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## Effect of Electrode Materials on electro kinetic remediation of Uranium Contaminated Soil

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# Effect of Electrode Materials on electro kinetic remediation of Uranium Contaminated Soil

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**Abstract.** In this study, three different electrode materials (graphite, stainless steel, and titanium rods) were used to explore the electro kinetic (EK) remediation of soil contaminated with uranium (U). All EK experiments were carried out in a soil cell reactor with a moisture content of 25.1% and a total uranium mixture of 90.6 mg/kg at a constant voltage gradient (1V/cm) for 5 days. The experimental results show that the EK repair process with graphite rod as the electrode material has the highest current peak, and the overall current level is higher than the other two electrode materials. Compared with stainless steel and titanium rods, the removal efficiency of using graphite as the electrode material U in contaminated soil reached 34.11%. However, the removal rates using stainless steel and titanium rods were lower, 15.79% and 18.77%, respectively. In the EK experiment, the main removal is from the exchangeable part of U to the carbon-bound U composition, while the remaining forms of uranium are difficult to remove under this condition, so in order to be more efficient, the uranium in the soil is removed with maximum reduction. It is necessary to use it in conjunction with other enhancement technologies.

## 1. Introduction

With the rapid development of the nuclear industry, the demand for uranium is also increasing year by year. It is understood that since the 1950s, China has identified more than 200 uranium deposits of different sizes, of which nearly 85% are distributed in Hunan, Fujian and Guangdong [1]. The mining and smelting of uranium mines is the main cause of uranium-contaminated soil. In the mining and smelting of uranium mines, a large amount of waste liquid and tail uranium mines are generated. These wastes cannot be effectively treated at this stage, generally taken near the mining area. Stacking or discharging, these tail uranium mines will release a large amount of radioactive elements U under the action of rain, differentiation, etc., which will cause pollution of water bodies and soils [2, 3], both at home and abroad for uranium-contaminated soil events. Related reports [4, 5]. Uranium is a highly toxic radioactive metal element, mainly inhaling uranium-containing aerosols, ingesting uranium-containing water or entering the human body through the food chain [6, 7], which not only affects the yield and quality of soil crops, but also there are potential long-term risks to human health that endanger human survival and are therefore necessary for the restoration of uranium-contaminated soil.

Electro kinetic remediation technology is a contaminated soil remediation technology developed in the 1980s. Because it has the characteristics of high repair efficiency and a certain degree to avoid re-



contamination, power saving and in-situ repair, it is called “green remediation technology” [8]. By applying direct current, chemical reactions such as electro migration, electroosmosis and electrophoresis of pollutants in the soil cause the pollutants to completely migrate out of the soil and achieve the purpose of remediation [9]. At present, most of the electro kinetic remediation technology is applied to removal of heavy metal contaminated soil such as cadmium, copper, lead, zinc, etc. There is only a small amount involved in the repair of radioactive element uranium contaminated soil [10-12]. Research at home and abroad has focused on how to control pH to improve the removal efficiency of electrosurgical repair. However, there are few studies on the migration and morphological changes of heavy metals for various factors in the electric process. The bioavailability and migration of heavy metals in soil depend on the form of heavy metals in the soil. Therefore, it is important to study the changes of heavy metal forms in the electro kinetic process. In the remediation process, the electrode material is a key factor affecting the efficiency of. The existing research shows that the electrode material can significantly affect the removal efficiency of the pollutant during electro kinetic remediation process. Suzuki [13] et al. studied the removal efficiency of lead in three different anode materials (graphite, Pt/Ti, IrO<sub>2</sub>/Ti), and the removal efficiency was Pt/Ti, IrO<sub>2</sub>/Ti and graphite from high to low. Yuan [14] et al. compared the removal efficiency of graphite, Pt/Ti and PET-CNT as cathode materials for electrically repairing heavy metal contaminated soil, and found that the new cathode material PET-CNT has the best repair efficiency. Therefore, selecting the appropriate electrode material in the electric repair is of great significance to the removal efficiency. However, at present, there are relatively few researches on the electric parameters of electric uranium-contaminated soil. Most of them focus on the remediation of heavy metals and organic matter. Therefore, the optimization of the electric parameters for radioactive uranium-contaminated soil is more practical for practical applications. Great promotion.

In this paper, the uranium-contaminated soil with uranium content of 100mg/kg was used as the research object. The EK treatment was carried out with different electrode materials. The transformation of U-form distribution in soil under different electrode materials and the migration of U in different soil sections in soil were investigated. Regularity, at the same time, the current density, soil pH and conductivity of the remediation process were also analysed, which provided some theoretical support for the restoration of the actual site of uranium tailings soil pollution.

## 2. Experiment

### 2.1. Materials

The experimental soil is 20cm deep from a uranium mine in Hengyang, Hunan Province. After being retrieved, it is chopped and air-dried, and then the stones, branches and other debris are removed. It is then ground through a 10 mesh screen for storage. The basic physical and chemical properties of soil samples are determined according to the Manual of Soil Monitoring and Analysis. The standard solution of uranium is prepared. According to the uranium content of the tested soil, 100mg/kg is added to a certain amount of standard solution for preparation. After stirring evenly, it is incubated for about 30 days at room temperature, dried and ground through a 10-mesh sieve, and stored for later use. The basic physical and chemical properties of the original soil and the water supply soil are shown in Table 1.

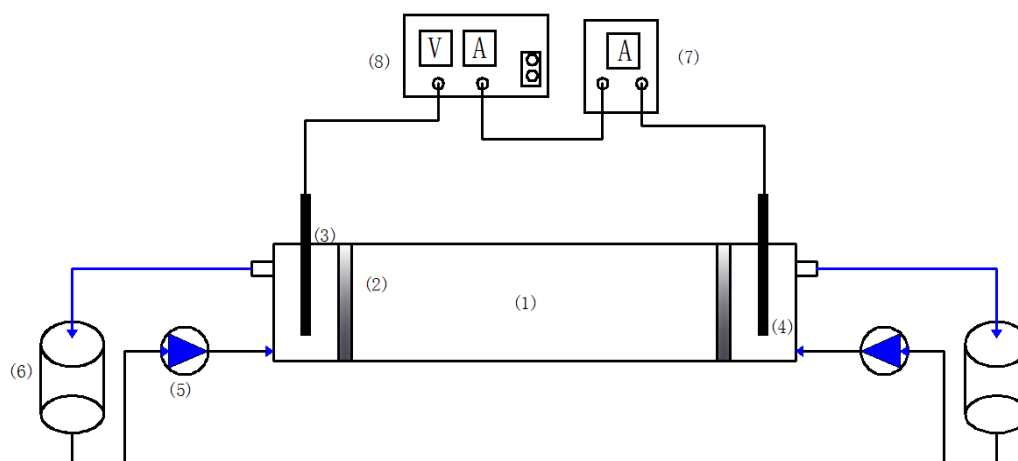
**Table 1.** The basic physical and chemical properties of soil

Measurement index	Moisture content/%	pH	Conductivity/(ds·m <sup>-1</sup> )	Organic mass/%	U(mg/kg)
Numerical value	25.1	4.51	2.83	3.5	90.6

### 2.2. Electro kinetic remediation installation

According to the needs of Electro kinetic remediation, the experimental device is a self-made reactor (Fig.1), wherein the soil chamber size is 15cm×5cm×6cm, and the electrolysis chamber size is 5cm×5cm×6cm,. Two peristaltic pumps (HL-2, Shanghai) were used to circulate electrolyte between the electrode compartment and the electrolyte reservoir; the DC power supply was applied to the EK

system with a specific constant voltage gradient (2.0V/cm). It adopts DC power supply (Hangzhou Apple Instrument Co., Ltd., China), the current range is 0A to 3A, and the voltage range is 0V to 30V. Electrode materials (20 mm in diameter, graphite, stainless steel, and titanium rods) were placed in the anode chamber (left) and the cathode chamber (right), respectively. Separated by a glass partition between the soil chamber and the electrolysis chamber, the separator is uniformly provided with a circular hole having a diameter of 1 cm, and a filter cloth having a pore diameter of 0.58  $\mu\text{m}$  is placed to prevent the soil from entering the electrolysis chamber.



**Figure 1.** A schematic view of the electro kinetic laboratory setup: (1) The cell for soil sample, length: 15cm, width: 5 cm, height: 6 cm. (2) Perforated polymethacrylate and a filter paper. (3) Electrode. (4) Electrode chamber. (5) Peristaltic pump. (6) Electrolyte reservoirs. (7) Logger. (8) DC power supply.

### 2.3. Experimental processes

Three types of electrode materials: graphite, steel iron, and Titanium were used for the cathode. Graphite was used for the anode. Sodium nitrate solution (0.01 mol/L) was used as anolyte and catholyte throughout the experimental. Each electrolyte reservoir was filled with 600 mL of catholyte or anolyte. The electrolytes were circulated from electrolyte reservoir into the corresponding electrode chamber using peristaltic pump at the rate of 5.6 mL/min and the electrolyte level in the electrode chamber was maintained equally. A 1.0 V/cm of potential gradient was applied for 120 h. EOF was calculated according to the volume changes of the two chambers. When EK experiment was terminated, the soil sample was sectioned into five equal parts and labeled as S1 to S5 from anode to cathode.

### 2.4. Analysis of Soil

Soil pH and EC were measured using a pH meter (S220 seven compact, Mettler – Toledo International Inc., Switzerland) and an EC meter (DDSJ-308A, Shanghai INESA Scientific Instrument Co., Ltd., China), respectively, by preparing slurries with soil to water ratio of 1:2.5 [15]. Stepwise chemical extraction process of uranium in soil: (F1) Exchangeable state (including water soluble state): Add 20 mL of 1 mol/L  $\text{MgCl}_2$  solution (pH=7), shake at room temperature for 2h, transfer to a 50 mL centrifuge tube and centrifuge at 8000 r/min for 10 min, and remove the supernatant in a 100 mL volumetric flask. Wash the conical flask twice with 30 mL of distilled water, carefully pour the washing solution into the original 50 mL centrifuge tube, centrifuge at 8000 r/min for 10 min, remove the supernatant in the same volumetric flask, add 1 mL of concentrated  $\text{HNO}_3$ , and set with distilled water. Allow to scale and shake for testing. (F2) Carbonate bound state: Take the residue of I, add 20mL 1mol/L NaAc solution (NaOH, HAc adjusted pH = 5.0), shake at room temperature for 7h, the following operation is the same as step I, dilute the supernatant with distilled water, shake and test. (F3) Organic matter binding state: Take the residue of II, add 20ml  $\text{H}_2\text{O}_2$ , react at room temperature for 1h, then keep in the water bath of 85°C for

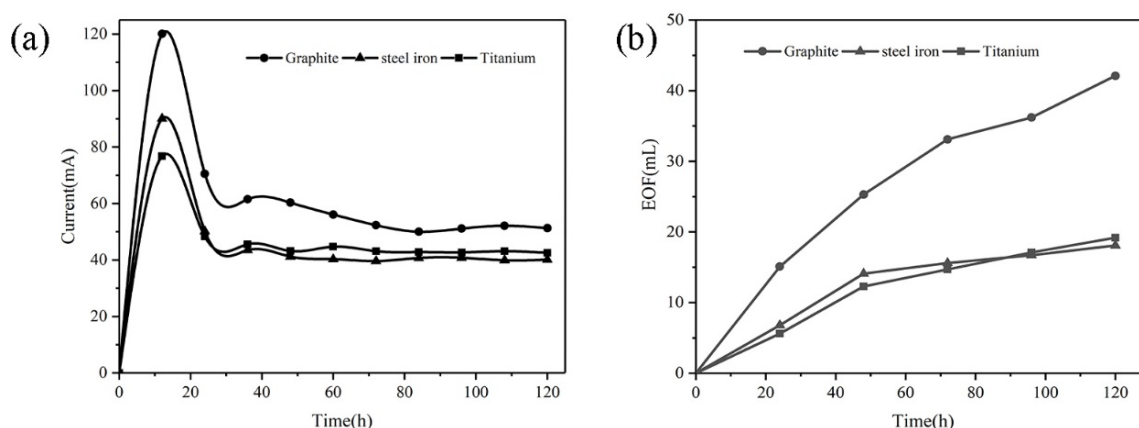
1h, evaporate to dry; add 20ml hydrogen peroxide, continue to heat in water bath at 85°C for 1h, evaporate to dry; add 50mL 1 mol/L ammonium acetate solution (pH=2 adjusted for HNO<sub>3</sub>) was shaken at room temperature for 2 h. The following supernatant was extracted in the same manner as in step I, and the supernatant was made to volume with distilled water, and shaken to be tested. (F4) Iron-manganese oxide binding state (include Amorphous iron manganese oxide-hydroxide bound state and Crystalline iron-manganese oxide-hydroxide bound state): The residue of III was taken, and 20 mL of Tamm's solution (10.9 g/L oxalic acid+16.1 g/L ammonium oxalate, pH=3.0) was added, and the mixture was shaken at room temperature for 5 hours. The following supernatant was extracted in the same manner as in step I, and the supernatant was made to volume with distilled water, and shaken to be tested; The residue of IV was taken, and 40 mL of sodium dithionite-sodium citrate-sodium bicarbonate (CDB) solution (pH = 7.0) was added thereto, and the mixture was shaken at room temperature for 5 hours. The following supernatant is extracted synchronously, and the supernatant is made to volume with distilled water and shaken to be tested. (F5) Residual state: Take the residue of V, add 15mL of aqua regia and 8mL of hydrofluoric acid, and then digest it with microwave. After completely dissolving, dilute to 100mL with ultrapure water and shake for testing.

### 3. Results and discussion

#### 3.1. Changes of electric current and EOF during the EK treatment

Fig.2a shows the change of electric current during the whole EK process using three different cathode materials. As seen in Fig.2a, Under three different electrode materials, the electric current will peak first in a short time, then gradually decline, and finally stabilize. There was no significant difference in the decreasing trend of electric current by using different electrode materials. The electric current in Graphite, Steel iron and Ti treatment strongly increased to 120.7mA, 90.8mA and 76.5mA respectively within approximately 12 h, then gradually decreased at the following 18 h, and finally reached the equilibrium after 90 h. The increase in current at the beginning may be related to the electrolysis of water and electrolyte. The generation of H<sup>+</sup> and OH<sup>-</sup> increases the amount of mobile ions in the system, and the entry of H<sup>+</sup> into the soil promotes the desorption of uranium in the soil. It can be seen from Fig.2a that regardless of the electrode, the current gradually decreases with time, mainly because the electrode is polarized during the test. The polarization phenomenon of the electrode includes both activation polarization and concentration polarization [8]. Activated polarization means that the hydrolysis reaction occurs in both the cathode and the anode during the test, and oxygen and hydrogen are generated. The generated bubbles will cover the surface of the electrode, making the conductivity of the electrode worse, and the electrochemical reaction becomes dull, thereby causing the potential of the electrode. Deviation from the equilibrium potential, eventually leading to a smaller current.

Cumulative EOF for different EK treatments is shown in Fig.2b. The EOF increased with increasing the operation time and the direction of the EOF were from the anode to the cathode in all the EK treatments. During the whole period of the experiment, the EOF in the Graphite treatment was always higher than that in the steel iron and Ti treatments. This result was proved by the previous studies, which reported that EOF was clearly dependent on the electric current [16].

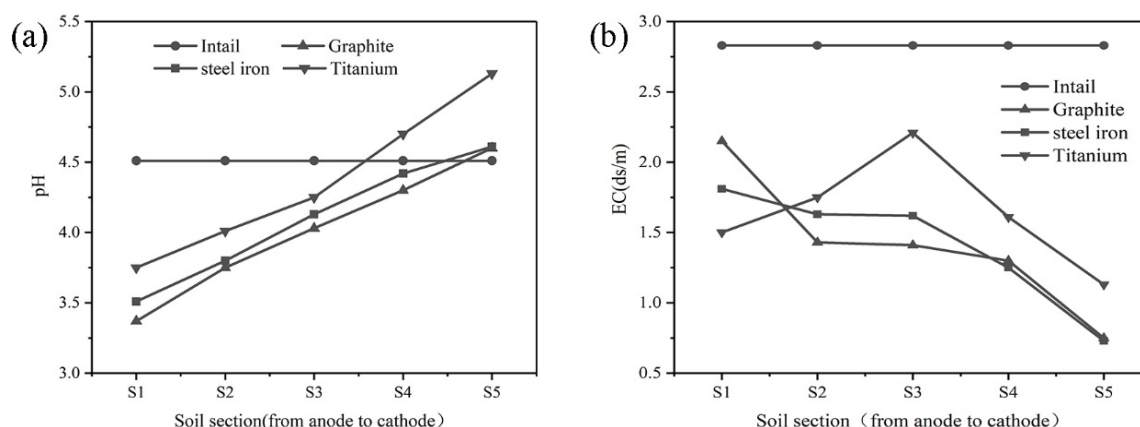


**Figure 2.** Changes of a) electric current and b) cumulative EOF with EK the prolongation of the treatment time.

### 3.2. Soil pH and EC after EK treatment

Soil pH significantly affected the existing form of uranium in the soil. In the low pH environment can enhance the solubilization of uranium in soil [10] and improve the removal of uranium in soil. Fig.3 (a) shows the pH of soil after 120h of different EK treatment. The initial pH of soil was 4.51. During the EK process, electrolysis reactions occurred at electrodes led to produce hydrogen ions at the anode, causing that the pH of anode fluid rapidly decreased. Meanwhile hydroxide ion were produced at the cathode, causing that the pH of cathode fluid rapidly increased. The acidic anode fluid was transported into the soil by electro migration and EOF resulting in a low pH of soil near the anode [15]. Hydroxide ions were transported into the soil by electro migration which was also participated in changing soil pH [13]. Compared to the initial pH value, the soil pH from S1 to S4 underwent an acidification process, however, the soil pH in S5 showed no significant change in graphite and steel iron. This is because that the hydroxide ions generated at cathode are neutralized by the hydrogen ions from anode. As the electro migration of hydrogen ion is 1.8 times faster than that of hydroxide ion [13]. But the soil pH in S5 increased to 5.13 in Ti. When graphite is used for the cathode, the acidification process is more pronounced. The pH curve of S1 to S4 in the graphite treatment is lower than that of the stainless steel and Ti treatment. Graphite as a cathode produces high current and EOF (Fig.2) and spontaneously accelerates the electrolysis of water [16]. Therefore, more hydrogen ions and hydroxide ions are generated at the anode and the cathode, respectively, resulting in a relatively lower pH of the soil near the anode in the graphite treatment than other treatments.

Soil EC significantly affected the EK remediation. In general, the low soil EC meant that the overall movement of ions by electro migration was low, the EK remediation process would take a great deal of time [17]. The EC value of the soil profile in different treatments after the EK experiment is shown in Figure3b. For stainless steel and processing, the EC value gradually decreases from anode to cathode. There was no significant difference from S2 to S4 in the graphite treatment and from S2 to S3 in the stainless steel treatment. And similar trends have been observed in previous studies [18]. When Ti is used for the cathode, the highest EC value is observed in the intermediate portion (S3) and decreases toward both sides.



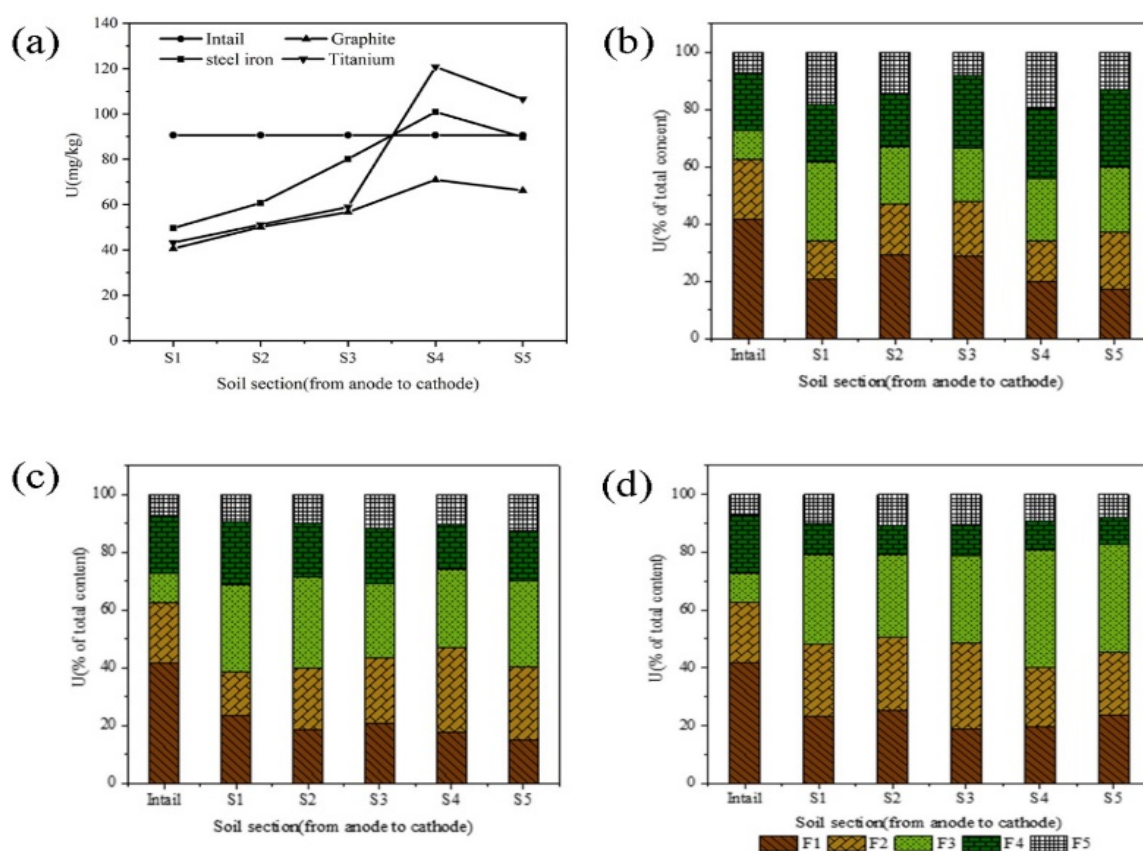
**Figure 3.** Soil a) pH and b) EC in different soil sections after EK treatments.

### 3.3. Heavy metals removal and Fractionation changes after EK treatment

Previous studies demonstrate that heavy metals are mostly removed through electromigration and electroosmosis during the EK treatment [13]. Fig.4 shows the residual concentrations of uranium in the soil sections after EK treatments. After all the different EK treatments, the highest uranium concentration in the S4 region contains, 70.9mg/kg, 100.9mg/kg and 110.7mg/kg in EK1, EK2 and EK3 respectively. Compared with stainless steel and titanium rods, the removal efficiency of using graphite as the electrode material U in contaminated soil reached 34.11%. However, the removal rates using stainless steel and titanium rods were lower, 15.79% and 18.77%, respectively and in the EK experiments,  $\text{UO}_2^{2+}$  in the soil migrated towards the cathode. The total distribution of total U(VI) in EK1, EK2, and EK3 were different because the different EK treatment have different the value of EOF, In the EK process with graphite as the electrode, the residual amount of uranium is the smallest due to its maximum electroosmotic flow [16] (Fig.2(b)).

As shown in Fig.4, a five-step sequential extraction was conducted to analyse residue Cr speciation in soil samples. In EK3 (Fig.4 (d)), the “EXCH” U fraction was mainly removed with a maximum removal rate up to 75.81% in S5. There is also an obvious removal for the “CAR” fraction in EK3 with a maximum removal rate up to 56.32% in S5. but Other fractions, such as FeMnOX, OMB, and RES, were hardly removed. The same results were obtained in EK1 (Fig.4 (b)) and EK2 (Fig.4(c)). Relatively speaking, the “EXCH” and the “EXCH” are easier to remove from the soil. This is because the hydrogen ions generated by the electrolyzed water can desorb it from the soil surface, but it is difficult to desorb from the soil surface into the soil pores such as FeMnOX, OMB, and RES [8].





**Figure 4.** a) Residual concentrations of heavy metals and b) Fractionation changes in different soil sections after EK treatments.

#### 4. Conclusion

This study explored the EK remediation of uranium (U)-contaminated soil using three different Electrode Materials. Compared to stainless steel and titanium electrodes, the degree of water electrolysis is more severe than that of the other two electrode materials due to the more active proton transport on the graphite electrode surface, which results in higher current values and electroosmotic flow, and the degree of change in soil pH is uniform and it has a certain correlation. Compared with stainless steel and titanium rods, the removal efficiency of using graphite as the electrode material U in contaminated soil reached 34.11%. However, the removal rates using stainless steel and titanium rods were lower, 15.79% and 18.77%, respectively. In EK repair, F1 and F2 removal can only be effectively achieved. The removal rate of the other three forms is extremely low. Therefore, different electrode materials cannot effectively remove uranium in other forms, so the development of other electric enhancement technologies is the focus of the work.

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