Enhanced electrokinetic remediation of high sorption capacity soil

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Abstract

In unenhanced electrokinetic remediation of metals, electrolysis reactions at the cathode generate a high pH medium that results in metal precipitation and immobilization in the soil. Different enhancement procedures could be utilized at the electrodes to prevent or hinder the generation and transport of this alkaline medium into the soil. This study investigates the feasibility of enhanced extraction of metals from high sorption capacity soils by the use of acetic acid to neutralize the cathode electrolysis reaction and also the use of an ion selective (Nafion™) membrane to prevent back-transport of the OH^- generated at the cathode. Synthetic soil samples spiked with lead were used in the testing. Synthetic soils were a mixture of 40% illite, 8% kaolinite, 5% Na-montmorillonite and 47% fine sand representing an illitic deposit. The results demonstrate the feasibility of extracting lead from the deposit. Acetic acid and Nafion enhancement resulted in better removal efficiencies and lead electrodepositions at the cathode compared to unenhanced tests. However, higher energy expenditure and longer processing periods were required when compared to enhanced extraction of lead from kaolinite. Acetic acid tests required less energy than membrane tests. © 1997 Elsevier Science B.V.

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1. Introduction

Electrokinetic soil processing is a primary emerging in-situ technology for extracting metals and radionuclides from soils. An electric current is applied across electrodes inserted in the soil to generate an electric field. The generated electric field results in transport of species that are in the system or introduced into the system (either by the electrolysis reactions at the electrodes, or through the cycling processing fluid at the electrodes). Species transport under electric fields is governed by electro-osmosis and ionic migration (Acar and Alshawabkeh, 1993). Electro-osmosis is used to mobilize the pore fluid and to flush the soil system, usually toward the cathode, while ionic migration effectively separates the negative and positive ionic species by their transport to the anode and cathode, respectively. This transport coupled with sorption, precipitation/dissolution, and complexation reactions comprise the fundamental mechanisms affecting the electrokinetic remediation process. Extraction and removal are accomplished by electrodeposition, precipitation or ion exchange either at the electrodes or in an external extraction system.

In unenhanced electrokinetic extraction of metals, electrolysis reactions of pore water are allowed to occur unaltered at the cathode and anode. Water electrolysis reactions generate an acidic medium at the anode, decreasing the pH to below 2, and an alkaline medium at the cathode, increasing the pH to above 10 (Acar et al., 1989, 1990, 1992). Proton mobility under an electrical field is about two times the hydroxyl ion mobility, resulting in a faster transport of the acid front than the base front. Furthermore, in most soils electro-osmosis promotes transport of the acid front and retards transport of the base front. Unless transport of protons is retarded by the soil buffering capacity, the soil between the electrodes will be acidified. This acidification results in solubilization of contaminants due to desorption and dissolution of species from soil. Once contaminants are present in ionic form in soil pore fluid, they migrate to the electrode opposite in polarity under the applied electric field leading to their extraction from soil. Bench-scale and pilot-scale experiments demonstrated feasibility of the process for extraction of metals and radionuclides from fine-grained soils (Lageman, 1989; Acar et al., 1989; Shapiro et al., 1989; Acar and Gale, 1992; Kelsh, 1992; Pamukcu and Wittle, 1992; Probstein and Hicks, 1993; Runnels and Wahli, 1993; Acar et al., 1993; Lageman, 1993; Acar and Alshawabkeh, 1993; Alshawabkeh, 1994; Alshawabkeh and Acar, 1996).

In unenhanced electrokinetic remediation, protons that transport across the soil mass meet hydroxyl ions close to the cathode compartment resulting in the generation of water within that zone. As a result, pH changes from about 2 to over 8 within this zone. It is necessary to consider the behavior of target species in an environment with such a widely varying pH values in assessment of transport. Some metals are amphoteric and can exist either in positive or negative ion forms, e.g. $Pb^{2+}/[PbO_2H]^-$, $Cr^{3+}/[Cr(OH)_4]^-$ depending on local pH conditions. These ions when complexed into a negatively charged species at high pH, could be transported towards the anode under electric fields. Therefore, in unenhanced electrokinetic remediation, a rise in catholyte pH may result in the complexation of heavy metals and their transport towards the anode. Such complexation should be considered and its effects should be evaluated in electrokinetic remediation. Furthermore, a rise in catholyte pH results in the precipita-

tion of metal hydroxides in adjacent soil (Acar and Alshawabkeh, 1993; Probstein and Hicks, 1993; Acar et al., 1994; Eykholt and Daniel, 1994). This precipitation decreases concentrations of ionic species in the pore fluid, decreases electrolyte strength, and renders a zone of low electric conductivity in the soil adjacent to the cathode compartment. Formation of this zone in unenhanced electrokinetic remediation results in a significant increase in the voltage drop across the soil and a commensurate increase in energy expenditure.

In view of fundamental understanding of the process developed, different schemes are proposed to enhance transport and extraction of cationic species under electric fields, and to prevent formation of immobile precipitates. The main objective of these schemes is to neutralize the cathode water electrolysis reaction to avoid generation and transport of high concentrations of OH^- ions into the soil and to enhance electrodeposition of metals. Neutralization of cathode water electrolysis reaction will also assist in decreasing the electrical potential difference across the electrodes and consequently decrease energy expenditure.

Envisioned enhancement schemes are expected to have the following characteristics: (i) the precipitate should be solubilized and/or any precipitate should be avoided, (ii) ionic conductivity across the specimen should not increase excessively in a short time as this may prematurely decrease the electro-osmotic advection which assists ion transport, (iii) the cathodic electrolysis reaction should possibly be depolarized to avoid generation of OH^- ions and their transport into the specimen, (iv) such depolarization will also assist in decreasing the electrical potential difference across the electrodes, (v) if any chemical is used, the metal precipitate with this new chemical should be soluble within the pH ranges attained, (vi) any special chemicals introduced should not result in any increase in toxic residue in the soil mass, (vii) cost of chemicals introduced should not make the overall cost of the process prohibitive.

This paper presents results of a study investigating the feasibility of electrokinetic extraction of lead from soils with a relatively high sorption capacity. Synthetic soil samples spiked with lead were used in the testing. The synthetic soils were a mixture of commercially available clay minerals (including kaolinite, illite and sodium montmorillonite) and fine sand, representing an illitic deposit. Enhanced extraction procedures were also investigated. The enhancement procedures addressed in this study are using organic acids to neutralize cathode electrolysis reaction and also using an ion selective membrane to prevent back-transport of OH^- generated at the cathode. The objective of these two schemes is to extract inorganic species by preventing formation of a high pH zone in the soil medium and avoiding precipitation of inorganic species at their hydroxide solubility values.

2. Enhancement techniques

Different options could be investigated to enhance extraction of inorganic species from soils: (1) to flush either or both ends using a fluid of controlled pH and chemistry (conditioning fluid), (2) to neutralize electrolysis reactions to allow the base/acid front to move across the soil, (3) to use specific complexing agents that may complex or

chelate with target species during transport, (4) to use special electrodes or membranes which would control the chemistry at the boundaries.

Neutralizing the cathodic electrolysis reaction is a feasible option to assist in extraction of positively charged species into the cathode compartment. Acetic acid is environmentally safe, biodegradable and it will not create a health hazard if it is used in conditioning the pore fluid in electrokinetic remediation of sites. Acetic acid is a weak acid that undergoes partial dissociation,

$$HA \leftrightarrow H^+ + A^- \tag{1}$$

where A represents the acetate anion (CH_3COO^-). Other advantages to using acetic acid in neutralizing cathodic processes are: (1) most metal acetates are highly soluble and the hydrogen ion is able to neutralize the cathodic electrolysis reaction, thereby reducing the energy necessary in electrolysis and avoiding formation of hydroxides, (2) migration of an acetate anion upstream will cause formation of a neutral acid and hence maintain a lower conductivity due to the association,

$$H^+ + A^- \Leftrightarrow HA \tag{2}$$

Other acids similar to acetic acid like oxalic acid and citric acid may also be used (Marks et al., 1995). Electrokinetics Inc. has developed the CADEX™ group of depolarizers that allow transport of species into cathode compartment and promote their electrodeposition and/or precipitation at the electrode.

The second enhancement technique that has been investigated in this study is using membranes at the cathode. The objective of using membranes, such as Nafion™, is to minimize or avoid transport of base generated at the cathode into soil. Nafion™ is permeable to many cations and polar compounds. Their size and ionic properties determine their mobility through the polymer. It is impermeable to anions and nonpolar compounds. Hence it was envisioned that Nafion™ can prevent upstream migration of OH^- from cathode to anode. The insolubility of Nafion™ in most solvents and its resistance to attack from strong oxidizing agents and strong bases increases its potential use in electrokinetic remediation.

3. Soil type

The efficiency of the enhancement techniques is evaluated in a soil with higher cation exchange capacity and activity (activity is defined as ratio of plasticity index to the percent soil passing through 2μ sieve size), by preparing a synthetic illitic mixture. The illitic mixture (referred to as synclay) was prepared using (by weight) 40% illite (Ward's Natural Science Establishment, Rochester, NJ), 8% kaolinite (Thiele Kaolin, Wrens, GA), 5% sodium montmorillonite (NL Baroid, Houston) and 47% fine sand (Easycrete, Greenwell Springs, LA). Compositional characteristics of the illitic mixture are presented in Table 1. One objective of using this clay was to assess whether the electrokinetic extraction process will be feasible in high sorption capacity clays. This mixture represents a relatively 'difficult' soil to remediate by electrokinetics. Lead sorption tests were conducted. Adsorption capacity (Fig. 1) of the mixture was about 10 000 μg of lead per gram of dry soil, which is about an order of magnitude higher

Table 1
Compositional characteristics of soils used in synthetic soil mixture

Characteristics	Na-M	K	I	Synclay
Liquid limit (LL)	425.0	64.0	38.5	36.5
Plastic limit (PL)	58.0	34.0	25.6	15.2
Plasticity index (PI)	367.0	30.0	12.9	21.4
−2 μ Sieve	80.0	90.0	34.0	24.8
Activity (PI/−2 μ sieve)	4.50	0.32	0.38	0.86
Cation exchange capacity ($\mu g/g$)	N/A	1100	N/A	10000

N/A = not available; Na-M = sodium montmorillonite; K = kaolinite; I = illite; synclay = 5% Na-M, 8% K, 40% I and 47% fine sand.

than sorption capacity of kaolinite (1100 $\mu g/g$) used in previous studies (Hamed et al., 1991; Acar and Alshawabkeh, 1996). Sorption capacity and behavior of this soil compares quite well with the sorption capacity of a natural illitic deposit (Drammen clay from Norway) reported by Rødsand et al. (1995) indicating that the synthetic mixture represents a typical illitic soil that may be encountered under natural conditions. This synthetic soil was spiked with lead at 2330 mg/kg (below the adsorption capacity) and at 18000 mg/kg (above the adsorption capacity). This variable spiking gives us the opportunity to assess the effect of concentration on metals transport.

4. Equipment and procedure

Experimental cells used in this study were made of acrylic and consisted of a cylindrical body of 10 cm (4 in) inner diameter, 11.4 cm (4.5 in) outer diameter, and 10
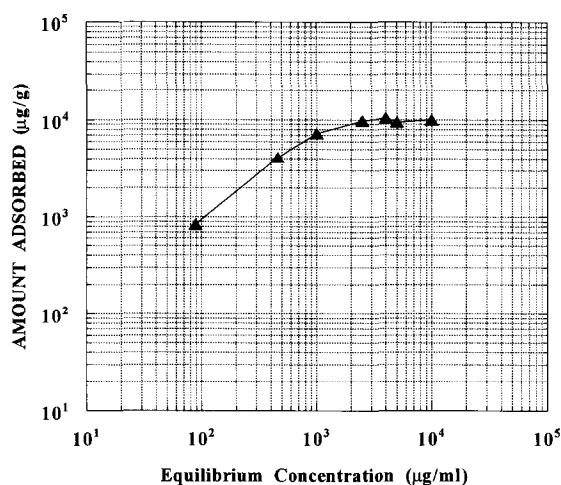

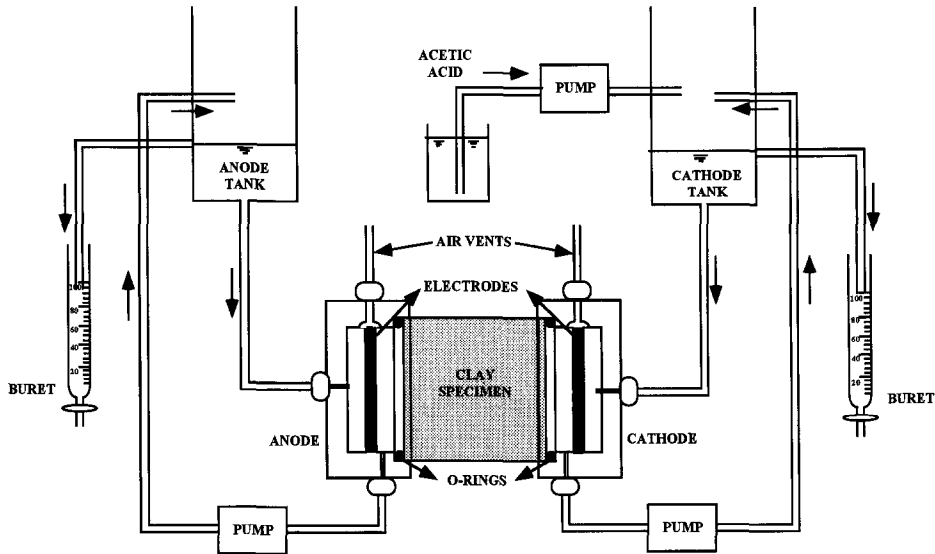Fig. 1. Lead adsorption isotherm for synthetic illitic soil (1:4 soil:water ratio).

Fig. 2. Bench-scale test set-up used in unenhanced and acetic acid enhanced tests.

cm long. The electrodes were held in place with acrylic cell caps, which are connected with 0.64 cm ($\frac{1}{4}$ in) all threaded steel rods. A schematic of test set-up used in acetic acid enhanced and Nafion™ membrane enhanced electrokinetic remediation tests are depicted in Fig. 2 and Fig. 3, respectively. Rubber O-rings were placed in between cell caps and
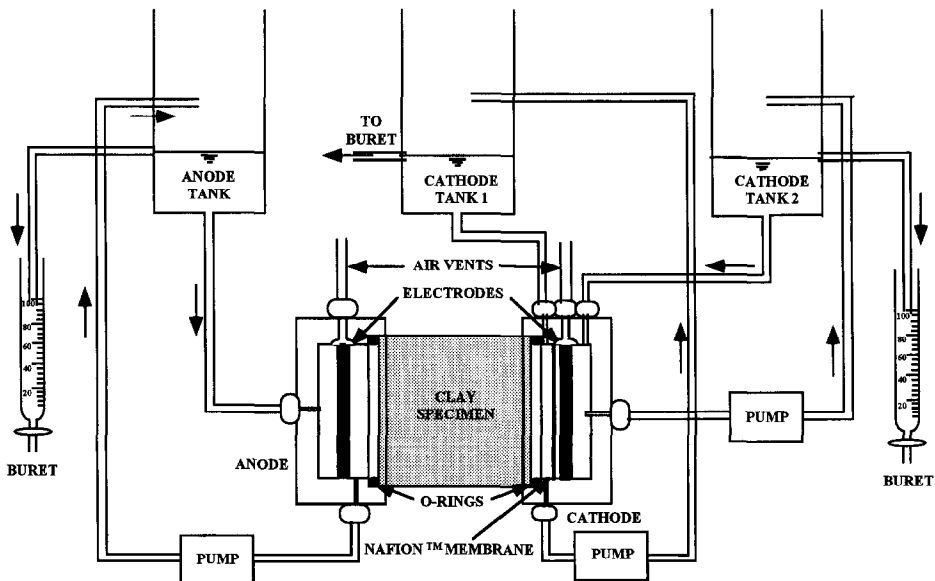

Fig. 3. Bench-scale test set-up used in Nafion™ membrane enhanced tests.

cell sleeves to prevent leakage of liquids. The cell caps were designed to prevent the electrodes from contacting the specimen directly. This arrangement facilitates control of chemical reactions between the soil specimen and the electrode. A liquid reservoir of 150 ml was available on each side of the electrode. In tests where the Nafion™ membranes were utilized, cell caps were slightly modified to accommodate a Nafion™ membrane in between the electrode and the specimen. Each end of cell caps (anode and cathode ends) was connected to an open reservoir having a volume of 1000 ml. However, in tests involving Nafion™ membranes, an extra reservoir was provided to differentiate two different zones on either side of the membrane. These reservoirs facilitate addition of chemicals like acetic acid. They also permit measurement of pH without any electrical interference.

Equipment and material used in this study include pH meters and electrodes, DC power supplies and carbon electrodes. Carbon electrodes were formed by cutting a 10.2-cm (4 in) diameter graphite rod into 0.32-cm (0.125 in) thick discs. Electrical wires were connected to the graphite electrodes by using a highly conductive silver epoxy. A pump was used for adding conditioning solutions to electrode compartments.

5. Specimen preparation

Soil specimens were prepared by mixing the soil with stock solutions of 0.015 M and 0.1125 M lead nitrate solutions. Lead solutions were sprayed on the soil to produce specimens at a water content of 16% and two lead concentrations of 2330 mg/kg and 18 000 mg/kg of dry soil. Soil specimens were then allowed to cure for 24 h. Compaction was accomplished in a single layer since layering adversely affects testing and evaluation of extraction (Puppala, 1994). A 2.5 kg (5.5 lb) hammer was dropped 25 times from a height of 30.5 cm (12 in). Soil and cell sleeves were removed from the compaction mold and excess soil was trimmed from sample ends. Specimens were taken from trimmings for initial pH, water content and total metal analyses.

6. Testing procedure

The testing procedure used was same for all unenhanced and enhanced recovery technique tests, except for Nafion™ enhanced test, which had an extra tank to recirculate liquid between Nafion™ membrane and soil cell (Fig. 3). In all enhanced recovery technique tests, both influent and effluent were continuously circulated from respective tanks to cell compartments using Masterflex pumps. For Nafion™ tests, a Nafion™ membrane was inserted in between the cathode electrode and soil specimen. In acid enhancement tests, 0.05 M acetic acid was added to either cathode tank or anode tank at a variable rate (controlled manually) to maintain the required pH level. The cell was placed in the test setup in a horizontal configuration. A direct current (4 or 20 mA) was applied to the specimen by a DC power supply. The cross sectional area of the specimens was 80 cm^2, rendering a current density of 50 or 200 μA/cm^2.

At the end of processing, soil specimens were removed from the cell caps and cut into 5 sections. These sections were analyzed for final pH, water content and species concentrations. In addition, filter papers, electrodes and liquids in reservoirs were analyzed for cation concentrations. In situ soil pH was measured by inserting pH electrode in the soil section. This procedure was described by Acar et al. (1989), Hamed (1990) and Hamed et al. (1991). Water content was measured according to ASTM (1991) D2216 procedure.

7. Soil chemical analysis

The soil sections were separately oven dried at 110°C for 24 h and then pulverized and mixed in a ceramic jar using a pestle to produce homogeneous samples. Three 3-g samples from each section were taken in 50-ml centrifuge tubes and 30 ml of 1.6 M HNO_3 were added. Resulting slurries were shaken continuously for 24 h at room temperature in a shaker. Subsequently, the slurries were filtered and filtrates were sent for inductively coupled plasma (ICP) [EPA (1992), Method 6010] analysis for cations. Similarly, cell electrodes were taken from cell caps and placed in 1000 ml beakers and soaked with 1.6 M HNO_3 for 24 h. Liquids from beakers were filtered and their volumes were measured. Both catholyte and anolyte solutions were analyzed by adding 100 ml of concentrated HNO_3. Samples were diluted to a final concentration values which fell within the ICP's linear range.

8. Results and analysis

Three different types of tests, (i) unenhanced, (ii) acetic acid enhanced and (iii) Nafion™ membrane enhanced tests, were conducted with synthetic soil specimens. Processing parameters for all tests are provided in Table 2. The tests were denoted as XY01; where XY represents type of test conducted (UE: unenhanced, AA: acetic acid

Table 2
Processing parameters in lead spiked synthetic soil specimens

Test name	Duration (h)	Current density ($\mu A/cm^2$)	Lead conc. (mg/kg)
UE01	1121	50.0	2330
UE02	2356	50.0	2330
UE03	3014	50.0–250.0	17950
AA01	1121	50.0	2330
AA02	2356	50.0	2330
AA03	3001	50.0–250.0	17950
NM01	1155	50.0	2330
NM02	2375	50.0	2330
NM03	3001	50.0–250.0	17950

enhanced and NM: Nafion™ membrane enhanced) and the two digits denote numerical identity of each test. Processing conditions for tests with 01 and 02 suffice are identical, but processing time is doubled in the second set of tests (02 suffice tests). A third set of tests (03 suffix), with different processing conditions, was also conducted to further substantiate the results obtained. The first two tests (XY01 and 02) were conducted at 2330 mg/kg lead concentration. Current density used in these tests was 0.05 mA/cm^2 (4 mA current). UE01 was processed for 1100–1200 h, while UE02 was processed for 2300–2400 h. The third test of each stage (numbered 03) was conducted on the illitic mixture at 17 950 mg/kg lead concentration and was processed for about 3000 h.

8.1. Unenhanced tests

8.1.1. Electrolyte pH and electrical gradients

An increase in catholyte pH (effluent) to about 10.5 and a decrease in anolyte pH (influent) to less than 2 occurred in all unenhanced tests during the first 100 h of processing. As discussed earlier, changes in catholyte and anolyte pH values are mainly due to electrolysis reactions at the electrodes. Since no enhancement agents were used in these tests, pH values remained same during processing.

Fluctuations in electrical gradients were observed during processing. In some instances, electrical gradients exceeded maximum capacity of the power supply (120 V or 12 V/cm for a 10 cm long cell). High electrical gradients (high soil resistivity) generated in some tests were attributed to precipitation of lead ions as hydroxides in regions close to cathode. Results of previous studies by Hamed (1990) demonstrated that during processing, voltage gradients erratically increase, possibly due to random rapid precipitation of species close to cathode compartment.

8.1.2. Final species profiles

A comparison between final lead distributions in the first two unenhanced tests (UE01 and UE02) is displayed in Table 3. Final lead distribution (as a percentage of

Table 3
Final lead distribution in unenhanced and acetic acid enhanced synthetic soil specimens

Section	UE01 (%)	UE02 (%)	UE03 (%)	AA01 (%)	AA02 (%)	AA03 (%)
Influent	0.01	0.19	9.93	0.14	1.59	13.09
Anode	0.07	0.04	0.09	2.12	0.08	0.02
A-filter	0.06	0.01	0.09	0.05	0.02	0.02
Section 1	12.21	12.74	3.85	12.35	3.68	0.80
Section 2	19.56	14.79	2.87	13.55	3.30	1.18
Section 3	15.27	4.88	5.33	12.94	3.90	12.23
Section 4	31.74	2.76	13.23	5.22	3.48	13.39
Section 5	4.19	67.62	32.47	52.11	55.78	13.76
C-filter	2.84	6.50	8.16	0.47	3.04	1.71
Cathode	0.15	0.19	24.43	0.07	27.23	39.53
Effluent	8.42	0.01	2.90	7.33	2.92	4.88
Error	5.39	9.73	3.35	6.35	5.03	0.60

total initial lead) is presented in this table using the following nomenclature; dissolved in anolyte (influent) and catholyte (effluent), precipitated or electrodeposited at electrodes, in soil (sections 1–5, from anode to cathode), precipitated at filter paper, and finally error in mass balance (error). The first unenhanced test (UE01) showed lead transport from the last section (section 5) towards the effluent. However, in UE02 a significant amount of lead (about 68% of initial total lead in soil) is found in section 5 due to lead hydroxide precipitation. Since processing time in UE02 is almost twice that of UE01, higher removal efficiency is noted in UE02 than UE01, specifically in sections 3 and 4. It should be noted that the required processing time for lead transport and accumulation in the last section near the cathode is affected by soil sorption capacity and lead concentration. In this case (illitic mixture), the sorption capacity of the mixture is 10 000 mg/kg, which is five times the initial concentration. Therefore, most of the lead is expected to be adsorbed on soil surface, particularly since lead is highly attracted by the clay surface. It is necessary to acidify the soil substantially to desorb and solubilize lead in the soil pore fluid. Although final pH values across the soil were less than 3 in both tests (UE01 and UE02), these pH values were not low enough for complete desorption and dissolution of lead; further acidification might be required. In addition, the desorption process is time dependent and not instantaneous (especially in high clay soils with high sorption capacities such as illite and montmorillonite). Therefore, time plays a critical roll in treating such soils, not only for transport of species but also for desorption and solubilization.

Initial lead concentration in the third unenhanced test (UE03) was about 8 times that of UE02. About 33% of total initial lead in UE03 (Table 3) was found in section 5, due to lead hydroxide precipitation compared to 68% in UE02. Another difference between the results of UE03 and UE02 is that 32% of initial lead was found electroplated and/or precipitated on cathode filter and cathode electrode in UE03 compared to almost nothing in UE02. Electrodeposition of lead on cathode in UE03 is due to high lead concentration in soil (17 950 mg/kg). Effluent is expected to be saturated with lead and consequently, reduction of lead will be favored at the cathode.

Results of the three unenhanced electrokinetic tests on lead-spiked illite mixtures show transport of lead across the cell to the cathode region. However, both UE01 and UE02 showed limited transport compared to UE03. The illitic soil can resist pH drop due to its high cation exchange capacity (compared to kaolinite), and therefore a significant amount of acid is necessary to desorb lead or other metals from the soil surface. Furthermore, illitic soils have high amounts of relatively free potassium ions that would compete with lead transport, and may hinder the electrokinetic extraction process. Higher currents might be necessary for treatment in this case (higher than 0.1 mA/cm^2). Higher currents, on the other hand, will increase energy expenditure (as demonstrated in UE03), and consequently cost of processing. Furthermore, precipitation of lead hydroxide in soil sections in direct contact with the cathode would develop a zone of low electric conductivity, resulting in a more pronounced drop in voltage, and a corresponding increase in energy expenditure. In summary, electrokinetic extraction of lead from illitic specimens will require higher current densities, processing periods, energy expenditure, and costs when compared to kaolinite. In such conditions, enhancement techniques are needed to minimize the cost.

8.2. Acetic acid enhanced tests

The procedure used in acetic acid enhanced tests involved adding 0.05 M acetic acid to catholyte to keep its pH at a value of less than 6.0. It was postulated that a pH of 6.0 would be sufficient to dissolve and remove the lead in the soil and aid in lead transport to cathode. Fig. 4 shows that catholyte pH was kept between 4.5 to 6 in acetic acid enhanced tests, compared to 10 in unenhanced tests.

At the time the third group of tests was initiated, results of first two groups of tests were not available. Therefore, processing conditions in the third test were kept identical to ongoing two tests. During the first 600 h of processing the third test, catholyte pH increased to 6, although 0.05 M acetic acid was added at intervals manually. Subsequently, when results of first two tests were available, catholyte pH was brought down to a value of around 4.0 by increasing the acid concentration (0.1 M acetic acid). The catholyte was replaced weekly by new 0.1 M acetic acid to keep catholyte pH less than 4.

Unenhanced tests resulted in lead accumulation in section 5 due to high pH of the catholyte (about 11). Decreasing catholyte pH in acetic acid enhanced tests to 6 was expected to minimize lead hydroxide precipitation in that section. Fig. 5 displays a comparison between lead distribution in the second acetic acid enhanced test (AA02) and the second unenhanced test (UE02). AA02 showed higher removal of lead from all sections when compared to UE02. However, section 5 still showed precipitation of about 55% of the total lead. This indicates that decreasing catholyte pH to 6 was not sufficient to prevent lead hydroxide precipitation. In any case, about 30% of initial lead in the acid enhanced test is found electrodeposited and/or precipitated at the cathode, compared to almost nothing in the unenhanced test. Although lead extraction is not complete, the results show the significance of decreasing catholyte pH on the process efficiency for electrodeposition of lead on the cathode.
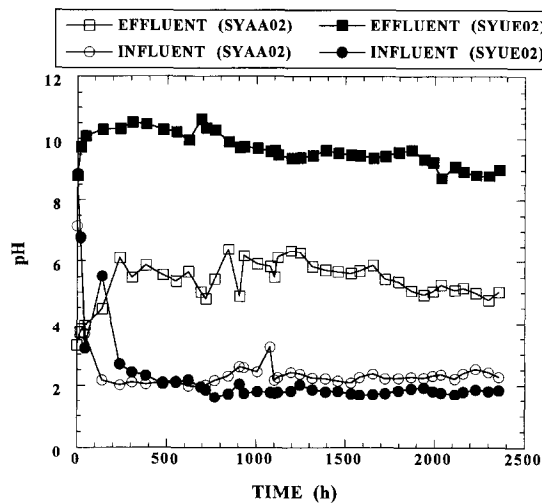

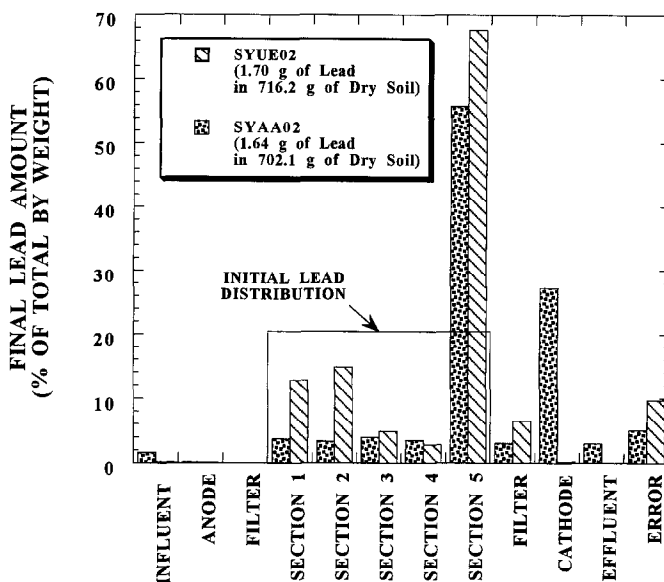Fig. 4. Catholyte and anolyte pH profiles in UE02 and AA02 tests (current density = 50 mA/cm^2.)

Fig. 5. Comparisons of distribution of final lead content and corresponding mass balance across specimen in UE02 and AA02 tests (current density = 50 mA/cm^2, processing duration = 2356 h).

Acetic acid enhancement tests result in substantial transport of the lead within the specimen in AA02 up to section 5. Higher removal rates (up to section 5) in AA02 over AA01 are due to the differences in processing periods (1121 h in AA01 and 2356 h in AA02). Lead electrodeposited at the cathode in AA02 is about 3 times that electrodeposited in AA01. Significant masses of lead were found in section 5 (up to 50% of the initial lead) in both enhanced tests. Further acidification and processing were required.

The third acetic acid enhanced test (AA03) had the best removal rates compared to other enhanced and unenhanced tests. Up to 40% of the total lead was precipitated and/or electrodeposited at cathode and at the base of the cathode in sludge form (Table 3). Test AA03 results better demonstrate the effect of decreasing the catholyte pH to 4 on process performance. In this test, sections 3–4 still contain 15% of the total lead each; however, longer processing periods may have decreased this amount. Initial concentration of lead was eight times the concentration in AA01 and AA02. Again, high adsorption capacity of the illitic soil necessitates longer processing times.

8.3. Nafion™ membrane enhanced tests

In the membrane enhanced tests, catholyte pH showed differences before and after the membrane (Fig. 6). A drop of two to three pH units occurred across the membrane. The pre-membrane (soil side of the membrane) pH value was at about 8 while the pH value at the electrode side of the membrane (post-membrane) increased up to 11.

At the beginning of the third test (NM03) processing conditions similar to NM01 and NM02 tests were employed. After 600 h of testing, it was realized that it would be
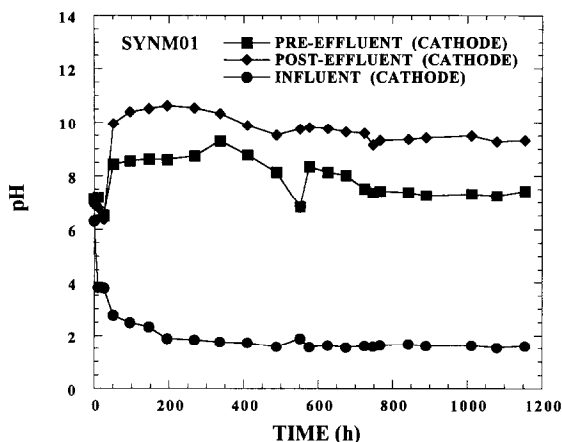
Fig. 6. Catholyte and anolyte pH profiles in NM02 test.

beneficial to decrease premembrane pH in NM03 to assist further extraction of lead. At that stage, 0.1 M acetic acid was introduced as premembrane processing liquid. In addition to adding 0.1 M acetic acid, a decision was taken to change both effluents periodically. The premembrane acid also worked as a self-cleaning solution for the Nafion™ membrane. It is noted that the premembrane effluent pH was brought down to a value of 3 from the earlier value of 8 realized in the NM01 and NM02 tests. Premembrane effluent pH remained steady at 3 throughout processing.

After about 600 h of processing NM01 and NM02 the potential difference across the electrodes increased, reaching gradients of up to 23 V/cm (maximum limit on the power supply). The second test NM02 showed that the potential difference across the electrodes fluctuated after the first 600 h. It is postulated that precipitation of a nonconducting salt on the membrane might be the reason for the increase in potential differences in these tests compared to the acetic acid enhancement tests.

Final lead distributions in the Nafion™ membrane enhanced tests are summarized in Table 4. Non uniform final lead distribution is noted across the specimen in NM01 and NM02 (Fig. 7). About 35% of the initial lead was found in section 5, most probably due to precipitation of lead as its hydroxide. About 5% of lead was found on the Nafion™ membrane and less than 2% on the cathode in NM01. In NM02, which was processed twice the processing time of NM01, 10% of the lead was found on the membrane and 2% on the cathode. Both tests showed limited transport of lead.

The specimen in the third Nafion™ membrane enhancement test (NM03) was spiked at an initial lead concentration of 17950 mg/kg and it was processed for 3001 h. Similar to acetic acid tests, lead was transported from sections near the anode (sections 1–4) to section 5 (Fig. 8). Up to 35% lead was accumulated in section 5. A significant amount of lead was transported out of the soil specimen into the cathode filter, cathode electrode and both effluents. The total energy expended in this test was significantly high (9958 kWh/m^3).

Table 4
Final lead distribution in Nafion™ membrane enhanced synthetic soil specimens

Section	NM01 (%)	NM02 (%)	NM03 (%)
Influent	0.26	0.00	15.56
Anode	0.02	0.04	0.53
A-filter	0.05	0.06	0.03
Section 1	10.07	9.84	2.56
Section 2	22.18	19.3	7.57
Section 3	20.64	9.88	0.72
Section 4	5.10	3.94	0.67
Section 5	34.94	32.62	38.55
C-filter	1.66	2.03	5.76
Pre-effluent	0.12	0.14	6.56
Nafion	3.07	9.31	4.63
Cathode	1.31	2.10	3.18
Post-effluent	0.05	0.50	3.02
Error	0.53	10.23	12.66

8.4. Energy expenditure

Table 5 summarizes the energy expenditure in all unenhanced and enhanced tests. Acetic acid enhancement tests resulted in less energy expenditure than unenhanced tests. Final lead distribution and energy expenditure demonstrate that acetic acid enhancement aids in efficient transport of lead out of the soil into the catholyte at a reduced energy
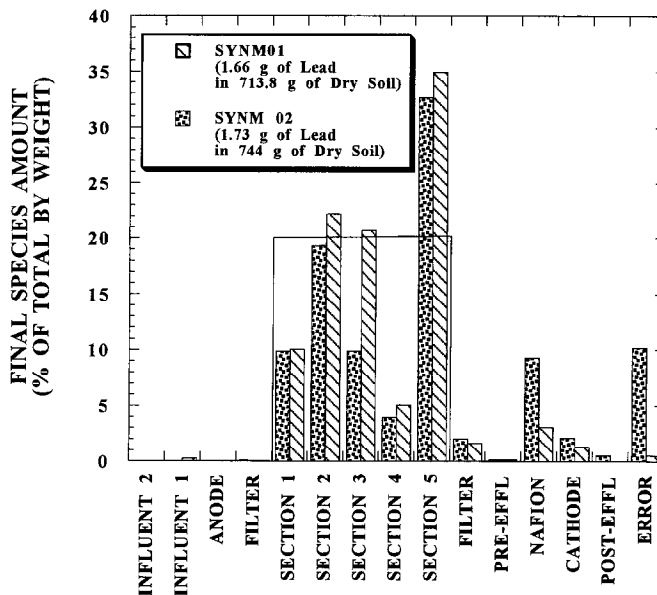

Fig. 7. Distribution of final lead content and corresponding mass balance across the specimen in NM01 (processed for 1155 h) and NM02 tests (processed for 2375 h).
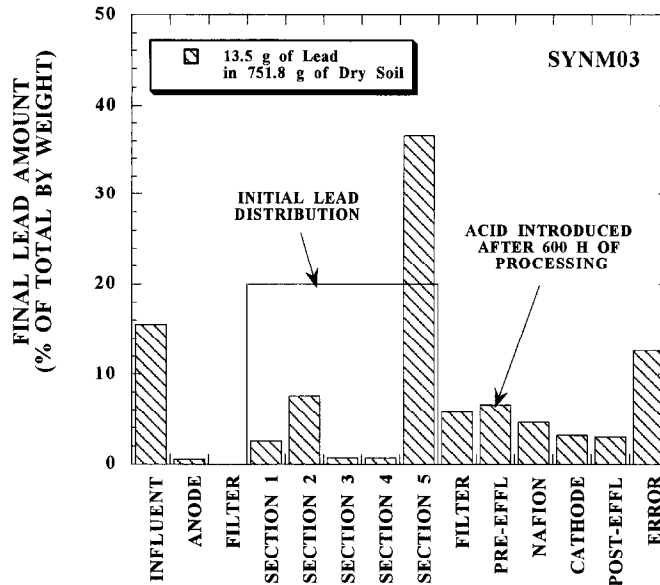
Fig. 8. Distribution of final lead content and corresponding mass balance across the specimen in NM03 test (processing duration = 2356 h).

expenditure. However, energy expenditures in these tests are higher than those reported by Hamed et al. (1991) for unenhanced removal of lead from kaolinite. Higher electric resistivity and higher energy expenditure is expected in the case of illitic mixture. First, high sorption capacity of this mixture will minimize solubilized lead in pore fluid. Ionic strength and electrical conductivity will be low, rendering a higher voltage gradient across the specimen. As a result, the energy expenditure will increase. Secondly, illite is the dominant mineral in the mixture, and soil tortuosity is expected to be less in this mixture than in kaolinite. This will result in a lower mobility of the ionic lead in the illite pore fluid under the applied electric gradient. Finally, free potassium ions in the pore fluid will compete with lead transport.

The third group of tests (unenhanced and enhanced tests) were conducted on the illitic mixture at an initial lead concentration of 18 000 mg/kg (8 times that used in the first two groups of tests). The applied current in the third group of tests were increased from an initial value of 4 mA (0.05 mA/cm^2) to 20 mA (0.25 mA/cm^2) after 400 h of processing. The decision to increase the current density in these test was made based on the results of the first two tests. It was concluded that it would be necessary to generate

Table 5
Energy expenditure

Test	UE01	UE02	UE03	AA01	AA02	AA03	NM01	NM02	NM03
Energy (kWh/m^3)	93	116	4171	49	90	4412	461	1248	9958

substantially more acid in this test to aid the desorption process. However, the voltage gradient increased significantly in the third tests (ranging from 10 V/cm in AA03 to 25 V/cm in UE03). The increase in voltage gradient is due to the high current used and due to the non-conductive zone developed at sections close to and in direct contact with the cathode, specifically in the unenhanced test. This behavior is often observed in tests with higher current densities (0.25 mA/cm^2) rather than in lower current densities (0.05 mA/cm^2) (Acar et al., 1994).

Energy expenditure in all Nafion™ membrane tests was high when compared to the other tests (Table 5). The potential differences across the electrodes increased in most membrane tests and reached gradients of up to 23 V/cm (maximum limit on the power supply). The energy expenditures in membrane tests were substantially higher (up to 1250 kWh/m^3) due to the resistance offered by the membrane. Lower expenditures are anticipated if (a) the membrane is changed periodically and cleaned, and/or (b) the postmembrane electrolyte is siphoned frequently for precipitation. These tests indicate that the membrane could be efficiently used in extraction only if its performance is closely maintained and its clogging is prevented.

9. Conclusions

It is feasible to extract metals from soils with high sorption capacity, such as illitic soils. However, higher currents and longer processing periods are necessary in order to clean-up the soil. This will require higher energy expenditure and increase the cost of remediation.

Neutralizing the cathode reaction to a pH level of 5–6 using acetic acid is relatively effective in extraction of the species; however, species are still found precipitated very close to the cathode end. It is essential to decrease the catholyte pH levels to 4 or less in order to increase the efficiency of species extraction.

Nafion™ membrane limits the transport of base. The membrane efficiency in preventing base transport is increased by using an acid as a premembrane fluid. The advantage of using this membrane is that there would not be a need to use a continuous neutralizing cathode. The cost of acid use will be significantly reduced. However, the Nafion membrane is relatively expensive and the cost of such a membrane may increase the cost of in situ remediation by electrokinetics unless the system is engineered and optimized to decrease the cost during field implementation. Cost-efficient field techniques should be devised if membrane could prevent premature precipitation.

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