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Leaching kinetics of selenium from copper anode slimes by nitric acid−sulfuric acid mixture

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Abstract: The leaching kinetics of selenium from copper anode slimes was studied in a nitric acid−sulfuric acid mixture. The effects of main parameters on selenium leaching showed that the leaching rate of selenium was practically independent of stirring speed, while dependent on temperature and the concentrations of HNO_3 and H_2SO_4. The leaching of selenium includes two stages. The activation energy in the first stage is 103.5 kJ/mol, and the chemical reaction is the rate controlling step. It was almost independent of H_2SO_4 concentration and dependent on HNO_3 concentration since the empirical reaction order with respect to HNO_3 concentration is 0.5613. In the second stage, the activation energy is 30.6 kJ/mol, and the process is controlled by a mixture of diffusion and chemical reaction. The leaching of selenium was almost independent of HNO_3 concentration.

Key words: selenium; kinetics; acid leaching; copper anode slimes

1 Introduction

Selenium, an essential element in advanced technologies, plays an important role in various fields, such as glass additive, solar cells and plain paper photocopies [1,2]. The independent deposit of selenium has been rarely found and 90% of selenium is extracted from copper anode slimes [2,3]. It has been reported that selenium presents mostly as intermetallic compounds containing silver, copper and selenides (Ag−Cu selenides) in the copper anode slimes [3−5].

Up to now, the approaches to recovering selenium from copper anode slimes include pyrometallurgical process [6,7] and hydrometallurgical process [8]. In the hydrometallurgical process, several agents have been employed, including sulfuric acid, sodium hydroxide, chlorine and chlorine-bearing oxidants [9]. 87% selenium can be extracted with 4 mol/L NaOH under atmospheric conditions [8] and 99% can be leached under pressure oxidation at a high temperature of 473.15 K [10]. Even so, it consumes more energy and needs alkali−acid conversion. Chlorine and chlorine-bearing oxidants can extract selenium efficiently, while the dispersal of Au and the product of poisonous chlorine cannot be avoided [11,12]. In sulfuric acid leaching process, the leaching efficiency is only 40%−50% even with high temperature and pressure [13]. To promote leaching efficiency, a new method with microwave assistance has been proposed by YANG et al [14], and hydrogen peroxide was added as oxidation agent. In that case, the high leaching efficiencies of 97.12% copper and 95.37% selenium were obtained, respectively. However, microwave is difficult to be applied in industry recently. Nitric acid, a strong oxidizing agent, which was used in INER process [9], can be added to sulfuric acid to improve the leaching efficiency of selenium. In previous work, leaching process with a nitric acid−sulfuric acid mixture has been proposed and selenium leaching can be divided into two stages. In the first stage, selenide is converted into elemental selenium (Reaction 1). In the second stage, the elemental selenium is converted to selenite (Reaction (2)) [15].

$$(Ag,\ Cu)Se+HNO_3 \rightarrow Cu^{2+}+Ag_2Se+Se+NO+H_2O \quad (1)$$

$$Se+HNO_3 \rightarrow SeO_3^{2-}+NO+H_2O \quad (2)$$

A remarkable extraction of selenium was successfully obtained. In this work, the leaching kinetics

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of selenium from copper anode slimes in this acid mixture system has been investigated by determining parameters of the empirical reaction order and the apparent activation energy.

2 Experimental

2.1 Materials

The process mineralogy of the copper anode slimes has been investigated in our previous work [16,17]. The samples are similar to the ones with copper anode slimes bearing a high lead concentration [17]. The previous work indicated that 84% of the particle size is below 35 μm and its composition is complex. The main phases of the copper anode slimes include Au, Au−Pb alloys, eukairite, sulfate, arsenate, antimonite and oxygen. In the copper anode slimes, copper sulfate is the matrix that cements the finer particles together and selenium exists in the form of Ag−Cu selenide, which appears as spherical or ring-like shape. XRF analysis has been conducted on the copper anode slimes and the results are shown in Table 1. The main elements have been analyzed by inductively coupled plasma-atomic emission spectrometry (ICP−AES) and atomic absorption spectroscopy (AAS). The results are given in Table 2. All the reagents used in this investigation were analytical grade, and the water used was deionized water.

Table 1 XRF results of copper anode slimes (mass fraction, %)

SO_3	CuO	PbO	Ag_2O	CO_2	SeO_2	BaO
20.36	18.06	14.12	10.13	9.15	6.45	4.41
As_2O_3	Sb_2O_3	SiO_2	TeO_2	NiO	Cl	Bi_2O_3
4.06	3.60	2.16	1.59	1.54	1.08	0.94
Fe_2O_3	Al_2O_3	Cr_2O_3	Au	CaO	Co_2O_3	HfO_2
0.76	0.35	0.26	0.23	0.16	0.14	0.10
ZnO	PdO	SrO	K_2O	P_2O_5		
0.09	0.08	0.08	0.06	0.05		

Table 2 Chemical composition of main elements in copper anode slimes (mass fraction, %)

Au	Ag	Cu	Pb	Se	Ba
0.31	8.38	13.06	13.25	3.40	4.54

2.2 Procedure

The mixture of copper anode slimes (8 g) and acid (560 mL) composed of various concentrations of HNO_3 and H_2SO_4 was firstly given into a 1000 mL flask. Then, it was agitated at various temperatures in a water bath with various stirring speeds. During the experiments, 2 mL samples were withdrawn periodically from the reactor and analyzed by ICP-AES to determine the content of selenium. The leaching efficiencies (E) for selenium were calculated using the following equation:

$$E=10^{-4}C/(2w\rho) \quad (3)$$

where C (mass fraction, 10^{-6}) is the concentration of selenium in the filtrate diluted to 100 mL, w (%) is the mass fraction of selenium in the copper anode slimes, and ρ (g/mL) is the solid−liquid radio in the flask.

As silver can also be leached from copper anode slime during the leaching process, sodium chloride was added to the lixivium to precipitate silver after leaching.

3 Results and discussion

3.1 Results on leaching of selenium from copper anode slimes

3.1.1 Effect of temperature on selenium leaching

The influence of temperature on selenium leaching from copper anode slimes was investigated in temperature range of 353−368 K, under the following conditions: 0.5 mol/L HNO_3, 1.25 mol/L H_2SO_4 and stirring speed 300 r/min. The results are shown in Fig. 1.

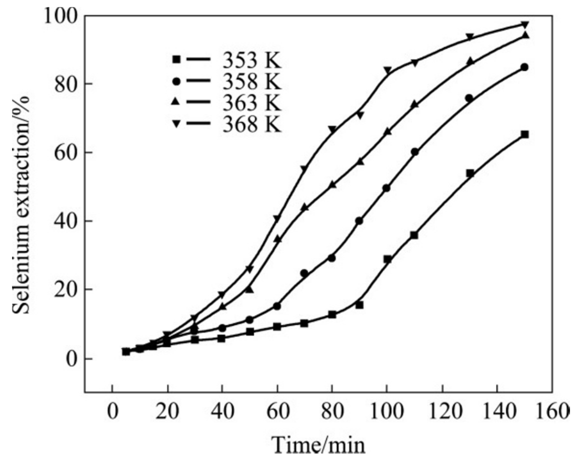

Fig. 1 Effect of temperature on selenium extraction (stirring speed: 300 r/min; HNO_3 concentration: 0.5 mol/L; H_2SO_4 concentration: 1.25 mol/L)

According to the slopes of curves in Fig. 1, selenium leaching curves can be divided into two stages. The slope value which can indicate the leaching rate of the process for the first stage is smaller and that for the second stage is larger. Temperature played an important role in the leaching rate. Time covered in the first stage decreased with the increase of leaching temperature. For example, at 353 K, the time covered in the first stage was 90 min, while it was 50 min at 368 K. At 353 K, 8.5% of selenium was leached in the first 90 min (the first stage) and the value increased to 65% in the following 60 min (the second stage). When the temperature increased to 368 K, 28.4% of selenium was leached in the first 50 min (the first stage) and the value increased to 97% in the following 100 min (the second stage).