

# Electromigration of cadmium in contaminated soils driven by single and multiple primary cells

Songhu Yuan<sup>1</sup>, Chan Wu, Jinzhong Wan, Xiaohua Lu\*

*Environmental Science Research Institute, Huazhong University of Science and Technology, Wuhan 430074, PR China*

Received 7 February 2007; received in revised form 7 June 2007; accepted 7 June 2007

Available online 13 June 2007

## Abstract

This study tentatively used an iron (Fe) and carbon (C) primary cell, instead of dc electric power, to drive the electromigration of cadmium in contaminated soils. The addition of acid to C compartment increased the electric potential, while the addition of acid to Fe compartment had a slight influence on the potential. It was feasible using the primary cell to drive the electromigration of cadmium in kaolin. The electromigration efficiencies were highly related to the soil pH. Lower pH led to greater migration efficiency. The mechanisms involved the desorption of cadmium from soils to pore solution and the electromigration of cadmium in the pore solution. The desorption was critical to the electromigration process. The series of primary cells could expand the treatment area, but the electromigration efficiencies of cadmium in each cell were less than that achieved by single primary cell. Since the potential gradient produced by the primary cell was rather low, the electromigration rate of pollutants was very low and remediation duration was long. The application would be acceptable in some specific sites, such as acidic soils or artificially controlled acid conditions so that heavy metals have been desorbed from soils.

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**Keywords:** Primary cell; Heavy metals; Soil remediation; Electrokinetic

## 1. Introduction

Electrokinetic (EK) remediation is a very effective technique to remove toxic metals from contaminated soils. A comprehensive review of EK soil remediation has been provided in several previous studies [1–5]. Briefly, with the application of electric field to the polluted site, pollutants will migrate towards anode or cathode by electromigration, electro-osmosis and electrophoresis [1–3]. Much interest has been focused on the electromigration of heavy metals in soils [6–13]. It has been well established that the removal mechanism of heavy metals by EK technique involved two steps, the desorption of heavy metals from soils to pore solution and the subsequent movement by electromigration, secondarily by electro-osmosis and diffusion [1–3]. It is impossible to move the pollutants adsorbed on soils by electromigration.

Generally, about 1 V/cm potential gradient was used in EK remediation in both experimental and field test [3–5,14,15].

Actually, the potential may attribute to the removal efficiencies of heavy metals from two aspects. On one hand, electrolysis of water on anode produces much H<sup>+</sup>, which forms an acidic front towards cathode by electromigration. The acid front may largely contribute to the desorption of heavy metal from contaminated soils into soil pore solution [1–3]. On the other hand, such a high potential may accelerate the electromigration rate of the positively charged heavy metals in the soil pore solution. Thus, relatively shorter remediation duration was achieved by EK process. High electric energy consumption is one of the most important factors restricting the application of EK technique [15,16], particularly in developing countries such as China. Therefore, it is very meaningful to develop new methods to reduce the energy consumption. Supposed that the contribution of potential to the desorption was subtracted or the heavy metals have been dissolved in soil pore solutions, much lower potential gradient can be used to drive electromigration. This supposition is reasonable in some specific cases, such as acidic soils or controlled acid conditions artificially so that heavy metals have been desorbed from soils.

In the present study, we tentatively used a primary cell, instead of the traditional dc electric power, to drive the

\* Corresponding author. Tel.: +86 27 87792159; fax: +86 27 87792159.

E-mail addresses: [yuansonghu622@hotmail.com](mailto:yuansonghu622@hotmail.com) (S. Yuan),

[lxh@hust-esri.com](mailto:lxh@hust-esri.com) (X. Lu).

<sup>1</sup> Tel.: +86 27 62798401; fax: +86 27 87792159.

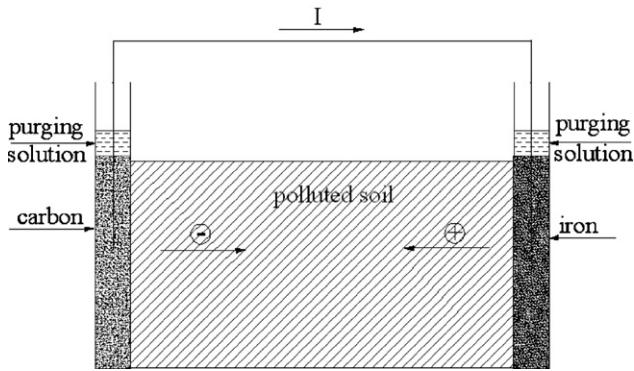
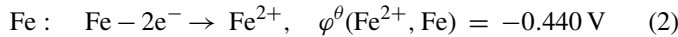
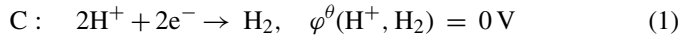


Fig. 1. Schematic diagram of the primary cell soil remediation process.

electromigration of heavy metals in soils. The schematic diagram of the technique is shown in Fig. 1. Iron (Fe) and carbon (C) are used as anode and cathode, respectively. When Fe and C are connected with wire, a primary cell is formed due to the difference of electrode potentials. Electrode reaction on C is the evolution of  $H_2$  (reaction (1)) and on Fe is the corrosion of iron (reaction (2)), so the electrode potential on C is higher than that on Fe. Electric current is from C to Fe in the wire and from Fe to C in the soil, as shown in Fig. 1. Cations migrate from Fe to C and anions migrate contrarily:



This study investigated the electromigration of cadmium, a representative heavy metal pollutant, in soils driven by the primary cell. The objectives are (1) to explore the feasibility of using Fe/C primary cell to drive the electromigration of cadmium in soils; (2) to research the effect of acid in Fe and C compartment on the electrokinetic properties and the electromigration of cadmium; (3) to investigate electromigration of cadmium by the series of several primary cells so as to increase the remediation area.

## 2. Experimental

### 2.1. Chemicals and materials

$CdCl_2 \cdot 2.5H_2O$  (Tingxin Chemical Reagent Factory, China, >99.0%) was used as the source of cadmium. Scrap iron was provided from the mechanical factory of Huazhong University of Science and Technology, China. It was first washed in boiling NaOH (1%) solution for 20 min to remove oil and then in  $H_2SO_4$  (1%) to remove rust. Finally, it was washed with tap water and deionized water to be neutral. Crustose carbon was purchased from Kexin Chemical Co. Ltd., China. It was washed by tap water and deionized water before use. All the other reagents used were above analytical grade.

Kaolin was often used as the model clay in EK laboratory experiments [6,8,11,17–19] because of its low buffer capacity, low organic content, low cation exchange capacity and inertia. The main characteristics of the kaolin (Shanghai Fengxian Fengcheng Chemical Reagent Factory, chemical purity)

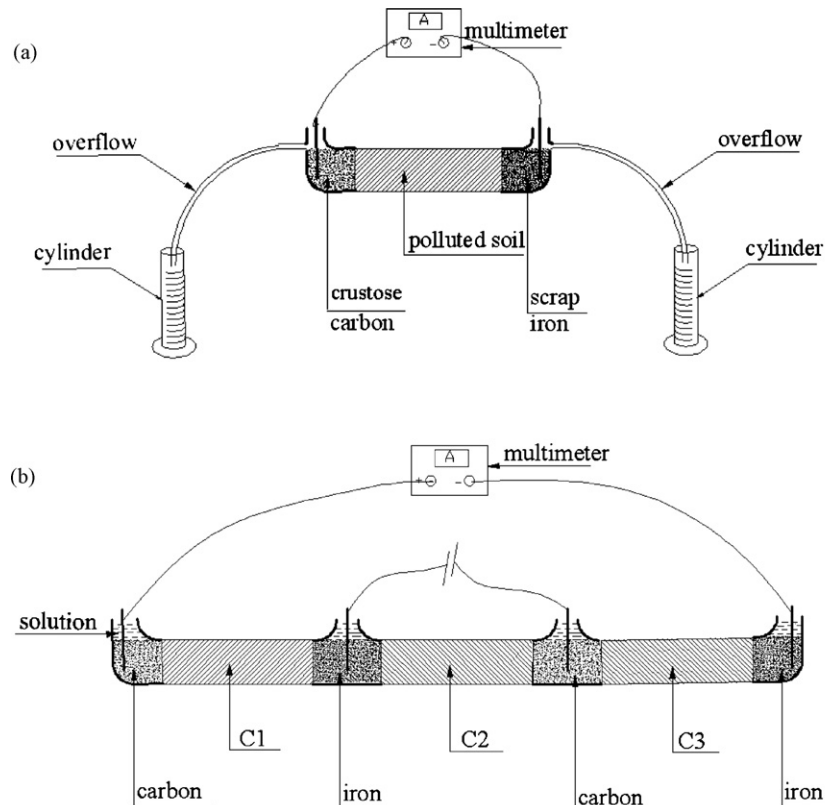


Fig. 2. Setup of primary cell soil remediation experiment: (a) in the first series; (b) in the second series.

used in this study have been provided in our previous work [20]. It is clayed, slightly acidic (pH 5.75), negatively charged (zero point of charge, ZPC, 3.36) and contains low content of organic matters (0.28%) and low cation exchange capacity (1.71 cmol/100 g).

## 2.2. Procedures and equipments

### 2.2.1. Effect of aqueous solution on the electric potential

The effect of aqueous solution on the electric potential between C and Fe was investigated in aqueous solution. The glass setup was the similar to Fig. 2(a) used in the following section. The anodic compartment (150 mL capacity) and cathodic compartment (150 mL capacity) were set in each end and a glass cylinder ( $\text{\O}5 \text{ cm} \times 8 \text{ cm}$ ) was placed in the middle. Both compartments were clotted to the cylinder with glass cement to avoid water leakage. Iron stick ( $\text{\O}25 \text{ mm} \times 90 \text{ mm}$ ) and graphite stick ( $\text{\O}25 \text{ mm} \times 90 \text{ mm}$ ) were placed in the anodic and cathodic compartments, respectively. Aqueous solution with different pH and ionic strength was filled in the cell. The solution pH was adjusted by 1 mol/L  $\text{H}_2\text{SO}_4$  or 1 mol/L NaOH and ionic strength was provided by powder NaCl. The electric potential between C and Fe was monitored by a multimeter (Hangzhou Huasheng Instrument Factory, China). The potential was obtained when it was stabilized after about 30 min.

### 2.2.2. Electromigration of cadmium by the primary cell

Cadmium-contaminated soil was prepared by spiking  $\text{CdCl}_2$  solution in kaolin. The soil and solution were stirred thoroughly to obtain a uniform contaminated soil. The water content of 45% was made by controlling the volume of  $\text{CdCl}_2$  solution added. The simulated soil was then settled for about 48 h, which was sufficient to achieve adsorption equilibrium [19]. The uniform distribution of cadmium in the soil was verified by the consistency of atomic absorbance spectrophotometer (AAS) analysis of three random samples. The content of cadmium was determined to be 185 mg/kg dry soil.

In the first series of experiments (T1–T5 in Table 1), the setup in Fig. 2(a) was used. A fraction of the moist soil was added to the glass cylinder ( $\text{\O}5 \text{ cm} \times 20 \text{ cm}$ ), followed by compacting with a glass rod to remove air bubbles. Another fraction was then added,

Table 1  
Parameters associated with the tests

Tests	C compartment	Fe compartment
T1	Deionized water	Deionized water
T2	0.2 mol/L HCl	Deionized
T3	Deionized water	0.2 mol/L HCl
T4	0.2 mol/L HCl	0.2 mol/L HCl
T5 <sup>a</sup>	0.2 mol/L HCl	0.2 mol/L HCl
T6 <sup>b</sup>	0.2 M HCl	0.2 M HCl
T7 <sup>c</sup>	0.2 M HCl	0.2 M HCl
T8 <sup>d</sup>	0.2 M HCl	0.2 M HCl

<sup>a</sup> An external potential of 2 V was supplied.

<sup>b</sup> The reference test with one primary cell.

<sup>c</sup> The setup in Fig. 2(b) was used and the middle cell was connected with wire.

<sup>d</sup> The setup in Fig. 2(b) was used and middle cell was disconnected.

and the procedure was repeated until the column was filled. A subsample of the remaining soil was extracted as described below to determine the initial concentration of cadmium and iron. Filter paper was placed in both ends of the column. The anodic compartment (150 mL capacity) and cathodic compartment (150 mL capacity) were assembled with the glass cylinder subsequently. A piece of silica gel circle was placed between the glass cylinder and the compartment to avoid solution leakage. Compartments and cylinders were connected with screw. Anodic and cathodic compartments were fully packed with 200 g scrap iron and 70 g crustose carbon, respectively. In order to make a good contact, thin iron stick and graphite stick were inserted to scrap iron and crustose carbon, respectively. Solutions were added to the compartments and wire was used to connect iron and carbon. The electric current and potential were monitored by a multimeter connected in the electric circuit. The electro-osmotic flow was collected by the cylinders. All the experiments were carried out at room temperature ( $30 \pm 3 \text{ }^\circ\text{C}$ ). In the test with external electric potential (T5 in Table 1), a dc power (GPC-H, 30 V/5 A, Taiwan Guwei Electronic Ltd. Inc., Taiwan) was used. The parameters associated with the experiments in the first series are presented in Table 1. In T1–T4, 0.2 mol/L HCl was added to Fe and/or C compartment to investigate the effect of acid on electromigration. As a comparison, the low electric potential of 2 V was supplied by a dc power in T5. The duration of T1–T5 were 25 d. Selected experiments were conducted in duplicate.

In the second series of experiments (T6–T8 in Table 1), the setup in Fig. 2(b) was used. C1, C2 and C3 refer to the first, second and third primary cell in the setup (Fig. 2(b)) and C refers to a reference test of T6. Differently, electro-osmotic flow was not collected because it has been found to be negligible; a polychloroethylene (PVC) cylinder ( $\text{\O}5 \text{ cm} \times 20 \text{ cm}$ ) was used instead of the glass cylinder; 100 g scrap iron and 50 g crustose carbon were placed in anodic (100 mL capacity) and cathodic (100 mL capacity) compartment, respectively. The compartments and cylinders were sealed with plastic glue. The other installation procedure was the same as that in the first series. The parameters associated with the experiments in the second series are also listed in Table 1. It should be noted that only one primary cell (similar to Fig. 2(a)) was used in T6, which was used as a reference test; three primary cells (Fig. 2(b)) were connected and the middle was connected and disconnected in T8 and T7, respectively. The duration of T6–T8 were 32 d. Selected experiments were conducted in duplicate.

## 2.3. Analysis of samples

In the running process, the solution pH in Fe and C compartment was measured by pH paper. At the end of the first series of experiments, soil in the cylinder were pushed out and sliced to eight pieces from Fe to C. At the end of the second series of experiments, the PVC cylinder was sawed to five or six pieces. Each piece was analyzed for pH, cadmium and iron concentration. The samples were dried at  $105 \text{ }^\circ\text{C}$  for 8 h, then ground and sieved by 0.25 mm screen. pH was measured by a pH meter (pHS-25, Shanghai Leici Instrument Factory, China)

by mixing 10 g soil sample with 20 mL deionized water. In the analysis of cadmium and iron, 1 g soil was digested with 5 mL concentrated nitric acid in a sealed vial (10 min, 170 °C), followed by centrifugation for 10 min (3000 rpm). The concentration of cadmium and iron in the supernatant was diluted and determined by AAS (WFX-110, Beijing Ruili Analytical Instrument Co. Ltd.). Each sample was prepared in triplicate. The recovery of cadmium in the processes was verified to be above 95%.

### 3. Results and discussion

#### 3.1. Effect of aqueous solution on electric potential

The standard potential between C and Fe is 0.440 V [21]. However, the potential was affected by the concentration of  $H^+$  and  $Fe^{2+}$ , which can be described by Nernst equation [21]:

$$E = \varphi(H^+, H_2) - \varphi(Fe^{2+}, Fe) \quad (3)$$

$$E = \varphi^\theta(H^+, H_2) - \varphi^\theta(Fe^{2+}, Fe) + RT/2F \ln[\alpha(H^+)^2\alpha(Fe)/\alpha(H_2)\alpha(Fe^{2+})] \quad (4)$$

$$E = 0.440 - RT/2F \ln[\alpha(Fe^{2+})p(H_2)] - 0.059pH \quad (5)$$

where  $R$  is the Avogadro number,  $T$  the standard temperature,  $F$  the Coulomb constant, and  $\alpha(H^+)$ ,  $\alpha(Fe)$ ,  $\alpha(H_2)$  and  $\alpha(Fe^{2+})$  are the activities of the corresponding species in the brackets. Generally, the activities of solid and gas reactants are 1 and the partial pressure, respectively [21]. So, Eq. (4) could be transformed to Eq. (5), indicating that pH had a negatively linear effect on the potential and the activity of  $Fe^{2+}$  and the partial pressure of  $H_2$  influenced the potential.

The effect of pH and ionic strength on the electric potential between C and Fe are displayed in Fig. 3. Ionic strength showed negligible influence on the electric potential, suggesting that the effect of ionic strength on the activity of  $Fe^{2+}$  was minute. However, the electric potential was about 0.60 V, which was higher than the standard potential of 0.440 V. Under this condition (pH 7.0), the electric potential was calculated from Eq. (5) to be

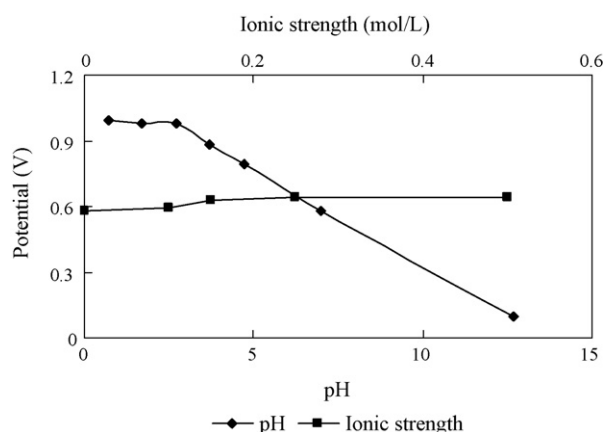


Fig. 3. Effect of pH and ionic strength on the electric potential between C and Fe.

$0.027 - RT/2F \ln[\alpha(Fe^{2+})p(H_2)]$ . The electric potential of about 0.60 V was stem from the effect of  $\alpha(Fe^{2+})$  and  $p(H_2)$ . The activity of  $Fe^{2+}$  was very low at the start of reaction and the partial pressure of  $H_2$  was negligible in an open system. The small values of  $\alpha(Fe^{2+})$  and  $p(H_2)$  led to the high electric potential. When pH rose from 2.70 to 12.70, a linear decline of electric potential was achieved. The regression equation was obtained as

$$E = 1.205 - 0.088pH, \quad R^2 = 0.999 \quad (6)$$

The coefficient (0.088) in Eq. (6) was higher than that (0.059) in Eq. (5). Compared with Eq. (5), the regression Eq. (6) apparently excluded the effect of  $\alpha(Fe^{2+})$  and  $p(H_2)$ . It is well known that the dissolution of iron and the evolution of  $H_2$  increased with the drop of aqueous pH. Eq. (5) suggested that lower values of  $\alpha(Fe^{2+})$  and  $p(H_2)$  resulted in higher values of electric potential. It can be inferred that the comprehensive effect of pH,  $\alpha(Fe^{2+})$  and  $p(H_2)$  made an increase of the coefficient from 0.059 (Eq. (5)) to 0.088 (Eq. (6)). When the aqueous pH further dropped from 2.70 to 0.70, the influence became minute. At pH below 2.70, the dissolution of iron and the evolution of  $H_2$  became significant. A negligible change of electric potential at pH < 2.7 suggested that the rise of electric potential due to the drop of pH was balanced by the decrease of electric potential due the increase of  $\alpha(Fe^{2+})$  and  $p(H_2)$ .

#### 3.2. Changes of electric potential and current

The changes of electric potentials in the first series of tests are shown in Fig. 4(a). The initial potentials in all the tests were ranged from 0.75 to 0.80 V. This can be well interpreted from the conclusions obtained in Section 3.1. The pH of kaolin spiked with cadmium was 5.08. Assuming that the pore solution in kaolin functioned as the electrolyte of the primary cell, we calculated the electric potential from Eq. (6) in Section 3.1 as 0.76 V, which was in good agreement with the initial electric potential obtained. The slightly higher initial electric potential in T2–T4 was due to the addition of acid in Fe and/or compartments.

With the increase of operation time, the electric potential gradually decreased in all the tests. It was found that the decrease was relatively slower when C compartment was filled with acid (T2 and T4). Since the electric potential increased with the decrease of pH and  $\alpha(Fe^{2+})$ , the addition of acid in C compartment may increase the electric potential and the addition of acid in Fe compartment may reduce the potential. However,  $H^+$  in C compartment was gradually consumed (rose to about 5 after 5 d in T2 and T4), which was partly accountable for the gradual decrease of electric potential with time.  $Fe^{2+}$  generated from the dissolution of iron in Fe compartment may enter into the soil and elevate  $\alpha(Fe^{2+})$  in the pore solution, which further led to a decrease of electric potential. The similar change of electric potential in T2 and T4 or in T1 and T3 indicated that the addition of acid in Fe compartment had no significant effect on electric potential.

The electric current was also monitored and shown in Fig. 4(b). In general, electric current is affected by many factors such as liquid conductivity, water content of soils, electrode



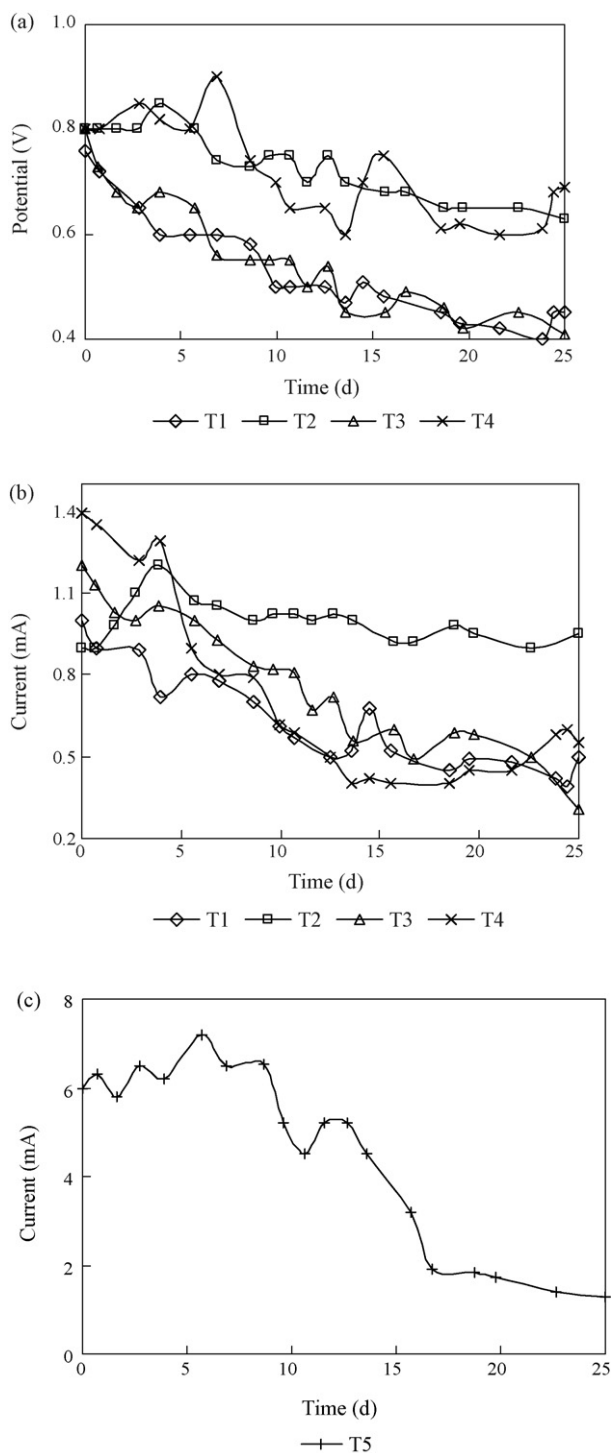


Fig. 4. Changes of electrochemical parameters in the first series of experiments: (a) electric potential in T1–T4; (b) electric current in T1–T4; (c) electric current in T5.

characteristics and electric field [1,19]. The initial currents of all the tests were different due to the different initial conditions, such as different solutions in Fe and C. In general, the maximum current reached at the start of test when the quantity of ions in the pore solution is greatest [8,19]. Fig. 4(b) shows that the current declined with time. However, the current in T3 was higher than that in T1 in the initial 14 d, though the potential in

T3 was approximately equal to that in T1. When 0.2 mol/L HCl was added to Fe compartment (T3), more ions were capable of transporting charges. As  $H^+$  in Fe compartment was consumed quickly and the direction of the electromigration of  $Cl^-$  was contrary to the direction of current, the influence of the addition of 0.2 mol/L HCl to Fe compartment became less and less significant with the further increase of time. Similarly, the current in T4 was higher than that in T2 in the first 4 d. However, it was surprising that the current in T4 was much lower than that in T2 when the duration exceeded 4 d. The addition of 0.2 mol/L HCl to Fe compartment may attribute to the corrosion of Fe and resulted in much ionized iron. With the consumption of  $H^+$  and the rise of pH (increased to about 6 after 0.5 d), these ions ( $Fe^{2+}/Fe^{3+}$ ) would be coated on Fe surface, which elevated the electric resistance of the circuit.

When a constant electric potential of 2 V was supplied by an external dc power (T5), the current was much higher (Fig. 4(c)). The current remained relatively high in the first 8 d. In the first stage, since the entering of  $H^+$  and  $Cl^-$  may lead to the release of cations from kaolin to the pore solution, the current was high. Then, the current dropped to below 2 mA at 16.5 d. This was due to the produce of  $OH^-$  on carbon cathode. Much  $OH^-$  produced may form precipitation with many cations contained in kaolin, which may reduce the species that transported charges and increase the electric resistance [2]. The polarization of both Fe anode and C cathode also made a decline of current [3].

### 3.3. Distribution of soil pH

At the end of tests, the distribution of soil pH along the cell is shown in Fig. 6, where  $x/L$  denotes the distance between sample and Fe divided ( $x$ ) by the length of soil column ( $L$ ). The initial pH of kaolin spiked with cadmium was 5.08. When deionized water was filled in iron and carbon compartment (T1), the soil pH dropped to 3.42 near Fe and rose to 5.11 near carbon. This could be explained from the electrode reactions on Fe and C and the subsequent electromigration of  $H^+$ ,  $OH^-$ , and  $Fe^{2+}/Fe^{3+}$ . In the Fe/C primary cell system, the electrode reactions involved the produce of  $H_2$  from  $H^+$  in C compartment and the generation of  $Fe^{2+}$  in Fe compartment. Since the anodic compartment was contacted with air,  $Fe^{2+}$  was possible further oxidized by  $O_2$  to  $Fe^{3+}$ , which was more favorable to form hydroxide precipitation [21]. Because  $OH^-$  may be consumed by  $Fe^{2+}/Fe^{3+}$  to form  $Fe(OH)_2/Fe(OH)_3$ , pH in Fe compartment was decreased. Likewise, pH in C compartment was increased due to the consumption of  $H^+$  on carbon. Subsequently, the electromigration of cations such as  $H^+$ ,  $Fe^{2+}$  and  $Fe^{3+}$  from Fe to C resulted in the drop of soil pH near Fe, while the electromigration of anions such as  $OH^-$  led to the rise of soil pH near C.

When 0.2 mol/L HCl was added to C compartment (T2), the soil pH in all the region was lower than that in T1. Since the  $H^+$  added externally may neutralize the  $OH^-$  produced in C compartment and diffuse into the soil, the soil pH dropped. With addition of 0.2 mol/L HCl to Fe compartment (T3), the pH near Fe became lower.  $H^+$  could enter into the soil by electromigration and diffusion. The soil pH in all the region became further lower

when both Fe and C compartments were filled with 0.2 mol/L HCl (T4).

As a comparison, the soil pH in T5 was much lower in most regions. When an external potential of 2 V was exerted to the system, the anodic reactions, including the dissolution of iron and the electrolysis of water, and the cathodic reactions, mainly the electrolysis of water, happened much more intensively. As a consequence, much more  $H^+$  and  $OH^-$  were produced in T5 than in the other tests. Since the transport rate of  $H^+$  is 1.76 times of that of  $OH^-$  [1–3], the pH in most regions dropped to less than 3.0.

### 3.4. Distribution of cadmium and iron

The distribution of cadmium at the end of tests is given in Fig. 6(a). A significant migration of cadmium from Fe to C was achieved. Negligible electro-osmotic flow was collected in T1–T4, so the effect of electro-osmosis on the migration of cadmium could be neglected. Fig. 6(a) revealed great removal of cadmium in the section near Fe. In this region, electromigration drove the migration of cadmium from Fe to C, while diffusion drove the migration of cadmium from C to Fe. Cadmium was found to be cumulated in the middle and/or near C in T1–T3, which suggested that the contribution of electromigration was more significant than that of diffusion.

Generally, the electromigration of heavy metals was achieved only when they were desorbed from soil and dissolved in the pore solution [1–3]. So, it is critical that cadmium was desorbed from kaolin. However, the desorption of cadmium from soils was highly affected by the pH of pore solution because the increase of pH resulted in the increasing adsorption of heavy metals on soils [22]. Previously, we systematically investigated the influence of pH on the desorption of cadmium from kaolin [20]. Results revealed that little desorption of cadmium appeared at pH above 4.8 and the desorption increased sharply and linearly with the decrease of pH below 4.8 (desorption =  $-0.163pH + 0.914$ ,  $R^2 = 0.983$ ) [20]. That is, the rise of one unit pH led to the drop of 16.3% desorption efficiency.

In T1, the content of cadmium increased greatly from Fe to the section of 0.31 (normalized distance from Fe) and maintained almost constant from the section of 0.31 to C. This result was highly related to the soil pH. Fig. 5 shows that the pH in T1 from Fe to the section of 0.19 was less than 4.8 and from the section of 0.31 to C was higher than 4.8. It can be proposed that the cadmium from Fe to the section of 0.19 was desorbed and dissolved in pore solution due to the low pH [20], the dissolved cadmium was subsequently moved to the next section from 0.31 to C by electromigration and was re-adsorbed due to the increase of pH. Thus, the slight accumulation of cadmium from the section of 0.31 to C was achieved. In T2–T4, the soil pH from Fe to the section of 0.19 was lower than that in T1 (Fig. 6), so a larger removal of cadmium was obtained in this region. As the pH from the section of 0.31 to C was higher than 4.8 in T2 and T3, the accumulation of cadmium was also observed in this region. While in T4, the pH from the section of 0.69 to C was less than 4.8, so the content of cadmium in this region was much lower.

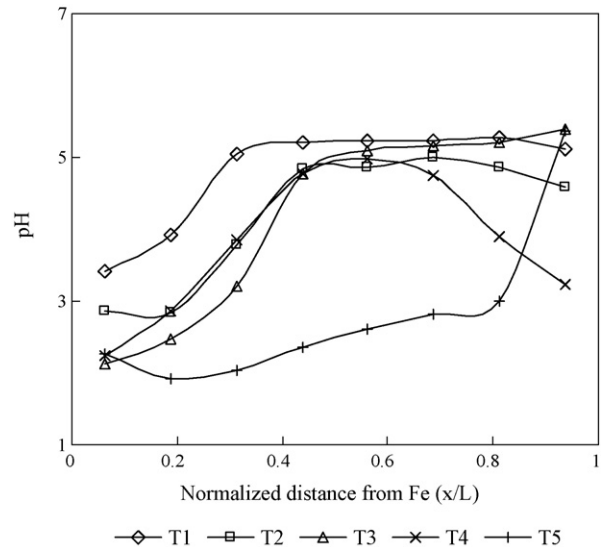


Fig. 5. Distribution of soil pH in the first series of experiments.

A remarkable removal of cadmium was achieved when an external potential of 2 V was supplied (T5). For 25 d treatment, cadmium was removed largely from Fe to the section of 0.19; no cadmium was detected from the section of 0.31 to the section of 0.81; a great accumulation of cadmium occurred in the section

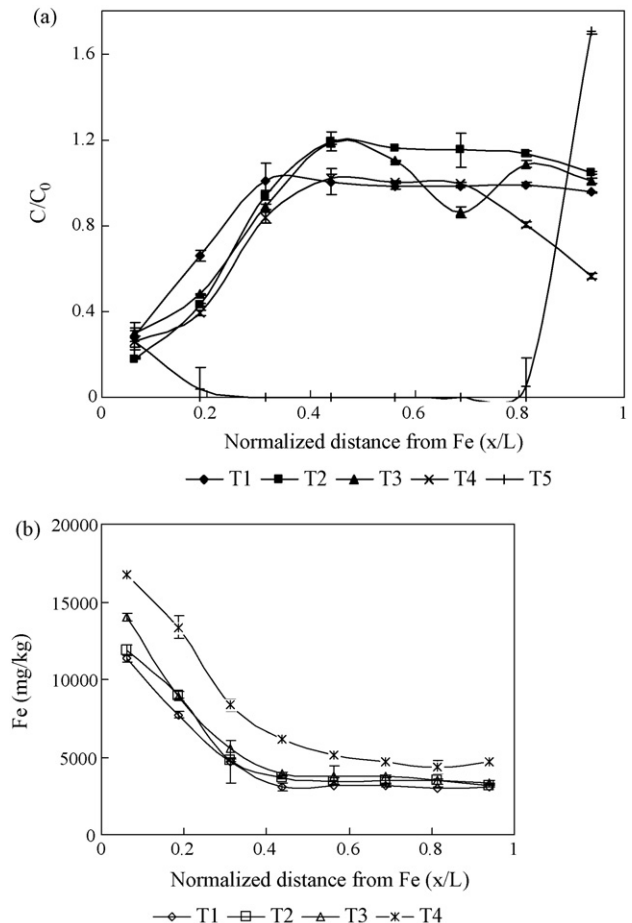


Fig. 6. Distribution of (a) cadmium and (b) iron in the first series of experiments.

near C. Likewise, the distribution of cadmium was related to soil pH. The soil pH from Fe to the section of 0.81 was below 3.0, at which cadmium could be desorbed from soils [20]. The soil pH near carbon cathode was 5.37, at which cadmium in pore solution could be re-adsorbed on soils [20]. The higher content of cadmium near Fe than in the middle was probably because the generation of  $\text{Fe}^{2+}$  from the dissolving of iron became far larger when 2 V external potential was exerted. So, the fraction of cadmium in the total ions that transported charges decreased. The electric current used to transport cadmium was reduced and the electromigration of cadmium near Fe was restricted [1,2].

The transport of iron ions in T1–T4 was measured and shown in Fig. 6(b). It has been stated that iron ions could be produced from the dissolving of iron in Fe compartment. The initial content of iron ions was measured as 3100 mg/kg. Fig. 6(b) revealed that quantities of iron ions entered into kaolin by electromigration and diffusion. The content of iron ions declined sharply from Fe to the section of 0.31. This tendency was also related to the distribution of soil pH. With the increase of pH, the adsorption of iron ions on kaolin increased and it was possible to form iron hydroxide precipitation. Fig. 5 shows the soil pH increased from Fe to the section of 0.31 and remained almost constant from the section of 0.31–0.69 in T1–T4. Consequently, iron ions migrated from Fe to the section of 0.31 successfully and the further migration was rather difficult. From the Fe content in soils, it was concluded that the entering of iron into soils was a problem for the application. This could be partly overcome by filling basic solution in Fe compartment or purging Fe compartment with water. Further work was under way.

In summary, it is feasible to use Fe/C primary cell to drive the electromigration of cadmium in contaminated soils, though the efficiency was much lower compared with that in the traditional dc power supply. The desorption process plays a very important role on electromigration. So, if heavy metals could be desorbed from soils into pore solution naturally or artificially, it is possible to drive their migration by primary cell.

### 3.5. Distribution of cadmium by series of primary cells

It has been found in the above sections, the electric potential and current across soils were very low. If a longer cylinder or larger area was treated, the electromigration efficiency would drop markedly. Hence, in this section, we investigated the electromigration of cadmium by the series of three primary cells. A longer duration of 32 d was lasted.

Fig. 7(a) revealed that the content of cadmium increased from Fe to C in all the three cells when Fe and C in the middle cell were connected (T7). The direction of current in T7 is depicted in Fig. 8(a). The soil in C2 was short circuited, current passed from C to Fe in wire and from Fe to C in soil. The direction of current in soils was in agreement with the electromigration of cadmium. From Fig. 7(a), the electromigration of cadmium in C1 and C3 was more significant than that in C2, and the electromigration in the reference test of T6 was the most obvious.

Previous results revealed the significant effect of pH on the electromigration of cadmium. Fig. 9(a) shows the distribution of

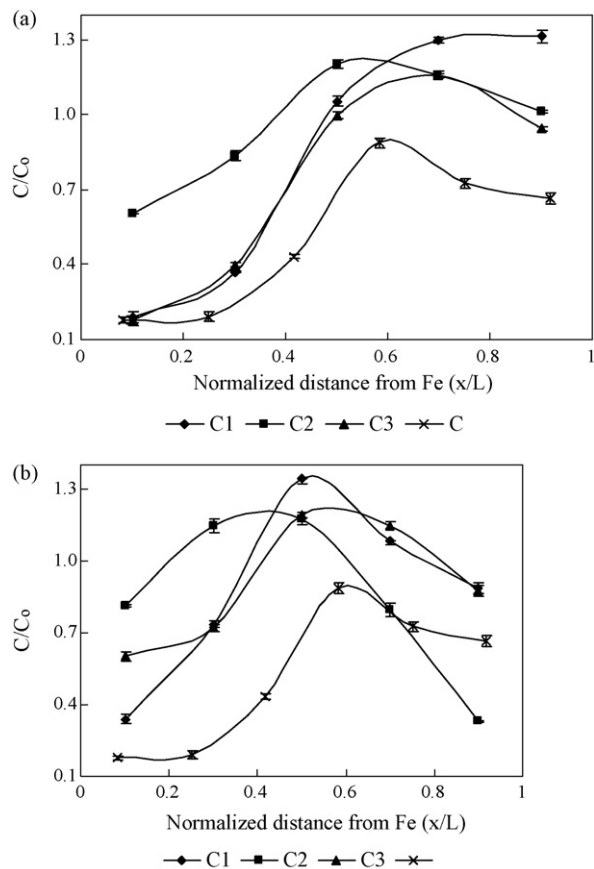


Fig. 7. Distribution of cadmium in the second series of experiments: (a) T7; (b) T8, C1, C2 and C3 refer to the first, second and third primary cell in the setup and C refers to T6.

soil pH at the end of T7. It is clear that the distribution of soil pH in C1, C3 and C (T6) were similar, while the soil pH in C2 was much higher. As a result, the electromigration rate of cadmium in C2 was slower. In C1, C3 and C (T6), the similar soil pH led to

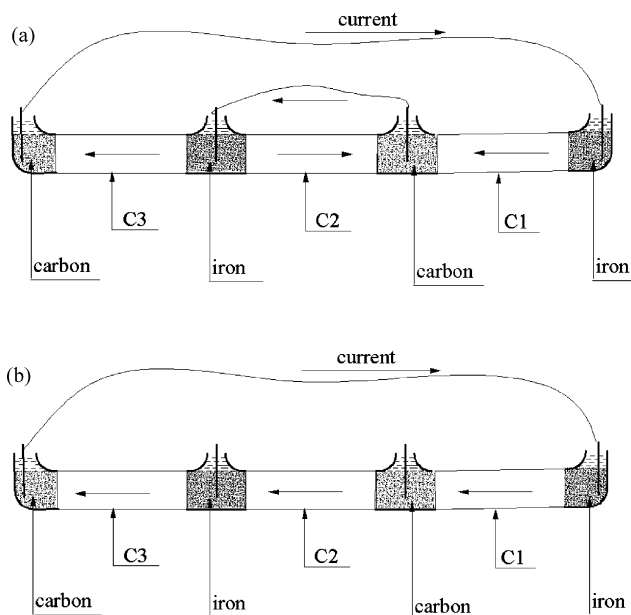


Fig. 8. Direction of electric current in the series of primary cells: (a) T7; (b) T8.

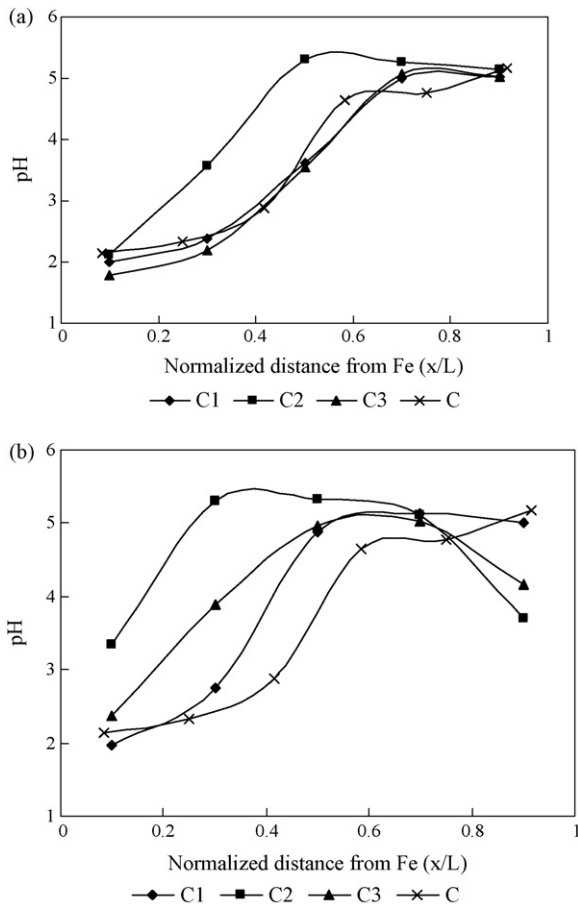


Fig. 9. Distribution of soil pH in the second series of experiments: (a) T7; (b) T8, C1, C2 and C3 refer to the first, second and third primary cell in the setup and C refers to T6.

different electromigration efficiency, indicating that the electric potential attributed to the migration. In the process, the total potential in T7 was about 1.0–1.5 times higher of the potential in T6 (data not shown). Fig. 8(a) indicated that the total potential in T7 was composed of the potential in C1 and C3. Since the total potential in T7 was less than two times of the potential in T6, the driving force exerted to the electromigration of cadmium in C1 and C3 (T7) was less than that in C (T6).

As a comparison, the electromigration in T8 was quite different from that in T7. Fig. 7(b) shows that the electromigration of cadmium was from Fe to C in C1 and C3 and from C to Fe in C2. The direction of current in T8 is depicted in Fig. 8(b). As the Fe and C in C2 were disconnected, the current in the whole cells passed from right to left despite the existence of Fe and C in the circuit. Fig. 9(b) shows that the soil pH gradually increased from Fe to C except the region closest to C in C1 and C3, while the contrary increase was obtained in C2. This result was consistent to electromigration direction of  $H^+$ . The soil pH in most regions was higher than that in T6. In addition, the total electric potential in T8 was measured to be approximately equal to that in T6. So, the potential exerted to each cell was much less than that in T6. Both led to the less electromigration efficiency in C1, C2 and C3 than that in C (Fig. 7(b)).

#### 4. Conclusions

The present study investigated the feasibility of using Fe/C primary cell to drive the electromigration of cadmium in soils. The effect of acid in Fe and C compartment on the electrokinetic properties and the electromigration of cadmium were studied. Furthermore, the electromigration of cadmium by the series of several primary cells was also researched. The main conclusions were drawn as follows:

- (1) In the primary cell system, the addition of acid to C compartment increased the electric potential, while the addition of acid to Fe compartment had a slight influence on the potential. The potential decreased with the increase of operation time. A similar decrease of electric current was also obtained.
- (2) It was feasible using the Fe/C primary cell, instead of dc electric power, to drive the electromigration of heavy metals such as cadmium in kaolin. The electromigration efficiencies were highly related to the soil pH. Lower pH led to greater migration efficiency. The mechanisms involved the desorption of cadmium from soils to pore solution and the electromigration of cadmium in the pore solution. The desorption was critical to the electromigration process.
- (3) The series of primary cells could expand the treatment area. However, the electromigration efficiencies of cadmium in each cell were less than that achieved by single primary cell.
- (4) Since the potential gradient produced by the primary cell was rather low, the electromigration rate of pollutants was very low and remediation duration was very long. The application would be acceptable in some specific sites, such as acidic soils or artificially controlled acid conditions so that heavy metals have been desorbed from soils.

#### Acknowledgement

This work was supported by the key project of Natural Science Foundation of Hubei Province (no. 2006ABD005).

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