

ELECTROREMEDIATION OF ZN(II) CONTAMINATED SOFT BANGKOK CLAY WITH CATHODE DEPolarIZATION TECHNIQUE

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ABSTRACT: Four electrokinetic experiments were performed to examine the application of electrokinetic remediation to remove heavy metals from the soft Bangkok clay. The experiments were carried out by applying a direct-current electric field of 20 V through the soil loaded with Zn(II) at the level of 1,000 mg per kg for 3 and 7 days. In addition, the cathode depolarization technique, in which hydroxide ions generated from electrolysis reactions are eliminated by flushing acidic solution into a cathode reservoir, was introduced to improve the efficiency of electrokinetic remediation. The experiment results showed that only electrokinetic remediation was able to remove 82 percent of the contaminants in a period of one week. During this period, the combination of electrokinetic remediation with the cathode depolarization technique has raised the removal efficiency after 7 days of the treatment by 15 percent while the energy expenditure was slightly increased from 273 kWh per m³ to 301 kWh per m³. Therefore, the application of electrokinetic remediation with the cathode depolarization technique can be considered as an efficient ground remediation method for the soft Bangkok clay.

Keywords: Electrokinetic, fine-grained soil, contamination, remediation, and heavy metals

INTRODUCTION

Remediation of the hazardous polluted soils is one of the most critical environmental problems in Thailand. Survey results show at least 26 sites around the central region of Thailand, situated on fine-grained soil, are susceptible to a high level of heavy metal contamination and have become a pollution source (PCD, 1998). Remediation of these contaminated sites is obligatory to reduce public health risks.

Electrokinetic remediation is considered as an innovative and cost-effective ground remediation technology for fine-grained soils (e.g. Acar and Alshawabkeh, 1993; Probst, 1993; Hicks, 1993; Puppala, et al., 1997; Mulligan et al., 2001; Reddy, and Chinthamreddy, 2003). In principle, electrodes are inserted into soil masses and a direct-current electric field is then applied to remove contaminants (Fig. 1). Although the concept of the electrokinetic remediation looks fairly simple, it involves numerous physico-chemical processes such as electrolysis reactions, adsorption and desorption of contaminants, and formation of secondary minerals, etc. The composition of the soil raises the remediation scheme to a highly

complex situation. The efficiency of the electrokinetic remediation varies from one soil type to another (Darmawan and Wada, 2002.)

This study attempts to apply the electrokinetic remediation technology to clean-up contaminated soft Bangkok clay. Four electrokinetic experiments were performed to investigate the efficiency of the electrokinetic remediation. In addition, an enhancement technique, namely the cathode depolarization technique, was introduced to improve the efficiency of the remediation as well as to reduce operating time and energy consumption.

BACKGROUND

The principle of electrokinetic remediation consists of the application of a direct-current electrical field through soil masses in order to promote the movement of contaminants through electrodes. Three transportation processes, which are electroosmosis advection, electromigration, and diffusion, are responsible for the movement of contaminants (e.g. Acar and Alshawabkeh, 1993; Shapiro and Probst, 1993; Baraud et al., 1999).

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Note: Discussion on this paper is open until December 2005

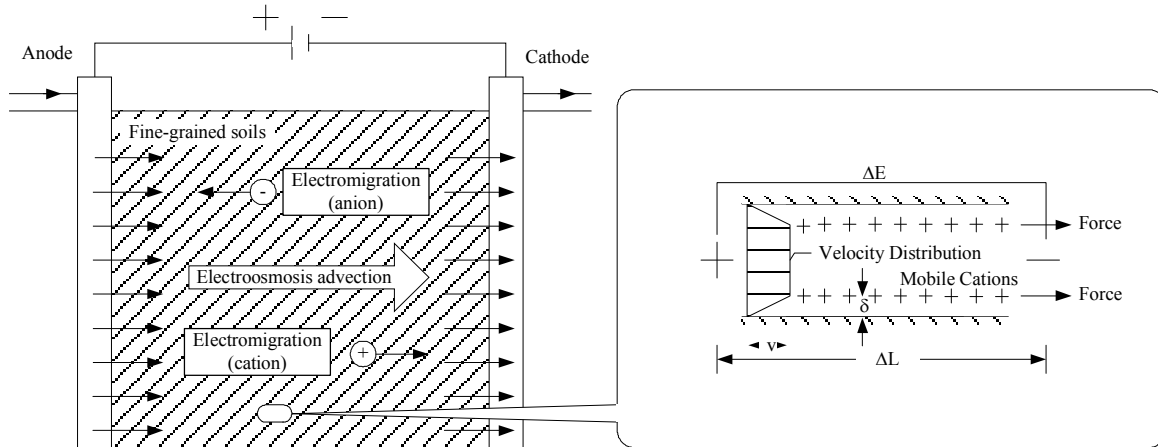


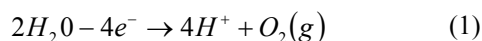
Fig. 1 Principles of the electrokinetic remediation

Briefly,

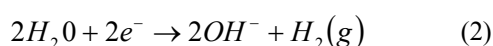
1. Electroosmosis advection is transportation of species due to the displacement of a liquid produced by an applied electrical force.
2. Electromigration is transportation of charged species by an applied electrical force.
3. Diffusion is a transportation process in which a chemical species migrates in response to a gradient in its concentration.

In addition, electrolysis reactions occur at the electrodes during the electro-remediation processes. These reactions dominate the chemistry at the boundaries as well as the soil chemistry in the electrokinetic remediation. In the case that the chemistry of boundaries is not controlled, the electrolysis reactions generate hydrogen ions and hydroxide ions at the anode and the cathode, respectively. These ions migrate into soils via electromigration and this result in changing the chemistry of soils. Since the hydrogen ions possess greater ionic mobility and the electroosmotic flow is towards the cathodes, by the end of the electrokinetic remediation processes, almost entire soil mass is subjected to acid conditions while the small fractions of soil masses near the cathode remain under alkaline conditions.

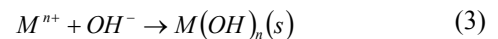
At the anode



At the cathode



Since pH values regulate the chemical kinetics of the heavy metals, the efficiency of electrokinetic remediation of heavy metal contaminated soils depends primarily on changes in pH values during the electrokinetic remediation processes (Hicks and Torndorf, 1994). In general, metals tend to desorb from the soil and present in solution as positively charged ions under acidic conditions. Under alkaline conditions, metals tend to precipitate by formation of hydroxides:



This precipitation significantly decreases the efficiency of electrokinetic remediation since this process results in accumulation of contaminants around the cathode regions (e.g. Hamed et al., 1991; Probst and Hicks, 1993; Acar et al., 1994). In order to improve the efficiency of electrokinetic remediation for heavy metals, the production of hydroxide ions, which results in precipitation, needs to be controlled.

MATERIALS

Soft Bangkok clay, collected from 3 to 4 m depth, was used as the soil medium. The physical properties, chemical properties, and mineralogical composition of the soil are summarized in Table 1.

EXPERIMENTAL PROGRAMME

Four electrokinetic experiments were performed to investigate the efficiency of electrokinetic remediation and to quantify the efficiency of the enhancement technique (Table 2). Experiment 1.1 and Experiment 1.2

aim to establish the base line of the efficiency of the electrokinetic remediation for the soft Bangkok clay. The direct current electrical field was applied through spiked clay for 3 and 7 days respectively. The anode reservoir was supplied with deionized water and the effluent was regularly collected at the cathode. Experiment 2.1 and Experiment 2.2 attempts to increase the efficiency of electrokinetic remediation by using the cathode depolarization technique. In this technique, the hydroxide ions, generated from electrolysis reaction at the cathode reservoir and results in decreasing the efficiency of electrokinetic remediation, were depolarized by purging acidic solution into the reservoir. Deionized water was supplied to the anode reservoir and the HCl solution at pH of 5 was continuously flushed the cathode reservoir by a peristaltic pump. The acid solution was flushed at the rate that allowed displacement of all solution in the cathode reservoir within a minute (20 mL/min).

EXPERIMENTAL SET UP

A diagram of the apparatus used in this study is presented in Fig. 2. The apparatus was designed according to the design criteria given by Yeung et al. (1992) and Yeung et al. (1997). The electrokinetic cell consisted of a specimen cylinder encapsulated within two end flanges. The cell was constructed entirely from acrylic since it allows visual inspection and is chemically inert. The specimen cylinder was 100 mm in diameter and 100 mm in length and had a capacity of approximately 0.8 liters of soil sample. The end flanges were made of an acrylic cube measuring 200×200×25 mm. The volume of the reservoir inside the end flanges was 20 ml and the influent was continuously supplied to

Table 1 Summary of properties of the soft Bangkok clay

Physical properties	
Natural water content (%)	90±2
Liquid limit (%)	100
Plastic limit (%)	40
Liquidity index	0.83
Plasticity index	65
Specific gravity	2.67
Total unit weight (kN/m ³)	14.9
Void ratio	2.4
Color	Dark gray
Permeability (m/sec)	~5×10 ⁻⁹
Grain size distributions	
Clay (%)	78
Silt (%)	22
Sand (%)	0
Chemical Properties	
Cation Exchange Capacity (meq/100g)	20.2
Exchangeable cations	
Na (meq/100g)	1.44
K (meq/100g)	0.39
Mg (meq/100g)	10.29
Ca (meq/100g)	4.99
Electrical conductivity (mS/m)	2.9±1
pH	7.3
Mineral Compositions	
Kaolinite (%)	58±5
Smectite (%)	28±5
Illite (%)	14±5

Table 2 Summary of electrokinetic experiments

No.	Series 1		Series 2	
	1.1	1.2	2.1	2.2
Initial contamination level	1000	1000	1000	1000
Initial water contents	100	100	100	100
Electrical gradient (V/m)	20	20	20	20
Anolyte	DW	DW	DW	DW
Catholyte	-	-	DW (pH =5)	
Duration (days)	3	7	3	7
Pore Volume (cc)	571	572	571	572
Flow volume (cc)	397	495	434	514
Average flow rate (cc/day)	132	71	145	73
K _e (×10 ⁻¹⁰ m ² /V·m)	938	5.21	10.7	5.41
K _i (×10 ⁻⁹ m ³ /A·sec)	15.8	32.1	16.5	32.5
Energy consumption (kWh/m ³)	244	301	273	304

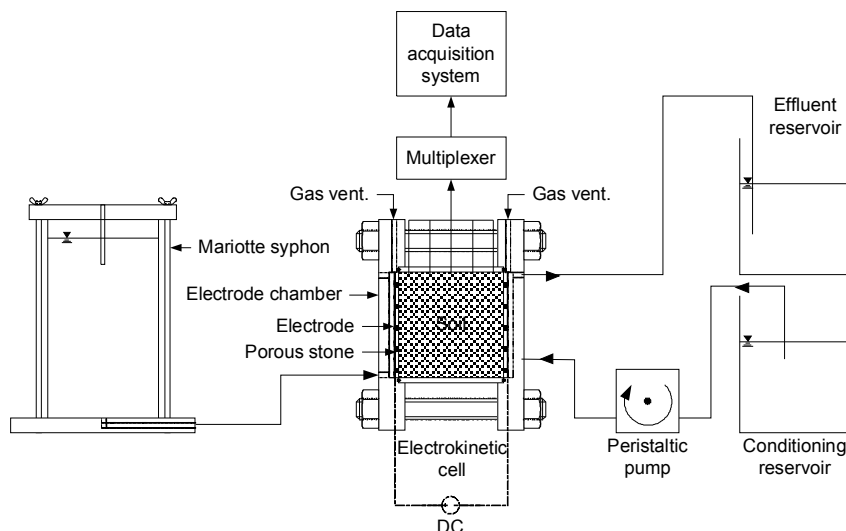


Fig. 2 Schematic diagram of the electrokinetic apparatus

the electrode reservoir by a Mariotte siphon. Titanium electrodes were held inside the flanges. Inert porous discs and filter papers were placed between the electrodes and the specimen. These porous discs held the specimen within the setup and prevented dispersion and/or collapse of soil particles into the electrode reservoirs.

EXPERIMENTAL PROCEDURES

Zinc was chosen as the contaminant in this study. Under acidic conditions, zinc is usually divalent and quite mobile. Zinc hydrolyzes at pH 7.0 to 7.5 and forms $Zn(OH)_2$ at pH values higher than 8. Natural levels of zinc in soils are 30 to 150 ppm. Levels of 10 to 150 ppm are normal in plants while 400 ppm is toxic (Mulligan et al., 2001). Zinc was loaded into the soil by mechanically mixing the soil with $ZnCl_2$ solution to reach the contamination level of 1,000 mg per kg and the initial water content of 100 percent. The slurry was poured into a specimen chamber and encapsulated by end flanges. The electrode reservoirs were then filled with deionized water and the specimen was allowed to equilibrate in the apparatus for 24 hours. The constant electrical potential of 20 V, corresponding to electrical gradients of 200 V/m, was applied across the specimen over the predetermined period. During the experiments, electrical potentials and temperatures along the specimen were monitored every 30 minutes. The effluent was collected every 3 hours and analyzed for its pH value.

Immediately after the experiments, the soil was extruded from the specimen chamber and was sliced into 10 sections. Each section was examined for physical

properties and chemical properties. The pH values were obtained by measuring the pH of a 1:5 mixture by weight of dry clay and distilled-deionized water. The residual Zn(II) was extracted from the soil by using the ammonium replacement method and the concentrations of Zn(II) were then determined by spectrophotometer.

RESULTS AND DISCUSSIONS

Flows and pH

The plot of the cumulative volume of the effluent against elapsed time is presented in Figures 3. The results from all experiments show that electroosmotic flow rates decreased with increasing operating time. For instance, the electroosmotic flow rate for Experiment 1.1 varied from 250 cc per day at initial time to 95 cc per day at the end of the experiment. In addition, the electroosmotic flow rates slightly increased when the cathode depolarization technique was applied. The increase in the flow rate provides the benefit to the contaminant removal efficiency since it increases of electroosmotic advection component.

The plot of pH values of effluent against elapsed time is presented in Figures 4, respectively. The results from the pH measurement verified that the cathode depolarization technique is able to control the production of hydroxide ions at the cathode reservoir. When the cathode was not depolarized, the pH values were above 12 within the experiment period. On the other hand, the pH values gradually decreased from 8 to 7 within 3 days after the experiments when the depolarization technique was applied. These pH values indicate that the technique

is able to maintain the pH values within satisfactory ranges but the cathode depolarization technique could not completely depolarize the generated hydroxides at the cathode reservoir. The pH values could be decreased below 7 throughout the experiments by either providing a faster flushing rate or providing a more acidic purging solution. The first method is preferred since the latter method may decrease efficiency of remediation due to development of the reverse electroosmotic flow conditions (Shapiro and Probst 1993; Eykhot and Daniel, 1994; West et al., 1995; Yang and Lin, 1998).

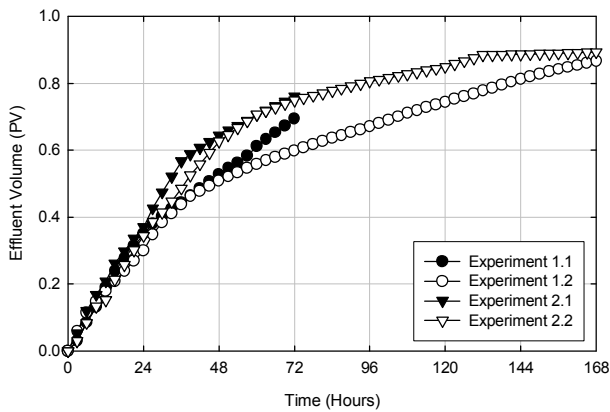


Fig. 3 Comparisons of cumulative electroosmotic flows

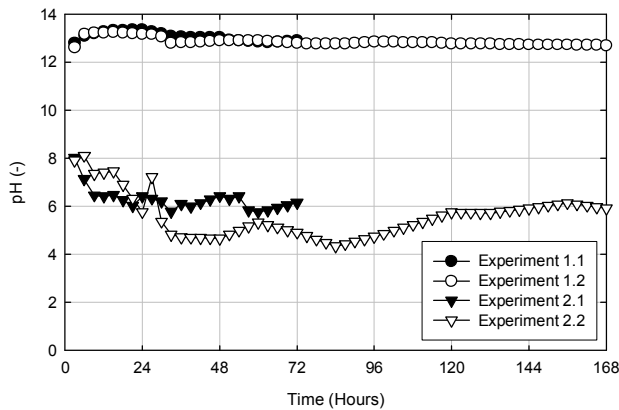


Fig. 4 Comparisons of pH of effluent during electroremediation

Current Density

The relative solubility of cations inside the soil specimen during electrokinetic remediation processes can be estimated from the magnitude of current densities. As the solubility of cations increases, the current density increases (Darmawan and Wada, 2002). Figure 5 shows the plot of current densities against elapsed time. The plot shows that the mode of variation of current densities

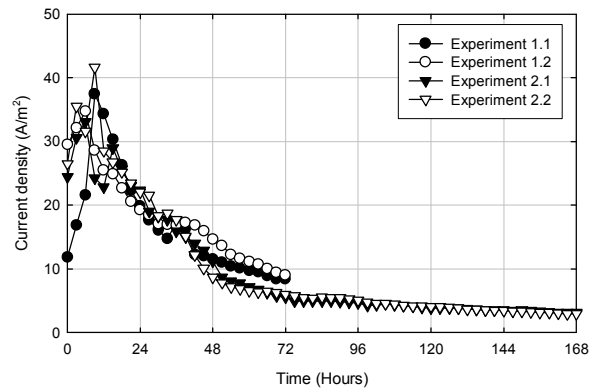


Fig. 5 Variation of current densities against time

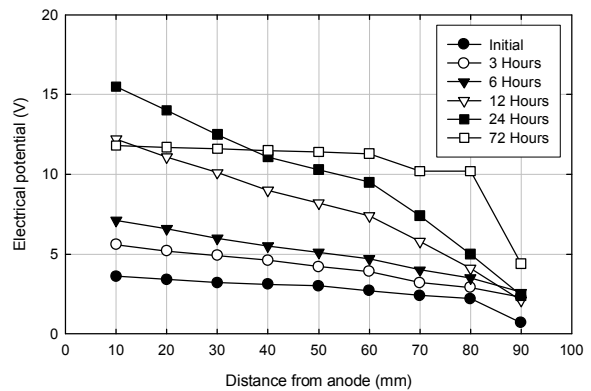


Fig. 6a Electrical potential distributions during the electrokinetic remediation of Experiment 1.1.

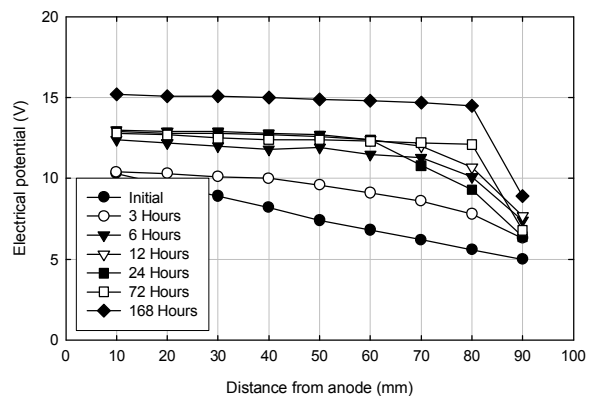


Fig. 6b Electrical potential distributions during the electrokinetic remediation of Experiment 1.2

was similar for all experiments. In general, the current densities increased from its initial value to a peak value of 38 A per m² approximately within 12 hours. The current then decreased exponentially to a value below 10 A per m² within 72 hours. Slightly higher current densities were observed in the experiments in which the cathode depolarization technique was applied, indicating that the cathode depolarization technique are able to increase the solubility of the cations during the experiments.

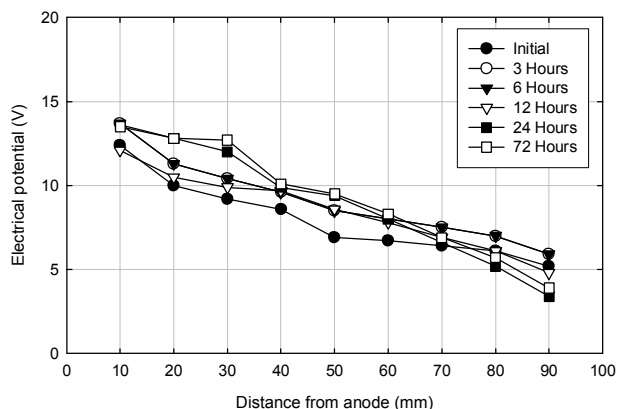


Fig. 6c Electrical potential distributions during the electrokinetic remediation of Experiment 2.1

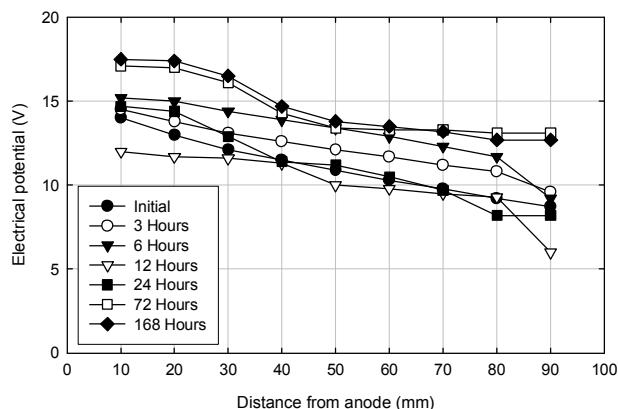


Fig. 6d Electrical potential distributions during the electrokinetic remediation Experiment 2.2

Electrical potential profiles

The changes in pore water chemistry during electroremediation processes could be roughly identified by using electrical potential profiles (Page and Page, 2002). The sharp drop in electrical potential indicates the position of pH jump (Cambefort and Caron, 1961) and therefore the position of precipitation of heavy metals contaminants as solid hydroxides (Hamed et al., 1991; Eykholt and Daniel 1994). Figure 6a to Fig. 6d show the distributions of electrical potentials during the electrokinetic remediation. Initially, the profiles of all experiments were relatively flat since the reservoirs were filled with distilled water, which is highly resistive. As time elapsed, the profiles turned steeper due to the relative increases in ionic concentration at electrodes resulting from electrolysis reactions. After 72 hours, the significant drop of the electrical potential was observed at a distance of 80 mm in Experiment 1.1 and Experiment 1.2 where the cathode depolarization technique was not applied (Fig. 6a and 6b). This drop in potential endured until the ends of experiments. The contaminants are, therefore, expected to precipitate and accumulate behind this area. Conversely, a drop in the electrical potential was not detected in Experiment 2.1 and 2.2 where the cathode depolarization technique was used (Fig. 6c and 6d). This indicates the strong possibility that the technique is able to maintain contaminants in soluble forms and does not permit contaminants to precipitate soil masses.

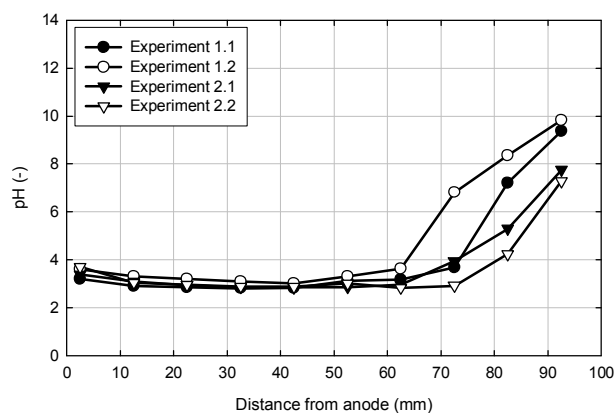


Fig. 7 Comparisons of pH distributions after electrokinetic remediation

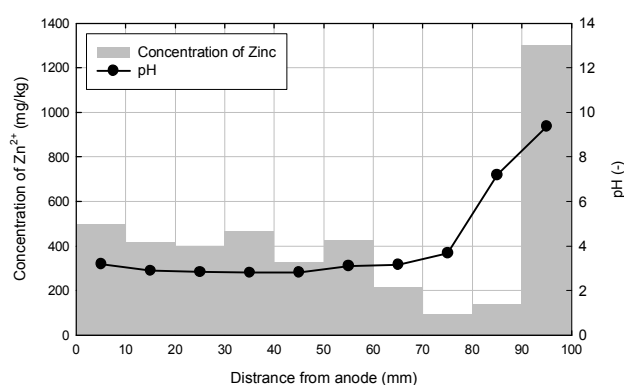


Fig. 8a Zn(II) and pH distributions in Experiment 1.1 (3 days, without cathode depolarization technique)

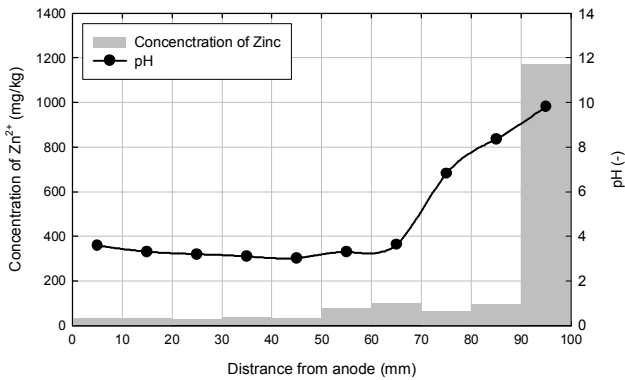


Fig. 8b Zn(II) and pH distributions in Experiment 1.2 (7 days, without cathode depolarization technique)

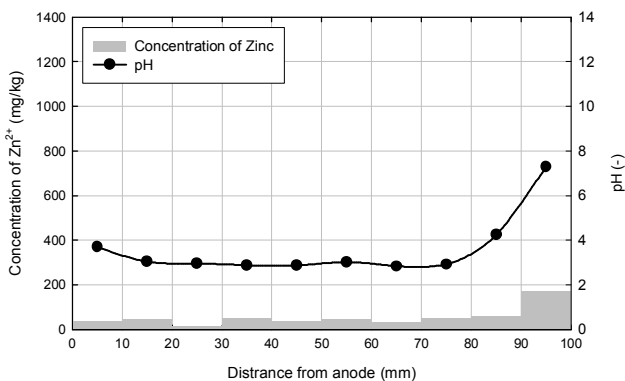


Fig. 8d Zn(II) and pH distributions in Experiment 2.2 (7 days, with cathode depolarization technique)

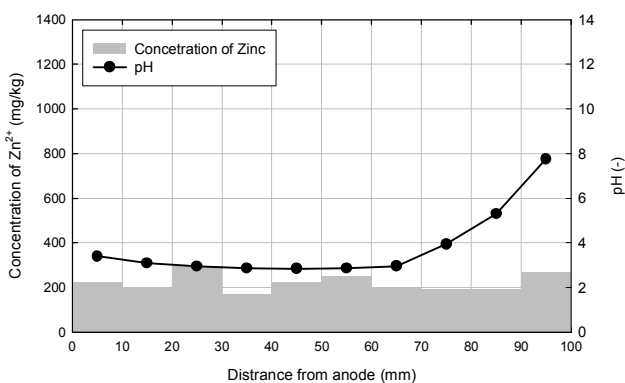


Fig. 8c Zn(II) and pH distributions in Experiment 2.1 (3 days, with cathode depolarization technique)

pH Distributions

The pH values dominate the chemical kinetic of heavy metals (Hicks and Tormdorf, 1994). Generally, metals tend to desorb from soils and present in solution as positively charged ions under acidic condition, and

tend to precipitate by formation of hydroxides under alkaline condition. The pH values of pore solution in electrokinetic remediation process need to be maintained within proper ranges to prevent the precipitation and accumulation of metal hydroxides (e.g. Hicks and Torndorf, 1994; Puppala et al., 1997; Reddy and Chinthamreddy, 2003). Figure 7 presents the pH profiles at the end of experiments compared with the initial value. Although the pH profiles look similar among experiments, significant decreases in pH values at the cathode region were observed when the cathode depolarization technique was applied. The pH values at the cathode end decreased from 12 to 7.5, indicating that the technique effectively controlled the backward migration of hydroxide ions into the soil specimen.

Zn Distributions

Figures 8a to 8d show the Zn(II) distributions along with the pH values in the soil after the experiments. The figures clearly demonstrate the effect of pH to the zinc removal efficiency. In all experiments, zinc was efficiently removed in the regions where the pH values were less than 7. Accumulation of zinc in the form of precipitations was observed at the cathode end when the cathode depolarization technique was not applied (Fig. 8a and 8b). The total amount of zinc was greater than 20 percent of its original value. More accumulation of zinc was expected to be presented in the soil if the experiments had been performed under lower electrical gradients since the lower applied electrical potentials promote slower electroosmotic flow rates. Therefore, hydroxide ions are able to migrate backward into soil masses to a larger extent. On the other hand, accumulation of zinc at the cathode end was eliminated when the pH of the cathode reservoir was controlled. The results of Experiment 2.1 and Experiment 2.2 show that the concentration of zinc at the cathode end was slightly greater than the concentration at the anode end (Fig. 8c and 8d).

Table 3 Comparisons of the removal efficiency and energy expenditure per unit volume of soils of the electrokinetic remediation in the soft Bangkok clay

No.	Series 1		Series 2	
	1.1	1.2	2.1	2.2
Duration (days)	3	7	3	7
Removal efficiency (%)	54	82	77	95
Energy expenditure per unit volume (kWh/m ³)	242	257	311	326

Efficiency and Economics of Electrokinetic Remediation

The efficiency and economics of electrokinetic remediation for the soft Bangkok clay without and with applying the cathode depolarization technique are presented in Figures 9 and 10 respectively. The amount of zinc removed from the soil was determined from the total concentration of the metal remaining in the clay after the experiment and the energy expenditure per unit volume of soil, E , is given as follows:

$$E = \frac{V}{AL} \int_0^t I(t) dt \quad (7)$$

where E is the energy consumption per unit volume of soil (kWh per m^3), V is the applied electrical potential (V), I is the current (A), A is the area of the specimen (m^2), L is the length of the specimen (m), and t is time (hour).

As indicated in Fig. 9 and Fig. 10, the efficiency of electroremediation can be significantly improved merely by adopting cathode depolarization technique. The application of this cathode depolarization technique not only accelerated the remediation processes, but also consumed less energy. For example, if the target of remediation is to remove 80 percent of contaminants from soil, the application of electrokinetics will decrease the operation time by 130 percent and will require less energy by 8 percent. These experiment results show that anode depolarization technique could significantly increase the efficiency of electrokinetic remediation. It is expected that efficiency of the technique shall be further increased in non-reactive fine-grained soils such as kaolinite. Furthermore, the application of the depolarization technique may significantly gain the efficiency of electrokinetic remediation in calcareous fine-grained soils where the metal carbonate compounds were formed under alkaline conditions (Ottosen et al., 2001)

CONCLUSIONS

This study covered four electrokinetic experiments with Zn(II) contaminated soft Bangkok clay. Based on the experiments conducted in this study, the following conclusions can be drawn:

- The efficiency of electrokinetic remediation for Zn(II) contaminated soft Bangkok clay was 54 and 82 percent after 3 and 7 days of operation time respectively.
- The efficiency of electrokinetic was significantly increased when the cathode depolarization technique

was applied. For similar operation times, the removal efficiency increased approximately by 15 percent. For a similar level of remediation, the operation time decreased by 130 percent.

- Application of the cathode depolarization technique results in slight increases in energy expenditure per unit volume of soil.

There is a strong possibility for application of electrokinetic remediation with the cathode depolarization technique to clean-up contaminated soft Bangkok clay. The weak acid such as acetic acid, which is biodegradable, may be used instead of hydrochloric acid for environmentally safe purposes. Careful examination of physico-chemical reactions in site specific situations is needed to understand the process better and to develop the technology for large-scale applications.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge the support from the European Commission under the Asia-Link Programme, Contract No. ASI/B7-301/98/679-12 for the experimental work presented here.

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