

ELECTROKINETIC REMEDIATION OF TRICHLOROETHYLENE CONTAMINATED KAOLINITE

Chih-Huang Weng*

Department of Civil Engineering
I-Shou University, Kaohsiung County
Taiwan 84008, R.O.C.

Yu-Hsiung Lin and Yung-Hsu Hsieh

Department of Environmental Engineering
National Chung-Shin University
Taichung, Taiwan 402, R.O.C.

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ABSTRACT

The effectiveness of electrokinetic (EK) process in removing artificially trichloroethylene (TCE) contaminated kaolinite ranging 5~137 mg/kg was investigated. The EK experiments were conducted with Pyrex glass cylindrical cells consisting of three compartments: anode reservoir, soil specimen chamber (17 cm in length and 3.8 cm in diameter), and cathode reservoir. Each reservoir contained 100 mL of synthetic groundwater. The electric gradients ranging from 1 to 3 V/cm were applied to induce the movement of electrolyte solution in the soil cell for 3 days.

The experimental results showed that the direction of electroosmosis flux in all tests was from anode toward cathode for all test. Because the electrolysis had taken place in the reservoir, the pH of anolyte and catholyte were kept at about 2.0~3.0 and 9.5~12.5, respectively. Increasing the electric potential (i_e) could further lower the soil pH across the soil profiles and could enhance the TCE removal efficiency. Although the acidification of clay could alleviate by controlling the processing fluid pH at 12.0, a trade-off TCE removal resulted. The values of electroosmotic permeability (K_e) obtained in this study ranged from 2.0×10^{-6} to 4.0×10^{-5} cm²/V-s. The results also reveal that the K_e values can be correlated to the initial TCE concentration in the clay (C_o) and i_e in accordance with the experimental data. The values of K_e are directly proportional to the values of i_e and the logarithm of C_o . When the processing fluid pH was controlled at 12.0, the K_e values increased about three times of the test run without controlling the pH. Up to 91.2% of TCE removal was achieved for a 3-day treatment at i_e of 1 V/cm. At the same EK conditions to process at C_o of 84 mg/kg and 137 mg/kg, the overall energy expenditure was 15.3 kWh/ton for the former and 8.6 kWh/ton for the later in order to achieve the TCE removal of 75.3% and 53.8%, respectively. This study displays that the cost-effective EK process may be feasible to remove TCE from clayey soils using a direct current.

INTRODUCTION

Trichloroethylene (TCE) is a toxic chlorinated hydrocarbon commonly found in many contaminated sites. Public concerns about the persistent behavior of TCE in soils are its hazard to the environment and a potential source of contamination to groundwater resources. Existing remediation technologies are not applicable for the removal of

chlorinated hydrocarbon, eg. TCE, from rather low hydraulic permeability media, eg. clay. More effective innovative technologies are needed for the decontamination of such kind of soils.

Electrokinetic (EK) remediation process is an innovative technology and has been demonstrated to be successful and cost-effective in removing both organic and inorganic contaminants from low hydraulic conductivity soils in many laboratories and field studies [1-16]. This process in-

* To whom all correspondence should be addressed.

volves the application of an electrical field across a porous medium to induce the movement of electrolyte solution and soluble contaminants toward the electrodes. In this process, the major mechanisms leading to the removal of contaminants from the soil include the advection of electroosmosis (EO) flow driven under electrical field, the movement of H^+ ions generated from H_2O electrolysis at the anode advancing through soil toward the cathode, and the migration of charged ions toward the opposite electrodes [12].

Many researchers have concentrated on studying the removal of heavy metal from contaminated soils by EK. Limited data on the removal of chlorinated hydrocarbon from soils can be found in the literatures. In particular, studies of remediation of TCE contaminated soils are scarce. Bruell *et al.* [5] have confirmed that the EK process has the potential to remove chemicals with relatively high water solubility and low distribution coefficients, such as TCE from kaolin clay. They have reported that a 25% removal was achieved for 3 days of treatment under 0.4 V/cm, and a 99% removal was predicted for 405 days. Most recently, Liu [16] has showed that a combined technology of electrokinetic remediation and Fenton-like process was capable to remove and destroy 88.9% of TCE from contaminated sandy loam soils by applying an electric potential of 1 V/cm. These studies have confirmed that the feasibility of removal of nonpolar chlorinated hydrocarbons, such as TCE by EK process, although the removal performance is not as obvious as the ionic species due to the lack of enhancement of ion migration toward respective electrode.

In this study, the feasibility and efficiency of EK process in the treatment of artificially TCE-contaminated kaolinite were investigated. The removal efficiency of TCE pertaining to the applied voltage, the processing fluid pH, and the soil TCE concentration were presented. An assessment of the EK phenomena including EO flux, electrochemistry, energy requirement affected by the above factors is also presented.

MATERIALS AND METHODS

The kaolinite used in this study was purchased from Associate Kaolin Ind. Co., Malaysia. The properties of the kaolinite are presented on Table 1. In this study, the artificially TCE contaminated kaolinite was prepared by adding appropriate amount of TCE solution and kaolinite into a 2000-mL PE bottle. The mixture was continuously agitated with a rotational agitator (Associate Design & Manufacturing Co., USA) at 30 rpm for 3 days. At the end of the agitating period, the

Table 1. Properties of kaolinite [14]

Characteristics	Values
Specific gravity, g/cm ³	2.60
BET-surface area, m ² /g	22.8
CEC, cmole/kg	1-15
pH _{zpc}	4.5
Soil pH	3.75
Organic matter content, %	0

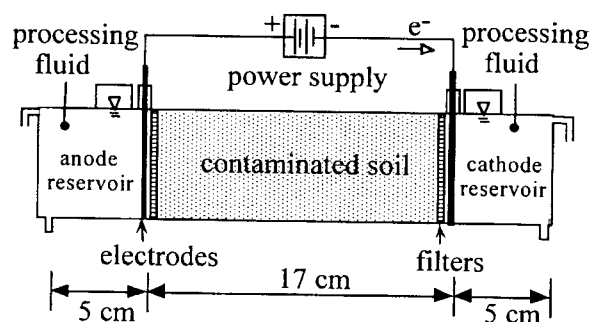


Fig. 1. Schematic of EK decontamination process.

0 meq/L		6.6		10	
Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺		
Cl ⁻	HCO ₃ ⁻		NO ₃ ⁻		
0	4.0		10		

Fig. 2. Recipe for preparation of synthetic groundwater.

wet clay was placed in a soil cell (as shown in Fig. 1). Each cell contained about 330 g of the contaminated clay with a moisture content of $80 \pm 3\%$. The TCE concentration of contaminated clay specimen was determined by gas chromatograph (GC). After the installation, the EK apparatus was sealed with silicon tape to prevent the TCE from vaporizing.

The EK experiments were conducted with a Pyrex glass cylindrical cell which consisted of three parts: an anode reservoir, a soil specimen chamber (17 cm in length and 3.8 cm in diameter), and a cathode reservoir. Each reservoir compartment had a diameter of 3.8 cm and a length of 5 cm (Fig. 1). Synthetic groundwater which filled up each of the reservoirs (100 mL) was used as the processing fluid (conductive medium). The composition of synthetic groundwater was prepared according to the average measured values from five groundwater monitoring stations in southern Taiwan between 1993 and 1996. The

Table 2. The summary of EK process conditions and their results

Test No.	TCE in kaolinite mg/kg	Electric gradient V/cm	Proc. fluid pH	Current density mA/cm ²	Energy expenditure kWh/ton	EO permeability $K_e \times 10^{-6}$ cm ² /V-s	TCE mass collected in the reservoir (%) ^a			% TCE removal ^c
							In Anode	In Cathode	Total ^b	
1	5	1.0	12.0	0.09	3.9	24.6	13	33	46	30.1
2	5	2.0	12.0	0.19	6.4	26.4	12	62	74	34.3
3	5	3.0	12.0	0.58	8.1	39.8	9	67	76	56.9
4	5	1.0	8.3	0.18	7.7	6.3	36	38	74	91.2
5	5	2.0	8.3	0.57	24.3	9.9	39	51	90	91.8
6	5	3.0	8.3	1.09	46.2	12.5	30	62	92	92.5
7	84	1.0	8.3	0.20	15.3	8.5	18	34	52	75.1
8	137	1.0	8.3	0.36	8.5	13.7	14	39	53	53.5
9	0	1.0	8.3	0.10	3.5	2.0	0	0	0	0

^a% TCE collected = (Cumulative TCE mass in the reservoirs ÷ TCE mass removed from the soil) × 100%

^bTotal % TCE collected = % TCE collected in the anode reservoir + % TCE collected in the cathode reservoir

^cTotal % removal = [(Initial TCE mass in the soil cell - Residual TCE mass in the soil cell) ÷ Initial TCE mass in the soil cell] × 100%

recipe of synthetic groundwater in terms of electroneutrality equilibrium diagram is presented in Fig. 2. Fiberglass filter paper was used to separate the clay from water solution at each end of the cell. Two sets of graphite rod electrodes (0.64 cm in diameter, AGKSP, Union Carbon Co., USA) were installed on each side of clay specimen and right behind the filters. The electrodes were connected with a direct-current power supply. In this study, the electrical potential gradients ranging from 1 to 3 V/cm were applied to induce the movement of electrolyte solution in the soil cell for a processing time of 3 days. The detailed experimental conditions are listed on Table 2. During the EK operation, the current, amount of EO flow, and reservoir pH were monitored at every 6 hours of the elapsed time. At the end of each experiment, the clay specimen was removed from the cell and sectioned equally into 6 segments. The soil pH and residual TCE concentration of each section were analyzed.

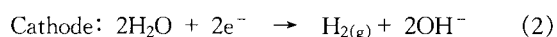
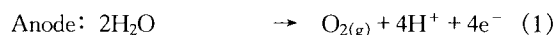
The controlled run (Test 9) without amendment of TCE in the kaolinite specimen while operating for 3 days was designed to compare the electrokinetic phenomena of clays with TCE and without TCE throughout the process. Assembly and disassembly of soil cells might result in a loss of TCE mass due to vaporization. To account for these losses, three sets of cell packed with clay contained identical TCE concentrations were carried for 3 days without the influence of electric potential. This procedure allowed for the correction of experiment data encountered by these losses. Right after sampling, 1~2 g of TCE contaminated clay and 5 mL of n-pentane were added to a glass centrifuge tube, with 10 cm in length and 1 cm in diameter, then it was tightly sealed and horizontally placed in a Branson model 2210 ultrasonic bath for 4 min. The mixture was centrifugally separated. The supernatants were then introduced

to a GC equipped with an electronic controlled detector (GC/ECD, Hewlett-Packard 5890II, USA) to determine the TCE concentration. The data acquisition was accomplished with an IBM-compatible computer equipped with HP3365 Series II ChemStation software. Chromatograph separation was performed on a HP5 capillary column of 30 m (L) × 0.53 mm (ID) at a carrier gas rate of 14 mL/min for He. The temperature programming was isothermally run from 50°C to 180°C for 1 min at an increasing rate of 12°C/min. The detection limit of TCE for such GC method was 5 µg/L.

RESULTS AND DISCUSSION

1. Variation of Reservoir pH

The pHs measured in the reservoirs at various time periods are presented in Fig. 3. This figure shows that the anode and cathode pHs are about 2.0~3.0 and 9.5~12.5, respectively. These values are in good agreement with the findings reported in many EK studies [3-14]. The build up of such reservoir pH values was attributed to the electrolysis of water under an electrical field. The primary electrolysis reaction is given as follows:



The oxidation of water at the anode generates H^+ (Eq. 1), while the reduction at the cathode produces OH^- (Eq. 2). Depending upon the total electric field applied, the reservoir pH can achieve values below 2.0 at the anode and above 12.0 at the cathode [3]. As seen in Fig. 3, increasing the applied electric potential gradient from 1 to 3 V/cm resulted in a decreasing in pH at

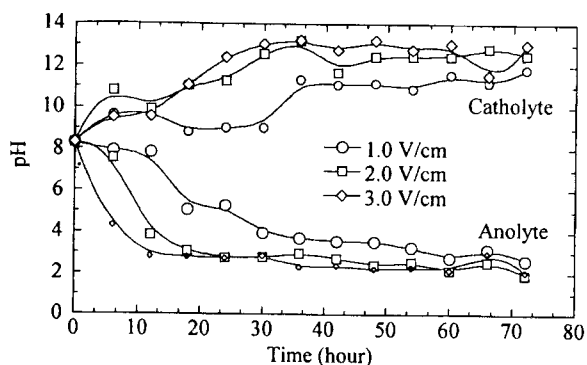


Fig. 3. Anode or cathode reservoir pH versus elapse time.

the anode and an increasing in pH at the cathode when compared with the pH values for the electric potential gradient of 1 V/cm. The enhancement of electrolysis reaction due to the strength of electric field has also been found by Weng *et al.* [14] in studying the removal of phenol contaminated sandy loam soil using tap water as the processing fluid. The occurrence of these reactions in the reservoirs not only could affect the operating fluid condition, but they can also cause the chemical change in soil system during electrokinetics. The movement of H⁺ and OH⁻ in an applied electric field producing acid and basic fronts in time would change the soil pH drastically during the EK process.

2. Electroosmosis Permeability

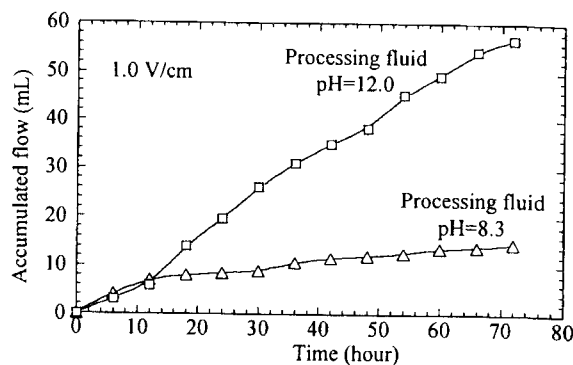
In EK system, the movement of electrolyte solution driven by an electrical field, which carried the desorbed TCE toward the electrodes, is thought to be the major mechanism leading to the removal of TCE from the clay. The movement of electrolyte solution, i.e., electroosmotic flow, Q_e (mL/d) for a cylindrical soil core of length of L and cross-section area of A under a potential difference of E (Volts), can be described by [1]:

$$Q_e = \frac{\zeta \epsilon q}{4\eta} \cdot \frac{E}{L} \cdot A \tag{3}$$

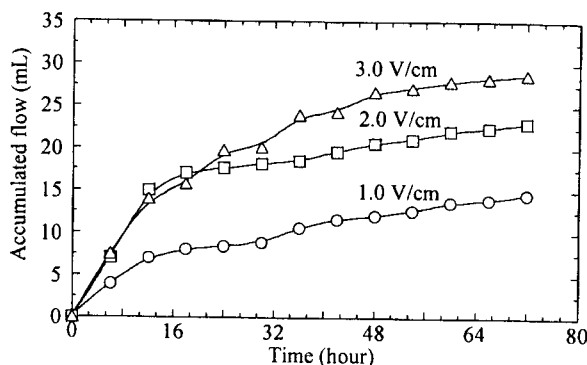
where ζ = zeta potential of the soil, η = viscosity of the fluid, ε = dielectric constant of the fluid, and q = empirical constant related to the soil physical properties. Unlike hydraulic flow which depends on the pressure, the EO flow rate is directly proportional to the applied electric potential gradient and the surface charge of hydrolyzed soil particle. Equation (3) can be rewritten in the form similar to Darcy's equation:

$$Q_e = K_e \cdot i_e \cdot A \tag{4}$$

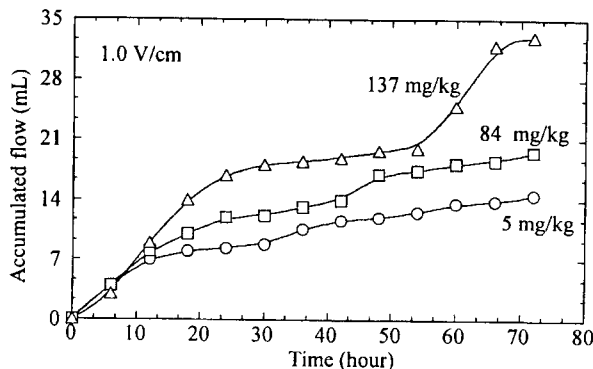
where K_e and i_e are defined as the EO permeability and the potential gradient, respectively. The ex-



(a)



(b)



(c)

Fig. 4. Cumulative EO flow versus time for the effects of (a) processing fluid pH, (b) electric gradient, and (c) initial TCE concentration in the clay.

perimental results showed that the direction of all EO flows was from the anode toward the cathode. The cumulative EO flow in the cathode reservoir as a function of time for the effects of processing fluid pH, electric gradient, and initial TCE concentration in the clay (C₀) is presented in Fig. 4. The calculated K_e values according to Eq. (4) are listed on Table 2. As indicated in Fig. 4, a higher flow rate in Test 1~3 for the processing fluid pH of 12.0 than that in Test 4~6 for pH of 8.3 (Fig. 4a) was observed. It is speculated that the cause

of such difference is related to more negative charged surface of kaolinite by the strong basic solution. Equation (3) shows that the value of Q_e is related to the zeta potential of the clay. The kaolinite has a pH_{zpc} of 4.5 (Table 1). Thus, it is expected that a higher pH environment (i.e. Test 1 ~ 3) exhibits a higher negative value of zeta potential for clay than for a lower pH (i.e. Test 1 ~ 3). As a result, a relatively high electroosmotic flow was found in Test 1 ~ 3. As indicated on Table 2, when the processing fluid pH was controlled at 12.0, the K_e values increased about three times of the test run without controlling pH in corresponding to each of the electrical potential gradient. For example, by applying an electric potential of 3 V/cm, a K_e value of $1.25 \times 10^{-5} \text{ cm}^2/\text{V-s}$ was obtained for Test 6 (pH = 8.3) and $3.98 \times 10^{-5} \text{ cm}^2/\text{V-s}$ for Test 3 (pH = 12.0). The above observation can be attributed to the strong basic solution enhancing the kaolinite surface charged more negatively, and consequently increasing the EO flow.

As shown in Fig. 4b and 4c, the quantity of the cumulated flow increased with increasing electric potential and initial TCE concentration in the clay. Table 2 shows that the values of K_e are in the range of 2.0×10^{-6} to $4.0 \times 10^{-5} \text{ cm}^2/\text{V-s}$ for all tests. It also indicates that K_e value increases with increasing i_e and C_0 . Normally, the K_e values are in the range of 1.0×10^{-6} to $3 \times 10^{-5} \text{ cm}^2/\text{V-s}$ for all soils. Segall and Bruell [6] have reported that K_e values range from 1.5×10^{-6} to $3.7 \times 10^{-5} \text{ cm}^2/\text{V-s}$ for the transport of nutrients in the kaolinite column treated by EO process. Values of K_e ranging from 1.3×10^{-5} to $2.79 \times 10^{-5} \text{ cm}^2/\text{V-s}$ has been reported by Coletta *et al.* [8] in studying cation-enhance removal of lead from kaolinite by electrokinetics. Acar and Alshawabken [15] have recorded K_e ranging from $1 \times 10^{-7} \text{ cm}^2/\text{V-s}$ to $1 \times 10^{-5} \text{ cm}^2/\text{V-s}$ for remediation of lead-spiked kaolinite by a pilot-scale EK process. Therefore, the obtained K_e values are in excellent agreement with the literature data.

An attempt was made to correlate the K_e values with C_0 and i_e in accordance with the values listed on Table 2. First, by plotting the value of K_e obtained from Test 4, 7, 8, and 9 for i_e of 1 V/cm against the logarithm of initial TCE concentration in the clay, C_0 , it yields a linear relationship with a slope of 4.63 and intercept of $2.0 \text{ cm}^2/\text{V-s}$. This linear relationship is formulated as follows:

$$K_e = S_i \cdot \log [C_0] + K_b \quad (5)$$

where S_i = constant related to the potential gradient of i_e , K_b ($\text{cm}^2/\text{V-s}$) = the K_e value of C_0 at 0 mg/kg. The value of K_b is $2.0 \text{ cm}^2/\text{V-s}$ which is directly obtained from Test 9 and is shown on

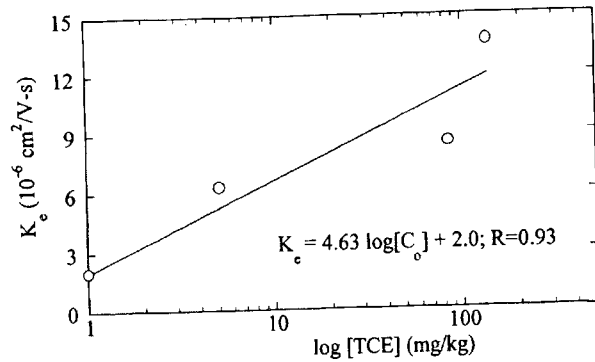


Fig. 5. EO permeability, K_e , as a function of initial TCE concentration in the clay. Electric gradient, i_e : 1 V/cm.

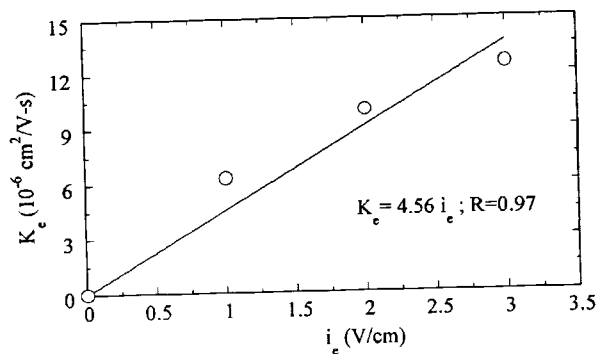


Fig. 6. EO permeability, K_e , as a function of electric gradient. Initial TCE concentration in the clay: 5 mg/kg.

Table 2. The slope, S_i , is 4.63 obtained from the linear plot of Fig. 5. The second approach is to plot K_e value against i_e for the run of Test 4 ~ 6 and that is depicted in Fig. 6. Another linear relationship for K_e and i_e is formulated as follows:

$$K_e = a_c \cdot i_e \quad (6)$$

where a_c ($\text{cm}^3/\text{V}^2\text{-s}$) represents the constant at any initial TCE concentration, C_0 . A value of $a_5 = 4.6 \text{ cm}^3/\text{V}^2\text{-s}$ is obtained for $C_0 = 5 \text{ mg/kg}$. From Eq. (5) and Eq. (6), it is possible to predict the a_c value under the condition of any C_0 while keeping the i_e below 3 V/cm. When C_0 values are 84 mg/kg and 137 mg/kg, the values of $a_{84} = 10.9 \text{ cm}^3/\text{V}^2\text{-s}$ and $a_{137} = 11.8 \text{ cm}^3/\text{V}^2\text{-s}$, respectively. Since K_e values can be correlated to C_0 , a_c , and i_e , the EO permeability coefficient at any applied i_e is therefore determined. It appears that the K_e values are directly proportional to the C_0 and i_e values. In a study of using EK to treat the phenol contaminated loamy sand soil, Weng *et al.* [14] have also reported that an increase in K_e value from 5.7×10^{-6} to $1.12 \times 10^{-5} \text{ cm}^2/\text{V-s}$ while increasing the phenol contaminated concentration

from 190 mg/kg to 1170 mg/kg.

3. Current Density

The decrease in current density with time reflects an increasing in electric resistance. Thus, when a constant voltage is applied to the EK system, the magnitude of current density is proportional to the potential gradient. The current density as a function of processing time for the effects of electric gradients is exemplified by Test 4, 5, and 6 and is depicted in Fig. 7. In the experiment of Test 4, for a constant potential gradient of 1 V/cm, the current density remains a near constant value of 0.2 mA/cm² throughout the processing period. With electric gradient of 2 V/cm (Test 4), the current density gradually increased from 0.3 mA/cm² at the beginning of the test to a maximum value of 0.7 mA/cm² at 45 hours elapsed, and then decreased to about 0.5 mA/cm² at the rest of test period. When the electric gradient of 3 V/cm was performed, the influence of electric potential on current became prominent. As seen in Fig. 7, the current density rose from 0.5 mA/cm² at the beginning of the test to a maximum value of 1.7 mA/cm² at the plateau then decreased to a value of 0.5 mA/cm².

A higher electric current is due to a lower electric resistance. This implied that the greater the constant voltage is applied to the system, the stronger the tendency of conquering the resistance is built up in the system. The primary reason of causing the increase of resistance is the formation of metal hydroxide precipitation near the cathode side consequently upon clogging the pores of the kaolinite. It is noted that the component of groundwater Ca²⁺ and Mg²⁺ are the species which likely interact with OH⁻ to form Ca(OH)₂(s) and Mg(OH)₂(s) near the cathode side. The drawbacks of this build up resistance in the system would lower the EO permeability and eventually retard the TCE transport from the anode toward the cathode end.

As seen in Fig. 7, the plateau becomes prominent while the electric gradient increasing from 1 V/cm to 3 V/cm in a 72 hours of elapsed time. At the beginning stage, the steady rising of the electric current was attributed to the establishment of EO flow channel. Upon reaching a certain time (hence about 45 hours), the formation of hydroxide precipitates resulted in an increase in resistance, and, consequently lowered the electric current. A higher current density results in a greater amount of cumulated EO flow in the cathode reservoir as comparing Fig. 4b and 7. In a study of treatment of TCE contaminated sandy loam soils by electrokinetics-Fenton process using de-ionized water as processing fluid, Liu [16] has re-

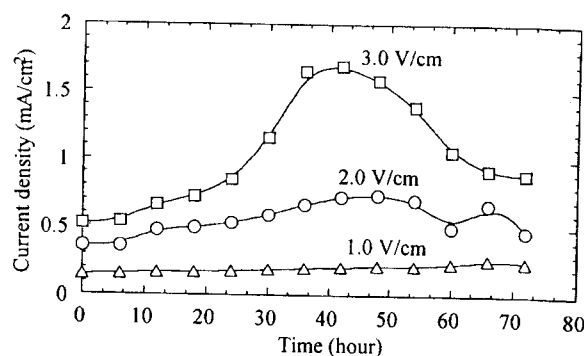


Fig. 7. Current density versus time for the effects of electric gradients.

ported that the current density started at 1.2 mA/cm² and gradually rises to 3.2 mA/cm² after 1.5 days of the operation, then continuously decreased to a steady state thereafter for 10 days. Yang and Long [10] have also observed that a higher electric density would result in a greater EO permeability and the flux of EO increases accordingly.

4. Cumulative TCE in the Reservoirs

Percentages of TCE mass collected in the reservoirs for all tests are listed on Table 2. Percentage of TCE collected less than 100% is attributed to vaporization during the EK experiments. The data shown on Table 2 reveals that TCE mass collected in the cathode (movement of TCE in the cell from anode toward the cathode and collected in the reservoir) rises with increasing potential gradient. An increase in constant electric gradient which resulted in an increase in EO flux has shown in Fig. 4b. Table 2 shows that the amount of TCE collected in the cathode reservoir is directly proportional to the applied voltage. However, the TCE collected in the anode reservoir is inversely proportional to the applied voltage. This finding is in a good agreement to the results of EK treatment of phenol contaminated kaolinite that was done by Weng *et al.* [14]. Since the direction of electroosmotic flow in all tests is from anode to cathode, a portion of TCE appeared in the anode side in all tests might be attributed to the diffusion of TCE causing by the concentration gradient in the vicinity of anode electrode.

5. Soil pH Profiles

The soil pH profiles along the cell affected by the electric gradients, initial TCE concentrations in the clay, and the processing fluid are shown in Fig. 8. The acid front generated at anode reservoir flushed across the clay specimen, consequently lowering the soil pH to values around 2.2~3.8

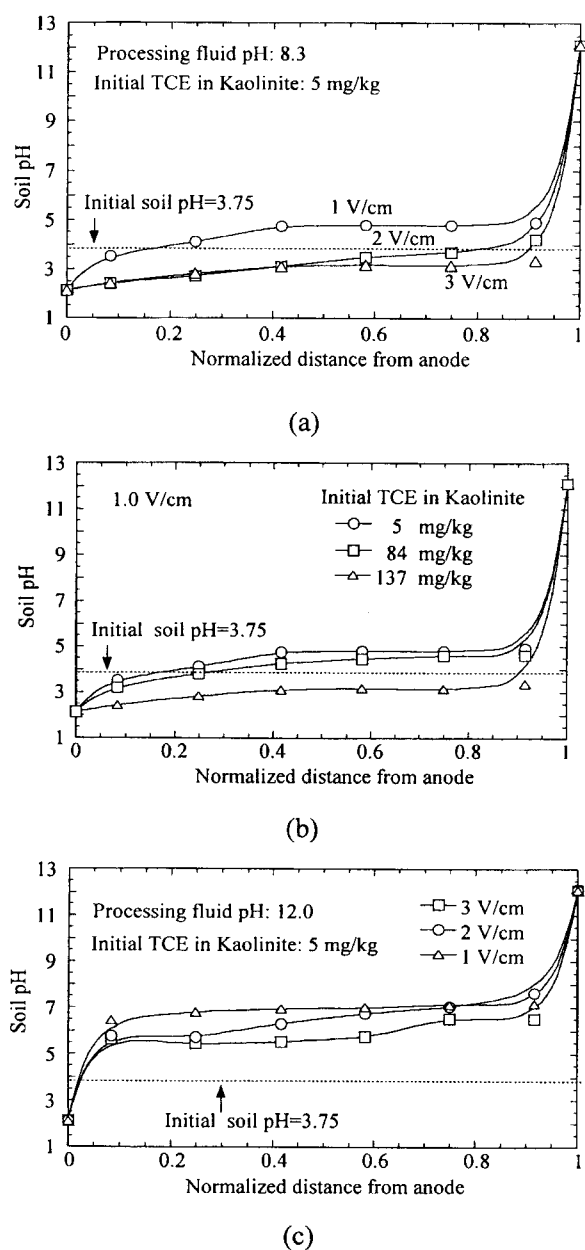


Fig. 8. Soil pH versus normalized distance from anode for the effect of (a) electric gradients (processing fluid pH 8.3), (b) initial TCE concentrations in the soil, and (c) electric gradients. (processing fluid pH 12.0)

in the vicinity of the anode for Test 4~8 except for the Test 1~3 in which the processing fluid pH was controlled at 12.0. Because the acid front was retarded by both the buffering capacity of the clay and the OH^- production at the catholyte which migrated into the soil, the soil pH along the cell did not decrease substantially for tests of electric gradient of 1 V/cm. Once the electric gradient was raised to 2 V/cm or 3 V/cm, it was expected that a stronger acidic electrolyte would produce in

the anode as indicated in Fig. 3. The acid front generated from these conditions would further lower the soil pH. This incident can be found in Fig. 8a. The figure indicates that the soil pH below the original pH of 3.75 across the cell was found as the electric potential increased by more than 2 V/cm.

On the cathode side, the migration of OH^- advances toward the anode and the OH^- ion concentration difference between the reservoir and soil would make the soil pH hardly decrease even though the H^+ ion was continuously swept into to this region. Figures 8a and 8b indicate that the soil pHs near the cathode side were about 3.5~5.0 for the Test of 4~8.

It is interesting to note that the soil pH across the cell is lowered as treating a rather high initial TCE concentration in the clay. The cause of such incidence is directly related to K_e . For a relatively high K_e which was exhibited in the EK system, it indicates that more H^+ ion would transport across the cell and eventually lower the soil pH. Since the K_e value is directly proportional to the initial TCE concentration, a decrease in soil pH as a result of the initial TCE concentration is expected. In the case of the controlling processing fluid at 12.0, all soil pH is greater than the original pH of 3.75 (Fig. 8c). Also, the applied electric potential plays an important role in affecting the soil pH.

In general, increasing the electric gradient and the initial TCE concentration in the clay resulted in a decreasing soil pH. Using a basic processing fluid in the EK process, the acidification of soil could be prevented, however, the removal of TCE from clay is trade-off.

6. TCE Removal

Table 2 summarizes the total removal of TCE from clay for the results from all tests. In Fig. 9, the percentages of TCE removal affected by the electric gradients, processing fluid pHs, and initial TCE concentrations in the clay are presented as a function of normalized distance from the anode for all tests. As seen on Table 2, when electric gradient increased from 1 to 3 V/cm, the total TCE removal is raised from 30.1 to 56.9% for Test 1~3. Apparently, the TCE removal is directly proportional to the applied voltage to the EK system. The profiles of TCE removal along the soil column from anode to cathode are shown in Fig. 9a for Test 1~3. It was found that a nearly 100% TCE was removed in the vicinity of anode side. However, it can be found that the residual TCE concentration near the cathode is still high.

With the processing fluid at pH of 8.3 throughout the EK experiments as for Test 4~6,

the total TCE removed from clay was drastically increased up to about 92%. It appears that this pH value (8.3) was more suitable for the previous pH value (12.0). By comparing the results shown on Table 2, the total TCE removal did not show a better result while the electric gradient rose from 1 to 3 V/cm. Even though the electrical potential gradient increased up to 3 V/cm, a 7% of TCE in the clay was hardly removed after 3 days of the EK treatment. The amount of residual TCE in the clay (0.35 mg/kg) might be accounted as the EK process limitation. A TCE removal profile along the soil cell is demonstrated in Fig. 9b for the results of Test 4~6. As shown in the figure, the TCE removal was not affected much by changing the potential gradient, and an average of 90% TCE removal is found in the soil profile.

As indicated on Table 2, normally, a greater removal of pollutants from clay is associated with a greater K_e value and a less electric resistance across the cell. However, by comparing the results of Test 1 and Test 4, it is seen that an increase in the processing fluid pH by 12.0 has decreased the TCE removal from 91.2 to 30.1%. The desorption of TCE was not affected by variations in pH, but it could decrease under a high ionic strength condition [17]. Since the ionic strength of the processing fluid pH 12.0 is much higher than that of pH 8.3, it gives a reasonable explanation for less TCE removal found in Test 1.

Initial TCE concentration in the clay was another factor affecting the removal efficiency. The results of Test 4, Test 7, and Test 8 for the initial TCE concentrations of 5 mg/kg, 84 mg/kg, and 137 mg/kg, respectively showed that the TCE removals were 91.2%, 75.1%, and 53.8%, respectively, for the EK process operated at 1 V/cm for 3 days. It is seen in Fig. 9d, only about 21% of the TCE was removed near anode and 70% near cathode for Test 8 of treating the 137 mg/kg initial TCE concentration. Under the same EK operating conditions, the higher the initial TCE concentration was processed, the less TCE removal could be expected. In the study conducted by Chen *et al.* [18], when high concentrations of pollutants were applied to the kaolinite surface, enhanced TCE either entered the layer of kaolinite structure or was bonded on the kaolinite surface. The occurrences of these phenomena led to decrease in efficiency of EK decontamination process. Although the outcome of less TCE removal was found at a higher TCE initial concentration in the clay, the total mass of TCE removed was remarkable. Besides, the residual of TCE in the clay could be further removed by changing the operating conditions such as switching the electrodes, prolonging the processing time, and increasing the applied voltage to the soil.

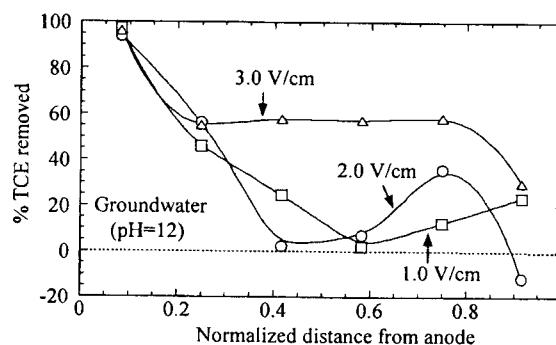
Based on the results described above, the electroosmotic advection is a primary transport mechanism responsible for the removal of nonpolar TCE from clay. Increasing the electric gradient and decreasing the initial TCE concentration in the clay can enhance the removal efficiency. The results also indicated that the removal were not improved by adjusting the pH to 12.0.

7. Energy Requirement

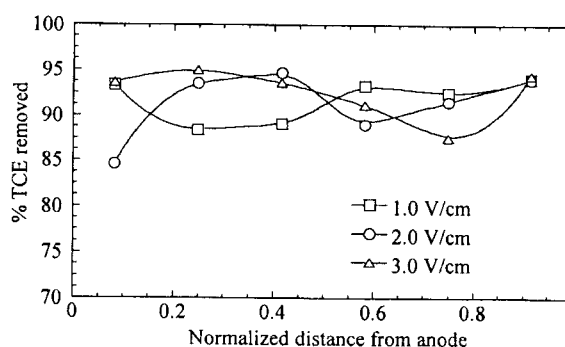
Energy expenditure per unit weight of soil processed is given as [4]:

$$E_u = \frac{P}{W} = \frac{1}{W} \int VIdt \quad (7)$$

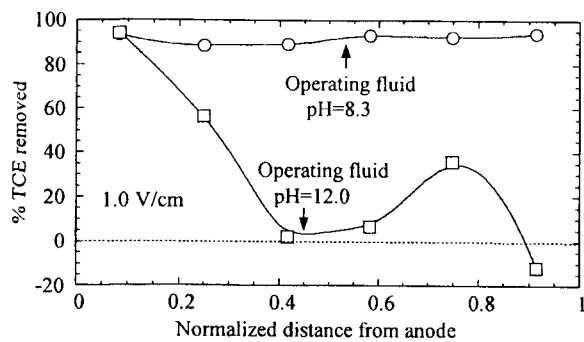
where E_u = energy expenditure per unit weight of soil (watt-hr/ton); P = energy expenditure (watt-hr); W = the weight of soil (ton); V = the voltage (V); I = the current (A); t = the time (hr). In the tests of constant-voltage conditions, the energy expenditure is directly related to the time integral of the current across the cell. As shown on Table 2, the calculated energy consumption upon the termination of the experiments is in the range of 3.9 to 46.2 kWh/ton for Test 1~8. In the absence of TCE in the clay, a relatively low energy expenditure of 3.5 kWh/ton is obtained for Test 9. By comparing the energy requirements of Test 5, 7, 8 with Test 9, it reveals that more electric energy is needed for treating a clay with rather high TCE concentration of 84 mg/kg and



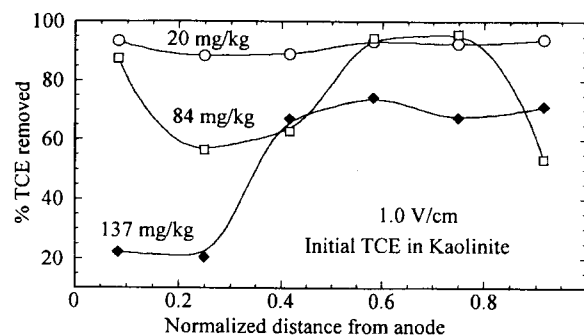
(a)



(b)



(c)



(d)

Fig. 9. TCE removal versus normalized distance from anode for the effect of (a) electric gradients (processing fluid pH 12.0), (b) electric gradients (processing fluid pH 8.3), (c) processing fluid pH, and (d) initial TCE concentrations in the clay.

137 mg/kg. Also, by comparing Test 1 with Test 3, the energy needed increased from 3.9 to 8.1 kWh/ton as the electrical potential gradient increased from 1 to 3 V/cm. A very similar trend was also found in the comparison of Test 4 and Test 6. The energy consumed increased from 7.7 to 46.2 kWh/ton for the same applied potential gradients. Apparently, the energy expenditure is proportional to the applied electrical voltage of the EK system. This study confirmed that EK process is a cost-effective and feasible technology in removing TCE from clay soil.

CONCLUSIONS

This study investigated electrokinetic removal of artificially TCE contaminated kaolinite using synthetic groundwater as the processing fluid. The effects of electric gradient, processing fluids, and TCE contamination levels on the electrokinetic phenomena and the TCE removal efficiency are

presented. The highlights of this paper are summarized as follows:

1. The anolyte and catholyte pHs were about 2.0 ~3.0 and 9.5~12.5, respectively. Decreasing pH order and increasing pH order were found for anolyte and catholyte when a relatively high electric gradient was applied to the cell.
2. The values of electroosmotic permeability, K_e , were in the range of 2.0×10^{-6} to 4.0×10^{-5} $\text{cm}^2/\text{V}\cdot\text{s}$. The observation is in a good agreement with literature data. The values of K_e are directly proportional to the i_e and the logarithm of C_o values. When the processing fluid pH was controlled at 12.0, the K_e values increased about three times of the test run without controlling pH.
3. The acid front generated from an electrical potential higher than 2 V/cm could further lower the soil pH to even below the original pH of 3.75 near the cathode.
4. The results show that TCE removal efficiencies can be enhanced by increasing the electric gradient. Still, about 0.35 mg/kg of residual TCE increasing the clay could not be further removed by raising the electric gradient from 1 V/cm to 3 V/cm for treating an initial TCE of 5 mg/kg kaolinite. The experimental results also show that the tests run with adjusting processing fluid pH to 12.0 did not show a higher TCE removal than the tests run without controlling pH (8.3), although they possessed a higher K_e values. Experimental results indicate that TCE in the kaolinite can be effectively removed by this EK process. Up to 91.2%, 75.1%, and 53.8% were achieved for processing initial TCE of 5 mg/kg, 84 mg/kg, and 137 mg/kg in the kaolinite, respectively, when the EK process operated at 1 V/cm for 3 days. It is believed that the remaining TCE concentration in the clay can be further removed by changing the operating conditions such as switching the electrodes, prolonging the processing time, and increasing the applied voltage.
5. The electric energy expenditure for all experiments was 3.9 to 46.2 kWh/ton, showing that electrokinetic is a cost-effective technology in removing TCE from clay.

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電動力法復育受三氯乙烯污染高嶺土之研究

翁誌煌

義守大學土木工程系

林裕雄 謝永旭

國立中興大學環境工程系

關鍵詞： 電動力、三氯乙烯、高嶺土、復育、土壤

摘 要

本研究目的為探討電動力復育受三氯乙烯 (Trichloroethylene, TCE) 人工污染高嶺土過程所發生之電動力現象及其去除效益。電動力試驗係以內徑3.8 cm、長17 cm 的玻璃試模進行，以人工地下水為操作液，高嶺土中 TCE 濃度為5 mg/kg 至137 mg/kg，施加恆定電壓坡降1~3 V/cm，處理3天。試驗結果發現，電動力進行時，電滲透流向為陽極至陰極，受到電解效應的影響，陰極槽液之 pH 值在操作期間大致維持於9.5~12.5左右，而陽極槽液 pH 值則下降至2.0~3.0左右。增加電壓坡降 (i_e) 及 TCE 污染濃度會增強土壤的酸化及鹼化；若以 pH 12.0之操作液進行電動力處理，雖可減緩酸化的程度，但卻降低 TCE 總去除率。研究結果顯示，電壓坡降小於3 V/cm 時，電滲透係數 K_e 值、TCE 污染濃度及電壓坡降 i_e 彼此間互有關聯： K_e 值與 TCE 濃度維持半對數線性正比例關係，而 K_e 值又與 i_e 成線性正比例關係。以1 V/cm 之電壓坡降，對5 mg/kg TCE 污染高嶺土處理3天，即達91.2%之去除率，而其電力耗損僅為7.7 kWh/ton；相同條件處理含84 mg/kg 和137 mg/kg TCE 的高嶺土，去除率分別達75.3%及53.8%，而電力耗損為15.3 kWh/ton 及8.6 kWh/ton，顯示電動力處理具經濟性可行性。本研究結果證實電動力適用於復育受 TCE 污染之黏質土壤，就經濟效益、安全性、可現地復育等觀點而言，其實場整治應用可行性頗高。

