

Toxic Elements in Soil and Groundwater: Short-Time Study on Electrokinetic Removal of Arsenic in the Presence of other Ions

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Abstract: The electrokinetic technique is an emerging technology presently tested *in situ* to remove dissolved heavy metals from contaminated groundwater. There is a growing interest for using this system to cleanse clayey soil contaminated by toxic metallic ions. Currently, there are very few available non-destructive treatment methods that could be successfully applied *in situ* on low permeable type of soil matrix. The main objective of presented study was to validate and possibly enhance the overall efficiency of decontamination by the electrokinetic technique of the low permeable soil polluted by the arsenic in combination with chromium and copper ions. The chosen mixture of ions was imitating leak of pesticide well known as chromate copper arsenate (CCA). The chosen technique is showing a big promise to be used in the future as a portable, easy to install and run on sites with spills or leaks hard to reach otherwise; such as in the dense populated and urbanized areas. Laboratory electrokinetic experiments were designed to understand and possibly manipulate main mechanisms involved during forced migration of ions. All tests were conducted on artificially contaminated kaolinite (low permeable clay soil). Electrokinetic migration was induced by the low voltage *dc* current applied through soil column. Series of experiments were designed to assess the efficiency of arsenic-chromium-copper remediation by applying (1) only *dc* current; and (2) by altering the soil environment. Obtained results showed that arsenic could be successfully removed from the soil in one day (25 hours) span. It was significant time reduction, very important during emergency response. Mass recovered at the end of each test depended on initial condition of soil and type of flushing solution. The best results were obtained, when soil was flushed with either NaOH or NaOCl (total removal efficiency 74.4% and 78.1%, respectively). Direct analysis of remained arsenic in soil after these tests confirmed substantial drop of the initial mass of arsenic in soil profile from 51.54 mg to 10.62 mg (NaOH) and 5.68 mg (NaOCl) after 25 hours of treatment.

Keywords: Toxic ions, electrokinetic technique, arsenic, CCA, remediation of low permeable soil

Introduction

Toxic ions in groundwater and/or soil pose a significant health hazard for the residents living in affected areas. The possible sources of these ions and their leak to the environment could range from the careless human activities, to the accidental or deliberate spills. In some parts of the globe, the natural formation of local ecosystems may deliver increased concentration of particular ions considered to be toxic, such as arsenic in groundwater in Bangladesh, or Chile [1, 2]. Adverse health effects on whole population that has to consume water with elevated level of arsenic (above 50 ppb) was studied and reported by various researchers, as is shown in chosen citations [1-5].

Apart from natural causes that result contamination of groundwater, the main source of pollution is, as

always, the human activities. Generally, spills or leaks on the surface of soil is washed down and ultimately cause contamination of groundwater. When metallic type of contamination in water or soil is detected, the proper remediation is usually based on either immobilization or extraction of contaminants of concern.

The soil and groundwater remediation techniques are mostly emerging technologies that require intensive studies to optimize general conditions of removal of toxic ions from either soil or water matrixes. Few available *in-situ* soil remediation techniques, such as bioremediation, permeable reactive barrier, soil flushing, and excavation have been applied for decontamination of heavy metals. The applicability of these techniques depends on soil type, hydraulic conductivity, costs and availability of equipment, as to

name a few. Most of the methods suffer from one or more technical difficulties or economic disadvantages. For example, excavation of contaminated soil is costly and exposes workers to health risk; injection of chemical and biological detoxifying agents may not reach regions of low permeability; purging by pressure driven flow may result in soil rupture or blow out in low permeability soils [6].

Electrokinetic Technique

The electrokinetic technique used in this study is a promising technology presently tested *in situ* to remove dissolved heavy metals from contaminated groundwater. There is a growing interest for using this system to cleanse soil contaminated by toxic metallic ions. Currently, there are very few available non-destructive treatment methods that could be successfully applied *in situ* on the low permeable type of soil matrix. The *in-situ* electrokinetic remediation method has shown suitable for clays contaminated with heavy metals [7-12], and it was applied to inaccessible sites, such as under-structures, where conventional techniques were not feasible to be successfully implemented [13, 14].

Generally, the transport of contaminants in the soil under low *dc* current is influenced by three main mechanisms: electromigration, electroosmosis and diffusion. Electromigration expresses movement of ions toward charged electrodes; transport by advection due to electroosmosis is typically towards cathode, and transport due to diffusion may be either towards anode or cathode depending on the concentration gradient of ions. At the end of the remedial process, contaminants that accumulated at the electrodes due to movements described by the above mechanisms have to be collected and disposed above the ground [7-12].

Overall cleanup/migration of contaminants highly depends on the physicochemical characteristics of the contaminated site. Soil pH, redox potential, presence of organic compounds, adsorption-desorption and precipitation-dissolution phenomena are important factors that influence the mobility of contaminants. Overall remediation could be improved by the control of pH, and maintaining or dissolving contaminants in pore-water. This could be done by the addition of the special augmentation solution to the soil. It was found that migration of copper was enhanced by lowering pH of the soil [11]; but arsenic and chromium migration favored alkaline soil conditions [11, 12].

Augmentation (flushing) solutions could be either used for changing the physicochemical conditions in the soil (pH and redox potential), or could form mobile complexes with the heavy metals [15]. Solution could be distributed between electrodes along with electroosmotic flow. It was found that the electroosmotic flow through experimental soil increased after addition of different complexants, such as citric acid, EDTA or HEDPA, when compared to distilled water [16]. The EDTA was found to enhance the removal of Pb and Zn from spiked soils [17, 18]. In fact, the fate of hazardous metals varies widely depending on soil environments and is a quite complex phenomenon.

CCA Pesticide: Chromate Copper Arsenate

Unfortunately, the copper, chromium and arsenic contamination in soil is widespread throughout the world. Spillage of CCA pesticide routinely used for the treatment of the construction wood is a very common problem at wood treatment facilities. For example, in Finland, over 200 sites have been identified with CCA contamination ranging from 50 to 100,000 ppm [19]. Soil samples collected from a wood impregnating plant located in Lammi, Southern Finland (in operation during 1956-1965) have shown the total concentrations of arsenic ranged 10-26100 mg/kg; chromium 32-18500 mg/kg and copper 26-7000 mg/kg [20]. The second wave of contamination comes from the leak of the CCA from constructions made from the treated wood. A study conducted in Florida showed that the average arsenic, chromium and copper concentration in soils collected below decks were 28, 34 and 40 mg/kg respectively [21].

The main objective of presented study was to validate and possibly enhance the overall efficiency of the electrokinetic technique applied to the low-permeable soil polluted by the arsenic in combination with chromium and copper ions. The chosen mixture of ions and their concentrations was imitating leak of CCA pesticide. Laboratory electrokinetic experiments were designed to understand and possibly manipulate main mechanisms involved during forced migration of ions. All tests were conducted on artificially contaminated kaolinite (low permeable clay soil). Electrokinetic migration was induced by the low voltage *dc* current applied through soil column. Series of experiments were designed to assess the efficiency of arsenic-chromium-copper remediation by applying only *dc* current; and by altering the soil environment.

Materials and Methods

Soil

The soil used for all experiments was supplied by the Imerys Kaolin Inc., Georgia. It was kaolin, a low buffering type of soil. As stated by the vendor, the composition of this soil consisted of kaolin $[Al_2Si_2O_5(OH)_4] > 97\%$, Crystalline Silica, Quartz $> 0.1\% \sim 1\%$ Sodium Polyacrylate/Soda Ash Dispersant $\sim 0.35\%$. Liquid limit of the soil was 44%, plastic limit was 29%, and hydraulic conductivity was 10^{-8} cm/s.

Spike Soil Preparation

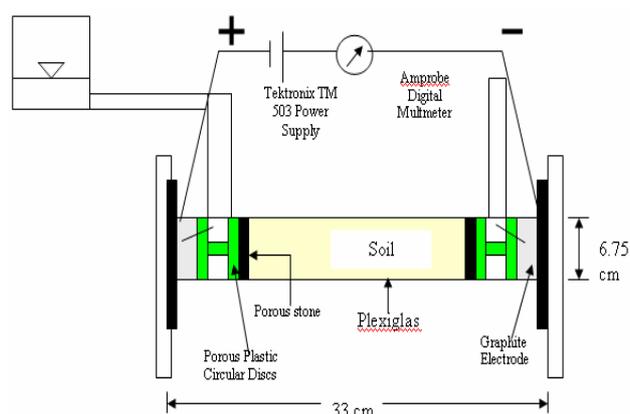
Soil was artificially contaminated at a target copper, chromium and arsenic concentration of 50 mg/kg to simulate/represent a typical concentration found in various contaminated sites. Dry soil of 1,350 g was used for each test. Preparation of standard solutions of copper sulfate, potassium dichromate, arsenic tri-oxide was performed following Standard Methods [19]. The chemicals were weighed, mixed and dissolved in de-ionized water for twenty-four hours. The copper sulfate, potassium dichromate, arsenic tri-oxide solution was added to the soil yielding the desired concentration of 50 mg/kg and desired water content of 35%. The flushing solutions were prepared by mixing tap water with appropriate chemicals to obtain the desired concentration shown in Table 1.

Table 1: Summary of Experimental Set-up

Parameters	Tests				
	EK-1	EK-2	EK-3	EK-4	EK-5
Initial soil pH	6.447	5.647	6.159	6.195	6.281
Soil Redox potential (mV)	477.3	464.3	459.8	458.3	487.9
Initial Soil conductivity ($\mu\text{S}/\text{cm}$)	1541	755	1176	1061	-
Purging Inlet solution	Potable water	H ₂ O ₂ (3%)	NaOH (0.1N)	NaOCl	Potable water
Electrode Position	Horizontal	Horizontal	Horizontal	Horizontal	45° Inclined (Cathode up)
Voltage gradient (V/cm)	1	1	1	1	1

Electrokinetic Reactor Setup

The electrokinetic cell shown in Figure 1 was fabricated using a Plexiglas tube. For each experiment, the fresh portion of the spiked soil was placed inside of the cell in 1-inch layers. After compacting, the soil was allowed to reach physicochemical equilibrium for 48 hours. Depending on the test, the fluid compartments were filled with either potable water or chosen flushing reagents. Potable water was selected as it is the most likely source of replenishing fluid at most contaminated sites [23]. Used for experiments: potable (tap) water had initial pH between 7.4 and 8.0, redox potential 395 ± 12 mV, and electrical conductivity between 275 and 300 $\mu\text{S}/\text{cm}$. The electrodes were connected to a electric power supply (Tektronix TM503 PS503A Dual Power Supply).

**Figure 1:** Electrokinetic Cell

Experimental Set-up and Measurements

Table 1 presents a summary of the series of experiments. First test (EK-1) was conducted as a baseline with the tap water as a flushing solution, while the EK-2, EK-3, EK-4, EK-5 used either different flushing solutions, or reposition of the electrodes.

Flushing solutions included water, hydrogen peroxide, sodium hypochlorite and sodium hydroxide.

A constant voltage gradient of 1 V/cm was applied to the apparatus. The electric current across the soil sample, electroosmotic flow, pH, redox potential, and electrical conductivity (EC) of the aqueous solutions in both the anode and the cathode reservoirs were monitored throughout the duration of the experiments. Current and voltage across the electrodes were measured periodically using Tektronix TM503 PS503A Dual Power Supply. Redox potential, pH, and electrical conductivity of the aqueous solutions from the electrodes were measured directly by immersing probes into the samples of the solutions. Electrical conductivity was measured by YSI 3100 probe; pH was measured using a Coring 350 probe; and redox potential was measured by Thermo Orion 230A probe. Each test was terminated after 25 hours, when the current stabilized and no significant change of water flow (electroosmotic flow) was observed.

At the end of the test, aqueous solutions from both the cathode (catholite) and anode (anolite) compartments were collected and their volumes were measured. Treated soil was extruded from the cell; it was sectioned into five parts and preserved in containers. From each soil section, a 10 g of soil was taken and mixed with 10 ml of deionized water in a glass vial. The mixture was shaken thoroughly by hand and the solids were allowed to settle. The pH, redox potential and the electrical conductivity was measured in prepared samples (soil), as well as in the aqueous solutions retrieved from the electrode's compartments.

Contaminants from the different soil sections were extracted by acid digestion in accordance with USEPA Method 3050, and fluid samples were digested following USEPA Method 200.2. Total concentrations of copper, chromium and arsenic were determined using an atomic absorption spectrophotometer (Shimadzu 6200A). Aqueous samples from the electrode reservoirs were directly tested.

Removal Efficiency

The total mass deposition in anolyte and catholyte was determined for each test. The mass loss due to adsorption onto electrodes, porous stones and reactor wall was neglected. Removal efficiency for each test was calculated dividing the total mass deposition in anolyte and catholyte by initial mass of contaminant of untreated soil.

Results and Discussion

Electric current

Figure 2 shows electrical current profile during tests. During tests EK-1, EK-3 (where tap water and NaOH were purged through the electro-osmotic flow), the current initially was as low as 19 and 22 mA, respectively, but with time, it increased to 67 and 82 mA. The electrical current profile for the test EK-5 (where the reactor was kept 45° inclined position with cathode at the top) was different. Initially it resembled the profile from the test EK-1, but for unknown reasons the voltage sharply decreased after 12 or 13 hours. Though it is difficult to explain this disruption, one of the causes might be development of a crack or vacuum at the upper portion of soil near the cathode compartment.

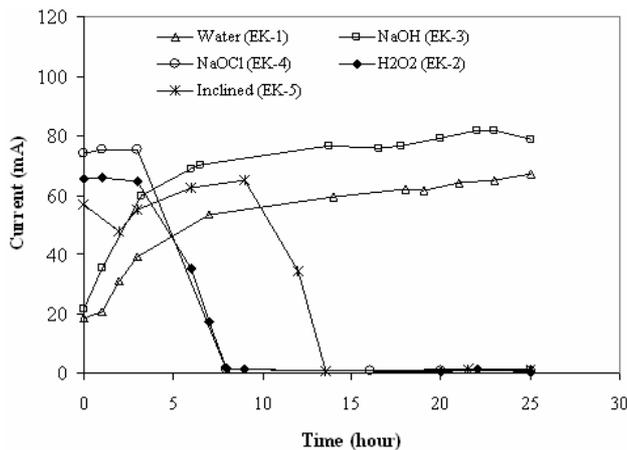


Figure 2: Current vs. Time

In tests EK-2 and EK-4, where H₂O₂ and NaOCl was purged, the current was initially quite high, ranging from 56-73 mA; after 3 to 12 hours (depending on the test) decreased, and finally stabilized at the 1-2 mA level. As is known, the measured electric current should be proportional to the dissolved species present in the solution.

Effluent Flow

The flushing solution moved from the anode to the cathode reservoir. Figure 3 shows changes in the volume of effluent over time. Recorded flow rate was relatively low in tests EK- 2 and EK-4 (purging chemicals were H₂O₂ and NaOCl, respectively) compared to tests EK-1, EK-3 and EK-5 (purging chemical for EK-1 and EK-5 was tap water and NaOH, respectively, and additionally the EK-5 was inclined). It was observed that for EK-2 and EK-4 the hydrodynamic flow ceased within 8 to 10 hours, but for the EK-1, EK-3 and EK-5 high fluid flow continued until the

end of experiment. The reason behind these phenomena was that electro-osmotic flow was directly proportional to current and dissolved contaminants in the pore fluid. When electrodes were in 45°-inclined position, the buoyancy force along with the low contaminant removal might have raised the hydrodynamic flow.

The average hydrodynamic velocity in the soil varied from 0.023 to 0.096 cm/h. The cumulative effluent collected from the EK-1, EK-3 and EK-5 ranged from 77-86 mL; while for EK-2 and EK-4 it was only 20.5-30.5 mL during the whole test duration of 25 hours.

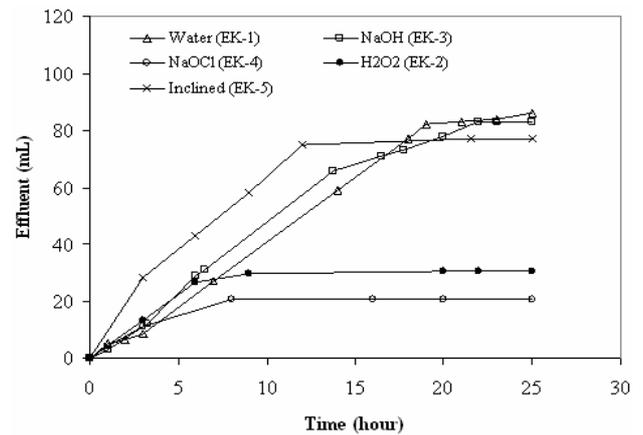


Figure 3: Cumulative Volume of Effluent vs. Time

Arsenic Migration

Figure 4 shows arsenic (total) concentration profiles all five tests. The initial total arsenic concentration for all these tests prior to treatment was maintained at the level of 50 mg/kg. These profiles show considerable arsenic removal during 25 hours of test.

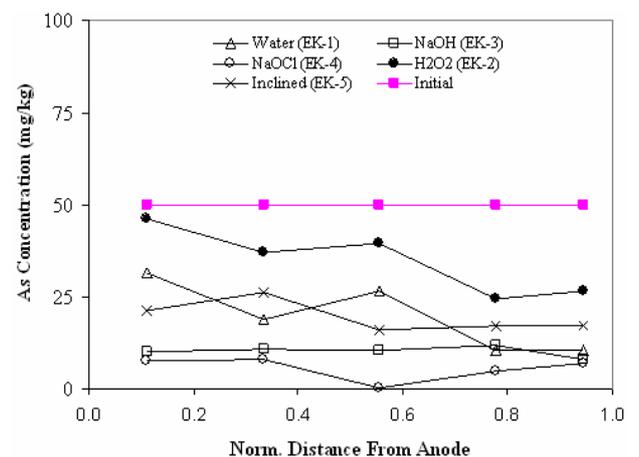


Figure 4: Arsenic Concentration Profile of Treated Soil

Total arsenic removal in the base line experiment was 39% (tap water), while maximum of arsenic removal was observed in EK-4, where NaOCl was applied as the purging agent. After the test, the arsenic concentration varied from 7.65 mg/kg near the anode to 6.87 mg/kg near the cathode. Overall removal efficiency calculated for this test was about 78% (Table 2). The solution of sodium hydroxide (EK-3) was also appeared to be an excellent purging agent. Arsenic removal was

74% and arsenic concentration varied from 10.1 mg/kg near the anode to 6.9 mg/kg near the cathode in EK-3.

Table 2: Arsenic Mass Balance and Removal Efficiency

Test	Initial mass (mg)	Contaminant mass after electro-kinetics			Removal efficiency (%) ¹	
		Anode	Cathode	Soil	% of initial mass	(%) ¹
EK-1 (Tap water)	51.54	10.19	10.13	20.24	78.7	39.26
EK-2 (H ₂ O ₂)	51.54	4.14	4.17	35.92	85.82	16.12
EK-3 (0.1N NaOH)	51.54	18.61	19.74	10.62	95.01	74.41
EK-4 (NaOCl)	51.54	20.02	20.23	5.68	89.11	78.09
EK-5 45° Inclined (Anode bottom)	51.54	4.13	14.19	20.14	74.62	35.55

¹Removal efficiency calculated neglecting loss of mass due to adsorption onto electrodes, porous stones, and reactor walls

Relatively poor performance was observed when the contaminated soil was purged with the oxidizing agent H₂O₂, which had an initial pH of 4.6 (EK-2). Removal efficiency was only 16%.

The summary of overall removal efficiency was shown in Table 2. The complexity of arsenic speciation, different in the oxidizing and reduction conditions was influencing final removal efficiency. Initial pH through soil profile was in the range of 5.6-6.3 for different flushing solutions, but only NaOH and NaOCl greatly improved removal of arsenic (measured as total). These solutions helped to wash up in average 79.6% (NaOH) and 88.9% (NaOCl) of arsenic from soil profile (Figure 4).

The influence of buoyancy forces was observed by comparing the experiment EK-1 (tap water) and EK-5 (tap water and 45° inclination, anode on the bottom). The amount of arsenic remained in the soil was identical (about 20 mg), while the total mass of arsenic in the anode compartment was substantially lower after EK-5 experiment was completed (4.1 mg) compared with EK-1 (10.2 mg). It shows that overall removal of arsenic depends rather on the properties of flushing reagent, but buoyancy forces have major influence in the direction of arsenic migration.

Conclusions

Removal of arsenic from the CCA-contaminated, hard to reach clayey soil could be feasible by electrokinetic method. The soil must be saturated with water and augmented with proper flushing solution for the optimal outputs.

The best results were obtained when soil was flushed with either NaOH or NaOCl (total removal efficiency 74.4% and 78.1%, respectively). Direct analysis of remained arsenic in soil after these tests confirmed substantial drop of the initial mass of arsenic in soil profile from 51.54 mg to 10.62 mg (NaOH) and 5.68 mg (NaOCl). The arsenic mass distribution in soil profile after treatment was independent from the direction of the flushing solution flow (from anode toward cathode), and the cumulative effluent collection (average 80 mL, and 25mL for flushing with NaOH and NaOCl, respectively).

The overall efficiency of the treatment without special augmentation solution (saturation with water only), and with standard set-up of electrodes (vertical) was recorded at the 39%, with remaining arsenic in soil profile of 20.2 mg.

Enforcing buoyancy forces (electrodes inclined) helped with better removal of arsenic mass from the region of anode (4.1 mg, and 10.2 mg), and also helped with better collection of arsenic mass at the cathode site (14.2 mg versus 10.1 mg,) inclined and standard set-up, respectively. In spite of the different mass distribution near electrode's sites, for inclined position of electrodes, the remaining arsenic in soil was basically the same (20.1 mg), as compared to the standard set up (20.2 mg).

The influence of the direction of flush solution flow on the remaining arsenic in the soil profile was better observed during experiments with lower (water) or halted (hydrogen peroxide) remediation efficiency. Obtained profile was pH independent, which suggested simple soil-flush effect.

The short duration of the successful remediation (25 hours) could consider this technique as a possible portable *in situ* technology.

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