

Enhancement of electrokinetic remediation of hyper-Cr(VI) contaminated clay by zero-valent iron

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Abstract

This paper investigated the effectiveness of incorporating zero-valent iron (ZVI) into electrokinetic (EK) to remediate hyper-Cr(VI) contaminated clay (2497 mg/kg). A ZVI wall was installed in the center of the soil specimen and was filled with 1:1 (w/w) ratio of granular ZVI and sand. Results show that transport of H⁺ is greatly retarded by the strong opposite migration of anionic chromate ions, whereupon a reversed electroosmosis flow (EO) was resulted and alkaline zone across the specimen was developed promoting the release of Cr(VI) from the clay. Chromium removal was characterized by high Cr(VI) concentration occurred in the anolyte and the presence of Cr(III) precipitates in the catholyte. The Cr(VI) reduction efficiencies for the process without ZVI wall were 68.1 and 79.2% for 1 and 2 V/cm, respectively. As ZVI wall was installed, the corresponding reduction efficiencies increased to 85.8 and 92.5%. The costs for energy and ZVI utilized in this process are US\$ 41.0 and 57.5 per cubic meter for the system with electric gradient of 1 and 2 V/cm, respectively. The role of ZVI wall effectively reducing Cr(VI) contamination and the operation simultaneous collection of Cr(VI) from the electrode reservoirs are two major advantages of this process.

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1. Introduction

Chromium (Cr) contamination has been found in many superfund sites, residential areas, and industrial areas, such as electroplating facilities and tannery industries [1]. The contamination incidences mainly caused by improper disposal of hazardous wastes and leakage from the dumping sites. Cr occurs primarily as two oxidation states, that is, Cr(III) and Cr(VI) in the soil. Due to its strong adsorption onto soils and forming insoluble Cr hydroxides in the aqueous solution, Cr(III) is relatively immobile and nontoxic compared to Cr(VI). The anionic Cr(VI) ions are of great concern owing to their carcinogenic and metallurgic to living organisms and their significantly mobility in subsurface. Therefore, remediation of Cr-contaminated sites is the top priority in many countries for environmental protection.

Ex situ remediation of Cr sites as a mean of excavation of the contaminated soil is usually followed by soil washing. Albeit, this remediation method can be a promising process to remove Cr from soil, the post treatment of the extraction fluids and the recovery of extracted soil after treatment are the two major concerns of adopting this costly process. Furthermore, the effectiveness of soil washing is much affected by soil types and chemical extracting agents. In situ or on-site clean up methods could be applied in terms of reducing environmental impacts and decrease the cost of remediation. In situ treatment of Cr-contaminated soils includes chemical and organic reduction [2,3], and bio-reduction [4]. However, these methods cannot effectively remove Cr from a low permeability soil, for example, clayey soil. The proven electrokinetic (EK) remediation has been known to be one of the in situ technologies, which is based on the application of a direct current across unsaturated soil. The major contaminant removal mechanisms involved in this process are the advection of electroosmotic (EO) flow driven under an electrical field, the movement of H⁺ ions generated from water electrolysis at the anode advancing through soil towards

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the cathode, and the electromigration of charged ions toward the opposite electrodes [5]. EK has been reported to be successful and cost-effective to treat both organic [6–8] and inorganic contaminants [5,9,10] from low permeability soils. Many studies have also shown that EK was capable of removing Cr from soils [11–19]. Most of the relevant studies performed were focused on the effects of soil types, multiple metal contaminants, composition of processing fluids, running period, and strength of electrical voltage.

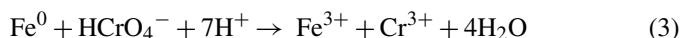
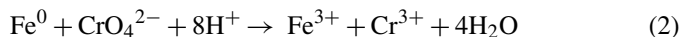
Although EK remediation has been extensively studied over the last two decades, limited data are available to describe the use of zero-valent iron (ZVI) wall to incorporate into this process [19,20]. ZVI aggregate is the most common reducing materials used in permeable reactive wall to remove certain persistent organic and inorganic contaminants such as dense of non-aqueous phase liquids (DNAPLs) and Cr(VI) [21–27]. Most recently, Chang and Cheng [20] performed the combination of EK and ZVI for remediation of the perchlorethylene contaminated soil and the results were promising. In the past relevant EK studies [11–19], Cr(VI) contamination in the tested soil was low. However, the effectiveness of EK remediation of Cr(VI)-contaminated soil is strongly affected by its concentration level and reductive media in the soil. In the present study, experiments were conducted to test the effectiveness of using ZVI in the EK process to remediate a hyper-Cr(VI) contaminated clay. The effects of electric potential gradient on the EK phenomena, the Cr removal efficiency, and the preliminary economic analysis of this process were presented. To obtain reduction information pertaining to the design of the wall, kinetic reduction of Cr(VI) by ZVI was conducted. It is expected that results of this study would provide useful information for the remediation of Cr(VI) contaminated sites.

2. Materials and methods

A Cr-free soil sample was collected from a depth of 0.7–1.5 m at Da-Hsu Township, Kaohsiung County in Taiwan. Upon collection, soil samples were air-dried, homogenized with a wooden mallet or by hand, and crushed to pass through a 2 mm ASTM standard sieve. The Cr-free soil was classified as clayey soil and has the following properties: organic content, 1.79%; moisture content, 31%; soil pH 7.54; pH_{zpc} 2.30; Fe, 36,183 mg/kg. The artificially Cr(VI) contaminated soil was prepared by adding an appropriate amount of dissolved $K_2Cr_2O_7$ solution and soil into a 2000 mL PE bottle. The slurry was continuously mixed with a rotational agitator at 30 rpm for two days to reach adsorption equilibrium. At the end of agitating period, the wet soil was analyzed and its Cr(VI) concentration was measured. An average concentration of 2497 mg/kg Cr(VI) in the dry soil was measured, which is below the maximum adsorption capacity (2.974 mg/g) of the soil determined from Langmuir adsorption isotherm. The major adsorbed chromate species would be $HCrO_4^-$ based on the initial Cr(VI) concentration of 4.027 mg/L (7.7×10^{-5} M).

In this work, ZVI aggregate and silica sand were used as fillings in the wall to create a reactive zone for Cr(VI) reduction. The iron aggregate sample (ETI CC-1004) with particle size

of US screen $-8 + 50$ mesh was obtained from Connelly-GPM Inc., USA. The major constituent of this sample is 89.82% Fe and minors are: 2.85% C; 1.85% Si; 0.15–0.2% Cu; 0.15% Mo; 0.132% P; 0.6% Mn; 0.107% S; 0.005–0.21% Ni; 0.003–0.17 Cr, and other trace substances. To ensure sufficient reaction time for Cr(VI) reduction and to avoid clogging, a weight ratio of 1:1 iron (5 g) to sand (5 g) was filled in the wall. Ottawa sand (Silica, Co., USA), which meets ASTM C778 classification, was used. Depending upon the Cr(VI) species involved, reduction of Cr(VI) by ZVI can be accomplished by the following reactions:



Chromate speciation is strongly dependent on the pH and the aqueous concentration. As shown in Fig. 1, $HCrO_4^-$ and CrO_4^{2-} are the dominant species of all the shown concentrations, and some $Cr_2O_7^{2-}$ would exist at the higher Cr(VI) concentration of 5×10^{-3} M. Based on Eqs. (1)–(3), one molar concentration of ZVI can reduce one molar of Cr(VI). To ensure all chromate species are completely reduced to Cr(III), an excess amount

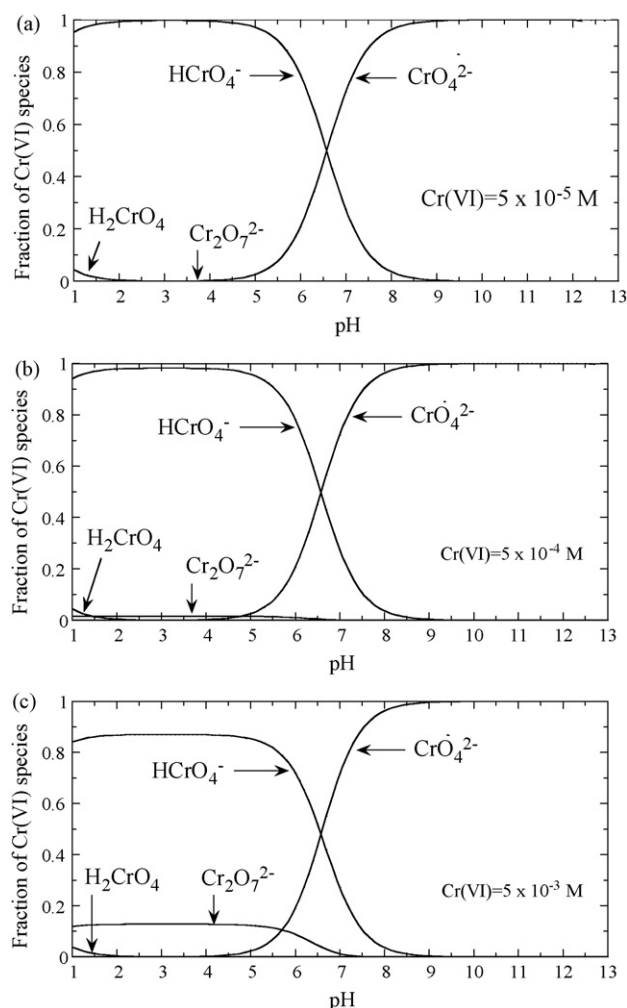


Fig. 1. The Cr(VI) speciation diagram as function of pH.

of ZVI ought to be applied. By accounting only 89.82% of Fe content in the Fe aggregate sample and 300 g soil in the EK experiment with a Cr(VI)-contamination level of 2497 mg/kg, the minimum ZVI requirement in the wall was estimated as follows:

$$\begin{aligned}
 & [\text{Cr(VI)}]_{\text{initial}} \times W_{\text{soil}} \times M_{\text{Fe}}/M_{\text{Cr}} = 2497 \text{ mg/kg} \\
 & \times 0.3 \text{ (kg)} \times 56 \text{ (g/mol)} / 52 \text{ (g/mol)} \\
 & \div 1000 \text{ (g/mg)} \div 0.898 = 0.902 \text{ g}
 \end{aligned} \quad (4)$$

where $[\text{Cr(VI)}]_{\text{initial}}$ (mg/kg) is the initial concentration of Cr(VI) in soil, W_{soil} (kg) is the weight of soil, and $M_{\text{Fe}}/M_{\text{Cr}}$ is the molar ratio of Fe and Cr. An amount of 5 g ZVI used in wall should prove sufficient ZVI for Cr(VI) reduction.

The reduction rate of Cr(VI) by ZVI is another important parameter to design the dimension of reactive ZVI wall. Kinetic experiments were carried out to establish the effects of time and pH on the reduction of Cr(VI) by ZVI. The experimental procedures are described as follows:

- (1) Prepare a series of 125 mL polyethylene bottles containing 100 mL of 5.2 mg/L Cr(VI) concentration with a constant strength of NaClO_4 (1×10^{-2} M).
- (2) Adjust initial pH to 3.5 or 6.9 by either 0.01 M HClO_4 or NaOH solutions.
- (3) Add a given amount of the ZVI (5 g/L) and sand (5 g/L) into the solution.
- (4) Shake these bottles on a reciprocal shaker at 150 excursions/min at 27 °C. At the completion of preset time intervals, 5 mL of solution was taken and immediately filtered through a 0.45 μm membrane filter (supor-450, 25 mm, Gelman Sci.) to collect the supernatant.
- (5) Determine the residual Cr(VI) concentration in the supernatant. The amount of Cr(VI) reduced was determined as the difference in concentration between samples withdrawn at two consecutive time intervals during the course of the kinetic experiments.

The EK experiments were conducted by a series of acrylic extruded cylindrical cell shown in Fig. 2. The cell has an inner diameter of 4.2 cm and consists of three compartments: anode reservoir (5 cm length), soil cell (12 cm length), and cathode reservoir (5 cm length). The soil cell contained approximately 300 g of the artificially Cr(VI) contaminated clay (2497 mg/kg) with a moisture content of $31 \pm 1\%$. Considering the possibility of using groundwater as processing fluid in the field remediation, simulated groundwater, which was filled up in each of the reservoirs, was used as processing fluid (conduc-

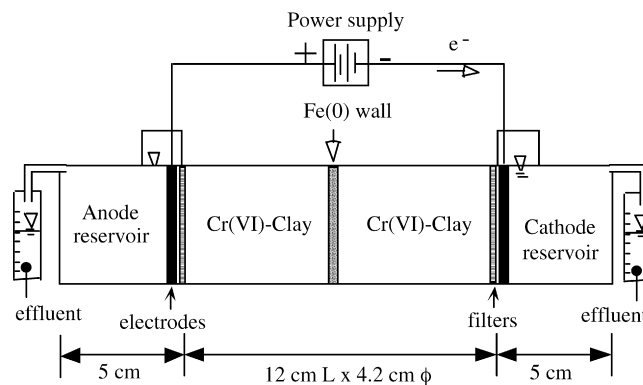


Fig. 2. EK process setup.

tive medium) and supplied continuously. The composition of simulated groundwater was prepared based on recent four-year data of five groundwater-monitoring wells in Kaohsiung County in Taiwan. The constituents of simulated groundwater in terms of equivalent per liter are as follows: Ca^{2+} 4.76; Mg^{2+} 1.84; Na^+ 1.12; K^+ 2.28; Cl^- 4.00; HCO_3^- 3.96; NO_3^- 2.04 mEq./L. Two pieces of fiberglass filter papers (0.45 μm , 47 mm in diameter, Advantec GS25, Japan) were attached on both inner sides of the anode and the cathode to separate the soil from the processing fluid. Two sets of graphite rod electrodes (0.64 cm in diameter, Union Carbon Co., USA) were installed at each side of the reservoirs. After the installation, the EK apparatus was sealed with silicon tape to minimize the water from vaporizing. The electrodes were connected with a DC power supply, which provided a constant electric potential gradient to induce the movement of electrolyte solution within the soil cell. Table 1 lists the detailed experimental conditions. During the EK operation, current density across the soil specimen, the amount of EO flow collected in the reservoirs, the amounts of dissolved Fe(II)/Fe(III) and Cr(III)/Cr(VI) in the reservoirs, redox potential, and reservoir pH values were monitored. At the end of the each test, the soil core was removed from the cell and sliced equally into six segments. The soil pH, redox potential, and residual Cr(III)/Cr(VI) in the soil of each segment were analyzed. A scanning electron microscope (SEM) equipped with energy dispersive X-ray spectroscopy (EDS) (Hitachi S2700) was used to characterize the photomicrography and constituents of precipitates in the catholyte. All experiments were operated at room temperature, that is 27 °C.

Cr(VI) in the solution was analyzed by reaction with diphenylcarbohydrazide and then the absorbance of the purple product was measured at a wavelength of 540 nm with a spectrophotometer (HACH DR2010, USA). Cr(III) in the solution

Table 1
Experimental conditions

Test no.	Initial soil Cr(VI) (mg/kg)	Electric gradient (V/cm)	Processing time (day)	ZVI/sand (g)/(g)
1	2497	1	12	0/0
2	2497	2	12	0/0
3	2497	1	6	5/5
4	2497	2	6	5/5

was measured by an atomic absorption spectrophotometer (AA, Varian 200). The total Cr concentration in the soil was determined by wet extraction analysis. Soil samples were digested with concentrated HNO₃ followed by the addition of concentrated H₂SO₄, HClO₄, and HF at volume ratio of 1:2:5 for 1 h at 60–80 °C. Cr(VI) in the soil was determined by alkaline digestion according to the method described in USEPA method: SW846-3060A. The soil sample was digested with 0.28 M NaCO₃/0.5 M NaOH solutions and heated at 90–95 °C for 1 h to dissolve the Cr(VI). The quantification of Cr(III) in the soil was determined by the difference between the total Cr and the Cr(VI). Fe(II) was analyzed by the 1,10-phenanthroline method at a wavelength of 510 nm. Total Fe was analyzed using HACH Ferrover iron reagent at 510 nm by the Ferrover method. Fe(III) was determined from the difference between the total Fe and Fe(II).

3. Results and discussion

3.1. Evaluation of thickness of ZVI wall

Kinetic study of Cr(VI) reduction by ZVI aggregates was conducted to provide information to design the thickness of ZVI wall. Fig. 3 shows the variation of Cr(VI) reduction with time for different pHs at 27 °C. It is evident that the reduction rate is fast at pH 3.5. When the pH increases to 6.98, the reduction rate becomes slower. Clearly, the results indicated that pH plays a significant role in the reduction of Cr(VI) by ZVI. As shown, a near 100% removal of Cr(VI) was found regardless the solution pH. The first-order kinetic equation is used to describe the adsorption kinetics data and has the form of:

$$C = C_0 e^{-kt} \quad (5)$$

where C_0 is the initial Cr(VI) concentration (mg/L); k is the rate constant (L/min); t is the reaction time (min). As shown in Fig. 3, the fitting results of kinetics reaction indicate that the experimental data were correlated well to the first-order kinetics with high correlation coefficient (>0.988). The rate constants are

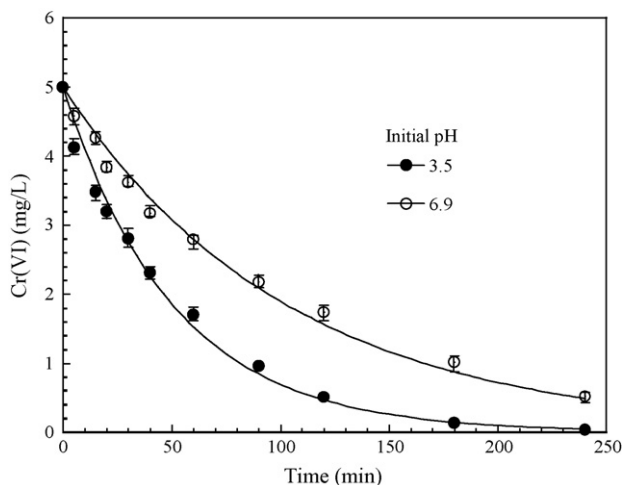


Fig. 3. Cr(VI) reduction by ZVI as a function of time. Solid lines are the best fit of 1st-order kinetic equation.

0.0198 and 0.0097 L/min, respectively, for initial pH 3.5 and 6.9. The thickness of wall (T_{wall} , cm) was calculated as follows:

$$T_{\text{wall}} = K_e \times i_e \times t_{\text{Cr}} \quad (6)$$

where K_e (cm²/V-s) is EO permeability; i_e (V/cm) is potential gradient; t_{Cr} (s) is the reaction time for Cr(VI) to be reduced to Cr(III) by ZVI. Depending upon the source of ZVI and the experimental conditions conducted, value of t_{Cr} would be different. Powell et al. [28] reported that the value of t_{Cr} was about 0.5 h for ZVI/sand filings while Liu et al. [29] showed that t_{Cr} was less than 6 min for a 99% reduction by ZVI under initial Cr(VI) concentration 5–30 mg/L and pH 6.3–8.5. In this work, by accounting a 99% Cr(VI) reduction efficiency, the values of t_{Cr} are about 4 and 8 h for pH 3.5 and 6.9, respectively. By adopting K_e value 8.36×10^{-6} cm²/V-s, determined from the results of EK experiments (Section 3.4), the least thickness of wall becomes:

$$T_{\text{wall}} = 8.36 \times 10^{-6} \text{ cm}^2/\text{V-s} \times 1 \text{ V/cm} \times 8 \text{ h} \times 3600 \text{ s/h} \approx 0.24 \text{ cm} \quad (7)$$

To make sure that those of Cr(VI) solution passing through the wall would be completely reduced to Cr(III), a thickness of 0.3 cm was adapted for the reactive wall which is far greater than the above calculated value.

3.2. Current density

In this work, the applied voltage to the system was kept constant between the electrodes and the current was allowed to vary in time. Current density was calculated by dividing the total current passing through the soil cell to the cross sectional area of the cell. The variations of current densities throughout the duration for the four EK experiments are depicted in Fig. 4. The current density reached a peak within 20 h operation was shown, and then it rapidly decreased to a stable low value after 60 h for all tests. Similar observation has been reported in many relevant studies [13,19]. By comparing the current density variation in Fig. 4, it was found that a higher current density peak was observed for the system with 2 V/cm (Tests 2 and 4) than the system with 1 V/cm (Tests 1 and 3). Results also showed

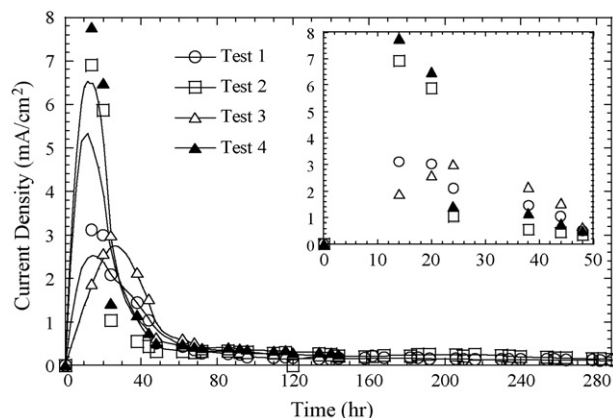


Fig. 4. Current density vs. processing time.

that installation of ZVI wall did not affect much on the current density. The sharp decrease of current with time, reflects the total electric resistance increased markedly in the system. The decrease in conductivity with time is due to a decrease in the concentration of dissolved ionic species, which is caused by the formation of precipitates at the cathode region. Thereby a much lower current was resulted. The precipitates that may be responsible for causing high resistance are Fe(III), Cr(III), Ca(II), and Mg(II) hydroxides because they are either initiated from the reaction products of the wall – such as $\text{Cr}(\text{OH})_3$, $\text{Fe}(\text{OH})_3$, and $\text{Cr}_x\text{Fe}_{1-x}(\text{OH})_3$, and the major components of conductive medium, that is groundwater – or originated from the constituents of the soil. The build-up of resistance in the system would lower the EO flow and eventually retard the further transport of soluble Cr and other soluble species from the anode towards the cathode.

3.3. EO flow

Fig. 5a and b show the cumulative EO volume collected in anode and cathode reservoir, respectively. At the beginning of the operation, accumulation of EO flow in the cathode reservoir was found (Fig. 5a) in all tests performed. After about 40 min,

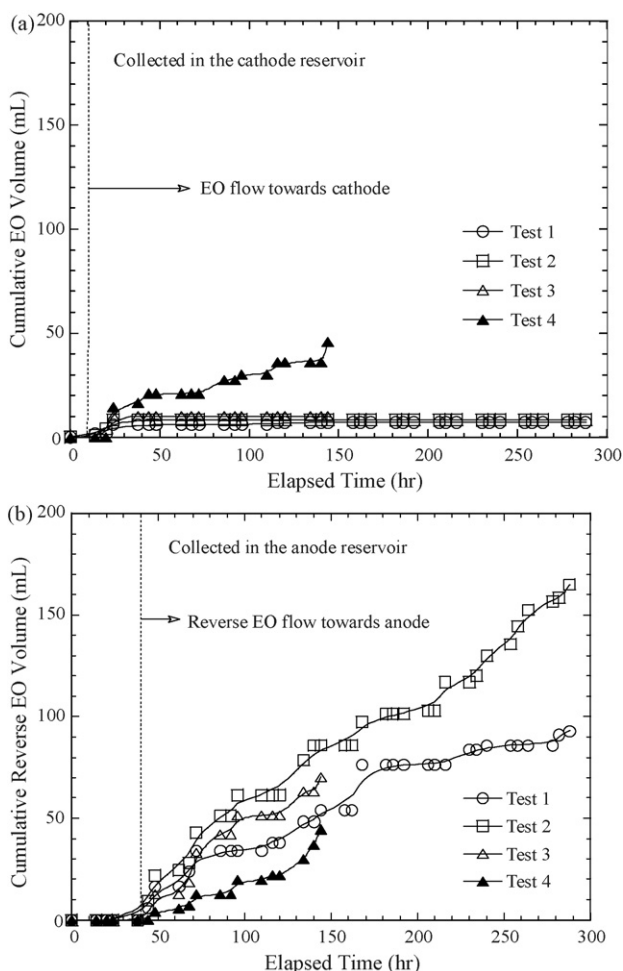


Fig. 5. Cumulative EO flow vs. time. Collected in (a) cathode reservoir (b) anode reservoir.

the movement of EO flux towards cathode disappears for Tests 1–3. Upon the disappearance of EO flow after 40 min, the EO flow began towards anode (Fig. 5b). Such kind of pronounced change in EO flow direction was not found in the relevant literatures. As compared in Fig. 5a and b, the reversed EO flow towards anode is much greater than the EO flow towards cathode, which was induced by the cationic ions. Normally as the solution pH is greater than the pH_{zpc} of the soil, the EO flux induced by the cationic ions would flow towards cathode. The developing of such kind of reversed EO flow was mainly attributed to the anionic chromate ions originated from the soil containing hyper Cr(VI) concentration (2497 mg/kg). Since chromate ions possessed a relatively higher ionic charge than those of major cations, that is, Ca^{2+} , Fe^{3+} , Fe^{2+} , and Mg^{2+} , reversed EO flow derived from the migration of chromate ions is faster than that of the EO flux induced by these cations. As shown in Fig. 5b, when voltage increased up to 2 V/cm (Test 2), more reversed EO flow was observed for the system without the wall. However, in the system containing ZVI wall, the reversed EO flow for the 2 V/cm (Test 4) is much less than that of 1 V/cm (Test 3). It would be reasonable to think that more Fe would be dissolved from the wall under a higher electric gradient. The dissolution of Fe^{2+} and Fe^{3+} into soil pore fluid would further increase the electrolyte concentration, thereby inducing more positive EO flow as depicted in Fig. 5a. However, the migration of anionic chromate ions towards the anode may have caused a hinder effect on the positive EO flow. On the basis of above findings, it is concluded that the ionic migration is one of the major mechanisms in removing Cr(VI) from soil. The formation of reversed EO flow was mainly caused by the migration of anionic Cr(VI) and such movement would result in an accumulation of Cr(VI) in the anode reservoir.

3.4. EO permeability

The EO permeability, K_e ($\text{cm}^2/\text{V}\cdot\text{s}$) was calculated as follows:

$$K_e = Q_e / (i_e \times A) \quad (8)$$

where Q_e is EO flow (mL/d); i_e is electric gradient (V/cm); A is cross-section area of the cylindrical cell (cm^2). The calculated K_e variation in time according to Eq. (8) for the EO flow (from anode towards cathode) and the reverse EO flow (from cathode towards anode) are plotted in Fig. 6a and b, respectively. The obtained K_e values are in excellent agreement with the literature data of 1.0×10^{-7} to $4 \times 10^{-5} \text{ cm}^2/\text{V}\cdot\text{s}$ for all soils [12,19]. Weng et al. [19] has shown that K_e values ranged from 6.73×10^{-6} to $7.74 \times 10^{-6} \text{ cm}^2/\text{V}\cdot\text{s}$ for the treatment of 1150 mg/kg Cr(VI)-contaminated clay with a constant potential gradient of 2 V/cm. All K_e values of EO flow (Fig. 6a) confirmed that a plateau at around 30 min elapsed time was found over the entire period in all tests. In general, a higher K_e value was observed for the process with a higher voltage. As shown in Fig. 6a, a slightly higher K_e value of EO flux over the entire period was found for the process without installation of ZVI wall. Fig. 6b shows that the K_e variation of reversed EO flow was within one order of magnitude, indicating low fluctuation. The obtained K_e values of

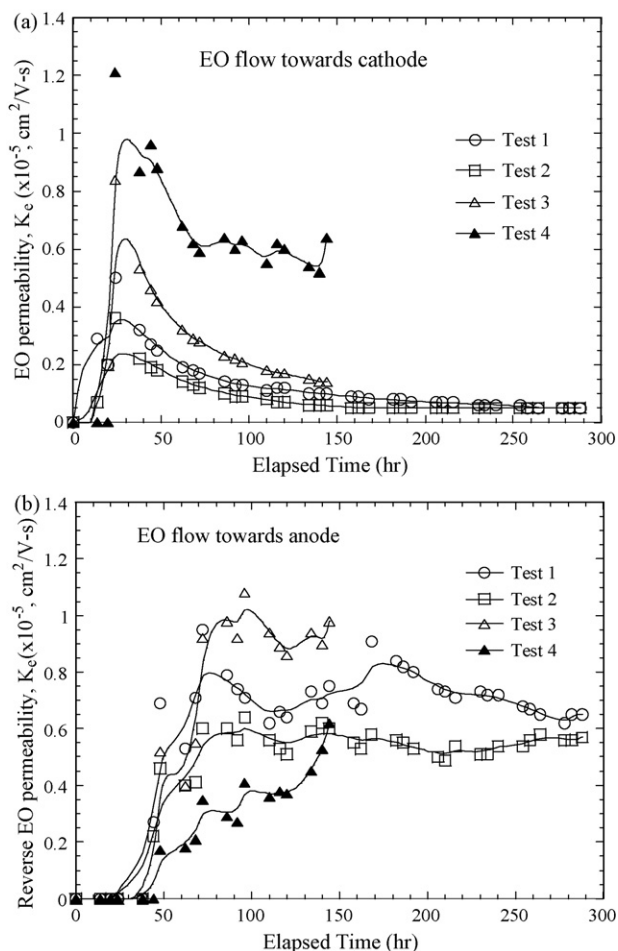


Fig. 6. EO permeability vs. processing time. (a) Towards anode; (b) towards cathode.

reversed EO flow ranged from 0.5×10^{-5} to $1.0 \times 10^{-5} \text{ cm}^2/\text{V}\cdot\text{s}$ are much greater than the typical hydraulic-induced flow in soils.

3.5. Reservoir pH and soil pH profiles

Results showed that the pH of anode fluid decreased rapidly from 8.3 to around 1.8–2.5 while the pH of the cathode fluid increased drastically to about 11.5–12.2 within 20 h elapsed time. Such variation of pH is attributed to the water electrolysis reaction which took place in the reservoirs. After EK treatment, in all four tests performed, a sharp soil pH gradient can be seen near the anode. Results show that a general trend in the soil pH profiles along the soil specimen was found: low (2.0) and high (12.0) in the vicinity of anode and cathode reservoir, respectively. Except for the soil near the anode, the soil pH across the cell increased from the initial value of 7.54 to approximately 10–11. These pH changes are greatly associated with the electrolysis reaction and the direction of the EO flow. Normally, for the cationic induced EO flow, because the mobility of the H^+ ion is higher than the OH^- ion, the migration of acid-front would be faster than that of base-front [30]. In this study, a reversed EO flow was produced in the system indicating that the base-

front did overcome the migration of acid-front. In addition, the acid-buffering capacity of clay is high enough to facilitate the migration of base-front to occur. Thus, the base-front generated from the cathode flushed across the soil specimen, consequently increasing the soil pH above the original pH of 7.54. Formation of alkaline zone caused a great increase in the current drop across the soil specimen (Fig. 4) and thus increased in energy expenditure. A slightly lower pH was found in Test 4, which is corresponding to a less amount of reversed EO flow (Fig. 5b). It has been noted that the condition of alkaline pH across the soil cell would cause further desorption of Cr(VI) from soil. At the anode side of the soil, because of the H^+ ion concentration differences between the reservoir and soil, that would lead the pH hardly increasing even though the OH^- ion was continuously swept into this region.

3.6. Redox potential

Because of the electrolysis reactions, the release of electrons from anode resulted in oxidative environment while the electrons were pushed into the cathode and resulted in reductive environment. Due to this oxidizing condition, which took place in the anodic reservoir, results show that the redox potential of anode fluid is maintained at about 300 mV. In addition, the reducing condition of the cathode reservoir made the redox potential of cathode fluid ranged from -300 to -320 mV. Generally, as the potential is greater than 200 mV, the system is considered as slightly oxidative environment, and when it is above 800 mV, it indicated highly oxidizing. The system having redox potential below 200 and 100 mV is considered as slightly and highly reductive environment, respectively [31]. Fig. 7b shows the variations of redox potential profiles along the cell. It seems that values of redox potential were not affected much by the installation of the wall. As seen from these results, slightly oxidizing condition exists only in the soil very next to the anode reservoir, while highly reductive environment prevails throughout the soil specimen of all tests. A highly reductive environment is definitely beneficial for Cr(VI) reduction. Moreover, the high pH across the soil specimen will facilitate Cr(VI) desorption and the precipitation of Cr hydroxide. It is expected that this precipitation will affect the performance of total Cr removal.

3.7. Cr migration and removal

Table 2 shows both Cr(III) and Cr(VI) accumulation in the electrode reservoir for all four tests. The overall mass balance is high (91.5–101.0%) indicating that the experimental error might be neglected. The total amounts of Cr (both Cr(III) and Cr(VI)) accumulated in the electrode reservoir ranged from 260 to 310 mg, indicating the removal of total Cr was not affected much by the installation of the wall. It was expected that the soluble anionic Cr(VI) would travel towards the anode, while cationic Cr(III) would migrate to the cathode during the EK process. As shown in Fig. 7a, the high pH condition that develops across the soil specimen are favorable for the Cr(VI) desorbed and resides in the pore fluid. Thus the migration of negatively

Table 2
Mass balance of Cr removed

Test	Initial soil	Residual soil	Anolyte		Catholyte		Mass balance (%)
	Cr(VI) (mg)	Total Cr (mg)	Cr(III) (mg)	Cr(VI) (mg)	Cr(III) (mg)	Cr(VI) (mg)	
1	738.0	450.5	16.4	157.1	42.5	47.0	91.5
2	739.6	453.5	58.3	112.9	51.0	58.7	98.2
3	740.2	434.8	51.2	128.9	67.4	60.7	101.0
4	736.6	465.8	20.3	52.3	87.1	98.1	95.2

Mass balance (%) = Total Cr in reservoir / (Initial Cr in soil – Residual Cr in soil) × 100.

charged Cr(VI) towards anode is effective. As shown in Table 2, a large portion of Cr migrated into anolyte, which presented mainly as Cr(VI) (52.3–157.1 mg) and the minor of Cr(III) (20.3–58.3 mg). In Test 4, the amount of Cr collected in the anolyte is much less whereas Cr accumulation in the catholyte is higher than the others. The occurrence of such phenomena can be attributed to the variation of EO flow in time (Fig. 5). As aforementioned, a prominent EO flow towards cathode was observed in Test 4 indicating that a higher amount of Cr migrated into catholyte. The low reversed EO flow produced in Test 4 resulted in less amount of Cr migration into anolyte.

In the anolyte, a yellow color was observed and the Cr(VI) concentration was as high as 0.1–0.255 mol/L in spite of the existence of Fe(II) (3.58×10^{-5} to 1.43×10^{-4} mol/L) (Table 3) and the dissolved organic substances that could possibly provide a good reduction source for Cr(VI). As comparing the chromate speciation diagram (Fig. 1), the major chromate specie occurring in the anolyte would be $\text{Cr}_2\text{O}_7^{2-}$ and HCrO_4^- while the major specie in the catholyte is CrO_4^{2-} . It must be noted that the continuously chemical reduction occurring is likely to happen upon the termination of EK process since Fe(II) and humic acid are the most likely electron donors for the reduction of Cr(VI). It is speculated that the existence of Cr(VI) in the anode reservoir is attributed to the diffusion of soluble Cr(VI) caused by the concentration gradient in the vicinity of anode and the migration of the anionic Cr(VI) ions towards the anode. Studies have shown that Cr(VI) could migrate into anode during the electrokinetic remediation [11–19]. The occurrence of Cr(III) in the anolyte might be attributed to:

- (1) The low pH condition that developed the vicinity of anode caused by the Cr(III) migration towards anolyte as reversed EO flow swapped into this region.
- (2) Reduction of Cr(VI) to Cr(III) in anode reservoir is expected because of the existence of Fe(II) (Table 3).
- (3) The slightly oxidative environment (>200 mV) created by electrolysis reaction that prevents possible reduction of Cr(VI) to Cr(III) as mentioned previously.

As shown in Table 2, both Cr(VI) and Cr(III) were found in the cathode reservoir. Similar findings have also been reported in the relevant studies [13,16]. In this study, since a hyper-Cr(VI) concentration exists in the soil, it is expected that more Cr(VI) species would diffuse into cathode, in particular at the beginning of the test. In the cathode reservoir, the concentration of Cr(III) is high due to the migration of Cr(III) into reservoir and the occurrence of secondary electrolysis reaction could reduce Cr(VI) to Cr(III) under such highly reductive environment (redox potential <100 mV). In test 4, a higher amount of Cr was measured in the catholyte, which resulted from a higher amount of EO flux in the test conducted (Fig. 5a). Because a basic medium was generated in the catholyte, all the cationic metal species, that is, Ca(II), Mg(II), Fe(III), and Cr(III) would precipitate as hydroxides in the catholyte when the concentration reaches their solubility limit. Insignificant amount of dissolved Fe(II) and Fe(III) were found in the catholyte as they already precipitated in hydroxide forms. Fig. 8 shows the S.E.M. image of

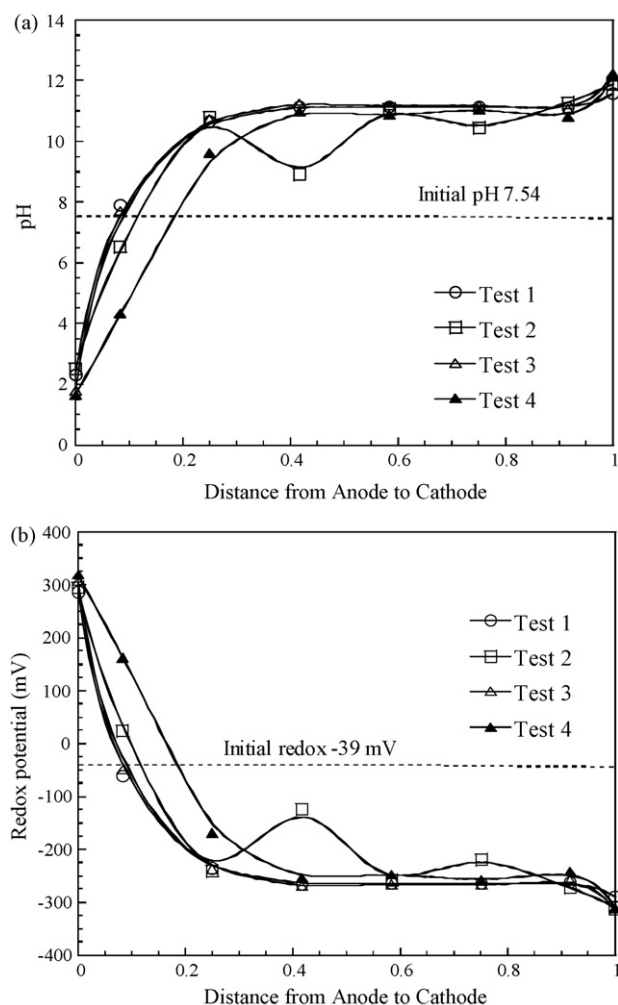


Fig. 7. (a) Soil pH profiles and (b) redox potential distribution in the soil core after EK treatment.

Table 3
Dissolved Fe(II) and Fe(III) measured in the electrode reservoirs

Test	Anode reservoir		Cathode reservoir	
	Fe (II) (mol/L)	Fe (III) (mol/L)	Fe (II) (mol/L)	Fe (III) (mol/L)
1	3.58×10^{-5}	2.63×10^{-3}	ND	3.58×10^{-5}
2	3.58×10^{-5}	4.05×10^{-3}	ND	1.79×10^{-5}
3	5.37×10^{-5}	2.44×10^{-3}	ND	ND
4	1.43×10^{-4}	4.37×10^{-3}	ND	ND

ND: under detection limit.

these mixed precipitates. The results of EDS analysis indicates that the major constituents by weight are O (35.3%), Ca (32%), Mg (19.23%), Si (9.33%), and with the minors of Fe (2.78%) and Cr (1.36%). As shown in Fig. 8, the crystalline structures were believed to be the mixture of $\text{Ca}(\text{OH})_2$ and $\text{Mg}(\text{OH})_2$ precipitates. The sources of Ca and Mg were mainly from the processing fluids.

Upon termination of electric power, the clay specimen was removed from the cell and sliced into six segments. Each segment was analyzed as well as its residual Cr(VI) and total Cr concentrations. Residual Cr(III) was determined by subtracting total Cr to Cr(VI). Fig. 9a–c show the profiles of residual Cr(VI), Cr(III), and total Cr along the soil cell, respectively. The results of all the tests performed showed a reduction of Cr(VI) to Cr(III) throughout the entire specimen. As shown, the major form of Cr remaining in soil was Cr(III), and the minor was Cr(VI). Clearly, the original form of Cr(VI) in soil has been converted to less toxic Cr(III) after EK treatment. Under acidic condition, Cr(VI) can be rapidly reduced to Cr(III) by both Fe(II) and/or organic matter [3,32,33]. During the EK remediation, albeit, the soil without contained the available reductive substances, the occurrence of Cr(VI) reduction was showed [13,14]. Table 4 lists the total Cr and Cr(VI) removal efficiencies after EK treatment. Results in Test 1 (Fig. 9a) show that the EK process could reduced Cr(VI) from 2497 to 395–2076 mg/kg after a 12-day of 1 V/cm treatment. As increasing the electrical voltage up to 2 V/cm (Test 2), the residual Cr(VI) in soil decreased to 329–927 mg/kg for the same treatment period. Albeit, the total removal efficiency of Cr(VI) for Tests 1 and 2 is as high as

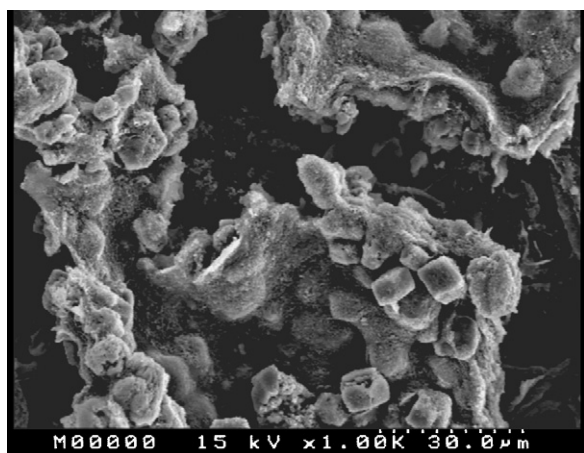


Fig. 8. S.E.M. image of the precipitates from cathode reservoir, 1000 \times .

68.1 and 79.2%, respectively, residual Cr(VI) in the whole soil cell was still high. As shown in Tests 3 and 4, when the wall was installed in the EK process, the Cr(VI) accumulation phenomenon apparently diminished—particularly near middle and cathode regions. With installation of ZVI wall in the EK process, a nearly 100% Cr(VI) reduction was achieved for Tests 3 and 4 in these regions (Fig. 9a). Once the EO flux containing Cr(VI), as it passed through the wall, ZVI can effectively reduced Cr(VI) to Cr(III). As such, the EK process with installation of ZVI wall

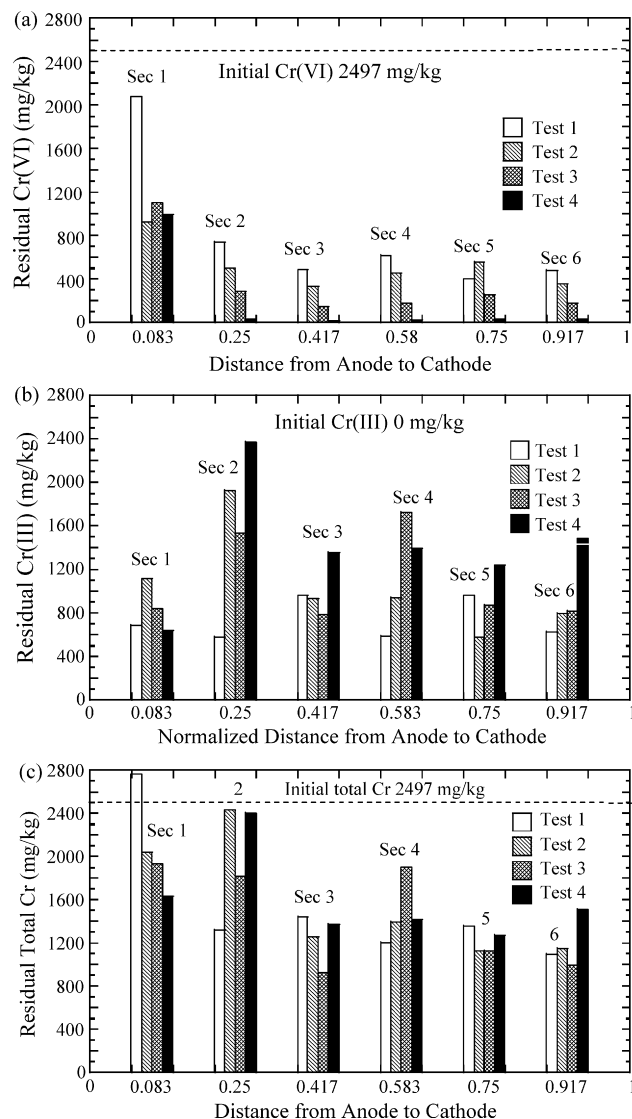


Fig. 9. Residual (a) Cr(VI), (b) Cr(III), and (c) total Cr distribution in the soil.

resulted in a greater Cr(VI) removal. The corresponding total removal efficiency for Cr(VI) increased to 85.8 and 92.5% for Tests 3 and 4, respectively. The results of Cr(VI) reduction in Tests 3 and 4 are consistent with the results of residual Cr(III) distribution (Fig. 9b). As shown, the tests with ZVI wall exhibit more Cr(III) remaining in the soil regions of middle and near the cathode (Fig. 9b), indicating the effectiveness of Cr(VI) reduction by ZVI. Fig. 9b also shows the soil near the anode having a much less Cr(III) remaining. As mentioned earlier, the reversed EO flux could flash the Cr(III) into anode reservoir under low pH condition. More Cr(III) was found in Sec 2 of Tests 3 and 4 of Fig. 9b for the system with ZVI. The phenomenon might indicate that the Cr(VI) in the reversed EO flux was reduced to Cr(III) by ZVI as it passed through the wall. The reaction product Cr(III) resided in the pore solution as it was hardly removed under high soil pH condition (pH 9.5–10.5). When 2 V/cm was applied to the system (Test 4), up to 2368 mg/kg Cr(III) was found in this region (Fig. 9b), indicating the effectiveness of Cr(VI) reduction preferring under a higher electrical voltage system. Because the migration of anionic chromates caused by the reversed flow, the mass of Cr removed near the anode side of the soil (Fig. 9c, first part) is low. In any of the test's results, the total Cr removal is not quite promising. In the second part of Fig. 9c, the residual Cr was equally distributed and about 50% total Cr removal was found in these regions. As shown in Table 4, total Cr removals were only 36, 37.5, 38.9, and 42.1%, for Tests 1–4, respectively. The results revealed that installation of ZVI wall in EK process did not enhance the total Cr removal for a highly Cr(VI) contaminated clay.

Based on the aforementioned findings, the EO advection and electromigration are the two dominant transport mechanisms responsible for the removal of Cr from clay. It is suggested that redox and adsorption/desorption reactions were active during the transport of Cr in the EK operation. Installation of ZVI wall can drastically enhance Cr(VI) reduction. Results of all tests indicated that the migration of reduction product, Cr(III), was hindered due to adsorption and precipitation of the Cr(III) in the soils under alkaline condition developed by reversed EO flow. Such kind of phenomenon would result in a low total Cr removal. In the United States, the current action level of cleanup criteria under Resource Conservation and Recovery Act (RCRA) corrective action for total Cr is 1000 mg/kg. Results of all Tests show that the residual total Cr in the second part of Fig. 9c is slightly over this level. Thus, measures for enhancing treatment of residual Cr concentrations beyond these standards

must be developed. Available effective operation conditions for removal of Cr(III) from soil may be applied including application of neutralization agents such as citric, oxalic, and acetic acids for pH control, switching the electropolarity, and increasing electric current [18,34]. Nevertheless, the EK treatment with ZVI wall has rendered the hyper-Cr(VI) contaminated soil to less toxic form of Cr(III). In this test, the use of a short sample length (12 cm) is critical because the boundaries impact may limit EK transport. In addition, metals in field soil are much more difficult to remove with respect to that of artificially contaminated soils being used in this study. Prior to field application approaches, scale-up researches need to be performed in terms of soil volume, process period, constituents of the processing fluid, electrode spacing, and the dimension of the wall.

3.8. Cost analysis for EK process

Electric power expenditure per cubic meter of soil treated, E_u (W-h/m³), is calculated as follows:

$$E_u = \frac{P}{V_s} = \frac{1}{V_s} \int VI dt \quad (9)$$

where E_u is the energy expenditure (W-h); V_s , the soil volume (m³); V , the applied voltage (V); I , the current (A); and t , processing time (h). For the process keeping a constant-voltage condition, the energy expenditures was expected to related to the time integral of the current across the soil specimen. Table 4 lists the energy consumption as determined from Eq. (9). The values of energy expenditure were 474, 685, 431, and 706 kWh/m³ for Test 1 (1 V/cm), Test 2 (2 V/cm), Test 3 (1 V/cm), and Test 4 (2 V/cm), respectively. Apparently, the value of E_u is directly proportional to the electrical gradient. As shown in Table 4, a higher Cr(VI) removal efficiency was also observed in the test that consumed more electrical energy by comparing Test 1 with Test 2 or Test 3 with Test 4. In comparison with the E_u values shown above, Tests 1 and 2 did not show a substantial increase in E_u while the processing time doubled from 6 to 12 days. Although installation of ZVI wall in the EK system may affect the energy expenditure, the results shown herein did not exhibit a substantial increase.

Table 4 shows the economic analysis of this process. It was noted that the analysis was preliminary because it only accounted the costs of energy expenditure and ZVI for this laboratory study. When it is applied to the field, capital costs, construc-

Table 4
Cr removal efficiency and economic analysis for EK remediation

Test	Total Cr ^a (%)	Cr(VI) (%)	Power expenditure (kWh/m ³)	Energy cost ^b (US\$/m ³)	ZVI cost ^c (US\$/m ³)	Total cost ^d (US\$/m ³)
1	38.9	68.1	474	28.4	0.0	28.4
2	37.5	79.2	685	41.1	0.0	41.1
3	42.1	85.8	431	25.9	15.1	41.0
4	36.0	92.5	706	42.4	15.1	57.5

^a Accounted for Cr(III) and Cr(VI) removals.

^b The current electricity fee in Taiwan is approximately US\$ 0.06 per kilowatt hour.

^c ZVI cost = (US\$ 500/ton) × (5 × 10⁻⁶ ton/g)/(166 cm³ × 10⁻⁶ m³/cm³) = US\$ 15.1 per cubic meter.

^d Total cost is the sum of energy and ZVI costs, which excludes the capital, construction of ZVI wall fees, maintenances and operation fees of EK apparatus.

tion of ZVI wall fees, maintenances, and running costs of EK apparatus should not be excluded. Energy requirement per unit volume of soil treated was 431–706 kWh/m³, equivalent to the energy cost of about US\$ 25–40 per cubic meter based on the current electricity fee in Taiwan. The cost of ZVI per cubic meter of soil treated is about US\$ 15.1 based on the unit price of ZVI (US\$ 500 per ton) and 5 g of ZVI used in the test. As indicated in Table 4, although the total costs for the process with ZVI wall is higher than the process without wall, the process with wall did showed promising Cr(VI) removal results.

4. Conclusions

This paper investigated the effectiveness of incorporating ZVI into EK process to remediate a highly Cr(VI) contaminated clay (2497 mg/kg). Major findings are as follows: a reversed EO flux towards anode was developed shortly after the disappearance of the EO flow, which has not been found in the relevant literatures. The pronounced change in EO flow direction was mainly attributed to the strong migration of anionic chromate ions towards anode. The obtained K_e for reversed EO flow ranged from 0.5×10^{-5} to 1.0×10^{-5} cm²/V-s. The reversed EO flow caused an alkaline condition across the soil cell and created a favorable condition for Cr(VI) desorption from soil. Therefore reverse EO flow promoted migration of Cr(VI) towards anode and consequently accumulated in the anodic reservoir or reduced by ZVI. The removal of Cr(VI) was accomplished by either EO flow or by the reduction of ZVI as the flow passing through the wall. A large portion of Cr ions migrated into anode reservoir as it was dragged by the reversed EO flow, and they presented mainly as Cr(VI) with the minor of Cr(III). Installation of ZVI wall in EK process could increase Cr(VI) removal. A nearly 100% Cr(VI) reduction in the soil was achieved with wall in the EK process under an electric gradient of 2 V/cm. Results show that the total Cr removal is not quite promising in any of the tests performed. The residual Cr was equally distributed and only about 36–42% of total Cr removal was achieved. Tests results indicate that the installation of ZVI wall in EK process did not enhance the total Cr removal for a hyper-Cr(VI) contaminated clay. Those findings indicate that the EO advection and electromigration are the dominant transport mechanisms responsible for the removal of Cr from clay. It is suggested that redox and adsorption/desorption reactions were active during the transport of Cr in the EK operation. The costs for energy and ZVI used in this process are US\$ 41.0 and 57.5 per cubic meter for the processing electric gradient of 1 and 2 V/cm, respectively. The EK treatment with ZVI wall has rendered hyper-Cr(VI) contaminated soil to less toxic form of Cr(III).

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