

Electrokinetic Remediation of Uranium Contaminated Soil by Ion Exchange Membranes

Z. H. Shi, T. J. Dou, H. Zhang, H. X. Huang, N. Zeng

Abstract—The contamination of significant quantities of soils and sediments with uranium and other actinide elements as a result of nuclear activity poses many environmental risks. The electrokinetic process is one of the most promising remediation techniques for sludge, sediment, and saturated or unsaturated soils contaminated with heavy metals and radionuclides. However, secondary waste is a major concern for soil contaminated with nuclides. To minimize the generation of secondary wastes, this study used the anion and cation exchange membranes to improve the performance of the experimental apparatus. Remediation experiments of uranium-contaminated soil were performed with different agents. The results show that using acetic acid and EDTA as chelating agents clearly enhances the migration ability of the uranium. The ion exchange membranes (IEMs) used in the experiments not only reduce secondary wastes, but also, keep the soil pH stable.

Keywords—Electrokinetic remediation, ion exchange membranes, soil, uranium.

I. INTRODUCTION

URANIUM is a radiotoxic and chemical toxic heavy metal. An extremely long decay half-life increases the risk of chemical toxicity over that of radiological toxicity, i.e. the radionuclide has a very low specific activity. For example, the decay half-life of ^{238}U is 4.47 milliard years. Only enriched uranium poses a radio toxicological problem [1]. Due to its α and β radioactivity, uranium compound may induce lung or bone cancer when ingested or inhaled. Like other heavy metals, the chemical toxicity of uranium may also cause kidney disease [2]. Actions, such as nuclear weapons testing and uranium mining, have contaminated significant quantities of soil and sediments with uranium and other actinide elements. For example, the total estimated volume of uranium mill tailing is $938 \times 10^6 \text{ m}^3$, which is produced at about 4,383 mines worldwide [3]. Another report estimated that the radioactive waste inventory from uranium mine and mill tailings in 2010 reached $438 \times 10^6 \text{ m}^3$, with a radioactivity of $1.1 \times 10^8 \text{ TBq}$ [4].

A variety of physical [5]-[7]; chemical [8], [9]; and biological methods [10]-[12] have been developed at field scale or laboratory scale in order to remediate uranium contaminated soil, such as capping, soil washing, leaching, vitrification, and

solidification. Most of these methods are problematic because of limited efficacy or applicability [13]. In this regard, the vitrification method costs a great deal, the thermal method disrupts the soil structure, and physical separation technology generates large amounts of secondary waste. In the last decade, researchers have taken interest in electrokinetic remediation for low permeability soils as a result of its efficient removal of high quantities of contamination and time efficiency [14]. Several electrokinetic remediation studies have been performed by researchers on nuclides, including Sr, I, Co, Cs, and U [15]. The electrokinetic remediation of uranium contaminated soil has had good results; for example, the uranium was removed from the soil at an efficiency rate of 96.8 % after 25 days in Kim's work [16]. However, the generation of secondary waste is a major problem for soil treatment. To reduce secondary waste, this study used electrodialysis (ED), an IEMs separation process [17]. Fig. 1 shows the principles of ED processing. When power supply turned on, the anions moved to the anode and passed through the anion exchange membrane (AEM), but could not pass through the cation exchange membrane (CEM). The anions accumulated in the anode concentrated zone. For the same reason, the cations collected in the cathode concentrated zone. Furthermore, the CEM in the cathode prevented the hydroxyl ions, which generated through the electrolysis of water in the cathode compartment, from moving to the soil. Hydroxide precipitates were avoided, and the removal efficiency was enhanced. This study improved the experiment apparatus with IEMs to reduce secondary waste and evaluated the performance of the apparatus. The study also investigated the removal efficiency enhanced by acetic acid and EDTA.

II. MATERIALS AND METHODS

A. Soil Characteristics

Experimental arable surface soil (10~20 cm depth), which contains a lot of sand, was sampled near a nuclear facility in Sichuan, China. The soil was first carefully air-dried, then homogenized, and put through a sieve (2 mm apertures). The experiment analyzed soil components with XRF spectra. The soil pH was measured using a pH meter (JENCO 6010) with a soil/water ratio of 1:2.5. The content of the organic matter was determined by baking the air-dry samples in a muffle furnace with 1,023 K for 6 hours. Table I shows the components of the soil composition and other properties.

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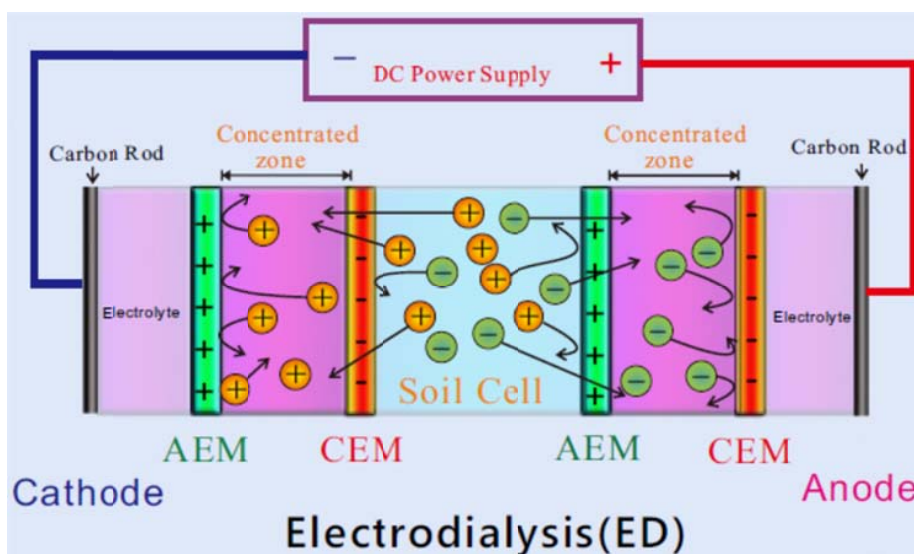


Fig. 1 The principle of electrodialysis

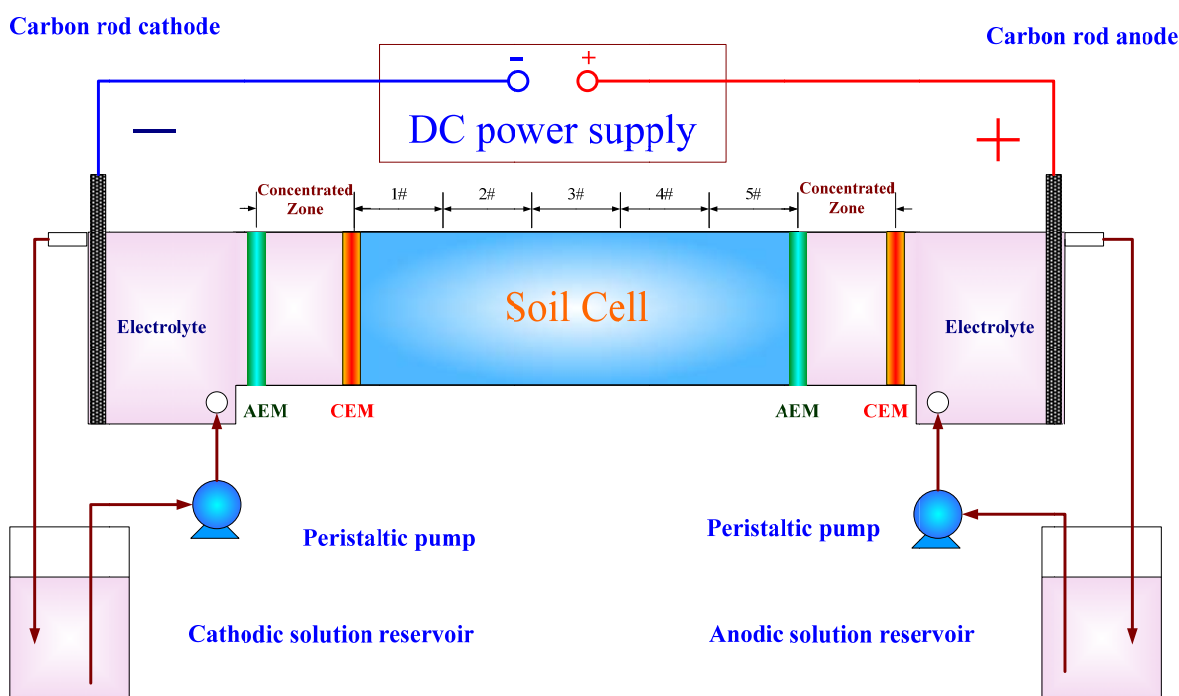


Fig. 2 Schematic diagram of the experimental apparatus

B. Experimental Set-Up

Fig. 2 shows the schematic diagram of the manufactured electrokinetic equipment. The equipment consists of five major parts: the soil cell ($15 \times 4 \times 5 \text{ cm}^3$), electrode compartments ($8 \times 8 \times 10 \text{ cm}^3$), electrolyte solution reservoirs, a power supply, and a concentrated zone ($3 \times 4 \times 5 \text{ cm}^3$). Each electrode compartment contained a sufficient amount of electrolyte solution to avoid sudden variations in pH. The same solution level was maintained in the electrode compartments, the concentrated zone, and the soil cell in order to avoid the

formation of soil channels by a hydraulic gradient. An electrolyte solution of 0.01 mol/L HAc with 0.01 mol/L NaAc was recirculated in both electrode compartments by using peristaltic pumps with a flow rate of 0.6 ml/s. Table II summarizes the characteristics of the tested IEMs.

C. Remediation Experiment

This study conducted three different experiments in order to evaluate their performances in the electrokinetic process. Table III shows the basic conditions for the experiments. In each experiment, approximately 300 g of air-dried soil mixed with

110 ml of specified solution was placed in the soil cell, and then stirred by hand for several minutes to achieve homogeneity. The soil was artificially contaminated with 10 $\mu\text{g/g}$ of uranium standard solution. In all three experiments, the sample was placed inside the cell and a constant DC voltage gradient of 15 V was applied for a treatment time of 120 hours. After the electrokinetic experiments, the treated soil was separated into five equal groups (from the cathode: 1#, 2#, 3#, 4# and 5#), and the data, which included the pH value and the uranium concentration, was subsequently measured.

TABLE I
MINERALOGICAL COMPOSITION AND PROPERTIES OF A SOIL NEAR NUCLEAR FACILITY

Soil components and properties	Value
Soil components	
SiO ₂	67.55 wt%
Al ₂ O ₃	13.85 wt%
Na ₂ O	0.69 wt%
CaO	0.46 wt%
MgO	1.05 wt%
others	16.45 wt%
Fresh moisture content	11.4 wt%
Air dried moisture content	3.9 wt%
Organic matter	3.9 wt%
pH	6.98
Uranium concentration	3.81 $\mu\text{g/g}$

TABLE II
THE CHARACTERISTICS OF COMMERCIAL IEMS

Test Items	CEM	AEM
Thickness(dry; mm)	0.32 ± 0.04	0.32 ± 0.04
Water content (wt %)	40~50	30~45
Selective penetration (%)	94	96
Exchange capacity(mol/kg)	2.0	1.8
Burst Strength(Mpa)	0.8	0.8
Coefficient of salt diffusion mmol NaCl/(cm ² •h•mol/L)	0.02	0.02
Resistance of membrane surface ($\Omega \cdot \text{cm}^2$)	12	13

TABLE III
EXPERIMENTAL CONDITIONS FOR ELECTROKINETIC EXPERIMENTS

Test	I	II	III
Anolyte and Catholyte	0.01 mol/L HAc-NaHAc		
Specified Solution	Distilledwater	HAc	EDTA
Concentration	10	10	10
Voltage	15 V	15 V	15 V
Duration	120 h	120 h	120 h

III. RESULTS AND DISCUSSION

A. Evaluate the Experiments Apparatus

To evaluate the efficacy of the experimental apparatus, this study examined the color and analysis methods of CuSO₄ solution to test the migration effectiveness of Cu²⁺ with. As Fig. 3 shows, 0.01 mol/L of CuSO₄ was deposited in the soil cell, and to avoid diffusion caused by hydraulic gradient, HAc-NaAc buffer filled in other compartments to maintain the same level of CuSO₄. The electric voltage was set at 15V, and the length of the experiment was 96 hours. Fig. 4 shows the

transport of Cu²⁺ versus the length of the experiment. With the time increased, the blue color in the soil cell became shallower. After 96 hours, the soil cell was achromatous, while the color in the cathode concentrated zone became deeper. From these results, it could be concluded that the Cu²⁺ was enriched in the cathode concentrated zone.

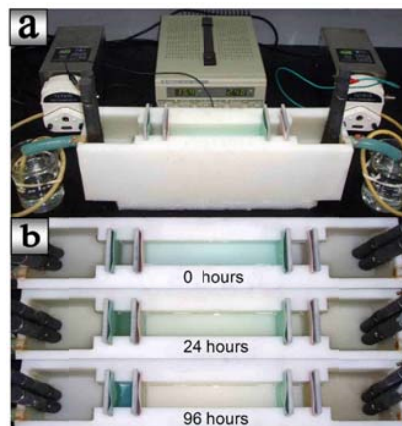


Fig. 3 Electromigration of CuSO₄ (a. Electrokinetic apparatus with CuSO₄ solution; b. Transport of Cu²⁺ versus experiment time)

The flame atomic absorption spectrometry (FAAS) method was used to determine the level of Cu²⁺ concentration in each compartment. Fig. 4 shows the results. The soil cell had an initial concentration of 190 mg/L of Cu²⁺. The Cu²⁺ concentration in the HAc-NaAc was 1.475 mg/L. After 96 hours, the Cu²⁺ concentration in the soil cell decreased to 2.675 mg/L, and increased in the cathode concentrated zone to 289.75 mg/L. Consequently, the electrokinetic apparatus improved by IEMs accumulated contaminates and protected the electrodes and electrolyte from pollution.

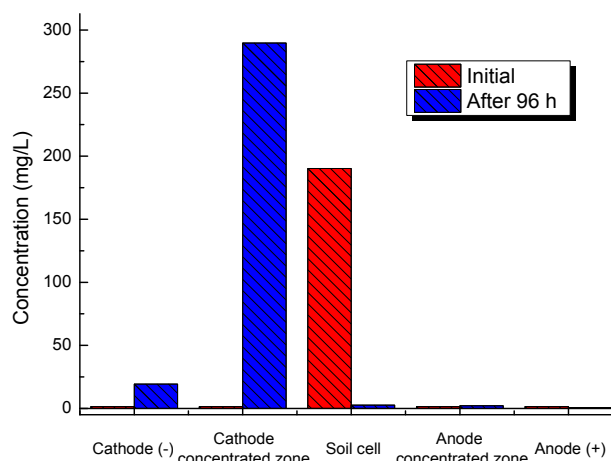


Fig. 4 Cu²⁺ concentration in each compartment

B. Soil pH

Two experiments of HAc, one with IEMs and one without IEMs, were performed to evaluate the relationship between IEMs and the soil pH. Fig. 5 depicts the soil pH in five groups

from the cathode: 1#, 2#, 3#, 4# and 5#. The initial pH value of the soil was 6.98. After 120 hours, the pH values of the soil with IEMs had little difference from the soil in the experiment with IEMs. Without IEMs, the H^+ and OH^- generated by electrolysis could directly contact the soil and move freely. When the IEMs were present, the transportation of OH^- could be blocked by the CEM, and the H^+ could be blocked by the AEM, according to their characteristics.

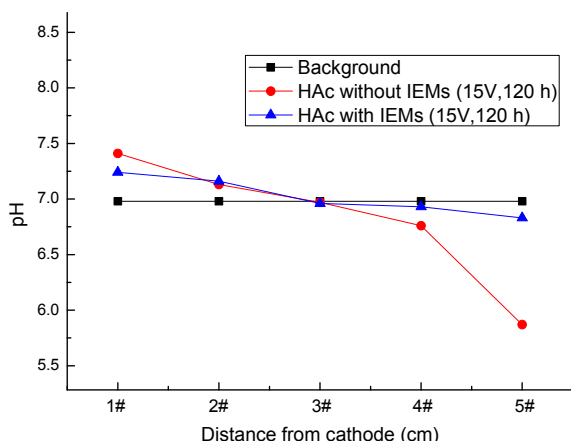


Fig. 5 pH variation in the soil

C. Uranium Distribution

The movability of uranium can be enhanced with chelating agents, as shown in Fig. 6. The highest removal efficiency happened in the third segment, which was 48.33%, 46.47%, and 63.77% for the experiments with distilled water, acetic acid, and EDTA, respectively. Therefore, when the electric voltage was set at 15 V and the experiment length was 120 hours, the removal efficiency of uranium from the radioactive soil of about 13.81 $\mu\text{g/g}$, with 0.01 mol/L EDTA, had best results. The concentration of uranium in the soil was 3.81 $\mu\text{g/g}$. The initial uranium concentration was 13.81 $\mu\text{g/g}$, when the soil was artificially contaminated with 10 $\mu\text{g/g}$ of uranium standard solution.

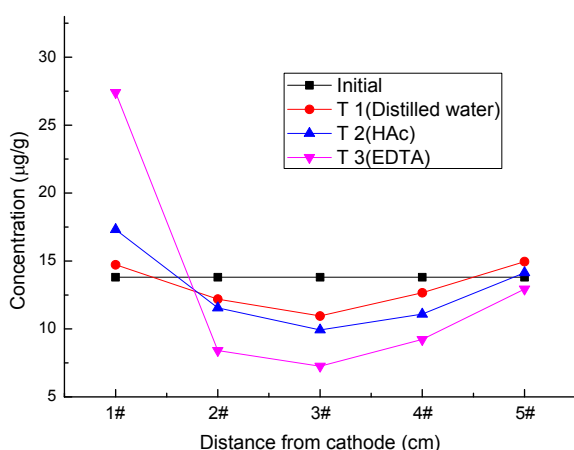


Fig. 6 Uranium distribution in soil

The uranium concentration in the solution was determined after the completion of the electrokinetic remediation experiments, and Fig. 7 shows the distribution results. The amount of uranium in the concentrated zone was higher than that in the electrode compartments. As discussed in Section I, the anions accumulated in the anode concentrated zone while the cations accumulated in the cathode concentrated zone. Generally, most concentrations of the solution were below the background level (about 0.6 $\mu\text{g/g}$). Only the concentration in the cathode zone in the experiment with EDTA was 1.03 $\mu\text{g/g}$. If the background level 0.6 $\mu\text{g/g}$ was treated as the clearance level, then the waste water produced by experiments little. Moreover, because the IEMs seclude the carbon rod electrodes from contaminates, the two electrodes were also clean. Thus, secondary waste was reduced.

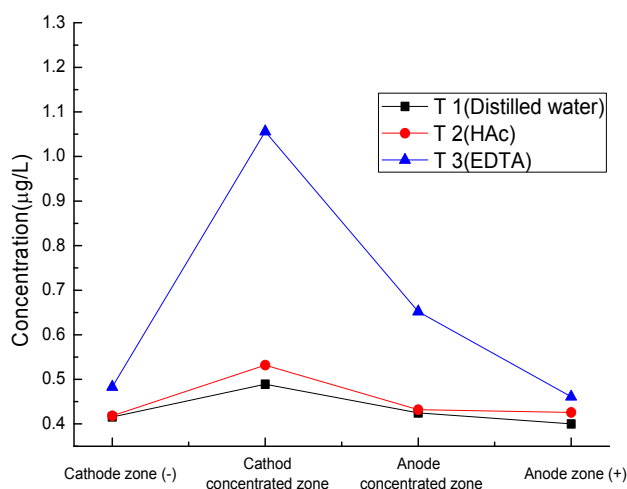


Fig. 7 Uranium distribution in solution

IV. CONCLUSIONS

It is very important to pay particular attention to the reduction of secondary waste in the remediation of soil contaminated by nuclides. Based on the results of the experiments, the following conclusions can be drawn:

- (1) Experiment apparatus improved with IEMs not only avoided H^+ and OH^- generation from the electrolysis reaction moving towards the soil, but also reduced secondary waste according to the ED principle.
- (2) The experiment with the CuSO_4 solution demonstrated the feasibility and efficacy of the IEMs. In all three experiments, the uranium concentration in the solution in all the compartments was mostly below or close to the background concentration. Therefore, this study concluded that IEMs improved the experimental apparatus and reduced the secondary waste of liquids.
- (3) Chelating agents enhanced the movability of the uranium. The EDTA experiment produced better results than the HAc and the distilled water experiments. The highest removal efficiency occurred in segment 3# in the experiment with the EDTA, which was 63.77 % for 120 h disposal with 12 V. Although the remediation efficiency

wasn't very high, this study believes that good results will be achieved after proper measures are taken.

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