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Soil Clean Up by *In-situ* Surfactant Flushing.
IV. A Two-Component Mathematical Model

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Abstract

A two-dimensional mathematical model is developed for *in-situ* surfactant flushing of contaminants from an aquifer by means of injection and recovery wells. The model tracks both surfactant concentration and contaminant concentration, and permits the use of the Langmuir, Freundlich, BET, or other adsorption isotherms for the contaminant-soil binding. The permeability of the aquifer is assumed to be constant and isotropic, and local equilibrium is assumed between adsorbed and solubilized contaminant.

INTRODUCTION

The remediation of groundwater and soils contaminated with organic chemicals tends to be costly and slow, and may itself have substantial environmental impact. The Superfund amendments have given strong impetus to the development of technologies which detoxify the contaminated material or drastically reduce the potential loading to the environment should a release occur. *In-situ* techniques, where they can be used, often have major advantages over other technologies in terms of cost, environmental impact, and destruction of the toxic contaminants. *In-situ* soil surfactant flushing and (*ex-situ*) soil surfactant washing show potential for the remediation of sites which are contaminated with organic compounds of low water solubility. These techniques are still in the developmental stage, but show promise for the removal of hydrophobic organics of low volatility, such as PCBs and polynuclear aromatic hydrocarbons, from contaminated soils and aquifers.

Techniques using surfactants remove hydrophobic organics of low solubility in water by virtue of the greatly enhanced solubilities of these compounds in solutions containing surfactants at concentrations above the critical micelle concentration (cmc). The hydrophobics are solubilized in the hydrophobic phases in the interiors of the micelles. Two early but excellent references on solubilization are McBain and Hutchinson's book (*1*) and a review article by Klevens (*2*).

Use of aqueous surfactants for remediation apparently dates back to work by the Texas Research Institute (*3*, *4*) on the recovery of gasoline by *in-situ* surfactant flushing. An extensive study was published by Ellis, Payne, and McNabb (*5*) in 1985; this reported on the use of nonionic surfactants for washing petroleum hydrocarbons, PCBs, and chlorinated phenols from soils. A small-scale lab study and field trial by Nash (*6*) yielded ambiguous results; good removals were obtained in the lab column work, but the field studies (on extremely greasy soil) were unsuccessful.

Castle (*7*) and his coworkers reported on a mobile soil-washing unit for use at Superfund sites in which surfactants, as well as other reagents, could be used. However, Tabak and Traver (*8*) and Traver et al. (*9*) reported some problems in the use of this unit with surfactants. Roy and Griffin (*10*) reviewed the decontamination of soils with surfactants and with chelating agents, and McDermott and his coworkers (*11*) reported on the removal of PCBs from soils by biodegradation and by surfactant extraction. Amdurer et al. (*12*) published information on a number of commercial surfactants, and they related surfactant properties to the possibility of improvements in surfactant flushing. Valsaraj and Thibodeaux (*13*) demonstrated a very useful correlation between octanol/water partition coefficients (available for a large number of compounds) and the micellar phase/water partition coefficients which arise in surfactant flushing and washing, relatively few of which have been determined. Kunze and Gee (*14*) recently investigated the use of Triton-X-100, as well as acids and CitriKleen, in removing PCBs from soil. They found improved removal of the PCBs, but use of a nonionic surfactant prevented easy separation of the surfactant solution from the contaminants for reuse. Dworkin et al. (*15*) and Khun and Piotek (*16*) indicated the possibilities of surfactant flushing for remediating soils contaminated at wood preserving sites.

Our group has done both lab-scale work and mathematical modeling of surfactant flushing and surfactant washing. Mathematical models include lab column surfactant flushing and flushing with an injection well and a recovery well, either unconfined in the aquifer or enclosed within a rectangular slurry wall to prevent escape of contaminated surfactant solution (*17*). These models follow the movement of contaminant only.

A second paper examined the nature of solubilization and developed a statistical mechanical method for estimating the partition coefficient of a hydrophobic contaminant between the aqueous phase and the micellar phase (*18*). Laboratory studies included the investigation of the solubilities of naphthalene, dichlorobenzene, and biphenyl in solutions having various concentrations of sodium dodecylsulfate (SDS), demonstration that SDS solutions are capable of extracting these model contaminants from sand and sand/clay mixtures with high efficiency, and demonstration that the contaminant-laden surfactant solutions could be reclaimed by gentle extraction with hexane or mineral oil. Valsaraj's correlation of octanol/water partition coefficients with micellar phase/water partition coefficients was also verified and extended to five more compounds (*19–21*).

More recently, we have presented data on the bench-scale removal of PCBs from high-clay soil by surfactant washing (*22*). Countercurrent liquid–liquid extraction was used for removal of nonvolatile contaminants from the spent surfactant solution, and thin film aeration was shown to remove volatiles. Models for batch-batch, batch-continuous flow, and countercurrent flow surfactant soil washing were developed.

Our previous model for *in-situ* surfactant flushing followed the movement of the contaminant only; it made the assumption that all of the fluid flowing through the zone of contamination between the injection and recovery wells was surfactant solution having the concentration of that in the injected solution. This approximation quite substantially reduces the memory and computer time requirements of the model. Currently available microcomputer hardware and software make this approximation much less necessary than it was previously, and in the present paper we describe a model in which both surfactant concentration and contaminant concentration are followed.

ANALYSIS

Development of the surfactant flushing model breaks down into four tasks. First is the analysis of the steady-state movement of the fluid in the zone of influence of the injection and recovery wells. Second is the description of the movement of the surfactant; how does the surfactant concentration distribution in the domain of interest evolve with time? Third is the investigation of the effect of the surfactant concentration in the aqueous phase on the adsorption isotherm of the contaminant on the porous medium (soil, sand, gravel). Fourth is the analysis of the movement of contaminant under the influence of the moving surfactant solution. In this model we make the local equilibrium assumption—that is, we assume that in any volume element the partitioning of contaminant between the stationary phase(s) and the surfactant solution is at equilibrium. We also assume that the aquifer is of essentially constant thickness, that the only recharge is through the injection and recovery wells, that the hydraulic permeability is constant and isotropic, and that a two-dimensional description is adequate. We shall use SI units throughout.

Calculation of the Flow Field

In an unbounded aquifer of the sort described above, the velocity v is given by the gradient of a solution to Laplace's equation (*17*),

$$v = \nabla W \tag{1}$$

where

$$W = \sum_{i=1}^{N} c_i \log_e [(x - a_i)^2 + (y - b_i)^2] + v_x^0 x + v_y^0 y \tag{2}$$

$$c_i = Q_i / 4\pi h \nu \tag{3}$$

and a_i, b_i = x–y coordinates of the ith well
v_x^0 = x-component of the background uniform flow
v_y^0 = y-component of the background uniform flow
Q_i = flow rate of the ith well (positive for injection, negative for recovery
h = aquifer thickness
ν = porosity of medium

The natural, unperturbed flow of the groundwater is assumed to be constant and uniform.

The steady-state velocity components of the fluid in the aquifer are then

$$v_x = \frac{1}{2\pi h \nu} \left[\sum_{i=1}^{N} \frac{Q_i (x - a_i)}{(x - a_i)^2 + (y - b_i)^2} \right] + v_x^0 \tag{4}$$

$$v_y = \frac{1}{2\pi h \nu} \left[\sum_{i=1}^{N} \frac{Q_i (x - a_i)}{(x - a_i)^2 + (y - b_i)^2} \right] + v_y^0 \tag{5}$$

If one is dealing with a domain which is bounded by slurry walls or other barriers, one must construct a solution to Laplace's equation, $\nabla^2 W = 0$, which satisfies the appropriate boundary conditions; see our earlier paper for details (*17*). The velocity components v_x and v_y are then calculated by finite difference techniques. For either type of domain, bounded or unbounded, streamlines for the fluid flow can then be calculated by numerical integration of Eqs. (6) and (7):

$$dx/dt = v_x(x,y) \tag{6}$$

$$dy/dt = v_y(x,y) \tag{7}$$

Dynamics of the Surfactant

Our second task is following the surfactant concentration distribution. This is done simply by carrying out surfactant mass balances on the volume elements into which the domain of interest is partitioned, noting that source and sink terms will be needed to model the effects of the injection and recovery wells. The notation for the velocities is as follows: through the top (T), bottom (B), left (L), and right (R) surfaces of the volume element, in plan view.

Let M_{ij} = mass of surfactant in the *ij*th volume element
S_{ij} = surfactant concentration in the *ij*th volume element
$S(u) = 0,\ u \leq 0;\ = 1,\ u > 0$

We have

$$S_{ij}\Delta x \Delta y v h = M_{ij} \tag{8}$$

A surfactant mass balance on the *ij*th volume element then gives

$$\begin{aligned}\frac{dS_{ij}}{dt} = \frac{1}{\Delta x \Delta y} [&\Delta y v_{ij}^L S(v^L) S_{i-1,j} + \Delta y v_{ij}^L S(-v^L) S_{ij} \\ &- \Delta y v_{ij}^R S(-v^R) S_{i+1,j} - \Delta y v_{ij}^R S(v^R) S_{ij} + \Delta x v_{ij}^B S(v^B) S_{i,j-1} \\ &+ \Delta x v_{ij}^B S(-v^B) S_{ij} - \Delta x v_{ij}^T S(-v^T) S_{i,j+1} \\ &- \Delta x v_{ij}^T S(v^T) S_{ij} + (Q_{ij}/vh) S^0]\end{aligned} \tag{9}$$

where the velocities are as mentioned above. S^0 is the surfactant concentration of the injected liquid, and Q_{ij} is the injection flow rate in the *ij*th volume element. Note that $Q_{ij} = 0$ unless there is an injection well in the ijth volume element. We ignore the surfactant concentrations in the volume elements which contain recovery wells.

Effect of Surfactant on Contaminant Adsorption Isotherm

Our third task is assessing the effect of surfactant concentration on the contaminant adsorption isotherm on the soil. In this section we focus on a single volume element, so we drop the subscripts i and j throughout the section. Let ΔV be the volume of the volume element.

m = mass of contaminant in ΔV
c^l = contaminant concentration in the surfactant solution, kg/m^3 of liquid
c^n = concentration of pure, neat contaminant (liquid or solid) in the soil, kg/m^3 of soil
c^a = concentration of sorbed contaminant in the soil, kg/m^3 of soil
c^w = contaminant concentration in the aqueous phase of the liquid, kg/m^3 of aqueous phase
c^m = contaminant concentration in the micellar phase of the liquid, kg/m^3 of micellar phase
νV = volume of liquid phase
$\beta \nu V$ = volume of micellar phase
$(1 - \alpha)\nu \Delta V$ = volume of aqueous phase

Note that β is slightly less than α; both are proportional to $(S - \text{cmc})$, where S is the surfactant concentration in the solution and cmc is the critical micelle concentration of the surfactant. Then

$$m = \Delta V[c^a + c^n + \beta \nu c^m + (1 - \alpha)\nu c^w] \tag{10}$$

We assume that the distribution law holds for the partitioning of contaminant between the aqueous phase and the micellar phase, so that

$$c^m = K_m c^w \tag{11}$$

Also, c^1 is related to c^m and c^w as follows:

$$\Delta V \nu c^1 = \Delta V[\beta \nu c^m + (1 - \alpha)\nu c^w] \tag{12}$$

Substitution of Eq. (11) into Eq. (12) and rearrangement then yield

$$\begin{aligned} c^w &= \frac{c^l}{\beta K_m + 1 - \alpha}, \qquad S \geq \text{cmc} \\ &= c^l, \qquad S < \text{cmc} \end{aligned} \tag{13}$$

Next, we need to calculate the concentration of adsorbed contaminant. We illustrate this for the Langmuir, Freundlich, and BET isotherms.

Langmuir:

$$c^a = c^a_{\max} \frac{c^w}{c^w + c_{1/2}} \tag{14}$$

We substitute Eq. (13) into Eq. (14) to obtain

$$c^a = c^a_{\max} \frac{c^l}{c^l + c_{1/2}(\beta K_m + 1 - \alpha)} \tag{15}$$

Evidently we still have a Langmuir isotherm, but $c_{1/2}$ is replaced by $c_{1/2}(\beta K_m + 1 - \alpha)$.

Freundlich:

$$c^a = a(c^w)^{1/n} \tag{16}$$

We substitute Eq. (13) into Eq. (16) to obtain

$$c^a = a\left[\frac{1}{\beta K_m + 1 - \alpha}\right]^{1/n} (c^w)^{1/n} \tag{17}$$

BET:

$$c^a = \frac{c^a_{\text{mono}} C x}{(1 - x)[1 + (C - 1)x]} \tag{18}$$

Here $x = c^w/c^w_{\text{sat}}$, c^a_{mono} is the contaminant concentration (kg/m^3) at monolayer coverage, C is the equilibrium constant for partitioning of contaminant between the first adsorbed layer and subsequent layers, and c^w_{sat} is the saturation concentration of the contaminant in water. See Adamson (*23*) for details on the BET and other adsorption isotherms.

Since Eq. (13) gives

$$c^l = (\beta K_m + 1 - \alpha)c^w$$

for all $c^w \leq c^w_{\text{sat}}$, we can write

$$x = c^l/c^l_{\text{sat}} \tag{19}$$

where

$$c^l_{\text{sat}} = (\beta K_m + 1 - \alpha)c^w_{\text{sat}} \tag{20}$$

This allows us to use Eq. (18) to calculate c^a for any given value of c^l, provided that we know the surfactant concentration.

The last three paragraphs relate the concentration of adsorbed contaminant, c^a, to the concentration of contaminant in the mobile liquid phase, c^l, for three adsorption isotherms; other isotherms could be handled in similar fashion. We now return to the general case.

A mass balance on the volume element gives

$$m = \Delta V(c^a + c^n + \nu c^l) \tag{21}$$

From the adsorption isotherm and our discussions above, we have

$$c^a = f(c^l) \tag{22}$$

where f is a known function. To calculate c^l given m, we proceed as follows. Assume $c^n = 0$ (that no neat contaminant is present). Then solve the equation

$$m = \Delta V[f(c^l) + \nu c^l] \tag{23}$$

by the method of bisection. (This method is relatively slow, but has the advantage of being extremely stable.) If the resulting value of c^l is $\leq c^l_{\text{sat}}$, this is the correct value of c^l and $c^n = 0$—i.e., there is no neat contaminant present in the soil. If the resulting value of c^l is $> c^l_{\text{sat}}$, then set $c^l = c^l_{\text{sat}}$ and, if desired, calculate c^n from

$$c^n = \frac{m}{\Delta V} - f(c^l_{\text{sat}}) - \nu c^l_{\text{sat}} \tag{24}$$

In either case, the outcome is a value for the contaminant concentration in the mobile liquid, given the contaminant mass in the volume element and the surfactant concentration in that volume element. We shall need this value of c^l (one for each volume element, actually) in the next section.

We still need to determine α and β in terms of observable quantities. β is the specific volume (m^3/m^3) of the micellar phase. This should be well approximated by

$$\beta = \beta'(S - \text{cmc}) \tag{25}$$

where

$$\beta' = 10^{-3}\overline{V}_{\text{tail}}/(\text{MW}) \tag{26}$$

Here

$$\overline{V}_{\text{tail}} = 32.67 + 16.23n_{\text{CH}_2} \tag{27}$$

is the molar volume of the surfactant hydrophobic tails, cm^3/mol, and n_{CH_2} is the number of CH_2 groups in the hydrophobic tail (11 for dodecylsulfate, for example). Equation (27) is obtained by means of a least-squares fit of the molar volumes for straight-chain hydrocarbons having 6 through 16 carbons and subtracting the molar volume of one of the terminal methyl groups (32.67 cm^3). MW is the molecular weight of the surfactant, g/mol.

Similarly, $1 - \alpha$ is the specific volume of the aqueous phase, m^3/m^3. This gives

$$\alpha = (S - \text{cmc})\overline{V}_{\text{surf}}10^{-3}/(\text{MW}) = \alpha'(S - \text{cmc}) \tag{28}$$

where $\overline{V}_{\text{surf}}$ is the molar volume of the surfactant, cm^3/mol. We can then rearrange Eq. (13) to give

$$c^l = [(\beta' K_m - \alpha')(S - \text{cmc}) + 1]c^w, \qquad S \geq \text{cmc} \tag{29}$$

$$= c^w, \qquad S < \text{cmc} \tag{30}$$

Also,

$$\beta K_m - \alpha = (\beta' K_m - \alpha')(S - \text{cmc}) \tag{31}$$

In all of our expressions, β, K_m, and α appear only as the combination $\beta K_m - \alpha$, so all that is really needed is the single surfactant constant K_s' ($= \beta' K_m - \alpha'$), the cmc, and the surfactant concentration S. K_s' is simply the slope K_s of a plot of c^l versus S for a saturated solution of contaminant in surfactant solutions of various concentrations S, divided by c_{sat}^w,

$$K_s' = K_s/c_{\text{sat}}^w \tag{32}$$

Therefore, the experimental parameters we need are the cmc, c_{sat}^w, and K_s, along with the isotherm parameters for adsorption of the contaminant onto the soil from pure water, and the various local values of the surfactant concentration, $S(x,y,t)$.

Movement of Contaminant by the Surfactant Solution

Our fourth and last task in modeling surfactant flushing is to develop equations which describe the movement of contaminant in the presence of the flowing surfactant solution. In the analysis of the contaminant's dynamics, we use the same velocity field as was used to distribute the surfactant in the first section. A mass balance on contaminant is carried out on the ijth volume element. Here c_{ij}^l is the contaminant concentration in the mobile liquid phase in the ijth volume element, m_{ij} is the contaminant mass in the ijth volume element, and the other notation is as before. The resulting equations are as follows.

$$\begin{aligned}\frac{dm_{ij}}{dt} = \nu h[&\Delta y v_{ij}^L S(v^L) c_{i-1,j}^l + \Delta y v_{ij}^L S(-v^L) c_{ij}^l \\ &- \Delta y v_{ij}^R S(-v^R) c_{i+1,j}^l - \Delta y v_{ij}^R S(v^R) c_{ij}^l \\ &+ \Delta x v_{ij}^B S(v^B) c_{i,j-1}^l + \Delta x v_{ij}^B S(-v^B) c_{ij}^l \\ &- \Delta x v_{ij}^T S(-v^T) c_{i,j+1}^l - \Delta x v_{ij}^T S(v^T) c_{ij}^l] \qquad (33)\end{aligned}$$

One starts with an initial distribution of contaminant, $\{m_{ij}(0)\}$, calculates the c_{ij}^l as described above, and then integrates Eqs. (9) (for the movement of surfactant) and (33) (for the movement of contaminant) forward in time. This process is repeated as many cycles as are needed to simulate the run. The velocities in an aquifer which is unconfined are given by Eqs. (4) and (5).

The progress of a surfactant flushing operation can easily be followed in either one of two ways. The first and most obvious is to plot the total mass of residual contaminant versus time:

$$m_{\text{total}}(t) = \sum_{i,j} m_{ij}(t) \qquad (34)$$

If a wider range is desired, one can plot $\log_{10}$ of the total mass.

The above approach gives no idea of the evolution of the spatial distribution of the contaminant. This distribution can be seen by calculating the quantities

$$J_{ij} = \text{Int}\,\{[\log_{10} n^9 m_{ij}(t)/m_{\max}(0)]/\log_{10} n\}, \qquad m_{ij} > m_{\max}n^{-9}$$
$$= 0, \qquad m_{ij} \le m_{\max}n^{-9} \tag{35}$$

These integers can be displayed in an array isomorphic to the domain of interest, and permit one to cover values of m_{ij} ranging from $m_{\max}$ down to $m_{\max}n^{-9}$.

RESULTS

This model was implemented in TurboBASIC and run on an MMG 386-SX microcomputer equipped with a math coprocessor and running at 16 MHz. The runs presented here typically required about 5–6 h of computer time each. All runs were made by using a surfactant concentration-dependent Langmuir adsorption isotherm for the contaminant, as discussed above. The parameters used are given in Table 1, except as indicated in the figures or their captions. Injection and recovery well flow rates, the coordinates of these wells, and the coordinates of the lower left and upper right corners of the rectangular domains of contamination are given for all runs in Table 2.

Figure 1 illustrates some of the effects resulting from variations in the placement of the injection and recovery wells. For the runs shown here (Runs 4, 5, and 8), such effects tend to be of importance both during the

TABLE 1
Default Values of the Parameters Used in the Model

Aquifer thickness	1 m
Dimensions of the domain of interest	30 × 24 m
Influent flow rate	0.02 m^3/s
Effluent flow rate	−0.02 m^3/s
Influent surfactant concentration	28.8 g/L
Surfactant critical micelle concentration	2.31 g/L
Unperturbed groundwater linear velocity	(0,0) m/s
Water-filled porosity of aquifer	0.3
Saturation concentration of contaminant in pure water	0.01 g/L
Slope of a plot of contaminant concentration versus surfactant concentration	0.0195
Langmuir parameter $C_{s\,\max}$	5 kg/m^3 of soil
Langmuir parameter $c_{1/2}$	0.1 g/L of solution
Initial contaminant concentration	0.1 kg/m^3 of soil
dt	50, 100 s

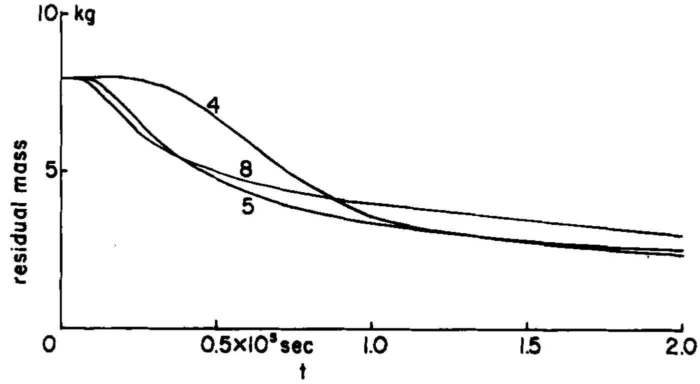

FIG. 1. Plot of residual contaminant mass versus time. Effect of well placement relative to the zone of contamination. Runs 4, 5, and 8 are plotted for the initial 2×10^5 s of the run. Parameters for this and subsequent figures are given in Tables 1 and 2.

initial portion of the runs and during the latter portions of the runs, in which exponential decays are observed. See Fig. 2. The slopes of these exponential decays depend quite markedly on the relationship between the locations of the wells and the contaminant distribution. The extent of this tailing is much greater than was observed with our earlier one-component model. Examination of the distribution of contaminant indicates that this

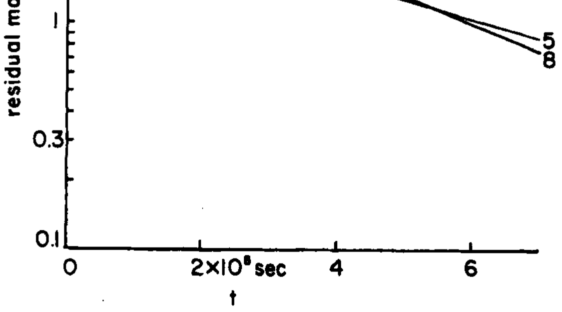

FIG. 2. Plot of residual contaminant mass versus time, logarithmic scale. Effect of well placement relative to the zone of contamination. Runs 4, 5, and 8 are plotted.

TABLE 2
Domain and Well Coordinates and Well Flow Rates for the Simulations

Run	Q_{in} (m^3/s)	Injection well coordinates	Q_{out} (m^3/s)	Recovery well coordinates	Contaminated zone coordinates
4	0.02	(4.5, 4.5)	0.02	(25.5, 19.5)	(10, 8), (20, 16)
5	0.02	(4.5, 11.5)	0.02	(25.5, 12.5)	(10, 8), (20, 16)
6	0.02	(4.5, 4.5)	0.024	(25.5, 19.5)	(10, 8), (20, 16)
7	0.02	(4.5, 4.5)	0.028	(25.5, 19.5)	(10, 8), (20, 16)
8	0.02	(14.5, 3.5)	0.02	(15.5, 20.5)	(10, 8), (20, 16)
9	0.02	(4.5, 11.5)	0.02	(25.5, 12.5)	(10, 10), (20, 14)
10	0.02	(4.5, 11.5)	0.022	(25.5, 12.5)	(10, 10), (20, 14)
11	0.02	(4.5, 11.5)	0.022	(25.5, 12.5)	(10, 8), (20, 16)
13	0.02	(4.5, 11.5)	0.02	(25.5, 12.5)	(10, 8), (20, 16)
14	0.02	(4.5, 11.5)	0.02	(25.5, 12.5)	(10, 8), (20, 16)

is associated with the flushing and dispersion of contaminant into volume elements in which the surfactant concentration remains relatively low throughout the run, so that the solution in these peripheral volume elements is unable to carry very much contaminant. Also, in these more outlying volume elements the linear velocity of the aqueous phase is much lower than it is in the volume elements which are located closer to a line drawn between the injection well and the recovery well, which exacerbates the difficulty.

Figure 3 shows the effect of overpumping the recovery well; here log plots of the residual contaminant mass versus time are made for Runs 4, 6, and 7 over a duration of 7 × 10^5 s (about 8 days). The latter portions of the curves for Runs 4 and 6 are virtually flat, indicating that the maximum contaminant removal which can be expected here is about 72% for Run 4 and 88% for Run 6. Run 7, however, shows rapid removal with an exponential approach to cleanup; in this run the recovery well is being overpumped by 40% (injection rate = 0.020 m^3/s; recovery rate = 0.028 m^3/s).

The dilution of surfactant solution as it moves out toward the periphery of the range of influence of the injection well-recovery well pair appears to present a major problem for *in-situ* surfactant flushing in unbounded aquifers. If, indeed, dispersive dilution of the injected surfactant solution occurs to a substantial extent (as these runs suggest), this would require extensive overpumping of the recovery well and would make necessary the reconcentration of rather diluted recovered surfactant before the surfactant solution could be recycled.

We note that the extent of this dispersion may be significantly overestimated by our mathematical model, inasmuch as the algorithm we are

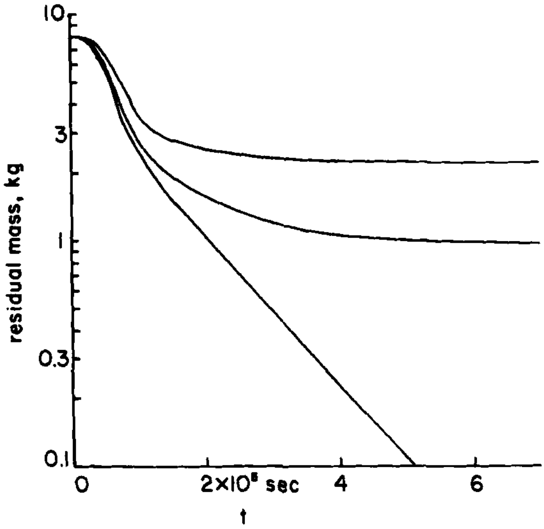

FIG. 3. Plot of residual contaminant mass versus time, logarithmic scale. Effect of overpumping the recovery well. Runs 4, 6, and 7 are plotted, top to bottom.

using for representing advection gives a substantial amount of numerical dispersion. It is hoped to get around this difficulty in a future model by the use of coordinates which follow the streamlines and equipotentials. This would eliminate entirely the transverse dispersion. The effects of longitudinal numerical and physical dispersion are much less troublesome than those of transverse and physical dispersion, since the former merely result in transport of solutes along the streamlines, rather than out into more peripheral domains.

One could get around the difficulty of surfactant dispersion and dilution by surrounding the domain of interest with a slurry wall, so that it is hydrologically isolated from the rest of the aquifer. In such a scenario the entire domain of interest is filled with surfactant solution, so that this problem of excessive dilution by dispersion does not arise. Installation of such a slurry wall barrier would, however, add substantially to the complexity and cost of *in-situ* surfactant flushing.

Tailing of the cleanup seems to be reduced significantly if the contaminant is present only in a region that is fairly close to a line between the injection well and the recovery well, as shown by a comparison of Runs 9 and 5 in Fig. 4. Apparently dispersive losses from the contaminated region in Runs 9 are relatively minor, due to the rapid flow and high surfactant concentration of the aqueous phase in this domain. The recovery well is

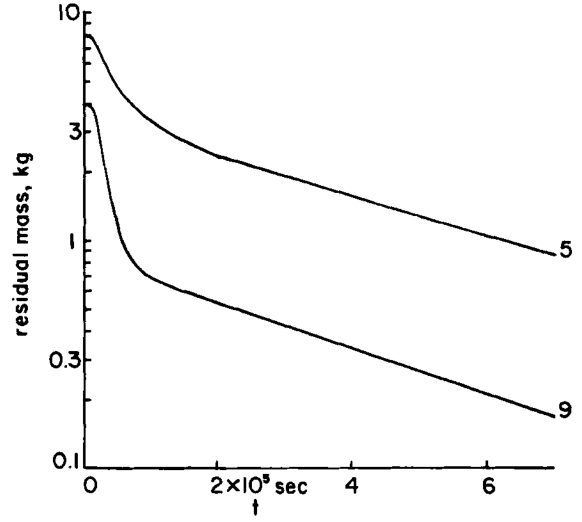

FIG. 4. Plot of residual contaminant mass versus time, logarithmic scale. Effect of contaminant spatial distribution relative to the line between the wells. The recovery wells in these runs are not overpumped. Runs 5 and 9 are plotted.

being pumped at the same rate as the injection well in both these runs. Note that the slopes of the exponential tails on these logarithmic plots are virtually identical.

In Fig. 5 we make a second comparison of the dependence of cleanup rate on location of the contaminated region with respect to the injection and recovery wells; the contaminated zone is confined more closely to a line drawn between the two wells in Run 10 than it is in Run 11. In both runs the recovery well is overpumped by 10% (injection flow rate = 0.02 m^3/s; recovery well flow rate = 0.022 m^3/s). Removals are quite a bit more rapid than those of Fig. 4, and, as in Fig. 4, cleanup is fastest for contaminant distributions which lie fairly near the axis between the wells.

Figure 6, Runs 5 and 13, shows the effect of the Langmuir parameter $c_{1/2}$ on the removal rate. The larger the value of $c_{1/2}$, the weaker the adsorptive binding. As expected, initial removal rates are more rapid the larger the value of $c_{1/2}$, but the slopes of the exponential tails on these log plots are virtually identical. In these three runs the flow rates of the injection well and the recovery well are identical (0.02 m^3/s).

In conclusion, we note that our modeling results suggest that dispersive dilution of the surfactant solution may be a serious problem in the surfactant flushing of unbounded aquifers under certain circumstances. This may be an artifact of the model, associated with numerical dispersion. However,

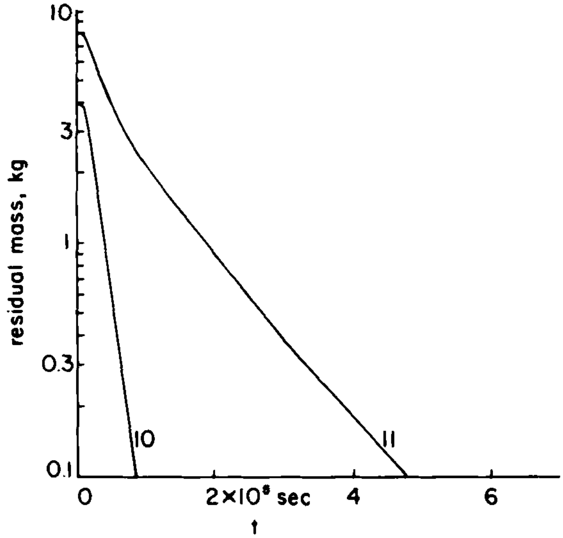

FIG. 5. Plot of residual contaminant mass versus time, logarithmic scale. Effect of contaminant distribution relative to the line between the wells. The recovery wells in these runs are overpumped by 10%. Runs 10 and 11 are plotted.

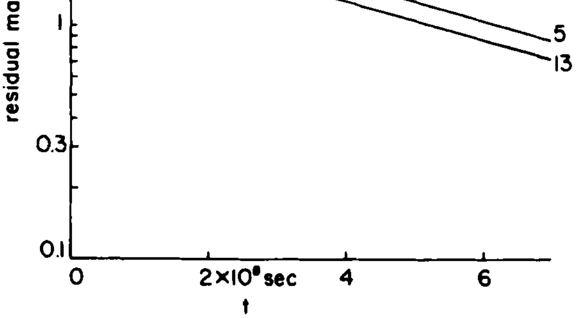

FIG. 6. Plot of residual contaminant mess versus time, logarithmic scale. Effect of Langmuir adsorption isotherm parameter $c_{1/2}$ on clean-up rate. $c_{1/2}$ = 0.02, 0.1, and 0.5 kg/m^3. The recovery wells in these runs are not overpumped. Runs 5, 13, and 14 are plotted.

if it is a real effect, it can be controlled either by the use of impervious slurry walls to confine the surfactant solution or by overpumping the recovery well(s). Unfortunately, both of these would add rather substantially to the cost of the technology, inasmuch as installation of slurry walls is not cheap nor is the concentration for recycle of large volumes of excessively dilute surfactant solution.

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