

## Removal of Cadmium from Clayey Soil by Electrokinetic Method

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Restoration of contaminated soils to an environmentally acceptable condition is important. One of the newer techniques in soil remediation is a method based on electrokinetic phenomena in soils. The technology uses electricity to affect chemical concentrations and water flow through the pores of soils. An important advantage of electrokinetic soil remediation over other in-situ processes such as soil flushing is the capability of control over the movement of the contaminants. Because the migration of the contaminants is confined by the electric field, there is little dispersion outside the treatment zone. Furthermore, the process is effective for soils with low and variable permeability.

In the present study, the distributions of cadmium in the electrokinetic processing of kaolinite under the condition of constant applied voltage are investigated. Cadmium accumulates near the cathode without reducing the diffusion of hydroxide ion into the soil. In keeping the catholyte pH at neutrality, cadmium migrates toward the cathode without any accumulation of cadmium near the cathode and is successfully removed at the cathode reservoir. It was also found that the progress of electrokinetic processing of cadmium could be grasped to a certain extent by monitoring the local voltage and the current density.

Keywords: Electrokinetics, Contaminated Soils, Soil Remediation, Cadmium

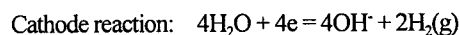
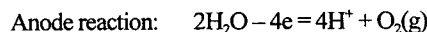
### Introduction

During the last decade, a great deal of research has been conducted to develop in-situ technologies for treating contaminated soils and ground water. In-situ methods are attractive because of the potential lower cost, less disruption to the environment and reduced worker exposure to the hazardous materials. However, most successful in-situ remediation technologies are restricted to soils with relatively high hydraulic conductivity so that they can not be used for fine-grained deposits. In recent years, there has been considerable interest in the application of electrokinetics as an in-situ method for cleaning up contaminants in fine-grained, low permeability soils [1-9]. The primary contaminant transport and removal mechanisms are electroosmotic advection and ionic migration. Electroosmotic 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. 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 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. Removal of heavy metals might be expected to be straight forward, because transport by ionic migration is rapid and is not affected by variations in the zeta potential. However, there are many complex physicochemical reactions occurring simultaneously during the process that may enhance or retard the cleanup process.

In the present study, the feasibility of using electrokinetics to remove cadmium from saturated kaolinite under controlled laboratory conditions is investigated and the results of the tests conducted for cadmium removal are provided.

### Background

The electrokinetic soil remediation process is governed in part by the electrode reactions which are inherent to the process. These reactions are typically the electrolysis of water at the electrodes which can be described by the following redox reactions:



The hydrogen ions produced at the anode and the hydroxide ions generated at the cathode migrate into the soil under the action of the electric field. When the acid front and the base front meet, the soil between the electrodes is divided into two zones, a low and a high pH zone, with a sharp pH jump in between. The location of the pH jump usually locates closer to the cathode, because hydrogen ion has about twice as high ionic mobility as hydroxide ion.

In the removal of heavy metals from soil, the generated acid front will enhance the dissociation of heavy metal cations from the negatively charged soil surface by ion exchange, and the dissociation of precipitates and complexes of heavy metals present in the soil. Meanwhile, the high pH zone near the cathode will favor the sorption of heavy metals by increasing their affinity for the soil surfaces, and favor formation of metal precipitates and / or complexes, thus decreasing the mobility of heavy metals. The high pH zone in the soil turns out to be a main obstacle to removal of heavy metals from the soil. Therefore, it is important to prevent the increase in pH near the cathode for the removal of heavy metals from the soil.

### Experimental

Experimental Procedures and Materials

The soil used in this study was a kaolinite (South Carolina, U.S.A.). The cadmium solution ( $Cd=8.9 \times 10^{-4}$  mol/dm<sup>3</sup>;  $NaNO_3=0.01$  mol/dm<sup>3</sup>) was mixed into kaolinite to form the saturated soil sample. The saturated kaolinite was packed into a polyvinyl chloride column (20 cm long, 2 cm diameter), which is connected on each end to an electrode reservoir containing a graphite electrode. A schematic of the experimental apparatus used for this study is shown in Fig. 1. The kaolinite is prevented from entering the reservoirs by filter paper supported on a stainless steel screen, which also serves as a reference electrode for measuring the potential across the kaolinite. Voltage probes are embedded along the length of the column to permit measurement of the potential profile. The ports for the voltage probe was also utilized for the periodical measurements of soil pH using pH test papers. The electrolyte solution used in the electrode reservoirs was 0.01 mol/dm<sup>3</sup>  $NaNO_3$ . The electrolyte solution was circulated continuously to electrode reservoirs with a micro tubing pump. Pressure-induced flow was prevented by equalizing the water level in both electrode reservoirs. In the experiment under the condition of catholyte pH kept at neutrality, catholyte pH was adjusted to around 7, periodically adding  $HNO_3$  solution with pH-stat. The applied voltage was 20 V DC across the electrodes. The current, applied voltage and local voltage were monitored. During the experiments, samples of solution were taken from the electrode reservoirs for determining cadmium concentration. At the end of the experiments, the kaolinite was sectioned into 10 segments, and each section was analyzed for pH and cadmium concentration. Final soil pH was measured using a pH meter. The cadmium content was determined using an atomic absorption spectrophotometer.

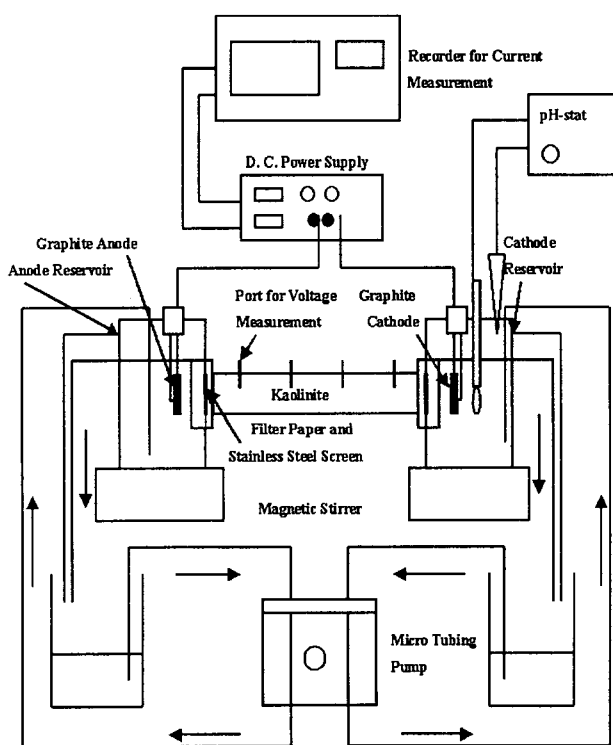


Fig. 1 Schematic diagram of experimental apparatus.

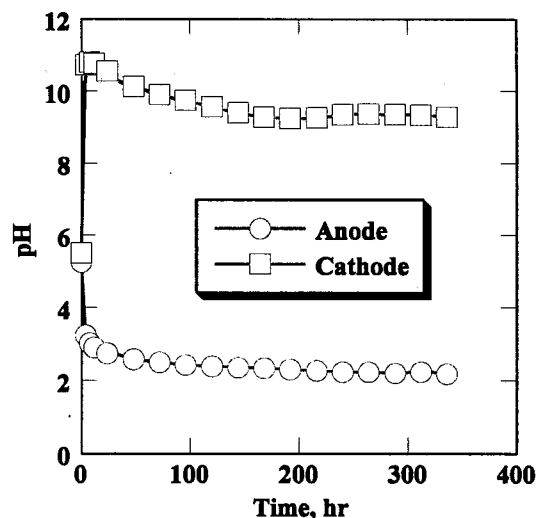


Fig. 2 pH profiles in electrode reservoirs.

## Experimental Results and Discussion

### Without Keeping Catholyte pH at Neutrality

#### *pH in Electrode Reservoirs*

Fig. 2 shows the pH profiles in the electrode reservoirs. The anolyte pH decreases sharply until 12 hr and remains nearly constant at pH 2.3 thereafter. Meanwhile, the catholyte pH increases initially and remains steady constant at pH 9.3 after 120 hr.

#### *pH Distribution in Kaolinite*

The measured distribution of pH in the kaolinite at 336 hr is shown in Fig. 3. The acid front generated at the anode advances toward the cathode and the base front generated at the cathode advances toward the anode. The both fronts meet and the sharp gradient in the pH (pH jump) is shown near the cathode.

#### *Cadmium Concentration Distribution in Kaolinite*

The measured distribution of cadmium in the kaolinite at 336 hr is shown in Fig. 4. The influence of the pH jump on the cadmium concentration distribution is clearly seen. Cadmium accumulates in the region of the pH jump to the cathode and cadmium is a low concentration except close to the cathode. Cadmium was not detected in the electrode reservoirs. Therefore, it is considered that almost all the cadmium in the kaolinite accumulated as cadmium hydroxide in this region.

#### *Electrical Potential Distributions and Current Density*

Fig. 5 shows the measured distributions of electrical potential across the kaolinite. The electrical potential

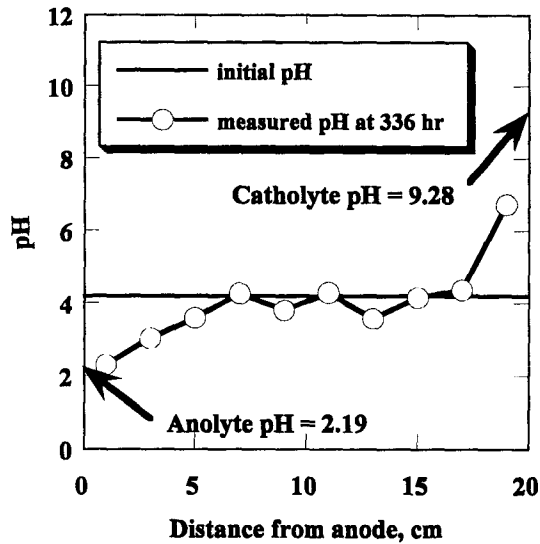


Fig. 3 Measured distribution of pH at 336 hr.

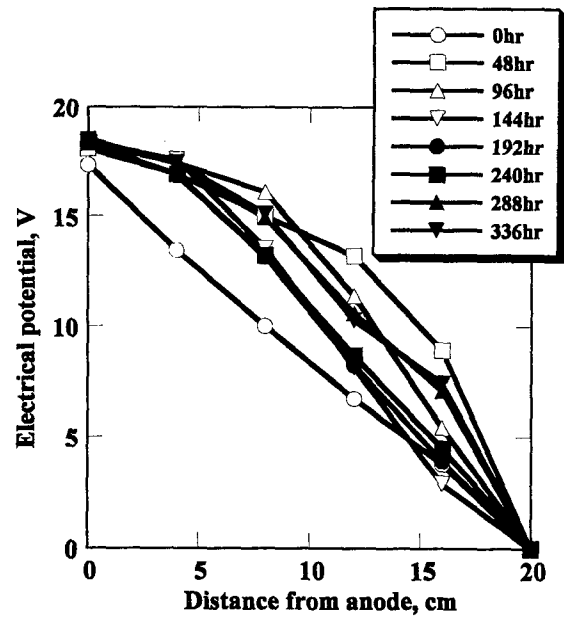


Fig. 5 Measured distributions of electrical potential.

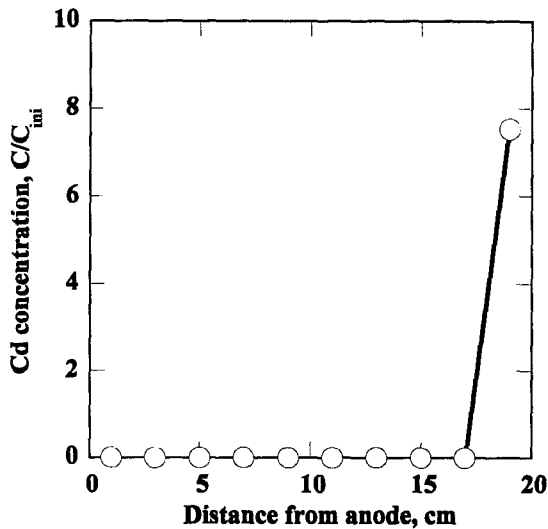


Fig. 4 Measured distribution of Cd concentration at 336 hr.

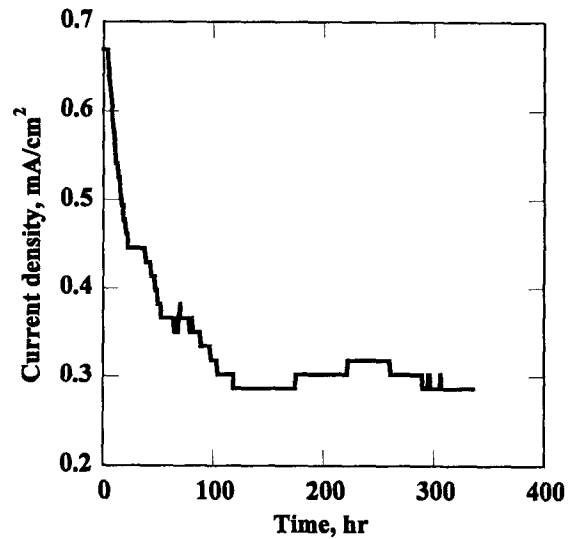


Fig. 6 Time history of current density.

gradients decrease near the anode and increase near the cathode. Cadmium forms the hydroxide precipitate and the electrical conductivity of the pore solutions decreases near the cathode. Consequently, the electrical potential gradient increases near the cathode compared with the anode region.

The time history of the current density is shown in Fig. 6. The current density is  $0.67 \text{ mA/cm}^2$  at the beginning of the experiment, but decreases sharply until 120 hr and then remains nearly constant ( $0.3 \text{ mA/cm}^2$ ).

#### In Keeping Catholyte pH at Neutrality

#### pH in Electrode Reservoirs

Fig. 7 shows the pH profiles in the electrode reservoirs.

The anolyte pH decreases sharply to the pH value of around 1 and is a lower pH as compared to the anolyte pH without keeping the catholyte pH at neutrality. Meanwhile, the catholyte pH is maintained at neutrality by adding  $\text{HNO}_3$  solution with a pH-stat.

#### pH Distribution in Kaolinite

The measured distribution of pH in the kaolinite at 336 hr is shown in Fig. 8. The pH is reduced to the strong acidity throughout most of the soil.

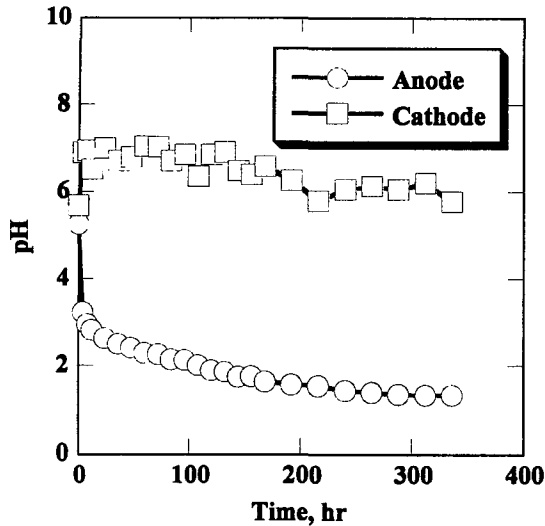


Fig. 7 pH profiles in electrode reservoirs.

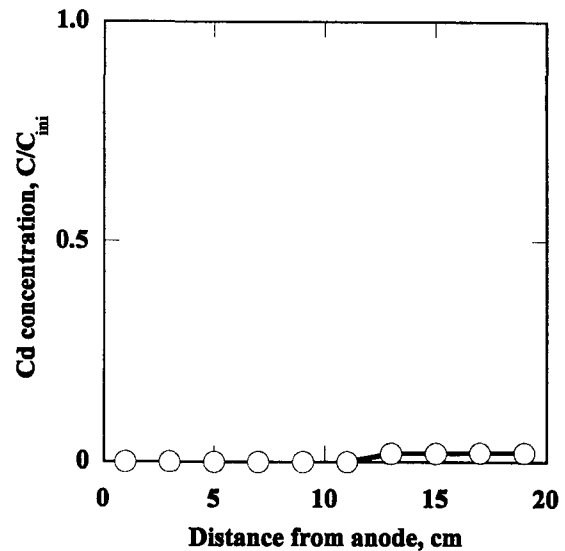


Fig. 9 Measured distribution of Cd concentration at 336 hr.

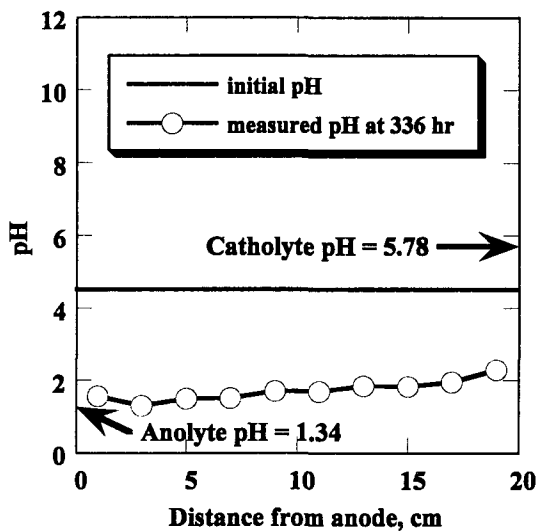


Fig. 8 Measured distribution of pH at 336 hr.

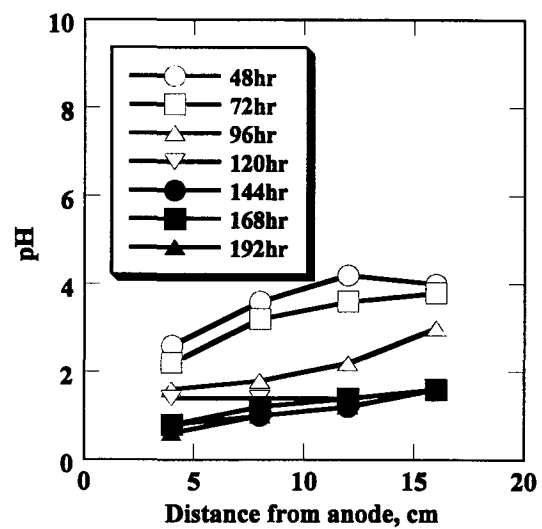


Fig. 10 Measured distributions of pH at various time.

#### Cadmium Concentration Distribution in Kaolinite

The measured distribution of cadmium in the kaolinite at 336 hr is shown in Fig. 9. The cadmium concentration decreases throughout most of the soil. Cadmium was detected in the anode reservoir. In particular, the cadmium concentration in the cathode reservoir increased after 72 hr. This is because the pH was particularly reduced to the strong acidity throughout most of the soil after 72 hr (Fig. 10) and the dissociation of cadmium from the soil surface was enhanced. Cadmium migrates toward the cathode without accumulation as cadmium hydroxide near the cathode and is successfully removed at the cathode reservoir.

#### Electrical Potential Distributions and Current Density

Fig. 11 shows the measured distributions of electrical potential across the kaolinite. Measurements at the beginning of the experiment show a linear increase in the potential values across the soil from the cathode to the anode. However, the electrical potential gradients increase near the cathode and relatively decrease except the cathode region after 144 hr. Fig. 12 shows the time history of the current density. The current density increases until 150 hr and decreases thereafter. The increased current density increases the production of hydrogen ion. Consequently, the anolyte pH and the soil pH significantly decrease. The increase in the current density is considered to be due to the nonformation of cadmium hydroxide near the cathode. From the results of the increased

electrical potential gradients near the cathode after 144 hr, the decreased current density after 150 hr and the increased cadmium concentration in the cathode reservoir after 72 hr, it is considered that the electrical conductivity is governed by hydrogen and hydroxide ions as cadmium transfers from the soil to the cathode reservoir. The electrical conductivity near the cathode kept at neutrality decreases and the electrical gradient consequently increases. Also, the removal of cadmium from the soil may be completed in about a week (168 hr). Fig. 13 shows the distribution of cadmium in the kaolinite at 168 hr. It is found that cadmium is removed from the soil at 168 hr.

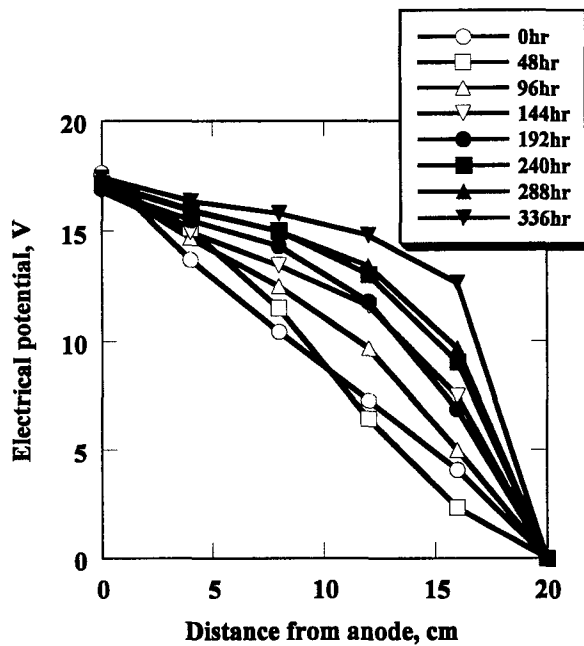


Fig. 11 Measured distributions of electrical potential.

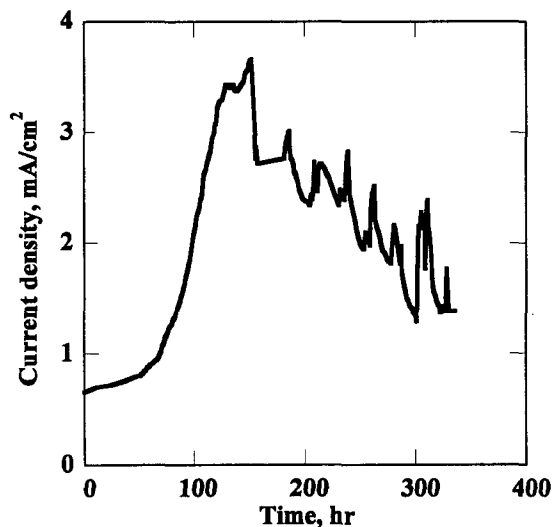


Fig. 12 Time history of current density.

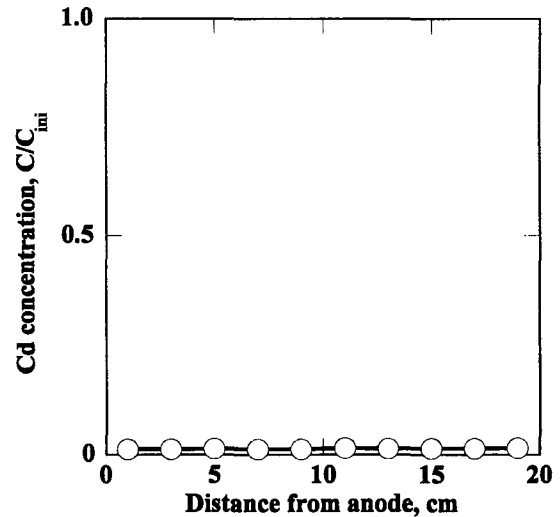


Fig. 13 Measured distribution of Cd concentration at 168 hr.

### Conclusions

Experiments have been presented for the electrokinetic removal of cadmium from kaolinite. Cadmium accumulates near the cathode without reducing the diffusion of hydroxide ions into the soil. The steepness of the pH jump and its influence on the distribution of cadmium are clearly seen. In keeping the catholyte pH at neutrality, cadmium migrates toward the cathode without any accumulation of cadmium near the cathode and is successfully removed at the cathode reservoir. It was also found that the progress of electrokinetic processing of cadmium could be grasped to a certain extent by monitoring the local voltage and the current density.

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