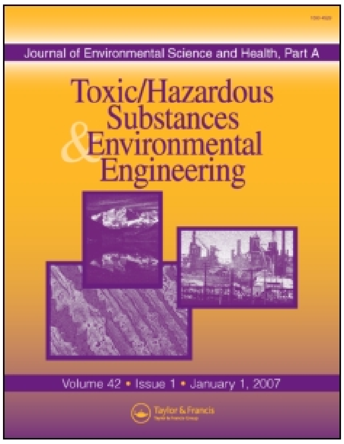
This article was downloaded by: *[National Taiwan University]*
On: *28 November 2008*
Access details: *Access Details: [subscription number 788846425]*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Environmental Science and Health, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597268

The Enhanced Removal of Cadmium and Lead from Contaminated Soils and the pH Effect by Electrochemical Treatment

Shin-Bin Chou [a]; Meng-Cha Cheng [a]; Shi-Chern Yen [a]
[a] Department of Chemical Engineering, National Taiwan University, Taipei, Taiwan

Online Publication Date: 27 December 2004

To cite this Article Chou, Shin-Bin, Cheng, Meng-Cha and Yen, Shi-Chern(2004)'The Enhanced Removal of Cadmium and Lead from Contaminated Soils and the pH Effect by Electrochemical Treatment',Journal of Environmental Science and Health, Part A,39:5,1213 — 1232

To link to this Article: DOI: 10.1081/ESE-120030327

URL: http://dx.doi.org/10.1081/ESE-120030327

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

JOURNAL OF ENVIRONMENTAL SCIENCE AND HEALTH
Part A—Toxic/Hazardous Substances & Environmental Engineering
Vol. A39, No. 5, pp. 1213–1232, 2004

The Enhanced Removal of Cadmium and Lead from Contaminated Soils and the pH Effect by Electrochemical Treatment

Shin-Bin Chou, Meng-Cha Cheng, and Shi-Chern Yen*

Department of Chemical Engineering, National Taiwan
University, Taipei, Taiwan

ABSTRACT

Electrochemical treatment is an emerging technology for decontaminating soil in-situ, which involves electrolysis, adsorption, desorption, precipitation, hydraulic or electroosmotic flow, and ionic transport. The removal of Pb and Cd ions from contaminated soils has been investigated in this study. The pH value of the soil significantly affects the removal of heavy metal ions. Besides the adsorption/desorption and precipitation are strongly affected by the pH of the soils, it can also influence the magnitude and direction of electroosmotic flow, and so the pH of the soil specimen must be regulated adequately. The appropriate range of pH values has been found to be $2 \sim 4$, and the pH must not exceed 6. Various enhancing methods of ensuring adequate pH distribution were employed herein, including methods that involve buffer solution, cation exchange membranes, and pretreatment with acetic acid and acetate buffered solution. Such methods proved to be highly effective in improving the removal efficiency in all instances. The removal efficiency of Cd^{+2} can reach 99%, and that of Pb^{+2} can reach 85%, when buffered solutions are used for the electrochemical treatment.

Key Words: Electrochemical treatment; Soil remediation; Pb removal.

---

*Correspondence: Professor Shi-Chern Yen, Department of Chemical Engineering, National Taiwan University, No. 1, Sec. 4, Roosevelt Road, Taipei, Taiwan 106; Fax: 886-2-23630397; E-mail: scyen@ccms.ntu.edu.tw.

DOI: 10.1081/ESE-120030327
1093-4529 (Print); 1532-4117 (Online)

www.dekker.com

INTRODUCTION

Conventional methods of soil remediation are soil flushing, soil washing, covering, solidification, vitrification or vaporization, reaction, and biological techniques.[1–6] Several methods may be combined to improve the efficiency of in-situ soil treatments. New promising treatment technologies have been proposed for on-site remediation, for use when the above traditional methods do not suffice. The electrochemical method has been proposed to treat heavy metals in soils effectively.[7,8] Generally the electrochemical method provides the following advantages: (i) on-site treatment[9]; (ii) control of the depth of the soil treated, by the depth of the inserted electrodes; (iii) the use of fewer chemicals in the treatment, and (iv) the collection of pollutants from effluents at the electrodes. In the past decade several studies on this aspect have been published in this field, addressing the pH distribution of the soil, the fluid flow, the efficiency of removal, and other aspects.[10,11] Some researchers tried to remove Pb from kaolinites.[12,13] The removal efficiency of Pb can be as high as 96% under some experimental conditions. However, most of these studies used sands and kaolinites as soil specimens. As the results obtained in the laboratory are applied to contamination of the field, the on-site results can be unexpected. In this work, soil specimens from a contaminated site were employed to ensure the practical relevance of the results.

Treatment by the electrochemical method involves the insertion of two inert electrodes (anode and cathode) into the soil, and the application of an electrical field using a power supply.[7] The heavy metal ions move to the cathode by fluid flow and electrical migration. The effluents, which contain the heavy metals, are collected from the cathode. Since H^+ and OH^- are produced at the anode and cathode, respectively, these ionic species move in opposite directions by diffusion and electric migration, and they are also carried by fluid flow induced by pressure gradient and electric field. The fluid flow induced in porous media by the electric field is called electroosmotic flow. At an electric field of about 1 V/cm, the effective mobility of hydrogen ions in the soil is approximately 2.73 cm/h.[14,15] By diffusion, migration, hydraulic and electroosmotic flow, the protons in the soils move toward cathode, strongly affecting the pH at various positions in the soils, and a pH distribution established along the soil specimen. In the soils near the anode, the pH can be reduced to 2, facilitating desorption of the adsorbed metal ions and increasing the solubility of the precipitates of heavy metal ions. Also the pH variations will influence the magnitude of the electroosmotic flow, and even its direction, if the sign of the zeta potential of the soils is changed due to more alkaline pH values. At the cathode, the effective mobility of OH^- at an electric field of 1 V/cm will be around 1.55 cm/h. The pH value of the soil increases to around 12 near the cathode.[8,12] The increase in the pH causes the precipitation of heavy metal ions near the cathode, reducing the removal efficiency, and plugging the pores, thereby retarding the flow. Regulating the pH of the soil is an important issue in soil electrochemical remediation. In this study a buffered solution at the cathode and/or in the soils is used to adjust the pH of the soil. Hence the pH at the cathode is kept at more acidic conditions to prevent the precipitation of metal oxides. Also the cation exchange membrane has been adopted to prevent the backward diffusion of the OH^- ion. They have been found to be effective for the removal of Pb and Cd ions.

Flow Phenomena During Soil Treatment

The pore fluid in soils is moved by hydraulic gradient and voltage gradient. According to Darcy's law, the water flow rate (Q_h) under a hydraulic gradient can be represented by

$$Q_h = v_h \cdot A = k_h \cdot A \cdot \nabla(-h) \tag{1}$$

where v_h represents the superficial velocity; A is the cross-sectional area of the soil specimen; k_h is hydraulic permeability; and h is the hydraulic head. Like Darcy's law, the electro-osmotic flow (Q_e) under an electric field can also be expressed as

$$Q_e = v_e \cdot A = k_e \cdot A \cdot (-\nabla\phi) \tag{2}$$

where v_e is the superficial velocity due to the electroosmotic effect, ϕ is the applied voltage, and k_e is the electroosmotic coefficient, which is dependent on pH and can be correlated to zeta potential by the Helmholtz–Smolchowskiz equation.[16,17]

$$k_e = -\frac{\varepsilon\zeta}{\mu}n \tag{3}$$

where ζ is the zeta potential; ε is the dielectric constant; μ is the viscosity; and n is the porosity. The value of k_e depends on the zeta potential of the soil, which in turn depends on the pH of the soil, its ionic strength, and the ionic species present. A larger ionic strength corresponds to a lower zeta-potential. If the zeta potential of the soil is negative, then the direction of electroosmotic flow is from the anode to the cathode.

Since the direction of hydraulic flow herein is from anode to cathode, electroosmotic flow in the same direction will better remove metal ions. Hence the pH of the soil must be maintained in a suitable range to prevent a reversal of electroosmotic flow. To apply the hydraulic head and electric field, the flow rate of the pore fluid in the soils is

$$Q_{\text{total}} = k_h \cdot A \cdot (-\nabla h) + k_e \cdot A \cdot (-\nabla\phi) \tag{4}$$

The ratio Q_e/Q_h is proportional to $1/d_p^2$ (d_p is the average pore size), so when the average pore size decreases, the electroosmotic flow in the soil becomes more important. The magnitude of Q_h and the flow path are affected strongly by the distribution of particle sizes, but Q_e is independent of this distribution.

Heavy-Metal Ions in Soils

Effectively treating pollutants in soils by the electrochemical method heavily depends on keeping the pollutants in a mobilized state. When the pollutants are in the ionized state, they move by electromigration. The ratio of the ionic effective migration mobility u_i^* to the k_e value is always between 10 and 300.[14] So the effect of the eletroosmotic flow is usually much smaller than that of ionic migration. Additionally, nonionic species must be dissolved or suspended in solution, and can be carried away from the soil by electroosmotic and hydraulic flow.

The reasons for the immobilization of heavy metal ions in the soil are: (i) organic acids are generated by biodegradation in the soils; (ii) –SiOH or –AlOH structures are present in the soil particles; (iii) carbonate ions are present in the calcium-contained soils; or (iv) other anions, such as OH^-, S^{-2}, SO_4^{-2}, PO_4^{-3}, or others.[18] Such ions precipitate easily with heavy metal ions. The former two factors can promote adsorption; the latter two factors can promote the formation of precipitates with metal ions.

Adsorption/Desorption

Since the surface of the soil particle carries negative charge at pH more than four, the cations in the pore fluid may adsorb onto it. The amount of adsorbed cations depends on the pH of the soil specimen. The adsorption fraction of Pb^{+2} increases from 0.3 to nearly 1 as the pH value changes from 4 to 5.5 and the adsorption fraction of Cd^{+2} increase from 0.5 to 0.9 as the pH value changes from 4 to 6.[13]

Precipitation

The solubilities of hydroxides and carbonates heavily depend on pH values, and the formation constants of lead hydroxides are

$$Pb^{+2} + OH^- \rightarrow Pb(OH)^+ \qquad \log k_1 = 7.82$$

$$Pb^{+2} + 2OH^- \rightarrow Pb(OH)_2 \qquad \log k_2 = 10.88$$

$$Pb^{+2} + 3OH^- \rightarrow Pb(OH)_3^- \qquad \log k_3 = 13.94$$

$$Pb^{+2} + 4OH^- \rightarrow Pb(OH)^{-2} \qquad \log k_4 = 16.30$$

where k_1, k_2, k_3, k_4 are equilibrium constants.[19] A calculation shows that $Pb(OH)_2$ precipitates as the pH value is between 8 and 13. At other pH values, most of Pb ions remain in the mobilized ionic state. For example, when the pH is below 5.6, most Pb ions are Pb^{+2}. When the pH is between 7 and 9, most Pb ions are in the form $Pb(OH)^+$. And when the pH exceeds 12, the major form is $Pb(OH)_4^{-2}$. With regard to cadmium, $Cd(OH)_2$ is precipitated at pH values of 9–13 .However, at most pH values, they are ionic. Cd^{+2} is present at lower pH values, and $Cd(OH)_4^{-2}$ at higher pH values, as for lead. However, Pb ions are adsorbed more tightly onto the surface of soil particles than are Cd ions.

The precipitates of lead and cadmium with other anions (carbonate, sulfate) behave differently from precipitates with hydroxides over a range of pH values. The solubility of sulfate precipitate is independent of the pH. The solubility of lead with the coexistence of carbonate and sulfate anions is about 0.1 mg/L over pH values from 4 to 11. Their solubility weakly depends on pH. However, when only carbonate anions are present, the solubility increases steeply from 0.2 to 300 mg/L as the pH declines from 6 to 4.[20]

In this study various enhancements have been employed, such as acid or buffer pretreatment, adding a buffer solution to the anode or cathode reservoirs, adding a cation exchange membrane at the cathode, among others, to increase the efficiency of removing heavy metals. The optimal ways of removing heavy metals from soils by electrochemical treatment are identified.

EXPERIMENTAL

The soil of silt clay used herein was taken from the Chung-fu District, the Lu-chu area of Tauyuan County, Taiwan. It has a higher organic content than typical silt clay. Table 1 lists the basic characteristics of the soil specimens. This soil taken from the site was contaminated and contained 1–10 ppm concentration of both lead and cadmium. For the convenience of experimental studies, the concentrations of lead and cadmium in the soils were increased to about 100 ppm in the following steps. Five hundred grams of the sieved soil was mixed with 500 mL of a solution that contained 100 ppm of lead and cadmium ions. The slurry was stirred for 24 h using a stirrer. Then, it was poured into a settling column with a diameter of 4 cm, and was allowed to settle for 24 h. After settling, the slurry was compacted under a 10 lb mass for 48 h, after which time, the upper clean solution of the column was removed. Filter paper was placed on the inside of each of the two perforated acrylic plates, and then the compacted soil sample was inserted between the two perforated acrylic plates to begin with the experiment.

Figure 1 schematically depicts the experimental setup. The acrylic cell has an inner diameter of 4 cm, and a length of 20 cm. The low overvoltage of evolution of hydrogen and oxygen at the inert electrodes of platinized titanium screen, such that the Pt/Ti screens were used at both sides of the acrylic cell as anode and cathode. The anode and cathode chambers were two cubic cells (4 cm × 4 cm × 4 cm), filled with anolyte and catholyte, which might be buffered solutions or regular solutions.

Table 1. Basic characteristics of the soil.

Texture	Silt loam with trace lime
Density	2.5081 g/cm^3
Initial pH	5.6
Point of zero charge	2.60
Initial water content	17.66%
Average particle size	104.9 μm
Porosity	0.3634
CEC	26.6 meq/100 g dry clay
Organic content	2.75%
Ion content of metal (by 1 M HNO_3 extraction)	Al (0.5721%) Ca (0.097%) Fe (0.2754%) Mg (0.0421%)

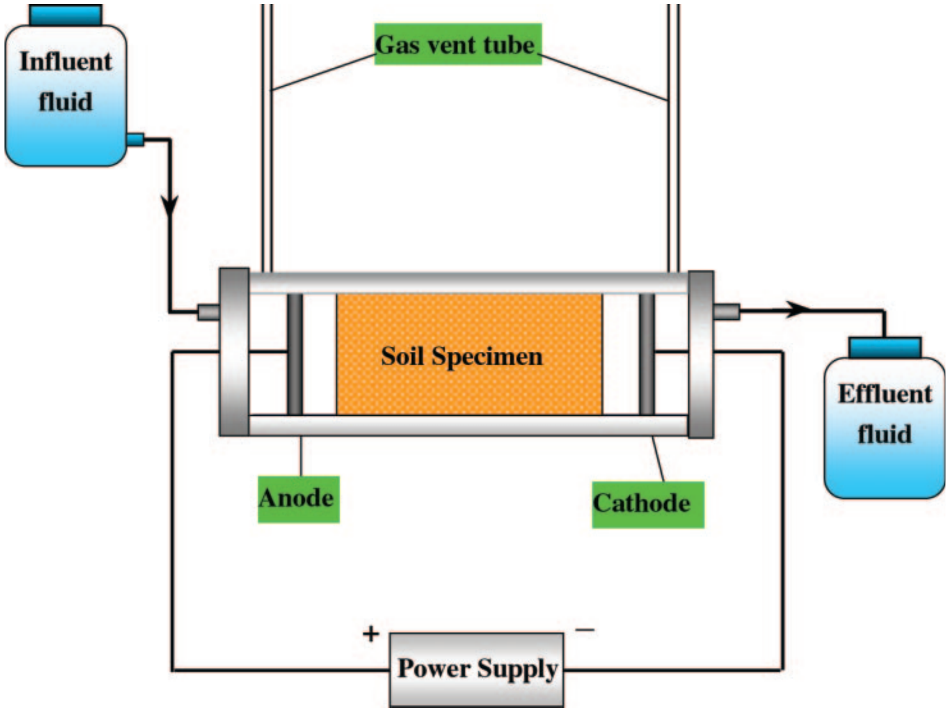


Figure 1. Experimental setup. *(View this art in color at www.dekker.com.)*

In the experiments, a 20 V dc voltage was applied to both electrodes. A 20 cm hydraulic head was added at anode. Table 2 lists the experimental conditions. The effluent from the cathode chamber during the treatment was analyzed. The pH, conductivity, and concentrations of heavy metal ions, and the volume of the effluent were measured. The voltage and current variation with time were recorded and the distribution of the water content in the soil after the treatment was also analyzed. The soil specimen was then divided into ten parts, weighing about 10 g each, dried in an oven, and 50 mL 1 M nitric acid solution was added. The mixture was shaken for 14 h in a shaker to leach out cadmium and lead ions. Then, the slurry was centrifuged to separate solution from the solid and the Pb and Cd concentrations in the solution were measured by ICP (Inductive Coupled Plasm Optical Emission Spectrometry).

RESULTS AND DISCUSSION

Treatment at Constant Applied Voltage Without Enhancement

Table 2 presents the experimental conditions and removal efficiency concerning the electrochemical soil treatment. Tests 1 and 2 are performed at constant applied voltage (20 V/20 cm) and hydraulic gradient (1 cm H_2O/cm soil). The durations of the experiments are 20 days, and 30 days, respectively. Figure 2 presents the residual

Table 2. Experimental conditions and removal efficiency.

	Test 1/2	Test 3	Test 4	Test 5	Test 6	Test 7	Test 8	Test 9	Test 10
Duration (days)	20/30	20	20	20	20	20	20	20	20
Anode reservoir	Water	Water	Buffer solution	Buffer solution	Water	Water	Water	Water	Buffer solution
Cathode reservoir	Water effluent	Buffer solution	Effluent	Buffer solution	Effluent	Effluent	Effluent	Effluent	Buffer solution
Pretreatment in soil	No	No	No	No	No	0.01 M acetic acid	Buffer solution	Buffer solution	Buffer solution
C.E.M.	No	No	No	No	Yes	No	No	Yes	No
Cd removal efficiency	42/50%	80%	83%	94%	94%	98%	98.5%	99%	98%
Pb removal efficiency	24/32%	54%	65%	79%	70%	49%	53%	77%	85%

Voltage gradient: 1 V/cm soil; hydraulic head: 1 cm H_2O/cm soil; buffered solution: 0.01 M CH_3COOH/0.01 M CH_3COONa (pH = 4.7).

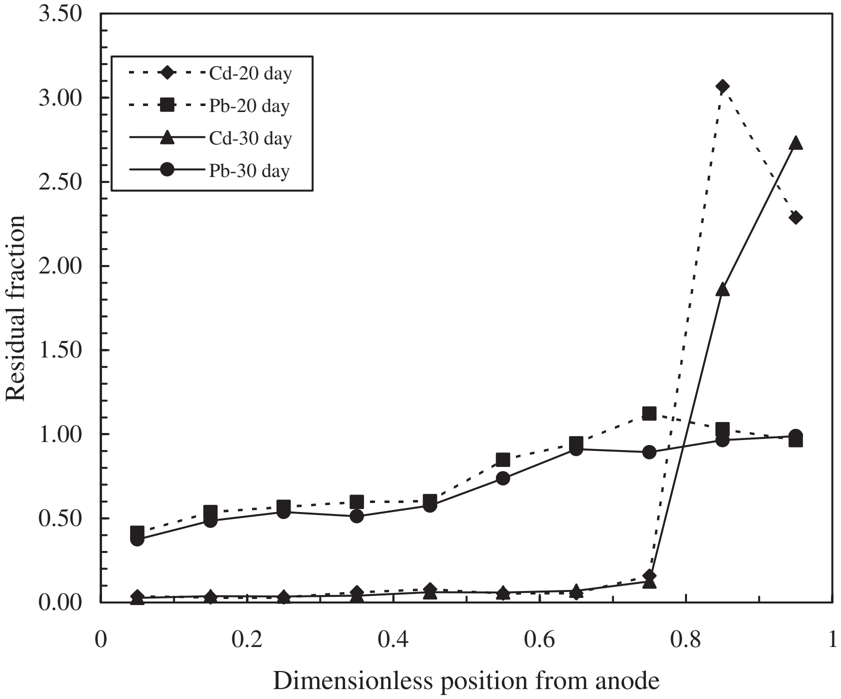


Figure 2. Residual fraction vs. position under constant voltage (20 V/20 cm).

distribution of Pb and Cd in the soil specimen after electrochemical treatment. The residual fraction of the Pb ion in the region near the anode remains approximately 40%. The distribution curves of Pb ions after 20-day and 30-day treatments are similar. The residual fraction near the cathode was even higher than the initial concentration. The average residual fractions of Pb in the soil specimens were 76% (20 days) and 68% (30 days). The concentration distribution of the Cd ions was similar to that of Pb ions. The removal efficiency of Cd was much higher than that of Pb. The residual concentration of Cd is small at the regions close to the anode, where the removal efficiency exceeded 99%, and higher near the cathode, reaching three times of the initial concentration. As shown in Fig. 2, the Pb and Cd ions began to accumulate at the dimensionless position of 0.75 from the anode. The Pb and Cd ions re-precipitate near the cathode because pH value increase, resulting from the backward transport of OH^- from the cathode. Figure 3 plots the pH distribution after the treatment, revealing higher pH values near the cathode. The pH of the whole section from the anode to the dimensionless position 0.75 is about 3.0, and the pH begins to increase to 9.0 at the dimensionless position of 0.95. Figures 2 and 3 show that the heavy metal ions begin to re-precipitate when the hydroxyl ion concentration is increased, and are more difficult to remove. The precipitates plug the pores, preventing the water from flowing smoothly, as clearly revealed later by both the plots of the water distribution in the soil specimen and the accumulated water volume (Figs. 4 and 7).

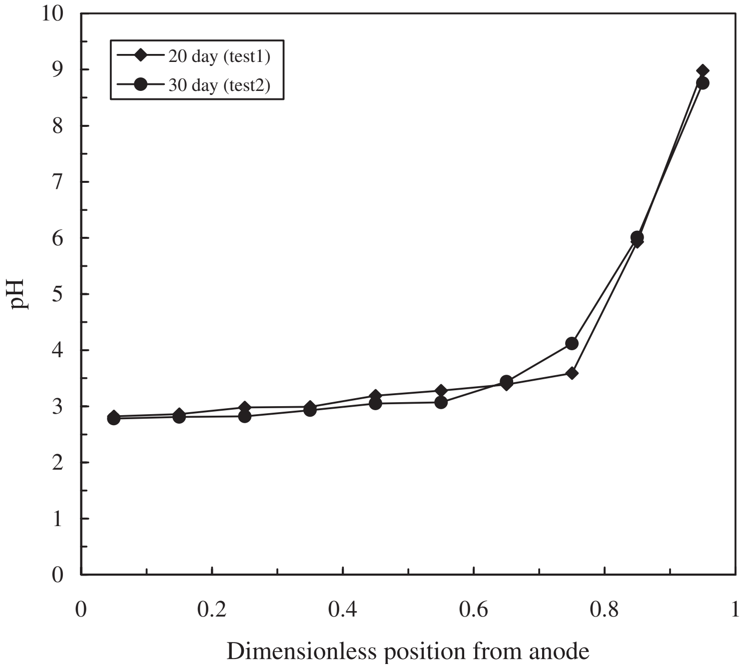


Figure 3. The pH distribution at applied voltage (20 V/20 cm).

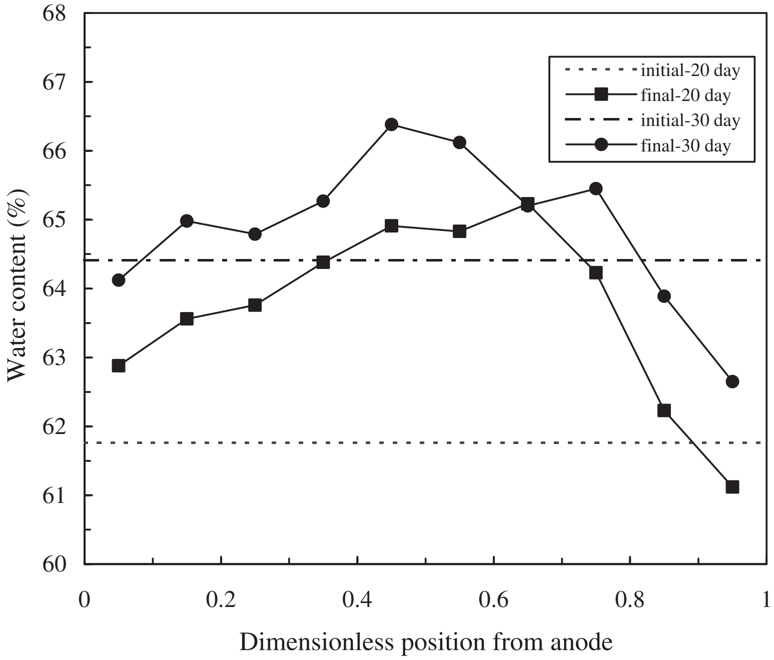


Figure 4. The distribution of water content at applied voltage (20 V/20 cm).

Table 3. The solubility product K_{sp} of hydroxides, carbonates, and sulfates of OH^-, CO_3^{-2}, SO_4^{-2}.

	OH^-	CO_3^{-2}	SO_4^{-2}
Ca^{+2}	1.3×10^{-6}	8.7×10^{-9}	6.1×10^{-5}
Pb^{+2}	1.2×10^{-15}	1.5×10^{-15}	1.3×10^{-8}
Cd^{+2}	5.9×10^{-15}	5.2×10^{-12}	Soluble

The removal of Cd ions is easier than that of Pb ions is primarily because the soil contains calcium carbonate. In the presence of carbonate ions, the concentration of mobilized Cd ions is much higher than that of mobilized Pb ions. Table 3 lists the relevant solubility products, K_{sp} for hydroxides, carbonates and sulfates.[21] The K_{sp} value of carbonate ions, and OH^- ions, are much lower than that of other anions, as shown in Table 3. Therefore, if the carbonate anions are present in the soil specimen, then the removal efficiency by the electrochemical treatment is reduced .If the soil has a trace of calcium carbonate, which is usually the case in soils and limestone, as well as sufficient water, then the concentration of carbonate can be estimated to be approximately 9.32×10^{-5} M according to the equilibrium calculation. At this concentration, the concentration of Pb^{+2} in water can only be of the order of 0.1 ppm, and the concentration of Cd^{+2} in the water will be about 6 ppm. This result explains why Cd^{+2} can be removed more efficiently than Pb^{+2}. As can be seen from Fig. 2, when most of the Cd ions have been removed, only a little of the Pb ions are removed. Controlling the pH of the soil specimen to avoid precipitation and increasing the concentration of mobilized Pb and Cd ions are important issues.

As shown in Fig. 4, the water content in the region near the cathode is lower than the rest part of the soil specimen. The rate of electroosmotic flow is high, since the pH near the cathode is high, and the electroosmotic flow near the anode is low because the pH at the anode is low. Precipitation occurs at the dimensionless position 0.75 and increasing the resistance to flow. Therefore, water accumulates from position 0.4 to 0.75.

Figure 5 shows the variation of current with time at applied voltage 20 V. The variation of the current over 30 days is similar to that over 20 days. The curve descends at first and then becomes flat. The beginning current in the 30-day periods (about 1.92 mA) is slightly higher than that in the 20-day periods (about 1.71 mA), because of the higher initial water content over 30 day periods, which allows the pore water to dissolve more ions. As the experiment begins, the ions in the pore solution migrate toward the electrodes due to the effect of electric field. The initial electric current is the highest because the ionic concentration is the highest. As the number of ions falls, the current descends gradually. If the reduction of the number of ions equals the number of ions dissolved out of the soil, then the current will maintain constant, as indicated by the conductivity of the effluent from the cathode, which can be seen in Fig. 6. Table 4 shows the result of metallic compositions at various locations in the soil. It can be seen in Table 4 that most of the metal ions in the cathode chamber are calcium ions. The analysis of the soil specimen at various

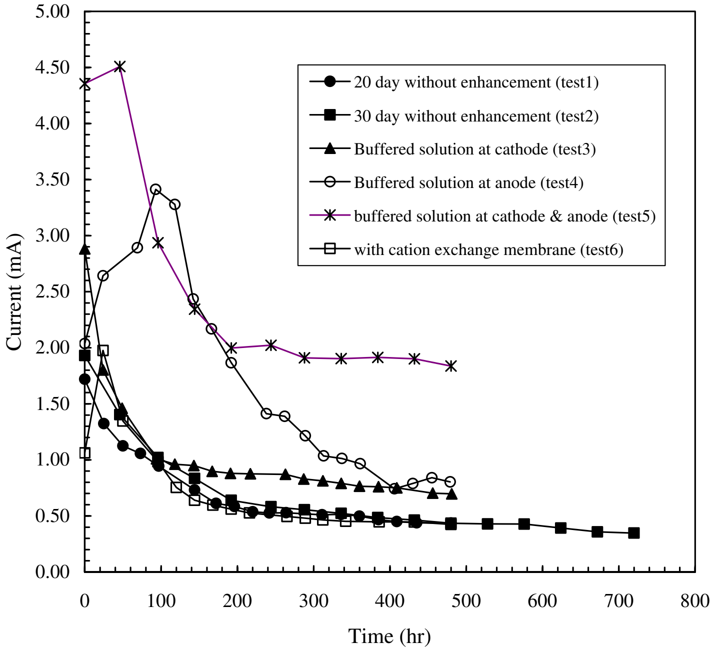


Figure 5. Current vs. time at constant voltage (20 V/20 cm). *(View this art in color at www.dekker.com.)*

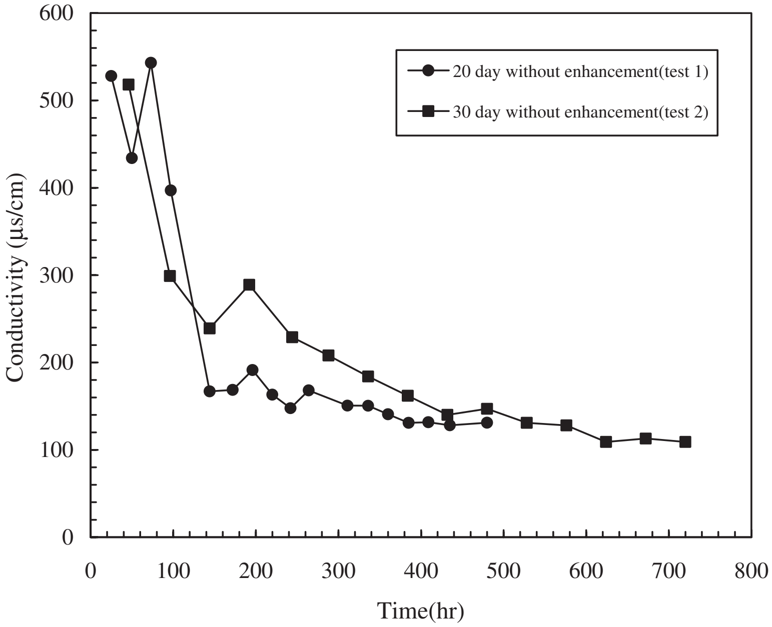


Figure 6. Conductivity of cathode effluent vs. time at applied voltage (20 V/20 cm).

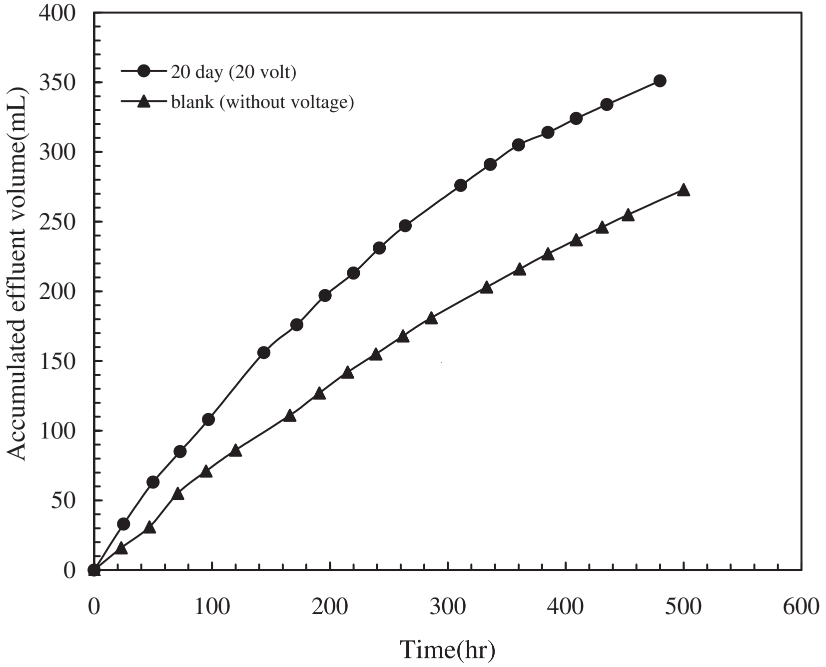


Figure 7. Accumulated effluent volume vs. time (hydraulic head: 20 cm H_2O).

Table 4. The cation analysis (ppm) of the original soil specimen and various points after 20 days' operation.

	Al (ppm)	Ca (ppm)	Fe (ppm)	Mg (ppm)	Pb (ppm)	Cd (ppm)
Original soil	1190	202	573	87.7	100	100
0.35 from anode	1360	23.2	589	64.1	59.7	6.04
0.85 from anode	1500	252	609	96.1	102.9	306
Cathode chamber	2.83	367	2.06	4.49	0.0115	0.0014

points reveals that calcium ions dissolve out and migrate toward the cathode. Calcium carbonate is an important factor in this study.

Figure 7 plots the accumulated volume of effluent versus time during 20 days' operation. The blank case involves the operation driven by only the hydraulic head, and the electroosmotic flow under the voltage gradient is added to the initial hydraulic flow. Figure 8 presents the electroosmotic coefficient k_e values with time, calculated from Eq. (4) with the data in Fig. 7. After a period, the flow rate decreases to a constant value. The pH of the pore solution strongly influences the electroosmotic flow rate. The plot of the pH distribution in Fig. 3 indicates that most of the soil is affected by the H^+ ions from the anode, and the pH is gradually reduced to about 3.0 at dimensionless position 0.7 from anode. So the zeta potential is

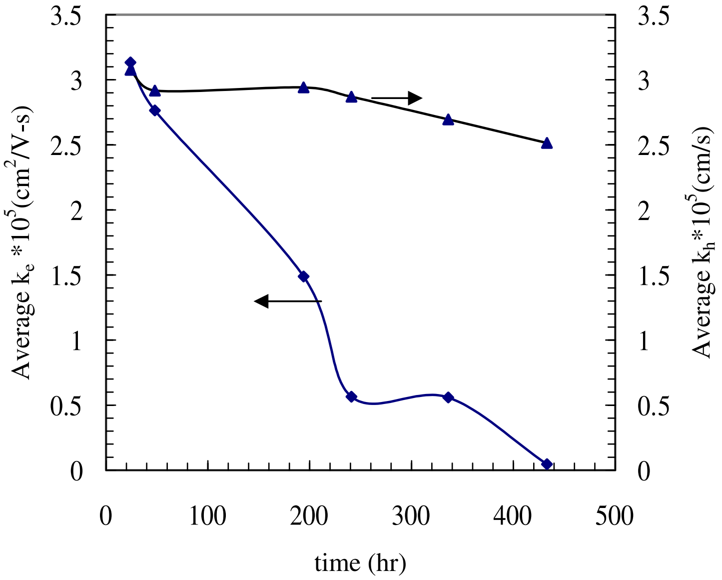


Figure 8. Average values of k_e and k_h vs. time (20 days). *(View this art in color at www.dekker.com.)*

decreased with time, and the average k_e value is smaller according to Eq. (3), explaining why the electroosmotic flow rate is getting smaller with time in this case.

The Effect of Buffered Solutions at Anode or Cathode

Because the metal removal in soil by an applied voltage only is not so effective, buffered solutions are employed at the cathode, the anode, or both, for tests 3–5, respectively, as shown in Table 2. The buffered solution is a mixed solution of 0.01 M acetic acid and 0.01 M sodium acetate. Diluted acetic acid solution is harmless to animals and plants, and most of the metal ions will not precipitate with acetate ions. Acetic acid is therefore suitable for adjusting the pH of the soil specimens.

During the remediation, OH^- ions are produced at the cathode. They move toward the anode, and the pH of the soil specimen increases near the cathode. A high pH will cause the heavy metal ions to precipitate and become immobilized. The removal efficiency is thus reduced. Buffered solution was applied to the cathode chamber to neutralize the OH^- ions and control the pH. The pH of the whole cell might be regulated by adding the buffered solution to the anode chamber. The effects of applying buffered solution at the cathode, the anode, and both electrodes have been investigated. First, the variation of the pH value was shown in Fig. 9. For the cases with buffered solution the pH values in soils after 20 days' treatment were all less than 6, and the soil tended to be acidic. When buffered solution was applied to both electrodes, the pH of the soil can be regulated between 2 and 5. Within this

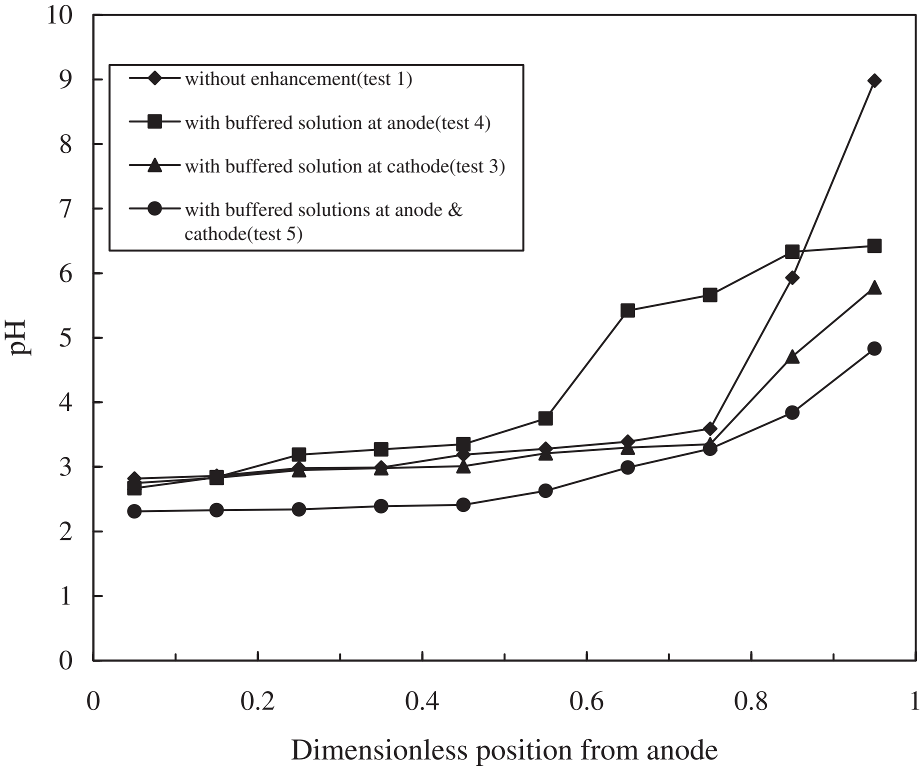


Figure 9. The pH Distribution for treatment with Buffered Solution (20 V/20 cm, 20 days).

pH range, no precipitates formed, and the removal of heavy metal ions would be enhanced significantly.

Figure 10 shows the Pb and Cd residual fraction distributions with and without buffered solution of 0.01 M acetic acid + 0.01 M sodium acetate at cathode. It has been found that the metal removal is enhanced by the addition of the buffered solution at cathode chamber. The presence of the buffered solution can prevent the accumulation of OH^- ion, which can form precipitated metal hydroxides.

The Pb and Cd residual distributions for the two cases of buffered solutions at anode and both electrodes, respectively, are shown in Fig. 11. Of course the removal efficiency is also enhanced, as can be seen in Table 2. The removal efficiency of buffered solutions at both anode and cathode can reach 94% for Cd and 79% for Pb, which is better than the other two cases of buffered solution at either electrode only.

The Effect of Cation Exchange Membrane

Besides the buffered solution for enhanced removal, the insertion of cation exchange membrane between the soil and the cathode chamber can also prevent the back diffusion of hydroxyl ions into the soil specimen. Thus no precipitates are

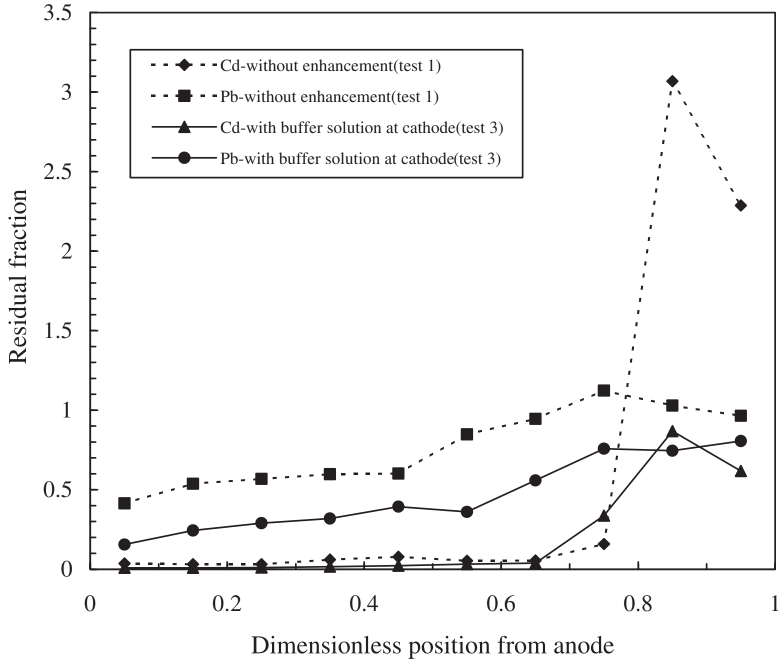


Figure 10. Residual fraction vs. position for applying buffered solution at cathode.

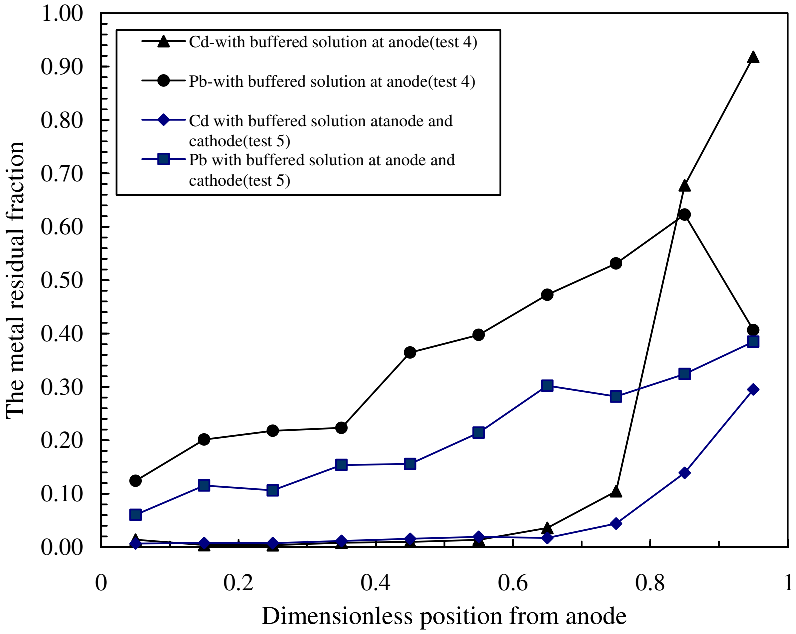


Figure 11. The metal residual distribution with buffer solution at anode (20 V/20 cm, 20 days). *(View this art in color at www.dekker.com.)*

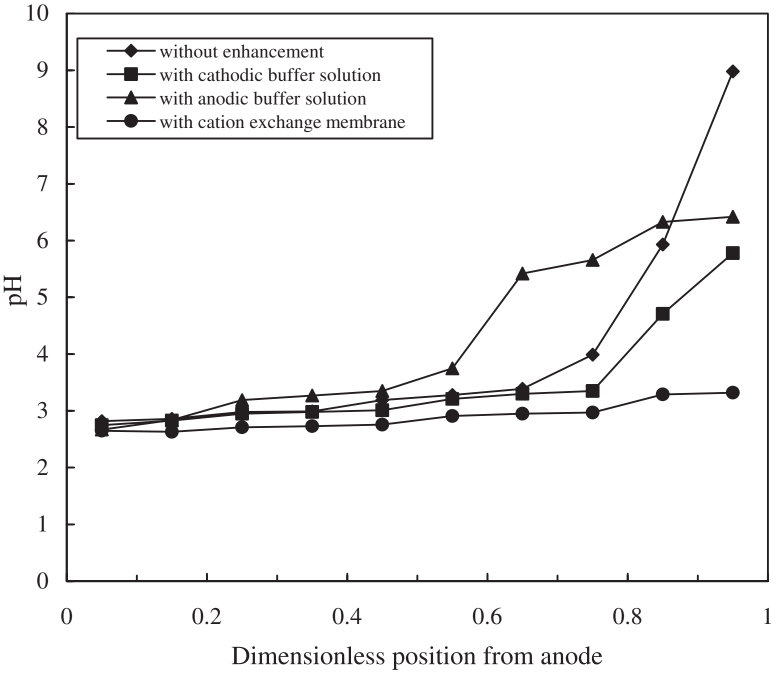


Figure 12. The pH distribution vs. position for various cases (including C.E.M.).

produced near cathode. A membrane of Nafion 117 (Dupont Company) was used. Figure 12 plots the pH distribution of the soil sample after the treatment. The pH across the whole section is below 3 and almost uniform when C.E.M was used. The OH^- ions are kept off of the soil specimen, so the H^+ ions migrate into the soil specimen without becoming neutralized. Therefore, the soil specimen is acidified gradually, and the heavy metal ions are mobilized easily. Figure 13 plots the residual distributions of Cd and Pb after the experiment was completed. The removal effect obtained by applying C.E.M. is much better than that obtained only by an applied voltage. In the region near the anode, Pb concentration is less than 12% and the Cd concentration is less than 0.5%. In the region near the cathode, Pb concentration is less than 54%, and the Cd concentration is about 41%. These values are much better than that obtained without a membrane. The overall efficiencies of enhanced removal with the cation exchange membrane are 94% for Cd and 70% for Pb, which is a little smaller than that with buffered solution at cathode and anode (test 5), as shown in Table 2.

The Addition of Pretreatment with 0.01 M Acetic Acid or Buffered Solution

In tests 7, 8, and 9 of Table 2, the soil specimens were pretreated with 0.01 M acetic acid or buffered solution. The anode chamber was supplied with pure water. A cation exchange membrane (C.E.M) was used in test 9. Figure 14 shows the pH

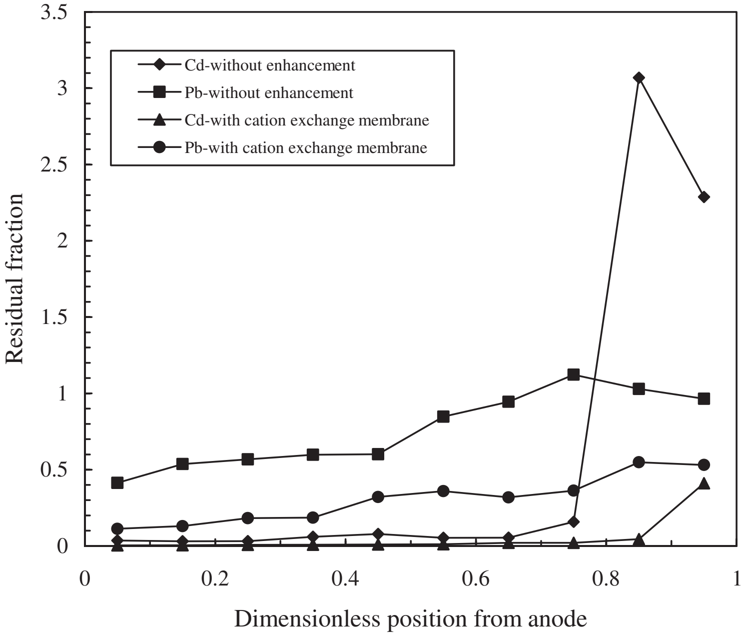


Figure 13. Residual fraction vs. position with C.E.M. (test 6).

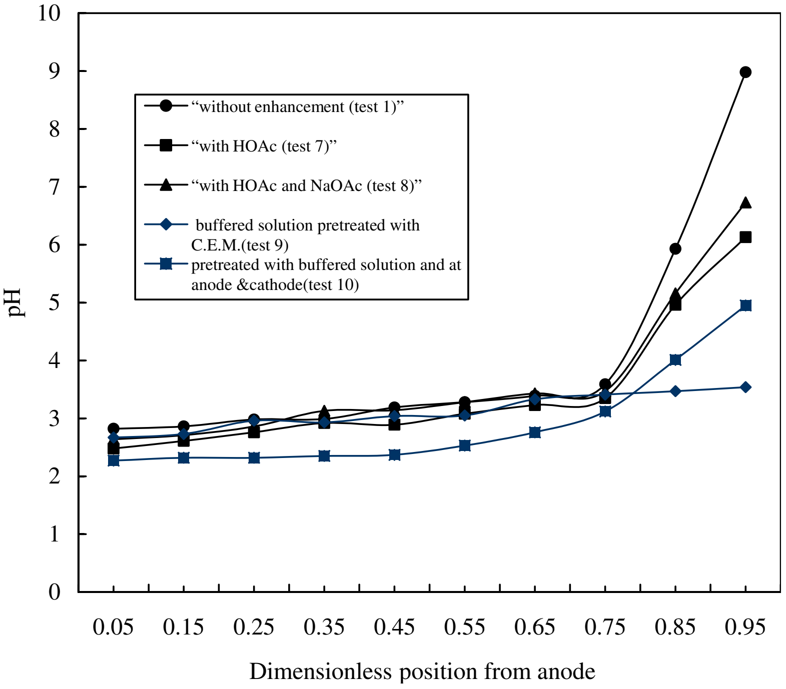


Figure 14. The pH distribution with the soil pretreatment of acetic acid and buffered solution (20 V/20 cm, 20 days). *(View this art in color at www.dekker.com.)*

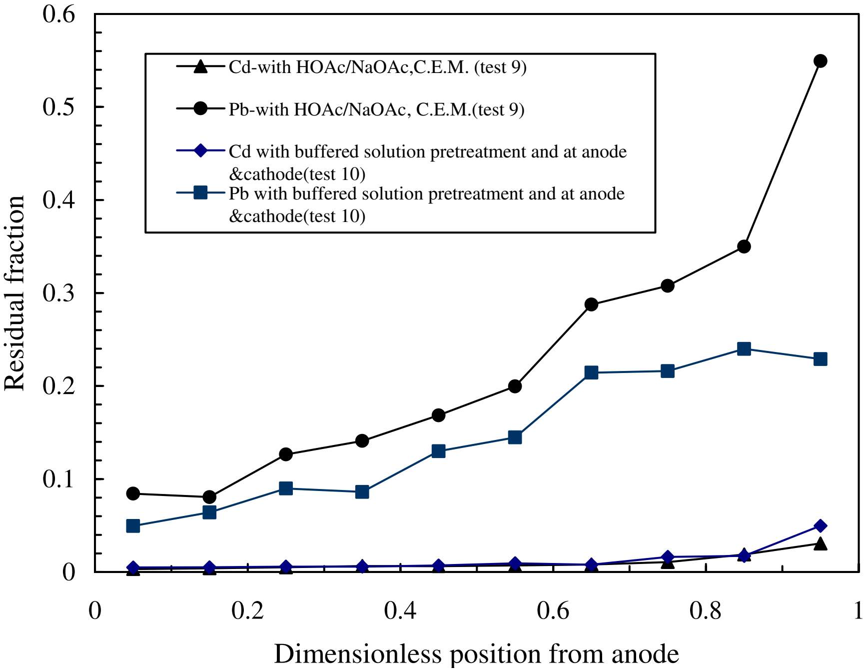


Figure 15. Metal residual distribution of Test 9 and 10. *(View this art in color at www.dekker.com.)*

distributions. After 20 days' treatment, the pH values were kept at nearly 3, from the anode to the dimensionless position 0.8. The pH increased to 6 from the dimensionless position 0.8 to the end. At the values of pH from 3 to 6, the heavy metal ions are mobilized easily. The removal efficiencies remain good with the pretreatment, especially combined with the C.E.M. They are 98, 98.5 and 99% for Cd, and 49, 53, and 77% for Pb, as shown in Table 2, in which the case of C.E.M. with pretreatment produces a better removal efficiency. In test 10 of Table 2, the soil was pretreated with buffer solution, and both chambers were supplied with buffer solution. Its residual distributions for Pb and Cd were pretty low, as shown in Fig. 15 and the removal efficiency was most satisfactory, 98% for Cd and 85% for Pb.

CONCLUSIONS

As the pH of the soil specimen is between 2 and 4, desorption of heavy metal ions in the soil is promoted and these ions are mobilized from precipitates. The pH must be maintained between 2 and 4, and never exceed 6. Various enhancing methods including buffered solution, cation exchange membrane, and pretreatment have been investigated in this study. Buffer solution, applied to the anode, the cathode or both electrodes can effectively consume the OH^- ions from the cathode. The removal efficiency in the cathode area and that through the soil specimen is much higher than that obtained only by applying a voltage. Applying cation exchange membrane at the cathode chamber can increase the removal effect. Pretreating the soil specimens with a weak acid or buffer solution can regulate the soil specimen under appropriate acidic conditions. The precipitation of the heavy metal ions near the cathode is apparently eliminated, and the removal effect through the soil specimen is much better than that obtained without pretreatment. In particular, the removal effect of Cd reaches 99% under these conditions. According to the removal efficiency of Pb and Cd, the enhancing methods of tests 5, 6, 9, and 10 are found to achieve better results.

REFERENCES

1. Dowdy, R.H.; Latterell, I.J.; Hinesly, T.D.; Grossman, R.B.; Sullivan, D.L. Trace metal movement in a aeric ochraqualf following 14 years of annual sludge applications. J. Environ. Qual. **1991**, *20*, 119–123.
2. Elliott, H.A.; Denneny, C.M. Soil adsorption of cadmium from solutions containing organic ligands. J. Environ. Qual. **1982**, *11*, 658–662.
3. Huang, C.P.; Ostoric, F.B. The removal of cadmium(ii) from dilute aqueous solution by activated carbon adsorption. J. Environ. Eng. Div., ASCE **1978**, *104*.
4. Iskandar, I.K.; Adriano, D.C. *Remediation of Soils Contaminated with Metals*; Science Review: Northwood, 1997.
5. Sheppard, M.J.; Thibault, D.H.; Mitchell, J.H. Element leaching and capillary rise in sandy soil cores: experimental results. J. Environ. Qual. **1991**, *16*, 273–284.
6. William, C.A. *Innovative Site Remediation Technology*; Annapolis: New York, 1993.
7. Ronald, F.P.; Hicks, R.E. Removal of contaminants from soils by electric fields. SCIENCE **1993**, *260*, 498–503.
8. Wu, Y.F.; Chou, W.L.; Yen, S.C. Removal of mercury and organomercury from contaminated soils by applying an electric field. J. Environmental Science and Health **2000**, *A35* (7), 1153–1170.
9. Lageman, R. Applications in the Netherlands. Environ. Sci. Technol. **1993**, *27* (13), 2648–2650.
10. Acar, Y.B.; Haider, L. Transport of low-concentration contaminants in saturated earthen barriers. Journal of Geotechnical Engineering **1990**, *116* (7), 1031–1052.
11. Acar, Y.B.; Gale, R.J.; Hamed, J.T.; Putnam, G. Acid/base distribution in electrokinetic soils processing. Transport Research Record **1991**, *1288*, 23–34.
12. Hamed, B.J.; Acar, Y.B.; Yalcin, B.; Gale, R.J. Pb(II) Removal from kaolinite by electrokinetics. Journal of Geotechnical Engineering **1991**, *117* (2), 241–271.
13. Yen, S.C.; Lu, I.M.; Chapman, T.W. *Electrokinetic Treatment of Contaminated Soils: Removal of Lead from Porous Kaolinite*, Emerging Separation Technologies for Metals 11 Conference, Hawaii, USA, June 16–21, 1996.
14. Acar, Y.B.; Alshawabkeh, A.N. Principles of electrokinetic remediation. Environmental Science and Technology **1993**, *27* (13), 2638–2647.

15. Hicks, R.E.; Tondorf, S. Electrorestoration of metal contaminated soils. Environ. Sci. Technol. **1994**, *28*, 2203–2210.
16. Mitchell, J.K. *Fundamentals of Soil Behavior*; John Wiley & Sons: New York, 1976.
17. Vane, L.M.; Zang, G.M. Effect of aqueous phase properties on clay particle zeta remediation processes. Journal of Hazardous Materials **1997**, *55* (1–3), 1–22.
18. Bohn, H.L.; McNeal, B.L.; O'Connor, G.A. The solid phase. *Soil Chemistry*, 2nd Ed.; A Wiley-Interscience Publication: New York, 1985; Chapter 4, 104–134.
19. Dean, J.A.; Lange, N.A. Table 5–7 Proton-transfer reactions of inorganic materials in water at 25°C. *Lange's Handbook of Chemistry*, 12th Ed.; McGraw-Hill Book Company: New York, 1979; 5–15.
20. Schock, M.R. Response of lead solubility to dissolved carbonate in drinking water. JAWWA **1980**, *72*, 695–704.
21. Zumdahl, S.S. Appendix 4 the K_{sp} values of ionic compounds. *Chemistry*, 3rd Ed.; D. C. Heath and Company: Lexington, Mass, 1993.

Received September 23, 2003

Downloaded By: [National Taiwan University] At: 07:08 28 November 2008

Request Permission or Order Reprints Instantly!

Interested in copying and sharing this article? In most cases, U.S. Copyright Law requires that you get permission from the article's rightsholder before using copyrighted content.

All information and materials found in this article, including but not limited to text, trademarks, patents, logos, graphics and images (the "Materials"), are the copyrighted works and other forms of intellectual property of Marcel Dekker, Inc., or its licensors. All rights not expressly granted are reserved.

Get permission to lawfully reproduce and distribute the Materials or order reprints quickly and painlessly. Simply click on the "Request Permission/ Order Reprints" link below and follow the instructions. Visit the U.S. Copyright Office for information on Fair Use limitations of U.S. copyright law. Please refer to The Association of American Publishers' (AAP) website for guidelines on Fair Use in the Classroom.

The Materials are for your personal use only and cannot be reformatted, reposted, resold or distributed by electronic means or otherwise without permission from Marcel Dekker, Inc. Marcel Dekker, Inc. grants you the limited right to display the Materials only on your personal computer or personal wireless device, and to copy and download single copies of such Materials provided that any copyright, trademark or other notice appearing on such Materials is also retained by, displayed, copied or downloaded as part of the Materials and is not removed or obscured, and provided you do not edit, modify, alter or enhance the Materials. Please refer to our Website User Agreement for more details.

Request Permission/Order Reprints

Reprints of this article can also be ordered at

http://www.dekker.com/servlet/product/DOI/101081ESE120030327