

Removal of Pb(II), Cd(II) and Cr(III) from sand by electromigration

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Abstract

This study presents the results of a new electrokinetic soil remediation technique in which a conductive solution is inserted between the cathode and the soil being treated. In this arrangement, the heavy metals will no longer precipitate in the treated soil. They are transported out of the soil and precipitated in the conductive solution. Furthermore, the decrease in conductivity, due to metals precipitated in the soil, has been avoided. Six laboratory tests have been carried out to remove lead (II), cadmium (II) and chromium (III) from sand. The experimental results show that metal removal efficiencies higher than 90% can be reached. © 1997 Elsevier Science B.V.

Keywords: Soil remediation; Heavy metals; Electromigration; Electrokinetics

1. Introduction

Soil contaminated with heavy metals is a serious environmental problem and unfortunately, up to now, no effective cleaning technology is available. In recent years a new technology has been developed: electrokinetic soil remediation. In this technology, a dc current is passed through the contaminated soil, causing contaminating species to be transported towards the electrodes and then removed from the soil. Using the technology, contaminants ranging from inorganic chemicals to organic compounds can be removed from soil [1–4].

Electrokinetic soil remediation has been studied by many scientists in both laboratory-scale and field-scale experiments [5]. Three principal mechanisms of contaminant movement in electrical field are involved in this technology: electromigration of ionic species [1,2], electroosmosis [4,6–10] and electrophoresis. Electromigration is the migra-

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tion of ionic species, which are present in the soil void fluid, in an electric field. Cations move towards the cathode, while anions move towards the anode. In some cases, electromigration probably contributes significantly to the removal of contaminants, especially in high concentrations of ionic contaminants and/or high hydraulic permeability of soil [2]. Electroosmosis in a pore occurs due to the drag interaction between the bulk of the liquid in the pore and a thin layer of charged fluid next to the pore wall that, like a single ion, is moved under the action of the electric field in a direction parallel to it. The thin layer of charged fluid, or electric double layer, has a typical thickness between 1 and 10 nm [1]. Electroosmosis produces a rapid flow of water in low permeability soils and probably contributes significantly to the decontamination process in clayey soils [2]. Many scientists have focused their studies on removal of contaminants by electroosmosis [4,6–10]. The removal of contaminants would have the advantage of these two concurrent movements of electromigration and electroosmosis. Electrophoresis is the migration of charged colloids in a soil–liquid mixture. Electrophoresis could be important in a system where the contaminants are bound to colloids.

In conventional use of the technology, the cathode is directly inserted in the soil being treated. Therefore, the hydroxyls generated at the cathode are transported into the soil, causing an increase in pH near the cathode. Because heavy metals precipitate at high pH and, furthermore, a high pH favours the sorption of heavy metals onto the soil surface, most heavy metals can be found in the cathode half of the soil after remediation. In our recent studies, a new method [11,12] relevant to the technology has been proposed and developed. In the proposed method, a conductive solution is inserted between the cathode and the soil being treated. In this way, heavy metals can migrate out of the soil before precipitating as hydroxides. To demonstrate the proposed method, experiments were conducted to remove lead, cadmium and chromium from artificially contaminated sand.

2. Theoretical

When a dc potential is applied to graphite electrodes, the primary electrode reactions of electrolysis will be: At the anode:



At the cathode:



The hydrogen ions produced at the anode and the hydroxide ions generated at the cathode will generate a proton and a hydroxide front at the respective electrode. Both fronts advance towards the opposite charged electrode by electromigration, diffusion and advection (including electroosmotic flow), if any. When the two fronts 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 depends on several factors and usually locates closer to the cathode. One factor affecting the location of the pH jump is

the relative mobility of hydrogen ions and hydroxide ions. Hydrogen ion has about twice as high ionic mobility as hydroxide ion. Electroosmotic flow typically favours transport towards the cathode and hence it favours the advancement of the acid front. The concentration and mobilities of other ions present in the solution will also affect the location of the pH jump by influencing the distribution of the electric field and forming complexes with hydroxide ions or hydrogen ions. Also, the pH buffer capacity and cation exchange capacity of the medium and interactions of the solution with the soil may affect the speed of advancement of the acid and base fronts and the location of the pH jump.

In the removal of some toxic metals from soil, the low pH solution near the anode will enhance the dissociation of toxic metal cations from the negatively charged soil surface by ion exchange, and the dissociation of precipitates and complexes of toxic metals present in the soil. On the other hand, the high pH solution near the cathode will favour the sorption of heavy metals by increasing their affinity for the soil surfaces, and favour formation of metal precipitates and/or complexes, thus decreasing the mobility of heavy metals. Therefore, heavy metals that are transported in the low pH zone cannot further migrate towards the cathode as they are transported into the high pH zone near the cathode. Tests of metal removal by electric field have shown that a metal pollutant may concentrate at some intermediate region between the electrodes [2]. Thus the high pH zone in the soil turns out to be a main obstacle to removal of heavy metals from the soil.

In our previous study, a new method was developed. In this method, to prevent penetration of the hydroxide ions created by cathode reactions into the soil, a conductive solution was inserted between the cathode and the soil to be treated, as schematically shown in Fig. 1. When a voltage is applied to the electrodes the hydroxide ions generated at the cathode will move in the electric field towards the anode, but because of the inserted conducting solution they cannot penetrate from the inserted solution into the soil. They will meet hydrogen ions produced at the anode in the inserted solution. In other words, the hydrogen ions generated at the anode sweep the treated soil and meet hydroxide ions produced at the cathode in the solution. This means that the soil is in a low pH condition during the remediation process. Thus the precipitation of heavy metals by hydroxide ions in the soil can be avoided. Heavy metals will migrate out of the soil before they precipitate as hydroxides.

To investigate the performance of the proposed method, six experiments were conducted. In all these experiments, no open flow arrangement is employed in the

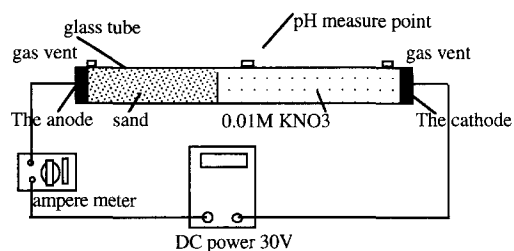


Fig. 1. Schematic diagram of the experimental arrangement.

system. In such a condition, electroosmotic flow can be neglected, and only electromigration of ionic species is taken into consideration. Therefore, whether or not the metals can be removed by electromigration alone can be verified. It is reasonable to anticipate that the combination of electromigration of ionic species and electroosmotic flow will make the process more effective.

3. Experimental

3.1. Materials

Washed sand with an average particle size of 0.15 mm, provided by KEBO Lab AB, is used in the experiments. The solution used in the experiments is 0.01 M potassium nitrate, simulating groundwater, which was prepared by dissolving commercial analysis grade potassium nitrate in deionized water. This solution has a higher conductivity than deionized water, so that a higher current (with constant cell potential) passes through the soil, thus speeding up the experiments. The initial pH value of the solution is neutral, 6.86. In practical soil remediation, if the groundwater contains sufficient electrolytes and has a reasonable conductivity, electrolytes probably need not be added to the conductive solution. In the case where the groundwater lacks electrolyte, some innocuous salt could be added at the electrode to increase the conductivity of the system.

The arrangement of equipment used in the experiments is schematically shown in Fig. 1. The sand is placed in a glass tube about 30 cm long and 35 mm in diameter, connecting to the anode at one end and to a column filled with 0.01 M potassium nitrate solution at the other end. The other end of the potassium nitrate solution is connected to the cathode. The length of the potassium nitrate column is 60 cm. Both the cathode and the anode are graphite disks with a diameter of 35 cm to avoid introduction of corrosion products at the electrode. A dc voltage of 30 V is applied to the electrodes. Between the soil and the anode, and at the interface of the soil and the conductive solution, glass filters are inserted.

3.2. Procedures

The sand sample was weighed and spiked with a known amount of cadmium nitrate, lead nitrate or chromium nitrate before being loaded into the glass tube. The glass tube, which was placed vertically, was first filled with 0.01 M potassium nitrate solution. Then the sand sample was slowly poured into the tube, displacing the solution. In this way, the air in the soil was removed, avoiding spurious electrical resistance due to air bubbles. The sand was allowed to settle for 10 min before a glass filter was placed on the soil and the glass tube was placed horizontally. Then the dc power was applied. During the experiments, the electrical current through the system was monitored with an APPA 98 digital multimeter. Periodic measurements of pH values in the conductive solution were made at a point about 10 cm from the boundary of the sand and the solution. Since the electric field affects the measurement of pH value, the power supply was turned off for a brief period during each measurement. Metal precipitates were

Table 1
Conditions in the six experiments

Test No.	Metal	Duration of test(h)	Composition of solution	Length of solution(cm)	Potential(V)
1	Pb(II)	78	0.01 M KNO ₃	60	30
2	Pb(II)	119	0.01 M KNO ₃	60	30
3	Cd(II)	118.8	0.01 M KNO ₃	60	30
4	Cd(II)	73	0.01 M KNO ₃	60	30
5	Cr(III)	100.92	0.01 M KNO ₃	60	30
6	Cr(III)	70.75	0.01 M KNO ₃	60	30

observed in the conductive solution after the current had been applied for a certain time. It could be observed through the glass tube that the amount of precipitate increased as the experiment continued. As it is difficult to judge the completion of metal removal, a series of experiments of different duration was made.

At the end of each experiment, the solution and precipitates outside the soil were collected in a volumetric flask. Nitric acid was added to dissolve the precipitates. Then the flask was filled with deionized water to the mark line. The concentrations of cadmium, lead or chromium in the solution in the flask were analysed by a DIONEX DX-300 ion chromatograph with an HPIC-CG5 separator column. The amount of metals removed was calculated on the basis of the measured concentration and the volume of the solution in the flask.

It was found that a white film covered the cathode after each cadmium experiment, which could be metallic Cd resulting from Cd²⁺ being reduced at the cathode. Therefore, after each experiment, the amount of cadmium in the sand was measured by leaching the contaminants out the sand by the USEPA (1986) TCLP method [13]. The procedure followed was: (A) 10 g of the sampled, dried sand was placed in a polyethylene bottle with a screw cap. Then 200 g of deionized water was added to the bottle, followed by adjustment of the pH value of the mixture to 3.5–4 by adding nitric acid. (B) The samples for the leaching experiments were kept in a shaker for a period of 24 h to achieve equilibrium. (C) A 5 ml soil–solution mixture was sampled, centrifuged, and the clear supernatant was analysed by a DIONEX DX-300 ion chromatograph with an HPIC-CG5 separator column. The final amount of the cadmium in the sand was calculated.

The removal efficiencies were calculated on the basis of a mass balance between the amount of metal removed (in cadmium experiments, this amount is equal to the difference between the initial amount and the amount remaining in the soil after the experiment) and the amount initially contained in the sand. The experimental conditions in each experiment, such as the duration of each experiment, the potential drop between the cathode and the anode and the composition of the pore fluid, as well as the length of the conductive solution, are shown in Table 1.

4. Results and discussion

The proposed method has been tested with the removal of Zn and Cu from sand [11] and the removal of Cr and Cu from naturally contaminated loam [12]. The results,

Table 2
Removal efficiencies

Test No.	Initial concentration C_i (ppm of sand)	Final concentration C_f in the solution (ppm of sand)	Final concentration C_s in the sand (ppm of sand)	Removal efficiency (% of initial)
1	948	790.5	—	83.4
2	948	863	—	91
3	674	208	14.8	97.8 ^a
4	674	216	32.4	95.2 ^a
5	108	97	—	90
6	108	89	—	82.4

^aRemoval efficiencies in experiments 3 and 4 were calculated as $(1 - C_s / C_i)$.

shown in Table 2, indicate that high metal removal efficiencies can be achieved. The experimental work presented in this paper is a demonstration of the proposed method for the removal of Pb, Cd and Cr from sand. The experimental results indicate that high metal removal efficiencies can also be achieved for these metals.

As mentioned before, in these experiments electroosmotic flow is not taken into consideration. This is because a low pH is needed for the removal of heavy metals, otherwise the metals will precipitate as hydroxides or adsorb onto the soil surface. Meanwhile, the soil surface charge density and its sign are pH dependent. Normally, the soil surface is negatively charged and the charge density will decrease with the decrease of the pH. In very low pH, the soil surface can become positively charged. Thus the direction and the rate of electroosmotic flow will also be pH dependent. So, if the soil has a low pH, electroosmotic flow is unlikely to be important.

In these experiments, sand is used and the metals are artificially spiked into the sand, for which the removal is probably not as difficult as for real contaminated soils. Natural soils usually contain fine particles such as clay particles, which have a high surface area, causing a larger retention time for heavy metals.

4.1. pH values at the pH measuring point

The pH values measured at the pH measuring point during each experiment are shown in Figs. 2–4. It is important to control the pH in the sand and in the conductive solution during removal of toxic metals since it affects the solubility of heavy metals.

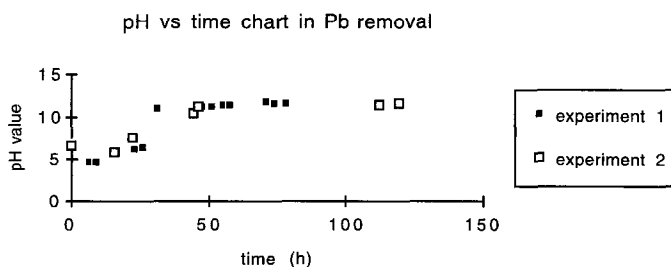


Fig. 2. pH measured in the experiments for Pb removal.

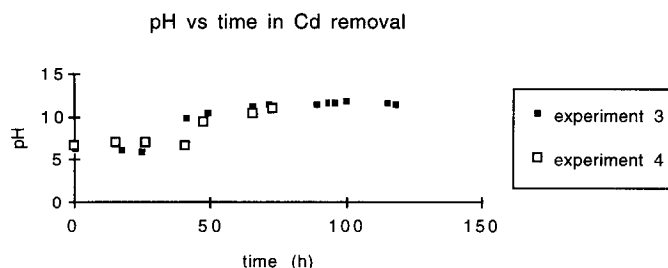


Fig. 3. pH measured in the experiments for Cd removal.

This could be achieved by adjusting the dimensions of the soil and the solution. It is observed that the pH value rises quickly at a certain time. This could be an indication that the position of the pH jump moves towards the anode during the experiments. Explanations could be as follows.

1. At the beginning of each experiment, hydroxides are consumed by forming precipitates with heavy metals. Thus the advancement of the base front is reduced, and the pH jump, established as the acid front and the base front meet each other, is closer to the cathode. As the test proceeds, the pH near the anode becomes lower and lower and the consumption of hydrogen ions on the soil surface by ion exchange, sorption mineral reactions, etc., increases in time and cannot be neglected. At the same time, the concentration of hydroxide ions also increases, which, however, does not result in mass transfer of hydroxide ions from the solution phase to an immobile phase. Consequently the pH jump moves towards the anode.

2. In these experiments, potassium nitrate was added to produce a conductive solution. NO_3^- , which is not at a trace level, could be reduced at the cathode, for example, to form NO as shown in Eq. (3), although it moves towards the anode during the experiment.



This means that the generation rate of hydroxide ions at the cathode is greater than that of hydrogen ions at the anode. According to Eq. (1), three electrons will generate three hydrogen ions at the anode, whereas, in Eq. (3), four hydroxide ions will be generated at the cathode.

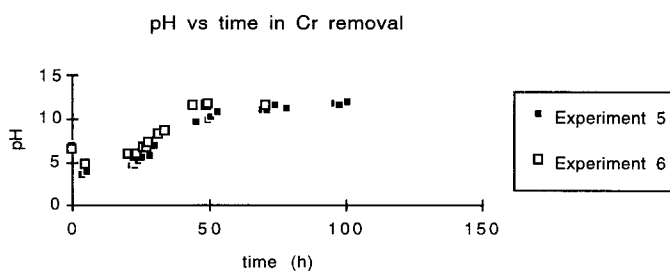


Fig. 4. pH measured in the experiments for Cr removal.

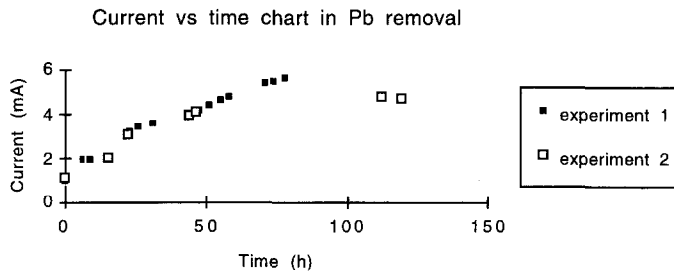


Fig. 5. Current measured in the experiments for Pb removal.

4.2. Electrical current and conductivity

The measured currents are shown in Figs. 5–7. The following observations are made. (1) Under constant potential employed in the six experiments, the current increased at the beginning of each experiment then kept almost constant through the remaining time of the experiment. (2) After several hours at the potential employed, precipitates appeared in the column of the conductive solution, the amount of the precipitates increasing with time. The increase in current at the beginning of each experiment was caused by the increase in concentration of ionic species due to their desorption from the soil surface and dissolution of precipitates in the low pH region.

The tendencies of current changes appear to be different from what are reported in other investigations. Hamed et al. [6] reported that, in tests for removal of Pb(II) by using electroosmosis, the potential drop needed to keep the current constant increased from 0.4–0.7 V cm⁻¹ at the beginning to 2.4 V cm⁻¹ at the termination of the tests; they demonstrated that this was due to a decrease in conductivity in the cathode section of the cell. The current is related to the apparent conductivity as shown in Eq. (4):

$$K_a = \frac{IL}{VA} \quad (4)$$

where I = the current; V = the potential drop between the cathode and the anode; L = the distance between the two electrodes; and A = the cross-sectional area of the soil.

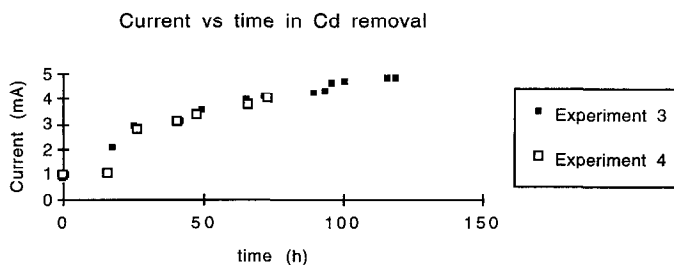


Fig. 6. Current measured in the experiments for Cd removal.

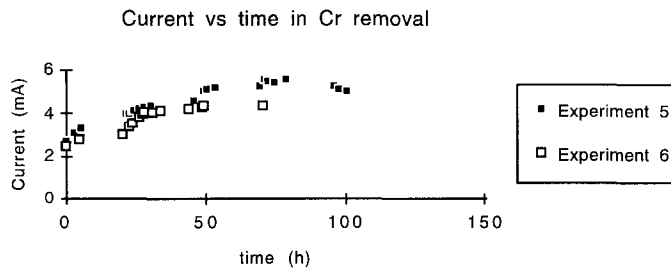


Fig. 7. Current measured in the experiments for Cr removal.

Conductivity can change due to variation in pore sizes (porosity), tortuosity in the porous medium and variation in pore fluid [9,14]. Since, in the three experiments, V , A and L in Eq. (4) are constant, the curves of apparent conductivity with time across the electrodes have the same shapes as that of the currents shown in Fig. 2. The difference of the tendencies of current and conductivity in our experiments from those in literature may be attributed as follows. (1) There was no open flow arrangement at the electrode in the three experiments. Therefore the electrolyte ions added to the system would not be depleted by using the proposed method. (2) Precipitation did not occur in the treated soil; thus the porosity of the medium and the tortuosity in the porous medium would be almost the same at the end of the test as it was at the beginning. Therefore, the apparent conductivity of the system was not much changed and the current through the system kept almost constant through a few days of treatment.

5. Conclusions

The main conclusions in this study are as follows:

1. By using the proposed technique, Pb(II), Cd(II) and Cr(III) can be removed from sand. A high percentage of heavy metal removal can be achieved.
2. The experimental results indicated that heavy metals can be removed by using electromigration alone.
3. Since the metal contaminants precipitated out of the soil, the porosity and the tortuosity of the soil did not change very much. The decrease in apparent conductivity reported in the literature, caused by precipitation of metal in soil, is thus avoided.
4. The proposed method is simple and easy to implement.

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