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Soil Clean Up by *in-situ* Surfactant Flushing. I. Mathematical Modeling

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Abstract

Mathematical models for the *in-situ* surfactant flushing of hydrophobic organic compounds from soil and aquifers and for the flushing of samples in laboratory columns are described, and numerical results obtained with the models are presented.

INTRODUCTION

The contamination of ground water with organic chemicals from underground storage tanks, from spills, and from waste disposal has become a major problem in the United States. Remediation is costly and slow, may not result in permanent solution of the problem, and may itself have substantial environmental impact. The development of cheaper, more efficient methods of soil and ground water clean up would result in significant savings, reduced environmental impact, and more rapid clean up. The National Priority List developed by EPA currently contains over 1200 sites, and clean-up cost estimates currently run in excess of $10 million per site.

In the past, remedial efforts have focused mainly on containment of contaminated materials and/or removal and off-site disposal in approved hazardous waste facilities. In either case, containment has typically been the solution, and the only reduction in toxic properties of these materials occurs through natural degradation processes. The recent Superfund amendments mandate that, where possible, remedial technologies be employed which detoxify the contaminated material or reduce the potential loading to the environment should a release occur. *In-situ* approaches, which manage the contaminated material in place, are attractive for several reasons, not the least of which is the much lower cost typically associated with *in-situ* methods where they are appropriate. Two *in-situ* methods shown to be effective in certain site-specific applications are *in-situ* biogradation of hydrocarbons (*2*), and *in-situ* soil vapor stripping (*1*, *3*, *5*, *7*, *21–24*). The general area of *in-situ* remediation has been reviewed by Clarke and Mutch (*4*).

Ellis, Payne, and McNabb (*6*) investigated the clean up of soils contaminated with nonvolatile organics by means of surfactant flushing; they described the use of aqueous nonionic surfactants for flushing PCBs, chlorinated phenols, and petroleum hydrocarbons from soils. They found removal efficiencies of over 90% with surfactant solutions containing 1.5% surfactants, and noted that these removals were orders of magnitude greater than those obtained by flushing with water alone. These workers used a 1:1 blend of two nonionic surfactants, and found that total surfactant concentrations below 0.5% resulted in very little clean up, while there was no significant further enhancement of clean up at surfactant concentrations above 1.5%.

These workers also carried out treatability studies of the aqueous surfactant-contaminant solutions resulting from surfactant flushing, and noted that a serious problem arose here. It was possible to remove the surfactant and the contaminant from the water, but they were unable to find a process that would allow recovery of the surfactant for reuse. Reuse of the surfactant, they noted, is essential for cost-effective application of the technique, and they suggested that future work be directed toward the problem of developing a surfactant flushing scheme which permitted recovery of the surfactant. They found that hydrolysis of the surfactant is effective as a primary treatment technqiue for removing both surfactant and hydrophobic organics from the leachate waters, but this destroys the surfactant, making recycling out of the question. Foam fractionation of these relatively concentrated surfactant solutions was not feasible, in that the bulk of the water being treated was removed in the foam. Adsorption techniques (activated carbon, clays, etc.) were also not feasible, again because of the high concentrations of surfactant present in the leachates. Ellis and his coworkers suggested that their limited testing indicated that ultrafiltration was a possibility. They regarded the development of a scheme in which the surfactant solution could be separated from the contaminants and recycled as a crucial next step in the development of the surfactant flushing technique.

A small-scale field trial of surfactant flushing was carried out by Nash (*13*) at Volk Air National Guard Base, Wisconsin. Soil heavily contaminated with oil and other hydrocarbons at a fire pit used for training purposes was treated both in laboratory columns and *in-situ* beneath small holes in the surface of the fire pit which were 1-ft deep. Nash reported that the laboratory studies were very encouraging, with extensive removal after the passage of 12 pore volumes of surfactant solution through the contaminated soil. The results of the *in-situ* work were not encouraging, however; several of the holes clogged during the course of the work, and the results were complicated by a heavy rain which may have washed material into the holes. Removal of hydrocarbons by *in-situ* surfactant flushing was not statistically significant. Nash suggested that the extremely high levels of oil and grease present in the soil may have led to severe channelling as well as the clogging of several of the test holes. The present author is of the opinion that this field test, involving soils containing in the range of 1000 to 13,500 mg/kg of oil and grease, and in which several of the holes clogged completely, may well be too stringent a test of surfactant flushing, and merely establishes the fact that surfactant solutions will not clean soils if they cannot penetrate them. Nash's lab column results are certainly encouraging.

The effectiveness of surfactant flushing is intimately related to the ability of these substances to solubilize water-insoluble compounds. The behavior of aqueous solutions of surfactants is discussed in a number of texts (e.g., *10*, *16*, *18*), and the salient features are as follows. Surfactant molecules or ions have a hydrophobic portion (often a long hydrocarbon chain) and a hydrophilic portion (an ionic or polar head, or a polyethoxyethylene chain). These species therefore tend to concentrate at polar–nonpolar interfaces (such as air–water), and, at sufficiently high concentrations, form aggregates (micelles) in aqueous solutions such that the polar or ionic portions of the molecules are presented to the aqueous phase, while the nonpolar hydrocarbon tails of the molecules are clustered together away from contact with the water molecules. These micelles may take a number of different shapes, although they are usually roughly spherical in dilute solutions. The interior of a micelle, consisting of the hydrocarbon tails of the surfactant species, is a nonpolar phase, and may dissolve appreciable quantities of nonpolar solutes which are virtually insoluble in normal aqueous solutions. This phenomenon is known as solubilization, and it plays a major role in secondary oil recovery, cleaning and laundering, micellar catalysis, etc. By means of solubilization, the amount of a hydrophobic solute which can be "dissolved" in water can be increased manyfold. Two early but useful references on solubilization are McBain and Hutchinson's book (*11*) and a review by Klevens (*9*). The thermodynamics of solubilization has been discussed by Hall and Pethica (*8*) and Mukerjee (*12*); Vold and Vold (*18*) have given an excellent review of the theories of micelle formation, which provide the foundation on which any approach to solubilization must rest.

The amount of solubilizate which is solubilized is approximately a linear function of the concentration of the surfactant, provided that this is above the critical micelle concentration (cmc, the surfactant concentration at which micelles first start to form). Below the cmc, solubilization does not occur, although the presence of a hydrophobic solute may reduce the cmc of surfactant in solution substantially.

We felt that the results obtained by Ellis et al. (*6*) and Nash's lab column results made a very strong case for pursuing the surfactant flushing technique further, to see if the crucial problem of treatability of the leachate and recycling of the surfactant could be overcome. These workers mostly used nonionic surfactants, which essentially rules out one potentially promising treatment technique, solvent extraction. Those solvents, which would be effective in extracting the hydrophobic contaminants, would also probably be effective in extracting the nonionic surfactants. We believed that the comparatively low cmc's of nonionic surfactants as compared to ionic surfactants was an advantage which might well be outweighed by the extremely low solubilities of many ionic surfactants in nonpolar organic solvents, which would make treatment by solvent extraction a possibility. Also, if the process were found to be feasible, a mathematical model to simulate it would be necessary for assisting in estimating clean-up times and costs and in designing field-scale surfactant flushing procedures.

In this paper we develop a mathematical model for simulating field-scale surfactant flushing. In subsequent papers we shall present data on the solubilization of three prototype contaminants (*p*-dichlorobenzene, naphthalene, and biphenyl) in solutions of sodium dodecylsulfate, a cheap, readily available, relatively nontoxic ionic surfactant. This is followed by data on the solvent extraction of the three prototype contaminants from the loaded surfactant solutions into hexane and mineral oil. Then some data on the leaching of these compounds from soil in lab-scale columns are given.

CALCULATION OF FLOW FIELDS

We first calculate the velocity field resulting from an array of injection and recovery wells in an aquifer in which the natural unperturbed flow of water is of constant direction and magnitude. We calculate the velocity potential W, which is related to the flow velocity by

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

where

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

is readily shown to be a solution of Laplace's equation in two dimensions. We restrict ourselves to two-dimensional flow in an aquifer of constant thickness and without recharge except for the injection and recovery wells. The constants c_i are related to the flow rates of the wells as follows. Let v_i be the velocity field associated wtih the ith well. Then

$$v_{ix} = \frac{c_i \cdot 2(x - a_i)}{(x - a_i)^2 + (y - b_i)^2} \tag{3}$$

$$v_{iy} = \frac{c_i \cdot 2(y - b_i)}{(x - a_i)^2 + (y - b_i)^2} \tag{4}$$

and the radial velocity is given by

$$v_r = (v_{ix}^2 + v_{iy}^2)^{1/2} = 2\frac{c_i}{r} \tag{5}$$

where

$$r = [(x - a_i)^2 + (y - b_i)^2]^{1/2}$$

The volumetric flow rate of the well is then given by

$$Q_i = \int_0^{2\pi} \nu h v_r r d\theta = 2\pi h \nu \frac{2c_i}{r} r = 4\pi h \nu c_i \tag{6}$$

so

$$c_i = Q_i/(4\pi h\nu) \tag{7}$$

where h = thickness of aquifer
ν = porosity of aquifer

The velocity components of the flow field are then given by

$$\mathrm{v}_x = \frac{1}{2\pi h\nu}\left[\sum_{i=1}^{N} \frac{Q_i(x - a_i)}{(x - a_i)^2 + (y - b_i)^2}\right] + v_x^0 \tag{8}$$

$$\mathrm{v}_y = \frac{1}{2\pi h\nu}\left[\sum_{i=1}^{N} \frac{Q_i(y - b_i)}{(x - a_i)^2 + (y - b_i)^2}\right] + v_y^0 \tag{9}$$

Here Q_i is positive for injection wells and negative for recovery wells. The natural, unperturbed flow of the groundwater is assumed to be constant and uniform, with velocity components v_{x0} and v_{y0}.

The above results are suitable for use when the region to be flushed is not bounded by any impermeable barriers. One of the concerns in connection with the surfactant flushing technique, however, is the possibility that surfactant-solubilized toxics may escape capture by a recovery well and be widely disseminated through the aquifer. This could be avoided by enclosing the zone of contamination within a slurry wall extending down to the aquitard beneath the contaminated acquifer. We therefore next address the calculation of the velocity field of an array of injection and recovery wells in a domain surrounded by an impermeable boundary.

The velocity potential function W satisfies Laplace's equation, as before:

$$\nabla^2 W = 0 \tag{10}$$

We include the effects of the injection and recovery wells by writing

$$W = \sum_{l=1}^{N} \frac{Q_l}{4\pi h\nu} \log_e [(x - a_l)^2 + (y - b_l)^2] + U \tag{11}$$

$$= S + U$$

where the logarithmic terms generate the sources and sinks corresponding to the injection and recovery wells. The function S is obviously a solution to Laplace's equation. The function U is also a solution to Laplace's equation; it is to be constructed such that W satisfies the desired boundary conditions. Let us choose the domain $0 \leqslant x \leqslant a$; $0 \leqslant y \leqslant b$ as the region to be enclosed. Then

$$\frac{\partial w}{\partial x}(0,y) = 0 \tag{12}$$

$$\frac{\partial w}{\partial x}(a,y) = 0 \tag{13}$$

$$\frac{\partial w}{\partial y}(x,0) = 0 \tag{14}$$

$$\frac{\partial w}{\partial y}(x,b) = 0 \tag{15}$$

are the equations specifying the presence of an impermeable boundary around the region of interest.

We next represent Eq. (10) by a discrete mesh approximation,

$$0 = W_{i-1,j} + W_{i+1,j} + W_{i,j-1} + W_{i,j+1} - 4W_{ij}, \qquad \begin{array}{l} i = 2, 3, \ldots, n_{x-1} \\ j = 2, 3, \ldots, n_{y-1} \end{array} \tag{16}$$

Here we have assumed that $\Delta x = \Delta y$, and that

$$W_{ij} = W[(i - \tfrac{1}{2})\Delta x,(j - \tfrac{1}{2})\Delta y]$$

This rearranges to

$$W_{ij} = \tfrac{1}{4}(W_{i-1,j} + W_{i+1,j} + W_{i,j-1} + W_{i,j+1}) \tag{17}$$

which, since S is a solution to Laplace's equation, gives

$$U_{ij} = \tfrac{1}{4}(U_{i-1,j} + U_{i+1,j} + U_{i,j-1} + U_{i,j+1}) \tag{18}$$

for the interior points of the mesh.

We next examine the boundary of the domain. From Eq. (12) we have

$$0 = W_{z,j} + W_{1,j-1} + W_{1,j+1} - 3W_{ij}, \qquad i = 2, 3, \ldots, n_{y-1} \tag{19}$$

which yields

$$U_{ij} = \tfrac{1}{3}(U_{2j} + U_{1,j-1} + U_{1,j+1} + S_{zj} + S_{1,j-1} + S_{1,j+1} - 3S_{1j}),$$
$$j = 2, 3, \ldots, n_{y-1}$$

Here

$$S_{ij} = S[(i - \tfrac{1}{2})\Delta x, (j - \tfrac{1}{2})\Delta y]$$

where S is defined in Eq. (11).

In similar fashion, Eq. (13) yields

$$U_{nx,j} = \tfrac{1}{3}(U_{nx-1,j} + U_{nx,j-1} + U_{nm,j+1} + S_{nx-1,j} + S_{nx,j-1} + S_{nx,j+1} - 3S_{nx,j}),$$
$$j = 2, 3, \ldots, n_{y-1} \tag{21}$$

Equation (14) gives

$$U_{i1} = \tfrac{1}{3}(U_{i,2} + U_{i-1,1} + U_{i+1,1} + S_{i,2} + S_{i-1,1} + S_{i+1,1} - 3S_{i,1}),$$
$$i = 2, 3, \ldots, n_{x-1} \tag{22}$$

and Eq. (15) gives

$$U_{i,ny} = \tfrac{1}{3}(U_{i,ny-1} + U_{i-1,ny} + U_{i+1,ny} + S_{i,ny-1} + S_{i-1,ny} + S_{i+1,1} - 3S_{i,ny}),$$
$$i = 2, 3, \ldots, n_{x-1} \tag{23}$$

Analysis of the situation at the four corners of the domain yields

$$U_{11} = \tfrac{1}{2}(U_{12} + U_{21} + S_{12} + S_{21} - 2S_{11}) \tag{24}$$

$$U_{nx,1} = \tfrac{1}{2}(U_{nx,2} + U_{nx-1,1} + S_{nx,2} + S_{nx-1,1} - 2S_{nx,1}) \tag{25}$$

$$U_{1,ny} = \tfrac{1}{2}(U_{2,ny} + U_{1,ny-1} + S_{2,ny} + S_{1,ny-1} - 2S_{1,ny}) \tag{26}$$

$$U_{nx,ny} = \tfrac{1}{2}(U_{nx-1,ny} + U_{nx,ny-1} + S_{nx-1,ny} + S_{nx,ny-1} - 2S_{nx,ny}) \tag{27}$$

Equations (18) and (20)–(27) completely define the problem. We have $n_x \times n_y$ linear inhomogeneous equations in the $n_x \times n_y$ unknowns U_{ij}, and physically we have a completely specified problem; we therefore may expect a unique solution.

This system of equations is then solved by simple iteration, starting out with zero values for the U_{kl} on the right-hand sides of the equations, and then simply iterating the values calculated until convergence occurs. This method is fairly slow, but appears to be extremely stable. We have run it with an 80 × 80 grid on a Zenith 150 (a PC clone) and an MMG 286 (an AT clone) in TurboBASIC with an 8087 or 80287 math coprocessor, and overnight runs result in complete convergence. We used this approach earlier in calculating airflow velocity fields in the modeling of soil vapor stripping (*7, 22*); it is modified from a method described by Shaw (*17*).

The major purpose in calculating the velocity potential is to use it as input in the equations modeling the movement of solubilized contaminants. Plots of the streamlines are of interest in their own right, however, since these can be used to determine from what regions in the zone of contamination clean up is likely to be particularly slow, and should also prove useful in optimizing the location of the slurry wall and the siting of the recovery and injection wells. If accurate data on the movement of water in the aquifer are available, these plots may be of help in assessing the need for a slurry wall. One should note, however, that this model is simple (two-dimensional, with an aquifer of uniform thickness and isotropic permeability), and that available data on a site are often sparse and uncertain. These facts dictate that conclusions from these model calculations be drawn prudently and conservatively.

If one is dealing with an unbounded domain, the velocity components can be calculated from Eqs. (8) and (9), and trajectories traced out by integrating the equations

$$dx/dt = v_x(x,y) \tag{28}$$

$$dy/dt = v_y(x,y) \tag{29}$$

numerically. We used a standard predictor-corrector method for doing the numerical integration (*14*). In the course of carrying out the numerical integration, oen obtains the time required for an element of liquid to transit the trajectory being mapped out; this allows one to identify regions in the domain from which contaminant removal will be particularly slow.

The trajectories can be classified into four categories: (1) those which originate at an injection well and end at a recovery well, (2) those which start at the boundary of the domain and end at the boundary of the domain, (3) those which originate at an injection well and end at the boundary of the domain, and (4) those which originate at the boundary of the domain and end at a recovery well. The first two categories are desirable. The third describes flow in which surfactant solution and solubilized contaminant are lost into the aquifer, an extremely undesirable result. The fourth corresponds to wasted effort in the recovery and treatment of water which is free from surfactant and solubilized contaminant.

Streamlines can also be computed from Eqs. (28) and (29) if the velocity potential W has been computed numerically by the relaxation method described above. The velocity components are calculated by the following procedure. If x is in the range $[(i-1)\Delta x, i\Delta x]$ and y is in the range $[(j-1)\Delta y, j\Delta y]$, then one can expand $W(x,y)$ in a Taylor's series about the point (x_i, y_j).

$$W(x,y) = w_{ij} + \left(\frac{\partial W}{\partial x}\right)_{ij} \delta x + \left(\frac{\partial W}{\partial y}\right)_{ij} \delta y + \frac{1}{2}\left(\frac{\partial^2 W}{\partial x^2}\right)_{ij} (\delta x)^2 + \left(\frac{\partial^2 W}{\partial x \partial y}\right)_{ij} \delta x \delta y + \frac{1}{2}\left(\frac{\partial^2 W}{\partial y^2}\right)_{ij} (\delta y)^2 \tag{30}$$

Here

$$\delta x = x - (i - \tfrac{1}{2})\Delta x$$

$$\delta y = y - (j - \tfrac{1}{2})\Delta y$$

Then

$$v_x = \frac{\partial W}{\partial x} = \left(\frac{\partial W}{\partial x}\right)_{ij} + \left(\frac{\partial^2 W}{\partial x^2}\right)_{ij} \delta x + \left(\frac{\partial^2 W}{\partial x \partial y}\right)_{ij} \delta y \tag{31}$$

and

$$v_y = \frac{\partial W}{\partial y} = \left(\frac{\partial W}{\partial y}\right)_{ij} + \left(\frac{\partial^2 W}{\partial y^2}\right)_{ij} \delta y + \left(\frac{\partial^2 W}{\partial x \partial y}\right)_{ij} \delta x \tag{32}$$

The derivatives needed in Eqs. (31) and (32) are calculated as follows:

$$\left(\frac{\partial W}{\partial x}\right)_{ij} = \frac{W_{i+1,j} - W_{i-1,j}}{2\delta x} \tag{33}$$

$$\left(\frac{\partial W}{\partial y}\right)_{ij} = \frac{W_{i,j+1} - W_{i,j-1}}{2\Delta y} \tag{34}$$

$$\left(\frac{\partial^2 W}{\partial x^2}\right)_{ij} = \frac{W_{i+1,j} - 2W_{ij} + W_{i-1,j}}{\Delta x^2} \tag{35}$$

$$\left(\frac{\partial^2 W}{\partial y^2}\right)_{ij} = \frac{W_{i,j+1} - 2W_{ij} + W_{i,j-1}}{\Delta y^2} \tag{36}$$

$$\left(\frac{\partial^2 W}{\partial x \partial y}\right)_{ij} = \frac{W_{i+1,j} - W_{i-1,j+1} - W_{i+1,j-1} + W_{i-1,j-1}}{4\Delta x\Delta y} \tag{37}$$

The streamlines of the fluid are then determined by calculating the velocity components from Eqs. (31) and (32) and numerical integration of Eqs. (28) and (29).

Streamlines calculated for an enclosed zone of contamination all originate at an injection well and terminate at a recovery well. The analysis assumes that the total rate of recovery is equal to the total rate of injection. This can be monitored by water level measurements in the zone of contamination. The absence of streamlines of the third type mentioned above makes the use of slurry wall isolation during surfactant flushing an intrinsically more secure procedure than surfactant flushing without a containing barrier.

MODELING OF SURFACTANT FLUSHING

Let us next turn to the use of the velocity fields constructed above for the development of two mathematical models for surfactant flushing. One of these is more realistic than the second, but requires more in the way of computer resources than are generally available in microcomputers. It is therefore hoped that the second, simpler model, which runs on AT clones, proves to be sufficiently accurate for practical work.

The development of the first model is as follows:

Let M = mass of surfactant per unit volume of soil
C = concentration of surfactant in the aqueous phase
m = mass of contaminant per unit volume of soil
c = concentration of contaminant solubilized and dissolved in the aqueous phase

Then the conservation equations for contaminant and surfactant are given by

$$\partial m/\partial t = \nabla(D\nabla c) - v\nabla(\bar{v}c) - f(m,c) \tag{38}$$

$$\partial M/\partial t = \nabla(D\nabla C) - v\nabla(\bar{v}C) - F(m,C) \tag{39}$$

The first terms on the right-hand side of Eqs. (38) and (39) model dispersion; D is a tensor which depends on the velocity. The second terms model advective transport. The third terms model loss of contaminant (f) and surfactant (F) by chemical and biological processes. These last are included for generality, and we shall assume that they are negligible on the time scale of interest.

We next assume that the contaminant is at local equilibrium with respect to its distribution between a stationary phase of some sort in the soil (adsorbed, nonaqueous liquid, or solid) and a mobile phase (solubilized in the surfactant micelles and actually dissolved in the water). The distribution function we assume for this is the following.

$$c(m,C) = [c_0 + S(C - \text{cmc})(C - \text{cmc})K_\text{D}]g(m) \tag{40}$$

$$g(m) = \frac{m}{m_{1/2} + m} \tag{41}$$

where $S(x) = 0, x \leq 0$
$= 1, x > 0$
cmc = surfactant critical micelle concentration

The constant K_D is the slope of a plot of the aqueous solubility of the neat contaminant in surfactant solution versus the surfactant concentration. These plots are typically linear at surfactant concentrations above the critical micelle concentration (*15*). The constant c_0 is the solubility of the contaminant in the absence of surfactant. The function $g(m)$ approaches unity for $m \gg m_{1/2}$ and approaches $m/m_{1/2}$ as m approaches zero. It is included to take into account any reduction in the ease of solubilization of contaminant at low soil contaminant concentrations, at which the residual contaminant may be strongly bound to the soil by adsorption.

Because of the complexity of the flow velocity v and because of the nonlinear coupling of Eqs. (38) and (39) through Eq. (40) even when the degradation terms f and F are dropped, the pair of partial differential equations (Eqs. 38 and 39) must be integrated forward in time numerically. It is reasonable to assume that $M = vC$ for anionic surfactants, in which case we can replace Eq. (39) by

$$\partial C/\partial t = \nabla(D\nabla C) - \nabla(\bar{v}C) \tag{42}$$

which is independent of m.

One then proceeds as follows. Equation (42) is integrated forward in time with a source term included wherever an injection well is located and with a sink wherever a recovery well is located. One starts with an initial surfactant concentration of zero throughout the domain. Equation (43) is then integrated one step forward

$$\partial m/\partial t = \nabla(D\nabla c) - v\nabla(\bar{v}c) \tag{43}$$

$$\bar{r} = \bar{x}\bar{i} + \bar{y}\bar{j}$$

in time; the initial distribution of contaminant, $m(\bar{r},0)$, is given, and this variable presumably has no source terms. This integration yields $m(\bar{r},\Delta t)$, from which, along with $C(\bar{r},\Delta t)$, the contaminant concentration $c(r,\Delta t)$ is calculated by Eq. (40). The integration process is then repeated as many times as necessary to model the surfactant flushing operation.

In actually doing the numerical integration, one would represent the two partial differential equations by two sets of ordinary differential equations defined on a discrete mesh of points (x_i, y_j, z_k) spanning the domain of interest. One could make use of the numerical dispersion intrinsic in finite difference approximations to the advection term to represent the physical dispersion terms $\nabla D\nabla C$ and $\nabla D\nabla c$. This can be adjusted by adjusting the mesh size and the dispersion inherent in the finite difference representation of the advection term; see Wilson (*19, 20*) for an application of this approach to gas chromatography column operation.

Even if one restricts the model to a two-dimensional representation, it exceeds the capabilities of most commonly available microcomputers.

We therefore turn to the construction of a model which retains the salient aspects of surfactant flushing but which is of somewhat reduced numerical complexity.

This second model assumes that the surfactant concentrations along all streamlines originating at an injection well are all equal to the surfactant concentration of the injected surfactant solution. Contaminated regions which are traversed by streamlines originating at an injection well will be cleaned up, sooner or later. Contaminated regions which lie outside the domain bathed by the injected surfactant solution will not be cleaned up. (We neglect the extremely slow clean up resulting from flushing hydrophobic compounds with water alone.) The first step in the use of this model is therefore the selections of an array of injection and recovery wells such that the domain of contamination is covered by streamlines originating at an injection well, and such that all streamlines originating at injection wells terminate at recovery wells. We then take

$$\partial m/\partial t = \nabla(D\nabla c) - \nu\nabla(\bar{v}c) \tag{43}$$

$$c = [c_0 + K_D(C - \mathrm{cmc})]m/(m + m_{1/2}) \tag{44}$$

where C is the concentration of surfactant in the injected fluid and all the other terms have been defined previously. Because of the numerical dispersion associated with discrete approximations of the advection term, we drop the dispersive term in Eq. (43) and use

$$\partial m/\partial t = -\nu\nabla(\bar{v}c) \tag{45}$$

as our starting point.

We approximate Eq. (45) by a set of ordinary differential equations.

$$\begin{aligned}\partial m_{ij}/\partial t = \nu\Delta x\Delta y h\{&(v_x)_{i-1/2,j}S[(v_x)s_{i-1/2,j}]c_{i-1,j}\}\\ &- (v_x)_{i+1/2,j}S[-(v_x)_{i+1/2,j}]c_{i+1,j} + (v_y)_{i,j-1/2}S[-(v_y)_{i,j-1/2}]c_{i,j-1}\\ &- (v_y)_{i,j+1/2}S[-(v_y)_{i,j+1/2}]c_{i,j+1} + [(v_x)_{i-1/2,j}S[-(v_x)_{i-1/2,j}]\\ &- (v_x)_{i+1/2,j}S[(v_x)_{i+1/2,j}] + (v_y)_{i,j-1/2}S[-(v_y)_{i,j-1/2}]\\ &- (v_y)_{i,j+1/2}S[(v_y)_{i,j+1/2}]]c_{ij}\end{aligned}$$

where $S(x) = 0, x \leqslant 0$
$\quad\quad\quad\;\, = 1, x \geqslant 0$
$\quad\; h$ = thickness of aquifer

and the velocities are given by formulas such as

$$(v_x)_{i-1/2,j} = (W_{i,j} - W_{i-1,j})/\Delta x \tag{47}$$

and

$$(v_y)_{i,j+1/2} = (W_{i,j+1} - W_{ij})/\Delta y \tag{48}$$

(Recall that the velocity potential values W_{kl} were calculated earlier.)

Equations (45) are then integrated forward in time by means of the predictor-corrector method. The overall progress of clean up is monitored by calculating the total mass of contaminant remaining in the domain of interest, given by

$$M_{tot}(t) = \sum_{i=1}^{n_x} \sum_{j=1}^{n_y} m_{ij}(t) \tag{49}$$

More detail can be obtained about the movement of contaminant by examining the masses of contamination in the various volume elements during the course of the run. This is most readily done by calculating the quantities

$$I_{ij} = \mathrm{Int}\,[9m_{ij}(t)/m_{ij}(0)] \tag{50}$$

and plotting these integers as an array of the same shape as the domain of interest. Here Int (u) is the largest integer less than u. The range of concentrations covered can be extended considerably by using a logarithmic scale, such as

$$J_{ij} = \mathrm{Int}\left[\frac{1}{\log_e 2} \quad \log_e\left(\frac{m_{ij}(0)}{m_{ij}(t)}\right)\right] \tag{51}$$

For this scale, as J_{ij} goes from 0 to 9, the contaminant concentration decreases to 1/512th of its initial value, with each integer increase in J_{ij} corresponding to a concentration decrease by a factor of ½. For an even wider range, one may use $\log_e 10$ instead of $\log_e 2$ in Eq. (51), which covers a concentration range down to 10^{-9}th of the initial concentration.

THEORETICAL RESULTS

In this section we first display a number of flow fields generated by an injection well and a recovery well in an unbounded aquifer of uniform thickness and constant porosity. Then we look at flow fields generated by an injection well and a recovery well enclosed by a slurry wall—an impermeable rectangular boundary. Lastly, we examine some surfactant flushing run simulations calculated from the second model described earlier. All these calculations were carried out on an MMG 286 microcomputer (an IBM AT clone) in TurboBASIC; a math coprocessor was used.

In the flow fields shown in Figs. 1 to 5, the aquifer is unbounded. The injection and recovery wells are 40 m apart, and both are located on the x-axis. The aquifer thickness is 1.0 m, and the porosity is 0.2.

The importance of having the recovery well fairly precisely downstream from the injection well is illustrated in Figs. 1 and 2. In Fig. 1 the unperturbed, natural flow (in the absence of the wells) has an x-component of velocity equal to 0.001 m/s, and a y-component equal to

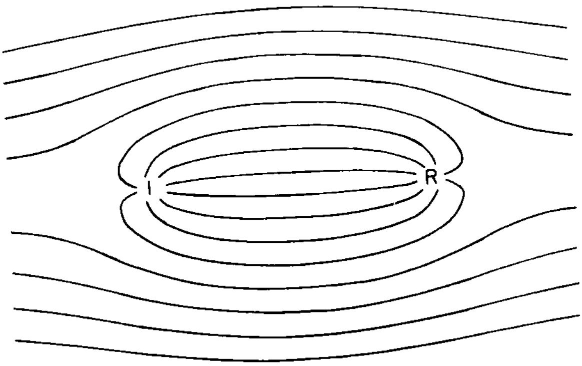


FIG. 1. Velocity field around an injection well and a recovery well in an unbounded aquifer, I = injection well, R = recovery well. The distance between the two wells is 40 m, the thickness of the aquifer is 1 m, and the porosity of the aquifer is 0.2. The unperturbed flow velocity in the x-direction (v_x) = 0.001 m/s; the unperturbed flow velocity in the y-direction (v_y) is 0. The injection flow rate is 0.01 m^3/s; the recovery flow rate is 0.01 m^3/s.

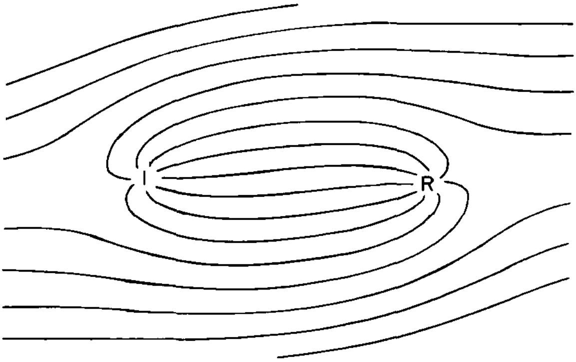


FIG. 2. Velocity field around an injection well and a recovery well in an unbounded aquifer. $v_x = 0.001$, $v_y = 0.0002$ m/s; all other parameters are as in Fig. 1.

zero. Both wells are being operated at a flow rate of 0.01 m^3/s. We see that all of the streamlines originating at the injection well (labeled *I*) terminate at the recovery well (*R*), indicating that the surfactant solution injected is completely recovered. (Note that here we are neglecting dispersive mixing.) In Fig. 2 the unperturbed x- and y-components of the flow velocity are 0.001 and 0.0002 m/s, and both wells are operated at a flow rate of 0.01 m^3/s. We see that two streamlines originating at the injection well do not terminate at the recovery well, but pass on to the right; evidently for this setup some of the injected surfactant solution is escaping into the aquifer.

One can overcome this problem of sensivity to proper alignment of the wells, but only at a price. The streamlines in Fig. 3 describe the motion of water when the unperturbed x- and y-components of the flow velocity are 0.001 and 0.0002 m/s (as in Fig. 2), the injection well is operating at 0.01 m^3/s, and the recovery well is pumping 0.0125 m^3/s. In this configuration all of the surfactant solution injected appears to be recovered, despite the fact that the recovery well is not directly downstream from the injection well. We see, however, three streamlines which do not originate at the injection well but which terminate at the recovery well. These describe the movement of surfactant-free groundwater which is pumped up the recovery well. This extra pumping is costly, and also results in undesirable dilution of the surfactant solution if it is to be recycled after treatment.

Increasing the flow rates through the injection and recovery wells broadens the area which is flushed by surfactant, as seen by comparing

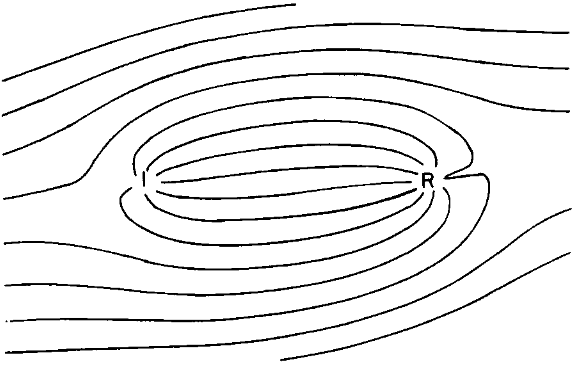


FIG. 3. Velocity field around an injection well and a recovery well in an unbounded aquifer. Recovery flow rate = 0.0125 m^3/s; $v_x = 0.001$, $v_y = 0.0002$ m/s; all other parameters are as in Fig. 1.

Fig. 4 (well flow rates = 0.02 m^3/s) with Fig. 1 (well flow rates = 0.01 m^3/s). A similar broadening of the domain of influence of the injection and recovery well pair is found if the unperturbed flow rate of the groundwater is reduced. This is seen by comparing Fig. 1 with Fig. 5. In Fig. 5 the unperturbed groundwater flow velocity components are zero; in Fig. 1 they are $v_x = 0.001$ m/s and $v_y = 0$. This suggests that one might improve the surfactant flow pattern in the contaminated zone by the judicious

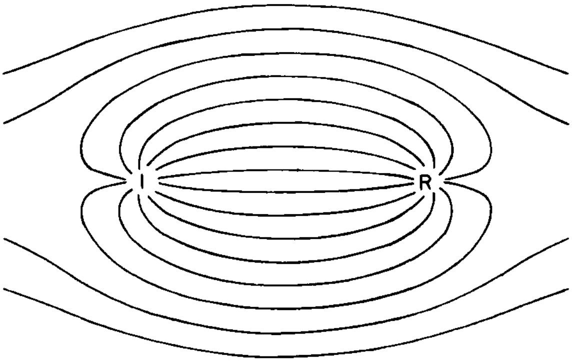


FIG. 4. Velocity field around an injection well and a recovery well in an unbounded aquifer. Injection flow rate = 0.02, recovery flow rate = 0.02 m^3/s; all other parameters are as in Fig. 1.

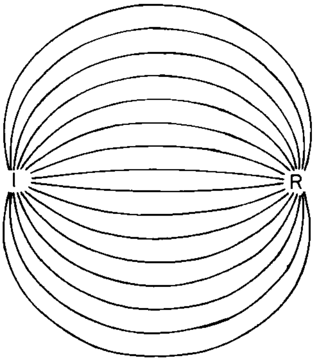


FIG. 5. Velocity field around an injection well and a recovery well in an unbounded aquifer. $v_x = 0$ m/s, $v_y = 0$ m/s; all other parameters are as in Fig. 1.

placement of a slurry wall or other barrier to reduce the natural flow velocity of groundwater in and near the domain of contamination.

A major concern with the surfactant flushing technique is the possibility of pollutant-laden surfactant solution escaping capture by the recovery well(s) and moving off the site. This could result from either improper design of the operation or failure of the pump on the recovery well. One possible technique for reducing the probability of contaminant escape is to place an impermeable barrier (a slurry wall) around the zone of contamination and extending down to the acquitard. Flow fields for an injection well and a recovery well operating at the same flow rates are shown in Figs. 6 and 7. In Fig. 6 the domain being flushed is a 60 × 60 m square, with the well located 5 m in from the middle of opposite sides. (Note that these drawings are somewhat distorted by the differences in the horizontal and vertical scales of the computer monitor.) The streamline pattern indicates fairly complete coverage of the domain, with relatively small regions of stagnation in the corners.

The wells are located in diagonally opposite corners of a 60 × 60 m domain in Fig. 7; the wells are 5 m in from each of the nearby sides. This configuration appears to leave two regions of stagnation in the two corners not containing wells. Qualitatively, the amount of soil being poorly flushed appears to be somewhat larger than is the case in Fig. 6. The numerical relaxation method described earlier was used to generate the velocity potentials from which the streamlines in these two figures were calculated.

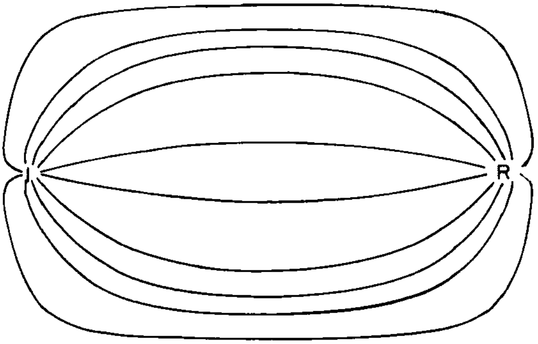


FIG. 6. Velocity field around an injection well and a recovery well within a domain surrounded by an impermeable rectangular barrier. The domain is 60 × 60 m in size; the injection well is located at (5,30), and the recovery well is located at (55,30). Both wells are operated at the same flow rate. Note that the scale factors are different for the horizontal and vertical axes.

Figures 8 and 9 are plots of the total mass of contaminant in the domain of interest as a function of the flushing duration. In both cases the domain of interest is 30 × 20 m in area and is surrounded by a slurry wall; the aquifer is 1 m thick, its porosity is 0.2, and the zone of contamination is a 10 × 10 m region located as shown on the insets to the figures. In Fig. 8 the two well are located near opposite corners of the rectangular domain of interest; in Fig. 9 the wells are located near the

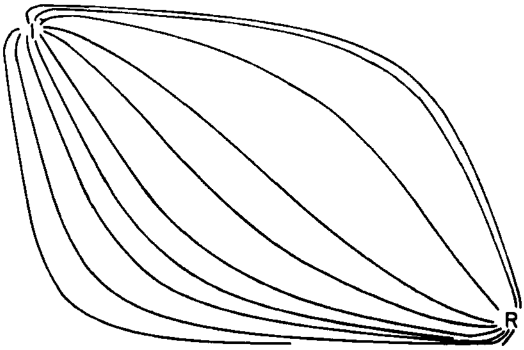


FIG. 7. Velocity field around an injection well and a recovery well within a domain surrounded by an impermeable rectangular barrier. The injection well is located at (5,5), and the recovery well is located at (55,55); all other parameters are as in Fig. 6.

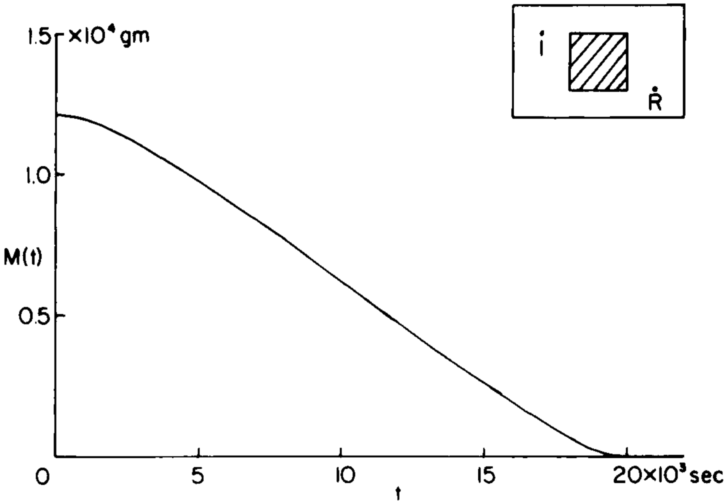


FIG. 8. Plot of total mass of contaminant versus time during a surfactant flushing operation. The model parameters are given in Table 1, and the geometry of the system is shown in the inset to the figure.

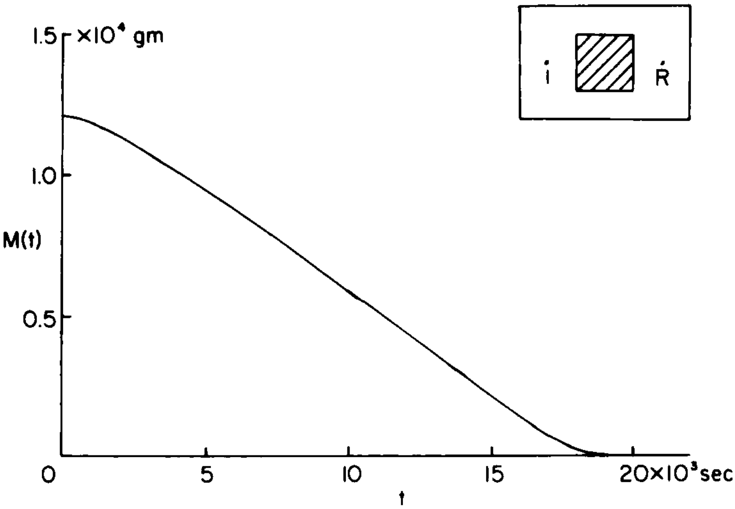


FIG. 9. Plot of total mass of contaminant versus time during a surfactant flushing operation. The model parameters are given in Table 1, and the positions of the wells and the contaminant are shown in the inset to the figure.

middles of the 20-m sides of the rectangle, as shown on the insets. The parameters for these runs are given in Table 1.

For both runs, removal appears to be rather linear with time after a fairly short period during which the slug of contaminant is being flushed over to the recovery well. This is in marked contrast to removal by soil vapor stripping, in which tailing can be quite substantial. One can obtain

TABLE 1
System Parameters Used for the Modeling of Surfactant Flushing

- Dimensions of domain of interest:
  - $x_{\min} = 0$
  - $x_{\max} = 30$ m
  - $y_{\min} = 0$
  - $y_{\max} = 20$ m
- Aquifer thickness = 1.0 m
- Aquifer voids fraction = 0.2
- Injection rate = 0.01 m^3/s
- Recovery rate = 0.01 m^3/s
- Location of zone of contamination:
  - $x_{\min} = 10$ m
  - $x_{\max} = 20$ m
  - $y_{\min} = 5$ m
  - $y_{\max} = 15$ m
- Location of injection and recovery wells:
  - Fig. 8:
    - Injection well:
      - $x = 5$ m
      - $y = 5$ m
    - Recovery well:
      - $x = 25$ m
      - $y = 15$ m
  - Fig. 9:
    - Injection well:
      - $x = 5$ m
      - $y = 10$ m
    - Recovery well:
      - $x = 25$ m
      - $y = 10$ m
- Initial contaminant concentration = 100 g/m^3
- Contaminant isotherm parameters:
  - Contaminant solubility in pure water = 1 mg/L
  - K_D, mg/L of contaminant per mg/L of surfactant = 0.01
  - Surfactant critical micelle concentration = 2300 mg/L
  - Influent surfactant concentration = 5000 mg/L
  - $m^{1/2}$, soil adsorption parameter = 10 g/m^3

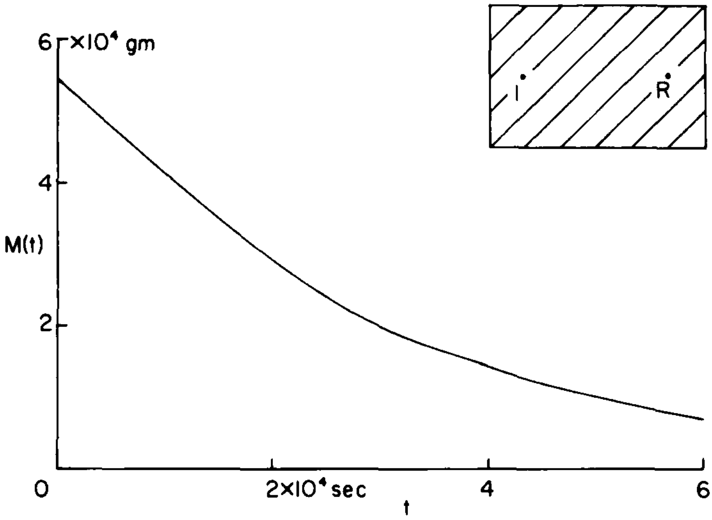


FIG. 10. Plot of total mass of contaminant versus time during a surfactant flushing operation. The model parameters are given in Table 1, and the positions of the wells and the contaminant are shown in the inset to the figure.

tailing with surfactant flushing, too, if one has a portion of the contaminated region in areas in the zone of interest through which movement of surfactant is quite slow, such as the corner of the rectangular regions enclosed by a barrier. This is shown by the run plotted in Fig. 10. The geometry of the setup is exactly as in Fig. 9, except that the zone of contamination fills the entire region which is enclosed within the slurry wall boundary. Note that the horizontal and vertical scales on this figure are different from those used in Figs. 8 and 9. It is quite apparent that one would be well advised to design slurry wall barrier systems in such fashion that the corners of the enclosed domain did not contain contamination. As seen in Table 2, removal remains relatively rapid down to quite low total contamination mass for the runs shown in Figs. 8 and 9, indicating that a properly designed system should be able to achieve very high levels of removal in a reasonable period of time.

In assessing the capability of the surfactant flushing technique, we must note that the results presented above are based on a rather simple adsorption isotherm; if one has sites in the aquifer material which very strongly bind the contaminant, the results could be quite different. We

TABLE 2
Total Contaminant Mass at Various Times during the Surfactant Flushing Operation, Figs. 8 and 9

Time	Total mass (g), Fig. 8	Total mass (g), Fig. 9
0×10^3	12,100	12,100
1	11,940	11,893
2	11,548	11,421
3	11,031	10,843
4	10,433	10,204
5	9,781.6	9,522.8
6	9,094.2	8,812.6
7	8,383.1	8,085.0
8	7,656.7	7,349.0
9	6,921.5	6,610.4
10	6,182.4	5,871.2
11	5,444.4	5,132.0
12	4,713.1	4,392.6
13	3,974.6	3,653.0
14	3,267.1	2,912.9
15	2,575.8	2,172.8
16	1,908.4	1,441.3
17	1,280.0	737.85
18	700.89	222.98
19	190.35	18.865
20	0.45962	0.10680
21	0.23947	0.0088053
22		0.0015778
23		0.0003721
24		0.0001010

therefore stress the importance of preliminary lab studies to determine the ability of the surfactant solution to move any particular contaminant through any particular aquifer material. The results of such studies should permit the assignment of parameters in the model which are at least qualitatively correct, and which should allow a determination of the suitability of the surfactant flushing technique in any particular application. This brings us to the next topic, which is the modeling of laboratory scale surfactant flushing.

MODELS OF LABORATORY SCALE SURFACTANT FLUSHING

In this section we first develop a model for batch surfactant flushing which may be used for either laboratory scale or batch field scale operations. In batch surfactant flushing, the contaminated material is flooded with surfactant solution and the contaminant is allowed to equilibrate between the soil/gravel/sand and the surfactant solution. The surfactant solution is then drained away, and the process is repeated until the desired reduction in contaminant level is achieved. In the field this could be carried out in suitably designed lined pits, with contaminated soil hauled to the pit, flushed, and then returned; this might be necessary if there is concern about possible mobilization of contaminant in the aquifer by *in-situ* treatment.

Let V = volume of material to be treated, m

ν = voids fraction

m = mass of contaminant in the material to be treated, g

m' = mass of contaminant in the material to be treated after flushing has taken place, g

c = contaminant concentration in the surfactant solution after equilibration, mg/L

C = surfactant concentration, mg/L

c_0 = solubility of contaminant in pure water, mg/L

K_D = slope of a plot of contaminant solubility versus surfactant concentration (above the cmc), both in mg/L

cmc = surfactant critical micelle concentration, mg/L

$m_{1/2}$ = adsorption parameter, g/m^3; small if adsorption is weak, large if adsorption is strong

We use the same adsorption isotherm for the contaminant as before,

$$c = [c_0 + K_D(C - \text{cmc})]\frac{m'}{m' + Vm_{1/2}} \tag{52}$$

A mass balance then gives

$$m' = m - \nu Vc \tag{53}$$

Let

$$A = \nu V[c_0 + K_D(C - \text{cmc})] \tag{54}$$

so

$$m = m' + \frac{Am'}{m' + m_{1/2}V} \tag{55}$$

This can be rearranged to give a quadratic equation in m', the desired solution of which is

$$m' = \frac{-(m_{1/2}V + A - m) + [(m_{1/2}V + A - m)^2 + 4mVm_{1/2}]^{1/2}}{2} \tag{56}$$

This can be solved recursively n times to determine the mass of contaminant left after n flushings.

A simple column would probably be a more common setup for laboratory scale experiments. This is modeled as follows.

Let L = column length, cm
r = column radius, cm
n = number of compartments into which the column is partitioned mathematically for analysis (number of theoretical plates)
m_i = mass of contaminant in the ith compartment
V = volume of one compartment = $\pi r^2 L/n$, cm^3
Q = surfactant flow rate, mL/s

The concentration of contaminant in the aqueous phase in the ith compartment is given by

$$c_i = [c_0 + K_D(C - \text{cmc})] \times 10^{-6} \frac{m_i}{m_i + m_{1/2}V \times 10^{-6}} \tag{57}$$

which is just our earlier isotherm modified for cgs units. Then

$$dm_i/dt = Q(c_{i-1} - c_i) \tag{58}$$

and

$$dm_1/dt = -Qc_1 \tag{59}$$

A computer program implementing this model was written and a number of runs were simulated. The common parameters used in these runs are given in Table 3. In Fig. 11 we see the effect of varying the number of theoretical transfer units used to model the column; as expected, we can use this number to model the effects of axial dispersion. A small number of theoretical transfer units corresponds to a large axial dispersion in the column.

Figure 12 shows the effects of the adsorption parameter $m_{1/2}$. A large value of this parameter produces the same sort of broadening of the

TABLE 3
Standard Parameters Used for the laboratory Column Model

Column length	20 cm
Column diameter	10 cm
Number of transfer units	10
Soil voids fraction	0.2
Soil density	1.6 g/mL
Initial contaminant concentration	100 mg/kg
Surfactant concentration	5000 mg/L
Critical micelle concentration	2300 mg/L
K_D parameter	0.1
$m_{1/2}$ parameter	50 g/m^3
Contaminant solubility in pure water	1 mg/L
Surfactant solution flow rate	1 mL/s
dt	1 s

elution front that is produced by high axial dispersion, but the plateau concentration before elution is nearing completion shows very marked changes as well, which are not observed as a result of axial dispersion. From the appearance of the plots in Fig. 11, one can in all probability construct columns such that the number of theoretical transfer units is at least greater than 5, at which point the dominant factor contributing to the width of the elution front is the adsorption parameter $m_{1/2}$.

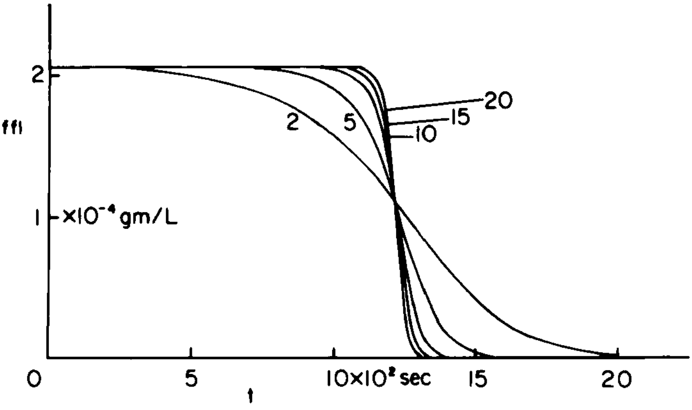


FIG. 11. Lab column surfactant flushing, plots of effluent concentration versus time. Effect of number of theoretical transfer units. $n = 2, 5, 10, 15$, and 20, as indicated; other parameters as given in Table 3.

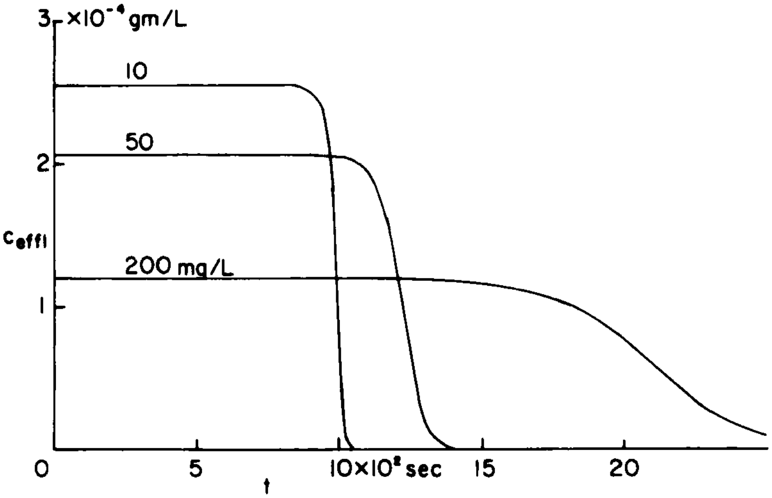
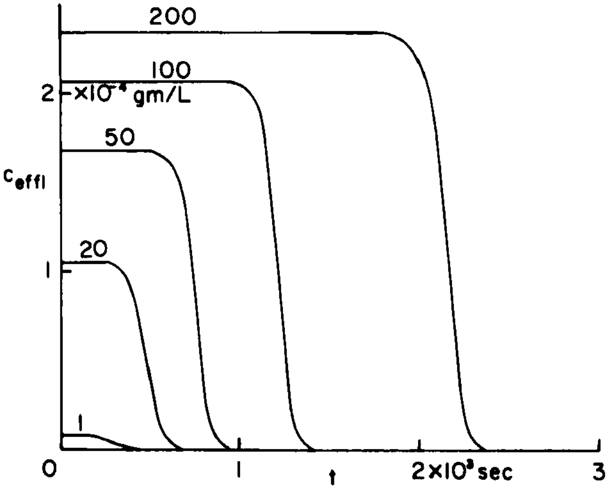


FIG. 12. Lab column surfactant flushing, plots of effluent concentration versus time. Effect of the value of the parameter $m_{1/2}$, $m_{1/2} = 10$, 50, and 200 g/m^3; other parameters as in Table 3.



13. Lab column surfactant flushing, plots of effluent concentration versus time. Effect of initial contaminant concentration. $m = 200$, 100, 50, 20, and 1 mg/kg; other parameters as in Table 3.

The effect of varying initial concentrations on the shapes of the elution curves is shown in Fig. 13. We see that both the height of the initial plateau concentration and its duration increase with increasing initial contaminant concentration. The ratio of front width to plateau duration is seen to decrease substantially with increasing initial contaminant concentration.

The isotherm parameters K_D, cmc, and c_0 can all be determined by measurements of the solubility of the contaminant in surfactant solutions of various concentrations. This leaves the parameter $m_{1/2}$ to be assigned by fitting theoretical elution curves to the experimental data. These parameters can then be used in the model of field surfactant flushing previously discussed.

Acknowledgments

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