

Ferritization treatment of copper in soil by electrokinetic remediation

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Available online 9 January 2007

Abstract

The usefulness of the combined use of the electrokinetic (EK) remediation and a ferrite treatment zone (FTZ) was demonstrated for a treatment of the contaminated soil with heavy metal ions. Copper ions in contaminated soil were transferred into the FTZ by the EK technology and were ferritized in this system. The distribution of copper in a migration chamber after EK treatment with FTZ for 48 h showed the large difference in the total and eluted concentration of copper. This indicated that copper ions transferred by EK into the FTZ were ferritized there with ferrite reagent in soil alkalinized by EK process. The copper–ferrite compound, which was not dissolved with diluted acid, was retained in the FTZ and accumulated there. The ratio of the ferritized amount of copper against total copper was 92% in the EK process with FTZ after 48 h.

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Keywords: Electrokinetic remediation; Copper; Ferrite; Insolubilization; Soil

1. Introduction

In our environment, there are many land sites contaminated with a variety of pollutants. If the contaminated soils are left without any adequate treatment, it leads to the subsequent contaminations of ecosystem and foods through river and ground water as well as lands. Therefore, the development of the technologies for cleaning up the contaminated soil is important from the viewpoint of the environmental protection. A variety of treatment techniques for the soil contaminated with metals or organic pollutants have been designed, using bioremediation [1–5], phytoremediation [6–10], physical and chemical remediation [11–13] and so on. These treatment methods for hazardous materials in soil can be categorized into the *in situ* and *ex situ* technology. The *in situ* technology, which treatment is performed at the position of the contaminated site, is more efficient in the total-cost and applied time than the *ex situ* technology, even though most of the current treatment methods applied to the actual contaminated sites are *ex situ* technology.

Electrokinetic (EK) remediation is one of the *in situ* technologies for removing pollutants from clayey soils on the basis of electrokinetic phenomena [14]. The EK process is suitable for treating various contaminants (e.g. heavy metals, organic pollutants and radionuclides) in many kinds of soils [15,16].

This method can be performed under a low-level voltage or current between the electrodes, which are inserted in the vicinity of the contaminated sites. The charged species can be removed by electromigration and also the electrically neutral species by electro-osmotic flow (EOF) in EK method if they are soluble in water.

Although the EK technology is effective to remove heavy metals in contaminated soil, the complete removal of heavy metals from soil by EK technology is sometimes difficult, because alkalization of soil by applying voltage caused the precipitation of heavy metal ions in soil. The redox condition of soil also influences the mobility of heavy metal ions and then the mobilities of metal ions in the presence of reducing and oxidizing reagents were investigated [17,18]. While, if heavy metal ions can be accumulated at the limited area of soil, it may become an alternative technology.

The reactive zone where the granular iron (Fe^0) was mixed with soil for entrapping or decomposing contaminants in groundwater has gained widespread acceptance in the environmental remediation and regulatory communities in recent years [19]. This reactive zone is called as a permeable reactive barrier (PRBs). Considerable investigation has been made toward understanding the interfacial chemistry of granular iron and the mechanisms of the degradation of contaminants. However, less attention has been paid to the means for introduction of ground water and waste water into PRBs. Ho et al. reported that TCE in the soil was removed and degraded by the combination of EK technology with PRBs (it is called as Lasagna technology) [20].

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Table 1
The chemical property of the kaolin soil before and after the acid washing

	Original kaolin	Treated kaolin
pH	3.62	6.54
Total organic carbon (TOC)	N.D. (ppm)	N.D. (ppm)
Ratio of mineral		
SiO ₂	79.72	79.55
Al ₂ O ₃	17.57	18.90
TiO ₂	0.76	0.37
K ₂ O	0.68	0.42
Cl	0.29	0.11
Fe ₂ O ₃	0.27	0.15
SO ₂	0.17	0.13
SrO	0.07	0.04

We also reported the removal and the degradation of TCE in the soil by the combination of EK technology with PRBs [21].

The ferrite method not only insolubilizes metal ions but also changes metal ions to the magnetic material. The ferritization is able to remove many kinds of harmful metal ions at the same time, and can be applied to the treatment of Cr⁶⁺ and Mn⁷⁺ without especial pre-treatment [22]. Ferritized metals can be separated easily by sedimentation or magnetic separation [23].

The purpose of this study is to confirm the usefulness of the combined use of the EK remediation and a ferrite treatment zone (FTZ). This system includes two treatment processes. One is an EK system, where heavy metal ions are removed from a contaminated soil by electromigration and electroosmotic flow, and the metal ions are introduced into the FTZ by EK.

The second is a FTZ system, where metal ions are ferritized to be immobilized as ferrite material. The immobilization of heavy metal ions by ferritization is effective for the treatment of the site contaminated with heavy metals of relative low concentration. In this case, a large amount of water produced by EK process should be treated. In the combined system of EK with FTZ, if metal ions are accumulated completely in FTZ, it is not necessary to treat water produced by EK. Generally, both of acidification and alkalization of soil caused by electrolysis of water at the EK system without a buffer supplying system and an ion exchange membrane filter [16]. However, the ferritization of metal ions was performed under alkali condition effectively. Alkalization of soil by EK process is suitable to the condition for ferritization.

2. Materials and methods

2.1. Soil and materials

Commercial available kaolin, which mainly consists of kaolinite, from Wako Pure Chemical Co. (Tokyo, Japan), was used as a model soil. Since this kaolin contains trace of metals (mainly iron), the kaolin was shaken with 0.1 M HCl (kaolin:HCl (w/w) = 1:4) for 24 h to remove heavy metals. After the procedure, the pH of the model soil was adjusted to 7.0 by addition of aqueous 0.1 M NaOH. The kaolin was filtered and then dried for 24 h in an oven. This treated kaolin was used as a model soil in this study. The chemical property of the kaolin before and

Table 2
The element of poly ferric sulfate solution

Specific gravity (20 °C)	1.506
Fe ³⁺	11.1%
Fe ²⁺	0.01%
Pb	2 ppm
Cd	N.D. (ppm)
Total-Hg	N.D. (ppm)
As	N.D. (ppm)
pH	0.26

after the acid washing was summarized in Table 1. The metal minerals of treated kaolin were analyzed by energy dispersive X-ray fluorescence spectrometer (EDX) EDX-700HS (Shimadzu Co., Japan). The transmission coefficient of the kaolin after acid treatment was $1.0 \times 10^{-8} \text{ cm s}^{-1}$ and the particle size by the soil classification method was the silt (0.02 mm – 2 μm) of 18% and the clay (>2 μm) of 82%.

Ferrite solution, which is called as ‘polyferric sulfate’, was obtained from Lasa Industries Ltd. (Japan) [24]. The components in this ferrite solution are summarized in Table 2.

2.2. Simulator for EK process

In order to investigate the behavior of pollutants in soil by EK technology, an apparatus having a small migration chamber (3.0 cm in diameter and 10 cm length) and two electrode chambers (3.0 cm in diameter and 5.0 cm length) was prepared with acrylic resins (Fig. 1). To prevent the soil in migration chamber from leaking into the buffer solution of the electrode chambers, each chamber was connected using a filter paper of 5B (Advantec, Japan) and an O-ring (Kokudo Co., Japan). Two meshed Ti electrodes coated with Pt were inserted into the electrode chambers, and the chambers were filled with 0.1 M phosphoric buffer solution [25].

The dc power supply AE-8270 (Atto Co., Japan) or MP-7612D (System Instruments Co., Ltd., Japan) was used to provide a constant electric potential across the two electrodes. The current during EK process was measured by this power supply as a function of time. The effluent by EOF was collected in a measuring cylinder and stored for analysis. The constant dc voltage of 20 V (the potential gradient is 2.0 V/cm) was applied through the soil for 0–96 h.

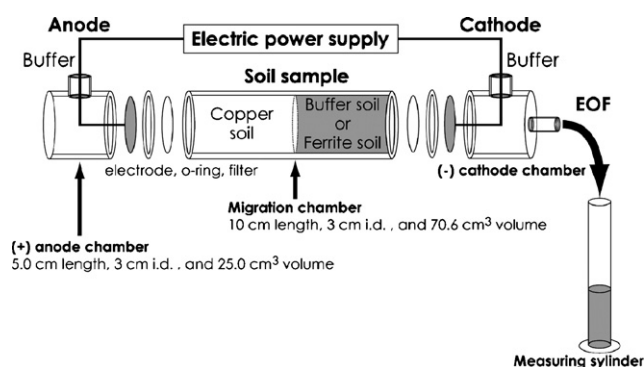


Fig. 1. Schematic diagram of electrokinetic remediation apparatus.

Table 3
The condition of all tests in the EK treatment

Test	Applied voltage (V)	Applied time (h)	FTZ	Result
1	20	3	EK only	Fig. 4a
2	20	6	EK only	Fig. 4b
3	20	12	EK only	Fig. 4c
4	20	48	EK only	Fig. 4d
5	20	96	EK only	Fig. 4d
6	20	24	EK-FTZ	Fig. 5a
7	20	48	EK-FTZ	Fig. 5b

By adding the copper ion solution prepared with $\text{Cu}(\text{SO}_4)$ into treated kaolin and mixing them well, the contaminated soil was prepared. The contaminated soil was filled in the half of an anode side of the migration chamber. The initial concentration of copper was 50.0 ppm and the water content in the all soils was adjusted at 30% using a buffer solution (pH 7.0, 0.1 M $\text{NaH}_2\text{PO}_4/0.1$ M NaOH buffer). The copper of 50 mg/kg was adopted in these experiments. The value is close to a natural content in soil and selected for the contamination with a relative low concentration. The total amount of copper in the migration chamber was 3.0 mg. The remaining area from the center in the migration chamber to the cathodic chamber, was packed with the soil containing only buffer solution. The total weight of the soil in the migration chamber was 120 g in every run.

In the case of experiments for EK combined with FTZ, the soil containing ferrite reagent was filled instead of the soil containing buffer solution. The concentration of ferrite in the FTZ was 1000 ppm (mg/kg) that was an excessive amount for copper of 50 mg/kg in the soil. The condition of the all tests was summarized in Table 3.

2.3. Analytical method

After the EK experiment, the soil sample was removed from the migration chamber and sliced into several sections. Each section was provided for the measurement of water content, pH and the concentration of copper by means shown in the following sections.

2.3.1. pH of soil

To measure pH of soil before and after EK treatment, 2.5 ml distilled water was added to 1.0 g of soil in each section (w:w = 1:2.5). The measurement method of soil pH in Japan was recommended by Soil Reaction Commission of International Union of Soil Sciences. And the mixture was shaken at 1500 rpm at room temperature for 1 h. The pH values of the extracted water were measured by a digital pH meter M-13 (Horiba Co., Japan).

2.3.2. Measurement of copper in soil

After EK treatment, the amounts of total copper in the soil, the solution of two electrode chambers and the overflow by EOF were determined by the following procedure. Copper ions were extracted from 3.0 g of soil in each sliced section by shaking it with 27.0 ml of 1 M HCl (w:w = 1:9) at 1500 rpm for 6 h using shaker M-1000 (EYELA, Japan). After shaking, the mixture

of soil and hydrochloric acid was centrifuged at 4000 rpm for 15 min using the centrifugal separator 2410 (Kubota Co., Japan). The concentration of total copper ion in the supernatant was analyzed by atomic absorption spectrophotometer (AAS), A-2000 (Hitachi Co., Japan). The extraction of copper ions from soil and analysis of copper concentration were carried out by Japanese Industrial Standard (JIS) K 0102. The mass balance for copper in the EK system was within the range of $\pm 10\%$.

To evaluate the amount of copper insolubilized with ferrite in soil, free copper ions in the soil was measured as well as the total amount of copper. After EK remediation treatment, the free copper ion was extracted from 3.0 g of soil in each section by adding 27 ml of Milli-Q[®] water (Millipore Co., USA) (w:w = 1:9) and then analyzed by the same method for the total copper.

3. Results and discussion

3.1. Ferritization of copper ion in solution

At first, the ferritization of copper ion in the solution was investigated at various pH. Fig. 2 shows the effect of pH and the amount of ferrite on the normalized concentration of free copper ion in the solution. After ferritizations, the concentration of free copper ion, which was eluted with Milli-Q[®] water from the ferrite, was determined by AAS. The concentration of copper ion at every run was almost not changed in acidic condition. In alkali solution, however, the concentration of copper was decreased in every runs. Even through Fe^{2+} and Fe^{3+} were not present, the eluted copper ion was decreased at the half level of the initial concentration, due to the formation of hydroxide precipitation in the alkali solution. In the presence of Fe^{2+} and Fe^{3+} in the alkali solution, the eluted copper ion was decreased largely in comparison with that in the absence of ferrite solution. This figure indicates that the pH condition from neutral to alkali is required for ferritization of copper. The ferritization is one of coprecipitation phenomenon to capture the heavy metal ions in ferric hydroxide. It was reported that the ferritization of copper was progressed through the reactions shown in the following Eqs. (1) and (2) [26–28]. Barrado et al. suggested the coprecipi-

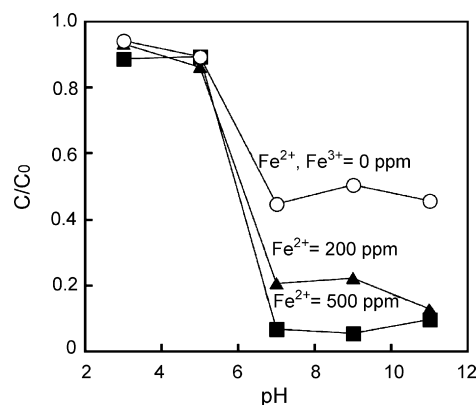


Fig. 2. Effect of pH generating ferrite of copper. Initial copper concentration = 100 ppm (1.53 mM), $\text{Fe}^{3+} = 200$ ppm (3.58 mM), buffer solution = 0.1 M $\text{NaH}_2\text{PO}_4/0.1$ M HCl or 0.1 M NaOH.

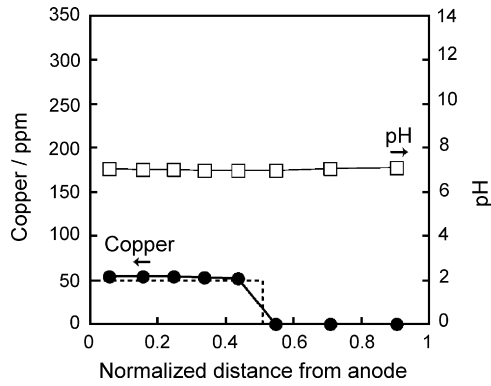
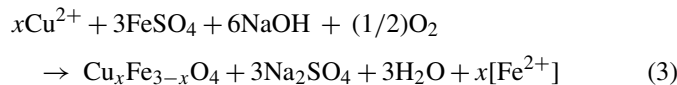
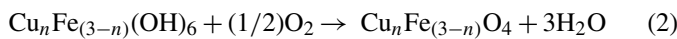
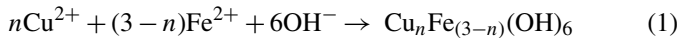


Fig. 3. Effect of diffusion of copper in soil. [Copper] = 50 ppm, applied voltage = 0 V, applied time = 72 h.

tation mechanism for Fe^{2+} and divalent or polyvalent metal ions as Eq. (3) [29]. The precipitation of copper after ferritization could be separated by the magnetic stirring bar. This indicates that the ferrite precipitation with copper become magnetic body and makes it easy to separate the precipitates from solution.



3.2. Removal of copper from soil by EK treatment

Since electrolysis of water in each chamber occurred by the applied constant dc voltage in EK treatment, the solution in the anodic chamber was changed to acid solution and the solution in the cathodic chamber was to alkali solution. Hydrogen ion generated by the electrolysis of water in the acidic chamber moved into the soil in the migration chamber if pH of the electrode chamber was not controlled. Consequently, the acidic and alkali zone in soil appeared during the EK process. The acidic soil condition is suitable for removal of metal in the soil, because metal and metal oxide in soil could be changed to metal ions in acidic condition. Metal ions are also adsorbing strongly by ion-exchanging mechanism on the clay mineral of soil. Therefore, in order to shift the ion exchanging equilibration, the acidic condition is essential. On the other hand, alkali condition near the cathodic chamber facilitates the ferritization of copper ions.

Fig. 3 shows the distribution of copper and pH of the soil in the migration chamber after for 72 h without EK treatment. The horizontal axis of this figure represents the normalized distance from the anode, that is, 0 of the axis means the edge of the anodic chamber and the 1 means the edge of the cathodic chamber. The initial copper concentration of the soil in the position of 0–0.5 (a dotted box) in the migration chamber was adjusted to 50 ppm, and the rest was 0 ppm. Initial pH in the soil was adjusted to 7.0. After 72 h without EK treatment, the distribution of copper ion in the soil and the pH of the soil did not change compared with

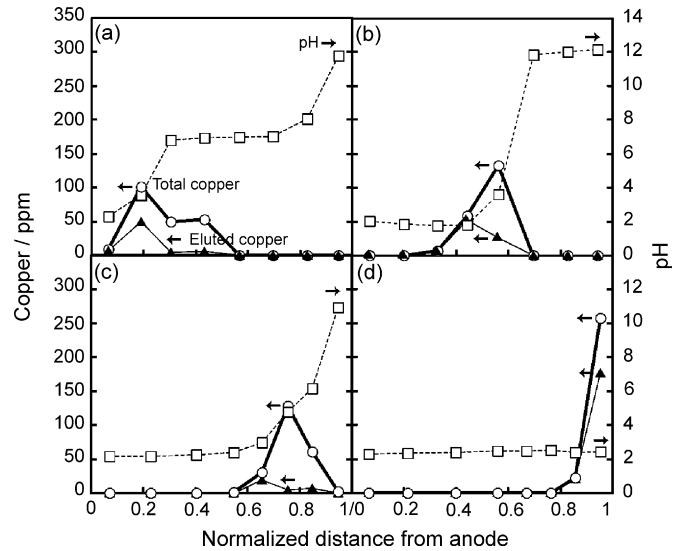


Fig. 4. Removal of copper in soil on EK. [Copper] = 50 ppm, applied voltage = 20 V. Applied time: (a) 3 h, (b) 6 h, (c) 12 h and (d) 96 h.

the initial condition. This shows that copper ions in the soil can not move only by diffusion, and that the analysis methods for copper ions and pH are adequate because the initial condition is represented by the analysis.

Fig. 4 shows the distribution of the concentration of total copper and eluted copper and pH of the soil in migration chamber after applying voltage in EK treatment. After 3 h (Fig. 4a), pH of the soil in nearly each chambers began to be changed by EK process. In acidic region, the copper concentration in 0–0.2 was decreased, whereas the copper concentration of 0.2–0.3 of the axis was increased. In neutral pH region in 0.3–0.4 of the axis, the copper concentration was not changed. This indicates that the copper ion in acidic condition can move in soil easily in the direction to the cathode [31], but in neutral pH region copper ion cannot move, because of ion-exchanging mechanism of clay mineral.

After 6 h, copper was detected even at central position of the soil in the migration chamber (Fig. 4b). This position is the front of acidic soil and also the front of alkali soil and it is called as the 'pH junction' or 'pH jump' [30]. The pH of soil was changed from 2 to 12 abruptly at this position. The total concentration of copper in the position of 0.4–0.5 was equal to the eluted copper concentration. However, the eluted copper in the position of 0.5–0.6 decreased largely compared with the total copper concentration at this position. This difference was due to the formation of hydroxide precipitate of copper in alkali soil. Fig. 4c shows the distribution of copper ions after 12 h. Copper moved more to cathodic chamber than that after 6 h.

After 96 h (Fig. 4d), all soils in the migration chamber was completely acidified and most of copper ions moved to the vicinity of the cathodic chamber. The total copper concentration in this position was equal to the eluted copper concentration. This indicates that copper in the soil is free ionic form and the hydroxide precipitate of copper ion is also dissolved when all soil in the migration chamber become acidic soil. Therefore, copper ions might move from migration chamber to cathodic cham-

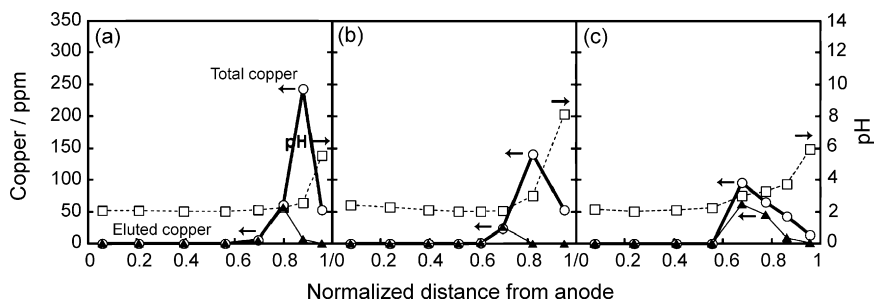


Fig. 5. Insolubilization of copper in soil by EK applied reaction wall of ferrite as a function of time. [Copper] = 50 ppm, [ferrite soil] Fe^{2+} = 500 ppm, Fe^{3+} = 1000 ppm, applied voltage = 20 V. Applied time: (a) 24 h, (b) 48 h (EK with PRBs) and (c) 48 h (EK treatment only).

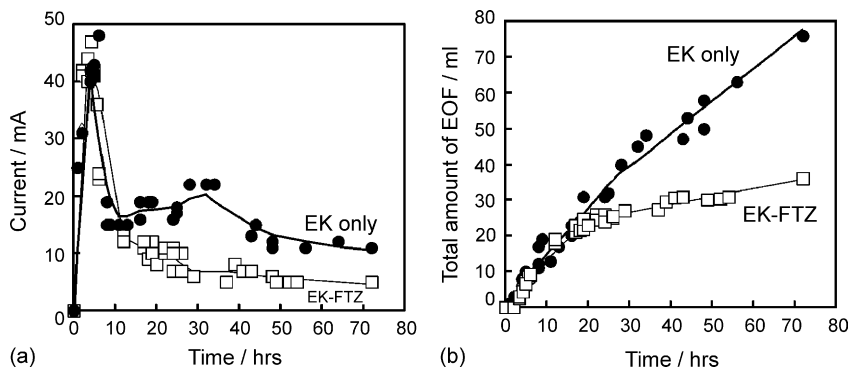


Fig. 6. Current and total amount of EOF during applied voltage by the EK treatment. (a) Current (mA), (b) total amount of EOF (ml). Applied voltage = 20 V, applied time = 72 h.

ber. However, copper ions were slightly detected in the solution of cathodic chamber and measuring cylinder. The solution in the cathodic chamber was strong alkali and the surface of soil in contact with the chamber, and the filter paper between the migration and cathodic chamber was also strong alkali and then copper ions existed there as hydroxide precipitations.

3.3. Insolubilization of copper ions in soil on EK with FTZ

Fig. 5 shows the distribution of the total copper and the eluted copper in the soil of migration chamber with FTZ after applying voltage by EK. After 24 h, copper ions moved to the cathodic chamber (Fig. 5a), but distribution of copper remained in the FTZ. The less amount of eluted copper suggested the evidence of ferritizing in FTZ. After 48 h, the large difference between total concentration and eluted concentration of copper was observed (Fig. 5b). While the large difference between total and eluted concentration of copper was not observed in the case of EK treatment without FTZ (Fig. 5c). The results in Fig. 5c shows the FTZ is effective for the immobilization of copper ion. That is, in FTZ, copper is insolubilized with ferrite reagent and accumulated in the zone. The ratio of the ferritization was 92% by EK with FTZ after 48 h.

Fig. 6 shows the current through soil and the overflow carried by EOF (total amount of EOF) as a function of EK treatment time. As shown in Fig. 6a, the current of both the treatment of EK with and without FTZ increased for at first 5 h, then the current suddenly decreased after 10 h. This decrement of the current was thought to be due to the loss of ionic species in soil by neutralization. That is, when the front of acidic and the

front of alkali contact each other, neutralization occurs there to vanish ionic species such as proton and hydroxide. As shown in Fig. 6b, the total amount of EOF by the EK with FTZ was decreased compared with the EK treatment without FTZ. The total amount of EOF after 72 h by the EK treatment was 76 ml only and 32 ml by the EK treatment with FTZ. This decrease was thought to be due to the difference of the current through soil as shown in Fig. 6a. The current is significant factor for removing copper ions from soil. Therefore, adding much ferrite reagent to soil leads to the decrease of the efficiency in the removal of copper from the soil although it is effective for ferritizing copper ions. The precipitation of copper in alkali condition of EK treatment sometimes stopped the flow of current and EOF. The velocities of EOF and electromigration of metal ions increased with increasing potential gradient and current density. However, Gray reported that the heat generation was caused by applying a current density over 5 mA/cm^2 [31]. In the present system with the voltage gradient of 2.0 V/cm, the heat generation was not observed.

The EK technology with FTZ could insolubilize and accumulate copper at the limiting position in the soil. The insolubilization as copper–ferrite of magnetic materials might facilitate the separation of heavy metals from the soil as well as from the solution.

4. Conclusions

The usefulness of the combined use of the EK remediation and the FTZ for treatment of the soil contaminated with copper ion was demonstrated. In the case of EK treatment with FTZ,

the large difference between total and eluted concentration of copper in the zone was observed. This shows that copper ions were insolubilized by the reaction with ferrite reagent in the zone and was accumulated as copper–ferrite in soil. Therefore, the EK system with FTZ has some advantages, for example: (1) it is able to collect heavy metals in a specific zone, then (2) to avoid the treatment of a large amount of water produced by EK system and (3) there is a possibility that copper–ferrite can be collected and separated by magnet. Although actual field scenario is a problem in future, the FTZ is made in the vicinity of the cathode around the contaminated site by injecting the ferrite solution into the narrow soil zone, and the electrode position is decided so that the contaminated water from the contaminated soil is introduced to the FTM by EK process. After EK treatment, the FTZ is dug over and then copper in FTZ is recovered by the adequate process, such as washing with acid and magnetic separation.

Acknowledgement

This work was supported in part by 21st Century Center of Excellence Program (E-01) funded by Ministry of Education (Culture, Sports, Science and Technology).

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