Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Electrokinetic Remediation. II. Amphoteric Metals and Enhancement with a Weak Acid

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

To cite this Article Wilson, David J. , Rodríguez-Maroto, José Miguel and Gómez-Lahoz, César(1995) 'Electrokinetic Remediation. II. Amphoteric Metals and Enhancement with a Weak Acid', Separation Science and Technology, 30: 16, 3111 — 3128

To link to this Article: DOI: 10.1080/01496399508013133

URL: http://dx.doi.org/10.1080/01496399508013133

SEPARATION SCIENCE AND TECHNOLOGY, **30**(16), pp. 3111–3128, 1995

Electrokinetic Remediation. II. Amphoteric Metals and Enhancement with a Weak Acid

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 the electrokinetic treatment of aquifers contaminated with an ionic salt. Electrokinetic removal of amphoteric metals such as zinc and lead is simulated. The use of a weak acid (acetic acid) to neutralize a portion of the OH^- generated electrolytically in the cathode compartment is explored in connection with the electrokinetic removal of nonamphoteric metals such as copper and cadmium.

INTRODUCTION

The removal of toxic metals from aquifers by pump-and-treat methods is generally limited by difficulties in mobilizing the metal ions, which may be dispersed in porous structures of low permeability (clay, silt, or till lenses and layers), adsorbed/ion exchanged on clays or natural soil organic matter, or present as slightly soluble solids—hydroxides, hydrous oxides, or carbonates. Discussions of the behavior of metals in soils have been given, for example, by McLean and Bledsoe (1) and by Freeze and Cherry (2).

An innovative technology which shows promise for the removal of toxic ionic compounds from contaminated aquifers is electrokinetic remediation. The technique has been described and 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 electrokinetic remediation technique for EPA; they noted that the technique shows promise for removing inorganics from fine-grained soils, a difficult, if not impossible, task for other methods. Lageman (7) described several electrokinetic remediation projects in the Netherlands; toxics removed included lead, copper, zinc, cadmium, and arsenate. Hamad, Acar, and Gale discussed the theory of electrokinetic remediation and presented a study of its use in removing Pb(II) from kaolinite (8). We have described a mathematical model for the enhanced electrokinetic removal of nonamphoteric divalent metals (9).

In principle, the technique is quite simple. Electrodes (generally inert) are placed in the contaminated zone of the aquifer and an applied potential generates a direct current between them. Cations, under the influence of the electric field, migrate toward the negative electrode, where (usually) OH^- ion is formed and hydrogen is liberated by the electrolytic reduction of water. Anions move 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 move 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 one must consider 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.

In fact, the situation is more complex than our description above indicates. There may be movement of ions in fluid flow resulting from gradients in hydraulic head. There is migration of ions in electroosmotic flow—the flow of water induced by an electric field in a porous medium having a charged surface. There is 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^-). The major factor contributing to 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 Ref. 3, 4, or 8.

In our previous paper (9) we analyzed the electrokinetic removal of a nonamphoteric ion such as Cd(II) or Cu(II) which forms an insoluble hydroxide. The process was enhanced by the partial or complete neutralization of the OH^- generated in the cathode compartment by the addition of H_2SO_4. One can anticipate, however, that the use of H_2SO_4 as an enhancing reagent would meet with serious and justified opposition from regulatory agencies and the public. There is little reason, aside from computational complexity, not to replace sulfuric acid with acetic acid, which is present in many foodstuffs and is biodegradable. We therefore model here the electrokinetic removal of a divalent nonamphoteric metal (Cd^{2+}) by means of a system in which acetic acid is added to the cathode compartment of the system as an enhancing reagent.

The modeling of electrokinetic remediation is made more complex if the metal is amphoteric (Zn, Pb, Al, for example), so that anionic hydroxy complexes must be taken into consideration. The second problem addressed in this paper is the modeling of the electrokinetic removal of Zn(II) with the use of sulfuric acid as an enhancing reagent.

ANALYSIS

The setup of the experiment is as described in our earlier paper (9), and the notation is the same except for some additions. See Fig. 1.

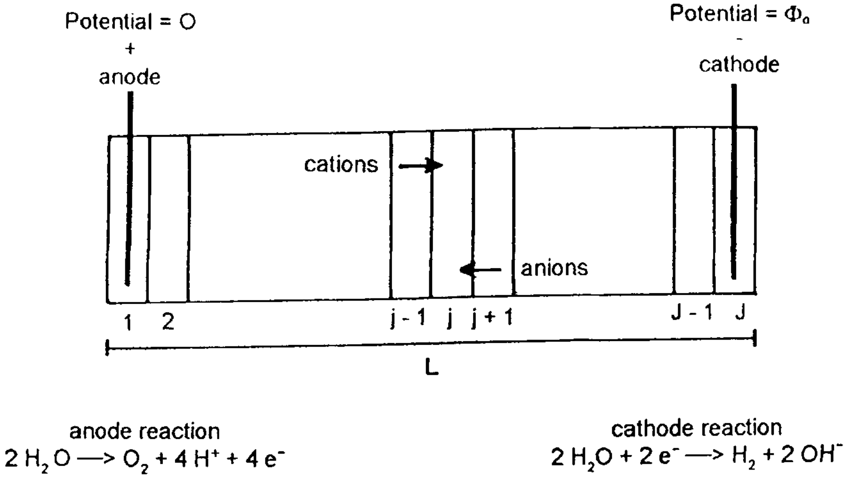

FIG. 1 Schematic diagram of a one-dimensional column configuration for electrokinetic remediation.

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, $ohm^{-1} \cdot cm^{-1}$
λ_i = molar conductivity of ith ion, $ohm_{-1} \cdot mol^{-1} \cdot cm^2$
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

Electrode Reactions

The half-reaction at the cathode is

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

The anode half-reaction is

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

As before, 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 equal to unity. As shown earlier, 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

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

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. We shall assume that the applied voltage is sufficiently large (about 100 V or so in our calculations) that we can neglect the voltage drop due to the electrode reactions.

Electrokinetic Migration

The handling of the electrokinetic migration of the ions in our models here is exactly the same as was used in our earlier work (9) and will not be duplicated here; the reader is referred to Eqs. (1)–(14) and (26)–(29) of that paper.

CHEMISTRY

Removal of Cadmium with Acetic Acid as the Enhancing Reagent

We first list the chemical reactions which are presumed to be at equilibrium during the course of electrokinetic remediation. This is followed by a decision tree which is used to determine the correct initial conditions for doing the equilibrium calculations. The section closes with descriptions of the various cases for which equilibrium calculations must be made in the course of the modeling.

The chemical equilibria involved in the system are as follows:

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

$$HOAc \Leftrightarrow H^+ + OAc^-$$

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

The corresponding equilibrium expressions are

$$[H^+][OH^-] = K_w = 10^{-14}$$

$$\frac{[H^+][OAc^-]}{[HOAc]} = K_a = 1.8 \times 10^{-5}$$

$$[Cd^{2+}][OH^-]^2 = K_{sp} = 2 \times 10^{-14}$$

In addition to these, we shall have equations for the conservation of acetate, cadmium, and total charge during the equilibration process.

We focus on a single volume element containing a volume V of aqueous solution. Initial concentrations of solutes and mole number of $Cd(OH)_2$, all calculated after a time increment in which one considers only electrokinetic migration, are as follows:

$$[H^+] = H_0$$

$$[OH^-] = OH_0$$

$$[HOAc] = HA_0$$

$$[OAc^-] = A_0$$

$$[Cd^{2+}] = Cd_0$$

$$\text{Moles solid } Cd(OH)_2 = M_0$$

We next construct a stoichiometry tree in which at each level we assume that the reaction between the strongest remaining acid and the strongest

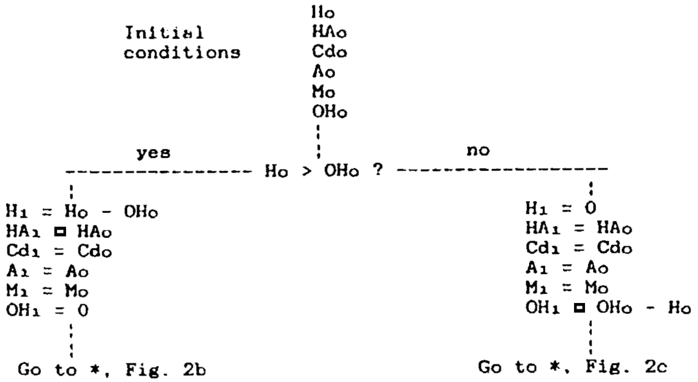

FIG. 2a Decision tree for Cd–HOAc, first branch.

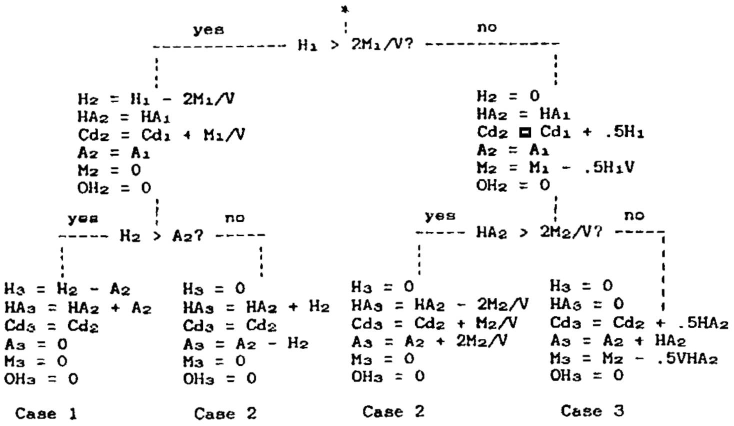

FIG. 2b Continuation of decision tree for Cd–HOAc, second branch.

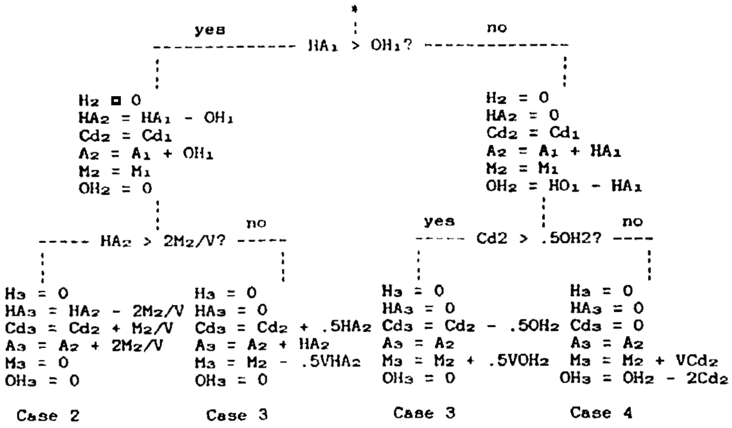

FIG. 2c Continuation of decision tree for Cd–HOAc, third branch.

remaining base goes to completion. At any level the concentrations are labeled with the number of branches needed to reach that level in the tree. The tree is shown in Figs. 2a, 2b, and 2c. Working down the tree from the initial conditions leads us to one of four possible cases for the equilibrium calculations, each of which splits into two options, depending upon whether solid $Cd(OH)_2$ is or is not present at equilibrium.

The calculations for the four cases are quite similar. We let H, HA, Cd, A, and OH be the concentrations at equilibrium, and M be the number of moles of solid $Cd(OH)_2$ which is present at equilibrium. Then we have

$$\mathrm{H{\cdot}OH} = K_\mathrm{w} \tag{1}$$

$$\mathrm{H{\cdot}A/HA} = K_\mathrm{a} \tag{2}$$

$$\mathrm{Cd{\cdot}OH}^2 = K_\mathrm{sp} \tag{3}$$

as our equilibrium equations,

$$\mathrm{HA} + \mathrm{A} = \mathrm{HA}_3 + \mathrm{A}_3 \tag{4}$$

for conservation of acetate,

$$\mathrm{Cd} + \mathrm{M}/V = \mathrm{Cd}_3 + \mathrm{M}_3/V \tag{5}$$

for conservation of cadmium, and

$$2\mathrm{Cd} + \mathrm{H} - \mathrm{A} - \mathrm{OH} = 2\mathrm{Cd}_3 + \mathrm{H}_3 - \mathrm{A}_3 - \mathrm{OH}_3 \tag{6}$$

for conservation of charge during the equilibration process. The values of H_3, HA_3, etc. are taken from the appropriate point at the bottom of the tree; of the eight possibilities, four are distinct.

One then makes the assumption that $M \geq 0$, and substitutes Eqs. (1)–(4) into Eq. (6) to obtain an equation for the cadmium concentration, Cd:

$$\begin{aligned} 2\mathrm{Cd} + K_\mathrm{w}(\mathrm{Cd}/K_\mathrm{sp})^{1/2} - \frac{(\mathrm{A}_3 + \mathrm{HA}_3)K_\mathrm{a}}{K_\mathrm{a} + K_\mathrm{w}(\mathrm{Cd}/K_\mathrm{sp})^{1/2}} \\ - (K_\mathrm{sp}/\mathrm{Cd})^{1/2} - 2\mathrm{Cd}_3 - \mathrm{H}_3 + \mathrm{OH}_3 + \mathrm{A}_3 = 0 \end{aligned} \tag{7}$$

The left-hand side of this equation is a monotonically increasing function of Cd, with a single positive root; it is readily solved by a simple binary search technique.

The number of moles of solid $Cd(OH)_2$ present is obtained from Eq. (5); it is

$$\mathrm{M} = \mathrm{M}_3 + V(\mathrm{Cd}_3 - \mathrm{Cd}) \tag{8}$$

If $M \geq 0$, then

$$\mathrm{OH} = (K_\mathrm{sp}/\mathrm{Cd})^{1/2} \tag{9}$$

$$H = K_w/OH \tag{10}$$

$$HA = \frac{H(HA_3 + A_3)}{K_a + H} \tag{11}$$

$$A = K_a \cdot HA/H \tag{12}$$

and the calculation is complete.

If M < 0, the assumption that solid $Cd(OH)_2$ is present at equilibrium is incorrect, and we have

$$M = 0 \tag{13}$$

$$Cd = Cd_3 + \frac{M_3}{V} \tag{14}$$

The charge balance equation can then be written in terms of H as

$$H - \frac{K_w}{H} - \frac{(HA_3 + A_3)}{(H/K_a + 1)} + \frac{2M_3}{V} - H_3 + A_3 + OH_3 = 0 \tag{15}$$

The left-hand side of this equation is a monotonically increasing function of H with a single positive root which we obtain by the binary search technique. M and Cd are given above; the other concentrations are given by

$$OH = K_w/H \tag{16}$$

$$HA = \frac{H(HA_3 + A_3)}{K_a + H} \tag{17}$$

$$A = K_a \cdot HA/H \tag{18}$$

This completes the calculation.

It should be noted that the use of a stoichiometry tree to get the correct initial conditions for the equilibrium calculations is unnecessary if one uses the exact equilibrium equations (i.e., no approximations are made). In our calculations here this is due to the fact that

$$HA + A = HA_3 + A_3 = HA_0 + A_0 \tag{4'}$$

for conservation of acetate,

$$Cd + M/V = Cd_3 + M_3/V = Cd_0 + M_0/V \tag{5'}$$

for conservation of cadmium, and

$$\begin{aligned} 2\mathrm{Cd} + \mathrm{H} - \mathrm{A} - \mathrm{OH} &= 2\mathrm{Cd}_3 + \mathrm{H}_3 - \mathrm{A}_3 - \mathrm{OH}_3 \\ &= 2\mathrm{Cd}_0 + \mathrm{H}_0 - \mathrm{A}_0 - \mathrm{OH}_0 \end{aligned} \tag{6'}$$

for conservation of charge during both the initial stoichiometric reactions and the final equilibration process, so that the initial concentrations could be used. Frequently, however, such equilibrium calculations are carried out approximately, with reactions which are of little importance being ignored until the calculations are nearly complete. In such cases the use of a stoichiometry tree is helpful in determining which reactions must be taken into account and which can be neglected until the final stages of the calculations.

Removal of Zinc with Sulfuric Acid as the Enhancing Reagent

As before, we first list the chemical reactions which are presumed to be at equilibrium during the course of electrokinetic remediation. This is followed by a decision tree based on the stoichiometry of the reactions which is used to determine the correct initial conditions for doing the equilibrium calculations. The section closes with descriptions of the various cases for which equilibrium calculations must be made in the course of the modeling.

The chemical equilibria involved in the system are as follows:

$$\mathrm{H_2O} \Leftrightarrow \mathrm{H^+} + \mathrm{OH^-}$$

$$\mathrm{Zn(OH)_2} \Leftrightarrow \mathrm{Zn^{2+}} + 2\mathrm{OH^-}$$

$$\mathrm{H_2O} + \mathrm{HZnO_2^-} \Leftrightarrow \mathrm{Zn^{2+}} + 3\mathrm{OH^-}$$

The equilibrium equations are

$$[\mathrm{H^+}][\mathrm{OH^-}] = K_w = 10^{-14} \tag{19}$$

$$[\mathrm{Zn^{2+}}][\mathrm{OH^-}] = K_{sp} = 5 \times 10^{-17} \tag{20}$$

$$\frac{[\mathrm{Zn^{2+}}][\mathrm{OH^-}]^3}{[\mathrm{HZnO_2^-}]} = K_{in} = 5 \times 10^{-14} \tag{21}$$

In addition to these equations we shall have conservation equations for Zn and the charge which must be satisfied during the process of equilibration.

As before, we focus on a single volume element containing a volume V of solution. Initial concentrations of solutes and mole number of solid

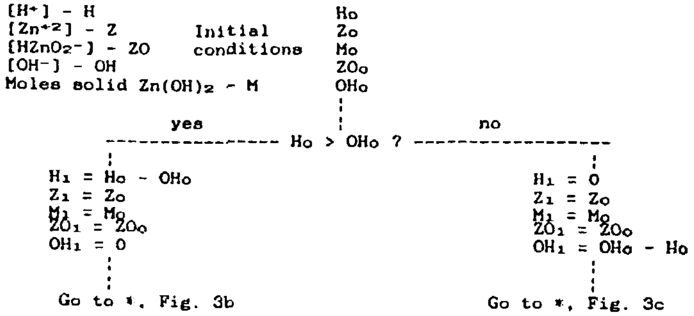

FIG. 3a Decision tree for Zn^{2+}–$Zn(OH)_2$–$HZnO_2^-$, first branch.

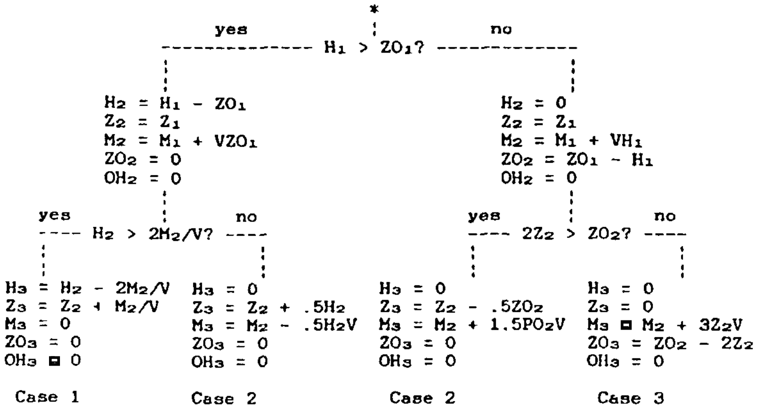

FIG. 3b Continuation of decision tree for Zn^{2+}–$Zn(OH)_2$–$HZnO_2^-$, second branch.

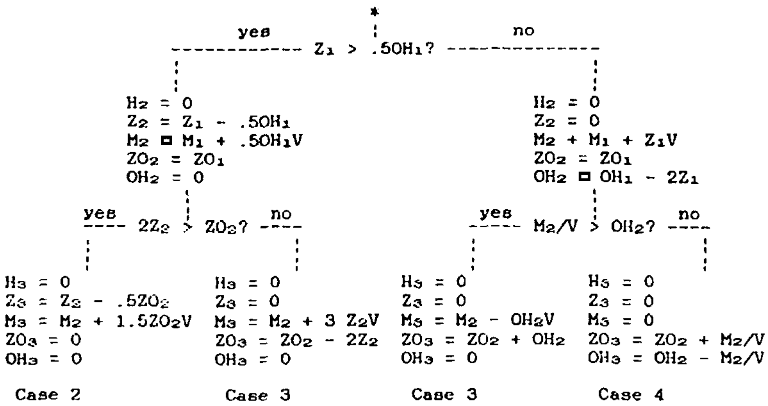

FIG. 3c Continuation of decision tree for Zn^{2+}–$Zn(OH)_2$–$HZnO_2^-$, third branch.

$Zn(OH)_2$ (all calculated after a time increment in which only electrokinetic migration is considered) are as follows:

$$[H^+] = H_0$$

$$[OH^-] = OH_0$$

$$[Zn^{2+}] = Z_0$$

$$[HZnO_2^-] = ZO_0$$

$$\text{Moles solid } Zn(OH)_2 = M_0$$

We next construct the stoichiometry tree in which at each level the reaction between the strongest remaining acid and the strongest remaining base goes to completion. At any level the concentrations are labeled with the number of branches needed to reach that level in the tree. The tree is shown in Figs. 3a, 3b, and 3c. As before, working down the tree from the initial conditions leads to one of four possible cases for the equilibrium calculations, each of which splits into two options, depending upon whether solid $Zn(OH)_2$ is or is not present at equilibrium.

In our abbreviated notation the equilibrium equations are

$$H\cdot OH = K_w \tag{22}$$

$$Z\cdot OH^2 = K_{sp} \tag{23}$$

$$Z\cdot OH^3/ZO = K_{in} \tag{24}$$

The conservation equation for zinc is

$$Z + ZO + M/V = Z_3 + ZO_3 + M_3/V \tag{25}$$

and the conservation of charge equation is

$$2Z + H - ZO - OH = 2Z_3 + H_3 - ZO_3 - OH_3 \tag{26}$$

Substitution of Eqs. (22)–(24) in Eq. (26) and rearrangement leads to the following equation for Z, the zinc ion concentration:

$$\begin{aligned} 2Z + K_w(Z/K_{sp})^{1/2} - (K_{sp}/K_{in})(K_{sp}/Z)^{1/2} \\ - (K_{sp}/Z)^{1/2} - 2Z_3 - H_3 + ZO_3 + OH_3 = 0 \end{aligned} \tag{27}$$

This is solved for Z by the binary search technique. ZO is then given by

$$ZO = K_{sp}^{3/2}/(K_{in}Z^{1/2}) \tag{28}$$

Then the quantity of solid $Zn(OH)_2$ present is calculated from

$$M = M_3 + V(Z_3 - Z + ZO_3 - ZO) \tag{29}$$

If $M \geq 0$, then

$$OH = (K_{sp}/Z)^{1/2} \tag{30}$$

$$H = K_w/OH \tag{31}$$

and the calculation is complete.

If $M < 0$, then set

$$M = 0 \tag{32}$$

$$Z + ZO = Z_3 + ZO_3 + M_3/V \tag{33}$$

Solution of this equation for ZO and substitution in Eq. (24) yields, after rearrangement,

$$Z = \frac{K_{in}(Z_3 + ZO_3 + M_3/V)}{K_{in} + OH^3} \tag{34}$$

Use of Eqs. (32) and (33) in the charge conservation equation, Eq. (26), and rearrangement, yields an equation involving only OH:

$$OH - \frac{K_w}{OH} - 3\frac{Z_3 + ZO_3 + M_3/V}{1 + OH^3/K_{in}} + 3Z_3 + H_3 - OH_3 + \frac{M_3}{V} = 0 \tag{35}$$

This equation is solved by binary search for OH. Then

$$H = K_w/OH \tag{36}$$

$$Z = \frac{K_{in}(Z_3 + ZO_3 + M_3/V)}{K_{in} + OH^3} \tag{37}$$

$$ZO = Z \cdot OH^3/K_{in} \tag{38}$$

and the calculation is complete.

RESULTS

These models were programmed in TurboBASIC and run on an MMG 386 DX microcomputer using a math coprocessor and operating at 33 MHz. Typical runs required between 45 minutes and 2 hours. A lab-scale electromigration cell was simulated; its length was 100 cm and its cross-sectional area was 100 cm^2.

The default parameters for the simulations of cadmium removal with acetic acid as the enhancing reagent are given in Table 1. Figure 4 shows the effects of increasing the percentage of electrolytically formed OH$^-$ which is neutralized with HOAc in the cathode compartment. In this set of runs no solid Cd(OH)$_2$ is present initially. As the percentage of OH$^-$

TABLE 1
Parameters Used in Modeling Enhanced Electrokinetic Treatment of Porous Medium Containing Sodium Sulfate; Removal of Cadmium with Acetic Acid as the Enhancing Reagent

---

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 ohm^{-1}·mol^{-1}·cm^3
z_2: −1 (OH$^-$)
λ_2: 198.5 ohm^{-1}·mol^{-1}·cm^3
z_3: +1 (Na$^+$)
λ_3: 50.1 ohm^{-1}·mol^{-1}·cm^3
z_4: −2 (SO$_4^{2-}$)
λ_4: 160 ohm^{-1}·mol^{-1}·cm^3
z_5: +2 (Cd^{2+})
λ_5: 108 ohm^{-1}·mol^{-1}·cm^3
z_6: −1 (OAc$^-$)
λ_6: 40.9 ohm^{-1}·mol^{-1}·cm^3
z_7: 0 (HOAc)
λ_7: 0
Δt: 100 seconds
Applied voltage: 100 V
Initial Na_2SO_4 concentration: 0.0005 mol/L of aqueous phase
Initial $CdSO_4$ concentration: 0.0005 mol/L of aqueous phase
Initial solid $Cd(OH)_2$ concentration (if present): 0.0005 mol/L of bulk porous medium
$K_{sp} = [Cd^{2+}][OH^-]^2 = 2 \times 10^{-14}$
$K_a = [H^+][OAc^-]/[HOAc] = 1.8 \times 10^{-5}$
$K_w = [H^+][OH^-] = 10^{-14}$

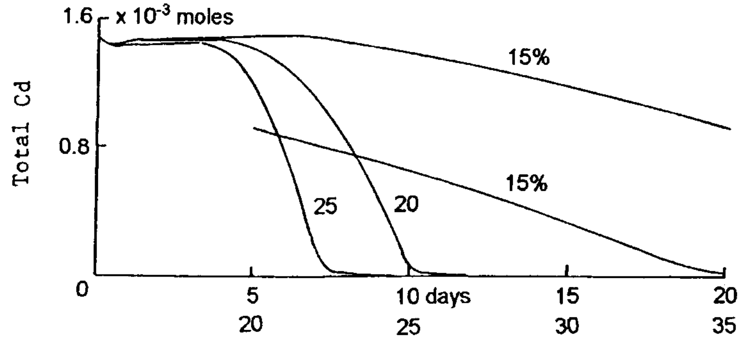

FIG. 4 Plots of total residual Cd versus time; effect of percent neutralization of electrolytically formed OH$^-$ with HOAc. Percent neutralization = 15, 20, and 25%, as indicated. Other parameters as in Table 1. No solid $Cd(OH)_2$ is present initially in these runs.

neutralized decreases much below 20%, the rate of remediation decreases very markedly. Under these conditions the concentration distributions of the ions in the volume elements in the cell and the total current passing through the cell show the formation of a region in the cell in which the ionic conductance is very low, since the reaction of H^+ with OH^- produces a very weakly ionized electrolyte, water. The bulk of the electric potential drop occurs in this region because of its high resistance, and so there is little potential gradient to move the ions in those regions in which the ionic conductance is high.

The simulations graphed in Fig. 5 had the bulk of the initial cadmium ion present as solid $Cd(OH)_2$. In these runs we show the dependence of the removal on the percent of electrolytically formed OH^- which is neutralized by the addition of HOAc; as in Fig. 4, the rate of Cd(II) removal is increased with increasing neutralization with HOAc, as expected.

The runs shown in Fig. 6 display the effect of the strength of the acid used to neutralize the OH^- formed at the cathode. In these runs the ionization constants of the acids range from 10^{-3} down to 10^{-6}. It is fortunate that acetic acid ($K_a = 1.8 \times 10^{-5}$) is no weaker than it is,

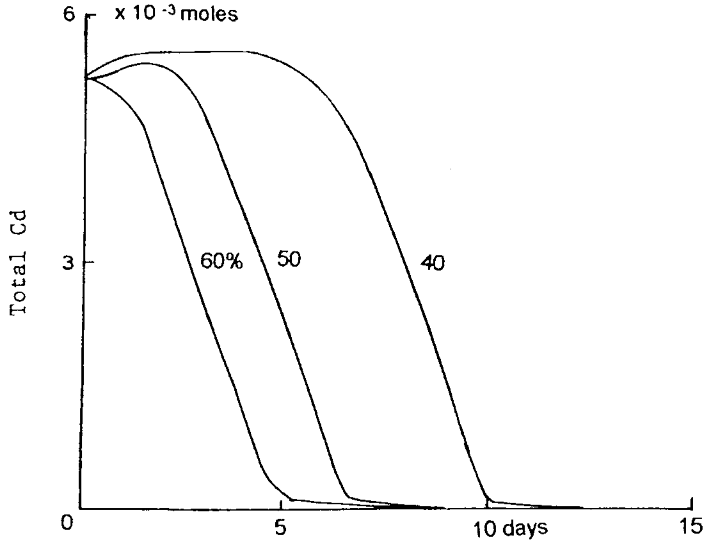

FIG. 5 Plots of total residual Cd versus time; effect of percent neutralization of electrolytically formed OH^- with HOAc. Percent neutralization = 40, 50, and 60%, as indicated. Other parameters as in Table 1. Solid $Cd(OH)_2$ is present initially in these runs at a concentration of 0.0005 mol/L of bulk porous medium.

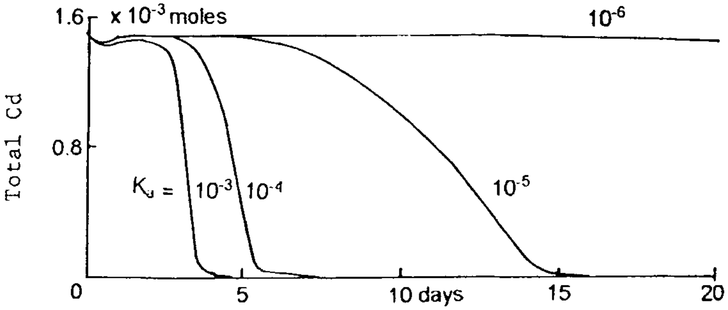

FIG. 6 Plots of total residual Cd versus time; effect of strength of the weak acid used to partially neutralize electrolytically formed OH^-. Percent neutralization = 20% in all runs. No solid $Cd(OH)_2$ is initially present. K_a of the acid = 10^{-3}, 10^{-4}, 10^{-5}, and 10^{-6}, as indicated. Other parameters as in Table 1.

because the effectiveness of weak acids as enhancers drops off spectacularly between $K_a = 10^{-5}$ and 10^{-6}. The results also indicate that stronger acids would be a good deal more effective than acetic acid; this suggests that formic acid ($K_a = 1.77 \times 10^{-4}$) or glycolic acid ($K_a = 1.48 \times 10^{-4}$) be considered for use as enhancing reagents in electrokinetic remediation. A number of other organic acids are stronger than acetic acid (acetoacetic, citric, maleic, malonic, and lactic), but can be expected to form stable chelate complexes, precipitates, or very weakly ionized salts with the metals, which would interfere with remediation.

We next turn to the electrokinetic removal of zinc(II) with sulfuric acid as the enhancing reagent. As mentioned above, zinc hydroxide is amphoteric, so it dissolves in excess base with the formation of soluble anionic zincate. Default values of the parameters used in the zinc runs are given in Table 2. In Fig. 7 the simulations pertain to runs in which initially no solid $Zn(OH)_2$ is present; we examined the effect of neutralizing various percentages of the OH^- formed electrolytically in the cathode compartment. As in our previous runs, we see that this enhancement results in greatly increased metal removal rates. During the course of the runs a good deal of solid zinc hydroxide and some zincate ion are formed in the regions of the cell which are alkaline. Eventually, however, H^+ succeeds in sweeping across the entire cell, converting both the zinc hydroxide and the anionic zincate ions into Zn^{2+}, which is then moved to the cathode compartment by electrokinetic migration.

Solid $Zn(OH)_2$ is present initially in the runs simulated in Fig. 8. Here, as before, the time required for remediation decreases as the percentage of electrolytically formed OH^- which is neutralized by the addition of

TABLE 2

Parameters Used in Modeling Enhanced Electrokinetic Treatment of Porous Medium Containing Sodium Sulfate; Removal of Zinc with Sulfuric Acid as the Enhancing Reagent

---

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 ohm^{-1}·mol^{-1}·cm^3
z_2: −1 (OH^-)
λ_2: 198.5 ohm^{-1}·mol^{-1}·cm^3
z_3: +1 (Na^+)
λ_3: 50.1 ohm^{-1}·mol^{-1}·cm^3
z_4: −2 (SO_4^{2-})
λ_4: 160 ohm^{-1}·mol^{-1}·cm^3
z_5: +2 (Zn^{2+})
λ_5: 105.6 ohm^{-1}·mol^{-1}·cm^3
z_6: −1 ($HZnO_2^-$)
λ_6: 40 ohm^{-1}·mol^{-1}·cm^3 (estimated)
Δt: 100 seconds
Applied voltage: 100 V
Initial Na_2SO_4 concentration: 0.0005 mol/L of aqueous phase
Initial $ZnSO_4$ concentration: 0.0005 mol/L of aqueous phase
Initial solid $Zn(OH)_2$ concentration (if present): 0.0005 mol/L of bulk porous medium
$K_{sp} = [Zn^{2+}][OH^-]^2 = 5 \times 10^{-17}$

$$K_{in} = \frac{[Zn^{2+}][OH^-]^3}{[HZnO_2^-]} = 5 \times 10^{-14}$$

$K_w = [H^+][OH^-] = 10^{-14}$

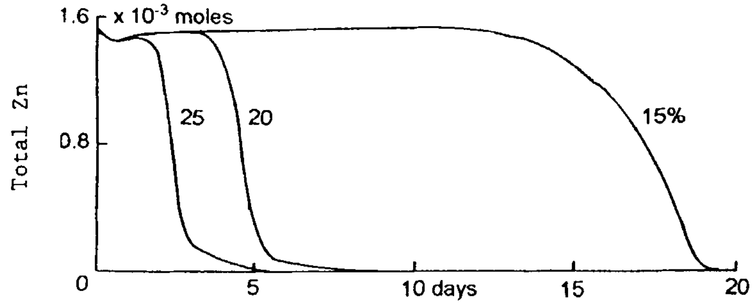

FIG. 7 Plots of total residual zinc versus time; effect of percent neutralization of electrolytically formed OH^- with H_2SO_4. Percent neutralization = 15, 20, and 25%, as indicated. No solid $Zn(OH)_2$ is initially present. Other parameters as in Table 2.

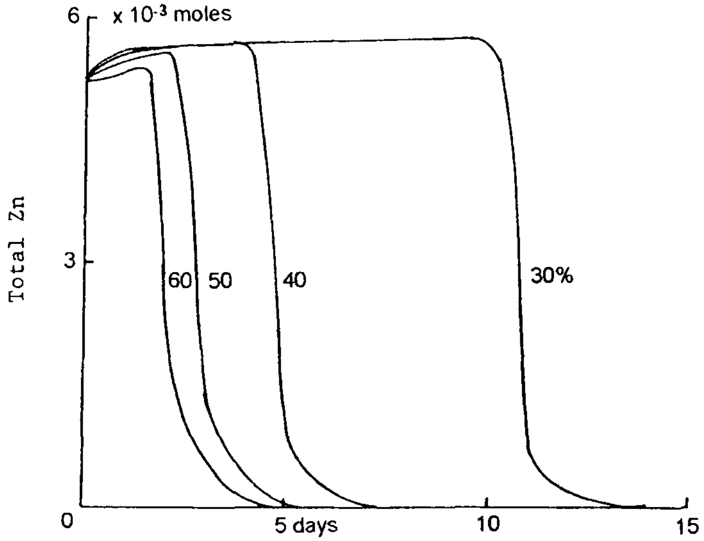

FIG. 8 Plots of total residual zinc versus time; effect of percent neutralization of electrolytically formed OH^- with H_2SO_4. Percent neutralization = 30, 40, 50, and 60%, as indicated. Solid $Zn(OH)_2$ is initially present at a concentration of 0.0005 mol/L of bulk porous medium. Other parameters as in Table 2.

acid to the cathode compartment is increased. One does not want to push the addition of acid to extremes, however, because this results in a very marked decrease in the electrical resistance of the cell. Since the power requirements of the system at constant voltage increase as the reciprocal of the electrical resistance of the cell, this increases power costs, and heat dissipation may be excessive, since this is also proportional to the inverse of the cell's electrical resistance.

CONCLUSIONS

The following conclusions can be drawn from the work described above.

- The use of decision trees facilitates the sorting out of the complex stoichiometry of many electrokinetic remediation systems, providing a systematic way for determining the initial conditions for the necessary equilibrium calculations. This is essential if the approximations which are commonly made in doing complex equilibrium calculations are used, but is not needed if the full system of equations is solved exactly.

- The complex equilibrium calculations which arise in the analysis of electrokinetic remediation systems appear to be readily solved by use of successive elimination to obtain from the charge balance equation an equation in one variable which is readily solved by a simple binary search technique.
- Acetic acid performs reasonably well as an enhancing reagent for the partial neutralization of OH^- in the cathode compartment of an electrokinetic remediation cell. Stronger weak acids, such as formic and glycolic acids, should perform significantly better than acetic acid. Acids which form quite stable un-ionized salts, precipitates, or anionic chelate complexes should be avoided.
- Amphoteric metals such as zinc are readily removed by electrokinetic remediation and do not introduce any significant difficulties.

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, New Jersey, 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. J. Wilson, J. M. Rodríguez-Maroto, and C. Gómez-Lahoz, "Electrokinetic Remediation. I. Modeling of Simple Systems," *Sep. Sci. Technol.*, *30*, 2937 (1995).
10. 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).

Received by editor January 30, 1995