

## EDTA-enhanced electroremediation of metal-contaminated soils

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### Abstract

Precipitation and sorption of heavy metals reduce their mobility and limit the effectiveness of in-situ remediation technologies. In electroremediation, metal mobility can be further impeded by the development of regions of elevated pH near the collecting electrodes. This paper investigates the feasibility of mobilizing precipitated heavy metals by delivering complexing agents into soils by ionic migration. Two metals, lead and zinc, were selected as contaminants, and EDTA, a widely available non-toxic chelating agent, was selected as the complexing agent. It was found that EDTA added to the catholyte can be readily delivered into a sandy soil where it solubilizes the precipitated metals. The resulting complexes are then transported to the anode with metal removal efficiencies, for the spiked laboratory samples, approaching 100%. The poor ligand utilization obtained in the tests is attributed to the low dissolution rate of the metals. Modifying the operating conditions to increase the concentration and the residence time of the ligand in the soil is expected to improve the utilization efficiency of the complexing agent. © 1997 Elsevier Science B.V.

*Keywords:* EDTA; Heavy metals; Electroremediation

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### 1. Introduction

In electroremediation, contaminants are removed from soil and groundwater by the action of an electric potential applied across electrodes embedded in the contaminated medium [1]. The electric field drives the contaminants to the electrodes from where they can be brought to the surface for treatment or safe disposal. An important advantage of electroremediation over other in-situ processes such as soil flushing is the degree of control over the movement of the contaminants. Because the motion of the contaminants

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is confined by the electric field there is little dispersion outside the treatment zone. Furthermore, the process is effective in soils of low and variable permeability.

The contaminants are transported toward the electrodes by processes of electroosmosis and ionic migration [2]. Electroosmosis is the flow of the pore water in the soil under the action of the electric field. The flow rate, which is proportional to the product of the electric field strength and the zeta potential, is typically around  $10 \text{ cm day}^{-1}$ . Dissolved substances are carried along with the flowing water and can consequently be removed at an electrode. Because drying of the soil would disrupt the electric field and interrupt the flow process, it is essential that the pore water that is removed at one electrode be replenished at the other electrode. This is accomplished by supplying a purge solution at the appropriate electrode [3].

Ionic migration is the motion of charged ions in an electric field. The velocity of the ions is proportional to the product of the electric field strength and the ion charge [2], and is generally more rapid than electroosmosis. Consequently, heavy metals are typically removed by the migration of their ions, whereas uncharged contaminants, usually organic chemicals, have to be removed by electroosmosis.

It is clear that electroremediation by electroosmosis and ionic migration is restricted to soluble substances. Contaminants that are adsorbed on the soil or are present as precipitates or immiscible liquids cannot be effectively removed unless they can first be absorbed into the aqueous phase. In particular, the solubility of most heavy metals may be significantly reduced at elevated pH values and in the presence of certain anions such as carbonates, sulfides and sulfates. Because these substances might be naturally present in the soil and because the pH can be elevated by the electroremediation process itself [1,4], reagents have to be introduced to enhance the solubility of metal contaminants.

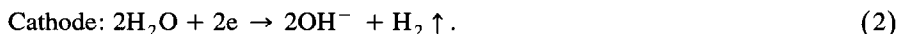
This paper examines the effectiveness of introducing a chelating agent to enhance the removal of precipitated metals from soils by ionic migration. The investigation was carried out in a laboratory-scale cell containing a fine sand which was contaminated either with lead carbonate or with a mixture of lead sulfate and zinc carbonate. The chelating agent selected was ethylenediaminetetraacetic acid (EDTA). Before describing the experiments, some background material is given covering the general use of reagents in soil remediation as well as the relevant chemistry of EDTA, lead and zinc.

## 2. Background

The electroremediation process is governed in part by the electrode reactions which are inherent to the process. These reactions are typically the electrolysis of water which, at the anode, produces hydrogen ions:



and, at the cathode, produces hydroxyl ions:



The hydrogen and hydroxyl ions migrate into the soil under the action of the electric field and produce acidic conditions near the anode and alkaline conditions near the cathode. The change in pH may be attenuated by the buffering action of the soil, and may be controlled by washing the electrodes to remove or neutralize the hydrogen or

hydroxyl ions. For example, acidic conditions can be promoted throughout the soil by washing the cathode to remove the generated hydroxyl ions while allowing the hydrogen ions generated at the anode to migrate into the soil [4].

Of interest here is that reagents such as surfactants and complexing agents can be added to the electrode rinse or purge streams, and will be introduced into the soil by electroosmosis [3] or, if charged, by ionic migration. These reagents have been widely used in other soil remediation technologies to either enhance or diminish the mobility of contaminants [5–7]. Surfactants are typically used for controlling the mobility of organic contaminants [8–10] whereas complexing agents are used for heavy metals [7].

### 2.1. Chelating agents and metals

The solubility of metals can be enhanced by lowering the pH with acids or by adding reagents that form metal complexes such as chelates. As stated, hydrogen ions are produced inherently in electroremediation (Eq. (1)), and acid conditions can be induced throughout the soil by rinsing away the hydroxyl ions generated at the cathode. However, acid enhancement may be undesirable in that it changes soil properties, and may not be effective in highly buffered, carbonate soils [11,12]. On the other hand, chelating agents are available that are environmentally benign and that do not interact with the soil. Many of these agents are ionic and can, in principle, be introduced into the soil by ionic migration.

Chelating agents contain two or more ligands that bond with the metal to form stable, ring-like coordination complexes called chelates. Extensive evaluations of numerous chelating agents [7,11,13] have shown that ethylenediaminetetraacetic acid (EDTA) is an excellent solubilizing agent for many metals including lead and zinc. It is of interest that EDTA has been used medically to promote removal of lead from the human body [14], and also as an additive to render floor polishes with zinc binders amenable to detergent washing [15]. In the latter example, the high pH of the detergent causes the zinc to complex with the EDTA, so destroying the polymeric structure of the polish.

Important considerations in selecting a chelating agent for remediation work include [7]:

- the chelates should be highly stable over a wide pH range and 1:1 ligand-to-metal molar ratio;
- neither the chelating agents nor their chelates should adsorb on the soil;
- the chelating agent should have low toxicity and low potential for environmental harm; and
- the chelating agent should be cost effective.

In addition, the chelating agent should have a greater affinity for the target metals than for other species that may be naturally present in the soil (for example the alkali and alkali-earth metals), and the reaction time to form the complexes should be short. Because chelating agents are relatively expensive, it is important that they can be readily separated from the metal complex and reused. In the case of electroremediation, it is desirable that the chelating agent and their chelates be charged so that they can be transported by ionic migration. These characteristics are now examined in more detail with specific reference to the use of EDTA for enhancing the mobility of lead and zinc.

## 2.2. EDTA

EDTA is generally available as the acid  $H_4L$  or the disodium acid salt  $Na_2H_2L$ . Here  $L$  represents the EDTA ligand,  $(NCH_2)_2(CH_2COO^-)_4$ . It is soluble at pHs above about 3.5 [11] and, in the absence of metals, is present in solution as  $H_nL^{(4-n)-}$ ,  $0 \leq n \leq 4$ , with the degree of protonation increasing with decreasing pH. The dependence of its speciation on pH, shown in Fig. 1, was calculated from the stability constants  $\beta$  defined by:

$$\beta_n = \frac{[H_nL^{(4-n)-}]}{[H^+]^n[L^{4-}]} \quad (3)$$

The stability constants for the metal complexes are defined analogously to those for hydrogen ions. For example, for sodium:

$$\beta_1 = \frac{[NaL^{3-}]}{[Na^+][L^{4-}]} = 10^{2.5} \quad (4)$$

Stability constants for hydrogen and selected metals are listed in Table 1 [16]. The larger the stability constant, the more stable the complex. Sodium has a relatively low stability constant and, as can be seen in Fig. 1, forms a stable complex with EDTA only at high pH where the competition from hydrogen ions is small. Because the stability constant for lead chelate ( $\beta = 10^{19.8}$ ) is some  $10^7$  times greater than that for calcium chelate ( $\beta = 10^{12.4}$ ), EDTA can be expected to selectively dissolve lead in the presence of high concentrations of calcium. There is some evidence, however, that at alkaline pHs calcium might in fact interfere with complexation with lead [17].

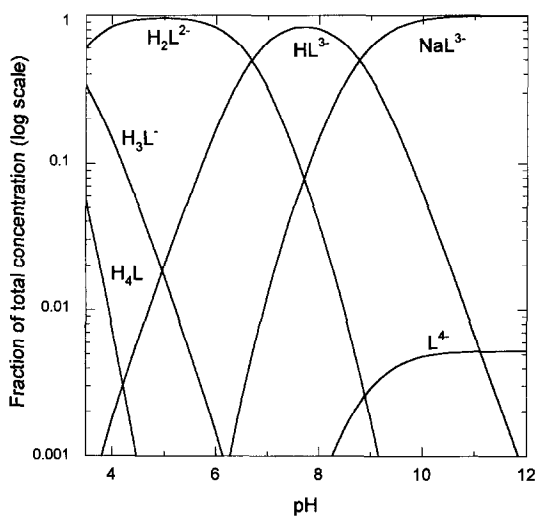


Fig. 1. Speciation of the sodium salt of EDTA as a function of pH ( $[Na] = 4[L]$ ).

Table 1  
Stability constants for EDTA [16]

Metal	Chelate	Log $\beta$	Metal	Chelate	Log $\beta$
Hydrogen	HL <sup>3-</sup>	11.12	Chromium (III)	CrL <sup>-</sup>	26.0
	H <sub>2</sub> L <sub>2</sub> <sup>2-</sup>	17.8		CrHL	28.2
	H <sub>3</sub> L <sup>-</sup>	21.04		CrOHL <sup>2-</sup>	32.2
	H <sub>4</sub> L	23.76	Copper (II)	CuL <sup>2-</sup>	20.5
Sodium	NaL <sup>3-</sup>	2.5		CuHL <sup>-</sup>	23.9
Calcium	CaL <sup>2-</sup>	12.4	Lead (II)	CuOHL <sup>3-</sup>	22.6
	CaHL <sup>-</sup>	16.0		PbL <sup>2-</sup>	19.8
Magnesium	MgL <sup>2-</sup>	10.6		Zinc	PbHL <sup>-</sup>
	MgHL <sup>-</sup>	15.1	ZnL <sup>2-</sup>		18.3
Iron (II)	FeL <sup>2-</sup>	16.1	ZnHL <sup>-</sup>	21.7	
	FeHL <sup>-</sup>	19.3	ZnOHL <sup>3-</sup>	19.7	

### 2.3. Lead and zinc

The solubility of lead and zinc (and the heavy metals in general) is not only strongly dependent on pH, but is also affected by the presence of other anions that may be present in solution. As shown in Fig. 2, relatively small concentrations of carbonates and sulfates reduce the solubility of lead by several orders of magnitude. It can also be seen that although zinc is significantly less soluble than lead, its solubility is reduced only moderately by small concentrations of carbonate (and is virtually unaffected by sulfate). Note that the solubility of lead was calculated for fresh lead hydroxide; aged precipitates of lead hydroxide are significantly less soluble [18].

The effect of EDTA on the dissolved metal concentration is shown in Fig. 3 for lead and Fig. 4 for zinc. In both cases the concentration of dissolved metal is essentially equivalent to the amount of added EDTA in the pH range from 4 to 12, in spite of the presence of the solubility-limiting sulfate and carbonate species. It is also seen that, for pHs above about 4 for lead and 5 for zinc, the metal is present as the doubly negatively charged chelate, ML<sup>2-</sup>.

### 2.4. Recovery and reuse

A process to recover the reagent for reuse is desirable, if not essential for the viability of enhanced remediation processes. One approach is to use a less powerful chelating agent that can be recovered from the metal by elevating the pH [20]. Although some metal–EDTA complexes might also be broken by pH elevation and calcium addition [17], they generally remain stable over a wide pH range and other techniques, such as electrochemical recovery [11,21,22], must be used. In the electrochemical process, the chelate solution (the catholyte) and a sodium carbonate solution (the anolyte) are separated by a cation exchange membrane. On applying a potential, metal is stripped from the chelate and plated on the cathode, while sodium ions that are transported

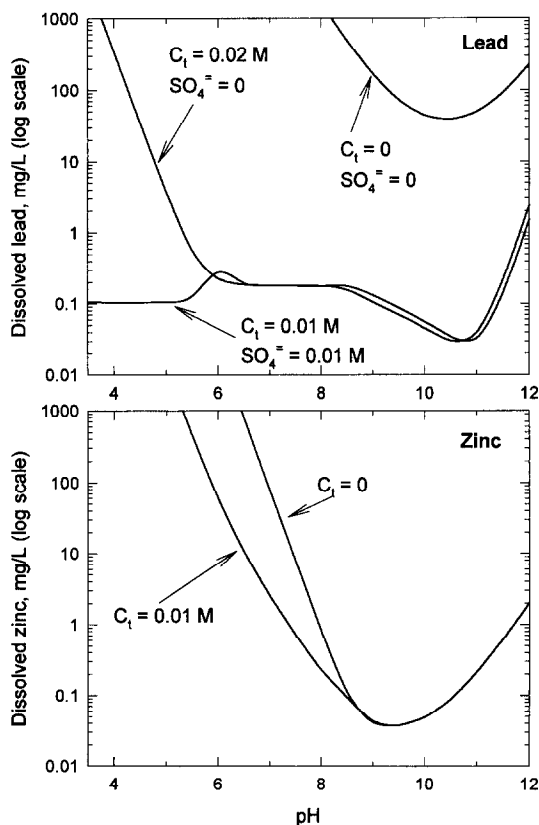
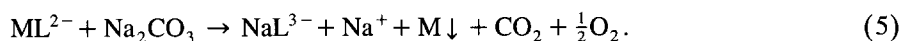
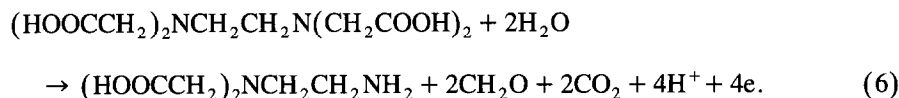


Fig. 2. Effect of carbonate and sulfate on the solubility of lead and zinc. Data for lead from [18] and for zinc from [19].  $C_t$  is the total inorganic carbon ( $\text{CO}_2$ ,  $\text{HCO}_3^-$ , and  $\text{CO}_3^{2-}$ ) present in solution.

through the membrane from the anolyte regenerate the EDTA in its sodium form. The overall electrochemical reaction is represented by:



The membrane prevents the EDTA from reaching the anode where it may be oxidized electrochemically [11]:



The electrochemical technique recovers EDTA and other carboxylic acid-based chelating agents from complexes with copper and zinc [21] as well as lead and copper [11], although not from nickel [21]. Recoveries and current efficiencies are reportedly high, but cost estimates for the process have not been given.

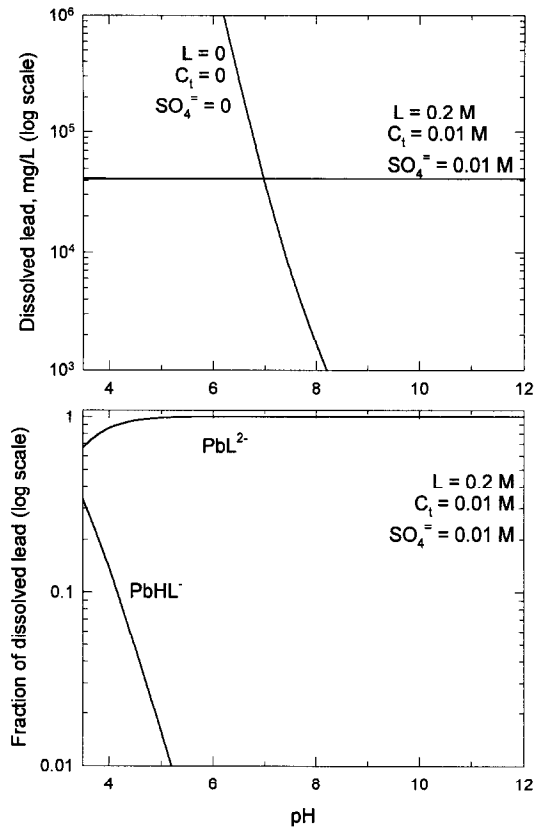


Fig. 3. Solubility of lead as affected by EDTA. L is the EDTA ligand, and  $C_t$  is the total inorganic carbon present in solution.

### 2.5. Dissolution kinetics

The rate of dissolution can be quantified with a pseudo first-order rate constant,  $k$ , defined in terms of the amount of solid present [23]:

$$\frac{d[M_{\text{aq}}]}{dt} = k[M_{\text{solid}}]. \quad (7)$$

Values of  $k$  reported for dissolution of plutonium hydroxides in 0.1 M EDTA are of the order of  $10^{-4} \text{ h}^{-1}$ , which is some two orders of magnitude greater than the dissolution rate in water [23]. However, the rate expressed in Eq. (7) appears to be an oversimplification in that the dissolution rate is found to depend on the surface area of the dissolving solid and also on the relative amount of ligand present [24]. In other words, the dissolution rate can be expected to increase with increasing ligand concentration and with the amount of exposed surface area of the precipitate.

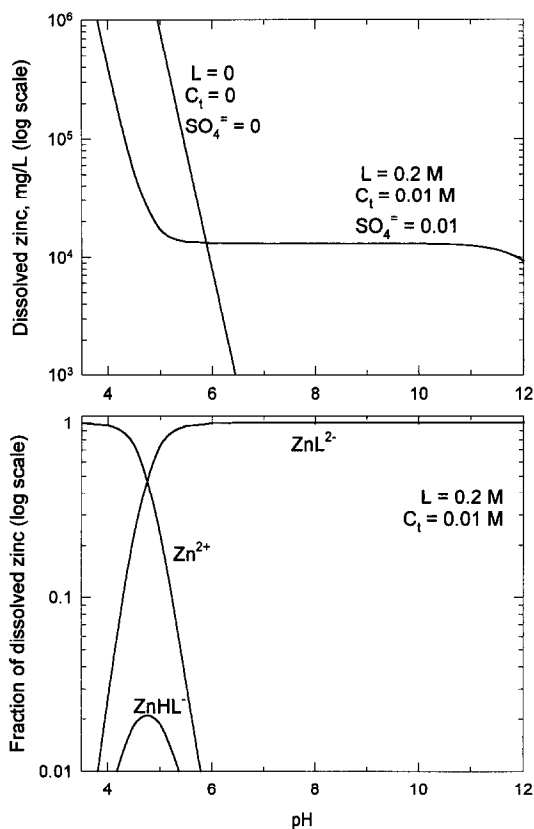


Fig. 4. Solubility of zinc as affected by EDTA.  $L$  is the EDTA ligand, and  $C_t$  is the total inorganic carbon present in solution.

The rate-controlling step is stated to be the rate at which the metal–ligand complex detaches from the solid [24]. Although this is true for dissolution in stirred beakers, it may not apply to precipitated metals in soil. In the latter case, simply getting the ligand to the metal may be a rate-limiting step. It is also important to bear in mind that rate data obtained with fresh precipitates may not apply to aged and ‘weathered’ solids in soils. Dissolution rates for aged precipitates are generally significantly slower [11,23].

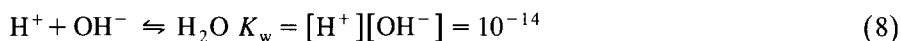
Peters and Shem [7] performed a series of batch experiments in which soil contaminated with lead at a concentration of  $100 \text{ mg kg}^{-1}$  was contacted with hydrochloric acid (HCl), EDTA and nitrilotriacetic acid (NTA). It was found that the three extraction agents reached pseudoequilibrium with the lead in soil in 0.5, 2 and 3 h respectively. These times are short compared to the duration of an electroremediation process which might continue for several weeks. It is of interest that, although the contact time needed for HCl is short, the concentration of lead in the effluent solution was nearly two orders of magnitude lower than that attained with EDTA.



## 2.6. Chelate-enhanced electroremediation

In electroremediation, the chelating agent is added to one of the electrode wells from where it is moved into the soil either by electroosmosis or, if ionized, by ionic migration. For example, EDTA added to the catholyte will migrate toward the anode. To maintain electroneutrality in the catholyte, negative ions must be generated (or positive ions consumed) by the electrode reaction at a rate equivalent to the rate at which the ligand ions leave and any positive ions arrive from the soil. Likewise, transport of a negatively charged ligand through the pore water requires a background of positive ions; these might be moving toward the cathode, or might be quasi-stationary as a result of a balance between diffusion and migration [2].

EDTA probably does not participate in any electrode reactions at the cathode. However, hydrogen ions released from this acid salt will react with the hydroxyl ions that are generated (Eq. (2)) so as to maintain the relative concentration of these ions as imposed by the equilibrium constant  $K_w$ :



Thus, in addition to providing a ligand to solubilize metals, the EDTA serves a secondary function of moderating the elevation of the pH in the vicinity of the cathode. In fact, it is sometimes stated that the primary purpose of adding acidic reagents to the catholyte is to ‘depolarize’ the cathode reaction, that is, to prevent the formation of high pH conditions near the cathode that would otherwise immobilize metals arriving there [25].

In some studies of enhanced electroremediation, weak acids such as acetic and citric acid have been used to depolarize the cathode reaction and to form soluble salts with metals such as lead, uranium, and copper [25,26]. In the case of a lead-contaminated soil containing high concentrations of calcium carbonate, addition of acetic acid to the catholyte did not prove useful in that the lead accumulated near the center of the specimen [25]. In the case of copper-contaminated kaolinite, addition of citric acid to either electrode was at best only slightly effective in mobilizing the copper precipitate that formed near the cathode [26]. However, in the case of uranium (present as the uranyl ion  $\text{UO}_2^{2+}$ ), the addition of acetic acid to the cathode did result in the metal being transported into the catholyte [25], preventing precipitation that occurred upstream of the cathode when the reagent was not used [27,28].

In a laboratory study with two lead-contaminated sandy soils [12], lead was removed from an acidic soil but not from a more buffered, alkaline soil. However, simple gravity washing with EDTA, at a rate of about 2.5 moles EDTA per mole lead, was sufficient to remove the lead from the alkaline soil. Although demonstrating the utility of a chelating agent in the case of buffered soils, these tests did not show that the reagent could be driven into the soil electrochemically nor that the complex could be removed electrochemically. Another laboratory study [29] did demonstrate moderate enhancement in removing plutonium by ionic migration. In control tests, only 33% of the plutonium was removed from the center compartment of the cell in 24 h. When the contaminant was premixed with EDTA, more than 56% of the plutonium was removed in the same time and, after 42 h, 74% had been removed with 36% reaching the anode.

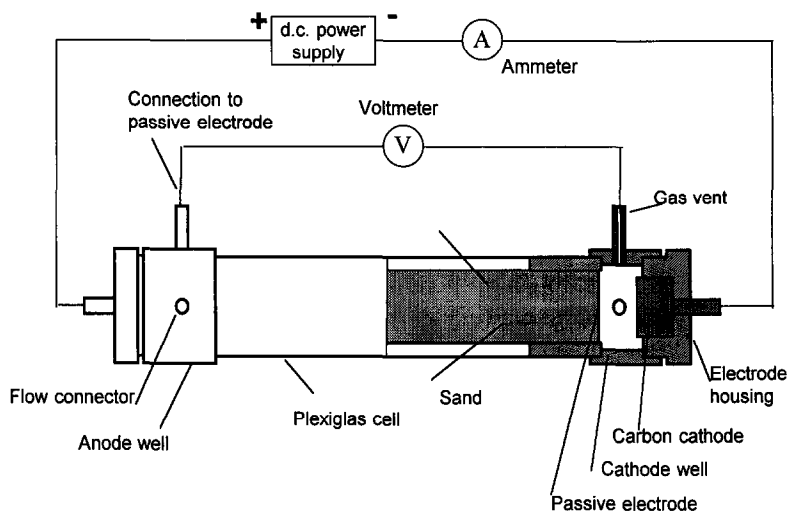


Fig. 5. Schematic of the experimental equipment.

In one series of tests in which a complexing agent was driven into the soil from the electrode well, only moderate success was achieved [30]. In these tests, ethylenediamine (EDA) was supplied to the anode chamber to enhance the removal of cobalt, mercury and lead from spiked kaolinite clay specimens. Although the accumulation of the metals near the cathode was reduced, the main effect of introducing the complexing agent was to increase the electroosmotic flow and the current efficiency. It was concluded that the EDA prevented the metals from precipitating and adsorbing on the clay, but that the complexes had low ionic migration rates and any enhanced removal that was realized occurred by electroosmosis [30].

Finally, before presenting the experimental results, it is noted that successful tests in the laboratory, particularly with spiked specimens, do not always translate into effective treatment in the field. For example, significantly higher removal efficiencies were found for EDTA-enhanced washing of metal salts added to soil samples in the laboratory than were obtained for samples taken directly from waste sites [31]. In the case of surfactant enhancement of soil washing, essentially no removal of organic solvents was obtained in the field despite repeated success in the laboratory with site samples [32].

### 3. Experimental

The experimental work was carried out in Plexiglas test cells, shown in Fig. 5, which are 3.2 cm in diameter and have an active length of 20 cm [4]. Because the transport process of interest is ionic migration, a relatively fine sand was used to simulate the contaminated medium. This eliminated transport by electroosmosis, which is significant only in fine pore soils such as clays [2]. The sand was air-dried US Silica F-50 purchased from Bos Sand Company (Frankfort, IL), which has a cation exchange capacity of less than  $0.07 \text{ equiv kg}^{-1}$ , a bulk density of  $1800 \text{ kg m}^{-3}$ , and a porosity of 0.348. When saturated, it contains about 0.191 of pore solution per kilogram of dry sand.

The sand and saturating pore solution were confined to the Plexiglas cell by placing Nucleopore polycarbonate membranes (hydraulic permeability coefficient of  $2.85 \times 10^{-11} \text{ m s}^{-1}$ ) at each end of the tube, supported on the aluminum passive electrodes shown in Fig. 5. The electrode wells on each end of the tube had a volume of 10 ml and contained carbon electrodes connected to a d.c. power supply capable of operating under constant voltage or constant current conditions. In all the tests described here, a constant voltage of 30 V was maintained across the passive electrodes. This is equivalent to a mean electric field of  $150 \text{ V m}^{-1}$ .

Both electrodes were rinsed with solutions that were circulated between large reservoirs and the electrode wells by peristaltic pumps. The hydrogen and oxygen generated at the electrodes by water electrolysis were entrained by the circulating rinse solutions and vented in the reservoirs. EDTA in the disodium salt form was added to the cathode rinse so that the negatively charged ligands (Fig. 1) would be transported through the sand toward the anode by ionic migration. The anode was rinsed with 0.2 M sodium hydroxide solution to neutralize the hydrogen ions generated there by water electrolysis (Eq. (1)). This was done to prevent an acid front from entering the soil, modifying the soil pH, and possibly amplifying the effect of the EDTA.

The lead-contaminated sand was produced by adding 10 ml of 0.1 M lead nitrate solution to the empty cell. This was followed by 1 ml of 1.0 M potassium carbonate solution to produce a precipitate of lead carbonate and enough sand to give a saturated medium. The bulk of the pore solution (about 45 ml of 0.2 M sodium chloride) was then poured on top of the sand, and the remainder of the sand added so as to fill the cell with saturated medium. This procedure served to confine the precipitated contaminant to a narrow band ( $< 4 \text{ cm}$  thick) in the sand adjacent to the cathode well. In this region the metal loading was about  $360 \text{ mg kg}^{-1}$  sand, or  $19000 \text{ mg l}^{-1}$  of pore solution. If uniformly distributed throughout the sand, the loadings would be  $715 \text{ mg kg}^{-1}$  and  $3700 \text{ mg l}^{-1}$ . This can be compared to the solubility of lead carbonate of about  $0.02 \text{ mg Pb l}^{-1}$ .

In the case of the mixed metal (lead and zinc) tests, 5 ml each of 0.1 M lead nitrate and 0.1 M zinc sulfate were added to the empty cell, followed by 1 ml of 1.0 M potassium carbonate. The metal loadings for the lead are then half of those given above, and for zinc they are  $575 \text{ mg kg}^{-1}$  and  $2970 \text{ mg l}^{-1}$  (non-distributed) or  $113 \text{ mg kg}^{-1}$  and  $584 \text{ mg l}^{-1}$  (if uniformly distributed). In these tests, the lead is precipitated as the sulfate, and the zinc as the carbonate. The solubility of lead sulfate is about  $29 \text{ mg Pb l}^{-1}$  and that of zinc carbonate about  $104 \text{ mg Zn l}^{-1}$ .

EDTA concentrations used in the catholyte ranged from 0.005 to 0.2 M. In one experiment, the metal precipitate was added in such a way as to distribute it more uniformly through the sand. In addition, different concentrations of electrolyte in the pore solution were used in some experiments. Preliminary runs were done to establish the basic operating conditions required to introduce the chelating agent. Thereafter, several runs were completed including two with a single metal (lead), and two with mixed metals (lead and zinc), as summarized in Table 2.

During the experiment, 10 ml aliquots were taken twice a day from the anode reservoir for determination of metal concentration, and 2 ml aliquots were taken from the cathode for checking the EDTA concentration. EDTA was analyzed by titration with

Table 2  
Summary of experimental runs

Run N <sup>o</sup>	Contaminant concentration (mg kg <sup>-1</sup> dry sand) <sup>a</sup>		NaCl concn in pore solution (M)	EDTA concn in catholyte <sup>b</sup> (M)
	Lead	Zinc		
1	715	0	0.2	0.2
2	715	0	0.1	0.1
3	358	113	0.1	0.1
4	358	113	0.05	0.05
5	715 <sup>c</sup>	0	0.2	0.2
6	715	0	0.1	0.2

<sup>a</sup>If distributed uniformly throughout the sand.

<sup>b</sup>Anolyte contained 0.2M NaOH.

<sup>c</sup>Distributed uniformly through sand.

magnesium chloride, and lead and zinc were determined using an inductively coupled plasma (ICP) spectrophotometer. Although the analytical accuracy is probably within a few percent, the sample volumes are small compared to the total volume of the system, so the calculated efficiencies are not expected to be better than  $\pm 10\%$ .

#### 4. Results and discussion

The experimental results are summarized in Table 3. Metal removal efficiencies, given in detail in Table 4, are plotted for selected runs in Fig. 6. Removal efficiencies were generally above 80% for lead carbonate, and essentially 100% for both lead sulfate

Table 3  
Experimental results

Run N <sup>o</sup>	Duration (days)	Current range(mA)	Removal efficiency(%)		Ligand efficiency <sup>a</sup> (%)
			Lead	Zinc	
1a	4	32–59	84	—	3.5
1b	6	31–61	~ 100	—	7.3
2a	5	21–65	68	—	3.2 <sup>b</sup>
2b	6	24–90	77	—	3.7 <sup>b</sup>
3	2	21–34	~ 100	~ 100	21.1
4	3	16–40	~ 100	96	18.8
5	3	29–56	96	—	8.2
6	5	22–35	87	—	4.5

<sup>a</sup>After removing 80% of the metal, unless noted. See text for definition.

<sup>b</sup>At conclusion of experiment (< 80% removal).

Table 4  
Experimentally determined metal removal efficiencies (mass percent)

Time (days)	Run N <sup>o</sup>									
	1a	1b	2a	2b	3		4		5	6
	Lead	Lead	Lead	Lead	Lead	Zinc	Lead	Zinc	Lead	Lead
1	8	55	6	10	44	80	24	55	82	14
2	40	86	32	20	108	104	100	88	96	56
3	66	83	52	37	104	104	108	96	92	79
4	84	93	68	59						85
5		100	68	74						87
6		104		77						

and zinc carbonate in the case of the mixed metal contamination. As can be seen in Fig. 6, removal rates were also generally more rapid in the case of the mixed metal precipitates than for lead carbonate alone. The one exception is run 5, in which the lead carbonate was distributed through the soil and was removed at about the same rate as the mixed metal contaminants.

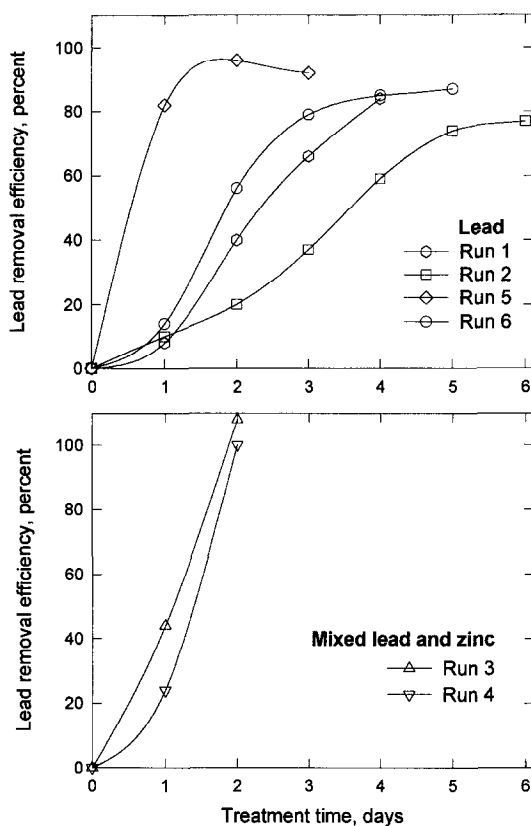


Fig. 6. Lead removal efficiencies measured during the runs.

The difference in removal rates is attributed to differences in the dissolution kinetics of the precipitates. It seems that lead sulfate was more readily dissolved than lead carbonate, possibly because it presented a greater amount of surface area or its surface provided more 'attack' sites for the ligand [24]. Although studies of dissolution kinetics were not done, an additional single-metal experiment was run in which lead was added to the soil in the form of lead chloride precipitate (solubility  $< 40 \text{ mg l}^{-1}$ ). In this case, the lead was removed at a rate similar to the mixed metal case, with 91% being removed in two days.

Some evidence for the importance of surface area for dissolution kinetics is to be gained from run 5. It is conceivable that distributing the lead precipitate through the soil, as was done in this run, would result in less clumping and so make more surface area accessible to the chelating agent. The dissolution rate in run 5 was much higher than in the other runs with lead carbonate, and in fact was similar to the dissolution rate of lead sulfate. In practice, aging and other factors might significantly alter the dissolution kinetics and so affect the removal process.

Typical variations of pH with time at the anode and cathode are shown in Fig. 7a. These pH changes occur as a result of the production of hydrogen and hydroxyl ions by the electrolysis of water (Eq. (1) and (2)), and can affect the ligand transport. For example, when the pH value increases above 12 at the cathode, the concentration of hydroxyl ions starts approaching that of the EDTA in the catholyte. Consequently, an increasing fraction of the current will be carried by the hydroxyl ions, and the amount of ligand entering the soil will decrease. Because the hydroxyl ions are more mobile than the EDTA ligand and chloride ions, the high pH at the cathode can be expected to be followed by an increase in the conductivity of the pore solution and the current. As shown in Fig. 7b, this increase in current occurred after two to three days, and did correspond with the pH value at the catholyte increasing to above 12. Also shown in Fig. 7b is that the current decreased significantly before increasing. This is because initially the hydroxyl ion concentration is insignificant ( $\text{pH} < 11$ ) and mainly EDTA ligand, which has a low mobility relative to chloride ions, enters the soil.

The data in Fig. 7a indicate that the pH throughout the soil remained above neutral for the duration of all the experiments. This means that the dissolution of the metals cannot be attributed to an acid front entering the soil. Furthermore, all the metal that was removed was found at the anode, with none found at the cathode. This indicates that the species that were mobilized were negatively charged and could not have been present in their usual cationic form. Although it is possible that some of the metal might have been present as negatively charged hydroxo complexes,



the concentration of these complexes at the pH prevailing in the soil is insignificant ( $< 0.001 \text{ mg l}^{-1}$  Pb and  $< 0.1 \text{ mg l}^{-1}$  Zn). It appears therefore that the metals must have been present as EDTA-bound complexes, probably mainly in the form  $\text{ML}^{2-}$ .

#### 4.1. Ligand utilization

In all experiments, the rate at which EDTA was delivered from the cathode into the soil remained fairly constant over the period of the run. As shown in Fig. 8a, the rate of

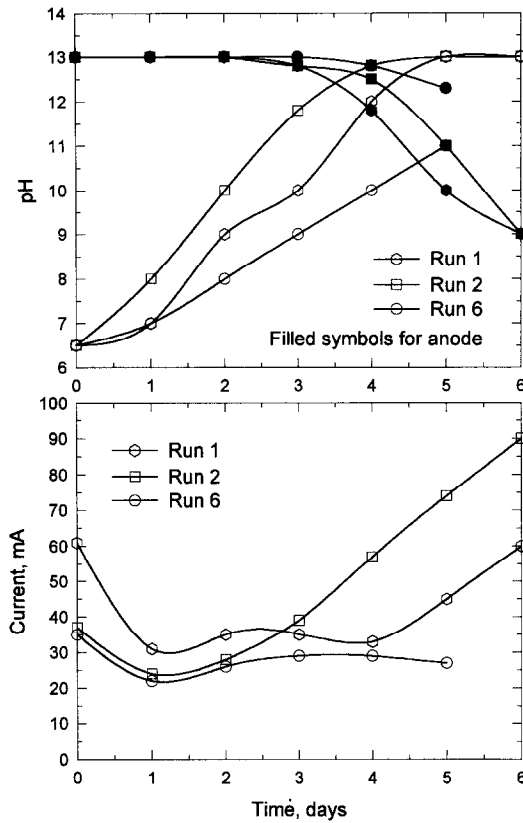
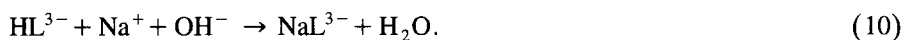


Fig. 7. Typical variations in pH and current with time. (a) pH in the anode and cathode wells. (b) Current through the cell at the constant applied voltage of  $150 \text{ V m}^{-1}$ .

delivery in runs 1–5 was proportional to the ion concentration ( $\text{NaCl}$  plus  $\text{KNO}_3$ ) in the pore solution. In these runs, the EDTA concentration in the catholyte was equal to the  $\text{NaCl}$  concentration in the pore fluid. For run 6, in which the EDTA concentration was double the pore fluid concentration, the delivery rate was some 40% higher than might have been predicted from the pore solution concentration.

The ability to increase the ligand delivery rate simply by increasing its concentration at the supply electrode is at first surprising in that, for an ionic migration process, the ion flux is equivalent to the current density and is governed by the conductivity of the pore fluid. As shown in Fig. 8b, the initial current for all runs is indeed proportional to the ion concentration in the pore solution and is not affected by the higher catholyte concentration of run 6. However, the increased ratio of EDTA concentration to current in run 6 resulted in a higher proportion of the generated hydroxyl ions being consumed in the catholyte (Fig. 1):



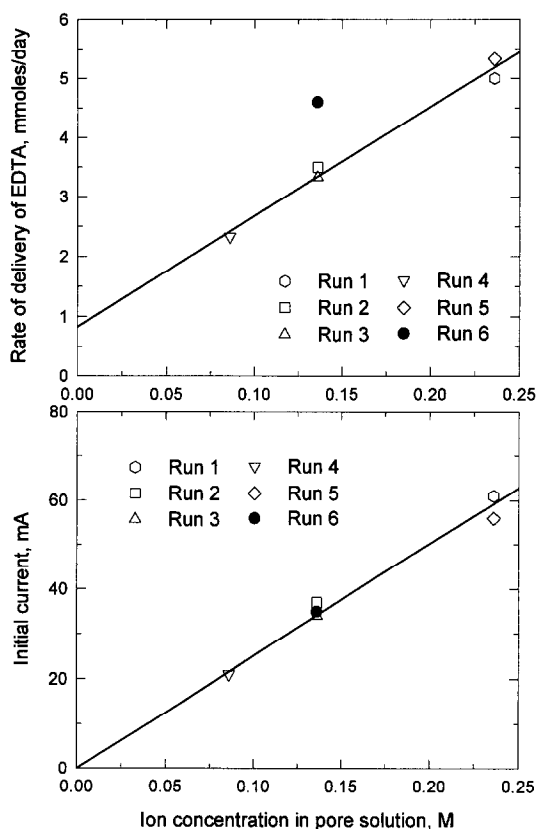


Fig. 8. Dependence of EDTA delivery rate and current on the ion concentration in the pore solution. (a) Mean delivery rate of EDTA into the soil. (b) Initial current. Runs 1–5: EDTA concentration = NaCl concentration. Run 6: EDTA concentration =  $2 \times$  NaCl concentration.

As a result, the pH of the catholyte rose more slowly (Fig. 7a), and a greater proportion of the current was carried by the ligand. Consequently, the ligand delivery rate is higher, and there is a greater concentration of ligand in the soil, than would occur in cases where the concentration of hydroxyl ions at the cathode approaches that of the EDTA.

From 5 to 30 mmol of EDTA were delivered into the soil during the course of a run, many times the 1 mmol of metal present. It is recalled that equimolar quantities of ligand and metal are theoretically required (Figs. 3 and 4), and, in gravity washing tests, about 2.5 mol of EDTA per mole of metal were found to be sufficient [12]. The fraction of the total EDTA that is utilized to form metal complexes is here called the ligand efficiency and is defined as the ratio of the moles of metal removed at the anode to the moles of ligand that are transported into the soil. As seen in Table 3, the ligand efficiency appears low at 3–21%. These low efficiencies cannot be explained in terms of the amount of ligand retained in the soil to replace the NaCl originally present. The low ligand efficiencies might be due to the high ligand flux compared to the metal dissolution rates. This would result in a substantial amount of ligand bypassing the metal without being



utilized for complex formation. It is noted that those runs with high metal dissolution rates also had the higher ligand efficiencies.

Ideally, a high concentration of ligand and an adequate residence time are required for efficient metal removal. As discussed above, increasing the concentration of ligand in the source electrolyte appears to be one method of increasing its concentration in the soil. To increase the residence time, the system should be operated at lower applied voltages. Another strategy would be to deliver the required amount of ligand into the soil and then interrupt the current for a time sufficient to achieve substantial dissolution of the metal. Polarity reversal might be practised to promote mixing and so enhance transport rates of ligand and complex to and from the solid metal phase.

## **5. Conclusions**

Freshly precipitated lead and zinc were effectively removed from contaminated sand by enhanced electroremediation in which EDTA was used as a solubilizing agent. Removal efficiencies approaching 100% were obtained for lead carbonate as well as for a mixture of lead sulfate and zinc carbonate contaminants.

The metals were transported to the anode by ionic migration, indicating that they were indeed solubilized by the EDTA as negatively charged complexes. Rinsing the anode with 0.2M sodium hydroxide maintained the pH in the soil above neutral and prevented an acid front entering the soil with consequent dissolution of metal cations.

The poor ligand utilization efficiency of between 3% and 21% is attributed to the low rate of metal dissolution, which results in a large fraction of the complexing agent being transported through the soil without participating in the solubilization process. Increasing the concentration of ligand in the source electrolyte increases the concentration of ligand in the soil and is expected to increase the metal dissolution rate. Operation at reduced applied voltages will increase the fraction of ligand utilized for solubilization by increasing its residence time in contact with the metal. Interrupting the current or alternating the polarity are other operating strategies expected to enhance ligand utilization.

The rate of metal removal depended on the type of metal precipitate and on the manner the precipitate was distributed through the soil. Dense, localized deposits of metal with low ratios of surface area to mass, and metal phases with relatively few active sites, will be more difficult to solubilize. Less amenable contaminants as well as the effects of aging and interactions with soil chemicals might make remediation in the field more difficult than is reported here for spiked laboratory samples. Tests with site samples to determine the optimum enhancing reagent and operating conditions are an essential prerequisite to success in the field.

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## References

- [1] R.F. Probstein and R.E. Hicks, Removal of contaminants from soils by electric fields, *Science*, 260 (1993) 498–503.
- [2] R.F. Probstein, *Physicochemical Hydrodynamics. An Introduction*, 2nd edn, Wiley, New York, 1994.
- [3] R.F. Probstein, P.C. Renaud and A.P. Shapiro, Electroosmosis techniques for removing materials from soil, US Patent 5074986, 24 Dec. 1991.
- [4] R.E. Hicks and S. Tondorf, Electrorestoration of metal contaminated soils, *Environ. Sci. Technol.*, 28 (1994) 2203–2210.
- [5] C.D. Palmer and W. Fish, Chemical enhancements to pump-and-treat remediation, Report N° EPA/540/S-02/001, US Environmental Protection Agency, Office of Solid Waste and Emergency Response, Washington, DC, 1992.
- [6] US Environmental Protection Agency, In situ remediation technology status report: Surfactant enhancements, Report EPA 542-K-94-003, Cincinnati, OH, April 1995.
- [7] R.W. Peters and L. Shem, Use of chelating agents for remediation of heavy metal contaminated soil, in: G.F. Vandergrift, D.T. Reed and I.R. Tasker (Eds.), *Environmental Remediation*, ACS Symposium Series 509, American Chemical Society, Washington, DC, 1992, pp. 70–84.
- [8] C.C. West and J.H. Harwell, Surfactants and subsurface remediation, *Environ. Sci. Tech.*, 26 (1992) 2324–2330.
- [9] R.C. Chawla, C. Porzucek, J.N. Cannon and J.H. Johnson, Importance of soil–contaminant–surfactant interactions for in situ soil washing, in: D.W. Tedder and F.G. Pohland (Eds.), *Emerging Technologies in Hazardous Waste Treatment II*, ACS Symposium Series N° 468, American Chemical Society, Washington, DC, 1991, pp. 316–341.
- [10] J.W. Mercer and R.M. Cohen, A review of immiscible fluids in the subsurface: Properties, models, characterization and remediation, *J. Contam. Hydrol.*, 6 (1990) 107–163.
- [11] H.E. Allen and P.-H. Chen, Remediation of metal contaminated soil by EDTA incorporating electrochemical recovery of metal and EDTA, *Environ. Prog.*, 12 (1993) 284–293.
- [12] G. Lefebvre, C. Couture and T.V. Pavate, Efficacité comparative de l'électro-osmose et d'un simple lessivage pour le traitement de sables silteux naturels contaminés au plomb, 1993 Joint CSCE–ASCE National Conference on Environmental Engineering, Montreal, Quebec, Canada, 12–14 July 1993.
- [13] US Environmental Protection Agency, A literature review summary of metals extraction processes used to remove lead from soils, Report N° EPA/600/SR-94/006, Cincinnati, OH, 1994.
- [14] D. Greninger, V. Kollonitsch and C. Kline, *Lead Chemicals*, International Lead Zinc Research Organization, New York, 1975.
- [15] M. Farnsworth and C. Kline, *Zinc Chemicals*, Zinc Institute, New York, 1983.
- [16] F.M.M. Morel and J.G. Hering, *Principles and Applications of Aquatic Chemistry*, Wiley, New York, 1993.
- [17] H.A. Elliott, G.A. Brown, G.A. Shields and J.H. Lynn, Restoration of Pb-polluted soils by EDTA extraction, in: J.-P. Vernet (Ed.), *Proc. 7th Int. Conf. on Heavy Metals in the Environment*, Vol. II, Geneva, 1989, pp. 64–67.
- [18] M.R. Schock, Response of lead solubility to dissolved carbonate in drinking water, *JAWWA*, 72 (1980) 695–704.
- [19] J.A. Dean, *Lange's Handbook of Chemistry*, 14th edn, McGraw-Hill, New York, 1992.
- [20] A.P. Hong, T.C. Chen and R.W. Okey, Chelating extraction of zinc from soils using N-(2-acetamido) iminodiacetic acid (ADA), Preprint Extended Abstract, I and EC Special Symposium, American Chemical Society, Atlanta, GA, Sept. 1993.

- [21] J.E. Etzel and D. Tseng, Cation exchange removal of heavy metals with a recoverable chelant regenerant, in: *Metal Speciation, Separation and Recovery*, J.W. Patterson and R. Passino (Eds.), Lewis Publishers, Chelsea, MI, 1987.
- [22] US Environmental Protection Agency, Bench-scale recovery of lead using an electromembrane/chelation process, Report N° EPA/600/SR-95/029, Cincinnati, OH, Feb. 1995.
- [23] J.R. Brainard, B.A. Strietelmeier, P.H. Smith, P.J. Langston-Unkefer, M.E. Barr and R.R. Ryan, Actinide binding and solubilization by microbial siderophores, *Radiochim. Acta*, 58/59 (1992) 357–363.
- [24] J.G. Hering, Implications of complexation, sorption and dissolution kinetics for metal transport in soils, in: *Metal Speciation and Contamination of Soil*, H.E. Allen, C.P. Huang, G.W. Bailey and A.R. Bowers (Eds.), Lewis Publishers, Boca Raton, FL, 1994.
- [25] Y.B. Acar and A.N. Alshawabkeh, Principles of electrokinetic remediation, *Environ. Sci. Technol.*, 27 (1993) 2638–2647.
- [26] G.R. Eykholt and D.E. Daniel, Impact of system chemistry on electroosmosis in contaminated soil, *J. Geotech. Eng., ASCE*, 120 (1994) 797–815.
- [27] Y.B. Acar, R.J. Gale, A.N. Alshawabkeh, R.E. Marks, S. Puppala, M. Bricka and R. Parker, Electrokinetic remediation: Basics and technology status, *J. Hazard. Mater.*, 40 (1995) 117–137.
- [28] A. Ugaz, S. Puppala, R.J. Gale and Y.B. Acar, Electrokinetic soil processing. Complicating features of electrokinetic remediation of soils and slurries: Saturation effects and the role of the cathode electrolysis, *Chem. Eng. Commun.*, 129 (1994) 183–200.
- [29] I. Triay, G. Miller and A. Mitchell, Electrochemical removal of actinides, in: *Proc. Electrokinetics Workshop*, US Department of Energy, Atlanta, GA, Jan. 1992.
- [30] J.K. Wittle and S. Pamukcu, Electrokinetic treatment of contaminated soils, sludges, and lagoons, Report N° DOE/CH-9206, Contract N° 02112406, Office of Research and Development, Technology Development, Environmental Restoration and Waste Management, US Department of Energy, Washington, DC, April 1993.
- [31] B.J.W. Tuin and M. Tels, Distribution of six heavy metals in contaminated clay soils before and after extractive cleaning, *Environ. Technol.*, 11 (1990) 935–948.
- [32] J. Nash, R.P. Traver and D.C. Downey, Surfactant-enhanced in situ soils washing, Report ESL-TR-87-18, Air Forces Engineering and Service Center, Tyndall AFB, Sept. 1987.