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Electrokinetic Remediation. III. Enhancement with Base

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ABSTRACT

One-dimensional models are developed for simulating the base-enhanced electrokinetic treatment of aquifers contaminated with As(V) and Zn(II). The effect of the fraction of H^+ generated electrolytically at the anode which is neutralized on the time required for remediation is investigated. The effect of the initial speciation of the contaminant [As(V) or Zn(II)] is also explored. Base-enhanced electrokinetic treatment is expected to be useful in the removal of anionic species (arsenate, selenate, fluoride, for example) and in the removal of amphoteric metal ions (lead, zinc, chromium, etc.) from aquifers containing large concentrations of calcium or magnesium carbonate which would interfere with acid-enhanced electrokinetic treatment.

INTRODUCTION

The removal of toxic substances from aquifers by pump-and-treat methods is often limited by the low rates with which one can mobilize the toxic substances, which may be dispersed in porous structures of low permeability (clay, silt, or till lenses and strata), adsorbed/ion exchanged on clays or natural soil organic matter, or present as slightly soluble solids—hydroxides, hydrous oxides, carbonates, or in some cases sulfates. The behavior of metals in soils has been described by, for example, McLean and Bledsoe (1) and Freeze and Cherry (2).

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A promising innovative technology for the removal of toxic ionics from contaminated aquifers is electrokinetic remediation. The technique has been described by Acar and Alshawabkeh (3) and by Acar et al. (4); Acar has also given a shorter nonmathematical treatment of the subject (5). Cabrera-Guzman et al. (6) evaluated the electrokinetic remediation technique for EPA. These authors noted that the technique shows promise for removing inorganics from fine-grained soils, a difficult to impossible task for other technologies. Lageman (7) described several electrokinetic remediation projects in the Netherlands; lead, copper, zinc, cadmium, and arsenate were removed. Hamad et al. discussed the theory of electrokinetic remediation and described its use in removing Pb(II) from kaolinite (8). Runnels and Larson (9) carried out a laboratory-scale study of the technique. We have described a mathematical model for the enhanced electrokinetic removal of nonamphoteric divalent metals (10); a later paper described the use of weak acids as enhancing reagents and the removal of amphoteric metals (11).

Conceptually, the technique is relatively simple. Electrodes (generally inert) are placed in the contaminated zone of the aquifer and an applied electric potential generates a direct current between them. Cations, under the influence of the electric field, migrate toward the negative electrode (the cathode) where (usually) OH^- ion and hydrogen gas are formed by the electrolytic reduction of water. Anions move toward the positive electrode (the anode), at which (usually) H^+ ion and oxygen are formed by the electrolytic oxidation of water. In addition to the ions initially present, the H^+ and OH^- generated at the electrodes are also driven in opposite directions through the aquifer. Chemical reactions may take place in the aquifer as H^+ and OH^- react to form water, and as hydroxide or hydrous oxide precipitates are formed by reaction with OH^- and/or dissolved by reaction with H^+. At high pHs there is the possibility of amphoteric behavior of metal hydroxides and hydrous oxides. One can modify the chemistry of the process by adding reagents to the electrode compartments, a process known as enhancement.

Actually, the situation is somewhat more complex than our description indicates. There may be movement of ions in fluid flow caused by gradients in the hydraulic head. There is migration of ions in electroosmotic flow—the flow of water induced by an electric field in a porous medium having charged surfaces. There is diffusion transport of ions caused by concentration gradients produced by electrode reactions and by reactions between the various species present (such as H^+ and OH^-). The major factor driving the flux of ionic species through the system, however, is ion migration—the dragging of the ions through the aqueous medium by the electric field.

For fuller descriptions of the theory of the process and the constitutive equations involved, see References 3, 4, and 8.

ANALYSIS

Arsenic(V) provides an example of a contaminant whose removal by electrokinetic migration is enhanced by a base. We examine first the equilibria which are involved, and then briefly recapitulate the handling of the electrokinetic migration described in detail previously (10). A simplified analysis of the use of base in the electrokinetic migration of amphoteric metals such as zinc or lead has been given earlier (11).

The setup of the experiment is as described in our earlier paper (10), and the notation is the same except for some additions. 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, $\text{ohm}^{-1}\cdot\text{cm}^{-1}$
λ_i = molar conductivity of ith ion, $\text{ohm}^{-1}\cdot\text{mol}^{-1}\cdot\text{cm}^3$
z_i = charge number of ith ion, integer

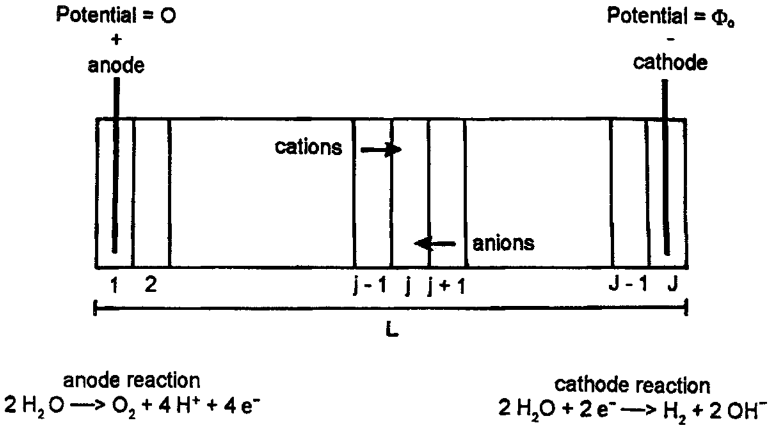

FIG. 1 Schematic of electrokinetic remediation.

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

Equilibration Processes with Arsenic and with Zinc

Arsenic

Arsenic acid, H_3AsO_4, dissociates as follows:

$$H_3AsO_4 \rightarrow H^+ + H_2AsO_4^-$$

$$H_2AsO_4^- \rightarrow H^+ + HAsO_4^{2-}$$

$$HAsO_4^{2-} \rightarrow H^+ + AsO_4^{3-}$$

Its ionization constants are given by Moeller et al. (12) as

$$K_1 = 6.5 \times 10^{-3}$$

$$K_2 = 1.1 \times 10^{-7}$$

$$K_3 = 3 \times 10^{-12}$$

We abbreviate as follows:

$$[H^+] = H$$

$$[OH^-] = OH$$

$$[H_3AsO_4] = H_3A$$

$$[H_2AsO_4^-] = H_2A$$

$$[HAsO_4O^{2-}] = HA$$

$$[AsO_4^{3-}] = A$$

Then

$$H \cdot OH = K_w \tag{1}$$

$$\frac{H \cdot H_2A}{H_3A} = K_1 \tag{2}$$

$$\frac{H \cdot HA}{H_2A} = K_2 \tag{3}$$

$$\frac{H \cdot A}{HA} = K_3 \tag{4}$$

Arsenic acid is sufficiently soluble in water that we do not expect a solid phase. The charge balance equation is

$$\begin{aligned} &\mathrm{H - OH - H_2A - 2HA - 3A} \qquad (5)\\ &= \mathrm{H_0 - OH_0 - H_2A_0 - 2HA_0 - 3A_0 = Ch} \end{aligned}$$

where the subscripts zero on the right-hand side denote the initial concentrations before equilibration. The equation for the conservation of total arsenic is

$$\mathrm{H_3A + H_2A + HA + A = H_3A_0 + H_2A_0 + HA_0 + A_0 = A_{tot}} \qquad (6)$$

Use of Eqs. (2)–(4) in Eq. (6) permits one to obtain

$$\mathrm{H_3A} = \frac{\mathrm{A_{tot}}}{1 + (K_1/\mathrm{H})\{1 + (K_2/\mathrm{H})[1 + (K_3/\mathrm{H})]\}} \qquad (7)$$

Use of Eqs. (2)–(4) yields

$$\mathrm{H_2A} = (K_1/\mathrm{H})\mathrm{H_3A} \qquad (8)$$

$$\mathrm{HA} = (K_1K_2/\mathrm{H}^2)\mathrm{H_3A} \qquad (9)$$

and

$$\mathrm{A} = (K_1K_2K_3/\mathrm{H}^3)\mathrm{H_3A} \qquad (10)$$

Then substitution of Eqs. (7)–(10) into Eq. (5) gives an equation in H alone:

$$\mathrm{Ch} = \mathrm{H} - (K_w/\mathrm{H}) - \frac{\mathrm{A_{tot}}(K_1/\mathrm{H})\{1 + (K_2/\mathrm{H})[2 + 3(K_3/\mathrm{H})]\}}{1 + (K_1/\mathrm{H})\{1 + (K_2/\mathrm{H})[1 + (K_3/\mathrm{H})]\}} \qquad (11)$$

Equation (11) is then solved for H by a simple binary search technique, after which OH, $\mathrm{H_3A}$, $\mathrm{H_2A}$, HA, and A are calculated from Eqs. (1) and (7)–(10). This completes the equilibrium calculations.

Zinc

The equilibria involved in the reactions of Zn(II) with $\mathrm{OH^-}$ are as follows:

$$\mathrm{Zn^{2+} + OH^- \rightarrow Zn(OH)^+}$$

$$\mathrm{Zn(OH)^+ + OH^- \rightarrow Zn(OH)_2(aq)}$$

$$\mathrm{Zn(OH)_2(aq) + OH^- \rightarrow Zn(OH)_3^-}$$

$$\mathrm{Zn(OH)_3^- + OH^- \rightarrow Zn(OH)_4^{2-}}$$

$$\mathrm{Zn(OH)_2(aq) \rightarrow Zn(OH)_2(s)}$$

We abbreviate by letting $OH^- = A$ and omitting charges and parentheses in formulas and brackets in the representation of concentrations. Thus, for example, $[Zn(OH)_3^-]$ is written as ZnA_3. The equilibrium equations for the above reactions are

$$\frac{ZnA}{Zn \cdot A} = K_1 \tag{12}$$

$$\frac{ZnA_2}{ZnA \cdot A} = K_2 \tag{13}$$

$$\frac{ZnA_3}{ZnA_2 \cdot A} = K_3 \tag{14}$$

$$\frac{ZnA_4}{ZnA_3 \cdot A} = K_4 \tag{15}$$

We shall also need the ion product for water.

$$H \cdot A = K_w \tag{16}$$

We set the solubility of un-ionized $Zn(OH)_2$ equal to S. The equilibrium constants for the zinc-hydroxy species were calculated from data given by Smith and Martell (13); they are

$$K_1 = 1 \times 10^5$$

$$K_2 = 2 \times 10^3$$

$$K_3 = 2 \times 10^5$$

$$K_4 = 2.5 \times 10^4$$

and

$$S = 1.3 \times 10^{-8}$$

in mol/L units.

In addition to the equilibrium expressions, we require equations for conservation of charge and of total zinc during the equilibration process; these are

$$2Zn + ZnA - ZnA_3 - 2ZnA_4 + H - A = Ch \tag{17}$$

$$Zn + ZnA + ZnA_2 + ZnA_3 + ZnA_4 + M/V = Zn_{tot} \tag{18}$$

where

$$Ch = 2Zn_0 + ZnA_0 - ZnA_3 - 2ZnA_{40} + H_0 - A_0 \tag{19}$$

and

$$\mathrm{Zn_{tot}} = \mathrm{Zn_0} + \mathrm{ZnA_0} + \mathrm{ZnA_{20}} + \mathrm{ZnA_{30}} + \mathrm{ZnA_{40}} + M_0/V \qquad (20)$$

The subscripts zero denote initial values before equilibration. M refers to the number of moles of solid $\mathrm{Zn(OH)_2}$ present, and V is the volume of water in the system.

We initially assume that solid $\mathrm{Zn(OH)_2}$ is present. The concentration of dissolved $\mathrm{Zn(OH)_2}$ is then equal to S, which, together with the equilibrium expressions Eqs (12)–(16), permit us to write Eq. (17) as

$$2S/(K_1K_2\mathrm{A}^2) + S/(K_2\mathrm{A}) - K_3S\mathrm{A} - 2K_3K_4S\mathrm{A}^2 + K_\mathrm{w}/\mathrm{A} - \mathrm{A} = \mathrm{Ch} \qquad (21)$$

This in turn can be rewritten as

$$S\{K_3\mathrm{A}(1 + 2K_4\mathrm{A}) - (1/K_2\mathrm{A})[1 + 2/(K_1\mathrm{A})]\} - K_\mathrm{w}/\mathrm{A} + \mathrm{A} = -\mathrm{Ch} \qquad (22)$$

the left side of which is a monotonically increasing function of A for positive A and can therefore readily be solved for A (the $\mathrm{OH^-}$ concentration) by the binary search technique.

The remaining concentrations are then given by

$$\mathrm{H} = \mathrm{A}/K_\mathrm{w} \qquad (23)$$

$$\mathrm{ZnA} = S/K_2\mathrm{A} \qquad (24)$$

$$\mathrm{Zn} = \mathrm{ZnA}/K_1\mathrm{A} \qquad (25)$$

$$\mathrm{ZnA_3} = K_3S\mathrm{A} \qquad (26)$$

$$\mathrm{ZnA_4} = K_4\mathrm{ZnA_3A} \qquad (27)$$

The quantity of solid $\mathrm{Zn(OH)_2}$ present at equilibrium is then given from Eq. (20) as

$$M = V(\mathrm{Zn_{tot}} - \mathrm{Zn} - \mathrm{ZnA} - \mathrm{ZnA_2} - \mathrm{ZnA_3} - \mathrm{ZnA_4}) \qquad (28)$$

If $M \geq 0$, the calculation of the equilibrium concentrations is complete.

If $M < 0$, one proceeds as follows. Set $M = 0$, so Eq. (18) becomes

$$\mathrm{Zn} + \mathrm{ZnA} + \mathrm{ZnA_2} + \mathrm{ZnA_3} + \mathrm{ZnA_4} = \mathrm{Zn_{tot}} \qquad (29)$$

Use of the equilibrium expressions Eqs. (12)–(15) then permits us to obtain

$$\mathrm{Zn} = \frac{\mathrm{Zn_{tot}}}{1 + K_1\mathrm{A}\{1 + K_2\mathrm{A}[1 + K_3\mathrm{A}(1 + K_4\mathrm{A})]\}} \qquad (30)$$

Use of the equilibrium expressions and Eq. (30) in Eq. (17) then yields an equation for A which after rearrangement can be written as

$$-\frac{\mathrm{Zn_{tot}}\{2 + K_1\mathrm{A}[1 - K_2K_3\mathrm{A}^2(1 + 2K_4\mathrm{A})]\}}{1 + K_1\mathrm{A}\{1 + K_2\mathrm{A}[1 + K_3\mathrm{A}(1 + K_4\mathrm{A})]\}} - K_w/\mathrm{A} + \mathrm{A} = -\mathrm{Ch} \tag{31}$$

This is solved by the binary search technique for A, H is given by K_w/A, Zn is calculated from Eq. (30), and Eqs. (12)–(15) are then used to calculate ZnA, ZnA_2, ZnA_3, and ZnA_4. This completes the calculation.

Electrode Potentials

The half-cell reaction at the cathode is

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

and the anode half-cell 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 are unity. Use of the Nernst equation and these half-reactions then yields the following expression for the electric potential drop resulting from the electrode processes as

$$E = -2.057 + 0.0592\{\log_{10}[H^+]_{\text{cathode}} - \log_{10}[H^+]_{\text{anode}}\} \text{ volts} \tag{32}$$

The effective potential which drives the electromigration process is then given by

$$\phi_{\text{eff}} = \phi_{\text{appl}} - E \tag{33}$$

Electrokinetic Migration

A number of the molar conductances needed for these calculations were unavailable, so were estimated from the tabulated values for similar ions. Fortunately, the range of values for ions of any given charge is not large, so the effect of these uncertainties on our calculations should be small. The molar conductance values used in the calculations are given in Table 1; estimated values are indicated by an asterisk (*).

The analysis of the movement of the various ions present under the influence of the effective potential difference ϕ_{eff} is as follows.

TABLE 1
Molar Conductance Values Used in the Calculations

Species	Molar conductance ($\text{ohms}^{-1}\cdot\text{cm}^2\cdot\text{mol}^{-1}$)
H^+	349.8
OH^-	197.6
Na^+	50.1
SO_4^{2-}	160
$H_2AsO_4^-$	55*
$HAsO_4^{2-}$	160*
AsO_4^{3-}	240*
Zn^{2+}	105.6
$Zn(OH)^+$	50*
$Zn(OH)_3^-$	40*
$Zn(OH)_4^{2-}$	150*

The specific conductance of the jth volume element is

$$\kappa_j = \sum_{i=1}^{n} \lambda_i c_{ij} \tag{34}$$

The resistance of the jth volume element is then

$$R_j = (1/A\omega)\left[\sum_{i=1}^{n} \lambda_i c_{ij}\right]^{-1} \tag{35}$$

The total resistance of the column is the sum of these resistances,

$$R = \sum_{j=1}^{J} R_j = (1/A\omega)\sum_{j=1}^{J}\left[\sum_{i=1}^{n} \lambda_i c_{ij}\right]^{-1} \tag{36}$$

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

$$I = \phi_{\text{eff}}/R \tag{37}$$

(Note that I here is negative, since our convention is that ϕ_{eff} is negative.)

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

$$\kappa_{j-1,j} = \sum_{i=1}^{n} \lambda_i[c_{i,j-1}S(z_i)S(c_{i,j-1}) + c_{i,j}S(-z_i)S(c_{ij})] \tag{38}$$

where

$$S(x) = 0, \quad x \leq 0$$

$$S(x) = 1, \quad x > 0$$

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

$$f^k_{j-1,j} = \frac{\lambda_k[c_{k,j-1}S(z_k)S(c_{k,j-1}) + c_{k,j}S(-z_k)S(c_{k,j})]}{\sum_{i=1}^{n} \lambda_i[c_{i,j-1}S(z_i)S(c_{i,j-1}) + c_{i,j}S(-z_i)S(c_{i,j})]} \tag{39}$$

The rate of migration of the kth ion into ΔV_j is then

$$F^k_{j-1,j} = (-I/Fz_i)f^k_{j-1,j}) \tag{40}$$

or

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

In similar fashion one obtains Eq. (41) for the rate of migration of the kth ion into the jth volume element from the $(j + 1)$th volume element.

$$F^k_{j+1,j} = \frac{-(I/Fz_k)\lambda_k[c_{k,j}S(z_k)S(c_{k,j}) + c_{k,j+1}S(-z_k)S(c_{k,j+1})]}{\sum_{i=1}^{n} \lambda_i[c_{i,j}S(z_i)S(c_{i,j}) + c_{i,j+1}S(-z_i)S(c_{i,j+1})]} \tag{41}$$

A mass balance for the kth ion in ΔV_j then gives

$$Al\omega \frac{dc_{kj}}{dt} = F^k_{j-1,j} + F^k_{j+1,j} \tag{42}$$

for $j = 2, 3, \ldots, J - 1$. Let the indices 1 and 2 correspond to H^+ and OH^-, respectively. For $j = 1$ we have

$$Al\omega \frac{dc_{k1}}{dt} = F^k_{2,1} \tag{43}$$

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

$$Al\omega \frac{dc_{11}}{dt} = F^1_{2,1} + |I|/F \tag{44}$$

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

$$Al\omega \frac{dc_{kJ}}{dt} = F^k_{J-1,J} \tag{45}$$

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

$$Al\omega \frac{dc_{2J}}{dt} = F^2_{J-1,J} + |I|/F \tag{46}$$

for OH^-. The term $|I|/F$ is added to Eqs. (44) and (46) to represent the electrochemical generation of H^+ and OH^+ at the anode and cathode.

We shall be interested in enhanced electrokinetic remediation in which the H^+ generated electrolytically at the anode is at least partially neutralized by the addition of sodium hydroxide. If a fraction p of the H^+ is neutralized, then Eq. (44) becomes

$$Al\omega \frac{dc_{11}}{dt} = F^1_{2,1} + (1 - p)|I|/F \tag{47}$$

Let the index $k = 3$ for Na^+. Then with the addition of sodium hydroxide we have

$$Al\omega \frac{dc_{31}}{dt} = F^3_{2,1} + p|I|/F \tag{48}$$

where the last term takes into account the added sodium ion.

The differential equations for describing the changes in the concentrations in the various volume elements due to electromigration and the prescription for calculating the equilibrium concentrations then constitute the model.

RESULTS

The models described above were implemented in TurboBASIC and run on MMG 386 SX and 386 DX computers equipped with math coprocessors and operating at 16 and 33 MHz, respectively. Use of the method of doing the equilibrium calculations described above makes unnecessary the tedious coding of the lengthy "stoichiometry trees" employed in our earlier programs to permit the use of approximations in the equilibrium calculations; this change actually seems to shorten the calculation times somewhat. In both the arsenic and the zinc calculations the domain being treated was partitioned into 16 volume elements, of which the two at either end were regarded as the anode/cathode compartment and its immediate surroundings, and the 12 other volume elements were regarded as the soil being treated. In all runs a reduced total number of moles of contaminant in all species in these 12 volume elements was plotted as a function of the time. This reduced mole number is given by the total number of moles of contaminant in these volume elements at time t divided by the total number of moles of contaminant in them initially.

TABLE 2
Default Parameters for the Electrokinetic Removal of As(V)

Length of soil bed	100 cm
Depth of soil bed	10 cm
Width of soil bed	10 cm
Soil porosity	0.4
Number of slabs into which soil bed is divided	16
Percent of H^+ at anode to be neutralized	25%
Applied voltage	−100 V
Duration of run	5 days
dt	1800 seconds

Arsenic

The default parameters for the runs simulating the base-enhanced electrokinetic removal of As(V) are given in Table 2. Other parameter values are given in the captions to the figures.

Figure 2 shows the effect of the percent of the H^+ generated at the anode which is neutralized by addition of NaOH to the anode compartment. In these runs all of the As(V) is initially present as H_3AsO_4. From the top down, the curves correspond to 5, 10, 15, 20, and 25% neutralization. In these base-enhanced systems the contaminated soil is swept by OH^- ion,

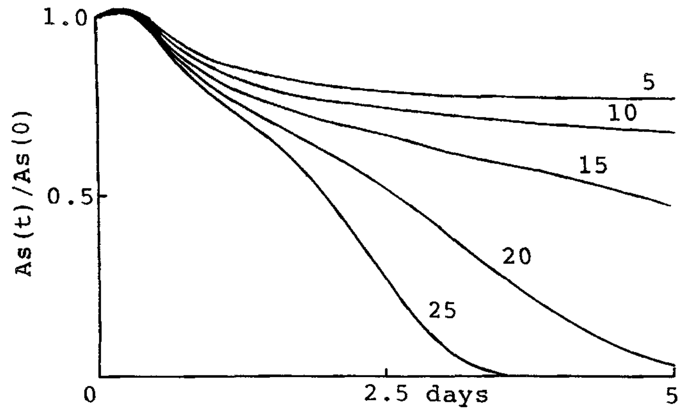

FIG. 2 Plots of total residual As(V) versus time; effect of percent neutralization of the H^+ generated at the anode. From top to bottom, percent H^+ neutralized = 5, 10, 15, 20, and 25%. Initial concentrations; $[Na^+]$ 0.001, $[SO_4^{2-}]$ 0.0005, $[H_3AsO_4]$ 0.0005, $[H^+]$ 10^{-7}, $[OH^-]$ 10^{-7} mol/L; other concentrations zero.

in contrast to the acid-enhanced systems described earlier (10, 11) in which the soil is swept by H^+. As before, however, increasing the concentration of the enhancing reagent results in large increases in the removal rate of the contaminant, here As(V). The slight increases in total arsenic seen at the beginnings of the runs are associated with an imbalance between the initial migration rates of As(V) away from the cathode and toward the anode. In the acidic region in the vicinity of the anode, As(V) is likely to have a less negative charge, and therefore to migrate more slowly, than in the alkaline region in the vicinity of the cathode. Migration of As(V) into the anode compartment is therefore expected to be initially slower than migration of As(V) out of the cathode compartment, resulting in the observed maxima.

In the runs plotted in Fig. 3 the effect of the initial speciation of As(V) on the rate of remediation is explored. In all the runs plotted in Fig. 3 the percent neutralization of the acid generated in the anode compartment is 25%. From right to left, the initial As(V) is present as H_3AsO_4, $H_2AsO_4^-$, $HAsO_4^{2-}$, and AsO_4^{3-}. As expected, the more highly ionized

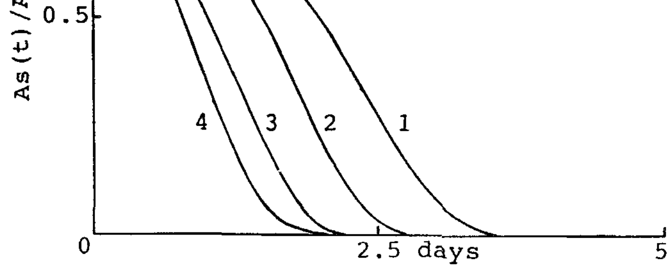

FIG. 3 Plots of total residual As(V) versus time; effect of the identity of the initial As(V) species. Percent neutralization of H^+ generated in the anode compartment = 25%. Initial $[H^+] = 10^{-7}$, initial $[OH^-] = 10^{-7}$. Other initial concentrations as follows. Curve 1: $[Na^+]$ 0.001, $[SO_4^{2-}]$ 0.0005, $[H_3AsO_4]$ 0.0005 mol/L, others zero. Curve 2: $[Na^+]$ 0.0015, $[SO_4^{2-}]$ 0.0005, $[H_2AsO_4^-]$ 0.0005, others zero. Curve 3: $[Na^+]$ 0.002, $[SO_4^{2-}]$ 0.0005, $[HAsO_4^{2-}]$ 0.0005, others zero. Curve 4: $[Na^+]$ 0.0025, $[SO_4^{2-}]$ 0.0005, $[AsO_4^{3-}]$ 0.0005, others zero.

the As(V) is initially, the more rapidly is it removed. If the As(V) is unionized, it cannot migrate until sufficient OH^- has been generated and has moved to where the As(V) can be converted into negative ions. Furthermore, the larger the negative charge on the As(V) anions, the larger their ionic conductivity.

The simulations indicate that base-enhanced electrokinetic remediation should be quite effective for the removal of As(V) from saturated contaminated soils. We note, however, that the results may be much less favorable if there are appreciable concentrations of cations which are not precipitated out by OH^- or tied up as hydroxy complexes so that they are available to form insoluble arsenates. This approach should also be suitable for the removal of selenium in anionic forms and of fluoride.

Zinc

The default parameters for the runs simulating the base-enhanced electrokinetic removal of Zn(II) are given in Table 3. Departures from these values are given in the captions to the figures.

Figure 4 shows runs in which the percentage of the H^+ generated at the anode which is neutralized is 20, 22.5, 25, 27.5, and 30%, from the top down. The cleanup times decrease very markedly with increasing percent neutralization; here cleanup for the run in which 20% of the H^+ is neutralized is nowhere nearly complete even after 10 days, while cleanup for the run in which 30% is neutralized is complete after 5 days.

These runs and those in Fig. 5 show quite substantial maxima; during the initial phase of a run the total Zn(II) in the domain of interest (volume elements 3 through 14) increases quite markedly above its initial value.

TABLE 3
Default Parameters for the Electrokinetic Removal of Zn(II)

Length of soil bed	100 cm
Depth of soil bed	10 cm
Width of soil bed	10 cm
Soil porosity	0.4
Number of slabs into which soil bed is divided	16
Initial concentration of solid $Zn(OH)_2$, mol/L of soil	0.0005
Percent of H^+ neutralized at anode	25%
Applied voltage	−100 V
Duration of run	10 days
dt	900 seconds

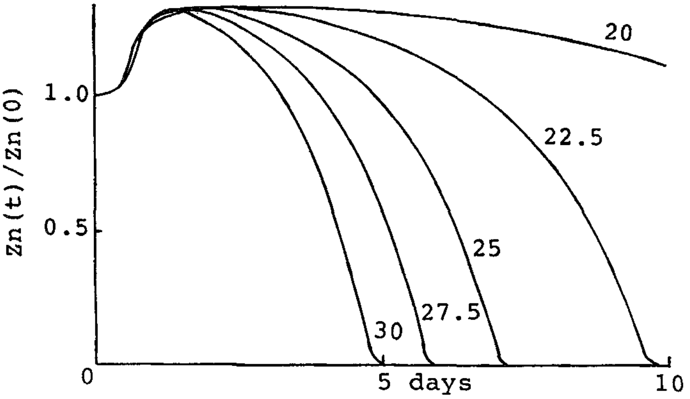

FIG. 4 Plots of total residual Zn(II) versus time; effect of percent neutralization of H^+ generated in the anode compartment. Initial concentration of solid $Zn(OH)_2$ = 0.0005 mol/L of medium. Initial aqueous concentrations: $[H^+]$ 10^{-7}, $[OH^-]$ 10^{-7}, $[Na^+]$ 0.002, $[SO_4^{2-}]$ 0.0005, $[Zn(OH)_4^{2-}]$ 0.0005 mol/L. Percent neutralization of H^+ generated in anode compartment = 20, 22.5, 25, 27.5, and 30%, from top to bottom.

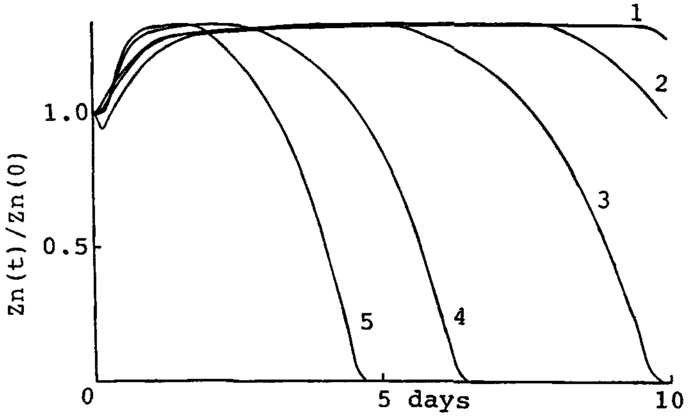

FIG. 5 Plots of total residual Zn(II) versus time; effect of the identity of the initial Zn(II) species. Percent neutralization of H^+ generated in the anode compartment = 25%. Initial $[H^+]$ = 10^{-7}, initial $[OH^-]$ = 10^{-7}. Initial concentration of solid $Zn(OH)_2$ = 0; other initial concentrations (mol/L) as follows. Curve 1: $[Na^+]$ 0.001, $[SO_4^{2-}]$ 0.001, $[Zn^{2+}]$ 0.0005, others zero. Curve 2: $[Na^+]$ 0.001, $[SO_4^{2-}]$ 0.00075, $[Zn(OH)^+]$ 0.0005, others zero. Curve 3: $[Na^+]$ 0.001, $[SO_4^{2-}]$ 0.0005, $[Zn(OH)_2(aq)]$ 0.0005, others zero. Curve 4: $[Na^+]$ 0.0015, $[SO_4^{2-}]$ 0.0005, $[Zn(OH)_3^-]$ 0.0005, others zero. Curve 5: $[Na^+]$ 0.002, $[SO_4^{2-}]$ 0.0005, $[Zn(OH)_4^{2-}]$ 0.0005, others zero.

The explanation is as follows. In the initial phase Zn^{2+} migrates from the acidic anode compartment into the domain of interest until it is immobilized as solid $Zn(OH)_2$; and anionic zinc hydroxy complexes migrate from the alkaline cathode compartment into the domain of interest until they are immobilized in the form of $Zn(OH)_2$ as the alkalinity decreases. It is then impossible for movement of Zn(II) into the anode compartment to take place until the advancing front of OH^- has moved across the domain of interest, at which point Zn(II) is dissolved as anionic complexes which can then migrate to the anode compartment.

Figure 5 shows the effect of the initial Zn(II) species which is present in the domain of interest. From bottom to top, the initial species is $Zn(OH)_4^{2-}$, $Zn(OH)_3^-$, $Zn(OH)_2$, $Zn(OH)^+$, and Zn^{2+}. Evidently cleanup is progressively more and more impeded the larger the quantity of OH^- which is needed to convert the Zn(II) into anionic forms which can be swept to the anode compartment by the electric field.

At first glance there appears to be no particular advantage to use base-enhanced electrokinetic migration rather than acid-enhanced treatment if one is dealing with amphoteric metals such as zinc or lead. Weak, nontoxic acids such as acetic acid are available for acid-enhanced treatment. On the other hand, strong bases such as NaOH involve hazards similar to those associated with strong acids, and the only readily available weak base, ammonia, is relatively toxic. However, if one is dealing with a medium rich in calcium carbonate, the capacity of the $CaCO_3$ for neutralizing acid may be quite large, resulting in high costs for reagent and power and in prolonged cleanup times. In such a case the use of base-enhanced electromigration provides a remedial option if the toxic metals are amphoteric.

REFERENCES

1. J. E. McLean and B. E. Bledsoe, "Behavior of Metals in Soils," *EPA Ground Water Issue* (US EPA Report EPA/540/S-92/018), October 1992.
2. R. A. Freeze and J. A. Cherry, *Groundwater*, Prentice-Hall, Englewood Cliffs, NJ, 1979, Ch. 3.
3. Y. B. Acar and A. N. Alshawabkeh, "Principles of Electrokinetic Remediation," *Environ. Sci. Technol.*, *27*, 2638 (1993).
4. Y. B. Acar, A. N. Alshawabkeh, and R. J. Gale, "Fundamentals of Extracting Species from Soils by Electrokinetics," *Waste Manage.*, *13*, 141 (1993).
5. Y. Acar, "Clean Up with Kilowatts," *Soils*, p. 38 (October 1993).
6. D. Cabrera-Guzman, J. T. Swartzbaugh, and A. W. Weisman, "The Use of Electrokinetics for Hazardous Waste Site Remediation," *J. Air Waste Manage. Assoc.*, *40*, 1670 (1990).
7. R. Lageman, "Electroreclamation: Applications in the Netherlands," *Environ. Sci. Technol.*, *27*, 2648 (1993).

8. J. Hamed, Y. B. Acar, and R. J. Gale, "Pb(II) Removal From kaolinite by Electrokinetics," *J. Geotech. Eng.*, *117*, 241 (1991).
9. D. D. Runnels and J. L. Larson, "A Laboratory Study of Electromigration as a Possible Field Technique for the Removal of Contaminants from Ground Water," *Ground Water Monit. Rev.*, pp. 81–91 (Summer 1986).
10. D. J. Wilson, J. M. Rodríguez-Maroto, and C. Gómez-Lahoz, "Electrokinetic Remediation. I. Modeling of Simple Systems," *Sep. Sci. Technol.*, *30*, 2937 (1995).
11. D. J. Wilson, J. M. Rodríguez-Maroto, and C. Gómez-Lahoz, "Electrokinetic Remediation. II. Amphoteric Metals and Enhancement with a Weak Acid," *Ibid.*, *30*, 3111 (1995).
12. T. Moeller, J. C. Bailar Jr., J. Kleinberg, C. O. Guss, M. E. Castellion, and C. Metz, *Chemistry with Inorganic Qualitative Analysis*, 2nd ed., Academic Press, Orlando, FL, 1984.
13. R. A. Smith and A. E. Martell, *Critical Stability Constants*, Vol. 4, Plenum Press, New York, 1976.

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