Dynamic Model and Experiment Research on Sulfuric Acid Heap Leaching of Uranium Mine

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Abstract- This document gives formatting instructions for authors preparing papers for publication in the journal. The authors must follow the instructions given in the document for the papers to be published. You can use this document as both an instruction set and as a template into which you can type your own text. The process of Sulfuric acid heap leaching for uranium mine is widely used in uranium mining and metallurgical industry in China, which includes chemical reactions, liquid membrane diffusion, solid membrane diffusion, etc. Deducing kinetics model and dynamics data will help to guide the work of uranium mine heap leaching. The process style and chemical reaction constants of sulfuric acid leaching for uranium mine are deduced by the curve relationship between the leaching rate and leaching time. Experimental results show that the leaching rate is linear with the leaching time when it is less than 60% and the leaching process is controlled by chemical reaction process. The chemical reaction leaching rate constant

is 1.5×10^{-7} s⁻¹ and the liquid-solid phase chemical reaction coefficient is 3.6×10^{-8} m/s in this experimental data. The experimental results also show that if oxidants were not added into the heap-leaching uranium ore, only 40% of the quadrivalent uranium could be oxidized into hexavalent uranium, so the oxidants must be added to improve the oxidizing ability for greater leaching rate of uranium.

Keywords- Heap Leaching; Uranium; Leaching Rate Constant; Dynamical Model

I. INTRODUCTION

The surface heap launching has being developed in most of uranium ore mountains and the process which gets uranium from heap leaching is still the main uranium mining technology. Uranium heap leaching is always the key study of uranium mining and metallurgical industry in China. The process of the uranium particles leaching is very complex and the leaching rate is related to the leaching time, ore grade, chemical composition, type and concentration of the solvent. Recently a lot of works have been done on uranium heap leaching and some related articles were published. Zhanxue Sun et al studied heap bioleaching of uranium fluoride and microbiological agitation leaching of uranium ore fines [1]. Chunlin Feng et al concluded that leaching performance of hexavalent uranium was still good without adding oxidants in low-grade uranium ore leaching experiments [2]. Xixin Chang et al studied alkaline heap leaching of uranium and the results showed that strengthening alkaline could improved the leaching rate [3]. Dexin Ding et al established a kinetic mode of tailings neutralizaton in the experiment of acidic leach uranium tailings neutralization with calcium oxide, sodium hydroxide and ammonia as neutralizer [4]. Xiaobo Wang et al concluded that the leaching rate of uranium ore could be accelerated with adding a small amount of leaching oxidants by increasing uranium concentration [5]. Wenge Shi et al studied the property, grain composition, distribution and leaching performance of uranium ore in Jiangxi province [6]. Jiafu Chen investigated the effects of particle size on the leaching rate, leaching period and acid consumption in the experiment of column leaching with different particle size [7]. Yingying Zeng et al advanced the new heap leaching process and apparatus for liquid fabric [8], and tested the atomized liquid fabric of uranium ore heap leaching column leaching [9].

However, the basic data of the chemical kinetics for uranium heap leaching have not been concluded and deduced, such as the uranium leaching rate of chemical reactions, chemical reaction constants of liquid-solid phase. The dynamic models for the process of uranium heap leaching in the published articles were too complex to guide the design and production. Technicians had to use the gray theory to describe the future behavior of the uranium leaching, which would exceed the limit error [10, 11]. Deducing kinetics model and dynamics data will help to guide the work of uranium mine heap leaching. This paper will deduce a simple practical dynamic model for the uranium leaching by sulfuric acid, judge the process style by the experimental data of the leaching rate and leaching time and get the dynamic parameters. These works may guide the design and production for the uranium leaching and provided the basic dynamic data for the gray theory on the uranium ore heap leaching by sulfuric acid.

II. LEACHING RATE AND TIME

An easy way to comply with the journal paper formatting requirements is to use this document as a template and simply type your text into it. When sulfuric acid leaches, the tetravalent uranium is oxidated to hexad one. Uranium trioxide UO_3 reacts with sulfuric acid, becomes the solubility uranium sulfate UO_2SO_4 , then UO_2SO_4 enters into the liquor:

$$UO_3 + H_2SO_4 = UO_2SO_4 + H_2O$$

$$2U_{3}O_{8}+O_{2}+6H_{2}SO_{4}=6UO_{2}SO_{4}+6H_{2}O_{4}$$

When alkali leaches:

$$UO_3 + 3Na_2CO_3 + H_2O = Na_4UO_2(CO_3)_3 + 2NaOH$$

Assume that the chemistry leaches from outside to inside [8], as shown in the Fig. 1. The solvent concentration is C and the shape of the uranium ore granule is ball. When the leaching begins, the radius of the granule is r_0 , the granule mass is G_0 , the surface area is S_0 , the ore density is ρ , the molar volume is Vm, the relative molecular mass is Mr and the uranium mass percent in the granule is η .



Fig. 1 Micro ring of granule reaction

After leaching time t, the leaching rate is β , the granule mass is G, the granule radius is r, the surface area is S and W is the product amount of chemical reaction.

A. Chemical Reaction Step Controlls Whole Process

Assume the uranium ore leaching is the first order chemical reaction. In the reaction of solid-liquid leaching, the chemical reaction rate is proportional to the surface area and the solvent concentration. The chemical reaction rate is expressed by the change of the product amount of the chemical reaction in the unit time.

$$\frac{\mathrm{d}\beta}{\mathrm{d}t} = (1 - \beta)^{2/3} \frac{3M_{\mathrm{r}}v_b}{r_o\eta\rho} k_{\mathrm{e}}C \tag{1}$$

When the solvent concentration is constant in the process of the heap leaching, integrate Eq. 1:

$$1 - (1 - \beta)^{\frac{1}{3}} = k_h t \tag{2}$$

Among them, the coefficient k_h is called the chemical reaction leaching rate constant.

$$k_h = \frac{M_{\rm r} v_b}{r_{\rm o} \eta \rho} k_{\rm e} C \tag{3}$$

If the whole process of uranium heap leaching is controlled by the chemical reaction step, the leaching rate and leaching time will fit the Eq. 2.

B. Solid Mebrane Diffusion Controls the Whole Process

If the reaction is controlled by the solid membrane diffusion, the reaction rate is proportional to the diffusion rate of the solid membrane and the surface area of the granule.

$$\frac{d\beta}{dt} = k_g \cdot \frac{(1-\beta)^{\frac{1}{3}}}{1-(1-\beta)^{\frac{1}{3}}}$$
(4)

When the solvent concentration C and the temperature are unchangeable, the k_{g} can be regarded as a constant.

Integrate Eq. 4, we get:

$$1 - \frac{2}{3}\beta - (1 - \beta)^{2/3} = \frac{2}{3}k_g t$$
(5)

When the ore is banded together closely, the leaching rate is controlled by the solid membrane diffusion and the relationship between leaching rate and time accord will fit Eq. 5.

C. Liquid Membrane Diffusion Controls the Whole Process

The follow deduction is similar to the above for the solid membrane diffusion controls the whole process.

$$\frac{\mathrm{d}\beta}{\mathrm{d}t} = k_{w} \frac{(1-\beta)^{\frac{1}{3}}}{1-(1-\beta)^{\frac{1}{3}}} \tag{6}$$

Integrate Eq. 6, we get:

$$1 - \frac{2}{3}\beta - (1 - \beta)^{\frac{2}{3}} = \frac{2}{3}k_{w}t$$
⁽⁷⁾

When the mass transfer resistance of the liquid membrane is big, the leaching rate is controlled by the liquid membrane diffusion and the relationship between leaching rate and leaching time will fit Eq. 7.

D. Three Factors Jointly Control the Whole Process

Actually, the process of heap leaching might be jointly controlled by chemical reaction, solid membrane and liquid membrane. Make three factors jointed, we get:

$$\frac{1}{3} \left\{ \frac{r_{o} \eta \rho}{M_{r} k_{h} v_{b} C} (1-\beta)^{-\frac{2}{3}} + \frac{r_{o}^{-2} \eta \rho}{M_{r} v_{b} C} \left(\frac{1}{k_{g}} + \frac{1}{k_{w}} \right) \left[(1-\beta)^{-\frac{1}{3}} - 1 \right] \right\} d\beta = dt$$
(8)

When the solvent concentration and temperature do not change, these coefficients k_h , $k_{g^{\circ}}$, $k_{w^{\circ}}$ can be regarded as constant. Integrate Eq. 8, we get:

$$\frac{1 - (1 - \beta)^{\frac{1}{3}}}{k_{\rm h}} + \left(\frac{1}{k_{\rm g}} + \frac{1}{k_{\rm w}}\right) \frac{r_{\rm o}}{2} \left[1 - \frac{2}{3}\beta - (1 - \beta)^{\frac{2}{3}}\right] = \frac{M_{\rm r}v_{\rm b}C}{r_{\rm o}\eta\rho}t$$
(9)

The relationship between leaching rate and leaching time can be got according to the Eq. 9. The Eq. 9 qualitatively shows that not only increasing the leaching time, but also increasing the mass transfer and reaction coefficients are the important methods to increase the leaching rate.

III. EXPERIMENTAL CONTENTS

All paragraphs must be indented. All paragraphs must be justified, i.e. both left-justified and right-justified. All paragraphs must be justified, i.e. both left-justified and right-justified. Some quantity of uranium mineral was got from the mineral remainder after tall pillar experiment. After being crushed and separated, the mineral's density is 2.8 g/cm3 and particle diameter is 10 mm. 910 kg mineral sample was got for the leaching experiment. Before heap the mine pillar, 30 mm thickness of pebble was laid at the bottom of the mine pillar, which is beneficial to the percolation of the lixivium, to avoid the export of the lixivium being blocked by the fine ore block. During the pillar being installed, some fine ore was put into the sampler and then the sampler was installed into the pillar. The sampler can not be overlapped in the vertical direction. These samplers were installed on three levels and four samplers every level. The distant of the neighbor levels were 0.8 m, and the lowest level was 1.0 m distant from the bottom of the pillar.

The grade of the experimented uranium mine and the content of the other composition were analyzed and the results were listed in Table 1.

TABLE 1 QUALITY PERCENTAGE OF THE URANIUM MINERAL

Items	U ⁶⁺	\mathbf{U}^{4+}	Fe ₂ O ₃	FeO	CaO	MgO	Al ₂ O ₃	SiO ₂	H ₂ O
Percentage(%)	0.055	0.051	5.93	0.900	1.020	0.100	14.630	69.790	3.1

The concentration of the leaching solvent (sulfuric acid) is $0.5\% \sim 4.0\%$, spraying liquid intensity is 15 to 25 L/m².h. The consumption of the sulfuric is about $3.0\% \sim 4.0\%$ of ore weight. The ratio of leaching liquid-solid is 2.5:1, the pH of the leaching solution is 2.0 ± 0.5 , and the leaching time is 60 days. The preparation of the leaching solvent is the artificial mixing method. At the beginning of the spray liquid, the concentration of the leaching solvent is 40 g/L and then adjusted according to the requirements of each stage and leaching data. When the flow rate of the leaching solution from the bottom of the experiment pillar is stable, determine three sampling time, then use liquid collection bottle to sample from these samplers. In order to reduce the error, sampling time should be longer and sampling time should be five hours. At the beginning of leaching, the ore is dry, and has certain capability of water absorption, so do not sample until the flow rate is stable.

The U content, remainder acid, pH, Fe^{3+} , Fe^{2+} , Ca^{2+} , Mg^{2+} , $SO4^{2-}$, Al^{3+} and electrical potential of the leaching solution from the bottom hole of the heaped column should be analyzed, then leaching rate will be got.

IV. EXPERIMENTAL RESULTS AND ANALYSIS

The experimental leaching rate of the uranium granule is shown in the Figure 2. From the Figure 2, it can be seen that: (1) when less than 60%, the leaching rate is proportional to the leaching time; (2) the leaching rate does not come until 5 days later; (3) the leaching rate reaches 64% in 20 days leaching; (4) the leaching rate increases slowly in 20 to 35 days; (5) 35 days later, the leaching rate could reaches 70%, but increases very slowly, with almost no change.



Fig. 2 Relationship between leaching rate and leaching time

Develop the Eq. 9, and combine the experimental data on actual, determine the parameters for the model.

$$(1-\beta)^{\frac{1}{3}} = 1 - \frac{1}{3}\beta - \frac{1}{9}\beta^{2} - \frac{5}{81}\beta^{3} - \dots$$
$$(1-\beta)^{\frac{2}{3}} = 1 - \frac{2}{3}\beta - \frac{1}{9}\beta^{2} - \frac{4}{81}\beta^{3} - \dots$$

When the leaching rate is not big, develop the equation and get:

$$\frac{\beta}{3k_{\rm h}} + \left(\frac{1}{k_{\rm g}} + \frac{1}{k_{\rm w}}\right) \frac{r_{\rm o}}{2} \frac{\beta^2}{9} = \frac{M_{\rm r} v_b C}{r_{\rm o} \eta \rho} t \tag{10}$$

Figure 1 shows that when the leaching rate is not big, the extraction rate and leaching time show linear relationship, so in the Eq. 10, the first one dominates the whole process, namely controls the whole heap leaching process.

Calculate the average $k_{\rm h}$ by the Eq. 10, get $k_{\rm h} = 1.5 \times 10^{-7} (s^{-1})$, take it into the Eq. 3, and get $k_{\rm e} = 3.6 \times 10^{-8} (m/s)$

During the 5th to 25th days, the leaching rate is stably increasing, but increasing slowly after 25th day. The content of quadrivalent uranium is a little more than the sexivalent uranium, and the quadrivalent uranium is difficult to be leached. The leaching rate can reach 70%, which shows 38% of the quadrivalent uranium has been turned into sexivalent uranium. To get more uranium be leached out from the ore in a relatively short time, the oxidant should be put into, make the quadrivalent uranium oxidized into sexivalent uranium which is easier to be leached.

V. CONCLUSION

Experimental results show that the whole process of sulfuric acid heap leaching of uranium ore is mainly controlled by the chemical reaction process, which is the same as literature 3. In the leaching experiment, the rate constant of chemical reaction is 1.5×10^{-7} s⁻¹ and the chemical reaction constant is about 3.6×10^{-8} m/s and 38% of the ore have been oxidized from quadrivalent uranium into sexivalent uranium. After that, if more uranium could be more quickly leaching from the ore, the oxidants should be added into the sulfuric acid solvent to improve the solution oxidation, then the leaching rate of uranium ore may be increased more.

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