

Extraction of uranium from tailings by sulfuric acid leaching with oxidants

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Abstract: Recovery of uranium have been performed by leaching uranium-containing tailings in sulfuric acid system with the assistance of HF, HClO₄, H₂O₂ and MnO₂. The effect of reagent dosage, sulfuric acid concentration, Liquid/solid ratio, reaction temperature and particle size on the leaching of uranium were investigated. The results show that addition of HF, HClO₄, H₂O₂ and MnO₂ significantly increased the extraction of uranium under 1M sulphuric acid condition and under the optimum reaction conditions a dissolution fraction of 85% by HClO₄, 90% by HF, 95% by H₂O₂ can be reached respectively. The variation of technological mineralogy properities of tailings during leaching process show that the assistants can break gangue effectively. These observations suggest that optimum oxidants could potentially influence the extraction of uranium from tailings even under dilute acid condition.

1. Introduction

As a zero carbon-emission source of energy, nuclear power has recently led to an unprecedentedly increased demand for uranium [1]. Furthermore, the number of nuclear power plants in industrial nations is increasing: China, India and Russia are planning to commission forty-six new nuclear power plants in the coming years. Therefore, uranium plays an important role in the search for alternative energies to nuclear fuels [2]. According to incomplete statistics, the current global stockpile of uranium tailings has reached 24 billion tons [3], which has become a potential secondary resource of uranium. However, there has been limited study on recovering uranium from uranium tailings due to the difficulty in recovering uranium. Due to depletion of uranium rich ore, recovering uranium from tailings is presenting significant opportunities to improve the nuclear fuel reserves [4,5]. Extraction of uranium from low-grade ores, however, requires greater efficiency in the leaching processes. It is necessary that hydrometallurgy processes has been identified as one of the optional way to solve the beforementioned problem.

The concentration of uranium in the tailings is normally range from 0.005% to 0.02%, which is much lower than the average concentration of 0.1% in the nature low grade ore [6]. Acid leaching has been largely used due to its low cost and relatively high uranium recoveries. The uranium leaching process was an oxidizing process in which sulfuric acid was normally utilized as lixiviant [7]. However, single acid condition was not enough to get satisfactory leaching efficiency for uranium tailings because low grade uranium often existed in the form of micro fine particles and disseminated inhomogeneous in high content of gangue. We found oxidants can destroy complex uranium gangue



structure to improve extraction of uranium [6]. Youlton[8] proposed can use the change of mineralogy parameters in acid leaching process to predict the dissociation pathways of uranium. The uranium dissociation from gangue mineral can achieves efficient extraction of uranium. Therefore, destroy complex gangue structure in uranium tailings and dissociated the uranium from the gangue are the important way to improve the leaching rate of uranium [9].

A series of strengthening methods for efficient recovery of uranium, including reinforced composite, ultrasound method, segmented cascade leaching, oxidation strengthen method and cavitations strengthen method, have been developed [10-13]. H_2O_2 , MnO_2 and SO_2/O_2 were usually used as oxidants to leach low-grade uranium ores. However, the uranium tailings mainly presence of high content of silicates, the effect of reactivity between these oxidants and silicates on uranium leaching is worthy of further study in sulfuric acid system. The aim of this paper analyse the effects of H_2O_2 , MnO_2 , HF and HClO_4 on uranium leaching ratio and revealing strengthening mechanism of these oxidants by investigating the mineral properties changes of uranium leaching residue.

2. Materials and methods

2.1. material

The samples used in this study were obtained from a tailings dam located in Hunan province at south of China. After drying at 110°C for 4 h, the samples were crushed in a laboratory vibration mill (RK/3ZM-100) and then screened using standard sieves to obtain particle size distribution. All samples were placed in a silica desiccator until use in the experiment. The deposit was a secondary formation containing about 0.01% uranium, mainly existed in tetravalent (U^{4+}). All chemical reagents used in experiments were of analytical grade.

2.2. Experimental methods

Chemical composition of uranium tailings were determined by inductively coupled plasma atomic emission spectrometry (ICP); The phase composition were determined by X-ray diffractometer analysis (XRD); The morphology were analyzed by scanning electron microscopy (SEM), The particle size distribution was analyzed using (LPSA); the uranium content in leaching solution were analyzed by ammonium vanadate titration method. The uranium leaching ratio were calculated using the following formula:

$$Y = \frac{V \times C}{m \times \beta} \times 100\%$$

In this equation: Y denotes the uranium leaching ratio, %; V is leaching solution volume, L; C is the uranium concentration in leaching solution, g/L; m is the mass of uranium tailings used in leaching experiments, g and β is the uranium grade in tailings, %.

3. Results and discussion

3.1 Mineralogy characteristic of uranium tailings

Chemical composition of uranium tailings analyzed by ICP were shown in reference [14]. The uranium concentration in tailings were about 0.008%, which belongs to the low grade uranium tailings; It contain high content of aluminum, while calcium and magnesium content was relatively low, sulfur element was contained in the tailings, thus, sulfuric acid was selected as leaching reagent to decrease acid consumption in the leaching process.

Morphology of uranium tailings and EDS analysis results were shown in figure 1. The minimum and maximum particle size of uranium tailings were around $10\ \mu\text{m}$ and $400\ \mu\text{m}$, the tailings need to be grind to decrease particle size before leaching. The energy spectrum analysis showed that the main elements of uranium tailings were Si, Al and Fe, which was consistent with the XRD results.

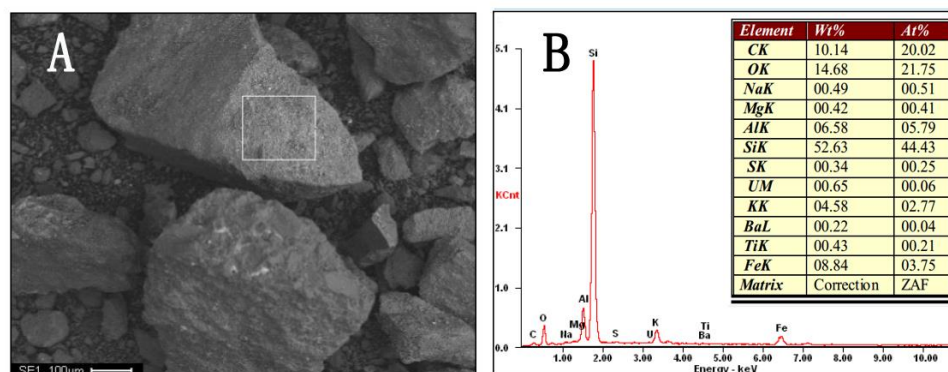


Figure 1. SEM-EDS results of uranium tailings

3.2 Discussion on acid leaching process of uranium tailings

3.2.1 Effect of MnO_2 concentration on the leaching of uranium. Sulfuric acid concentration of 1M, liquid to solid ratio of 20: 1, temperature 30 °C, time under 2h. (All the basic conditions of the experimental were the same.) Figure 2A shows that compared with H_2O_2 , lower concentrations of MnO_2 have stronger oxidation resistance and the leaching rate of uranium was obviously increased. While in high concentrations, as excessive MnO_2 has been adsorbed to uranium in solution, uranium leaching rate was not increased as strong as in low concentrations. In the whole process, the reasons for the inflection in MnO_2 and H_2O_2 leaching rate of uranium are the same.

3.2.2 Effect of H_2O_2 concentration on the leaching of uranium. The effect of H_2O_2 on uranium extraction from uranium tailings at different temperatures was examined. The extraction result was shown in figure 2C, the rate of uranium extraction with 0.2 M of H_2O_2 was always higher than the situation when the oxidant was absent.

Figure 2C shows that within 22 hours of leaching time, as the concentration of H_2O_2 increased from 0 M to 1 M, uranium leaching rate increased from 75% to almost 100%. On account of the strong oxidizing of H_2O_2 , the next uranium leaching rate was raised. Part of the adsorbed uranium tailings were dissolved by H_2O_2 , and some uranium ions have been re-released into the solution, and then the uranium leaching rate will be increased.

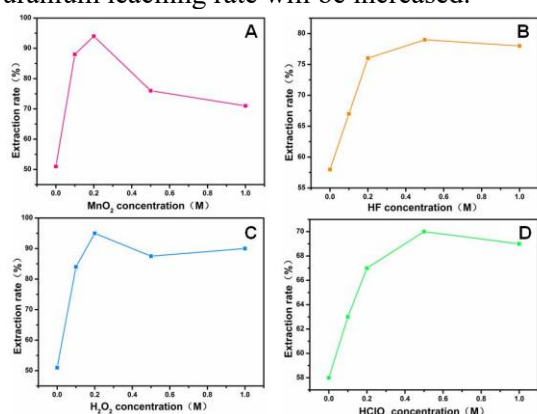


Figure 2. Effect of oxidant concentration on leaching of uranium

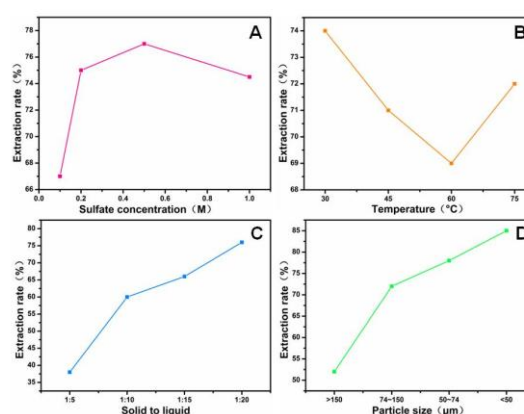


Figure 3. Effect of different variables on leaching of uranium

3.2.3 Effect of HF and $HClO_4$ amount of uranium leaching. Examined the impact of uranium leaching by HF and $HClO_4$, the results shown in figure 2B, D. When the concentration was less than 0.4M, leaching rate of uranium increased with the amount of supplements; however, when further increased the amount of enhancer, uranium leaching rate has decreased in some extent. Adding $HClO_4$, the

leaching rate of uranium has dropped significantly more than HF, which indicating that HF and HClO_4 excess would added adversely affected in uranium leaching. The main reason of phenomenon was HF and HClO_4 added in excess, let silicate gangue structure was strongly disrupted in uranium tailings, formed a lot of holes in uranium tailings particles. Therefore, the leaching process inverse adsorption of uranium tailings particles was increased [15], result in an apparent leaching rate of uranium declined. Therefore, the concentration of HF and HClO_4 were 0.4M in subsequent trials.

3.2.4 Effect of sulfuric acid concentration of uranium leaching rate. The effect of sulfuric acid concentration of uranium leaching rate, sulfuric acid concentration of 0.1 ~ 1 M, respectively.

The figure 3A shows that the concentration of sulfuric acid was lower than 0.5 M, the uranium leaching rate was increased with time. While the sulfuric acid concentration reached 0.5 M, the concentration of sulfuric acid was raised, the leaching rate of uranium was not increased. Because the 0.5 M of sulfuric acid was sufficient to extract uranium from uranium tailings, it is not feasible to increase the concentration of sulfuric acid to increase the leaching rate of uranium.

3.2.5 Effect of temperature on the leaching rate. To study the effect of temperature on the uranium leaching of uranium tailings in sulfuric acid solution, tailings in accordance with the solid-liquid ratio of 1:20 and 1 M sulfuric acid (20 g: 400 ml) into a 1000 ml beaker. The figure 3B shows that at 45°C or lower, uranium leaching rate decreased with increasing temperature, and the leaching rate increased with increasing time. 45°C or higher, with the temperature was increased, the possibility of collision between molecules was increased and the molecules were more likely to react, so uranium leaching rate raised with increasing temperature. After six hours, with the increase of dissolution rate and surface area of uranium tailings in high temperature environment, the adsorption of impurity ions to uranium in the solution was increased, and the leaching rate of uranium was decreased slightly.

3.2.6 Effect of solid-liquid ratio on the leaching rate. Figure 3C shows that the uranium leaching rate augment with time; when the solid-liquid ratio was greater than 1:10, leaching rate of uranium was rapid incresed within 6 hours. After 6 hours, the uranium leaching rate remained unchanged; when the solid-liquid ratio less than 1:10, the tailings and sulfuric acid solution reached reaction equilibrium at 4 hours. In addition, as the solid-liquid ratio increased uranium leaching rate was decreased. Because of the solid-liquid phase reaction, if the solid and liquid ratio of the uranium content was larger, the concentration difference between the two is greater. When the reaction equilibrium, the uranium concentration difference in solid and liquid was zero, therefore, the smaller the solid-liquid ratio, leaching of uranium rate was increased.

3.2.7 Effect of particle size on leaching rate. The effect of particle size on the uranium tailings in uranium leaching rate with 100 mesh, 200 mesh and 270 mesh standard sieve, sieved milled uranium tailings is > 150, 74 - 150, 53 to 74 and < 53 four size range.

The figure 3D shows that as the particle size decreased, the growth of time and uranium leaching rate was increased. When uranium tailings particle size greater than 150, within 22 hours leaching time, uranium leaching rate was increased. When the particle size less than 150, the uranium leaching rate was increased rapidly within 6 hours, and then the leaching rate was increased slowly. Compared with the large particle tailings, the small particle tailings were more susceptible to the reaction of sulfate acid penetration, the chemical control reaction time was shorter and the reaction ratio was faster.

3.3 Uranium tailings acid leaching process phase variation

After the leaching uranium tailings milled to 74 μm , four kinds of oxidant were added in leach residue, then analyzed by XRD. After the phase composition, the results shown in figure 4, which represents without added any oxidant but directly used sulfuric acid leaching slag (the same below).

Because the main mineral content in the tailings included SiO_2 and $\text{Fe}_3\text{FeSiO}_4$, the key to improve the uranium extraction rate was destroy the structure of these gangues. The main component of

uranium tailings SiO_2 diffraction peaks did not changed significantly (except MnO_2), under conditions of sulfuric acid and oxidizing reagent, SiO_2 without be damaged significantly. We selected H_2O_2 , MnO_2 , HF and HClO_4 as the oxidizing reagent. When the HF as oxidant, the iron salts of silicic and aluminum peaks completely disappeared in leaching slag, indicating silicate gangue minerals was extremely damaged by HF. When the oxidizing reagent was MnO_2 , silicate peaks not completely disappeared, but the phenomenon of wide appeared clearly. These observations suggest that, the crystal structure of silicate collapse occurred at the same time.

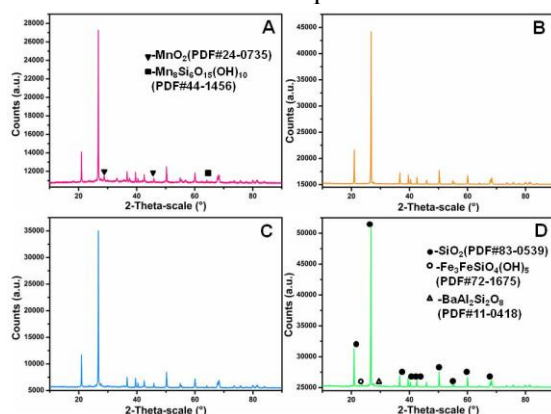


Figure 4. XRD results of uranium leaching residue

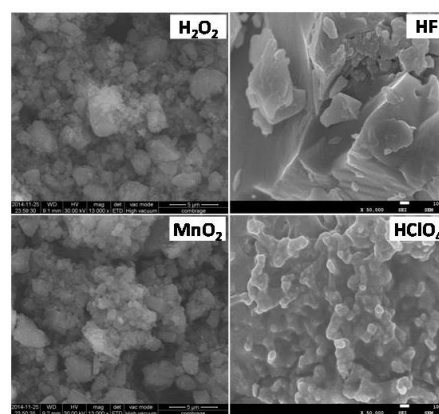


Figure 5. SEM results of uranium leaching residues

The main component of SiO_2 characterized derivative peak was significantly reduced. Not only appeared a peaks of a salt manganese silicate, indicating that MnO_2 and SiO_2 simultaneously had the ability of destroy the silicate under acidic conditions, but also the formation of new manganese silicate crystals were promoted. Thus, the leaching of low-grade uranium tailings may have a dual effect. When add less MnO_2 , which play a major role in destructed gangue structure, it was conducted the decomposition of uranium, if add more MnO_2 , the crystallization and the new manganese silicate crystals were promoted, the phase of uranium be repacked, therefore, the leaching rate of uranium was reduced. Adding HClO_4 and H_2O_2 as the oxidant, the silicate peaks have been weakening, there were much less than that large extent of the damage to silicates compared with HF and MnO_2 , it advantage was that a new crystalline impurity was not formed in the leaching process.

3.4 Morphology changes of uranium tailings in Acid Leaching Process

The speciation analysis of the leaching residue was shown in figure 5. The MnO_2 and H_2O_2 were magnificated 13000 times; the HF and HClO_4 were magnificated 50000 times.

According to figure 5, the damage effect of H_2O_2 on gangue structure was also obvious and the main fine gangue granular was leached as well. When the MnO_2 as oxidant, the particle size of the leaching slag was reduced significantly and the agglomeration between the particles was obvious. Because the MnO_2 had strong impact on the destruction of the silicate structure, the manganese silicate salt can form new nuclei, the tiny particles of gangue re-growth are promoted. In a word, morphology and results of phase analysis were consistent. On the one hand, When HF as oxidant, leaching residue shows irregular lamellar structure characteristics. It reflects that HF plays a strong corrosive role in silicate gangue, which had deep effect on the gangue stripping structure and this structure greatly strengthens the contact with uranium leaching liquid phase, thus the leaching efficiency of uranium was greatly improved. The mechanism of HClO_4 on the gangue was totally different from HF. The leaching slag was sharply presented on the surface of particles' sticking phenomenon, which shows that HClO_4 was useful in the "dissolution" gangue. On the other hand, although the failure mode of gangue did not change the particle size of ore, the intraparticle pores were increased. Therefore, the dissociation of uranium was enhanced.

4. Conclusion

The main ingredient of uranium tailings was SiO₂, polysilicate ferric and aluminum silicate salt, uranium content was only about 0.008%. The positive effect of oxidants on uranium extraction from uranium tailings can enhance leaching ratio and speed, along with the recovery and mechanism of extraction. The results demonstrated that oxidants shows advantageous effects in improving uranium extraction by reducing agglomeration, damaging gangue structure and improving dissolution of the uranium tailings. The study revealed maximum recovery efficiency at a temperature of 50 °C, a time of 1.5 h, a concentration of H₂SO₄ of 1.5M, and a solid-liquid ratio of 1:20, the order of leaching ratio was H₂O₂>MnO₂>HF>HClO₄.

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