial gas velocity, $\text{m}^3/\text{m}^2\cdot\text{s}$
 v_z = z -component of the superficial gas velocity, $\text{m}^3/\text{m}^2\cdot\text{s}$

The boundary conditions for the system are

$$P(r, h) = P_0, \quad 0 < r < \infty \quad (19)$$

$$\frac{\partial P(r, 0)}{\partial z} = 0, \quad 0 < r < \infty \quad (20)$$

Then

$$\begin{aligned} P^2(r, z) = W(r, z) = P_0^2 + A \sum_{n=-\infty}^{\infty} & \left[\frac{1}{\{r^2 + [z - 4nh - a]^2\}^{1/2}} \right. \\ & + \frac{1}{\{r^2 + [z - 4nh + a]^2\}^{1/2}} - \frac{1}{\{r^2 + [z - (4n - 2)h - a]^2\}^{1/2}} \quad (21) \\ & \left. + \frac{1}{\{r^2 + [z - (4n - 2)h + a]^2\}^{1/2}} \right] \end{aligned}$$

where

$$A = \frac{P_w^2 - P_0^2}{S} \quad (22)$$

and

$$S = \sum_{n=-\infty}^{\infty} \left[\frac{1}{\{r_w^2 + [-4nh]^2\}^{1/2}} + \frac{1}{\{r_w^2 + [2a - 4nh]^2\}^{1/2}} \right. \\ \left. - \frac{1}{\{r_w^2 + [- (4n - 2)h]^2\}^{1/2}} - \frac{1}{\{r_w^2 + [2a - (4n - 2)h]^2\}^{1/2}} \right] \quad (23)$$

Darcy's constant is given in terms of observables by

$$K_D = \frac{RTQ}{2\pi} \frac{S(r_w, a, h)}{(P_w^2 - P_0^2)} \quad (24)$$

The superficial velocities, given by

$$\mathbf{v} = -K_D \nabla P \quad (25)$$

are expressed in terms of $W(r, z)$ as

$$v_r = -\frac{K_D}{2W^{1/2}} \frac{\partial W}{\partial r} \quad (26)$$

$$v_z = -\frac{K_D}{2W^{1/2}} \frac{\partial W}{\partial z} \quad (27)$$

where the derivatives are obtained by differentiating Eq. (21) with respect to r and z .

This completes our sketch of the calculation of the gas flow field.

2. Analysis of Equilibrium and Diffusion Processes

The linear equilibrium isotherm is widely used in modeling work for describing the equilibrium partitioning of a contaminant between the mobile gaseous phase (C^g) and the various stationary phases (C^s) because of its simplicity, the fact that one must determine only a single constant, K_L , from either the literature or the experimental data available for the site. We write the isotherm as

$$C^g = K_L C^s \quad (28)$$

We shall use the linear isotherm here, but note in passing that it is not even approximately correct if one has nonaqueous phase liquid present, which would yield values of C^s in excess of what is allowed by the pure liquid SVOC, C_{sat}^g . Our treatment can readily be modified to make use of the Freundlich, BET, or other isotherms.

Let us next turn to the diffusion processes by which SVOC migrates from the interiors of the clay lenses to their surfaces, at which it may be swept away by the advecting steam. Let

v_c = porosity of the clay in the low-permeability lenses

f = volume fraction of the soil which consists of clay lenses

$2l$ = thickness of the clay lenses, m

A_{ij} = total cross-sectional area of the clay lenses in the volume element ΔV_{ij} , m². Note that $2A_{ij}$ = area available for diffusion transport, since SVOC can diffuse from both faces of the lenses

ΔV_{ij} = volume of the ij th volume element, m³; see Fig. 2.

Δu = l/n_u = thickness of one of the slabs into which a clay lens is partitioned for analysis. See Figs. 3 and 4 for the locations, shape, and partitioning of the lenses

Now $f\Delta V_{ij}$ gives the volume of clay lenses in ΔV_{ij} . This volume is also given by $2lA_{ij}$, from which we obtain

$$2A_{ij} = \frac{f\Delta V_{ij}}{l} \quad (29)$$

Let m_{ijk} = total mass of SVOC in the k th slab of the ij th volume element. The volume of the k th slab (which includes material in the k th layer of all the lenses in ΔV_{ij}) is given by $f\Delta V_{ij}/n_u$. Then

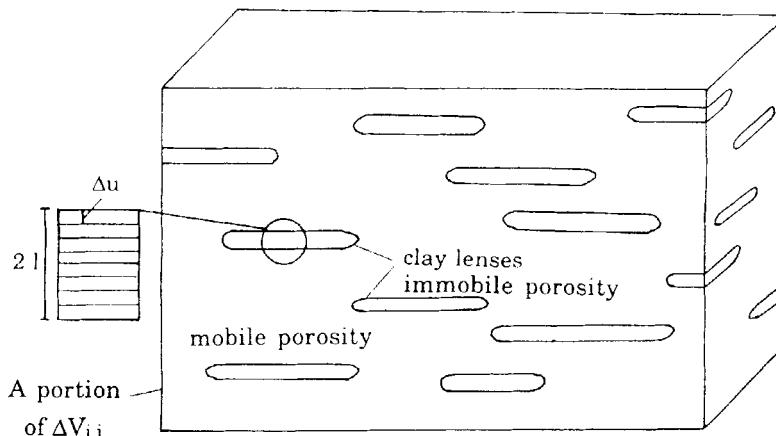


FIG. 3 A portion of a volume element, showing the distribution of porous low-permeability structures of clay, silt, or till.

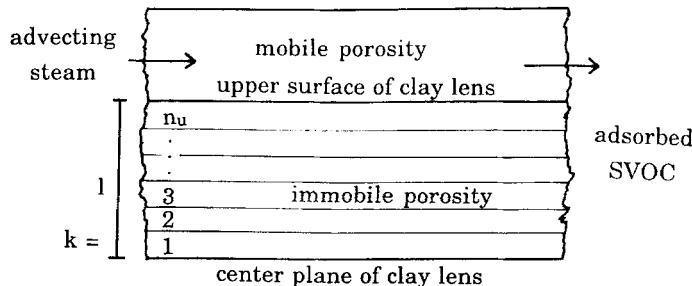


FIG. 4 The upper half of a clay lens, showing its mathematical partitioning into slabs for computational analysis and the adjacent mobile porosity through which the advecting steam moves.

$$m_{ijk} = \frac{f \Delta V_{ij}}{n_u} [v_c C_{ijk}^g + C_{ijk}^s] \quad (30)$$

where C_{ijk}^g = vapor phase SVOC concentration in (i, j, k) , kg/m^3 of gas
 C_{ijk}^s = stationary phase SVOC concentration in (i, j, k) , kg/m^3 of bulk soil

The adsorption isotherm, whatever it may be, gives

$$C_{ijk}^g = F(C_{ijk}^s) \quad (31)$$

if we assume that the gas phase and stationary phase(s) are at equilibrium with respect to SVOC transport in the k th slab of the ij th volume element. Here the function F is defined to correspond to the linear, Freundlich, BET, etc. isotherm. Then

$$m_{ijk} = \frac{f \Delta V_{ij}}{n_u} [v_c F(C_{ijk}^s) + C_{ijk}^s] \quad (32)$$

If F is linear, or for certain other special cases (the Langmuir isotherm, for example), Eq. (32) can be solved explicitly. Generally it must be solved numerically. A very simple, not very efficient, but extremely stable algorithm for doing this is by a binary search, which, while slower than other approaches, is never plagued by instabilities. Then, having C_{ijk}^s , one calculates C_{ijk}^g from Eq. (31). For our case, a linear isotherm, we simply have

$$m_{ijk} = \frac{f \Delta V_{ij}}{n_u} [v_c C_{ijk}^g + K_L^{-1} C_{ijk}^g] \quad (33)$$

from which

$$C_{ijk}^g = \frac{n_u}{f\Delta V_{ij}[\nu_c + K_L^{-1}]} m_{ijk} \quad (34)$$

This completes the analysis of the equilibrium partitioning of SVOC between the gaseous and stationary phases. We now turn to diffusion transport within the clay lenses. This is basically a simple one-dimensional Fick's law diffusion problem.

In the k th slab of the ij th volume element,

$$\frac{dm_{ijk}}{dt} = \frac{f\Delta V_{ij}}{l} D \frac{1}{\Delta u} [C_{i,j,k+1}^g - 2C_{ijk}^g + C_{i,j,k-1}^g] \quad (35)$$

$$\begin{array}{ll} \text{area} & \text{concentration gradients,} \\ & k = 2, 3, \dots, n_u - 1 \\ \text{diffusivity} & \end{array}$$

where D = effective diffusivity of the SVOC in the porous clay, m^2/s .

For the innermost slab (bordering the center plane of the lens),

$$\frac{dm_{ij1}}{dt} = \frac{f\Delta V_{ij}}{l} D \frac{1}{\Delta u} [C_{ij2}^g - C_{ij1}^g] \quad (36)$$

For the outermost slab, at the surface of the lens,

$$\frac{dm_{i,j,n_u}}{dt} = \frac{f\Delta V_{ij}}{l} D \left[\frac{C_{ij}^{gm} - C_{i,j,n_u}^g}{\Delta u/2} + \frac{C_{i,j,n_u-1}^g - C_{i,j,n_u}^g}{\Delta u} \right] \quad (37)$$

where C_{ij}^{gm} = gas phase SVOC concentration in the mobile porosity in ΔV_{ij} , kg/m^3 of gas.

The term in Eq. (37) with $\Delta u/2$ in the denominator corresponds to diffusion transport between the lens and the mobile gas phase. This diffusion process contributes to the mass balance for SVOC in the mobile gas phase, too. Let ν_p = porosity of the permeable medium—the mobile porosity.

The first diffusion term on the right-hand side of Eq. (37) gives

$$\nu_p(1 - f)\Delta V_{ij} \left[\frac{\partial C_{gm}}{\partial t} \right]_{\text{diffusion}} = \frac{2f\Delta V_{ij}D}{l\Delta u} (C_{ij}^{gm} - C_{i,j,n_u}^g) \quad (38)$$

so

$$\left[\frac{\partial C_{ij}^{gm}}{\partial t} \right]_{\text{diffusion}} = \frac{2fD}{\nu_p(1 - f)l\Delta u} (C_{ij}^{gm} - C_{i,j,n_u}^g) \quad (39)$$

This completes our second task, analysis of the sorption/desorption equilibrium and diffusion mass transport.

3. Final Development of the Model

We still need to determine the effect of advective transport on the C_{ij}^{gm} , and to merge this with the effect of diffusion transport exhibited in Eq. (39). See Fig. 2 for the geometry. Let

$$r_i = (i - 1)\Delta r \quad (40)$$

$$z_j = (j - 1)\Delta z \quad (41)$$

Then

$$\Delta V_{ij} = (r_{i+1}^2 - r_i^2)\Delta z \quad (42)$$

Let v_{ij}^I = superficial gas velocity normal to the Inner surface

v_{ij}^O = superficial gas velocity normal to the Outer surface

v_{ij}^T = superficial gas velocity normal to the Top surface

v_{ij}^B = superficial gas velocity normal to the Bottom surface

Note:

$$v_{ij}^I = v_r[(i - 1)\Delta r, (j - 1/2)\Delta z] \quad (43)$$

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

$$v_{ij}^T = v_z[(i - 1/2)\Delta r, j\Delta z] \quad (45)$$

$$v_{ij}^B = v_z[(i - 1/2)\Delta r, (j - 1)\Delta z] \quad (46)$$

where v_r and v_z are defined by Eqs. (26) and (27).

Define

$$A_{ij}^I = 2\pi r_i \Delta z = \text{area of Inner surface of } \Delta V_{ij}$$

$$A_{ij}^O = 2\pi r_{i+1} \Delta z = \text{area of Outer surface of } \Delta V_{ij}$$

$$A_{ij}^T = A_{ij}^B = \pi(r_{i+1}^2 - r_i^2) = \text{areas of Top and Bottom surfaces of } \Delta V_{ij}$$

Also, define

$$S(v) = 0, v < 0 \quad (47)$$

$$= 1, v > 0$$

Then the advective mass balance for SVOC in ΔV_{ij} gives

$$\begin{aligned} (1 - f)v_p \Delta V_{ij} \left[\frac{\partial C_{ij}^{gm}}{\partial t} \right]_{\text{advective}} &= v_{ij}^I A_{ij}^I [S(v^I)C_{i-1,j}^{gm} + S(-v^I)S_{ij}^{gm}] \\ &+ v_{ij}^O A_{ij}^O [-S(-v^O)C_{i+1,j}^{gm} - S(v^O)C_{ij}^{gm}] \\ &+ v_{ij}^B A_{ij}^B [S(v^B)C_{i,j-1}^{gm} + S(-v^B)C_{ij}^{gm}] \\ &+ v_{ij}^T A_{ij}^T [-S(-v^T)C_{i,j+1}^{gm} - S(v^T)C_{ij}^{gm}] \end{aligned} \quad (48)$$

where $S(v^X)$ is used to represent $S(v_{ij}^X)$, $X = I, O, B, T$.

Finally, the system of differential equations governing the C_{ij}^{gm} is

$$\frac{dC_{ij}^{gm}}{dt} = \left[\frac{\partial C_{ij}^{gm}}{\partial t} \right]_{\text{diffusion}} + \left[\frac{\partial C_{ij}^{gm}}{\partial t} \right]_{\text{advection}} \quad (49)$$

$$= \frac{2fD}{\nu_p(1-f)l\Delta u} (C_{ij}^{gm} - C_{i,j,n_u}^g) + \left[\frac{\partial C_{ij}^{gm}}{\partial t} \right]_{\text{advection}} \quad (50)$$

from Eq. (39). The SVOC masses in the slabs, m_{ijk} , are calculated from Eqs. (35), (36), and (37). The C_{ijk}^g are calculated by use of Eq. (34). The total residual mass of SVOC in the system is given by

$$M_{\text{total}} = \sum_i \sum_j \left[(1-f)\nu_p \Delta V_{ij} C_{ij}^{gm} + \sum_k m_{ijk} \right] \quad (51)$$

This completes the model.

B. Results

The model was implemented in TurboBASIC and run on an Alpha System computer equipped with a 80486 DX microprocessor and running at a clock speed of 50 MHz. A typical run took 17 minutes. The numerical integration was done by means of the simple Euler method. Default values of the model parameters are given in Table 1.

The effect of the diffusion constant of the SVOC on the rate of cleanup is shown by the plots of $M_{\text{total}}(t)/M_{\text{total}}(0)$ versus time shown in Fig. 5. This is the diffusion constant of the SVOC in the vapor phase in the low permeability lenses, so it includes the tortuosity factor. The expected decrease in cleanup rate with decreasing diffusion constant D is observed. We see a very short period of rapid fall-off as the contaminant diffusing from the outermost slab in the clay lenses is exhausted. Even if this small segment is eliminated, the decrease of M_{total} with time is not a simple exponential (plot not shown), indicating the inadequacy of a simple lumped parameter approach.

The effect of the mean thickness of the clay lenses is shown by the plots of $M_{\text{total}}(t)/M_{\text{total}}(0)$ versus time shown in Fig. 6. The rate of diffusion of SVOC from the lenses increases with increasing concentration gradient, which in turn increases with decreasing thickness of the low permeability lenses, so cleanup rates increase with decreasing lens thickness. The effect is not extremely large for these parameter sets, indicating that diffusion is not severely rate-limiting in these runs.

Figure 7 exhibits the effect of the linear sorption isotherm parameter K_L on plots of $M_{\text{total}}(t)/M_{\text{total}}(0)$ versus time. Decreasing K_L results in

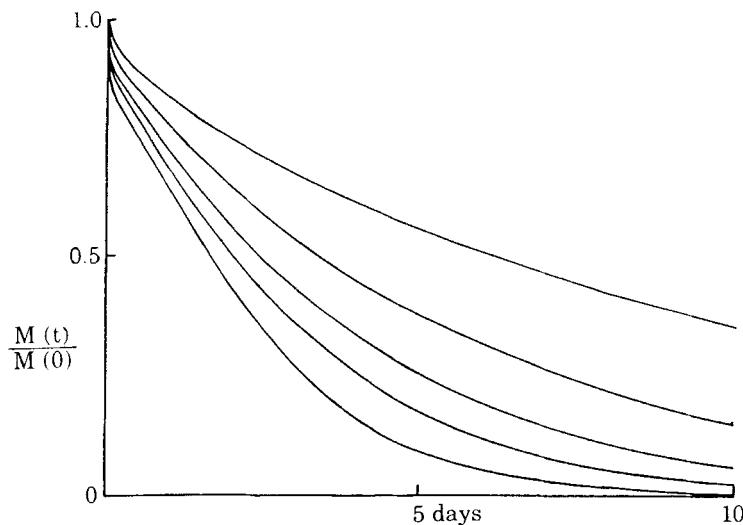


FIG. 5 Plots of $M_{\text{total}}(t)/M_{\text{total}}(0) = M(t)/M(0)$ versus time; effect of the diffusion constant D of the SVOC within the clay lenses. $D = 2, 5, 10, 20$, and $100 \times 10^{-8} \text{ m}^2/\text{s}$, from the top down; other parameters as in Table 1.

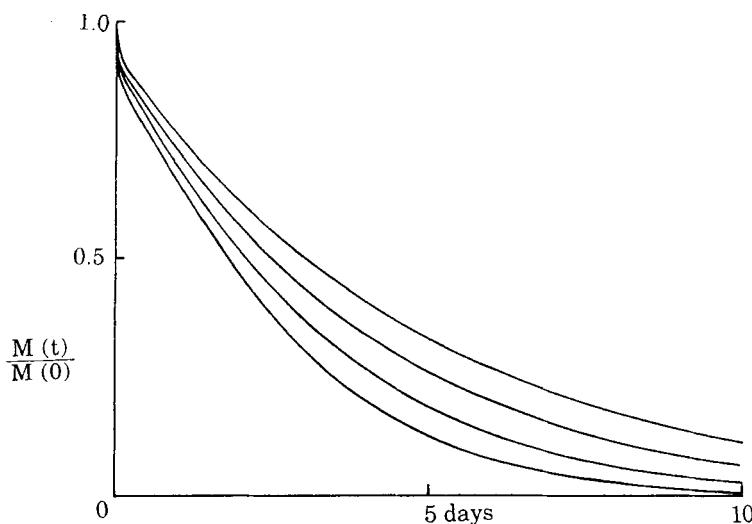


FIG. 6 Plots of $M(t)/M(0)$ versus time; effect of the thickness of the low-permeability porous clay lenses. Lens thickness = 5, 4, 3, and 2 cm, from the top down; other parameters as in Table 1.

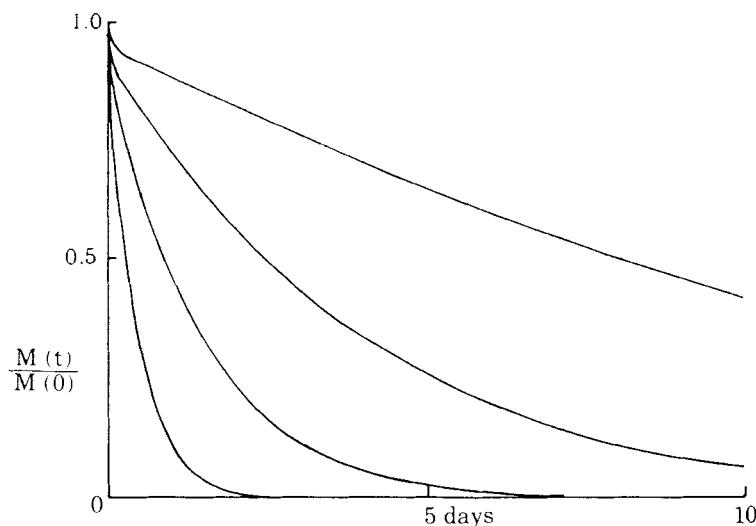


FIG. 7 Plots of $M(t)/M(0)$ versus time; effect of the linear sorption isotherm parameter K_L . $K_L = 0.005, 0.01, 0.02$, and 0.05 (dimensionless); other parameters as in Table 1.

quite large decreases in the rate of cleanup. Evidently in these runs equilibrium control is a major factor, a conclusion consistent with the finding that diffusion is not severely rate-limiting under the conditions used to make these runs. A point still to be explored is the extent to which variations in the functional form of the sorption isotherm (linear, Freundlich, BET, Langmuir, etc.) affects the shapes of the cleanup curves.

The effect on plots of $M_{\text{total}}(t)/M_{\text{total}}(0)$ versus time of the extent to which the contaminant has spread is explored in Fig. 8. As expected, the more widely the contaminant has spread, the more slowly does the cleanup take place, but the effect is not particularly large until the contaminated domain extends out beyond the region around the well which receives a substantial flux of steam. This is the case with the run which generated the top curve; the radius of the zone of contamination was 15 m and its depth was 10 m, so this run has a lot of contaminated soil out toward the periphery of the steam flow.

The effect of the rate of steam flow on plots of $M_{\text{total}}(t)/M_{\text{total}}(0)$ versus time is shown in Fig. 9. Steam flow rates are 1, 3, 5, 7, 10, and 15 kg/h from the top down. At the lower end of the range it is evident that the rate of removal of SVOC by the advecting steam is the controlling factor in the cleanup. For the runs with steam flow rates of 10 and 15 kg/h it is evident that equilibrium control and advective removal are no longer the

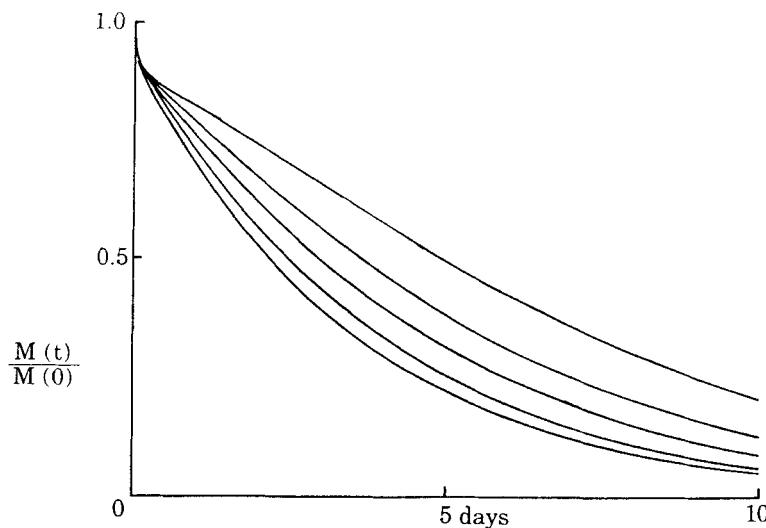


FIG. 8 Plots of $M(t)/M(0)$ versus time; effect of radius r_c and depth d_c to which a given mass of SVOC has spread. $(r_c, d_c, C_0) = (6, 3, 237.04), (8, 4, 100.00), (10, 5, 51.20), (12, 6, 29.63)$, and $(15 \text{ m}, 10 \text{ m}, 11.38 \text{ mg/kg})$ from the bottom up; other parameters as in Table 1.

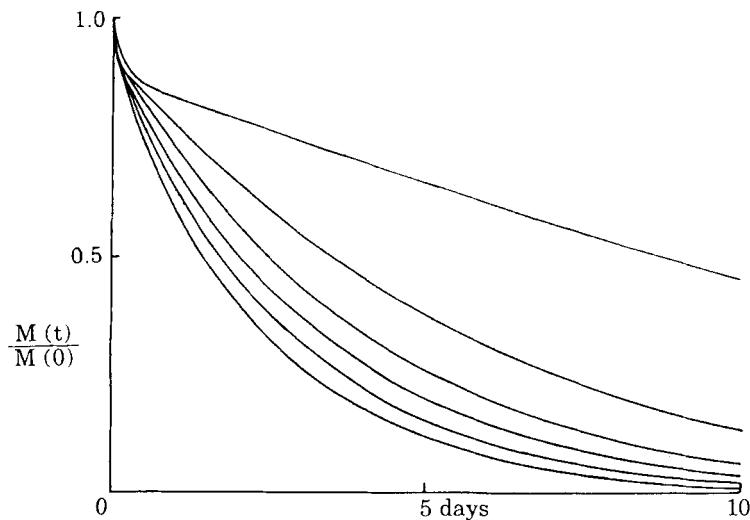


FIG. 9 Plots of $M(t)/M(0)$ versus time; effect of rate of steam flow. Rate of steam flow = 1, 3, 5, 7, 10, and 15 kg/h, from the top down. Other parameters as in Table 1.

bottleneck, and that the diffusion of SVOC from the clay lenses is rate-limiting for these runs. As with soil vapor extraction, operation at excessively high gas (or steam) flow rates does not yield significant increases in cleanup rates.

Figure 10 exhibits the effect of well depth on plots of $M_{\text{total}}(t)/M_{\text{total}}(0)$ versus time. The bottom of the contaminated domain is at a depth of 4 m in these runs, and the well depths are 2, 3, 4, and 8 m. Evidently wells should be screened underneath the bottom of the contaminated domain to avoid excessively prolonged cleanups. However, little appears to be gained by screening the well very far below the bottom of the contaminated domain.

The effect of the depth of the water table is seen in Fig. 11. Plots of $M_{\text{total}}(t)/M_{\text{total}}(0)$ versus time are shown for water table depths of 5, 6, 8, and 10 m. The well depth is 4 m, and the bottom of the contaminated domain is at a depth of 4 m. The runs do show some differences, but they are small. We conclude that the depth of the water table is not likely to be an important parameter in controlling cleanup rates by steam stripping, provided that the steam injection well and the contaminated domain do not extend down into the water table or the capillary fringe.

The effect of initial contaminant concentration on plots of $M_{\text{total}}(t)/M_{\text{total}}(0)$ versus time was explored as a check of the analysis and the

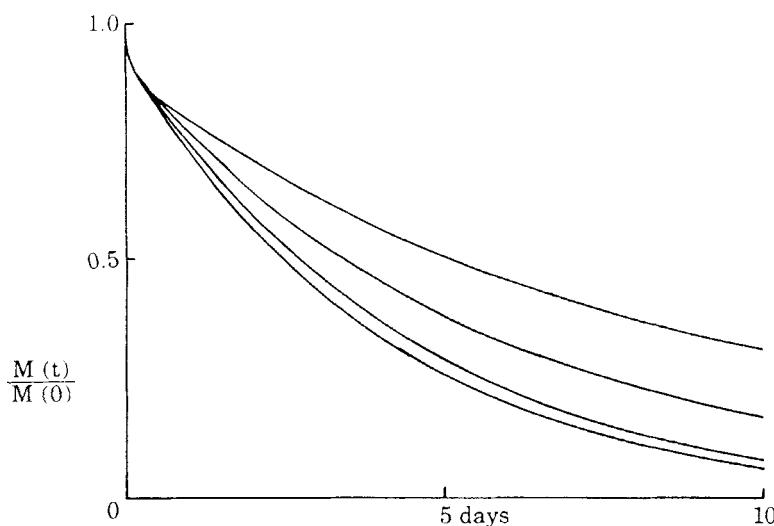


FIG. 10 Plots of $M(t)/M(0)$ versus time; effect of well depth. Well depth = 2, 3, 4 and 8 m, from the top down. Other parameters as in Table 1.

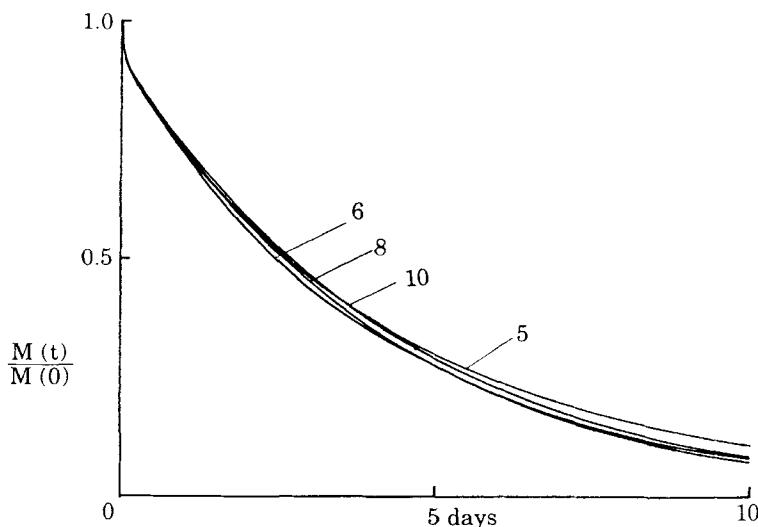


FIG. 11 Plots of $M(t)/M(0)$ versus time; effect of depth of water table. Depth of water table = 5, 6, 8 and 10 m, as indicated; depth of well = 4 m; other parameters as in Table 1.

coding. The equations of the model are all linear in the contaminant concentrations, so one expects that the size of the initial contaminant concentration will have no effect on plots of this type. This was found to be the case for runs made with initial SVOC concentrations of 50, 100, and 500 mg/kg.

The effect of the fraction f of the medium which consists of porous clay of low permeability on plots of $M_{\text{total}}(t)/M_{\text{total}}(0)$ versus time is presented in Fig. 12. From the top down, values of f are 0.5, 0.4, 0.25, and 0.1. We find that cleanup rates increase very markedly with decreasing fraction of low-permeability clay, f . This is consistent with our earlier conclusion that those runs having a steam flow rate less than 10 kg/h are mainly equilibrium/advection controlled. The steam flow rate in these runs was 5 kg/h. As the fraction of low permeability clay increases while the total initial contaminant SVOC concentration in the bulk medium is held constant, the concentration of SVOC in the clay lenses decreases correspondingly. This, combined with our assumption of a linear isotherm, results in decreasing SVOC vapor pressure and, therefore, decreased cleanup rate.

If, on the other hand, the rate of steam flow is sufficiently large that the cleanup process is diffusion controlled, one expects little or no effect

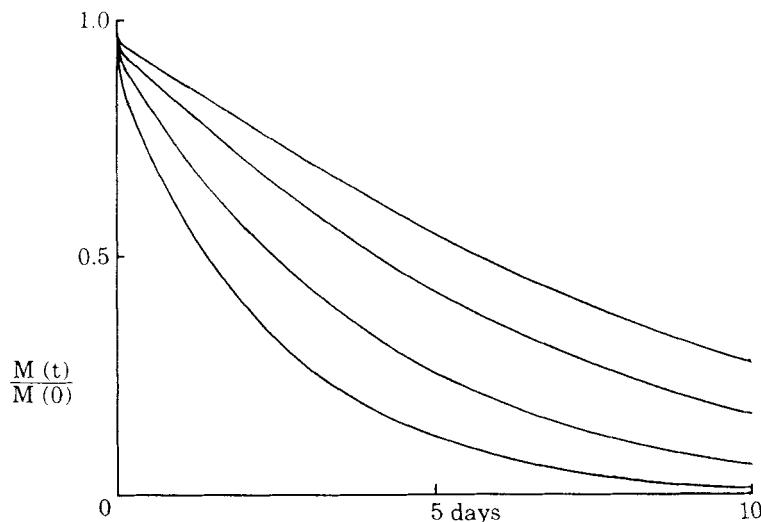


FIG. 12 Plots of $M(t)/M(0)$ versus time; effect of fraction f of soil which is low-permeability clay. $f = 0.1, 0.25, 0.4$, and 0.5 , from the bottom up; other parameters as in Table 1.

of f on the rate of cleanup. As f increases, the surface area of clay lenses from which SVOC can diffuse increases proportionally and the vapor pressure of the SVOC decreases inversely, resulting in virtually no net effect. The runs plotted in Fig. 13, for which the steam flow rate has been increased to 15 kg/h, show a very marked reduction in the size of the effect of f on remediation rates, in agreement with the above analysis.

Conclusions from Diffusion-Limited Steam-Stripping Model

A model for in-situ steam stripping of SVOCs has been developed which includes the effects of diffusion kinetics and which can readily be run on currently available microcomputers. Runs made with the model allow one to draw the following conclusions.

- 1) Remediation rates decrease with decreasing diffusion constant of the SVOC in the porous medium and with increasing thickness of low-permeability clay lenses in which SVOC is adsorbed.
- 2) Remediation rates increase very markedly with increasing linear soil/vapor partition coefficient of the SVOC.
- 3) Remediation rates decrease with increasing extent of spreading of a given quantity of contaminant. The effect is not large as long as all portions of the contaminated domain receive a substantial steam flux from

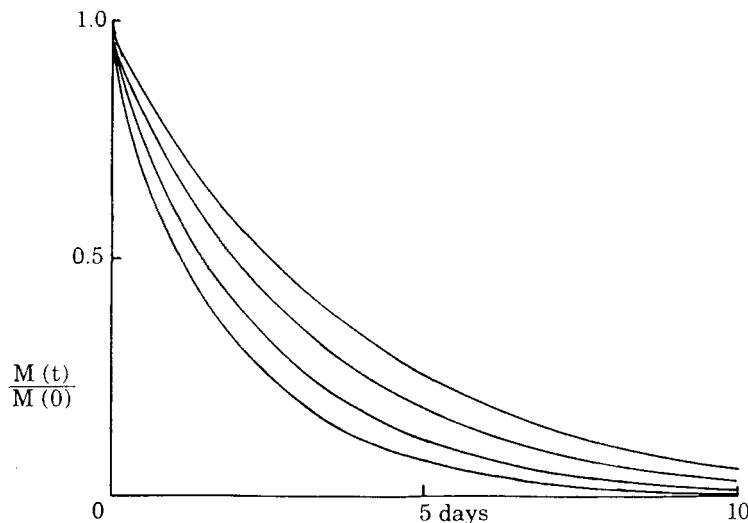


FIG. 13 Plots of $M(t)/M(0)$ versus time; effect of fraction f of soil which is low-permeability clay. $f = 0.1, 0.25, 0.4$, and 0.5 , from the bottom up; steam flow rate = 15 kg/h ; other parameters as in Table I.

the well, but cleanup rate decreases very markedly when contaminant migrates into regions which do not receive a good flow of steam.

4) At low steam flow rates equilibrium/advection is controlling, and increasing steam flow rate results in increased removal rate. At high steam flow rates diffusion/desorption processes are controlling, and increasing steam flow rate results in little increase in removal rate.

5) Well depth and water table depth have little effect on cleanup rates, provided that the steam is injected underneath the bottom of the contaminated domain of soil and provided that the water table and its capillary fringe lie below the bottom of the zone of contamination and below the point of steam injection.

6) Initial contaminant concentration has no effect on the rate of percent SVOC removal, due to the fact that a linear adsorption isotherm is used in the model.

7) If the steam-stripping well is being run at a relatively low flow rate, so that the system is equilibrium-controlled, then an increase in the fraction of the porous medium being stripped which is low-permeability clay results in a marked decrease in cleanup rate. If, on the other hand, high steam flow rates are being used, so that the system is diffusion/desorption

kinetics limited, the effect of an increase in the low-permeability clay fraction is substantially less.

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