

Electrokinetic treatment of firing ranges containing tungsten-contaminated soils

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Abstract

Tungsten-based alloys and composites are being used and new formulations are being considered for use in the manufacturing of different types of ammunition. The use of tungsten heavy alloys (WHA) in new munitions systems and tungsten composites in small caliber ammunition could potentially release substantial amounts of this element into the environment. Although tungsten is widely used in industrial and military applications, tungsten's potential environmental and health impacts have not been thoroughly addressed. This necessitates the research and development of remedial technologies to contain and/or remove tungsten from soils that may serve as a source for water contamination. The current work investigates the feasibility of using electrokinetics for the remediation of tungsten-contaminated soils in the presence of other heavy metals of concern such as Cu and Pb with aim to removing W from the soil while stabilizing in situ, Pb and Cu.

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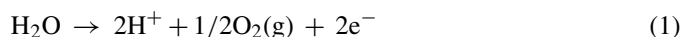
1. Introduction

The use of tungsten heavy alloys (WHA) in new munitions systems and W-composites in small caliber ammunition could potentially release substantial amounts of this element into the environment. Under prevailing environmental conditions, metallic tungsten and WHA may corrode and leach into the aqueous phase resulting in dissolved tungsten concentration in the mg/L level. Previous research efforts [1–3] have provided a substantial amount of information regarding the environmental fate and transport of tungsten and tungsten heavy alloy alloying elements but many questions regarding environmental and human health risks remain unanswered. The potential release of dissolved tungsten species may necessitate the development of remedial technologies to contain and/or remove tungsten from W-bearing soils that may serve as a W-source for water contamination.

Electrokinetic soil remediation is an emerging technology that has shown promising results in different laboratory, pilot-scale investigations and field deployment. Primarily, elec-

trokinetics is designed to remove heavy metal contaminants from soils having low permeability. Typically, direct current is applied to contaminated soils using electrodes inserted into the ground. This creates an electric field which leads to the migration of charged ions (electromigration). Positively charged ions move towards the cathode and negatively charged ions towards the anode. It has also been proven that non-ionic species are also transported in the electroosmotic water flow occurring in the electrokinetic cell. Recent research efforts have been geared at optimizing the process as well as better understanding of the various mechanisms and variables that are involved in the process [4–6]. The technique has been applied to heavy metal remediation, organics remediation and even the enhancement of established bioremediation processes.

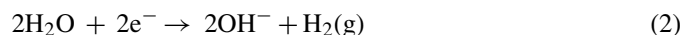
Several transport mechanisms come to play in the overall electrokinetic process. These include advection, hydraulic gradients, and diffusion of the resulting acid front to the cathode which are in addition to the migration of cations and anions to the electrodes. The electrolysis of water, shown by Eqs. (1) and (2), is the dominant electron transfer reaction in the electrokinetic process and can be expressed as:



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Table 1
Sandy-clay properties

Property	
Specific gravity	2.65
% Fines	24.2
% Sand	75.8
Unified soil classification	SM
% Organic carbon (US EPA SW-846)	0.134
CEC (US EPA SW-846)	9 meq./100 g soil
pH (ASTM D-4972)	5.51



Hydrogen ions produced in this reaction decrease the pH near the anode while the production of hydroxide ions increases the pH near the cathode. Under an electric field, three processes are responsible for the transport of charged species in the subsurface. These have been defined as:

1. Electroosmosis: The movement of soil moisture or groundwater from the anode to the cathode of an electrolytic cell.
2. Electromigration: The transport of ions and ion complexes to the electrode of opposite charge.
3. Electrophoresis: The transport of charged particles or colloids under the influence of an electric field; contaminants bound to mobile particulate matter can be transported in this manner [7].

Metal removal as high as 90% have been recorded for clayey, low permeability soils while porous, high-permeability soils have recorded 65% removal [7]. Laboratory and field experiments suggest that removal efficiencies are highly dependent on soil moisture content, soil grain size, ionic mobility, pore water amount, current density and contaminant concentration.

Electrokinetic remediation is often times used in the remediation of multiple contaminants present in the soil. The effect of having multiple contaminants as opposed to a single contaminant on removal efficiency has not been extensively studied. Redistribution of the metal ions in different fractions of the soil has been reported after the application of the electric field. One report shows the dependence of removal efficiencies of Pb, Zn and Cu on the number of contaminants present [5]. Removal

Table 2
XRF results for sandy-clay soil before EK experiment (mg/kg)

	Sandy clay
Ti	1595.05
Mn	69.22
Fe	6170.52
Ni	40.14
Cu	284.26
Zn	38.29
Se	27.19
Rb	12.75
Sr	10.96
Zr	179.25
W	1007.11
Pb	1103.53

Table 3
Model parameters for Freundlich model

	<i>K</i>	<i>n</i>	<i>R</i> ²
Na ₂ WO ₄	43174	0.21	0.99
Sodium metatungstate	52104	0.18	0.97
Ammonium metatungstate	57239	0.16	0.93
Mix 1	49464	0.18	0.98
Mix 2	95035	0.16	0.92
W/Cu	59755	0.14	0.79
W/Fe	27861	0.48	0.99

efficiencies of 48%, 92% and 34% were reported for Pb, Zn and Cu respectively when soils were contaminated separately and 32%, 37% and 31% respectively, when the soils were contaminated with the three altogether. The soil sample used in the current study contained tungsten, lead and copper which are typically present in firing ranges. Unlike most other metals, tungsten typically exists in anionic form in solution. Tungsten species are expected to migrate towards the anode while lead and copper ions will migrate to the cathode. It was theorized that the high pH at the cathode resulting from the dissociation of water would help stabilize the lead and copper while tungsten could be removed in the anolyte fluid.

While electrokinetics has been proven to be effective for the removal of several metals from contaminated soils, the removal of tungsten from range contaminated soils has not been attempted. The main goal of this study was to determine the effectiveness of electrokinetics to remove tungsten from range contaminated soil in the presence of two other metals of concern; lead and copper. A batch test was conducted using representative contaminated soils and pre-selected electrokinetic parameters.

2. Materials and methods

2.1. Description of soil

The soil sample used in the study was prepared as follows: 2% dry weight lead bullet fragments from contaminated ranges, were added to each of two 210 L barrels containing 180–220 kg of sandy clay soil (lateritic, iron rich quartzose soil containing quartz and expandable and no expandable clays representative of several firing ranges across of United States). The lead was added in two size ranges, less than 3.35 mm (71.6% of the lead added) and 3.35–6.7 mm (28.4% of the lead added). The amended soil was then fired upon with tungsten bullets. The current study was

Table 4
Model parameters for Langmuir model using linear regression

	<i>Q</i>	<i>b</i>	<i>R</i> ²
Na ₂ WO ₄	110824	0.23	0.97
Sodium metatungstate	102384	0.77	1.00
Ammonium metatungstate	99349	2.15	1.00
Mix 1	95312	0.79	0.98
Mix 2	258695	0.06	0.96
W/Cu	103812	0.27	0.95
W/Fe	344596	0.03	0.91

conducted approximately three years after the soils mixture was prepared. The mixture was sieved and the fraction smaller than 1.7 mm was used in the experiments. Relevant soil properties are listed in Table 1. The final concentrations of the metals of interest in the soil mixture were measured using a portable X-ray fluorescence (XRF) and are presented in Table 2. Approximately 1150 cm³ of soil was used in the setup which approximately corresponds to 1.7 kg ($\rho_{\text{bulk}} \approx 1.5$).

2.2. TiO₂ adsorption studies

Preliminary experiments were conducted to assess the viability of using TiO₂ as a sorbent for removing aqueous tungsten from contaminated solutions. Adsorption model parameters were derived for the adsorption of tungsten on granular TiO₂ in batch adsorption experiments. Various sources of tungsten were used in order to study the effects of speciation and the presence of other metals on the uptake process. The experiments were carried out using solutions of different tungsten salts (i.e., sodium tungstate—Na₂WO₄·H₂O, sodium metatungstate—3Na₂WO₄·9WO₃·H₂O, and ammonium metatungstate—(NH₄)₆H₂W₁₂O₄₀·H₂O), solutions obtained by dissolving metallic powders in proportions corresponding to certain tungsten alloy formulations (i.e., Mix 1 (W/Ni/Co), Mix 2 (W/Fe/Ni/Co)) and solutions obtained by dissolving bimetallic powder combinations of tungsten and another metal in weight proportions of 9:1 (i.e., W/Fe, W/Cu).

Granular TiO₂, developed by Meng et al. [8] and produced by agglomerating nano-crystalline anatase, was obtained from Hydroglobe Corp. The particle size of the grains ranged between

Table 5
Model parameters for Langmuir model using non linear regression

	Q	b	R^2
Na ₂ WO ₄	104025	0.30	0.97
Sodium metatungstate	95431	2.12	0.98
Ammonium metatungstate	94088	9.76	0.98
Mix 1	80603	8.80	0.97
Mix 2	281290	0.03	0.97
W/Cu	112077	1.84	0.96
W/Fe	400516	0.02	0.99

#30 and #100 US standard mesh (0.16–0.6 mm) with BET surface area of 250.7 m²/g.

Five solutions (volume 60 mL) containing 100, 75, 50, 25 and 10 mg/L of tungsten respectively, were prepared for each of the three different tungsten salts (Na₂WO₄, sodium metatungstate, ammonium metatungstate), by dissolving them in 0.01 M NaCl solution and adjusting pH to ~8. Initial tungsten concentrations of the solutions of dissolved metals were determined by ICP-OES as follows; Mix 1: 71.45 mg/L, Mix 2: 288.67 mg/L, W/Fe: 236.77 mg/L, W/Cu: 214.76 mg/L. Five solutions (60 mL) of various concentrations were then prepared by diluting each of these samples to obtain proportions similar to those obtained with the tungsten salts.

Approximately 25 mg of granular TiO₂ was added to each of the sample solutions prepared and the mixtures were rotated end-over end in Rugged Rotator mixers for 2 days. After two days, approximately 15 mL of the each of the mixtures were filtered and the filtrates analyzed using ICP-OES. Freundlich and Langmuir adsorption isotherms were used to fit the exper-

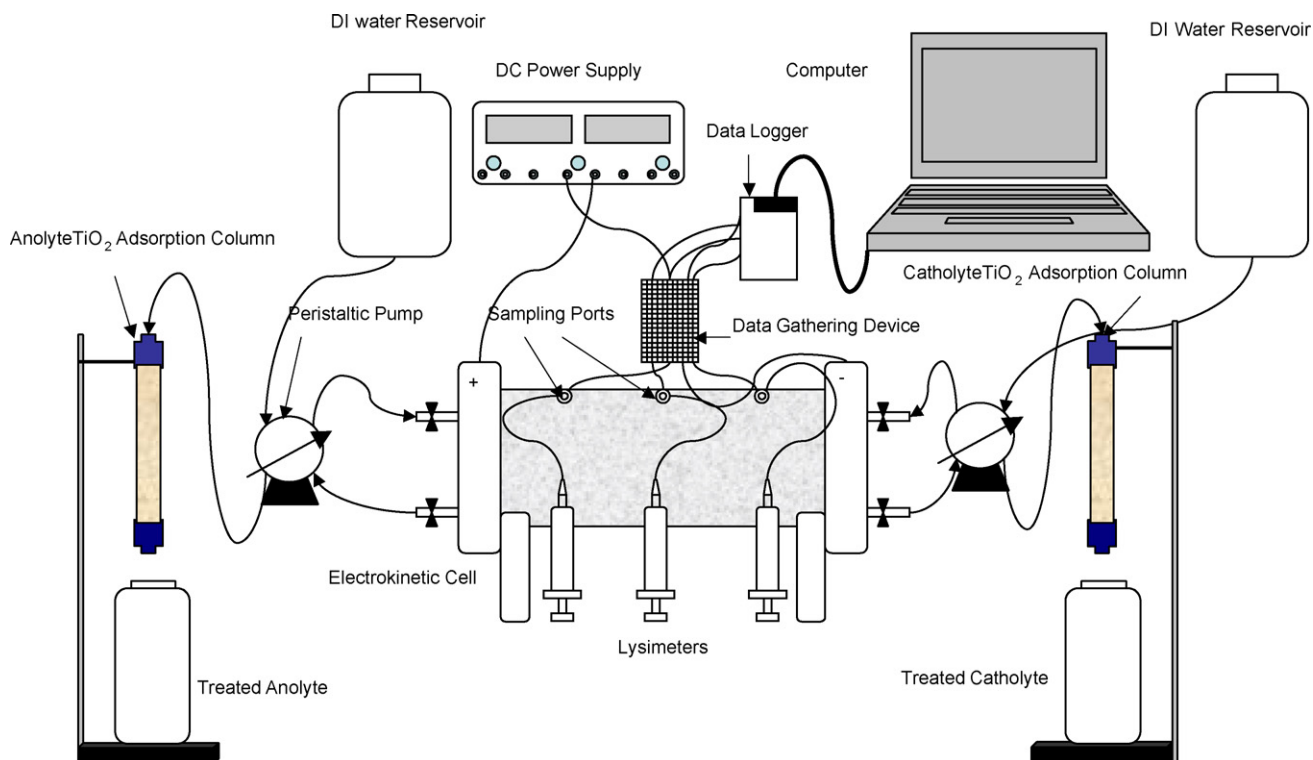


Fig. 1. Schematic of the electrokinetic cell and adsorption column setup.

imental data. Tables 3–5 present the Freundlich and Langmuir parameters obtained.

The Langmuir model provided an overall better fit to the data. Similar results were obtained for Q from both linear and non-linear regression methods. Although values obtained for b were different for some samples, the order is the same. From the results, it appears that the affinity of TiO_2 adsorbent is higher for the polytungstate species than for the monomeric species as indicated by the values of b . It can also be inferred that the adsorbent maximum capacity for the W-bearing species is quite high, about 100,000 mg/kg (around 10%) which suggests that the use of this type of adsorbent for removal of W from contaminated water is feasible.

2.3. Experimental setup

A two stage remediation scheme incorporating an electrokinetic cell and adsorption columns using granular TiO_2 was setup. Fig. 1 shows a schematic of the setup. The electrokinetic (EK) cell was constructed using a Plexiglass[®] tube. The cell was 26.5 cm in length and 7.5 cm in diameter (Fig. 1). Two chambers were provided for the graphite electrodes. The setup also consisted of two electrode reservoirs, a power source and a data logger system. Each electrode compartment had two valves to control the flow into the cell, a porous graphite electrode, a Plexiglas screen plate, and a 250 μm polypropylene mesh. The gases generated during the electrokinetic process were allowed to escape from the electrode cells by thin Plexiglas tubes (gas vents). The electrode compartments, which contained distilled water, were connected to the anode and cathode reservoirs by Tygon type tubing. Migration of charged species towards the electrodes occurred when a voltage was applied across the electrokinetic cell. The electrolyte solutions at the anode (anolyte) and cathode (catholyte) contained negatively charged and positively charged species respectively. The DC power supply provided the required voltage drop across the cell. Sampling ports on the electrokinetic cell were used to measure the drop in voltage across intervals of the cell over the period of the experiment. Data collected were recorded at pre-set intervals by a data logging programmable controller. A computer was used to display real time and logged data and for final data transfer and storage. Micro lysimeters, 5 cm in length, were used to intermittently collect pore space liquid samples from the sampling ports.

An absolute voltage of 30 V was applied at the anode. The potential gradient was not constant along the soil profile and it changed over time. On a daily basis, anolyte and catholyte liquid samples, the effluents from both columns and pore liquid collected in the lysimeters were taken. The pHs of the samples were measured and the concentrations of the three metals of concern (W, Pb, and Cu) were determined by ICP-OES. Recorded voltage data was also transferred from the data logger to the computer. The flow rate of DI water into the cell was regulated with the same pump used to extract electrolyte from the cell so a constant volume of liquid was maintained in the cell. Daily adjustments were made to compensate for the pore liquids extracted by the lysimeters. The experiment ran for 75 days.

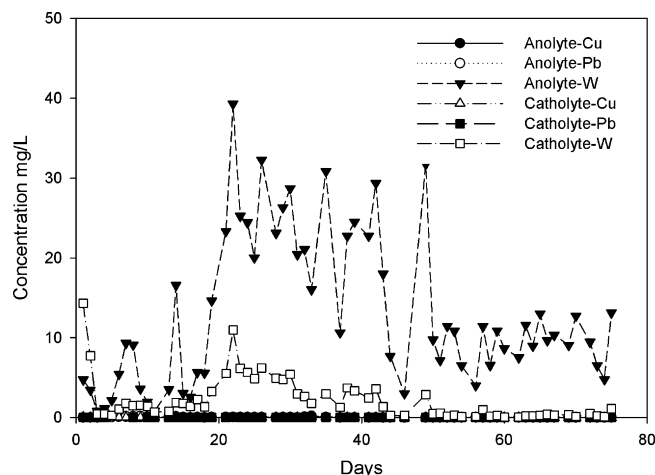
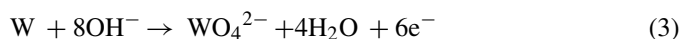


Fig. 2. Electrolyte concentrations over time.

3. Results and discussion

Changes in the concentration of the three metals of interest, Cu, Pb and W, in the anolyte and catholyte fluids over time are presented in Fig. 2. Tungsten exists as a wide variety of species in solution depending on concentration, pH, and aging time. Monotungstate, WO_4^{2-} , is however, the predominant specie above pH 7. When the pH decreases, WO_4^{2-} undergoes several polycondensation reactions forming negatively charged polyoxotungstates. As expected, the anolyte is consistently rich in tungsten as these species migrate towards the anode. A spike in the tungsten concentration of the catholyte is, however, observed between 15 and 45 days. This is attributed to the alkaline pH occurring at the cathode which favors the dissolution of tungsten from the metallic state according to the following half cell reaction:



Hence, the increase in tungsten concentration at the cathode is due to dissolution rather than electromigration.

The decrease in W concentration on both electrolyte fluids observed after 45 days appears to be the result of the electrode polarization which reduces the mobility of charged species. The values of copper and lead measured in both electrolytes are very low (<0.05 mg/L).

The pH of the anolyte and catholyte over time were consistently acidic and alkaline respectively as shown in Fig. 3. pH values for the anolyte decreased steadily from neutral to become steady at between 2 and 3. The catholyte pH increased to slightly steady values between 8 and 9 for the first 25 days eventually stabilizing at around 6 after 58 days. The variations in pH in the first 58 days are believed to be the result of the simultaneous production and consumption of OH^- at the cathode. The electrolytic process produces OH^- (Eq. (2)) while the dissolution of tungsten consumes the OH^- (Eq. (3)).

Anode-side lysimeter and cathode-side lysimeter refer to the lysimeters closest to the anode and cathode respectively. The concentration of tungsten in the pore liquids obtained from the three lysimeters over the period of the experimental run is shown

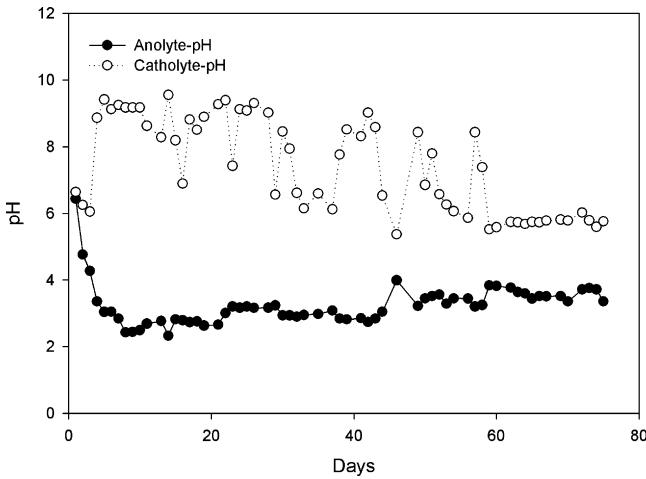


Fig. 3. Electrolyte pH over time.

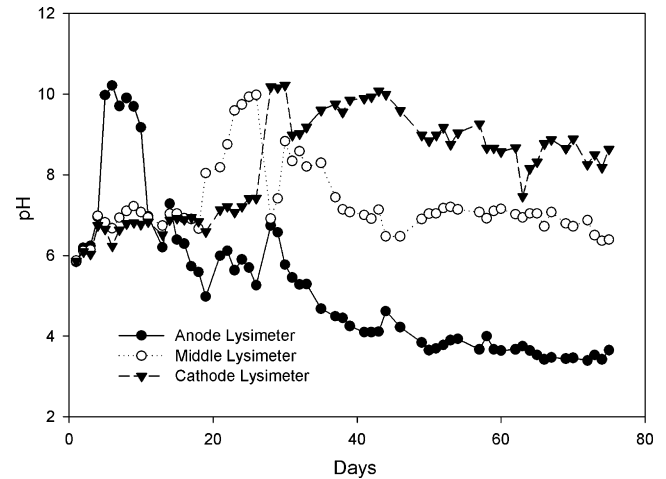


Fig. 5. Lysimeter pH over time.

in Fig. 4. The concentration of tungsten in the pore liquid for the area closest to the anode and in the middle of the EK cell are observed to have initially risen but decreased steadily over time. This indicates the removal of tungsten from these regions. In the area closest to the cathode however, the concentration of tungsten in the pore liquid increased after 10 days and remained higher than the other two regions until day 30 to stabilize around 80 mg/L after 40 days. The high concentration of tungsten in this region is likely due to the alkaline pH of the cathode, which helps tungsten dissolution and desorption. Although other phenomena may have an influence in the observed behavior, the constant pH and constant W concentration in the liquid phase suggest that the desorption and dissolution of W in the near the cathode area occurs at least at a similar rate to the generation of OH^- and the electromigration of tungsten species.

The pH of the pore liquid in the region closest to the anode increased sharply to about 10 at the beginning of the experiment and then decreased steadily to acidic (Fig. 5). The pore liquid in the region closest to the cathode maintained a slightly neutral pH at the beginning, and then increased to about 10. For the last 40 days of the run, the pH was alkaline with values ranging

between 8 and 10 with an average of 9. The pH of the pore liquid in the middle region also maintained a close to neutral value, then increased steadily to about 10 before decreasing back to values between 6 and 7. These variations are the result of several phenomena occurring simultaneously and with different intensities such as, generation of hydrogen cations in the anode and their movement towards the cathode, generation of hydroxyl anions in the cathode and their movement towards the anode, dissolution of metals with the associated pH increase (i.e., Fe, Cu, Pb) or decrease in pH (i.e., W), adsorption-desorption of the different dissolved metallic species resulting in the uptake/release of H^+ and OH^- .

By day 75, approximately 630 mg of tungsten had been removed; 530 mg in the anolyte fluid, 100 mg in the catholyte fluid (Fig. 6). The corresponding values of lead and copper were 1.6 and 1.3 mg, respectively. These removals conform to the expected behavior in which lead and copper are stabilized (precipitated) in the alkaline soil close to the cathode.

As it can be seen from Fig. 7, the voltage across the column decreased over time and the potential difference between the anode (i.e., anode side sampling port) and the cathode increased

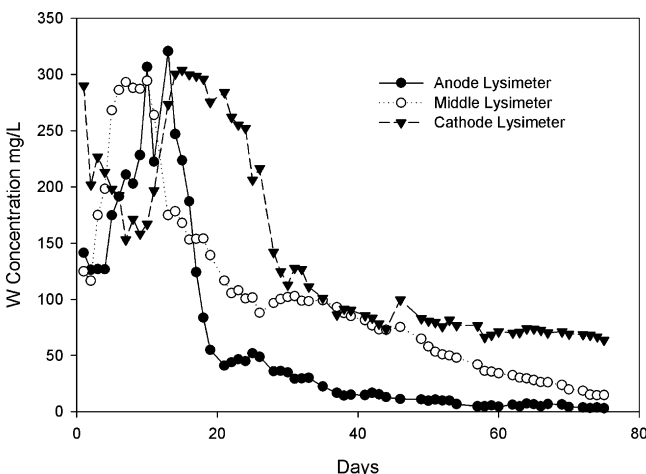


Fig. 4. Lysimeter concentrations of tungsten over time.

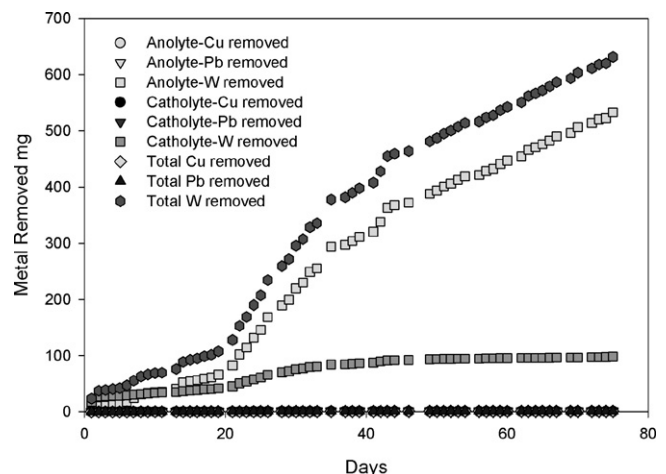


Fig. 6. Cumulative amount of metal removed over time.

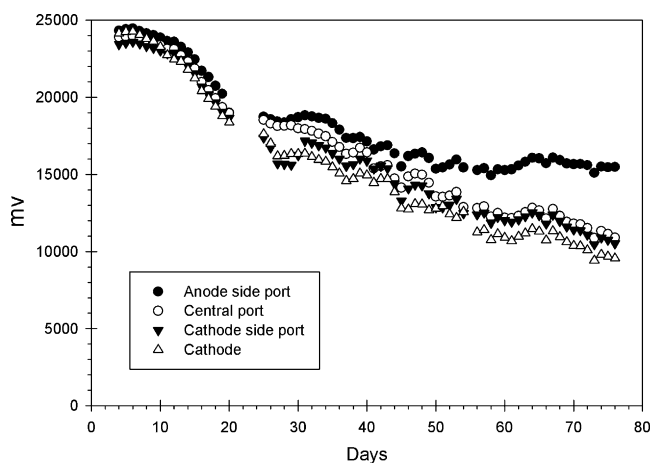


Fig. 7. Absolute voltage with respect to ground along the soil profile.

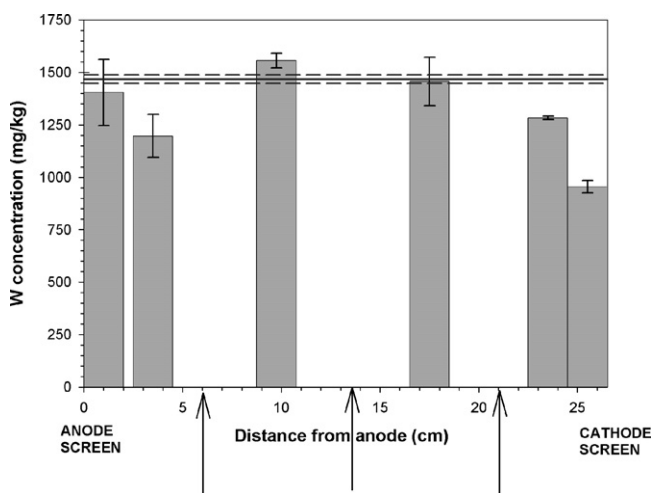


Fig. 8. Tungsten concentration in soils after the run. Error bars are the range of duplicate samples.

over time indicating and increase in the resistance of the soil profile to the transport of electrical current.

After the experiment was terminated, the soil was removed in layers from the electrokinetic cell. Aliquots of the soil were acid digested with the aid of microwave radiation and the metals of concern were measured in the digestates using ICP-OES [1]. A summary of the results is presented in Fig. 8. The arrows indicate the position of the sampling ports and lysimeters. The error bars represent the range of duplicate samples. The Figure suggests a reduction of the soil's W concentration in the near cathode region (i.e., dissolution, desorption, migration of tungstate towards the anode and removal of tungsten in the cathodic fluid). It appears

that the soil's W concentration in the near anode region has a smaller decrease from the original value than the decrease observed near the cathode of the cell. The standard deviation of the measurements in the anode side was larger than for the cathode side.

4. Conclusions

Electrokinetics has been shown to be a feasible method for removal of tungsten from firing ranges soils in the presence of Cu and Pb. TiO_2 has also been shown to effectively recover dissolved tungsten from electrolyte solutions for a complete remediation scheme. Approximately 630 mg of tungsten were removed from the test soil over a 75 day period. This procedure has also resulted in the simultaneous immobilization of lead and copper. Further studies are recommended to address other soil types and to assess the effects of parameters such pH, absolute voltage, Zeta potential, depolarization effects, and electrolyte removal/replenishment rates, on electrokinetic removal efficiency.

Acknowledgement

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