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# Use of Auxiliary Electrode to Prevent Alkalinization of Soil in Electrokinetic Remediation

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We devised an improved electrokinetic remediation method in which an auxiliary electrode was placed at the cathode–side end of the soil to be treated. The electric potential difference between the anode and the auxiliary electrode was fixed constant while that between the cathode and the auxiliary electrode was controlled to make the auxiliary electrode function as a secondary anode. To test the performance of the method, we carried out a bench scale remediation experiment on cadmium–contaminated soil, in which the electrodes and soil etc. were arranged in the following order; anode|anolyte|soil–auxiliary electrode|electrolytic diaphragm|H–saturated cation exchange resin|catholyte|cathode. During 112 h of the treatment, the net voltage applied to the soil could be maintained and the alkalinization of the soil could be prevented partly due to the acid–neutralization in the cation exchange resin, and partly due to the secondary anode. These results indicated the auxiliary anode was effective to improve the efficiency of electrokinetic remediation of heavy metals contaminated soils.

## INTRODUCTION

Pollution of soils with various harmful substances poses insidious effects on human health through direct ingestion of contaminated soils and crops and vegetables grown therein. Ground and surface waters are also polluted if contaminants in soils are transported by infiltrating and surface–running waters, which is also a threat to ecosystem health. Needless to say, the best way to remove the threat is to decontaminate the soils. Decomposing and detoxifying methods have been devised and successfully applied to some organic contaminants (Cantrel and Kaplan, 1997) including chlorinated aromatic compounds (Sayles *et al.*, 1997). However, these methods are not effective for heavy metals primarily because heavy metals would not decompose and some other methods to extract them from soils are needed for complete rehabilitation of heavy metals contaminated soils.

The electrokinetic remediation technology is one of a few methods for extracting heavy metals from soils and has been subjected to extensive experimental and theoretical studies. In the method, paired electrodes are inserted into a contaminated soil and a direct electric current is applied to create an electric potential gradient between the electrodes. Cations and anions are transported via electromigration to cathode and anode,

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respectively. Although the principle is simple, some problems have to be solved before practical implementation of the technology, one of which is the alkalinization of the soil at the cathode (Acar and Alshawabkeh, 1993).

As a direct electric current is applied to the electrode, hydroxyl ions are produced by the electrolysis of water at the cathode and they migrate toward anode. The soil neighboring the cathode becomes strongly alkaline and heavy metal cations that migrate toward cathode precipitate when they meet the alkalinized zone. To avoid the hydrolytic precipitation of heavy metal cations, some researchers applied acids to catholyte to maintain it acidic (Reed *et al.*, 1995) and others separated the catholyte and the soil with ion–selective membrane to prevent permeation of hydroxyl ions into the soil (Li *et al.*, 1998). The both methods successfully work in the bench scale experiments, but the latter solution method is difficult to employ in the field–scale remediation site because of insufficient mechanical strength of the membrane. The injection of acid into catholyte is a relatively easy and promising way but additional equipment is needed to inject acid, maintaining pH and circulate the catholyte.

An another problem encountered in the electrokinetic remediation is that the applied electric potential difference tends to fall within a small portion between the anode and cathode (Wada and Umegaki, 2001). In other portion of the soil, the electric potential gradient almost vanishes and, in turn, the electromigration diminishes.

In the present study an alternative method is devised and tested to avoid the alkalinization and localization of the electric potential gradient. In the proposed method an auxiliary electrode is inserted at the cathode–side end of the soil and an electric potential difference between the anode and the additional electrode is fixed, while the electric potential between the cathode and the third electrode is controlled so that cathodic reaction does not occur at the auxiliary electrode.

## THEORY

Fig. 1–a shows the equivalent electric circuit of the electrode configuration in the conventional electrokinetic soil remediation, where $R$a, $R$s, $R$c stand for the resistivities of anolyte, soil and catholyte, respectively. In this configuration, following electrolytic reactions take place at the electrodes. They are

$$2H_2O = 4H^+ + O_2 + 4e^- \tag{1}$$

at the anode and

$$4H_2O + 4e^- = 4OH^- + 2H_2 \tag{2}$$

at the cathode. The hydroxyl ions generated at the cathode migrate toward anode and the soil is alkalinized from the cathodic end.

Fig. 1–b the equivalent electric circuit for the electrode configuration proposed in the present study. The auxiliary electrode is placed at the cathode–side end of the soil and two independent power suppliers are connected as described in the diagram. The electric current in the auxiliary electrode, $i_2$, is given by

$$i_2 = \frac{E_2}{R\mathrm{c}} - \frac{E_1}{R\mathrm{a} + R\mathrm{s}} \tag{3}$$

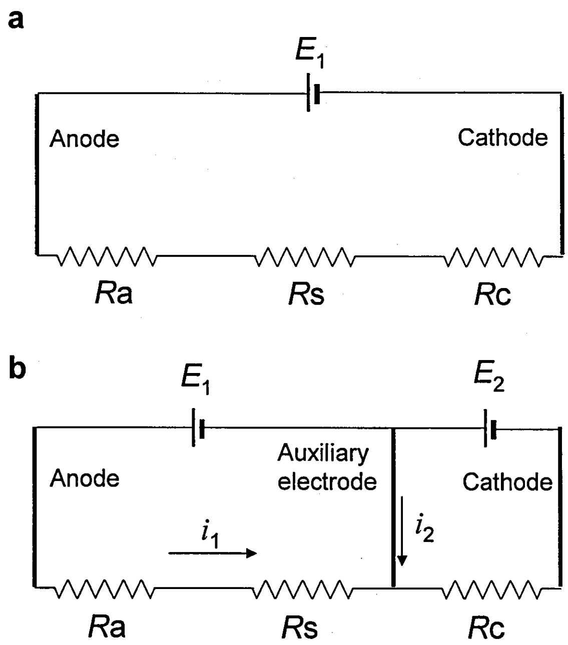

**Fig. 1.** The circuit diagrams for (a) conventional and (b) proposed apparatuses. $E_1$ and $E_2$ represent the main and secondary power sources, respectively. *R*a, *R*s and *R*c stand for the resistances which occur at the part of anolyte, soil and catholyte, respectively.

If $i_2>0$, the auxiliary electrode works as secondary anode and hydroxyl ions do not generate at this electrode. For a given $E_1$, $i_2$ can be kept positive by controlling the voltage generated by the second power supplier.

## MATERIALS AND METHODS

To test the effect of the auxiliary electrode, experimental device depicted in Fig. 2 was constructed. The devise is composed of four compartment including anode and cathode chambers at the both ends. The soil sample was packed in the largest compartment having a length of 12 cm and cation exchange resin was packed in the small cell between the soil and cathode chamber to trap heavy metal cations migrated from soil. The soil and the cation exchanger was separated by electrolytic diaphragm. Graphite plates were used for cathode and anode and a thin platinum foil was used as the auxiliary electrode. Three passive electrodes were placed in the soil and another passive electrode was inserted in the resin to monitor the electric potential distribution. Two independently controlled power supplies were connected between the anode and auxiliary electrode and between cathode and auxiliary electrode. Three ammeters were connected to monitor the electric current.

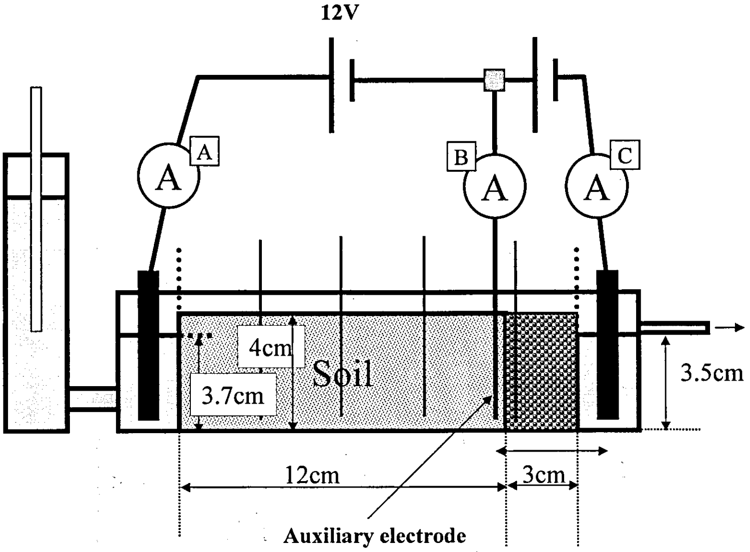

**Fig. 2.** Schematic diagram of the experimental device to test the effectivity of the auxiliary electrode. The size of soil compartment was 12 cm × 4 cm × 5 cm. The depth of anolyte was 3.7 cm. Catholyte was drained using the pump in order to maintain the depth of catholyte at 3.5 cm.

A soil contaminated with cadmium (Cd) was used in the present study. The total Cd content of the soil was 6.80 mg $kg^{-1}$ and soil pH was 5.58. The collected soil sample was air–dried and passed through a 2–mm screen.

After setting up the apparatus, the central chamber was packed with 248 g of the soil sample and saturated with 10 mmol $L^{-1}$ NaCl solution that was supplied from constant head device connected to the anode chamber. The voltage applied between the anode and auxiliary electrode was fixed at 12 V, namely the average potential gradient was 1 V $cm^{-1}$. The output of the second power supply was controlled manually so that $i_2$ is kept positive and around 1 mA.

After the treatment, the soil samples was sliced in to four sections of equal length and the subsamples were analyzed for the total Cd (Asami and Kato, 1977) content and soil pH.

## RESULTS AND DISCUSSION

Figs. 3 and 4 show the readings of the ammeters and the voltage applied between the cathode and auxiliary electrode, respectively. Fig. 3 shows that the electric current at A was always a sum of those at A and B. Since the second power generator was controlled manually, the change in its output was not smooth but stepwise. Accordingly, the change in the electric current at the ammeters A, B and C were also stepwise. The electric current in the auxiliary electrode (ammeter B) was kept nearly at 1 mA during the period from 0 to about 70 h. The comparison of Figs. 3 and 4 shows that the voltage loaded

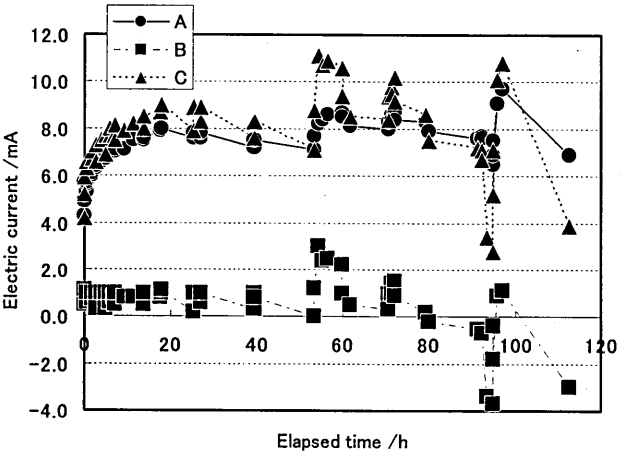

**Fig. 3.** Time courses of the electric currents on ammeters indicated in Fig. 2.

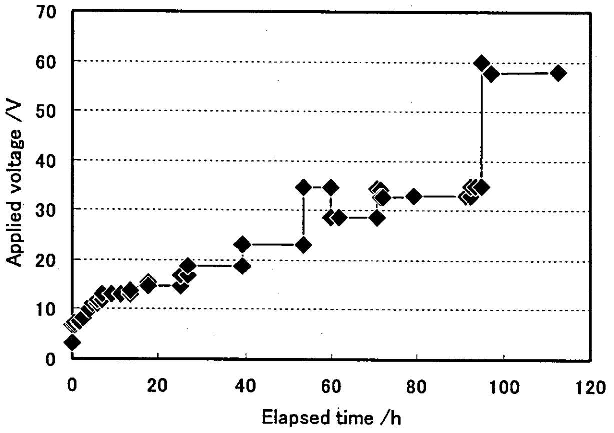

**Fig. 4.** The voltage output from the secondery power supply.

between the cathode and auxiliary electrode had to be increased from $<10$ V to about 30 V to maintain the electric current in the auxiliary electrode constant at around 1 mA. At and after 90 h, much more voltage was needed to maintain the electric current in the auxiliary electrode and the output was raised up to 60 V, which was a maximum output of the power supplier used in the present experiment.

To analyze the cause of the unsuccessful control of the electric current in the auxiliary electrode, the resistivities of anolyte plus soil ($R\text{a}+R\text{s}$) and catholyte plus resin ($R\text{c}$) were calculated from the measured electric current at A and C and the electric potential differences between the anode and auxiliary electrode ($E_1$) and between the cathode and auxiliary electrode ($E_2$) and plotted against elapsed time in Fig. 5. The initial resistivity of the soil plus anolyte was about 2600 Ω and it gradually decreased to about 1500 Ω after 40 h and on. On the contrary, the resistivity of the catholyte plus resin increased from 500 Ω to 4000 Ω in 90 h and grew suddenly at 93 h. With these values in the resistivity, the second term in Eq. (3) takes the values in a range from $4.3\times10^{-3}$A to $8\times10^{-3}$A. Therefore, if the resistivity of the anolyte plus resin was constant at 500 Ω, i. e., the initial value of $Rc$, throughout the experiment, the necessary magnitude of $E_2$ to maintain $i_2$ at 1 mA is calculated to be 2.65 V to 4.5 V. Actually, however, $Rc$ grew rapidly to 4000 Ω or more with time as described above and much higher voltage had to be loaded between the cathode and auxiliary electrode. Since the catholyte became strongly alkaline in the present experiment, desaltation in the cation exchange resin layer and/or electrolytic diaphragm would have been the major cause of the rapid increase in $Rc$. The addition of some salt solution instead of water would be effective to keep the resin layer more conductive.

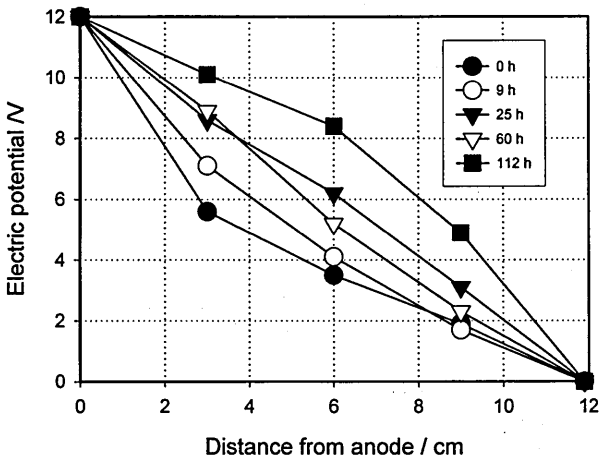

**Fig. 5.** The variation of the electric potintial profiles during the electrokinetic remediation.

Fig. 6 shows the electric potential distribution across the soil after 0, 9, 25, 60 and 112 h, where the potential at the anode was arbitrary set to 12 V. Fig. 7 shows the total Cd and pH distribution after 112 h. The initial electric potential gradient was not uniform but the gradient in the segment neighboring the anode was largest. After the application of the voltage, the potential distribution curve gradually straightened and finally became convex, suggesting that the electric potential gradient in the segments near the anode decreased relative to that in the segment facing the auxiliary electrode. This is indubitably due to the acidification of the segment near the cathode as evidenced by the pH distribution shown in Fig. 7.

Fig. 7 shows that after 112 h the soil pH at the segment neighboring the cathode was as low as 2 whereas that at the opposite end was near neutral. In many electrokinetic remediation experiments, the electric potential gradient diminished in extremely acidic region and it maximized at the zone of neutral reaction (Wada and Umegaki, 2001). In the present experiment, the electric potential gradient was fairly uniform irrespective of the extremely acidic reaction in one end and neutral reaction in the other end of the soil. Fig. 7 also shows that Cd was almost depleted in the soil segment neighboring the cath-

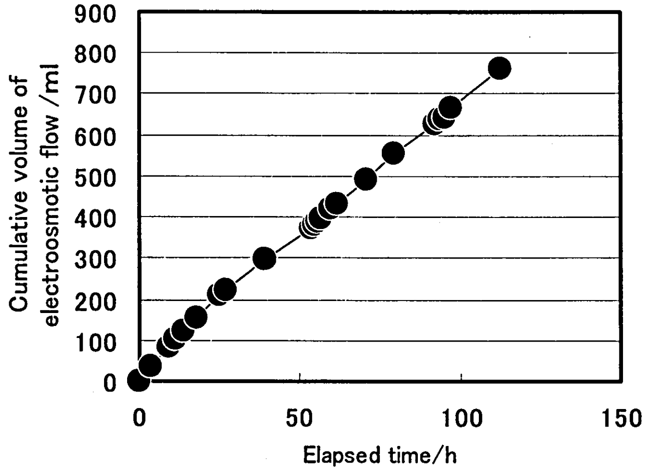

**Fig. 6.** The cummulative volume of electroosmotic flow drained from the catholyte.

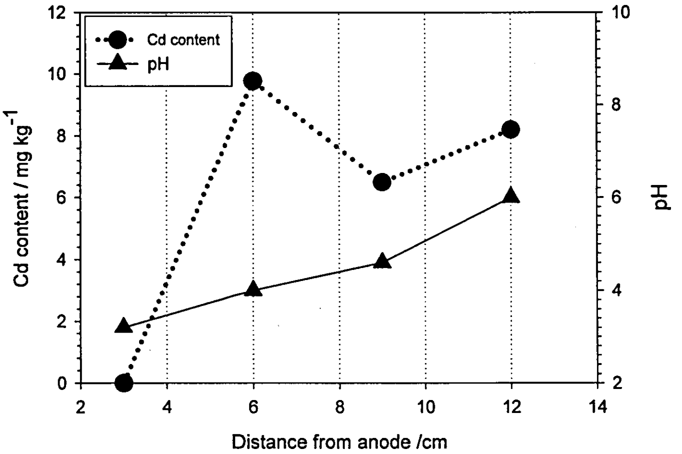

**Fig. 7.** Soil pH and total Cd content of the soil segment after the experiment. The soil pH was measured as to 1:5 water extraction, and the concentration of retained Cd was analyzed with hot hydrochloric acid method. The initial content of Cd was 6.8 mg kg$^{-1}$.

ode and accumulated in the next segment, while the Cd content was not significantly changed in the third and fourth segments. The 1:5 water extractions of the soil samples recovered from the cell revealed that 1.1 mg kg$^{-1}$ of water soluble Cd was present in the second segment whose pH was 4.0. This indicates that Cd can be successfully removed from the soil after prolonged treatment.

As seen from Fig. 7, the movement of Cd and soil acidification was synchronized. This is because the surface complexed Cd is released into soil solution as the soil is acidified and transported via electromigration (Darmawan and Wada, 2002; Mori and Wada, 2002). To accelerate this process, supply of dilute acid instead of 10 mmol L$^{-1}$ NaCl (Fig. 2) would have been effective. In addition, the electric conductance of the cation exchange resin layer should have been increased by addition of some electrolyte.

In the present experiment with an auxiliary anode, the net voltage applied to the soil could be maintained throughout the experiment. In addition, the alkalinization of the soil could be prevented partly due to the acid-neutralization in the cation exchange resin, and partly due to the second anode. These results indicate the auxiliary anode is effective to improve the efficiency of electrokinetic remediation of heavy metals contaminated soils. However, the desaltation of the cation exchange resin layer caused the increase in its electric resistivity and the voltage to keep the auxiliary electrode anodic increased with time and, finally, exceeded the capacity of the power supplier used. For the successful application of the electrode configuration proposed in the present study, the causes of the resistivity increase have to be elucidated.

As discussed above, one of the factors that prevent the electrokinetic remediation procedure is the desaltation of the cation exchange resin layer. Another possible cause would be associated with the electrolytic diaphragm. It is unlikely that the micropores of the diaphragm were clogged up physically because no noticeable decline of electroosmotic flow was noticed (Fig. 8). But deposition of carbonate or hydroxide of metals that were

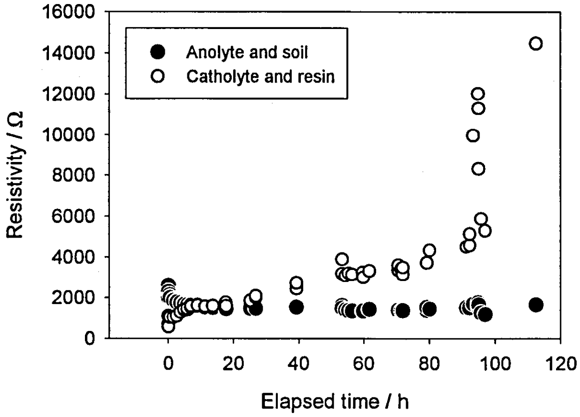

**Fig. 8.** The time courses of the resistivities of the anolyte-soil and catholyte-resin-electrolytic diaphragm. The resistivities were calculated from the readings of the ammeters and the voltages applied to the electrodes.

migrated from the soil on the wall of its micropores can not be excluded. The approximately constant electroosmotic flow rate (Fig. 8), may have resulted from the compensation of the increased resistivity with the increased voltage load.

## REFERENCES

Acar, Y. B. and A. N. Alshgawabkeh 1993 Principles of electrokinetic remediation. *Environ. Sci. Technol.*, **27**: 2638–2647

Asami, T. and K. Kato 1977 Comparison of analytical methods for total cadmium, zinc, lead and copper in soils. *Jpn. J. Soil Sci. Plant Nutr.*, **48**: 335–336

Cantrell, K. J. and D. I. Kaplan 1997 Zero–valent iron colloid empleacement in sand columns. *J. Environ. Eng.*, **123**: 497–505

Darmawan and S. –I. Wada 2002 Effect of clay mineralogy on the feasibility of electrokinetic soil decontamination technology. *Appl. Clay Sci.*, **20**: 283–293

Li, Z., J. –W. Yu and Y. Neretniels 1998 Electroremediation: Removal of heavy metals from soils by using cation selective membrane. *Environ. Sci. Technol.*, **32**: 394–397

Mori, Y. and S. –I. Wada 2002 Acid–extractability of cadmium from Cd–contaminated smectitic paddy soil. *J. Clay Scil. Soc. Jpn.*, **41**: 196–201

Reed, B. E., B. T. Berg, J. C. Thompson and J. H. Hartfield 1995 Chemical conditioning of electrode reservoirs during electrokinetic soil flushing of Pb–contaminated silt loam. *J. Environ. Eng.*, **121**: 805–815

Sayles, G. D., G. You, M. Wang and M. J. Kupferle 1997 DDT, DDD, and DDE dechlorination by zero–valent iron. *Environ. Sci. Technol.*, **31**: 3448–3454

Wada, S. –I. and U. Umegaki 2001 Major ion and electrical potential distribution in soil under electrokinetic remediation. *Environ. Sci. Technol.*, **35**: 2151–2155