

Electrokinetic remediation of soft clay soil contaminated with heavy metals



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ABSTRACT

This study was carried out to investigate the effectiveness of electrokinetics to remediate soft kaolinite clay soils contaminated with copper and cadmium at concentration of 150 mg/kg. The tests were performed in four identical electrokinetic columns. An electric field intensity of 140 V/m was applied during 118 hr of remediation with the top electrode serving as the anode and the bottom electrode serving as the cathode. The results showed that electrokinetics was effective in removing water from the contaminated soil and the highest removed volume was 2070 ml compared to 693 ml in the control. Electrokinetic was effective in removing part of the heavy metals from most of the contaminated soil with the highest removal of 89% near the anode.

RÉSUMÉ

Cette étude a été réalisée pour étudier l'efficacité de l'électrocinétique pour assainir les sols mous argile kaolinite contaminée avec du cuivre et du cadmium à une concentration de 150 mg / kg. Les tests ont été effectués dans quatre colonnes identiques électrocinétique. Une intensité de champ électrique de 140 V / m a été appliqué au cours de 118 h de l'assainissement avec le haut électrode servant d'anode et le fond électrode servant de cathode. Les résultats montrent que électrocinétique a été efficace pour éliminer l'eau du sol contaminé et le volume le plus élevé a été supprimé 2070 ml contre 693 ml dans le contrôle. Électrocinétique a été efficace pour éliminer une partie des métaux lourds de la plupart des sols contaminés par le plus grand retrait de 89% près de l'anode.

1 INTRODUCTION

Heavy metal contamination of soil is a major environmental concern that in general occurs from mining waste, particularly from abandon mines, improper treatment of industrial waste, leakage of landfill leachate, accidental spills and military activities (Gidarakos and Giannis 2006). In the presence of a hydraulic gradient, the heavy metal pollutants, especially the ones with high solubility in water, can spread to the surrounding areas and nearby water resources and pose health hazards for human and animal life.

Electrokinetic remediation is an emerging technology for cleaning up contaminated soils. It can be particularly effective in fine-grained soil as the technology has the ability to promote fluid and mass migration through soil with low permeability. The contaminants are mobilized and eventually recovered by passing a low-level direct current (dc) between a row of positively charge electrodes (anode) and negatively charged electrodes (cathode) inserted into the ground (Acar and Alshawabkeh 1993; Lynch et al. 2007). The technology exploits two transport mechanisms: electro-osmosis and electro-migration. Electro-osmosis is the movement of water in the soil pores from the anode toward the cathode that results from an applied electric field gradient and electro-migration is the movement of ions in solution toward the oppositely charged electrodes. The flow rate of water, q_e (m³/s), drained by electro-osmosis process from a soil mass with a cross-sectional area perpendicular to the direction of flow A (m²) is given by:

$$q_e = k_e E A \quad [1]$$

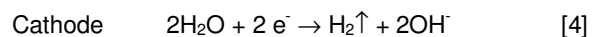
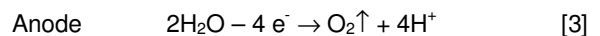
where k_e (m²/sV) is the electro-osmotic permeability, E (V/m) is the electric field intensity defined as $E = -\nabla U$, U is the electric potential (V), and ∇ is the del vector.

In electro-migration, the rate of ionic movement towards the oppositely charged electrode is quantified by the effective ion mobility, u_i (m²/sV), which is defined as the velocity of the ion in the soil under the influence of a unit electrical field intensity and can be evaluated by (Koryta 1982):

$$u_i = \frac{D_i z_i F}{RT} \tau n \quad [2]$$

where D_i (m²/s) is the diffusion coefficient of ion species j in dilute solution, z_i is the valence of ion species j , F is the Faraday's constant (96487 C/mol), R is the universal gas constant (8.314 J/(mol K)), T is the absolute temperature (K), τ is the tortuosity factor, and n is the porosity of the soil.

Electrolysis reactions occur at the electrodes in an electrokinetic process. The reactions results in oxidation at the anode generating an acid front and reduction at the cathode producing a base front as:



This experimental study was carried out to investigate the effectiveness of electrokinetics to remediate soft kaolinite clay contaminated with two heavy metals, namely, copper and cadmium. Copper and cadmium were

selected as a representative of heavy metal pollutions because of their toxicity and extensive existence.

2 EXPERIMENTAL PROGRAM

2.1 Soil Properties

The clay soil tested in this study was obtained from Plainsman Clay in Medicine Hat, Alberta. Kaolinite is the predominant mineral in the clay. The Unified Soil Classification System (USCS) group symbol for the soil is CL (lean clay). Table 1 summarizes the properties of the kaolinite clay.

Table 1. Characteristics of the kaolinite clay

Characteristics	
Liquid limit	35
Plastic limit	20
Water content (%) [*]	50
Clay size (%)	42
Silt size (%)	50
Sand size (%)	8
Specific gravity	2.67

*water content of soil specimen after preparation

2.2 Experimental Apparatus

The experimental equipment consisted of four identical electrokinetic testing columns. The column, 500 mm high, was made of a 6 mm thick and 190 mm inside diameter clear Plexiglas cylinder. A drainage valve was installed at the base of the column. The electric current was provided with a dc power supply with a capacity of 300 W and maximum ratings of 60 V and 5 A. Figure 1 shows the schematic of the electrokinetic column.

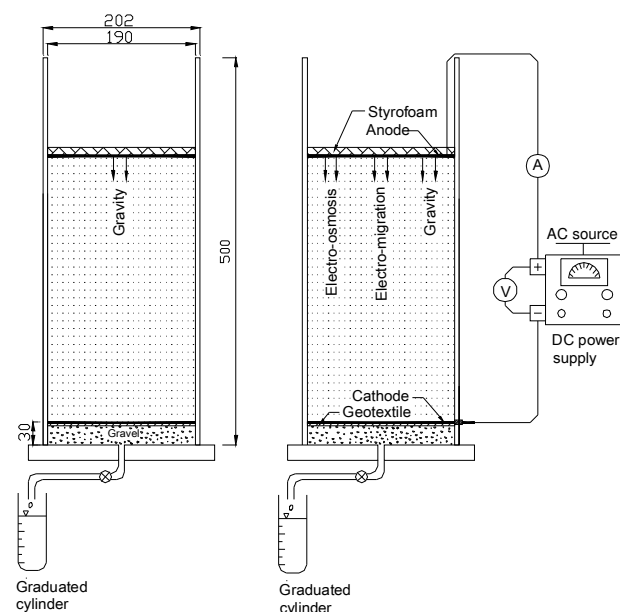


Figure 1. Elevation view of electrokinetic testing column

2.3 Testing Procedure

In test 1, the dry kaolinite clay was thoroughly mixed with cupric nitrate trihydrate ($\text{Cu}(\text{NO}_3)_2 \cdot 3(\text{H}_2\text{O})$) and distilled water using a heavy duty kitchen mixer to achieve a concentration of 150 mg of copper per kg of dry soil and water content of 70% (2 times the liquid limit). In test 2, the dry kaolinite was mixed with cadmium nitrate ($\text{Cd}(\text{NO}_3)_2 \cdot 4(\text{H}_2\text{O})$) to a concentration of 150 mg of cadmium per kg of dry soil and water content of 70%. The two soft contaminated soils were then stored in separate bails with airtight covers.

A layer of gravel, 5-6 mm grain size in diameter, was placed at the bottom of the column as part of a drainage layer, which was overlain by a geotextile filter as shown in Figure 1. A perforated graphite electrode (cathode), 190 mm in diameter and 3 mm thick, was placed on the top of the geotextile filter for a total of 30 mm drainage layer. After 48 hr of preparing the soil, each of the two pre-contaminated soils was placed into a cell in five layers for a total height of 250 mm. Each layer was rodded 25 times using steel rod, 16 mm in diameter and 600 mm long with a hemispherically shaped tip, to prevent the entrapment of air buckets. The high water content of the soil and the thorough rodding during placement in the cell insured that the soil specimen was nearly, if not fully, saturated. A second perforated graphite electrode (anode), 190 mm in diameter and 3 mm thick, was placed on the top of soft soil. Styrofoam was fixed to the anode to keep it in direct contact with the soil. A dc voltage of 35 V (corresponding to E of 140 V/m) was applied via the graphite electrodes for 118 hr of remediation. Electric current and water collected in the graduated cylinder (see Figure 1) were monitored and reported during the test. For each of the two electrokinetic tests performed in the study, an identical control test with no applied electric field was carried out to provide baseline data for comparison.

At the end of each test, the soil was extruded from the cell and divided into 5 equal layers from top to bottom. Part of the soil from each layer was tested for water content. The remaining of the sample was air-dried for 48 to 72 hr and then grounded and sieved by 0.425 mm screen. Each sample was analyzed for pH and copper or cadmium concentration. pH was measured with a pH meter by mixing 5 g of dry soil with 10 ml of deionizer water. For analysis of copper and cadmium concentration, 2 g of dry soil was mixed with 10 ml of concentrated nitric acid. The mixture was agitated in a digital shaker for 1 hr at 150 rpm. Afterward, the mixture was centrifuge for 20 min at 500 rpm. The concentration of cadmium in the supernatant was then determined using inductively coupled plasma-optical emission spectrometry (ICP-OES).

3 RESULTS AND DISCUSSION

3.1 Electric Current

Figure 2 shows the electric current during the remediation for test 1 (copper contamination) and test 2 (cadmium contamination) for an applied voltage of 35 V. As seen in the figure, for both tests the maximum current (0.65 and

0.52 A) was observed at the start of the remediation and the minimum current (0.17 and 0.16 A) at the end of the remediation. The decrease in current resulted from the decrease in electrical conductivity of the soil during the remediation process. The change in the conductivity of soil during an electrokinetic process is a result of two opposing mechanisms. The bulk electrical conductivity of a soil is a product of the electrical conductivity of the two components of the soil, namely, the soil pore fluid (water) and soil solids. In general, the electrical conductivity of the pore fluid is much higher than that of the soil solids and thereby dominates the bulk conductivity of the soil. Therefore, as water is drained out during an electrokinetic remediation process, the bulk electrical conductivity of the soil decreases. However, for water still remaining inside the soil pores, the electrical conductivity increases with the remediation time as a result of electrolytic reactions associated with the electrokinetic process (Narasimhan and Ranjan 2000; Mohamedelhasan and Shang 2003). Therefore, as the drainage of water during an electrokinetic remediation decreases with time, the increase in the electrical conductivity of the pore fluid by the electrolytic reactions may become more dominant than the decrease in soil conductivity resulting from the draining of water. Thus, the bulk conductivity of the soil and thereby the electric current through the soil may increase during the remediation. The increase in electric current during the remediation was clearly observed in test 2 (Cd contamination).

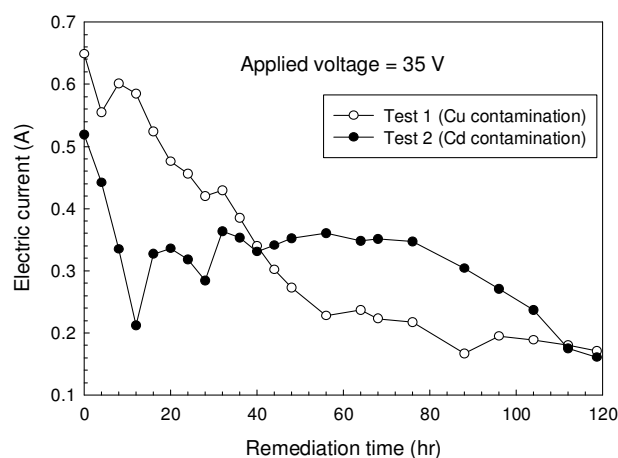


Figure 2. Electric current versus remediation time

3.2 Water Collected and Water Content

The cumulative volume of water drained from the soil during the electrokinetic remediation is shown in Figure 3. As seen in the figure, in test 1 (copper contamination) a cumulative volume of 2070 ml was collected by the end of the electrokinetic remediation compared to only 693 ml in the control test. In test 2 (Cd contamination), 1822 ml was collected by electrokinetic remediation compared to 839 ml in the control test. The much larger volume collected in the electrokinetic remediation test is due to electro-osmotic flow represented by Equation 1. While the

volume of water collected in the control test was due to gravity alone, the water collected in the test with electrokinetic remediation was due to electro-osmosis along with gravity.

Figure 3 shows the rate of water collected during the early hours of the remediation to be higher than that during the late hours of the remediation. This is to be expected as more water was available at the start of the remediation process. This is particularly obvious in test 1 where 50% of the drained water was collected during the first 22 hr of electrokinetic remediation. The concentrations of the copper and cadmium in water collected after electrokinetic remediation in tests 1 and 2 were 126 $\mu\text{g/l}$ and 2 $\mu\text{g/l}$, respectively, representing a negligible amount ($< 0.02\%$) of the initial metal mass. The means that while electro-osmosis was effective in draining the contaminated soil from water, it was ineffective in removing the contaminant from the soil.

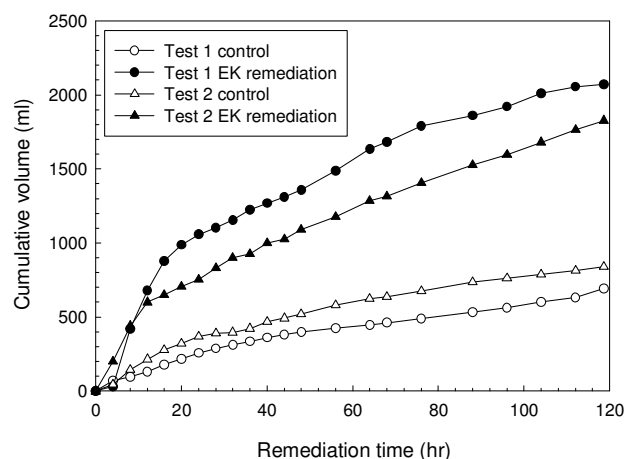


Figure 3. Cumulative volume of water collected during the tests

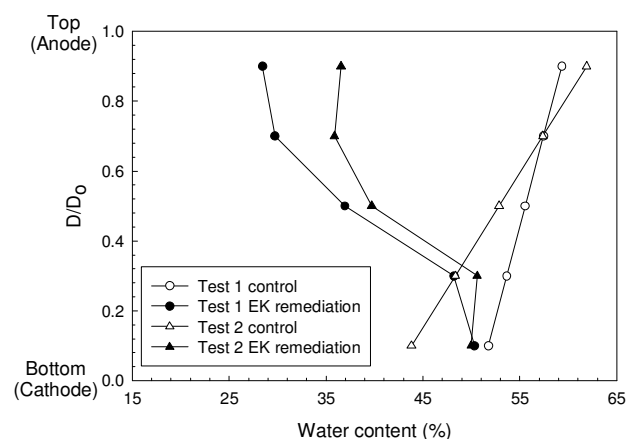


Figure 4. Water content along the electrokinetic column after the tests

Figure 4 shows the water content of the five layers along the soil sample. D is the vertical distance between the mid of the layer and the bottom of the column and D_0 is the total length of the soil samples. Thus, the water content at $0.1 D/D_0$ represent the bottom layer while at $0.9 D/D_0$ represents the top layer. Consistent with the higher volume of water drained by electrokinetics, lower water contents were observed after electrokinetic remediation as compared with the control test which demonstrates the effectiveness of electrokinetic in dewatering contaminated soil. Figure 4 shows that after electrokinetic remediation, the water contents along the soil sample in test 1 (Cu contamination) were lower than the water contents in test 2 (Cd contamination). This was to be expected as more water was drained in test 1 (see Figure 3). In the control tests, Figure 3 shows that the water content along the soil increased along the height of the soil while after electrokinetic remediation tests the water content decreased along the soil. This is in agreement with electro-osmosis as water is drained from the anode (top) toward the cathode (bottom) resulting in a higher water content near the cathode. In the control test, the soil with the shortest drainage path (bottom layer in this test configuration) will drain more water by gravity and has the lowest water content which was the case in both control tests (see Figure 4).

Figure 4 show the water content at $0.3 D/D_0$ (i.e. ~ 75 mm from the bottom) remained high and relatively similar to the water content at $0.1 D/D_0$ (i.e. ~ 25 mm from the bottom). The high water content at $0.3 D/D_0$ is a result of the water generated when the acid and base front meet. The acid front generated at the anode (see Equation 3) travels toward the cathode and the base front produced at the cathode (see Equation 4) travels toward the anode by electro-migration. Due to its smaller size, H^+ typically travels a longer distance through the soil than OH^- , resulting in an acid-base meeting closer to the cathode. As they meet, water is formed. The formation of water at the acid-base front junction in this study is in agreement with results in the literature (e.g. Narasimhan and Ranjan 2000; Mohamedelhassan and Shang 2003).

3.3 pH and Heavy Metal Concentration

Figure 5 shows the pH along the soil specimen after tests 1 and 2. As shown in the figure, the top 60% of the soil reported $pH < 7$ (i.e. acidic) with the lowest pH near the anode (pH of 1.9 and 2). The bottom 40% of the soil column reported $pH > 7$ and the highest pH of 9.5 was reported near the cathode in test 2. The pH profile is in agreement with the electrolysis reactions at the electrodes and the distance travelled by the H^+ and OH^- ions.

The dewatering of the soil by electro-osmosis removed negligible amount of the initial copper and cadmium in the soil. This clearly indicates the ineffectiveness of removing heavy metals by electro-osmosis. Figure 6 shows the concentration of the heavy metals along the soil specimen after the electrokinetic remediation. C is the concentration of the heavy metal (copper or cadmium) after the electrokinetic remediation and C_0 is the initial concentration (150 mg/kg of soil). The figure clearly shows that electrokinetics was effective in

moving both metals from the anode toward the cathode. The movement the heavy metals in the soil is via electro-migration and can be quantified by Equation 2. In test 1, the lowest concentration of copper after the remediation was 33% of initial concentration (67% removed) and was observed near the anode ($0.9 D/D_0$). The copper concentration increases toward the cathode with the maximum concentration of 119% of initial concentration at $0.3 D/D_0$ (the location where acid and base fronts meet). In test 2, electrokinetics was effective in reducing the cadmium near the anode ($0.9 D/D_0$) to 11% of the initial concentration (89% removed). The cadmium concentration increases toward the cathode with the maximum concentration of 184% at $0.3 D/D_0$ (the location where acid and base fronts meet). The maximum concentration of copper and cadmium at $0.3 D/D_0$ is a result of the precipitation of the metal as the soil medium change from acidic to basic (see Figures 5 and 6).

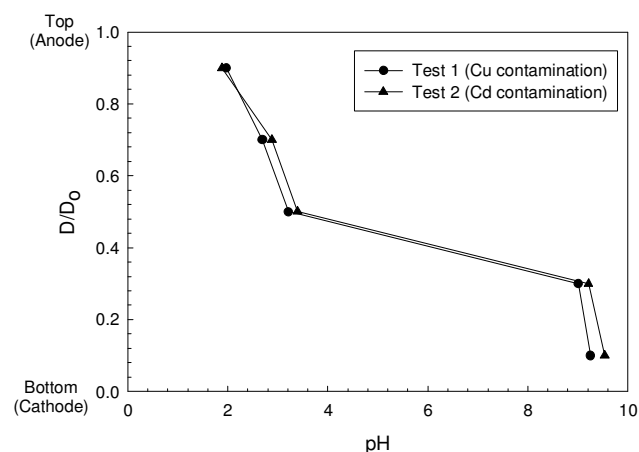


Figure 5. pH of soil along the electrokinetic column after the electrokinetic remediation

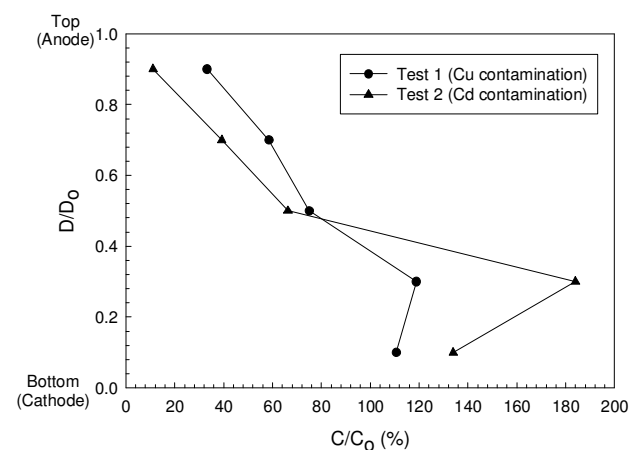


Figure 6. The concentration of the heavy metals relative to the initial concentration along the electrokinetic column after the electrokinetic remediation

Concentrating the heavy metal in the soil near the cathode by electrokinetic remediation can be very beneficial. For instance, forcing the heavy metals in part of the soil can significantly reduce the volume of the contaminated soil. This can reduce the cost of digging, transporting and landfilling the contaminated soil.

4 CONCLUSIONS

An experimental study was carried out to investigate the effectiveness of electrokinetics to remediate soft kaolinite clay soil contaminated with copper and cadmium to a concentration of 150 mg/kg. The tests were performed in four identical electrokinetic remediation columns. A voltage of 35 V (140 V/m) was applied during 118 hr of testing with the top electrode serving as the anode and the bottom electrode serving as the cathode. The results showed that:

- Electrokinetics was effective in removing water from the contaminated soils and the volumes of water were 1822 and 2070 ml compared to 693 and 839 ml in the control tests.
- Electrokinetic was effective in decreasing the water content along the soil column with the lowest water contents reported in the layer near the anode (top). The lowest water content in the control tests was reported in the bottom layer.
- The pH profile along the soil column after electrokinetic remediation was consistent with the electrolysis reactions.
- Electrokinetic was effective in removing part of the heavy metal from most of the contaminated soil with the highest removals of 67% in test 1 (copper) and 89% in test 2 (cadmium) in the layer near the anode.

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