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Electrokinetic Processing for the Removal of Radionuclides in Soils

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ABSTRACT

Electrokinetic soil remediation is one of the most promising soil decontamination processes because it has high removal efficiency and time effectiveness in low permeability soils, such as clay. Uranium and strontium were efficiently removed from kaolinite by electrokinetic remediation. In the case of cesium, the rate of removal may be

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significantly slower than those of the uranium and strontium. Acetic acid was effective as enhancement agent for buffering hydroxide ions produced by the cathode reaction, resulting in the prevention of the precipitation of uranium ions in the cathode region. This also decreased energy consumption because hydroxide precipitation increased the resistance and the electrical gradient across the soil cell. The use of citric acid was not efficient in removing uranium from kaolinite because the direction of electromigration was opposite to that of electroosmosis. Since most metal–citrate chelates are negatively charged, they were transported towards the anode by electromigration, whereas electroosmosis flowed toward the cathode, resulting in lowering removal efficiency. Uranium was not effectively removed from the weathered soil of black shale by electrokinetic remediation process. This may be due to the low proportion of the mobile ions because most of uranium exists in the residual fraction.

Key Words: Electrokinetic remediation; Enhancement agent; Radionuclides; Removal efficiency.

INTRODUCTION

The development of atomic power energetics and possible emergencies of the nuclear fuel cycle at a plant imposes strict requirements on the development of a cost-effective method to remove radionuclides from contaminated soils.[1] Long-lived strontium, cesium, and transuranium radionuclides, which may cause a potential hazard to human beings and animate nature for as long as a 1000-year period, are of the most importance in biogeochemistry.[2]

Electrokinetic remediation uses electric currents to extract radionuclides, heavy metals, certain organic compounds, or mixed inorganic species and organic wastes from soils and slurries.[3] Electrokinetics includes the movement of water (electroosmosis), ions and polar molecules (electromigration), and charged solid particles (electrophoresis) relative to one another between two electrodes under the action of an applied direct current.[3] When direct current is passed through soil, the aqueous phase will move toward the negative electrode (cathode) by the phenomenon of electroosmosis. In addition, ion migration takes place; cations migrate to the cathode, whereas anions migrate towards the anode. These processes, together referred to as electrokinetics, can be used to remediate contaminated soil in place without excavation. The electroosmotic permeability of clays is several orders of magnitude larger than their hydraulic permeability and, therefore, is useful for efficient transport of water in tight soil types, such as clay.[3]

The major advantages of the electrokinetic remediation have been clearly set out in numerous research reports: (1) a specific applicability to low permeability soils (clays, silts, and layers). Such soils have greater ability to adsorb pollutants, but are resistant to common in-situ remedial techniques, such as pump-and-treat method which would require in this case a very high hydraulic gradient to be efficient; (2) a high degree of control of flow direction, unlike soil flushing; (3) the capability of removing a wide range of contaminants, e.g., heavy metals, radionuclides, and organic compounds; and (4) a low electric power consumption.[3–11]

The objectives of this study were to assess the feasibility of radionuclide removal from kaolinite by electrokinetic remediation, to investigate the effect of enhancing agents, to explore the optimum condition for the efficient removal and energy consumption, and to examine the applicability of the technique to field soil.

EXPERIMENTAL

Soils used in this experiment were kaolinite and the field soil weathered from uraniferous black shale. Kaolinite was selected because of its low activity and permeability. Typical physicochemical properties of kaolinite are given in Table 1.

Kaolinite was prepared by mixing the soil with uranyl nitrate solution ($UO_2(NO_3)_2 \bullet 6H_2O$) and by spiking with Sr-85 and Cs-134 stock solutions obtained commercially. The anion present in stock solutions was only nitrate ion because the nitrate forms of U, Sr-85, and Cs-134 and deionized water were used to make stock solutions. Four kilograms of oven-dried kaolinite were mixed with 2 L of uranium, Sr-85, and Cs-134 solution to give 50% water content (defined as the ratio of water to soil, L/kg). Mixtures were allowed to settle down for more than 7 days to attain the uniform distribution of contaminants and to complete adsorption in the soil samples. The air-dried field soil was mixed with distilled water for the equivalent water content. Specimens were taken from soil samples for the measurement of initial pH and water content and for the analysis of uranium concentration and radioactivities of strontium and cesium.

A schematic of the electrokinetic test apparatus is shown in Fig. 1. The soil cell, which accommodated the soil sample, was made of acryl and had a size of 20 cm × 7 cm × 20 cm. This cell was connected to the anode compartment of 700 mL capacity at one end and to the cathode compartment

Table 1. Physicochemical properties of kaolinite soil used.

Parameter	Measured value
Group symbol according to USGS	CL
Liquid limit (%)	78
Plastic limit (%)	32
Specific gravity	2.64
pH of soil at 50% water content	4.93–5.20
Hydraulic conductivity (cm/sec)	1×10^{-7}
Initial water content (%)	50

at the other end. Between each compartment and soil cell, a porous polyethyleneterephthalate (PET) filter was inserted to prevent clay particle from flowing into electrode compartments. Anode and cathode compartments were connected to anode and cathode reservoirs to circulate the electrode solution using peristaltic pump (Masterflex, 1 to 100 rpm, 3 heads, USA). An electrode was placed in each compartment. Platinum mesh (20 cm × 7 cm) was used as anode to prevent introduction of extraneous products due to electrolytic reaction of the electrode itself whereas titanium mesh (20 cm × 7 cm) was used as s cathode. Two mass cylinders (2 L) were used as anode

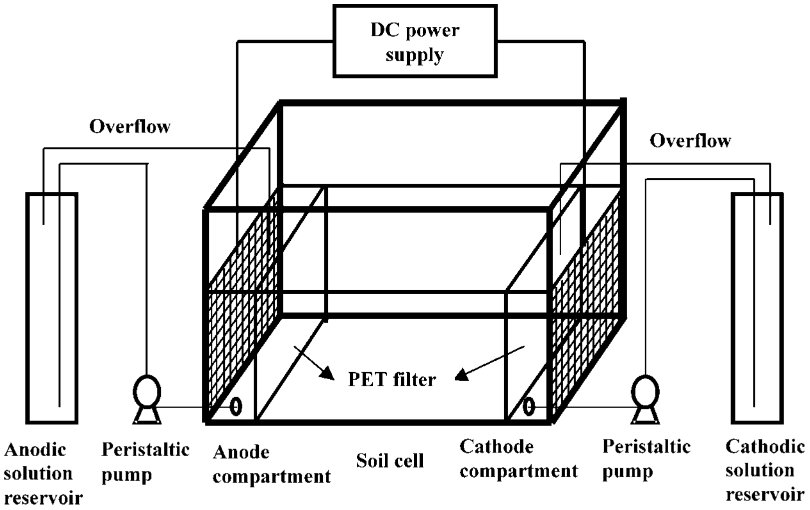

Figure 1. Schematic diagram of experimental apparatus.

and cathode reservoirs to measure the solution volume transported by electroosmosis.

Three different types of tests, enhancement tests (unenhanced vs. enhanced tests), enhancing agent tests (acetic vs. citric acids), and application to the weathered soil from uraniferous black shale, were conducted. Processing parameters are provided in Table 2. All experiments were carried out under the equivalent conditions, such as applied current, area, and length of soil cell. Only initial concentrations of contaminants and cathode-enhancing agents were different according to the testing program. Water (distilled water) was added to the anode reservoir on a daily basis to make up water deficiency due to electroosmotic flow toward the cathode. Cathode-enhancing agents of 0.4 M acetic acid or citric acid were used to

Table 2. Testing program for the electrokinetic removal of radionuclides.

	Enhancement tests		Enhancing agent tests		
Parameter	Unenhanced	Enhanced	Acetic acid	Citric acid	Application test
Soil specimen	Kaolinite	Kaolinite	Kaolinite	Kaolinite	Weathered soil from uraniferous black shale
Contaminants and initial concentration	U: 968.5 mg/kg	U: 1027 mg/kg			
	Sr-85: 4833 Bq/kg Cs-134: 280.9 Bq/kg	Sr-85: 4892 Bq/kg Cs-134: 286 Bq/kg	U: 1000 mg/kg		U: 11.1 mg/kg
Area of soil cell (cm^2)	140		140		140
Length of soil cell (cm)	20		20		20
Applied current (mA)	100		100		100
Current density (mA/cm^2)	0.714		0.714		0.714
Duration (h)	120		114	96	
Anodic solution	Distilled water		Distilled water		Distilled water
Cathodic solution	Distilled water	0.4 M Acetic acid	0.4 M Acetic acid	0.4 M Citric acid	0.4 M Acetic acid

maintain the pH below 4 at the cathode compartment. Both influent and effluent were continuously circulated from the respective reservoirs into the electrode compartments using a peristaltic pump. The cell was horizontally placed to diminish a hydraulic gradient. A constant direct current (0.1 A) was supplied to the specimen by a DC power supply (Biorad, model: PowerPac 200, 5 to 200 V, 0.01 to 2 A, 200 W, USA). The cross sectional area of the specimen was 140 cm^2, rendering a constant current density of 0.7 mA/cm^2. Five soil samples were obtained at different locations of the soil cell during and after the treatment. These samples were used for the analysis of final soil pH, water content, and species concentrations. In-situ soil pH was measured by inserting a pH electrode in the soil samples. A flowchart of the whole experimental procedure is shown in Fig. 2. The soil samples were separately oven dried at 105°C for 24 h and then pulverized. Two different methods were used for the analyses of U and Sr-85 and Cs-134. For the analysis of U, firstly, 3g of each sample was taken with 50-mL centrifuge tubes and 30 mL of 1 M HNO_3 was added. The resultant slurries were mechanically mixed for 24 h at room temperature. Subsequently, the slurries were filtered and the filtrates were analyzed with inductively coupled plasma atomic emission spectrometry (ICP-AES, Thermo Jarrel Ash, USA) for uranium. Secondly, in case of analyses of Sr-85 and Cs-134, their radioactivities in each oven-dried soil sample were determined by γ-ray spectrometry. A HPGe detector (Model EGPC 45-1.90, USA) with a counting efficiency of 45% and FWHM of 1.9 keV was used. Twenty grams of each sample from each section of the soil cell was oven-dried at 105°C for 24 h, ground, and filled in 20 mL plastic vials. In all cases, the samples prepared were counted for 20,000 seconds by γ-ray spectrometry. The radioactivities of Sr-85 and Cs-134 were determined from the peak at 514.01 keV and 795.84 keV, respectively.

RESULTS AND DISCUSSION

Unenhancement and Enhancement Tests

Radionuclides may be precipitated by hydroxyl ions generated from electrolysis of water in the cathode. Enhancing agent injected as cathode electrolyte can buffer those hydroxyl ions, and enhance the effectiveness of the process in removing radionuclides from soils. In order to compare the effectiveness of enhanced processing with that of unenhanced processing, distilled water and 0.4 M acetic acid were used as cathode electrolyte in unenhanced and enhanced tests, respectively. Acetic acid is known as one of

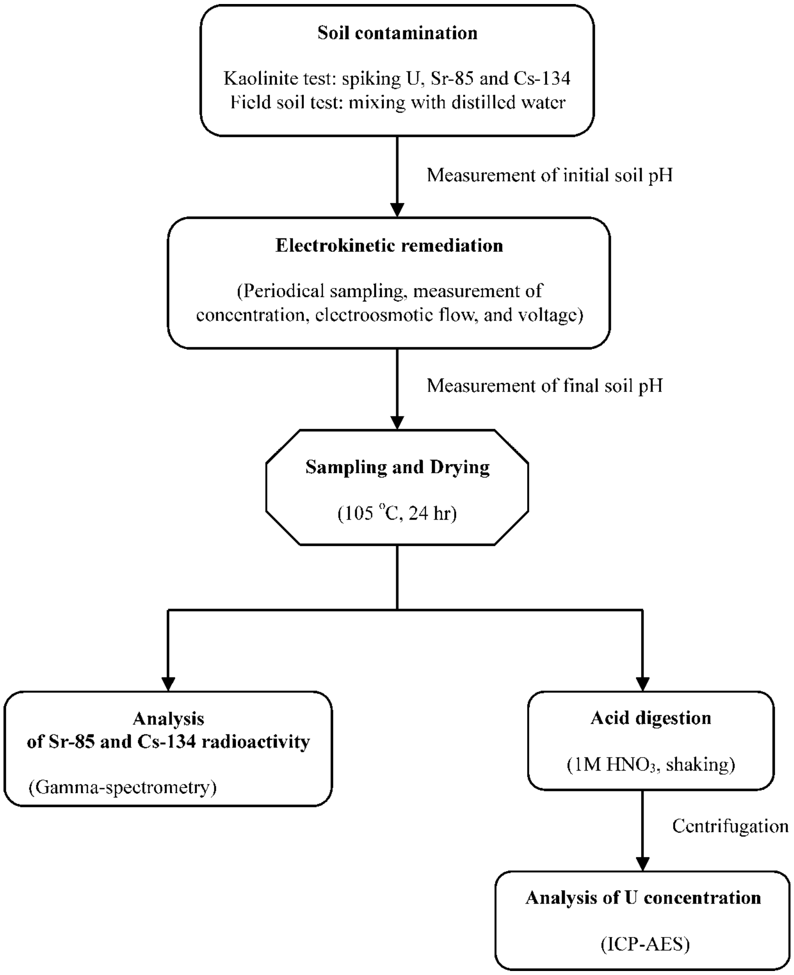

Figure 2. Flowchart of experimental procedure.

the environmentally safe and biodegradable chemicals. It will not cause a health hazard, when it is used for conditioning the pore fluid in electrokinetic remediation. As shown in Table 2, distilled water was injected as make-up water (influent) at the anode in both the unenhanced and the enhanced tests.

Figure 3 presents the variation of soil pH values in the unenhanced and the enhanced tests. In the unenhanced test, the pH profile of the unenhanced test was

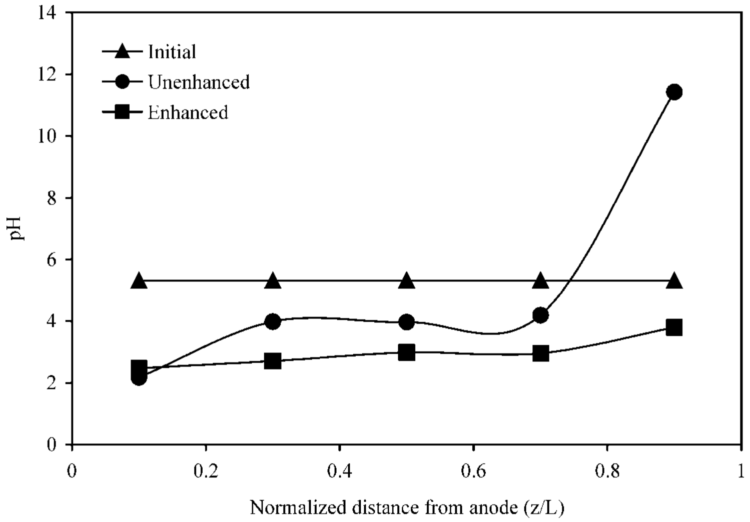

Figure 3. pH profile of the soil cell in the unenhanced and the enhanced tests. z = distance from anode; L = length of soil cell.

significantly similar to those of other researchers, with lower pH values at regions closer to the anode and increasing toward the cathode.[3,12,13] When the DC electric gradient was applied to the electrodes, and causing the primary electrode reactions of electrolysis, the hydrogen ions produced at the anode and the hydroxide ions produced at the cathode generate an acid and base front at the respective electrode. Both fronts advance toward the opposite charged electrode by electromigration, diffusion, and electroosmotic advection. When two fronts meet, the soil between the electrodes may be divided into two zones, low and high pH zones, with a sharp pH jump at section close to the cathode (see Fig. 3). The location of the pH jump depends on several factors and normally appears closer to the cathode. One factor affecting the location of the pH jump is the relative mobility of hydrogen ions and hydroxyl ions.[3,7,14] The Hydrogen ion has approximately twice as much ionic mobility as hydroxyl ion. In addition, electroosmotic flow typically enhances the transport of the acid front. As shown in Fig. 3, the final soil pH dropped to below 2 at the regions near the anode; whereas it increased up to 12 at the regions near the cathode.

To prevent the electrolysis of water at the cathode, the cathode compartment was filled with acetic acid. It was expected that introducing a weak acid might not tend to significantly increase the ionic strength in the system, and might not affect the electroosmotic flow as much as that in the addition of an equivalent of strong acid. Moreover, the acetate ions would migrate toward the anode and would not precipitate with the uranyl ions, since uranyl acetate is a soluble salt. This ensures that the uranyl ions may elute with the effluent. The acetic acid was added into the cathode compartment and replaced daily by fresh acid. Variation of the pH in the enhanced test using acetic acid is shown in Fig. 3. The final soil pH decreased at the region near the cathode, compared with that of the unenhanced test, because the base front was neutralized by the acetic acid. It was reported that uranium was quantitatively precipitated by the addition of ammonium hydroxide at a pH of 4 or greater. Therefore, it was desirable to maintain the pH value below 4 at a the cathode compartment to prevent precipitation of uranyl hydroxide.

Electroosmosis is the flow of the pore water in the soil under the action of the electric field. Electroosmotic velocity on a plane surface, U (m/sec), is expressed as[15]:

$$U = -(\varepsilon \zeta E_x)/\mu \tag{1}$$

where, ε is the permittivity of the medium (C/V m), ζ is the zeta potential (V), E_x is the electric field strength or gradient (V/m) in a direction parallel to the electroosmotic flow, and μ is the viscosity of the medium (N sec/m^2). This formula of the electroosmotic velocity on a plane charged surface is known as the Helmholtz–Smoluchowski equation. According to this equation, the electroosmotic velocity (U) is significantly affected by the electric field strength (E_x) and the zeta potential (ζ). On the other hand, the zeta potential of clay has a strong dependence on the local pH of the saturation solution. Typical ζ values of clay ranges between 0 to 100 mV, with more negative values at high pH. For silica particles, the point of zero charge (PZC) is reported to be at a pH of 3 to 5.[16] Below PZC, silica surface is positively charged and ζ is positive. Therefore, electroosmotic flow ceases or reverses. In electrokinetic remediation, the hydrogen ions on the soil surface cause the decrease of electroosmotic flow with time, resulting from the decrease of soil pH. In addition, the effect of high ionic strength on the zeta potential (ζ) can be written as[17]:

$$\zeta = A - B \log C \tag{2}$$

where, C is the ion concentration and A and B are empirical constants. The ionic strength is directly proportional to the ionic concentration. The high ionic strength causes the zeta potential to become less negative, which influences directly on the electroosmotic flow. The zeta potential of kaolinite ranges from $+0.7$ mV (at pH $= 2.0$) to -54 mV (at pH = 10).[16] Accordingly, the decrease of soil pH makes the electroosmotic velocity decreased.

Figure 4 show the volume of water transported by electroosmosis. In the unenhanced test, the electroosmosis increased steadily because the overall soil pH was kept relatively high during the remediation process (5 days). On the contrary, the flow of water was slowly diminished during the process and eventually stopped in the enhanced test. The magnitude of zeta potential became decreased as the ion concentration increased by injection of enhancing agent from cathode compartment. If the chemistry of the soil–fluid–contaminant system was changed by a prolonged application of a DC electric field, the direction of electroosmotic flow would be reversed, i.e., from the cathode toward the anode. The phenomenon was due to the acidic environment in the soil, resulting from the migration of hydrogen ions generated by electrolysis of water at the anode and the neutralization of hydroxyl ions by injection of enhancing agent (acetic acid) into the cathode compartment. The low pH in the soil reversed the polarity of zeta potential of kaolinite, as already mentioned. Hence, the initial negative zeta potential of the soil surface approached zero value and finally became positive below the pH around the original PZC. When the polarity of zeta potential was reversed, the direction of electroosmotic flow was reversed. Consequently, high ionic strength and low pH by injection of acetic acid caused a decrease of electroosmotic flow in the enhanced test compared to the unenhanced test.

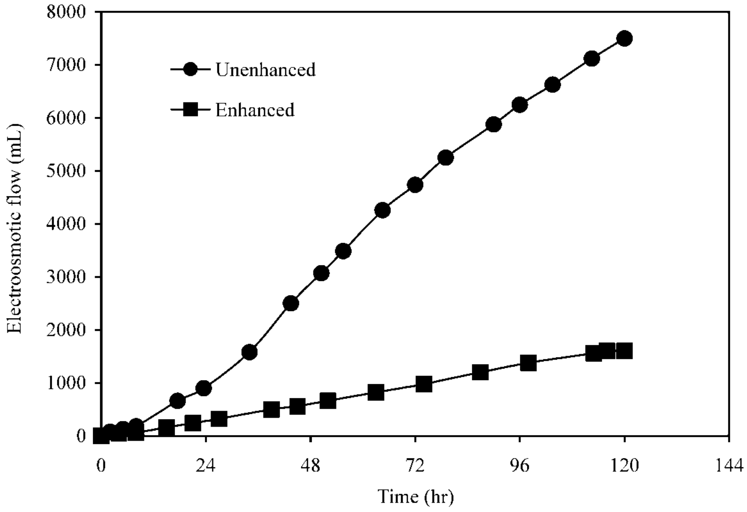

Figure 4. Volume of water transported by electroosmosis in the unenhanced and the enhanced tests.

The normalized concentration profiles of uranium during the unenhanced and enhanced tests are presented in Fig. 5. As shown in Fig. 5(a), there was a continuous increase in the residual uranium concentration toward the cathode. Since the high pH condition near the cathode favored the hydroxide precipitation, the removal efficiency remarkably decreased at the region near the cathode. The precipitates close to the cathode might be uranium hydroxide [$UO_2(OH)_2$]. This premature precipitation of the migrating ions, when confronted with the hydroxide ions generated at the cathode, was the dominant reason that enhancement techniques are required. When the acetic acid was added to the cathode, the migration of acetate (anion) into the system created soluble complexes with uranyl ions because most acetate salts were soluble. Uranium accumulation appeared at the region near the cathode in the unenhanced test due to high pH of catholyte. The low catholyte pH value (about 4) of the acetic acid enhanced test was expected to minimize uranium hydroxide precipitation. Figure 5(b) shows the uranium concentration profiles of the enhanced test. Although the electroosmotic flow was relatively small compared to that of the unenhanced test, uranyl ions were considerably transported toward cathode, as shown in the concentration profile (Fig. 5(B)). This transport was contributed to electromigration rather than electroosmosis, since electroosmosis appeared significantly diminished. Acar et al. reported that for a specific charged species, electromigration could be at least one order of magnitude larger than electroosmotic transport.[3] However, it was not possible to quantify the amount of ions transported by either transport mechanism. The introduction of 0.4 M acetic acid in the cathode compartment increased the uranium removal close to the cathode. Therefore, acetic acid was effective in neutralizing the cathode reaction to the pH level of 3 to 4, resulting in the prevention of the precipitation of uranium on the cathode. The increase of the removal close to the cathode was attributed to the neutralization of the hydroxyl ions by direct action of the acetic acid, or the effect of acetate ions forming a soluble salt with the uranyl ions. Table 3 shows the residual concentration and removal efficiency of uranium according to the distance from anode after treatment.

Figure 6 shows the normalized concentration profile of strontium. The removal trend of strontium appeared significantly similar to the test of uranium, as shown in Figs. 5 and 6. There was a large accumulation of the strontium in the region near the cathode compartment after 5 days of treatment in the unenhanced test. This accumulation might be due to precipitation and speciation of the strontium. Soil retention of cations increases with increase of pH, resulting in the precipitation and anionic complexation. As shown in Fig. 3, the pH of the soil close to the cathode compartment increased to 11.4. This may render salt precipitates or anionic species of most metals, which are

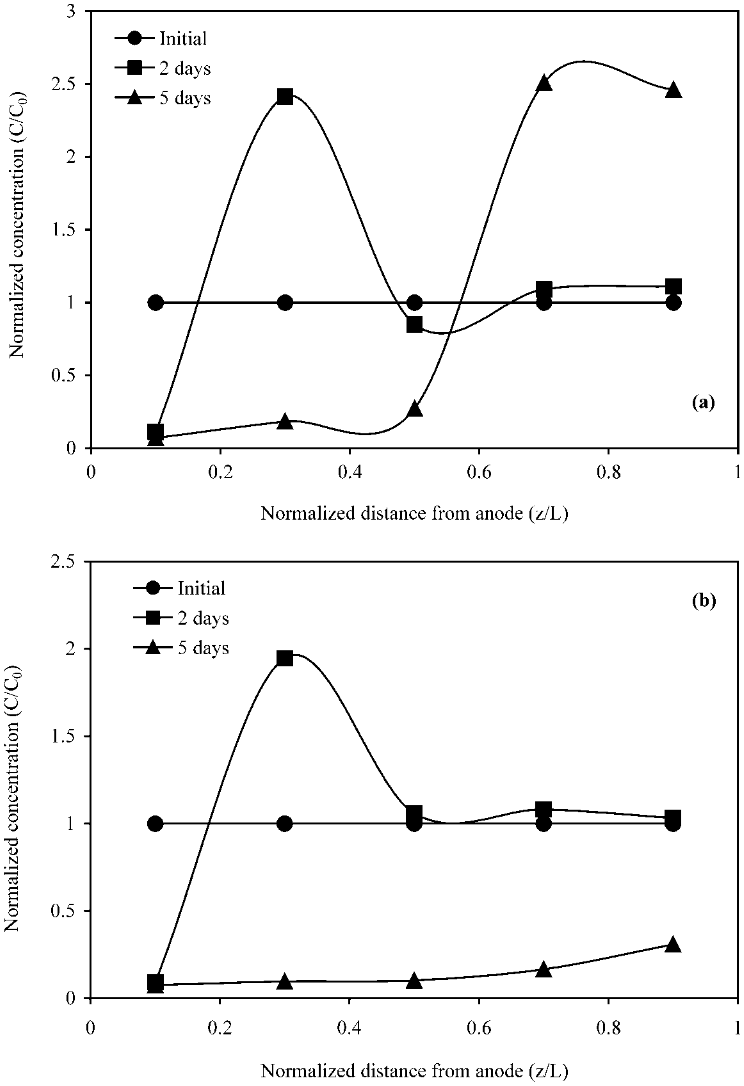

Figure 5. Uranium concentration profile, (a) unenhanced test; (b) enhanced test. C_0 = initial concentration; C = residual concentration; z = distance from anode; and L = length of soil cell.

Table 3. Residual concentration and removal efficiency of uranium in the soil cell after unenhanced and enhanced electrokinetic tests.

	Unenhanced test		Enhanced test	
Normalized distance from anode	Residual concentration (mg/kg)	Removal efficiency (%)[a]	Residual concentration (mg/kg)	Removal efficiency (%)[a]
0.1	47.8	95.1	76.7	92.5
0.3	117.8	87.8	98.5	90.4
0.5	204.1	78.9	105.7	89.7
0.7	2231.0	− 130.4	170.8	83.4
0.9	2186.0	− 125.7	316.6	69.2
Initial	968.5	—	1027.0	—
Average	957.3	1.2	153.7	85.0

[a] Removal efficiency = [(Initial concentration − Residual concentration)/Initial concentration] × 100 (%).

immobile or tend to move to the opposite direction of the electroosmotic water flow. In case of the enhanced test, a minor amount of strontium was found in the region near the cathode (see Fig. 6(b)). The results indicates that the cathode reaction (generation of hydroxyl ions by the electrolysis of water) was successfully depolarized, and the base front was not allowed to enter into the soil system where it did not cause the precipitation or soil retention of strontium. Table 4 shows the residual concentration and removal efficiency of strontium in each section of the soil cell after treatment.

The cesium distribution during experiments is shown in Fig. 7. In the case of cesium, the rate of removal appeared to be much slower than those of strontium and the uranium. This may be due to the lower ionic mobility of cesium, which resulted in lowered electromigration velocity. Additionally, the large affinity of the clay to cesium contributed to the delayed response. There was not a considerably different feature in the enhanced test using the acetic acid. These results demonstrated that the application of the technique was highly dependent on the chemistry of the contaminants. Table 5 shows the residual concentration and removal efficiency of cesium for each section after treatment.

Energy consumption is an important factor in the overall economics of an electrokinetic remediation process and needs to be carefully taken into account. The energy consumption per unit weight of soil processed, E_u

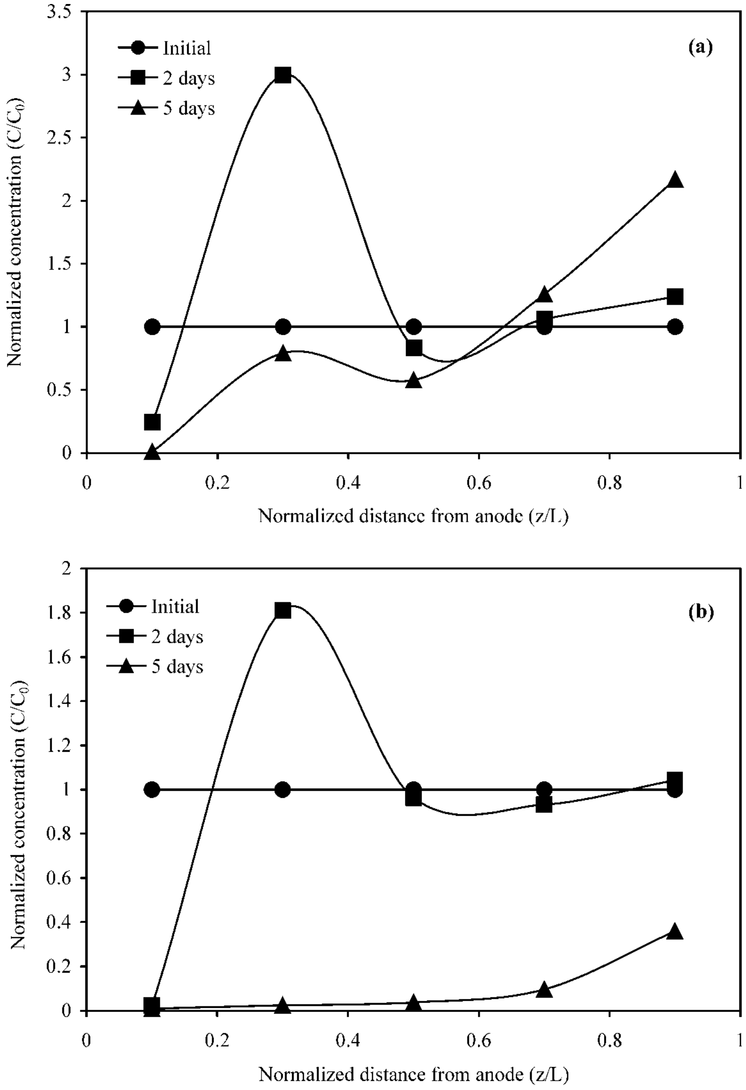

Figure 6. Strontium concentration profile, (a) unenhanced test; (b) enhanced test. C_0 = initial concentration; C = residual concentration; z = distance from anode; and L = length of soil cell.

Table 4. Residual concentration and removal efficiency of strontium in the soil cell after unenhanced and enhanced electrokinetic tests.

	Unenhanced test		Enchanced test	
Normalized distance from anode	Residual concentration (Bq/kg)	Removal enhanced (%)[a]	Residual concentration (Bq/kg)	Removal efficiency (%)[a]
0.1	46.0	99.0	42.2	99.1
0.3	3822.0	20.9	115.9	97.6
0.5	2787.0	42.3	181.2	96.3
0.7	6083.0	− 25.9	470.6	90.4
0.9	10480.0	− 116.8	1756.0	64.1
Initial	4833.0	—	4892.0	—
Average	4644.0	3.9	513.2	89.5

[a] Removal efficiency = [(Initial concentration − Residual concentration)/Initial concentration] × 100 (%).

(kWh/ton), was calculated using the following equation[12]:

$$E_u = \frac{E(t)}{W_s} = \int \frac{I \cdot V(t) \cdot dt}{W_s} \tag{3}$$

where, W_s is the dry weight of soil processed (ton), V(t) is the voltage (V) as a function of time (t), I is the current (A), and t is the processing time (h). Figure 8 shows the energy consumption in the unenhanced and the enhanced tests. The enhanced test showed less energy consumption than the unenhanced test. The high energy consumption in the unenhanced test was attributed to the increase of resistance in the soil cell, resulting from the precipitation of ions as hydroxides in sections close to the cathode. Residual concentration profiles of uranium and strontium and energy consumption indicate that uranium and strontium can be more effectively removed by the enhanced treatment with small energy than by unenhanced treatment.

Enhancing Agent Tests

Two electrokinetic tests were conducted to compare the effectiveness of different enhancing agents. The first test was aimed to neutralize the hydroxyl ions generated by electrolysis of water at the cathode using the acetic acid.

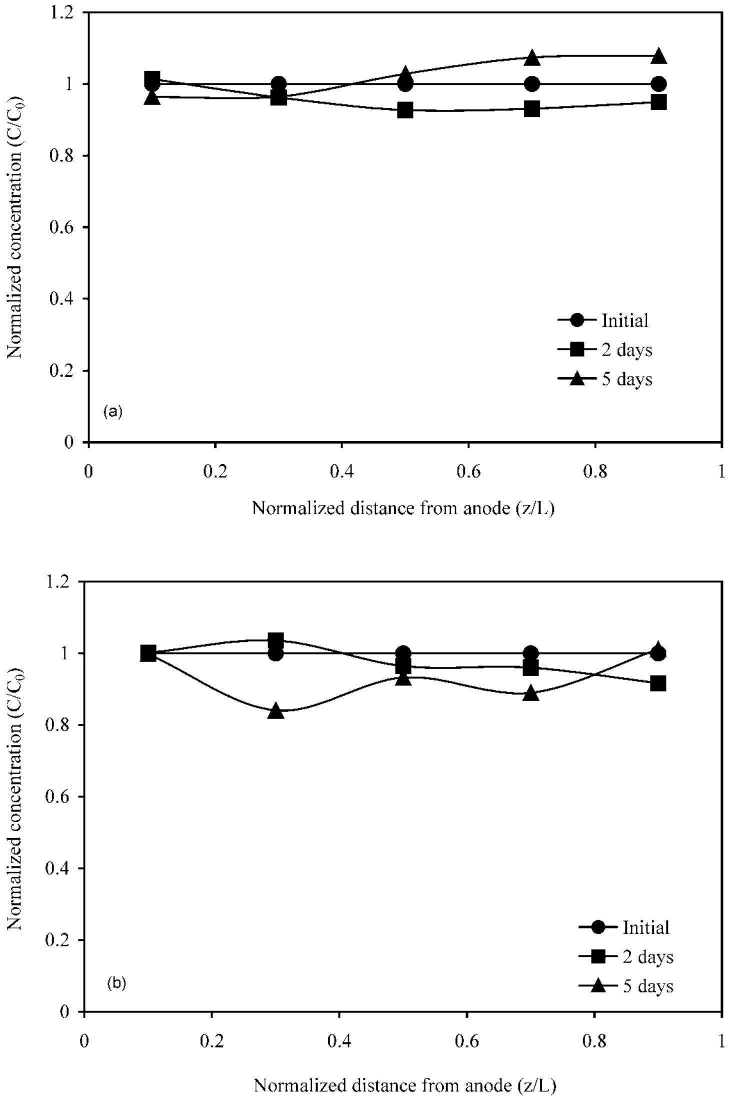

Figure 7. Cesium concentration profile, (a) unenhanced test; (b) enhanced test. C_0 = initial concentration; C = residual concentration; z = distance from anode; and L = length of soil cell.

Table 5. Residual concentration and removal efficiency of cesium in the soil cell after unenhanced and enhanced electrokinetic tests.

	Unenhanced test		Enhanced test	
Normalized distance from anode	Residual concentration (Bq/kg)	Removal efficiency (%)[a]	Residual concentration (Bq/kg)	Removal efficiency (%)[a]
0.1	274.4	2.3	285.4	0.2
0.3	274.5	2.3	240.5	15.9
0.5	276.0	1.7	266.8	6.7
0.7	284.3	− 1.2	254.5	11.0
0.9	285.1	− 1.5	289.2	− 1.1
Initial	280.9	—	286.0	—
Average	278.9	0.7	267.3	6.5

[a] Removal efficiency = [(Initial concentration − Residual Concentration)/Initial concentration] × 100 (%).

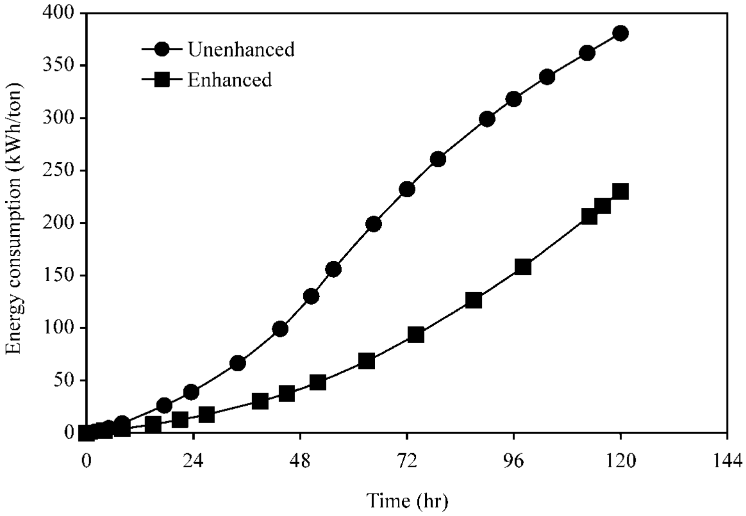

Figure 8. Energy consumption of the unenhanced and the enhanced tests.

The other test was to use specific complexing agents that may complex or chelate with target species during the transport by injecting the citric acid as a catholyte. All the other experimental conditions were identical to those of previous tests.

The initial and final soil pH in these two tests is shown in Fig. 9. After remediation process, the soil pH values were achieved significantly low in both tests. Because dissociation constant of citric acid ($pK_a = 7.1 \times 10^{-4}$) is greater than that of acetic acid ($pK_a = 1.76 \times 10^{-5}$), the final soil pH of the test using citric acid was lower than that of the test using acetic acid.

Figure 10 presents the electroosmotic flow profiles for both enhancement tests using acetic acid and citric acid. The trend was similarly observed in both tests. At the initial stage, water flowed toward cathode since surface of kaolinite was negatively charged. As the test processed, the overall soil pH became gradually low because the acid front moved toward cathode and base front was neutralized by acetic acid and citric acid. At the same time, the flow rate started to decrease.

The uranium distribution of the enhanced tests using acetic acid and citric acid is shown in Fig. 11. Herein, the difference between Figs. 5(b) and 11(a) is described before comparing the effectiveness of two different kinds

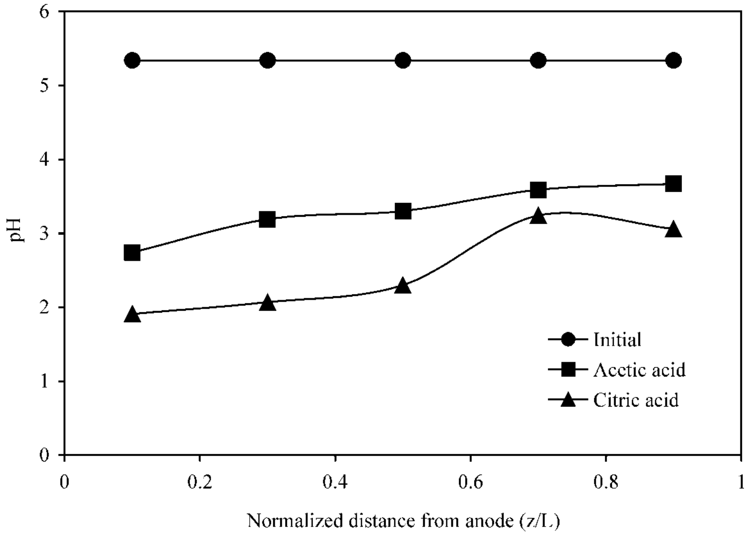

Figure 9. pH profile of the soil cell in the enhancing agent tests. z = distance from anode; L = length of soil cell.

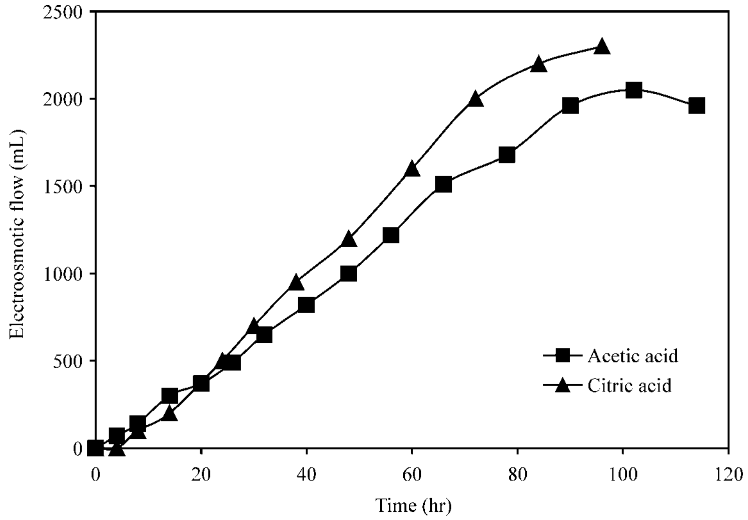

Figure 10. Volume of water transported by electroosmosis in the enhancing agent tests.

of enhancing agent. There was the slightly different trend of uranium removal presented in Figs. 5(b) and 11(a), although those two experiments were conducted using a same kind of enhancing agent, 0.4 M acetic acid, as shown in Table 2. In Fig. 5(b), the normalized amount of uranium after 2 days was low at the anode (a distance of 0.2), equal to 2 at a distance of 0.3, and unchanged at 0.5, 0.7, and 0.9. In Fig. 11(a), after the same time, however, the normalized amount of uranium was low at the first two sampling points from the anode (0.1 and 0.3) and unchanged at 0.5, 0.7, and 0.9. After 5 days, Fig. 5(b) shows all the amounts less than about 0.2, whereas Fig. 11(a) presents a value of 1 at a distance of 0.9. This difference between the two results may be due to the presence of other contaminants (strontium and cesium) in the experiment corresponding to Fig. 5(b) and the small experimental duration in the experiment shown in Fig. 11(a). In Fig. 5(b), the competitive removal among three kinds of contaminants brought about a significant delay of uranium transport at a distance of 0.3 after the 2-day operation, compared with that presented in Fig. 11(a), the experiment using only one kind of contaminant, uranium. In addition, the experiment in Fig. 11(a) was conducted for 114 hours, and the normalized amount of uranium at a distance 0.9 was larger than that in Fig. 5(b)

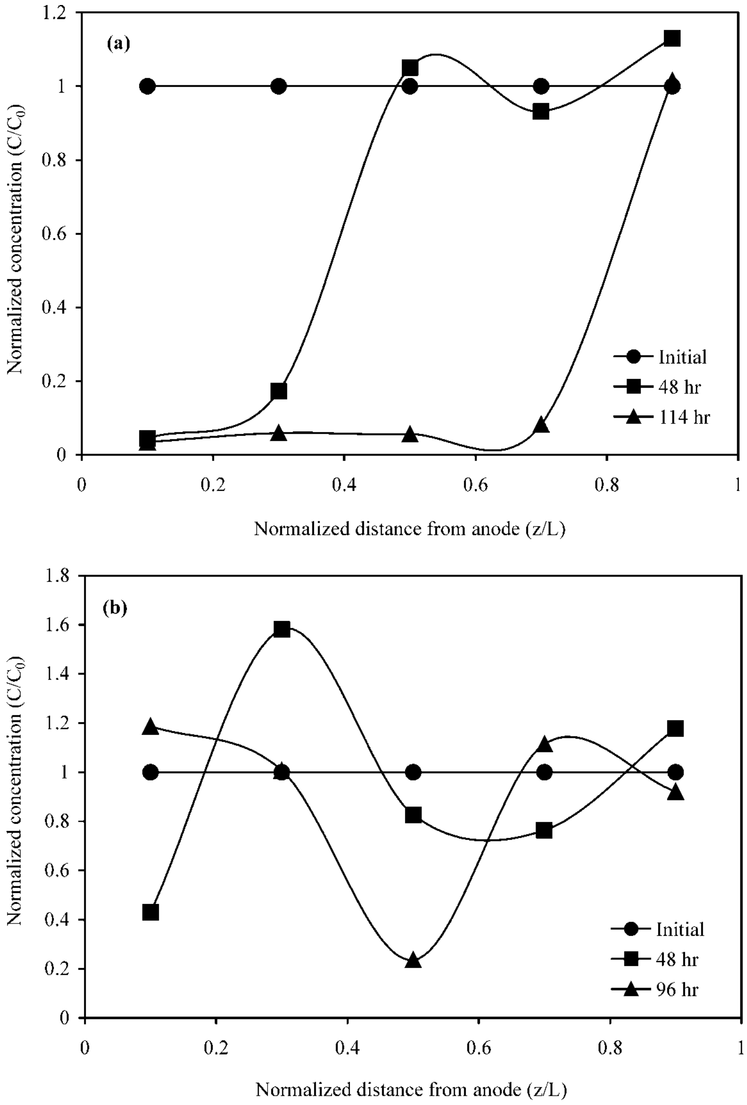

Figure 11. Uranium concentration profile in the enhancing agent tests, (a) acetic acid test; (b) citric acid test. C_0 = initial concentration; C = residual concentration; z = distance from anode; and L = length of soil cell.

obtained by the experiment undertaken for 120 hours. The value at a distance 0.9 in Fig. 11(a) will significantly decrease if the experimental duration is extended. The effectiveness of two kinds of enhancing agent are compared and evaluated. The uranium concentration profile shows that uranyl ions were significantly transported into cathode reservoir and there was no precipitation in the cathode section. The removal trend of the citric acid test was similar to that of the acetic acid test until 2 days. Uranium migrated toward the cathode only at the region near the anode. On the other hand, the final concentration profile showed much less uranium removal efficiency compared to that in the acetic acid test. In case citric acid solution (0.4 M) was injected into the soil from the cathode reservoir, the citrate ions were transported toward the anode. These ions competed with negatively charged soil particle surfaces for the retention of UO^{2+} ions. Since most metal–citrate chelates were negatively charged, they moved toward the anode by electromigration while electroosmosis occurred toward the cathode, and removal efficiency became low.[18] The use of citric acid was not efficient in removing uranium from kaolinite because the direction of electromigration was opposite that of electroosmosis. This result indicates that the selection of an enhancing agent be contaminant specific and considered depending on site characteristics. For example, citric acid may be effective in removing contaminants from cathode toward anode in soils where the reverse electroosmotic flow appears. The dissolved anionic complexes in the pore fluid can be removed by electroosmotic advection and electromigration toward the anode where they are collected and extracted. Table 6 shows the residual concentration and removal efficiency of uranium after the enhancing agent tests using acetic and citric acids.

Application to the Soil Weathered from Uraniferous Black Shale

Electrokinetic remediation was applied to the field soil weathered from uraniferous black shale at the Duck-Pyung area in Korea. Most of the in-situ cleanup techniques, such as electrokinetic extraction, are remarkably effective in removing mobile contaminants from contaminated soils. To maintain the uranium in the dissolved phase, a low pH condition is required. In other words, a low pH environment can promote the removal of uranium from soils. Figure 12 presents the final in situ pH distribution across the specimens after electrokinetic treatment. Final soil pH profile shows a uniformly low pH distribution with almost no significant rise of pH values close to the cathode, owing to the neutralization of hydroxide ions by acetic acid in the cathode compartment. The electroosmotic flow during treatment is shown in Fig. 13.

Table 6. Residual concentration and removal efficiency of uranium in the soil cell after enhancing agent tests.

	Acetic acid test		Citric acid test	
Normalized distance from anode	Residual concentration (mg/kg)	Removal efficiency (%)[a]	Residual concentration (mg/kg)	Removal efficiency (%)[a]
0.1	34.5	96.6	1187.0	− 18.7
0.3	59.2	94.1	1007.0	− 0.7
0.5	55.8	94.4	236.0	76.4
0.7	82.2	91.8	1114.0	− 11.4
0.9	1015.0	− 1.5	920.3	8.0
Initial	1000.0	—	1000.0	—
Average	249.3	75.1	892.9	10.7

[a] Removal efficiency = [(Initial concentration − Residual concentration)/Initial concentration] × 100 (%).

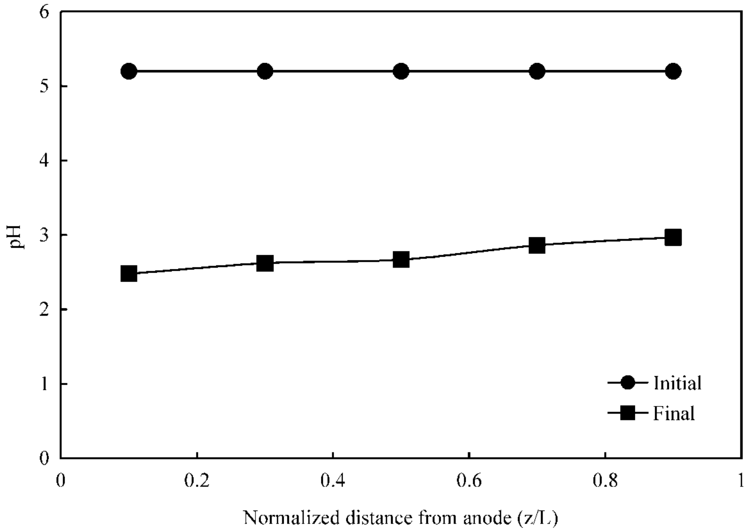

Figure 12. pH profile of the soil cell after the electrokinetic remediation of the field soil from uraniferous black shale area. z = distance from anode; L = length of soil cell.

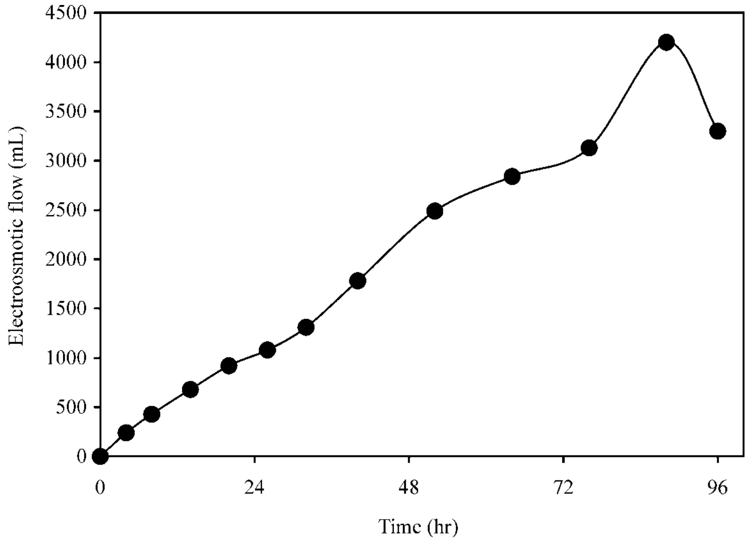

Figure 13. Volume of water transported by electroosmosis during the field soil test.

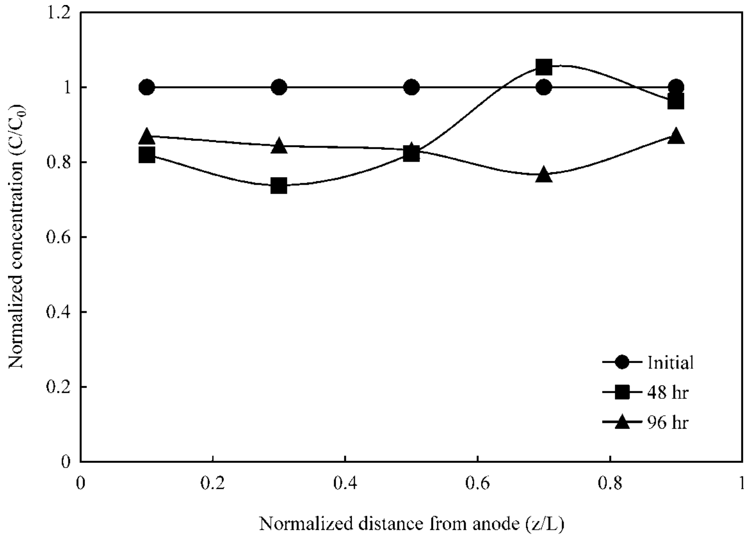

Figure 14. Uranium concentration profile during the field soil test C_0 = initial concentration; C = residual concentration; z = distance from anode; and L = length of soil cell.

Table 7. Partitioning of uranium in the field soil prior to electrokinetic treatment.

Fractions	Concentration (mg/kg)	Percentage (%)
Extractable (water soluble)	0.6	5.6
Reducible (bound to Fe/Mn oxides)	0.6	5.7
Oxidizable (bound to organic matter and sulfides)	0.7	6.3
Residual	9.2	82.4
Total	11.1	100.0

The flow rate of initial stage was significantly higher than that obtained in kaolinite tests, since the soil pH was maintained relatively high due to the high pH buffering capacity of hydrogen ions migrating from anode. However, the flow ceased after 95 h processing time, and reverse flow was observed (from cathode to anode). Figure 14 shows the uranium concentration profile during treatment. Uranium migrated slightly toward the cathode for 2 days, and then moved back from cathode to anode due to reverse electroosmotic flow. From the result of the field soil test, the overall removal efficiency of uranium was very low. The ratio of the final to the initial uranium concentration was close to 1 in most of soil samples, although the pH value of the soil cell was as low as 3 and significant electroosmotic flow was observed during the test. This low removal efficiency may be explained by the uranium speciation of the field

Table 8. Residual concentration removal efficiency of uranium in the soil cell after the field soil treatment.

Normalized distance from anode	Residual concentration (mg/kg)	Removal efficiency (%)[a]
0.1	9.68	12.8
0.3	9.39	15.4
0.5	9.24	16.6
0.7	8.54	23.1
0.9	9.69	12.7
Initial	11.10	—
Average	9.30	16.2

[a] Removal efficiency = [(Initial concentration − Residual concentration)/Initial concentration] × 100 (%).

soil. According to Kim et al. (2000) and Kim and Kim (2001), the more strongly bound fractions of metal contaminants, the less efficiently removed by electrokinetic treatment.[19,20] To determine the partitioning of uranium in the field soil prior to electrokinetic treatment, sequential extraction analysis was conducted. The sequential extraction method used in this study was suggested by Thomas et al.[21] Table 7 presents the result of sequential extraction analysis. As shown in Table 7, most of the uranium in the field soil exists in immobile and strongly bound fractions, such as residual and oxidizable fractions, resulting in the very low removal efficiency of uranium. Table 8 shows the residual concentration and removal efficiency of uranium in the soil cell after treatment.

CONCLUSION

Experimental study seems to demonstrate that the feasibility of electrokinetic soil remediation for the removal of radionuclide contaminants from soils. The experimental results indicate that the technique is effective in radionuclide contaminants from soils with a relatively small amount of energy. From the results of the study, the following conclusions can be made.

Uranium and strontium were efficiently removed from kaolinite by electrokinetic remediation. In the case of cesium, the removal rate may be significantly slower than those of uranium and strontium. This is due to the lower ionic mobility and the affinity of cesium onto kaolinite.

Acetic acid was effective as enhancing agent for buffering hydroxide ions produced by the cathode reaction, and prevented the precipitation of uranium ions in the cathode region. Accordingly, the acetic acid increased the removal efficiency and decreased energy consumption.

The use of citric acid was not efficient in removing uranium from kaolinite, because the direction of electromigration was opposite to that of electroosmosis. Since most metal–citrate chelates were negatively charged, they were transported toward the anode by electromigration while electroosmosis flowed toward the cathode. Therefore, removal efficiency significantly decreased. This result indicates that the selection of enhancement agent should be considered with respect to contaminant type and site characteristics.

The electrokinetic removal of uranium from the soil weathered from uraniferous black shale was not efficient. This was due to the low proportion of the mobile fraction, since most uranium exists as residual fractions derived from enriched uraniferous parent rocks.

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