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David J. Wilson[a]; José Miguel Rodríguez-Maroto[b]; César Gómez-Lahoz[b]
[a] DEPARTMENT OF CHEMISTRY, VANDERBILT UNIVERSITY, NASHVILLE, TENNESSEE [b] Departamento De IngenierÍA QuÍMica Facultad De Ciencias, Campus Universitario De Teatinos Universidad De MÁLaga, MÁLaga, Spain

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Electrokinetic Remediation. I. Modeling of Simple Systems

DAVID J. WILSON
DEPARTMENT OF CHEMISTRY
VANDERBILT UNIVERSITY
NASHVILLE, TENNESSEE 37235

JOSÉ MIGUEL RODRÍGUEZ-MAROTO
and CÉSAR GÓMEZ-LAHOZ
DEPARTAMENTO DE INGENIERÍA QUÍMICA
FACULTAD DE CIENCIAS
CAMPUS UNIVERSITARIO DE TEATINOS
UNIVERSIDAD DE MÁLAGA
29071 MÁLAGA, SPAIN

ABSTRACT

A one-dimensional model is developed for simulating the electrokinetic treatment of saturated porous media contaminated with an ionic salt. Simulations of simple, unenhanced electrokinetic treatment for the removal of a nonamphoteric salt such as cadmium sulfate exhibit a severe drop-off in electric current and in remediation rate after about 50–60% of the cation has been removed. Simulation of electrokinetic treatment in which the OH^- generated in the cathode compartment is partially neutralized by the addition of acid show rapid and complete removal of the cation. Partial neutralization of H^+ in the anode compartment by addition of base results in immobilization of the toxic metal as the solid hydroxide, although this should be a useful technique for the removal of arsenate and selenate.

INTRODUCTION

The removal of ionic contaminants (most commonly toxic metals) from water-saturated porous media by pump-and-treat methods is often limited by difficulties in the mobilization of metal ions which may be dispersed in porous structures of low permeability (such as clay lenses), adsorbed/

ion exchanged on clays or natural soil organic matter, or present as slightly soluble precipitates (such as hydroxides, hydrous oxides, or carbonates). The behavior of metals in soils has been summarized, for example, by McLean and Bledsoe (1) and by Freeze and Cherry (2).

One of the innovative technologies which shows some promise for addressing the problem of removing toxic ionic compounds from contaminated aquifers is electrokinetic remediation. The technique has been described in detail and critically reviewed by Acar and Alshawabkeh (3) and by Acar, Alshawabkeh, and Gale (4); see also Acar's shorter nonmathematical treatment of the subject (5). Cabrera-Guzman, Swartzbaugh, and Weisman (6) assessed the "state of the art" of electrokinetic remediation for EPA; they noted that the technique seemed to be particularly promising for removing inorganics from fine-grained soils, traditionally a quite difficult task. Lageman (7) described several electrokinetic remediation projects carried out by Geokinetics in the Netherlands since 1987; toxics removed included lead, copper, zinc, cadmium, and arsenate. Hamad, Acar, and Gale published a discussion of the theory of electrokinetic remediation and a study of its use in removing Pb(II) from kaolinite (8).

The technique is relatively simple in concept. Electrodes (generally inert) are placed in the saturated porous medium and a direct current is passed between them. Cations are drawn by the electric field toward the negative electrode, where (usually) OH^- ion is formed and hydrogen is released by the electrolytic reduction of water. Anions are drawn toward the positive electrode, at which (usually) H^+ ion is formed and oxygen is released by the electrolytic oxidation of water. In addition to the ions initially present, the H^+ and OH^- generated at the electrodes migrate through the porous medium. A number of chemical reactions may take place in the porous medium as H^+ and OH^- react to form water, as hydroxide or hydrous oxide precipitates are formed by reaction with OH^-, and/or dissolved by reaction with H^+. At high pHs the possibility of amphoteric behavior of metal hydroxides and hydrous oxides must be taken into account. The system is illustrated schematically in Fig. 1.

The situation is actually somewhat more complex than the above description would indicate. There may be movement of ions in fluid flow resulting from hydraulic head differences. There will be movement of ions in electroosmotic flow—the flow of water induced by an electric field in a porous medium having a charged surface. There will be diffusion transport of ions resulting from concentration gradients produced by electrode reactions and by reactions between the various species present (such as H^+ and OH^-, for example). The major factor contributing to the flux of ionic species through the system, however, is ion migration (electromigra-

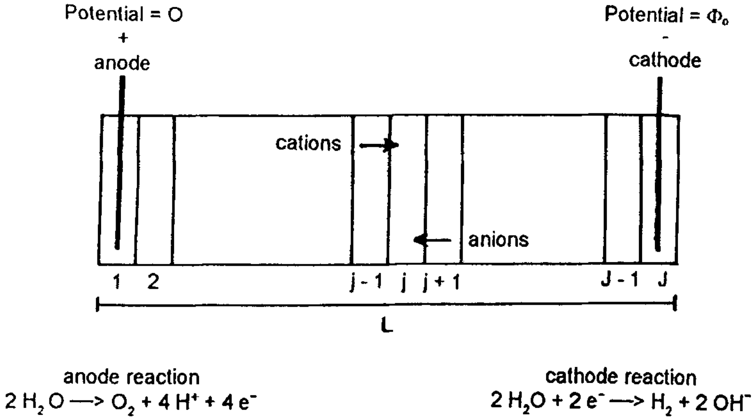

FIG. 1 Schematic diagram of a one-dimensional column configuration for electrokinetic remediation.

tion) resulting from the dragging of the ions through the viscous aqueous medium by the electric field.

For more detailed descriptions of the underlying theory of the process and presentation of the constitutive equations involved, see Refs. 3, 4, or 8.

ANALYSIS

Here we consider the electrokinetic migration of a chemically inert salt (such as sodium sulfate) in aqueous solution, dispersed in a porous medium contained between two inert (graphite) electrodes. See Fig. 1. Let

ϕ_0 = potential difference between the cathode and the anode ($\phi_- - \phi_+$, negative), V
L = length of column, cm
A = cross-sectional area of column, cm^2
J = number of volume elements into which the column is partitioned
ω = porosity of the medium filling the column, assumed saturated
l = L/J, the thickness of one volume element, cm
κ_j = specific conductance of jth volume element, ohm^{-1}·cm^{-1}
λ_i = molar conductivity of ith ion, ohm^{-1}·mol^{-1}·cm^2
z_i = charge number of ith ion, integer
c_{ij} = concentration of ith ion in the jth volume element, mol/cm^3

I = current passing through the column, A
F = Faraday's constant, 96,485 C/equivalent

Electrokinetics

The half-reaction at the cathode is

$$2H_2O + 2e^- \rightarrow 2OH^-(aq) + H_2(gas), \qquad E^\circ = -0.828 \text{ V}$$

The anode half-reaction is

$$2H_2O \rightarrow 4H^+(aq) + O_2(gas) + 4e^-, \qquad E^\circ = -1.229 \text{ V}$$

We assume that the only factor which needs to be taken into account in the system is electrokinetic migration, and that the activity coefficients of all species can be assumed equal to unity. Use of the Nernst equation and the above half-reactions then allows us to write the electric potential drop resulting from the electrode processes as

$$E = -2.057 - 0.0592 \log_{10}[H^+]_{\text{anode}}[OH^-]_{\text{cathode}}$$

This result can be expressed in terms of the pHs of the anode and cathode compartments as

$$E = -1.228 - 0.0592[\text{pH}_{\text{cathode}} - \text{pH}_{\text{anode}}]$$

After the system has been in operation for a time, these pHs are of the order of 12 and 2, respectively, so the voltage drop associated with the electrode reactions is about −1.820 V. Here we shall assume that the applied voltage is sufficiently large that the voltage drop at the electrodes due to the electrode reactions can be neglected.

The specific conductance of the jth volume element is given by

$$\kappa_j = \sum_{i=1}^{n} \lambda_i c_{ij} \tag{1}$$

The resistance of the jth volume element is then

$$R_j = (1/A\omega)\left[\sum_{i=1}^{n} \lambda_i c_{ij}\right]^{-1} \tag{2}$$

The total resistance of the column is

$$R = \sum_{j=1}^{J} R_j = (1/A\omega)\sum_{j=1}^{J}\left[\sum_{i=1}^{n} \lambda_i c_{ij}\right]^{-1} \tag{3}$$

Ohm's law then gives the current I through the column; it is

$$I = \phi_0/R \tag{4}$$

(Note that I here is negative, since our convention is that ϕ_0 is negative.)

We next examine the movement of ions into the jth volume element from the $(j - 1)$th volume element. At the volume element between these two, there are cations entering V_j from the left and anions leaving V_j to the left. The total conductivity at the boundary between the two volume elements is given by

$$\kappa_{j-1,j} = \sum_{i=1}^{n} \lambda_i[c_{i,j-1}S(z_i)S(c_{i,j-1}) + c_{i,j}S(-z_i)S(c_{ij})] \tag{5}$$

where $S(x) = 0, x \leq 0$
$ = 1, x > 0$

The fraction of the conductivity which is associated with ion k at the boundary between ΔV_j and ΔV_{j-1} is given by

$$f^k_{j-1,j} = \frac{\lambda_k[c_{k,j-1}S(z_k)S(c_{k,j-1}) + c_{k,j}S(-z_k)S(c_{k,j})]}{\sum_{i=1}^{n} \lambda_i[c_{i,j-1}S(z_i)S(c_{i,j-1}) + c_{i,j}S(-z_i)S(c_{i,j})]} \tag{6}$$

The rate of movement of the kth ion into ΔV_j is then given by

$$F^k_{j-1,j} = (-I/Fz_k)f^k_{j-1,j}) \tag{7}$$

or

$$F^k_{j-1,j} = \frac{-(I/Fz_k)\lambda_k[c_{k,j-1}S(z_k)S(c_{k,j-1}) + c_{k,j}S(-z_k)S(c_{k,j})]}{\sum_{i=1}^{n} \lambda_i[c_{i,j-1}S(z_i)S(c_{i,j-1}) + c_{i,j}S(-z_i)S(c_{i,j})]} \tag{8}$$

A similar analysis leads to Eq. (9) for the rate of movement of the kth ion into the jth volume element from the $(j + 1)$th volume element.

$$F^k_{j+1,j} = \frac{(I/Fz_k)\lambda_k[c_{k,j}S(z_k)S(c_{k,j}) + c_{k,j+1}S(-z_k)S(c_{k,j+1})]}{\sum_{i=1}^{n} \lambda_i[c_{i,j}S(z_i)S(c_{i,j}) + c_{i,j+1}S(-z_i)S(c_{i,j+1})]} \tag{9}$$

A mass balance for the kth ion in ΔV_j then gives

$$Al\omega \frac{dc_{kj}}{dt} = F^k_{j-1,j} + F^k_{j+1,j} \tag{10}$$

for $j = 2, 3, \ldots, J - 1$.

Let the indices $k = 1$ and $k = 2$ correspond to H^+ and OH^-, respectively. For $j = 1$

$$Al\omega \frac{dc_{k1}}{dt} = F^k_{2,1} \tag{11}$$

for $k = 2, 3, \ldots, n$, and

$$Al\omega \frac{dc_{11}}{dt} = F^{k}_{2,1} + |I|/F \tag{12}$$

for H^+. For $j = J$,

$$Al\omega \frac{dc_{kJ}}{dt} = F^{k}_{J-1,J} \tag{13}$$

for $k = 1, 3, 4, \ldots, n$, and

$$Al\omega \frac{dc_{2J}}{dt} = F^{2}_{J-1,J} + |I|/F \tag{14}$$

for OH^-. The term $|I|/F$ is added to Eqs. (12) and (14) to represent the electrochemical generation of H^+ and OH^- at the anode and cathode.

Chemistry

Up to this point it has been assumed that all of the ions present are chemically inert, except for the formation of H^+ and OH^- at the electrodes. We must take into account, however, the extremely rapid reaction between H^+ and OH^- to form H_2O:

$$H^+ + OH^- \Leftrightarrow H_2O$$

The concentrations of H^+ and OH^- are therefore constrained by the requirement that

$$c_{1j}c_{2j} = K_w = 10^{-20}\ (\text{mol/cm}^3)^2 \tag{15}$$

In the course of integrating the differential equations modeling the system, therefore, it is necessary to adjoin the stoichiometry of this reaction and the ion product requirement, Eq. (15). This is done as follows.

Let us assume that after electrokinetic migration for a time increment Δt we have concentrations of H^+ and OH^- in the volume element ΔV_j of c_a and c_b, respectively. There are two possibilities: $c_a \geq c_b$, and $c_a < c_b$.

If $c_a \geq c_b$, let x be the OH^- concentration at equilibrium. The reaction stoichiometry and Eq. (15) then give

$$(c_a - c_b + x)x = K_w \tag{16}$$

from which we obtain

$$x = (1/2)\{-(c_a - c_b) + [(c_a - c_b)^2 + 4K_w]^{1/2}\} \tag{17}$$

Then

$$c_{1j} = c_a - c_b + x \tag{18}$$

and

$$c_{2j} = x \tag{19}$$

give the equilibrated concentrations of H^+ and OH^- in the jth volume element.

If $c_b > c_a$, let y be the H^+ concentration in the volume element after equilibrium has been achieved. Then

$$y(c_b - c_a + y) = K_w \tag{20}$$

and

$$y = (1/2)\{-(c_b - c_a) + [(c_b - c_a)^2 + 4K_w]^{1/2}\} \tag{21}$$

from which

$$c_{1j} = y \tag{22}$$

and

$$c_{2j} = c_b - c_a + y \tag{23}$$

The model then consists of the differential equations governing the electrokinetic migration of the ions (Eqs. 10–14) and the definitions of the fluxes in these equations given by Eqs. (8) and (9), and the prescriptions for equilibrating the H^+ and OH^- concentrations given by Eqs. (17)–(19) or (21)–(23).

The value of J used in the calculations was generally taken to be 16. The two volume elements at either end of the column were regarded as the anode (left; $j = 1, 2$) and cathode (right; $j = J - 1, J$) compartments, and the mass M_k of an ion remaining in the volume elements 3, 4, . . . , $J - 2$ after a period t of electrokinetic treatment was calculated by Eq. (24).

$$M_k = \sum_{j=3}^{J-2} lA\omega c_{kj} \tag{24}$$

The electrical neutrality requirement must be satisfied by the solution in each volume element at all times; this gives the relationship

$$\sum_{i=1}^{n} z_i c_{ij} = 0, \qquad \text{all } j \tag{25}$$

which provides a rather stringent test of finite difference algorithms which might be used to approximate the differential equations which represent the system. We explored several such algorithms which looked quite reasonable but which were unsuccessful in satisfying, even approximately, the electrical neutrality requirement even after only short periods of simulated operation of the system. The algorithm described here appears to maintain electrical neutrality to within the limits of round-off errors in the computations.

RESULTS

The results presented here describe the treatment of a column of porous medium. Sodium sulfate was used as the electrolyte. Modeling parameters are given in Table 1.

In unenhanced electrokinetic migration we find that the removal of the salt is nowhere complete even after extended periods of treatment. As treatment proceeds, the central volume elements of the column become depleted of sodium and sulfate ions, so their electrical resistance becomes quite large. This results in greatly reduced values of the current through the column, with correspondingly reduced rates of migration of the ions.

TABLE 1

Parameters Used in Modeling Unenhanced Electrokinetic Treatment of Porous Medium Containing Sodium Sulfate

Column length: 100 cm
Column cross-sectional area: 100 cm^2
Porosity of soil: 0.4
Number of volume elements used to represent column: 16
z_1: +1 (H^+)
λ_1: 349.8 $\mathrm{ohm}^{-1}\cdot\mathrm{mol}^{-1}\cdot\mathrm{cm}^3$
z_2: −1 (OH^-)
λ_2: 198.5 $\mathrm{ohm}^{-1}\cdot\mathrm{mol}^{-1}\cdot\mathrm{cm}^3$
z_3: +1 (Na^+)
λ_3: 50.1 $\mathrm{ohm}^{-1}\cdot\mathrm{mol}^{-1}\cdot\mathrm{cm}^3$
z_4: −2 (SO_4^{2-})
λ_4: 160 $\mathrm{ohm}^{-1}\cdot\mathrm{mol}^{-1}\cdot\mathrm{cm}^3$
z_5: +1 (K^+)
λ_5: 73.5 $\mathrm{ohm}^{-1}\cdot\mathrm{mol}^{-1}\cdot\mathrm{cm}^3$
z_6: +2 (Cd^{2+})
λ_6: 108 $\mathrm{ohm}^{-1}\cdot\mathrm{mol}^{-1}\cdot\mathrm{cm}^3$
Δt: 100 seconds
Applied voltage: 50, 100 V
Initial Na_2SO_4 concentration: 0.05, 0.005 mol/L
$K_{sp} = [Cd^{2+}][OH^-]^2 = 2 \times 10^{-14}$

Figures 2–5 show plots of residual total moles of Na^+ in the column (calculated by Eq. 24) and electric current through the column as functions of time. These show the decrease of the current to very low values as the run proceeds. Figure 2 pertains to a column operated at a voltage of − 100 V with an initial sodium sulfate concentration of 0.005 M. Two runs were made, with the column partitioned into 16 and 23 volume elements as indicated. We see an initial increase in the magnitude of the current as the conductance is increased near the ends of the column by the formation of H^+ and OH^-. This is followed by a decrease in the current as volume elements near the middle of the column become depleted in ions. The H^+ and OH^- ions react with each other, so that they are unable to provide a high conductivity in the domain where they are meeting and being destroyed. Eventually the current dwindles to nearly zero, and the rates of migration of sodium and sulfate ions to the ends of the column become extremely slow.

Figure 3 shows similar plots (J = 16 only) for a column containing 0.005 M sodium sulfate and operated at −50 V. The current is decreased by half, and the time scale of the removal is doubled, as expected. Figures 4 and 5 show similar plots for columns initially containing 0.05 M Na_2SO_4 and operated at − 100 and −50 V, respectively. The currents and sodium

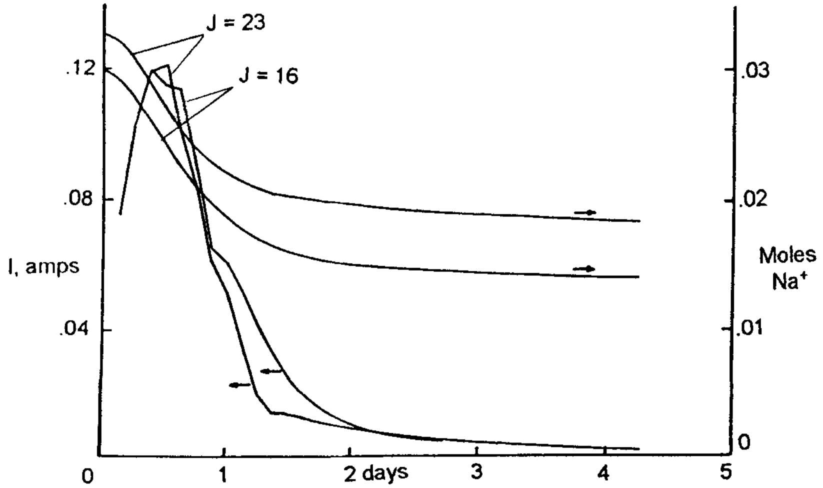

FIG. 2 Plots of current and total residual moles Na^+ versus time for two simulations of the removal of Na^+ from a column initially containing 0.005 M sodium sulfate. The applied potential is − 100 V. The numbers of volume elements into which the column is partitioned are 16 and 23, as indicated. Other parameters are as in Table 1.

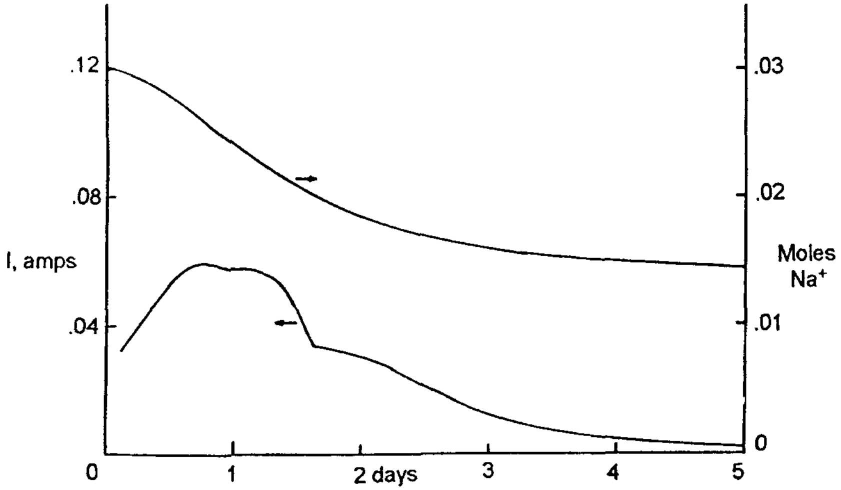

FIG. 3 Plots of current and total residual moles Na^+ versus time for a simulation of the removal of Na^+ from a column initially containing 0.005 M sodium sulfate. The applied potential is −50 V. The column is partitioned into 16 volume elements. Other parameters are as in Table 1.

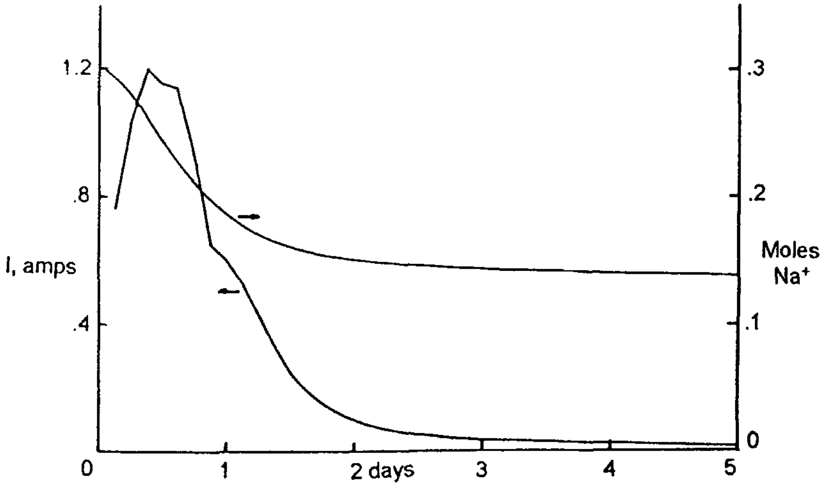

FIG. 4 Plots of current and total residual moles Na^+ versus time for a simulation of the removal of Na^+ from a column initially containing 0.05 M sodium sulfate. The applied potential is −100 V. The column is partitioned into 16 volume elements. Other parameters are as in Table 1.

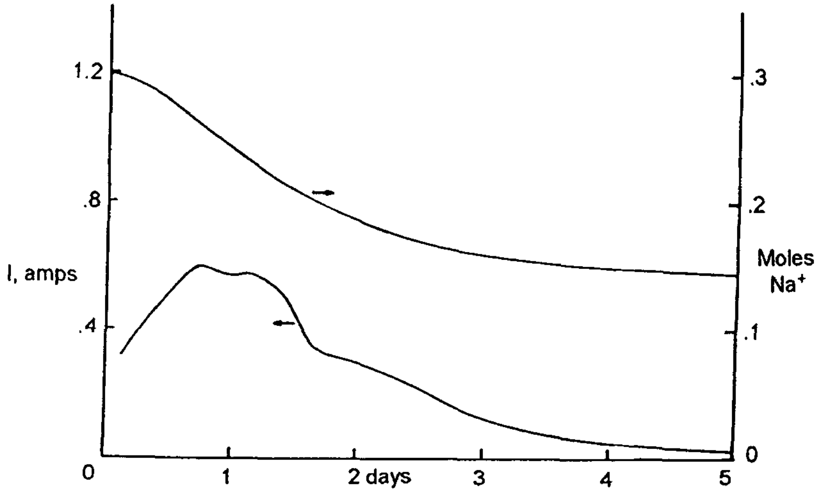

FIG. 5 Plots of current and total residual moles Na^+ versus time for a simulation of the removal of Na^+ from a column initially containing 0.05 M sodium sulfate. The applied potential is −50 V. The column is partitioned into 16 volume elements. Other parameters are as in Table 1.

TABLE 2

Distributions of Specific Conductance, Ion Concentrations, and Electrical Neutrality Sums for the Run Plotted in Fig. 2 ($J = 16$), after 6.3 Days of Treatment

J	Specific conductance	H^+	OH^-	Na^+	SO_4^{2-}	Electrical neutrality sums
1	3.10E-2	7.18E-5	1.39E-16	1.45E-6	3.66E-5	1.02E-10
2	1.50E-2	3.44E-5	2.90E-16	1.76E-6	1.81E-5	−1.46E-11
3	9.94E-3	2.25E-5	4.45E-16	2.13E-6	1.23E-5	−6.91E-11
4	6.52E-3	1.45E-5	6.92E-16	2.35E-6	8.40E-6	−2.73E-11
5	2.84E-3	6.09E-6	1.64E-15	1.74E-6	3.91E-6	7.27E-12
6	3.54E-4	7.46E-7	1.34E-14	2.58E-7	5.02E-7	1.32E-11
7	2.10E-6	2.46E-11	4.06E-10	1.56E-8	7.64E-9	−9.72E-12
8	1.97E-5	1.26E-13	7.92E-8	7.99E-8	3.85E-10	2.92E-12
9	9.53E-5	2.61E-14	3.83E-7	3.87E-7	1.85E-9	3.92E-12
10	3.84E-4	6.48E-15	1.54E-6	1.56E-6	7.25E-9	1.48E-11
11	1.08E-3	2.31E-15	4.33E-6	4.37E-6	1.86E-8	4.32E-12
12	2.11E-3	1.18E-15	8.49E-6	8.55E-6	2.99E-8	−1.56E-11
13	3.34E-3	7.45E-16	1.34E-5	1.35E-5	3.44E-8	−1.68E-11
14	4.92E-3	5.04E-16	1.98E-5	1.99E-5	3.31E-8	6.70E-11
15	7.85E-3	3.16E-16	3.17E-5	3.17E-5	3.01E-8	−6.20E-11
16	1.74E-2	1.43E-16	7.01E-5	7.02E-5	2.87E-8	−3.90E-12

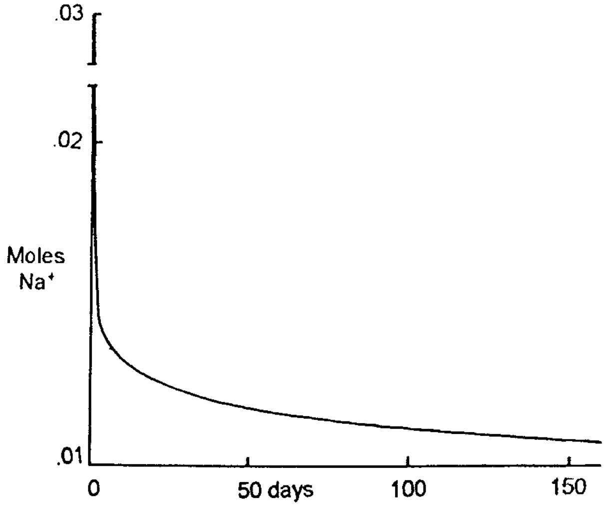

FIG. 6 Extended plot of total residual moles Na^+ versus time. Run parameters are as in Fig. 2, with the column partitioned into 16 volume elements. Note that the vertical scale starts at 0.01 mole and has a break between 0.02 and 0.03 mole.

ion mole numbers are increased by a factor of 10 as compared to Figs. 2 and 3, as expected.

Table 2 gives the values of the ion concentrations and the specific conductances of the solutions in the volume elements at the completion of one of the runs, and shows the marked decrease in specific conductance near the center of the column which is associated with ion concentrations which are near zero. This appears to be an inherent limitation to the effectiveness of unenhanced electrokinetic remediation. A simulated run carried out for 160 days showed relatively little removal of Na^+ after the first 10 days; see Fig. 6. Evidently either H^+ or OH^- must be replaced by a nonreactive ion if high conductivities are to be maintained throughout the column during the entire course of the remediation.

POSSIBLE ELABORATIONS OF THE MODEL

The model as described to this point handles only the most simple case of unenhanced electrokinetic migration of ions. We summarize here a number of interesting variations and elaborations of the model which it is planned to explore. These include the following.

1. One may modify the compositions of the anode and/or cathode compartments by adding reagents or by removing solution for treatment and possible amendment. In particular, one might replace the hydroxide formed electrolytically in the cathode compartment by chloride or sulfate, thereby preventing the destruction of H^+ as it migrates through the column from the anode. This should allow one to maintain a high column conductivity throughout the entire run, thereby greatly increasing the extent of removal of toxic cations from the column. The high acidity of the column should also prevent the formation of hydroxide precipitates and lead to the solution of any solid hydroxides, hydrous oxides, and carbonates. Two such enhancements, the neutralization of OH^- in the cathode compartment by its titration with sulfuric acid, and the neutralization of H^+ in the anode compartment by titration with KOH, are discussed in the following section.
2. The porous medium may contain one or more ions which form insoluble hydroxides/hydrous oxides if the solution is sufficiently basic. Copper and cadmium are two examples of practical interest in this connection. Inclusion of such ions would require one to permit the metal ion and OH^- to come to equilibrium in each volume element after every increment in time, and to keep track of the quantities of precipitated metal hydroxide in each volume element. Systems of this type are explored in a following section.
3. One may have a metal ion which forms a solid but amphoteric hydroxide, which redissolves at sufficiently high pHs. Representative examples of such metals include lead, zinc, and aluminum.
4. Very commonly, clays in the porous medium will have ion-exchange capacities for the cations involved, and these equilibria will then need to be included in the model. In addition, there may be sorption of metal ions on naturally-occurring organic material in the soil.
5. The soil may contain calcium carbonate or other buffer compounds which will react with H^+ if the pH is sufficiently low.
6. There may be dead-end capillaries in the porous medium from which metal ions must move by diffusion before they can undergo electrokinetic migration.
7. At low applied voltages the voltage drops at the electrodes may not be negligible, and it may be necessary to include a Nernst equation correction for these, as described above.
8. The model, as presently formulated, does not include diffusion and electroosmotic flow of water. These are described in the literature as being of much less significance than electrokinetic migration, but should probably be included if this can be done without drastically increasing the computation time required to simulate a run.

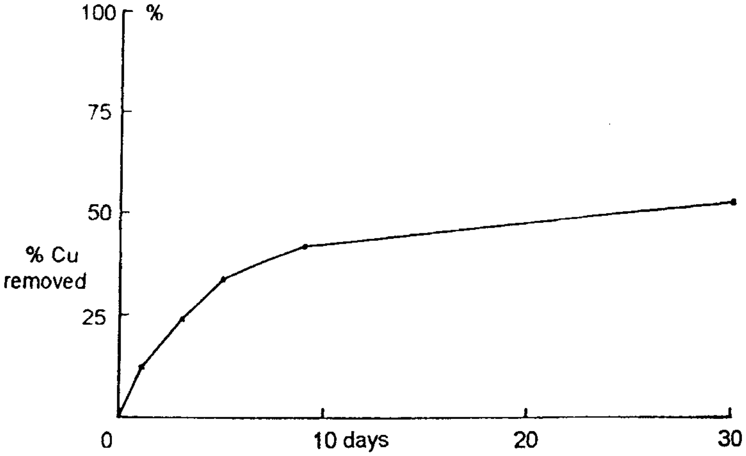

FIG. 7 Experimental data on % Cu removal versus time on electrokinetic treatment of a porous medium containing $CuSO_4$; data from Runnels and Larson (9).

Figure 7 shows some experimental results of Runnels and Larson (9) for the removal of copper by electrokinetic treatment. These results appear quite similar to those we obtained by calculation for unenhanced electrokinetic treatment.

ENHANCED ELECTROKINETIC REMEDIATION

It was seen above that the reaction of H^+ and OH^- in the column to produce nonionic H_2O results in the formation of regions of extremely low conductance, which drastically decrease the electric current through the column and, with it, the rate of migration of the cations one wishes to remove. If the OH^- is replaced by an ion which does not react with H^+, such as sulfate (assuming that the pH is not too low), one should be able to avoid this difficulty.

This is accomplished by simply titrating the hydroxide in the cathode compartment as fast as it is generated by adding sulfuric acid. The model equations are modified as follows. Equation (14) is replaced by

$$Al\omega \frac{dc_{2J}}{dt} = F^2_{J-1,J} \qquad (26)$$

and the corresponding equation for sulfate ion (for which $k = 4$ in our calculations) becomes

$$Al\omega \frac{dc_{4J}}{dt} = F^{4}_{J-1,J} + |I|/(2F) \tag{27}$$

The results of a typical calculation in which sodium ion is being removed from the column are shown in Fig. 8. Run parameters are as in Table 1; the applied potential is −100 V, and the initial Na_2SO_4 concentration in the column is 0.005 M. Cleanup of the column is virtually complete within 5 days, in marked contrast to the results obtained with unenhanced electrokinetic treatment. One does pay a price for this greatly improved efficiency, however, in terms of increased current requirements, as seen in the figure. It should prove possible to reduce electric power requirements by replacing H^+ as it is formed in the anode compartment by another cation which is less mobile than H^+.

Another possible strategy for reducing the current requirement is to add sufficient sulfuric acid to neutralize only a fraction p of the OH^- produced electrolytically in the cathode compartment. This requires that Eq. (26) (for H^+) and Eq. (27) (for sulfate) be modified; Eqs. (28) and (29) are the result.

$$Al\omega \frac{dc_{2J}}{dt} = F^{2}_{J-1,J} + p|I|/F \qquad (H^+) \tag{28}$$

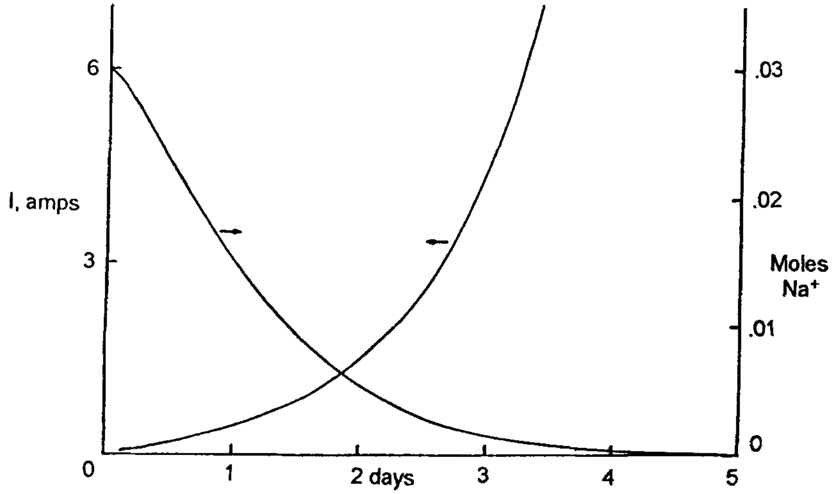

FIG. 8 Plots of total residual moles Na^+ and current versus time for a simulated run in which H_2SO_4 is introduced into the cathode compartment to completely neutralize the electrolytically formed OH^-. The initial sodium sulfate concentration in the column is 0.005 M, the applied voltage is −100 V, and the other parameters are as given in Table 1.

$$Al\omega \frac{dc_{4J}}{dt} = F^4_{J-1,J} + (1-p)|I|/(2F) \qquad (SO_4^{2-}) \qquad (29)$$

Figure 9 shows plots of Na^+ removal versus time for runs in which 0, 10, 15, 20, 25, and 100% of the OH^- generated in the cathode compartment is reacted with sulfuric acid. In these runs the titration of only 20% of the hydroxide produced is sufficient to yield cleanups which are essentially as rapid as that resulting when 100% of the OH^- is destroyed. The current requirements for these runs are shown in Fig. 10, and are far less than required if 100% of the hydroxide is to be destroyed. The results indicate that, for this system, addition of sufficient sulfuric acid to the cathode compartment to react with 20–25% of the generated hydroxide is sufficient to yield cleanup of the column within 5 days, and that the power requirements are a quite small fraction of that needed if all of the hydroxide is reacted.

In similar fashion one can modify the model to include the titration or partial titration of H^+ formed in the anode compartment by strong base. Here we simulated reaction with KOH. A representative run of this type is shown in Fig. 11, and indicates that this approach is also effective in

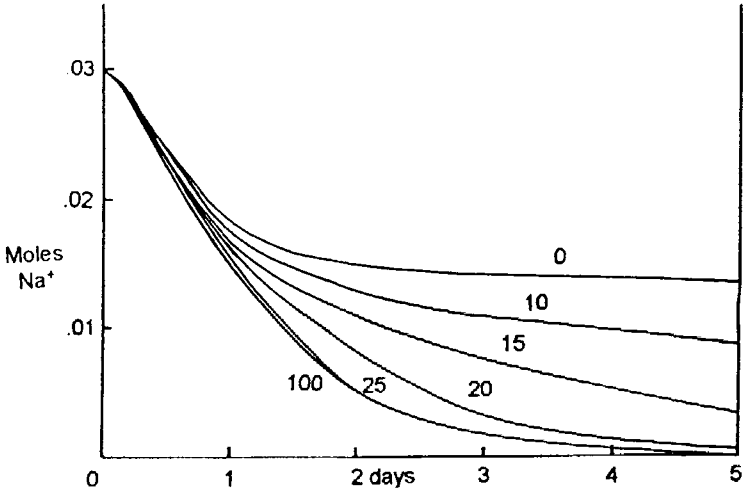

FIG. 9 Plots of total residual moles Na^+ versus time for simulated runs in which H_2SO_4 is introduced into the cathode compartment to partially neutralize the electrolytically formed OH^-. The initial sodium sulfate concentration in the column is 0.005 M, the applied voltage is −100 V; the other parameters are as given in Table 1. Zero, 10, 15, 20, 25, and 100% of the OH is neutralized, from the top down.

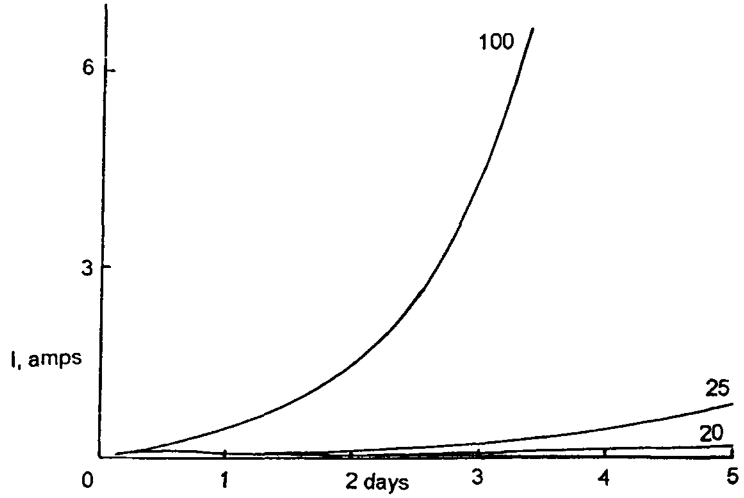

FIG. 10 Plots of electric current versus time for simulated runs in which H_2SO_4 is introduced into the cathode compartment to partially neutralize the electrolytically formed OH^- See Fig. 9. The initial sodium sulfate concentration in the column is 0.005 M, the applied voltage is −100 V; the other parameters are as given in Table 1. Twenty, 25, and 100% of the OH^- is neutralized from the top down; plots with 0, 10, and 15% neutralization lie below the plot with 20% neutralization.

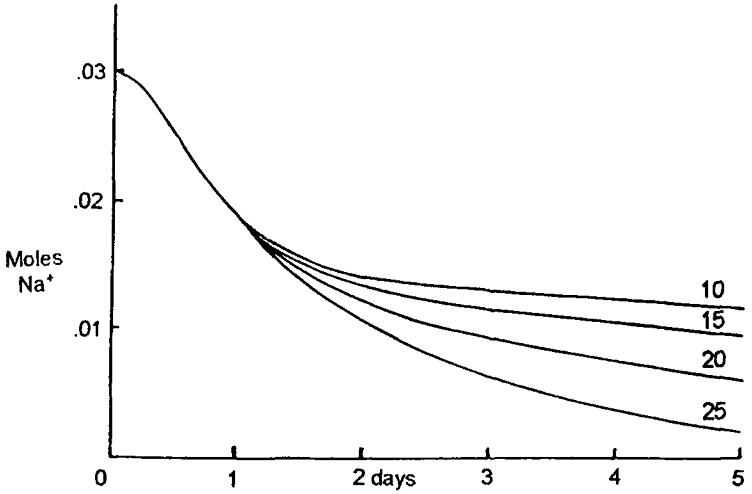

FIG. 11 Plots of total residual moles Na^+ versus time for simulated runs in which KOH is introduced into the anode compartment to partially neutralize the electrolytically formed H^+. The initial sodium sulfate concentration in the column is 0.005 M, the applied voltage is −100 V; the other parameters are as given in Table 1. Ten, 15, 20, and 25% of the H^+ is neutralized, from the top down.

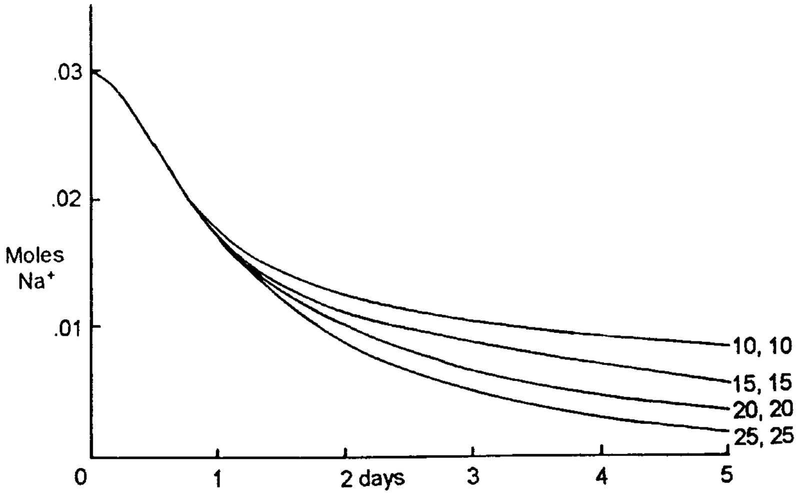

FIG. 12 Plots of total residual moles Na^+ versus time for simulated runs in which KOH is introduced into the anode compartment and H_2SO_4 is introduced into the cathode compartment to partially neutralize the electrolytically formed H^+ and OH^-, respectively. The initial sodium sulfate concentration in the column is 0.005 M and the applied voltage is − 100 V; other parameters are as in Table 1. Ten, 15, 20, and 25% of the electrolytically formed H^+ and OH^- are neutralized, from the top down.

maintaining the conductivity of the column, although not quite as effective as the addition of sulfuric acid to the cathode compartment.

Lastly, it is possible to add KOH to the anode compartment to partially replace H^+ by K^+, and H_2SO_4 to the cathode compartment to partially replace OH^- by SO_4^{2-}. Modification of the modeling equations to describe this case produced the results shown in Fig. 12. The results do not justify the additional complexity and expense; partial titration of the base electrolytically formed in the cathode compartment seems to produce the optimal results, although addition of base to the anode compartment should enhance the removal of anionic contaminants such as arsenate and selenate.

REMOVAL OF CADMIUM OR COPPER BY ELECTROKINETIC REMEDIATION

Analysis

We next turn to a case of more direct environmental interest—the removal of nonamphoteric divalent metals having slightly soluble hydroxides, such as cadmium or copper, by means of electrokinetic remediation. We illustrate with cadmium.

The chemistry here is somewhat more complex than in the case considered previously; the equilibria which must be taken into account are

$$H_2O \Leftrightarrow H^+ + OH^-$$

and

$$Cd(OH)_2(s) \Leftrightarrow Cd^{2+} + 2OH^-$$

with equilibrium expressions

$$K_w = [H^+][OH^-] \tag{30}$$

and

$$K_{sp} = [Cd^{2+}][OH^-]^2 \tag{31}$$

In simulating electrokinetic remediation it is necessary to allow the reagents in each volume element to chemically equilibrate with each other after each time increment in the numerical integration. The unknowns involved in the equilibrations are $[Cd^{2+}]$, $[H^+]$, $[OH^-]$, and M, the mass of solid $Cd(OH)_2$ present in the volume element.

The numerical solution of the equilibrium equations must be done in different ways, depending on the values of these variables. This is facilitated by the construction of a stoichiometry tree in which the various reactions are assumed to take place stoichiometrically (i.e., each to completion). This then yields the initial conditions for the particular equilibrium calculations which are necessary. Such stoichiometry trees are essential when dealing with more complex cases such as systems involving metals having amphoteric hydroxides, systems in which a weak acid (acetic acid) is used to partially neutralize the OH^- formed in the cathode compartment, systems containing buffer minerals (i.e., calcium carbonate), etc.

The stoichiometry tree for the electrokinetic removal of cadmium is shown in Fig. 13. The scheme for constructing the tree is simply to completely react the strongest remaining acid completely with the strongest remaining base until one can go no further. This then leads one to three possible cases (in the tree, Case 2 occurs two times); for each of these cases there are two possibilities—after equilibrium has been reached there is, or there is not, solid $Cd(OH)_2$ present. In each case, one carries out the equilibrium calculation assuming that solid cadmium hydroxide will be present. One then calculates the number of moles of $Cd(OH)_2$ present from the conservation equation for total cadmium. If this figure is nega-

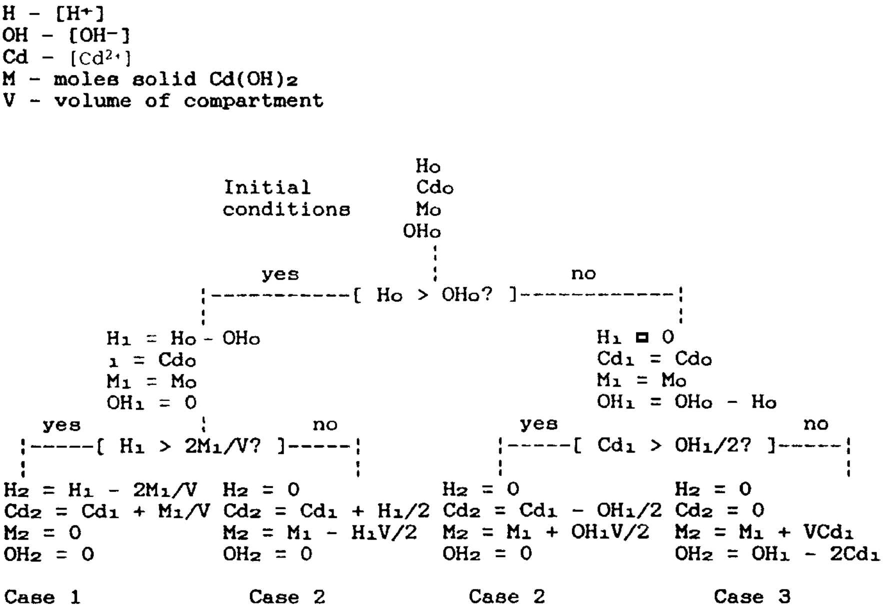

FIG. 13 Stoichiometry tree for the equilibrium calculations for electrokinetic migration of cadmium.

tive, one redoes the equilibrium calculation assuming that no solid $Cd(OH)_2$ is present.

We next turn to the equilibrium calculations; we first deal with Case 1, for which the initial $[H^+]$ is H_2, the initial $[Cd^{2+}]$ is Cd_2, and the initial values of M and OH^- are zero. We let $H = [H^+]$, $Cd = [Cd^{2+}]$, $OH = [OH^-]$, and $M =$ moles solid $Cd(OH)_2$, all at equilibrium. We assume initially that $M > 0$. Then conservation of total moles of Cd gives

$$\mathrm{Cd} + \mathrm{M}/V = \mathrm{Cd}_2 \tag{32}$$

and conservation of charge gives

$$\mathrm{H} + 2\mathrm{Cd} - \mathrm{OH} = \mathrm{H}_2 + 2\mathrm{Cd}_2 \tag{33}$$

Equations (30) and (31) give

$$\mathrm{OH} = (K_{\mathrm{sp}}/\mathrm{Cd})^{1/2} \tag{34}$$

and

$$\mathrm{H} = K_{\mathrm{w}}(\mathrm{Cd}/K_{\mathrm{sp}})^{1/2} \tag{35}$$

Substitution of these results in Eq. (33) and rearrangement gives

$$2\mathrm{Cd} + K_w(\mathrm{Cd}/K_{sp})^{1/2} - (K_{sp}/\mathrm{Cd})^{1/2} - \mathrm{H}_2 - 2\mathrm{Cd}_2 = 0 \tag{36}$$

This is easily solved by a simple binary search algorithm to give the value for Cd, the cadmium ion concentration. The value of M, the number of moles of solid $\mathrm{Cd(OH)_2}$ present, is then given by Eq. (32); it is

$$\mathrm{M} = V(\mathrm{Cd}_2 - \mathrm{Cd}) \tag{37}$$

If $\mathrm{M} \geq 0$, one then calculates OH and H from Eqs. (34) and (35), and the computation is complete.

If $\mathrm{M} < 0$, one sets $\mathrm{M} = 0$, $\mathrm{Cd} = \mathrm{Cd}_2$. Equation (33) becomes

$$\mathrm{H} - \mathrm{OH} = \mathrm{H}_2 \tag{38}$$

which on use of Eq. (30) becomes

$$\mathrm{H} - K_w/\mathrm{H} = \mathrm{H}_2 \tag{39}$$

This could be solved by rearranging and using the quadratic formula; this, however, under some circumstances leads to inaccurate results and it is safer to solve Eq. (39) by the binary search technique. OH is then given by use of Eq. (30), and the calculation is complete.

For Case 2, $\mathrm{H}_2 = \mathrm{OH}_2 = 0$, and Cd_2 and $\mathrm{M}_2 > 0$. Conservation of cadmium during the equilibration process gives

$$\mathrm{Cd} + \mathrm{M}/V = \mathrm{Cd}_2 + \mathrm{M}_2/V \tag{40}$$

and conservation of charge gives

$$\mathrm{H} + 2\mathrm{Cd} - \mathrm{OH} = 2\mathrm{Cd}_2 \tag{41}$$

Use of Eqs. (34) and (35) in Eq. (41) and rearrangement then yields

$$2\mathrm{Cd} + K_w(\mathrm{Cd}/K_{sp})^{1/2} - (K_{sp}/\mathrm{Cd})^{1/2} - 2\mathrm{Cd}_2 = 0 \tag{42}$$

This is solved by binary search for Cd. The quantity of solid $\mathrm{Cd(OH)_2}$ present is obtained from Eq. (40); it is

$$\mathrm{M} = \mathrm{M}_2 + V(\mathrm{Cd}_2 - \mathrm{Cd}) \tag{43}$$

If $\mathrm{M} \geq 0$, H and OH are calculated from Eqs. (34) and (35) and the calculation is complete.

If Eq. (43) yields $\mathrm{M} < 0$, however, we set $\mathrm{M} = 0$, $\mathrm{Cd} = \mathrm{Cd}_2 + \mathrm{M}_2/V$. The charge balance equation becomes

$$\mathrm{H} - \mathrm{OH} + 2\mathrm{M}_2/V = 0 \tag{44}$$

which yields

$$\mathrm{H} - K_w/\mathrm{H} + 2\mathrm{M}_2/V = 0 \tag{45}$$

This, as with Eq. (39), is most reliably solved by binary search for H, from which OH is readily calculated, completing the computation.

For Case 3, $H_2 = Cd_2 = 0$, and M_2 and $OH_2 > 0$. Conservation of cadmium during equilibration gives

$$\mathrm{Cd} + \mathrm{M}/V = \mathrm{M_2}/V \tag{46}$$

and conservation of charge gives

$$\mathrm{H} - \mathrm{OH} + 2\mathrm{Cd} = -\mathrm{OH_2} \tag{47}$$

Use of Eqs. (34) and (35) in Eq. (47) then gives

$$2\mathrm{Cd} + K_w(\mathrm{Cd}/K_{sp})^{1/2} - (K_{sp}/\mathrm{Cd})^{1/2} + \mathrm{OH_2} = 0 \tag{48}$$

This is solved by binary search for Cd, and M is obtained from Eq. (46) as

$$\mathrm{M} = \mathrm{M_2} - V\mathrm{Cd} \tag{49}$$

If $M \geq 0$, then H and OH are given by Eqs. (34) and (35), as before. If $M < 0$, then $M = 0$, $Cd = M_2/V$, and Eq. (47) becomes

$$\mathrm{H} - K_w/\mathrm{H} + 2\mathrm{M_2}/V + \mathrm{OH_2} = 0 \tag{50}$$

As before, this is solved by binary search. Calculation of OH then completes the computation.

The remainder of the model, which describes the electrokinetic migration of the cations and anions and the possible amendment of solutions in the electrode compartments, is virtually identical to the previous model for nonreactive ions.

Results

The model was implemented in TurboBASIC and runs made on an MMG microcomputer using an 80386 chip and a math coprocessor, and operating at 33 MHz. Typical runs took from 0.5 to 2 hours.

The effect on cadmium removal of the percent of the OH^- formed at the cathode which is neutralized by the addition of sulfuric acid is shown in Figs. 14 and 15. For the runs in Fig. 14, initially no solid $Cd(OH)_2$ is present; for those in Fig. 15, 0.0005 mol/L of soil of solid $Cd(OH)_2$ is present. The drastic acceleration of the rate of cleanup with increasing percent neutralization is associated with the higher conductivities which are maintained throughout the length of the cell when the ions which are generated, in effect, at the anode and cathode are H^+ and SO_4^{2-}, which do not react with each other to produce a nonconductive species, unlike H^+ and OH^-. One pays a price for the accelerated rate of cleanup

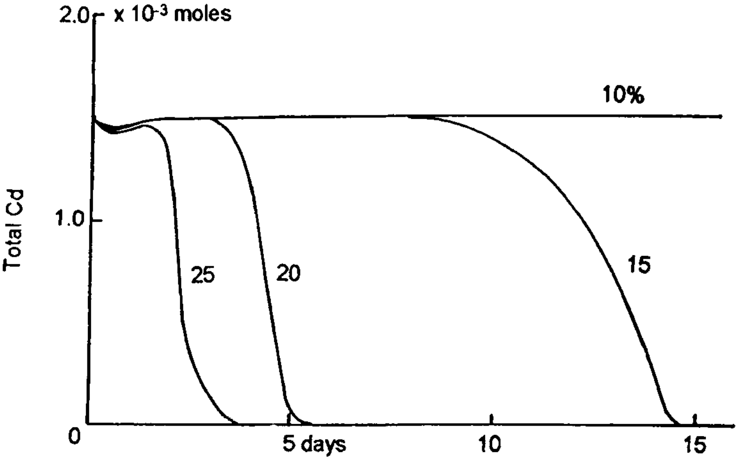

FIG. 14 Removal of cadmium. Plots of total residual moles Cd^{2+} versus time for simulated runs in which 10, 15, 20, and 25% of the OH^- formed in the cathode compartment is neutralized with sulfuric acid. Initially $[Cd^{2+}] = 0.0005$, $[Na^+] = 0.001$, $[SO_4^{2-}] = 0.001$ M; solid $Cd(OH)_2$ concentration = 0 mol/L of soil. Applied potential = 100 V, length of cell = 100 cm, width and breadth of cell = 10 cm.

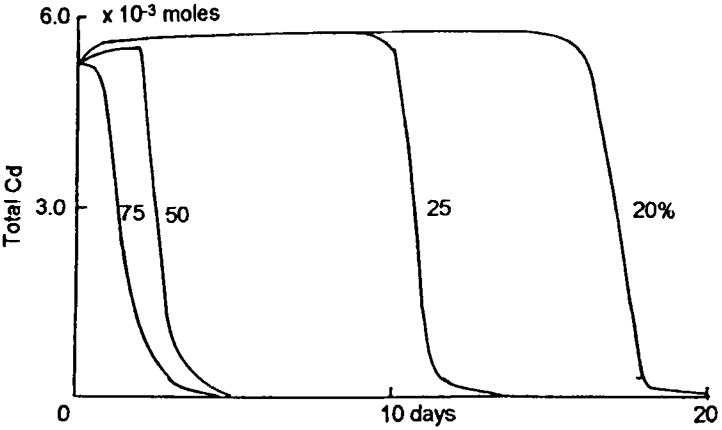

FIG. 15 Removal of cadmium. Plots of total residual moles Cd^{2+} versus time for simulated runs in which 20, 25, 50, and 75% of the OH^- formed in the anode compartment is neutralized with sulfuric acid. Operating conditions are as for the runs in Fig. 14, except that the initial solid $Cd(OH)_2$ concentration is 0.0005 mol/L of bulk soil.

achieved with enhanced electrokinetic migration, in that electric power requirements are greater and reagent costs are greater than in the unenhanced process. However, the extreme slowness of the unenhanced process would probably be unacceptable in most applications.

The effect of the initial concentration of chemically inert sodium sulfate is shown in Fig. 16. Here, as before, we find that overall increased conductivity results in faster cleanups (and higher currents), although here cleanup is complete in 26.5 days even for the run with no sodium sulfate present initially.

As expected, runs made in which OH^- was added to the anode compartment were disastrous. Cd^{2+} precipitated rapidly as solid $Cd(OH)_2$, which could never be redissolved and moved to the cathode compartment. This technique should be effective (but probably not economical) for the electrokinetic migration of amphoteric metals such as lead, zinc, and aluminum. And it should be quite useful in applications involving arsenate, selenate, and perhaps fluoride.

In conclusion, we note the following points.

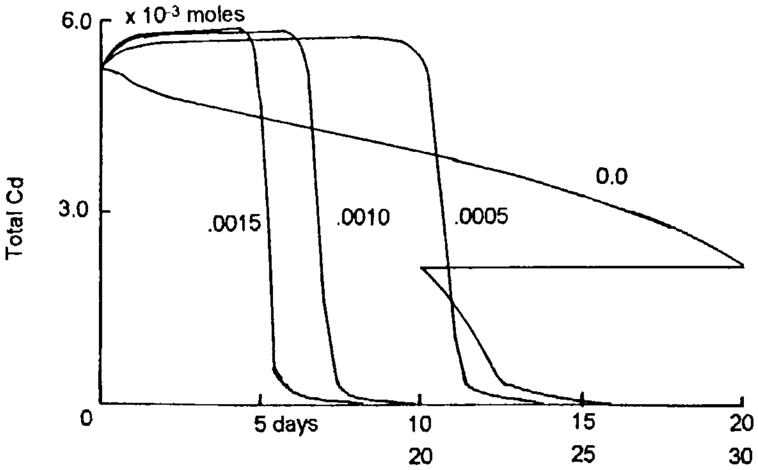

FIG. 16 Removal of cadmium. Effect of initial sodium sulfate concentration on plots of total residual moles Cd^{2+} versus time. In these runs 25% of the OH^- generated in the cathode compartment is neutralized with H_2SO_4. Initially $[Na_2SO_4]$ = 0, 0.0005, 0.0010, and 0.0015 M, as indicated. The initial solid $Cd(OH)_2$ concentration is 0.0005 mol/L of soil; initial $[Cd^{2+}]$ = 0.0005 M; other parameters are as given in Fig. 14. Note that the plot for which $[Na_2SO_4]$ = 0 is folded back to keep it on scale; Cd removal for this run was complete after 26.5 days.

- It appears that inclusion of even rather complex aqueous chemistry (amphoteric metals, weak salts, weak acids, etc.) in the modeling of electrokinetic remediation is not difficult.
- The results of modeling are in agreement with the great increases in remediation rate observed experimentally when electrokinetic remediation is enhanced by modification of the compositions of the solutions in the electrode compartments.
- Mathematical modeling should facilitate the exploration of a wide range of variations in electrokinetic remediation to optimize its performance in a variety of applications.

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