

The effect of critical operational parameters on the circulation-enhanced electrokinetics

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Abstract

Electrokinetics (EK) is a technique for soil remediation. However, the acid produced due to the water electrolysis at the anode will cause soil acidification, which may destroy the soil constituents, and reduce contaminant removal efficiency. The formation of a base front produced at the cathode will result in the precipitation of metal hydroxides and a concomitant clogging of pore space. In this study, a circulation-enhanced EK (CEEK) system is designed to neutralize the pH of the working solution and soils for avoiding the above problems. Experiments are conducted by controlling different voltage gradients, electrode materials, and electrode emplacement, respectively. According to the experimental results, the CEEK system could effectively stabilize the current and the pH of processing solution at a neutral range. The strength of voltage gradient is proportional to the current magnitude of the CEEK system. The graphite electrode for CEEK is the better choice than the metal electrodes because graphite electrodes can achieve the lower electricity consumption. The electrode installed in the reservoir without attachment on soils can decrease the pH deviation of the soil matrix.

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1. Introduction

The electrokinetics (EK) has been developed for several decades. In the early stage, EK is used to dewater the soil to enhance the soil mechanical stress. Applied to soil remediation, EK process has been regarded as an effective means to clean the sites contaminated by different pollutants such as heavy metals, organic chemicals, and radio nuclide waste [1–5]. The main features of EK techniques (DC, AC) comprise: (1) serving either as an in situ or an ex situ technology, (2) possessing high removal efficiency for different contaminants, (3) producing an electroosmotic (EO) flow in the heterogeneous soils, (4) applicability for the contaminated soils of low hydraulic conductivity, (5) exerting high economical effectiveness, and (6) integrating with other chemical or biological technologies [6,7]. Although EK presents many advantages, the drawbacks of EK process have also been considered. One major disadvantage is the soil acidification dur-

ing EK operation (even the soil acidification may be beneficial to the release of heavy metals from the soil), which may dramatically destroy the soil constituents and cause the failure of the EK system [8]. Especially for the agricultural lands, the fertile soils may not be cultivated after EK treatment due to the loss of organic nutrients and the low pH condition. In Taiwan, most sites contaminated by heavy metals are agricultural lands, therefore, it is expected that the contaminated soils can be recovered for the agricultural usage.

In order to overcome the soil acidification of EK system from the anode compartment toward the cathode compartment (high soil-pH gradient between the anode and the cathode), several innovative techniques have been established such as: (1) the continuous addition of acetic acid (CH₃COOH) at the cathode to buffer the pH of solution and (2) the installation of ion selective membrane such as Nafion membrane between the soil and the cathode for the prevention from metal precipitation [9,10]. In contrast to a simple EK process, these innovative techniques are called “the enhanced EK system”. In this study, an EK process with circulation system is designed to avoid the high pH gradient and soil acidification. According to our previous studies,

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this circulation-enhanced EK (CEEK) demonstrated a slight pH gradient, a stable EO flow rate, and the low current consumption [11].

One pair of electrodes installed into the subsurface with DC current basically constructs an EK system. When the DC current is applied to the EK system, several transport mechanisms will be induced to remove contaminants including electroosmosis, electromigration, and electrophoresis. The electroosmosis is attributed to the excess charges on the soil surface. Under the electrical field, the hydrated ions in the double layer of the soil will be driven from one end to the other, which will move the pore-liquid in the soils simultaneously. When the electroosmotic flow through the soil matrix, contaminants can desorb from soils into the pore-liquid and flush along with the electroosmotic flux. The electromigration and electrophoresis, respectively, represents that the ions and soil particles in the pore-liquid flow from one electrode to the other. For ionic contaminants, the electromigration is the major driving force to transport through soils. In addition to transport mechanisms induced in the soil, some electrochemical reactions occur on the electrode surfaces such as water electrolysis and ion redox reactions [12]. These reactions description can be written as follows with exemplification of the sodium carbonate as the working electrolyte [13]:

Anode:



Cathode:



Moreover, some other chemical reactions including ions precipitation, electroplating, and organic electrolysis also occur in the soil matrix or electrode surfaces [14]. These reactions may occur simultaneously and complicate the process.

Among electrochemical reactions, the water electrolysis is related to the EK performance. According to Eqs. (1) and (3), water molecules will be oxidized into oxygen and protons (H^+) at the anode; simultaneously, water molecules will be reduced to hydrogen and hydroxide ions (OH^-) at the cathode. Depending on the electric current and the charge transform at the electrodes, the pH of solution at the anode may decrease around 2.0 and that at the cathode may increase to 12.0 [15]. The protons will be transported from the anode to cathode under the electrical field and pass through the soil matrix. When these protons react with the soil, it will change the surface charge of the soil, which decreases the EO flow rate and removal efficiency. Chang et al. [16] reported that the EO flow would even cease when the pH of the soil is lower than the pH_{ZPC} of the soil. The value of pH_{ZPC} presents the zero surface charge of soils at this certain pH value, which is relevant to soil mineralogy and pore-liquid composition [17]. The soil acidification may ultimately make the EK system fail due to low pH soil without the EO flow. For the OH^- at the cathode, the formation of a base front will results in the

precipitation of metal hydroxides and a concomitant clogging of pore space.

In comparison with the above EK system, the CEEK system can be operated under relatively neutral pH, stable current and EO flow rate conditions [18]. Although the CEEK has obtained some satisfactory results, several critical operational parameters for real-field application including voltage gradient, electrode material, and electrode emplacement have not been clearly understood. It is essential to learn of the correlations among these operational parameters and CEEK system performance to optimize applying conditions. The purpose of this research is to study and explain the electrochemical effects of voltage gradient, electrode material, and electrode emplacement on the CEEK system. By means of monitoring the pH of working solution and soil, solution conductance, water content of soil, and system current, the electrochemical characteristics of the CEEK system are interpreted and the feasible parameters are found.

2. Materials and methods

Soil samples were collected from an agricultural site near Chaoyang University of Technology located in Taichung County, Taiwan. After 24 h air-dried process, the soil characteristics including soil texture, specific gravity, pH, soil water content, and organic matter content are determined. Table 1 presents the obtained results and their analytical methods. According to Table 1, the soil sample is categorized as a sandy soil with a neutral pH. The water content and the extent of the organic matter is 1.9 and 2.2%, respectively. After putting in the 550 °C oven for 24 h, the extent of organic matter of soil is determined by the weight loss of the soil sample.

Fig. 1 shows the sketch of the laboratory EK reactor. The EK cell is made of PVC with the dimension of 20.0 cm in length, 8.0 cm in width and 10.0 cm in height. It is divided into two compartments: the central one is for storing soil sample and the other is for working solution as reservoir. The soil sample is mixed with electrolyte solution (about 20% water content), then, carefully stowed in the central compartment. To avoid soil leakage to the water reservoir, a pair of nylon meshes (Spectrum model PP, mesh opening 149 μm), and a filter paper (Whatman No. 1) were placed between the soil sample and electrodes. The electrodes are punctured to make the pore-liquid pass from specimen to the solution reservoirs. Constant voltage is delivered by a DC power supply (IP 200-21 DS). A circulation pump is used to carry the working solution from the cathode to the anode for neutralizing its pH.

Table 1
Basic characteristics of the soil

Characteristics	Values	Method
Texture	Sand	ASTM D2217-85
Specific gravity (g/cm^3)	2.1	ASTM D854-92
Soil pH	7.0	NIEA S410.60T
Water content (mass%)	1.9	NIEA S280.61C
Organic matter content (%)	2.2	[19]

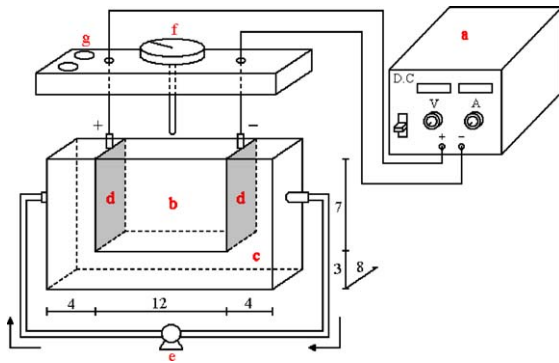


Fig. 1. The schematic diagram of CEEK system: (a) power supplier, (b) soil matrix, (c) solution reservoir, (d) electrodes, (e) circulation pump, (f) thermometer, and (g) sampling hole.

The experimental factors for conducting the EK tests include voltage gradient, electrode material, and electrode emplacement. The voltage gradient of 0.5, 1.0, and 2.0 V/cm is used individually. The electrode material is graphite, titanium coated by platinum (PT), and stainless steel (SS), respectively. In order to test the factor of electrodes position, electrodes are placed at each electrolytic compartment right behind the membranes (electrodes attached on the membranes) and suspended in the reservoir (electrodes hanged in the middle of compartment), respectively. The pH and conductivity of working solution, the system current are measured at selected time intervals; while pH and water content of the soil are determined at the completion of electrokinetic experiments. For obtaining the EO flow rate of CEEK, an individual experiment is conducted. For the experiment, a cathodic electrode without punctures is attached on the specimen and a sampling hole on the central compartment close to cathode end is set, which causes the pore-liquid can be collected to determine the EO liquid volume. The working electrolyte is 0.01 M Na_2CO_3 solution for all experiments. All chemicals were purchased from Fluka Co and the purity is greater than 97.0%. The electric conductivity of working solution is monitored by a conductivity meter (Suntex Co., model SC-170).

3. Results and discussion

For an in situ engineering technique, the operational parameters and the construction of facilities are critical. Because the electricity consumption is a major operation-cost for the EK technique, the well-controlled voltage apparently is a top priority among operational parameters. In addition, the selection of electrode's materials relates not only to electrochemical reactions on the electrode surface but also to the remediation cost. The installation position of electrode will influence the construction engineering and may induce some impacts on the EK system. Accordingly, the voltage gradient, electrode material, and electrode emplacement play the critical roles for the CEEK process.

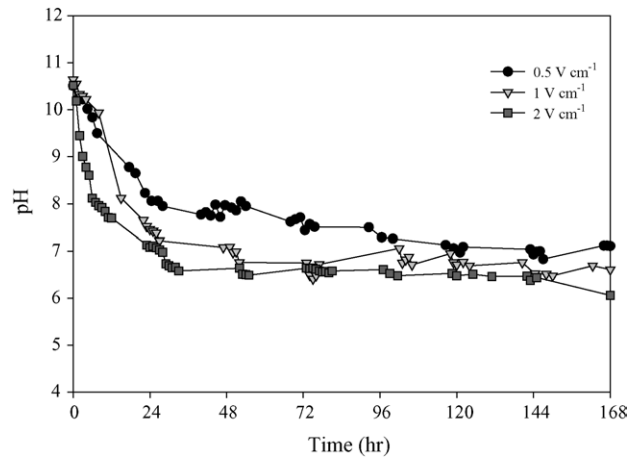


Fig. 2. pH of working solution vs. operation time under different voltage gradients.

3.1. Effect of voltage gradient

High voltage may enhance ionic contaminants mobility and increase electrochemical reactions rates particularly at the anode, thus producing more protons and decreasing electroosmotic transport. In contrast, low voltage may not sufficiently clean up the contaminated soil. Hence, it is necessary to gain insight into the effect of voltage gradient on the CEEK and find out the appropriate operational values.

3.1.1. pH and conductivity

Figs. 2 and 3 show, respectively, the pH and conductivity variation of working solution as a function of operation time under different voltage gradients. It can be seen that all pH and conductivity variations approach to a similar trend, that is, pH and conductivity decreased in the beginning and gradually reached a stable status. During the CEEK operation, the processing solution is continuously neutralized with H^+ and OH^- by circulation system because water electrolysis produces acid and base at anode and cathode, respectively. The pH of the solution, thus, changes and gradually reaches the equivalent titration point of the electrolyte. In other words, the reaction of water electrolysis

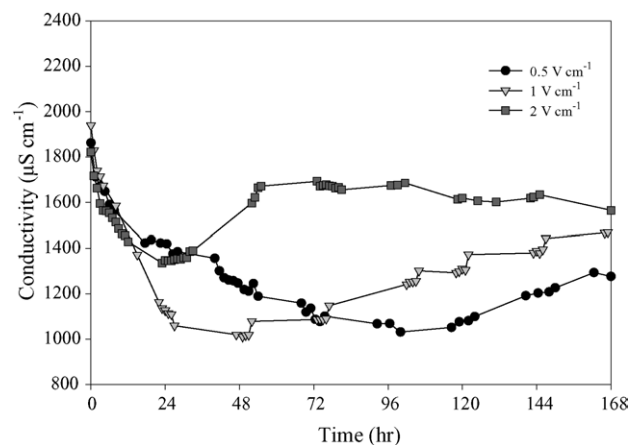


Fig. 3. Conductivity of working solution vs. operation time under different voltage gradients.

dominates the pH kinetic behavior. Since the reaction rate of water electrolysis is related to the electric potential, electrode surface properties, temperature, etc., it is difficult to quantify the dynamic phenomenon in detail. However, the change rate of solution pH increases with the increase of voltage gradient as expected. When the CEEK reaches the steady state, the magnitude of stable pH is attributed to the electrolyte species. As the solution is in the presence of the electrolyte with high equivalent titration point (i.e., high pK_a value), its pH is relatively high. In this study, the equivalent point of carbonate ($pK_a = 6.37, 10.33$), which causes the average solution pH under 0.5, 1.0, and 2.0 V/cm maintain around 7.1, 6.6, and 6.0, respectively. All pH values in the CEEK system are close to the equivalent point of carbonate and different voltage gradients alter the pH of processing solution slightly.

From Fig. 3, it can be observed that the conductivity dropped in the beginning, then, it increases gradually depending on the applied potential. The magnitude order of solution conductivity followed the sequence of $0.5 < 1.0 < 2.0$ V/cm. This can be attributed to the voltage gradient that influences the solution pH which in turn has a significant correlation with the solution conductivity. In general, the solution conductivity can be roughly calculated by the total conductivities of ions in CEEK system. As exemplified by sodium carbonate, the equation of computing total conductivity presents as follows:

$$\begin{aligned} \kappa_{Na_2CO_3(aq)} = & \Lambda^{\circ}_{H^+} \cdot C_{H^+} + \Lambda^{\circ}_{OH^-} \cdot C_{OH^-} \\ & + \Lambda^{\circ}_{H_2CO_3} \cdot C_{H_2CO_3} + \Lambda^{\circ}_{HCO_3^-} \cdot C_{HCO_3^-} \\ & + \Lambda^{\circ}_{CO_3^{2-}} \cdot C_{CO_3^{2-}} + \Lambda^{\circ}_{Na^+} \cdot C_{Na^+} \end{aligned} \quad (5)$$

where κ represents the conductivity (S/m); $\Lambda^{\circ}_{H^+}, \Lambda^{\circ}_{OH^-}, \dots, \Lambda^{\circ}_{Na^+}$ represent the molar ionic conductivity ($S\ m^2/mol$) at infinite dilution; $C_{H^+}, C_{OH^-}, \dots, C_{Na^+}$ represents the concentrations of different ions (mol/m^3). Among all ionic species in the CEEK system, high ratio of conductivity contributed by H^+ and OH^- due to their high molar ionic conductivities ($H^+ = 349.8$ and $OH^- = 199.2\ S/(m^2\ mol)$). It indicates that the solution conductance is dominated by the water electrolysis. When the pH value is close to 7.0, the total concentration of H^+ and OH^- is the lowest in comparison with other pH value. Therefore, values of conductivity increase with decreasing pH.

3.1.2. pH and water content of soils

After 168 h treatment, the soil matrix is divided into four sections A, B, C, and D from the anode to cathode. Fig. 4 shows the distribution of soil pH of each section under different voltage gradients. Results present that the soil pH in section A ranged from 3.0 to 8.5, those in section B ranged from 6.5 to 9.5, those in section C ranged from 10.0 to 11.0, and those in section D ranged from 10.5 to 11.5, respectively. Considering the average value of each section, soil pH close to anode is the lowest (section A) and that close to the cathode is the highest, which is in agreement with the results reported by Narasimhan and Ranjan [20]. This can be attributed to the H^+ produced at the anode that acidified the soil vicinity (section A) resulting in the lowest pH. In contrast, the OH^- from the cathode causes the highest soil

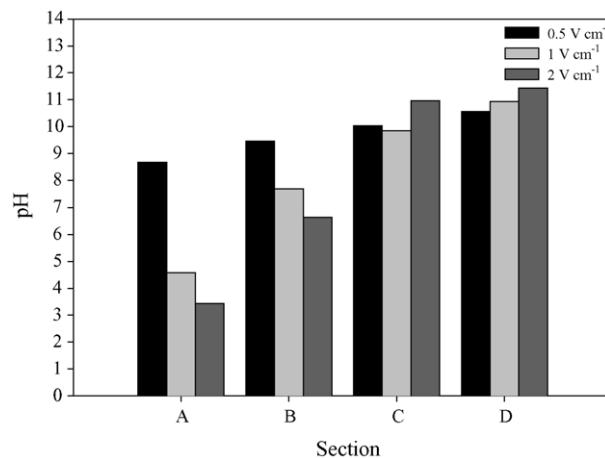


Fig. 4. Distribution of soil pH under different voltage gradients.

pH of section D. In addition, the soil pH will be also influenced by the pH of working solution since the solution in the reservoir will enter the soil specimen by electroosmosis. Therefore, the soil pH of sections B and C depends on the mixing status of acid and base front induced by water electrolysis and electroosmosis. It is noticed that the soil matrix possessed a higher pH gradient when the EK system employs high voltage gradient. This phenomenon is also influenced by the reaction of water electrolysis, which may result in the system failure especially after a long-term operation. For the consideration of water content of soils, the water content of soil in all sections remain from 18 to 22% based on experimental data (not shown in the paper). Comparing with the initial water content (20%), results indicate that water content of soil in this CEEK system can be maintained stable regardless the voltage gradient. This implies that the EO flow rate and the infiltration rate of the tested soils (i.e., sandy soils) can reach certain balanced status.

3.1.3. Current and EO flow rate

Fig. 5 shows the current of CEEK as a function of time for different voltage gradient values. Each current results from 0.5, 1.0, and 2.0 V/cm operation decreases initially, then, maintains around 15, 20, and 60 mA, respectively. The current is pro-

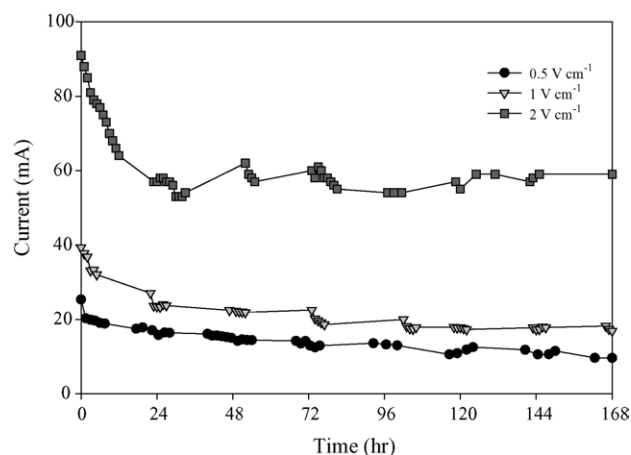


Fig. 5. Current vs. operation time under different voltage gradients.

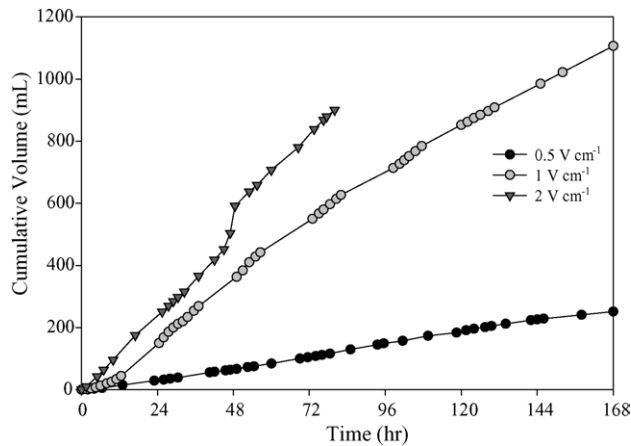


Fig. 6. EO Cumulative volume vs. operation time under different voltage gradients.

portional to the voltage gradient in certain degree. Since the system current is related to the electric resistance of electric wire, solution conductivity, soil properties, etc., the correlation of the current with the various factors is complex. However, the current decreases initially and approaches to a stable value, which is similar to the varying trend of pH and conductivity. For the current, not only the solution conductivity but also the electric resistance of the soil specimen influences its variation. The various current may reflect the various electric resistance of the soil specimen when the solution conductivity remains stable.

Fig. 6 shows the cumulative fluid volume of EO flow versus operation time under three different voltage gradients. Results present that the EO flow rate increases with increasing voltage gradient. Since the pore volume of the soil specimen is around 280 mL, it needs 13, 21, and 85 h, respectively, as each EO flow under 2.0, 1.0, and 0.5 V/cm replaced one pore volume of the specimen. That is, the EO flow rate under 2.0 V/cm is almost two times and six times faster than that under 1.0 and 0.5 V/cm, respectively.

For consideration of EO flow rate, the EO permeability coefficient, K_e , serves as the critical index to present the EO flow characteristics of the soil. The K_e value can be obtained by the equation of EO volumetric flow rate, Q_e , which correlates with the physical–chemical properties of soil, the characteristics of electrolyte, and voltage gradient [21]. The formula is as Eq. (6) and simplified as Eq. (7).

$$Q_e = \frac{\zeta \varepsilon}{4\pi\eta} \cdot \frac{E}{L} \cdot A \quad (6)$$

where Q_e is the EO volumetric flow rate (mL/s), ζ the soil zeta potential (V), ε the dielectric constant of pore-liquid (C/(V cm)),

η the kinetic viscosity of pore-liquid (N s/cm²), L the soil column length (cm), E the electric potential (V cm), and A the cross sectional area (cm²).

$$Q_e = K_e \cdot i_e \cdot A \quad (7)$$

where Q_e is the EO volumetric flow rate (mL/s), K_e the EO permeability coefficient (cm²/(V s)), i_e is the voltage gradient (V/cm).

Table 2 lists the EO flow data through the CEEK system that computed by Eq. (7). The EO flow rate is 4.16×10^{-4} , 1.83×10^{-3} , and 3.13×10^{-3} mL/s at the voltage gradients of 0.5, 1.0, and 2.0 V/cm, respectively. The corresponding EO permeability coefficients are 1.48×10^{-5} , 3.27×10^{-5} , and 2.79×10^{-5} cm²/(V s). For the values, Acar et al. [22] reported K_e values generally ranged from 10^{-6} to 2×10^{-5} cm²/(V s); Lin [23] reported K_e values ranged from 4.8×10^{-6} to 2.2×10^{-5} cm²/(V s) as the voltage gradient ranged from 1.0 to 3.0 V/cm; Musso [24] reported most K_e values ranged from 0.3×10^{-5} to 10.0×10^{-5} cm²/(V s) for different soil types and electric employment. Compared with the above research, the EO permeability coefficients of the CEEK are slightly high among those of other EK systems. Although, this result cannot guarantee that the CEEK system is the better EK system due to the comparison based on different soil samples, the CEEK system presents the acceptable EO flow performance.

3.2. Effect of electrode materials

Since different electrode materials may induce different oxidation or reduction reactions, various products will be produced in the CEEK system. Besides, the diffusion, adsorption, and desorption behaviors of the reactants on the electrode surface will also differ with various electrode materials. Accordingly, the electrode material will influence the CEEK performance and the electrode material is thus a critical operation factor.

3.2.1. pH, conductivity, and current

Fig. 7 shows the pH variation versus operation time with different electrode materials. In the beginning of operation, the pH curves of all used electrode materials overlap. After 24 h, the pH of electrolyte of the graphite electrode approaches stable condition maintained around 7.0. The two metal electrodes result in a lower pH (around 4.0). On the electrode surface, the chemical reactions consist of water electrolysis and other reactions. The dynamics of electrochemical reactions correlates to the over-potential, which is the gap between the practical and ideal reaction potential. Different electrode materials will possess different over-potentials for the same electrochemical

Table 2
EO permeability coefficient under different voltage gradients

Voltage gradient (V/cm)	Operation time (h)	Cumulative volume (mL)	EO volumetric flow rate (mL/s)	Cross section area (cm ²)	EO permeability coefficient (cm ² /(V s))
0.5	168	251.4	4.16×10^{-4}	56	1.48×10^{-5}
1	168	1106.48	1.83×10^{-3}	56	3.27×10^{-5}
2	80	900.5	3.13×10^{-3}	56	2.79×10^{-5}

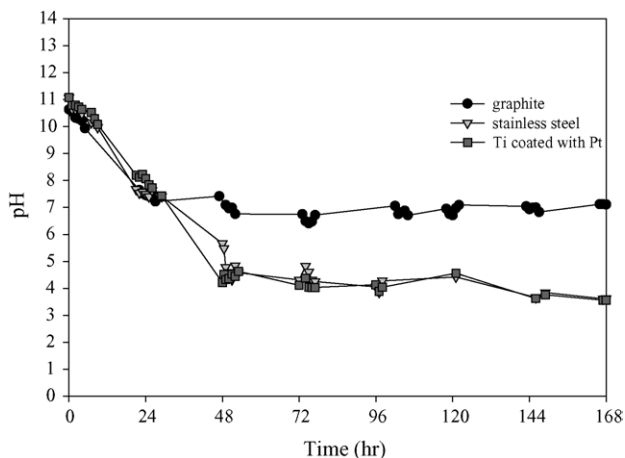


Fig. 7. pH of working solution vs. operation time with different electrode materials.

reaction. Since the pH is mainly controlled by water electrolysis, the low pH indicates that the over-potential of water electrolysis on the metal electrodes is relatively low. In contrast, the over-potential of water electrolysis on the graphite is relatively high.

Fig. 8 shows the conductivity variation as a function of operation time with different electrode materials. The variation trend of conductivity is similar to that of pH, i.e., the conductivity decreased in the beginning of 24 h. At that moment, the pHs for all electrodes are around 7.0, which results in quite identical conductivity. Afterwards, the conductivity for TP and SS gradually increases since the pH value decreases to acidic condition as shown in Fig. 7. Additionally, the metal electrode may produce ionic products because of the oxidation reaction occurrence at the anode. However, the conductivity for graphite behaves relatively stable due to its noble feature and the pH maintains at neutral stage throughout the whole testing time. Considering the conductivity, the graphite electrode performs better effectiveness than metal electrodes.

Fig. 9 presents the current variation versus operation time with different electrode materials. The current decreases dramatically in the beginning of operation time and gradually reaches a steady state for all electrode materials. As mentioned in the sec-

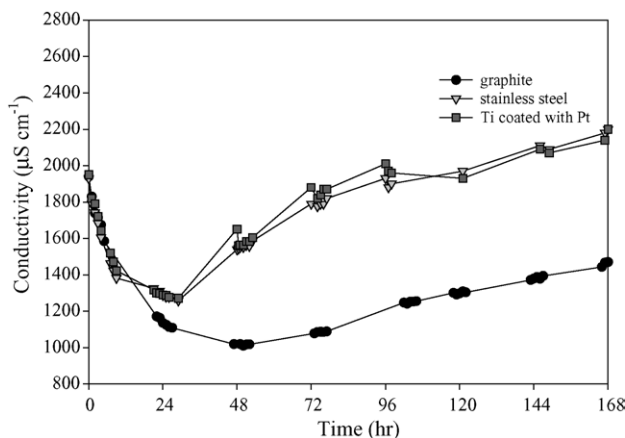


Fig. 8. Conductivity of working solution vs. operation time with different electrode materials.

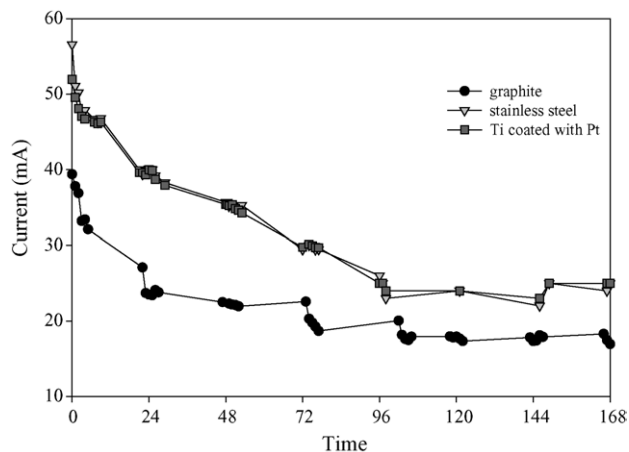


Fig. 9. Current vs. operation time with different electrode materials.

tion for discussing effect of voltage gradients, the various current reflects the various electric resistance of the soil specimen when the solution conductivity remains stable. Results imply that the electric resistance of the soil specimen increased in the beginning of test, then, approaches to a steady value. For the TP and SS electrodes, the currents are similar to each other, which may be attributed to their metal characteristics. In comparison with the two metal electrodes, the current of graphite is relatively low at the same voltage gradient. Because the electricity consumption is a major operational cost for CEEK, the low current is preferred as an operation condition. Therefore, graphite for CEEK is the valid electrode due to its features of neutral pH, low conductivity, and current.

3.2.2. pH and water content of soils

Fig. 10 shows the pH of soils treated by different electrode materials. Results indicate that the pH of soil at anode ranges from 3.2 to 4.8 and that of soil at cathode ranges from 11.0 to 12.0. It is noticed that the soil pH variation disagreed with the pH of working solution shown in the previous section. If the neutral pH of solution passes through the soil matrix, the soil pH should maintain in a neutral range. However, the pH

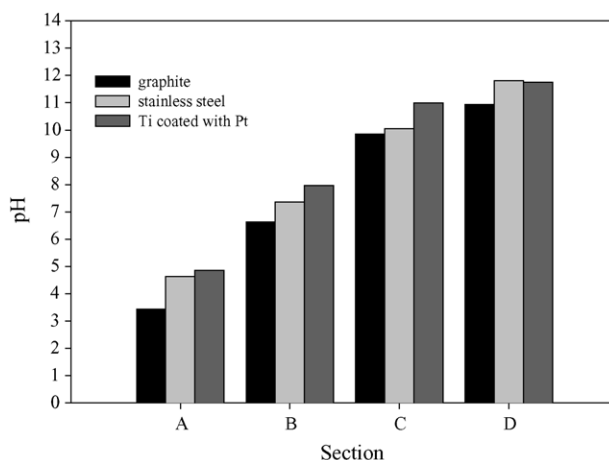


Fig. 10. Distribution of soil pH with different electrode materials.

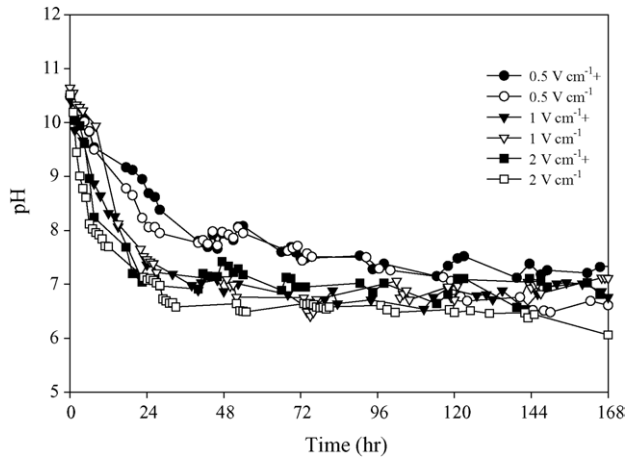


Fig. 11. pH of working solution vs. operation time with different electrode emplacements.

deviation of graphite electrode is greater than that of the two metal electrodes. This reveals that the acid and base produced at anode and cathode surfaces enter the soil matrix directly. Thus, it can be extended that the pH deviation between the soil and electrolyte may increase under a long-term operation. Like other experimental results, the water content of soils still ranges from 18 to 22% after 168 h running.

3.3. Effect of electrode emplacement

According to the previous study, the pH gradient of the soil matrix is still too high in the CEEK system. Since the products of the anode and cathode may pass through the soil directly, we suspend the electrodes in the reservoir to avoid the electrode attachment with the soil. By comparison with the previous results, we can distinguish the difference of two electrode emplacements.

3.3.1. pH, conductivity, and current

Fig. 11 shows the pH versus operation time with two electrode emplacements and three voltage gradients. The curves with notation of “+” are the results from tests with the electrode suspension. According to the figure, the pH of working solution is similar to the previous results that the electrodes attached on the soil surface. That is, the pH decreased dramatically in the beginning, then, maintained at a certain range. Likewise, the current variation versus operation time with two electrode emplacements is similar (data not shown). However, the conductivity variation of working solution based on electrode suspension presents more stable than that based on the electrode attached on the soil surface.

3.3.2. pH and water content of soils

Fig. 12 shows the pH of soils treated by different electrode emplacements. All soil pHs of four sections maintain around 8.0 when the electrodes are suspended in the reservoir. Even when the voltage gradient varies, the soil pH remains constant. Therefore, the new emplacement can prevent the soil from acid and base entrance and effectively improve the deviation of the soil pH. To the consideration of the water content, the water con-

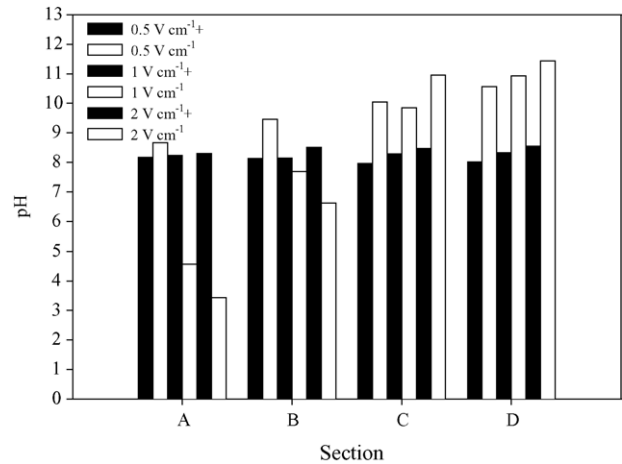


Fig. 12. Distribution of soil pH with different electrode emplacements.

tent of soils under different electrode emplacements still ranged from 18 to 22% after 168 h, which is similar the previous data. To sum up the above illustration, the emplacement of electrodes in the reservoir is a feasible alternative.

4. Conclusions

The CEEK process that can maintain a stable electroosmotic flow and the neutral pH range is with highly potential to remediate the agricultural soils in Taiwan. For the well-control application to real sites, several conclusions can be drawn according to the experimental results and theoretical interpretations:

1. The CEEK system can effectively stabilize the pH of processing solution at neutral range and the current at stable status with graphite electrode.
2. The high voltage gradients caused the fast electrochemical reaction rate, which resulted in the soil acidification rapidly. The voltage gradient is proportional to the current in the CEEK system.
3. Under an identical voltage, the operational current of metal electrode is higher than that of graphite. Because graphite electrode can obtain the neutral pH and low current consumption, it is an appropriate electrode material for CEEK.
4. The pH of working solution, conductivity, and current is almost the same regardless of the electrode suspended in the solution reservoir or attached on the soil surface. The electrode installation in the reservoir can improve the pH deviation of the soil matrix, which avoided the soil acidification in the CEEK.

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