Study on immobilization and migration of nuclide u in superficial soil of uranium tailings pond

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Abstract. The uranium tailings in southern China was used as the object of study to study the fixation and migration characteristics of nuclide U in shallow tailings. The results showed that the precipitation of tailings in the tailings soil was not linearly related to the depth during the acid rain leaching process. Tailings soil in the role of fixatives, when the lime as a fixative, the tailings of different soil uranium in 20 days after the re-precipitation. However, when lime and ammonium phosphate were used as fixing agents, the cumulative precipitation of U had a significant effect, and the migration of uranium was inhibited.

1. Introduction
Since the 1940s, nuclear energy has been developed and exploited, uranium demand is increasing, resulting in a large number of uranium tailings. It is expected that by 2020, Chinese nuclear uranium demand will reach 3180 to 6540 t [1]. The diffusion of radionuclides in the uranium mining tailings has become a serious problem that needs to be solved in contemporary society because of the lack of understanding of the pollution problem after the retreat of uranium and metallurgical tailings. Uranium tailings during the long-term open dumping process, the residual radioactive elements and toxic heavy metals susceptible to rain, surface and groundwater and other environmental factors to a certain extent precipitated, resulting in uranium tailings into a Radioactive-heavy metal composite pollution sources[2,3]. The acid leaching process is becoming more and more widely used in the hard rock uranium mine, Waste residue produced during the mining process is used before the entry into the tailings reservoir, and the lime is neutralized and then transported to the tailings reservoir [4-6]. With the passage of time, the nuclides that have been deposited are re-precipitated due to the acid reflux phenomenon. The radionuclides can disperse into the air with the weathering effect and reach the surface water from the surface soil around the polluted reservoir area by lateral migration, But also through the vertical migration of infiltration to reach the groundwater and with the flow of land around the migration, thus the reservoir area of the ecological environment poses a serious threat [7, 8].

Domestic research on the migration of radionuclides mainly focuses on the geological work of low and medium-sized radioactive waste repository, and few studies have been reported on the migration and control of radionuclide migration in waste disposal sites. In this study, the leaching test of uranium tailings was carried out to study the uranium removal of uranium tailings in acid rain and the fixation effect under the action of fixing agent. The reference was made to the safe operation and decommissioning of uranium tailings as well as the basis for studying the chemical and kinetic behavior of radionuclides in uranium tailings.
2. Experimental Part

2.1. Collection and Treatment of the Test Samples
The soil used for the test was taken from uranium tailings in southern China. Sampling point takes a point every 20 cm in vertical sampling, just a total of 4 samples. Samples is collected on the sample bag, and edit the corresponding number from 1 to 4, which is naturally air-dried. And then the collection of each sample is broken, mixed, shrinked, and other processes to deal with.

2.2. Test Reagents
Test simulate acid rain in acidic liquid with $c(\text{SO}_4^{2-}) : c(\text{NO}_3^-) = 5:1$ and adjust pH at 4.8 with deionized water [9].

2.3. Test Methods

2.3.1. pH Determination of Uranium Tailings. According to the International Standard for the Determination of Soil Quality-pH (ISO10390: 2005) [10]. The sample was air-dried at room temperature, a sample of 1: 5 by volume and a suspension of water, weighing the dried sample of 2 mm diameter sieve 20 g in 100 ml high beaker, adding 100 ml of deionized water to remove $\text{CO}_2$, stirring the stirrer for 1 min. After standing for 30 min, the pH was measured with a PH-3C acidity meter.

2.3.2. Leaching experiment design. Three parallel leaching columns were made of 10mm Plexiglas with an inner diameter of 7 cm and a height of 130 cm. Sampling ports were set at 20 cm, 40 cm, 60 cm, 80 cm. Loading 30 cm high gravel firstly, and then getting the 4 to 1 soil samples of the uranium tailings into it, height 80 cm, after compaction, the bulk density of the packed soil was consistent with the measured soil bulk density as 1.41 g·cm$^{-3}$.Leaching device was controlled by peristaltic pump, the flow rate of the peristaltic pump was set to 17 ml·min$^{-1}$ and the time was set to 60 min. The total amount of leaching was 1020 ml. A part of the supernatant was taken out for sampling and filtering, the solution was measured with PH-3C acidity meter, and the 5-Br-PADAP spectrophotometric method for the determination of uranium, the schematic diagram of the test device is shown in Figure 1.

No. 1 column for direct leaching uranium tailings sampling soil, No.2 column surface covered with 50 grams lime and leaching uranium tailings sampling soil, No.3 column surface covered with 25 grams of lime and 25 grams of diammonium phosphate and leaching uranium tailings sampling soil, Three leaching columns were leached for 50 days at simulated acid rain (pH ~4.8). Eight sampling ports on both sides of tailing soil at the depth of 20 cm, 40 cm, 60 cm, 80 cm, each sample port collects 50 ml of leachate. Take two symmetrical sampling ports to determine the average uranium concentration and pH value as the final uranium concentration and pH for each depth, collecting totally 400 ml per day, the bottom sampling port collects 600 ml of leachate per day.
3. Experimental results and analysis

3.1. Chemical composition

Table 1 for uranium tailings samples using inductively coupled plasma emission spectrometry (ICP-MS) measured uranium and X-ray diffraction analyzer measured part of the heavy metal content analysis results. The total amount of tailings per kilogram of tailings U is 142 mg·kg⁻¹, and the initial pH values of the samples 1 to 4 of the uranium tailings were 4.38, 4.36, 4.37, 4.22 respectively.

| Element     | U  | SiO₂ (%) | Al₂O₃ (%) | Fe₂O₃ (%) | CaO (%) | K₂O (%) | Na₂O (%) | MgO (%) |
|-------------|----|----------|-----------|-----------|---------|---------|---------|---------|
| Average Value | 142| 84.15    | 8.31      | 1.54      | 0.25    | 1.58    | 0.12    | 0.53    |

3.2. Uranium Tailings in the Nuclide Uranium Content and the Dynamic Changes

After 50 days of continuous leaching of simulated acid rain on uranium tailings in different depths, three column precipitation out of uranium cumulative precipitation shown in Figure 2.

![Diagram of experimental device.](image-url)
Figure 2. The changing curve of cumulative release of uranium with time

From Figure 2, the cumulative precipitation of uranium over time shows that: different leaching column in the 50 days acid rain leaching, the precipitation law of uranium at different depths is similar, but only the total amount of precipitation is different. No.1 column direct leaching in the uranium tailings soil. Uranium precipitation increased rapidly in the initial period of the leaching cycle, and precipitation tends to be stable and gradually reduced in late period. Due to simulated acid rain leaching tailings, Precipitated the surface of the surface covered by the aged oxide film to produce a new surface.

It improves the adsorption capacity of the tailings, and the precipitation is controlled by internal diffusion, and the precipitation rate is slowed down. No.2 column cover 50 grams lime in the uranium tailings soil, 20 days before the cumulative precipitation of uranium close to zero. Adding lime makes the soil in the alkaline environment, uranium through complex precipitation, uranium element activity is inhibited. So that the nuclide in the alkaline environment deposition and not spread, 20 days after the cumulative precipitation of uranium gradually increased. The precipitation of uranium in the surface of the No.3 uranium tailings is 25 grams of lime and 25 grams of diammonium phosphate, and the precipitation concentration of uranium is increasing. However the amount of uranium precipitates is very small. It may be due to the fact that the soil is in the alkaline environment. And at that time, the addition of diamines causes the strong adsorption of UO$_2^{2-}$ by phosphate ions to form a precipitate of uranium phosphate, which prevents the migration of uranium.

3.3. Vertical distribution of nuclides in uranium tailings

The distribution of uranium in uranium tailings can reflect the degree of uranium pollution and the potential environmental risk of uranium in uranium tailings soil. In this experiment, uranium tailings soils were treated with simulated acid rain leaching under different fixatives uranium content precipitated after 50 days and shown in Figure 3.
Figure 3. Uranium content at different depths

It can be seen from Figure 3 that the distribution of uranium in No.1 column soil is not uniform and does not have a linear relationship with depth. The content of uranium in 80 cm tailings is the highest, and Uranium content in 20cm tailings soil followed. The precipitated concentrations of uranium in the different depths were 3.71 mg·Kg\textsuperscript{-1}, 3.54 mg·Kg\textsuperscript{-1}, 3.61 mg·Kg\textsuperscript{-1}, 3.74 mg·Kg\textsuperscript{-1} respectively. The soluble uranium in the simulated acid rain will dissolve and migrate downwards, Wu X Y et al.\cite{11} have shown that rainfall has seriously affected the migration and diffusion of radionuclide uranium in groundwater, Cations in acid rain (such as H\textsuperscript{+}) also accelerate uranium replacement and precipitation, So that the uranium in the tailings soil at 80 cm the highest content. 20 cm tailings soil in the soil surface, with high oxygen content, uranium is prone to migration in the oxidation conditions. The contents of No.2 column and No.3 column uranium increased with the depth, the fixative was placed in the tailings soil surface, after 50 days of acid rain leaching, the fixative dissolved with the infiltration, and uranium content in the different depths is in the range of 0.68 to 2.02 mg·Kg\textsuperscript{-1}, and the uranium content in No.3 column is in the range of 0.36 to 0.38 mg·Kg\textsuperscript{-1} at different depths. Through the intuitive analysis of the data, when lime and diammonium phosphate were used as fixing agents, more conducive to control the precipitation of nuclides uranium.

4. Conclusion
The vertical distribution of nuclide U in tailings soil is not regular, and the maximum amount of radioactive precipitates is reached at 60cm to 80 cm. The amount of uranium precipitate in the soil surface to 20 cm deep may be in the oxidized environment or in the soil, resulting in uranium precipitation is higher than 20 cm to 60 cm precipitation. In the leaching experiment, the cumulative release and the release rate of uranium are larger and the precipitation increases with time, and it is easy to leach out in the process of simulated acid rain. When the lime is used as the fixing agent, the initial fixation effect is good. Uranium has been deposited over time has been re-precipitated due to the acid reflux phenomenon. When the lime and diammonium phosphate are used as the fixing agent, the migration of uranium is inhibited, suitable for long-term treatment of uranium tailings.

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