

## URANIUM AND THORIUM LEACHED FROM URANIUM MILL TAILING OF GUANGDONG PROVINCE, CHINA AND ITS IMPLICATION FOR RADIOLOGICAL RISK

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The paper focused on the leaching behaviour of uranium (U) and thorium (Th) from uranium mill tailing collected from the Uranium Mill Plant in Northern Guangdong Province, China. Distilled water (pH 6) and sulphuric acid solution (pH 4 and 3) were used as solvent for the leaching over 22 weeks. It was found that the cumulative leach fraction from the mill tailing was 0.1, 0.1 and 0.7 % for U release, and overall 0.01 % for Th release, using distilled water, sulphuric acid solution of pH 4 and pH 3 as leaching agents, respectively. The results indicate that (1) the release of U and Th in uranium mill tailing is a slow and long-term process; (2) surface dissolution is the main mechanism for the release of U and Th when sulphuric acid solution of pH 3 is employed as the leaching agent; (3) both U and Th are released by diffusion when using sulphuric acid solution of pH 4 as the leaching agent and (4) U is released by surface dissolution, while Th is released by diffusion when using distilled water as the leaching agent. The implication for radiological risk in the real environment was also discussed.

### INTRODUCTION

In the wake of Japan's nuclear crisis in 2011, approvals for constructing new nuclear power plants were temporarily suspended because of safety concerns over nuclear contamination in China. However, little public attention has been paid to the radioactive and environmental hazards behind the booming exploration activities of uranium resources in many developing countries like China, due to secular increased demands for energy consumption. Extensive extraction of uranium ores has been producing numerous tailing, waste-rock piles and slime dams, which were randomly disposed<sup>(1–2)</sup>. These chemical and radioactive metallurgical wastes could be activated during the long-term process of oxidation–reduction and weathering. Since non-target elements like Th, and target element U still have high content in wastes, abandoned uranium mine tailing may become a source of radioactive pollutants (i.e. U, Th, Ra and their daughter elements)<sup>(3)</sup>.

Many low-grade uranium deposits have been identified in China. Mining and processing of these ores commenced several decades ago in the northern part of Guangdong Province, China<sup>(1)</sup>. Sulphuric acid

was used to dissolve and oxidise the uranium. The spent acids and tailing were piped from slurry to unlined ponds<sup>(4)</sup>. An estimated 0.1 million tonnes of tailing were disposed into a 20-acre square, constituting an eco-environmental problem of extraordinary spatial dimensions. The predominant environmental concern regarding these residues is the release of contaminants by leaching. To evaluate the environmental impacts from the residues, it is necessary to quantify this leaching and gain a detailed knowledge about the mechanisms controlling leaching and release of contaminants. Semi-dynamic leaching tests are usually employed to elucidate the dominant leaching mechanism from a stabilised/solidified waste in which the leaching agent is renewed periodically<sup>(5)</sup>. Many authors have used such tests to perform a long-term projection of the system evolution<sup>(6, 7)</sup>. The main leaching mechanism of an element will depend on the immobilising reagents, the physical properties of the leaching material, the leaching agent and on the environmental conditions of the system.

The knowledge of the trends of release of radionuclides (U, Th) due to geochemical processes like weathering is essential to predict their mobility and possibility of reaching groundwater. However, few studies are known about the behaviour of uranium

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tailing regarding long-term leaching and release of relevant contaminants. In the present work, the mobility of U and Th from the typical uranium tailing was studied under semi-dynamic leaching conditions. As many uranium mill plants in China make use of heap leaching with sulphuric acid, the local area usually suffers rainfalls with low acidity. For instance, pH values of rain in Guangdong Province, China in this study ranged from 3.5 to 4.7<sup>(8)</sup>, sometimes even reaching 2<sup>(9)</sup>. Therefore, the environmental impacts of the uranium tailing pond under eluviations with acid rains should be seriously considered. In an attempt to investigate the leaching processes under simulated rainfall, two representative pH values (pH 3 and 4) were adopted as simulated acid rain and pH 6 served as simulated normal rain as a comparison. The main objectives of this study are: (1) to investigate the leaching characteristics of the key elements U and Th of the uranium tailing and (2) to determine their controlling leaching mechanisms. The study is necessary to understand environmental behaviour and to assess their environmental impacts of radioactive U and Th in uranium tailing over long-term weathering in nature.

## MATERIALS AND METHODS

### Experimental samples and setup

The leaching material (uranium tailing) was sampled from a large uranium plant in Guangdong Province, China, where low-grade but massive granite uranium ores were found (the U- and Th-containing mineral contents in relative percentage:  $UO_2$ , 27.6–59.3 %;  $UO_3$ , 22.3–52.8 % and  $ThO_2$ , <3 %)<sup>(10)</sup>. The total contents of U and Th in tailing were 472.5 and 8.2 mg  $kg^{-1}$ , respectively. Leaching experiments were carried out in the brinell funnels (20 cm in diameter) each installed with 1 kg of tailing, using three kinds of simulated rain as leaching agents. Deionised water (pH 6) represents normal rain, acidified deionised water with sulphuric acid (pH 3 and 4, respectively) as acid rains. In each leaching period, the three tailing samples were sprayed slowly for 2 min with a plastic watering pot that charged with 800 ml of the above simulated rains which just cover the tailing's surface and soaked for 1 h. Then the leachate was discharged completely and 100 ml was collected and acidified with 1 ml of 5 % nitric acid, preparing for equipment analysis after measuring its pH, redox-potential and the electric conductivity. After that, the tailing was exposed to the experimental conditions again and kept for the next leaching period after 7 d. Thus, the semi-dynamic leaching tests were carried out periodically. To date, 22 periods/weeks (154 d) of leachate have been collected. Such methods were actually equilibrium experiments to ensure good simulations of the natural conditions.

### Analytical techniques and agents

U and Th were determined by inductively coupled plasma (ICP) mass spectrometry (Elan 6100 DRC-e, PerkinElmer, Inc., USA) in the South China Institute of Environmental Science, Ministry of Environmental Protection. The detection limit of the elements ranged from 0.005 to 0.01  $\mu g l^{-1}$ . The low standard deviations of triplicates indicate a good reliability of the applied methods. The pH value and redox potential were determined by a redox potential-acidity meter (PB-10, Sartorius, Inc., Germany). The standard solutions of U and Th were prepared from ICP Single-element Standard Solution of U and Th (Ultra Scientific, Kingston, USA), respectively. Ultra-pure water acidified with suprapure nitric acid was used as the calibration blank for all dilutions. The quality control standards were run at selected intervals to ensure consistent instrument performance over the length of the analysis. All glassware and vessels were soaked in a 15 % (v/v) nitric acid solution for 24 h and subsequently rinsed with deionised water. Reagents were all of super-pure grade. All analysis was carried out using ultra-pure water (18.25 M $\Omega$  cm) produced by Milli-Q System (Millipore, Bedford, USA).

### Methods of analysis

Pertinent studies showed that in semi-dynamic leaching tests, the main leaching mechanism could be explored according to the slope of the linear regression of the logarithm of cumulative flux versus time<sup>(11)</sup>. The cumulative flux ( $B_{ac\ i}$ , mg  $m^{-2}$ ) can be obtained from Eqs (1) and (2):

$$B_{ac\ i} = \sum B_i \quad (1)$$

$$B_i = C_i \frac{V}{A} \quad (2)$$

where  $B_i$  is the single element release in each leaching period (mg  $m^{-2}$ ),  $B_{ac\ i}$  is the cumulative release flux until period  $i$  (mg  $m^{-2}$ ),  $C_i$  is the concentration of single element in the leachate in each leaching period (mg  $l^{-1}$ ),  $V$  is the volume of the leachate liquid (l) and  $A$  is the surface area of the leachate liquid contacting the uranium tailing ( $m^2$ ).

In accordance with Fick's diffusion theory, leaching processes are controlled by three main mechanisms: (1) surface wash-off, which is controlled by the rapid release of the most soluble material on the surface of the leaching material; (2) diffusion transport of the solubilised species through the pore space beneath the leaching material and (3) the slow portion of dissolution, where the leaching material dissolves with the aqueous phase in contact. If the slope of the straight line fitting the experimental

data is near 0 (slope  $\leq 0.35$ ), the surface wash-off will be the controlling leaching mechanism; for slope values close to 0.5 ( $0.35 < \text{slope} \leq 0.65$ ), the main mechanism will be diffusion; and for slope values similar to 1 (slope  $> 0.65$ ), the dissolution mechanism will be the dominant leaching mechanism<sup>(12)</sup>.

## RESULTS AND DISCUSSION

### Leaching characteristics of U and Th

As displayed in Figure 1, no significant difference was observed in the total U content in the leachate between the leaching test with simulated acid rain of pH 4 and that with simulated normal rain of pH 6 in 22 weeks. The accumulated extraction rate was almost the same, both around 0.1 %. However, leaching test with simulated acid rain of pH 3 extracted 0.7 % of total U content, notably higher than the sum of the extract rates in former two tests.

Specifically, the U concentrations in the leachate of each week were shown in Figure 2. According to the Regulations for Radiation and Environmental Protection of Uranium Mining and Milling (GB 23727-2009) in China, the guided maximum release level is  $50 \mu\text{g l}^{-1}$  for U in the effluent from uranium tailing pond without recipient water downstream. Evidently, the U content in all the leachate overwhelmingly exceeds the regulation limit by a factor of 3–9 under the simulated acid rain of pH 3. The U contents in leachate from the simulated acid rain of pH 4 at the early stage were also obviously higher than the limits. The release of Th was relatively low, with no visible differences among three cases.

### The controlling leaching mechanism

The cumulative flux of radionuclides U and Th versus time during the leaching process is presented in Figure 3 in order to understand the leaching mechanism and predict the leaching potential. The

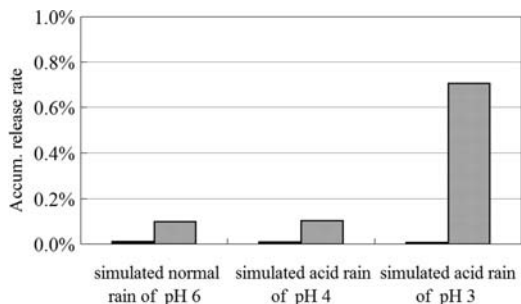


Figure 1. Accumulated release rate of U and Th in leachate with different leaching agents. Black histogram indicates Th, while shadow histogram indicates U.

cumulative fluxes of U were remarkably higher under the leaching condition of pH 3 than that of pH 4 as well as pH 6, which was quite different from that of Th. One possible reason was that Th could easily precipitate in sulphate solution. The higher the concentration of sulphate, the stronger the precipitation of Th that could occur. In contrast, the element U tends to form solvable uranyl sulphate ( $\text{UO}_2\text{SO}_4 \cdot n\text{H}_2\text{O}$ ) or uranyl monopersulphate (i.e.  $\text{M}_2[\text{UO}_2(\text{SO}_4)_2]$  and  $\text{M}_4[\text{UO}_2(\text{SO}_4)_3]$ ) in the case of low pH and high concentration of  $\text{SO}_4^{2-}$ <sup>(13)</sup>. However, minerals such as uraninite, pitchblende are insoluble under the conditions of  $\text{pH} \geq 4$ , which sharply decreased the U level of the leachates in test with the simulated rain of pH 4 and 6.

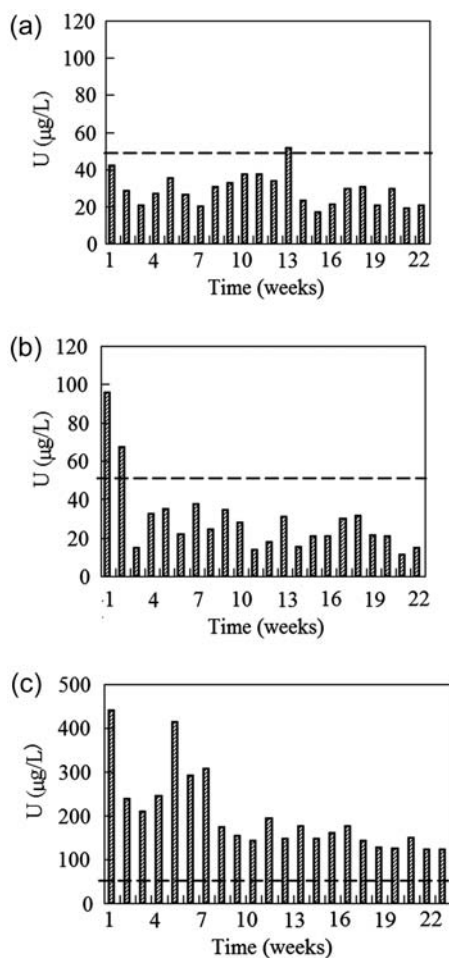


Figure 2. Separate U concentrations in leachate as a function of time period: (a) simulated normal rain of pH 6; (b) simulated acid rain of pH 4 and (c) simulated acid rain of pH 3. The dotted lines indicate the regulation limit of U release in China.

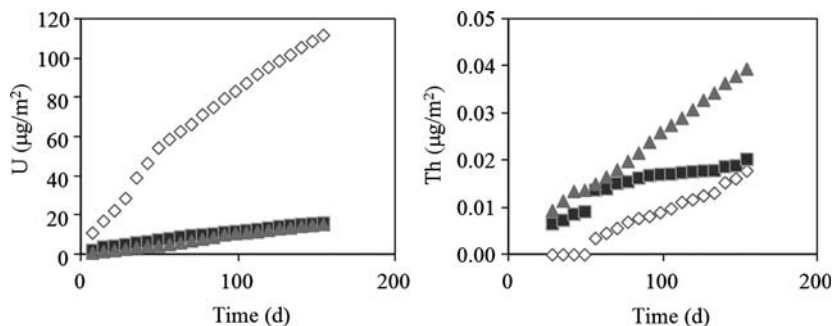


Figure 3. The cumulative flux of U and Th in the leachate of uranium tailing with different leaching agents: (open diamonds, simulated acid rain of pH 3; closed squares simulated acid rain of pH 4; closed triangles, simulated normal rain of pH 6).

Table 1. Slopes of the regression lines corresponding to the calculated concentration of U and Th versus time in logarithmic scale, which indicates the mechanism of the leaching.

Element	Slope	Mechanism	Element	Slope	Mechanism	Element	Slope	Mechanism
pH 3 U	0.772	Surface dissolution	pH 4 U	0.615	Diffusion transport	pH 6 U	0.918	Surface dissolution
Th	1.363	Surface dissolution	Th	0.564	Diffusion transport	Th	0.416	Diffusion transport

Simultaneously, this precipitation may promote co-precipitation of Th on the surface of the tailing.

The slopes of the regression line of the calculated cumulative release versus time in logarithmic scale are shown in Table 1. Both U and Th showed a surface dissolution controlled leaching mechanism under the leaching conditions of pH 3. This indicates that in the strong acidic environment, surface dissolution of the elements could be easily induced and released from the tailing. Under the condition of pH 4, leaching of U and Th was mainly controlled by diffusion. By the eluviation with deionised water (pH 6), Th presented a diffusion-controlled leaching mechanism, while U was predominantly controlled by surface dissolution.

#### Implication for radiological risk

The semi-dynamic leaching tests indicate different mobility of U and Th from uranium mill tailing under three leaching agents with varied pH. Generally, the lower the pH of the leaching agents, the higher the possibility for U to release from the tailing. However, the acidity plays no role on the leaching potential of Th. The results suggest that U residues in the huge amount of uranium tailing in the real environment could continuously release and enter the surface water or ground water system,

especially under the acid rain with pH range of 3–4. Apart from the radioactivity of U and Th, radon and further decay products might also become a threat to the safety of the water environment and even the whole ecological system. Therefore, countermeasures like adding non-toxic alkaline material (e.g. lime) into the tailing should be taken to ensure the immobility and stability of the U and Th, and thus minimise the radiological risk of the uranium tailing.

#### CONCLUSION

During semi-dynamic leaching tests of 22 weeks, the cumulative leach fraction was 0.1–0.7 % for U, and all around 0.01 % for Th from uranium mill tailing, using three different leaching agents. Furthermore, the results indicate that the release of U and Th from tailing was quite a slow process; in other words, the environmental impacts due to radioactive hazards of the uranium tailing would last even longer. However, the U concentrations in each period of leachate with the leachant of pH 3 largely exceeded the regulation limit ( $50 \mu\text{g l}^{-1}$ ) proposed by uranium industry administration in China, which suggests the uranium mill tailing could be a significant source of radiation pollution under acid rain within possible pH ranges. Both U and Th indicate

surface dissolution as the dominant leaching mechanism under the leachant of pH 3 while they show a diffusion mechanism simultaneously under the leachant of pH 4. However, under the leachant of pH 6, they show a different leaching mechanism (U-surface dissolution; Th diffusion), suggesting the easier release of U than Th even under normal environmental conditions. Countermeasures like adding alkaline material into the tailing are necessary to attenuate the mobility and leachability of the U and Th in tailing. On the other hand, acid rain should be effectively controlled in uranium mill areas.

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