OPTİMİZATİON OF THE PYRO-HYDROMETALLURGİCAL METHOD TO RECOVER SELENİUM FROM COPPER ANODE SLİME

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Abstract: Copper anode slime is a byproduct of electrolytic copper refineries which usually contains many valuable elements such as Au, Ag, PGMs (platinum-group metals), Cu, Se, Pb, As, and Sb. Anode slime is generally considered as the main source of the world's selenium and one of the important sources for the extraction of precious metals. Several methods have been used for processing and recovery of selenium from anode slime. One of the prevalent common industrial methods is sulfation roasting. In this research, the sulfation roasting method was optimized to recover selenium from copper anode slime whichthat is able to minimize the environmental pollutions and energy consumption. A D-optimal design based on response surface methodology was used for modeling of the roasting stage. The effect of two parameters was investigated on the roasting process;of liquid to solid ratio (L/S), and temperature on the roasting process was investigated. The selenium recovery was optimized and at the optimum condition of the L/S ratio of (1.9 mL/g) and temperature of (247.3 °C), the selenium recovery was found to be 99.99%. The head sample of the copper anode slime was characterized by x-ray diffraction (XRD), x-ray fluorescence (XRF), and inductively coupled plasma atomic emission spectroscopy (ICP-AES). The selenium purity was determined to be 97.08 % by ICP.

Keywords: Copper anode slime, Sulfation roasting, Selenium, Optimization.

1- INTRODUCTION

Copper anode slime is a by-product of copper electrorefining process, and a source of valuable elements such as Se, Te, Cu, Ag, Pb, Sb, Sn, Au, and PGMs (Li et al. 2015). There are three general methods of pyrometallurgy, hydrometallurgy, and hybrid processes to recover these valuable metals from copper anode slime. The hybrid process is a combination of pyrometallurgy and hydrometallurgy methods to reach the maximum recovery of metals (Chen et al. 2015; Narinder and Mathur 1976). Sulfation roasting is one of the prevalent industrial pyro-hydrometallurgical (hybrid) methods among the methods of recovering copper anode slime which benefits from simple and available technologies, using a low-cost acid (sulfuric acid). In this method, sulfuric acid sulfatizes the base metals and oxidizes selenium in the presence of air. Selenious acid will be made as a result of SeO_2 reacting with water. The SO_2 gas produced in the roasting process reduces the selenious acid to elemental selenium, and the sulfuric acid that was used in the process is restored. Selenides are transformed to sulfates during the sulfation roasting process. Outokumpu Company and Sumitomo Metal Mining Company are two of the greatest companies using the sulfation roasting process to recover selenium from copper anode slime (Narinder and Mathur 1976; Elkin and Schloen 1950) The Outokumpu process is operated at three stages. At first, the copper anode slime is leached in an autoclave. Selenium and silver are precipitated by SO_2 and separated through filtering. Finally, the wet filter cake is roasted at 600 °C by SO_2 to recover selenium. Same as the Outokumpu process, the Sumitomo process is operated at 3 stages. The copper anode slime is roasted in sulfuric acid and leached in water to recover the copper content. At the third stage, the leach filter cake is roasted at 600-800 °C and selenium is recovered (Elkin and Schloen 1950)(Hait et al. 2009). In both processes high energy consumption and the need to perform the process in multiple stages, which can produce gaseous and liquid effluents, are considered as the main drawbacks of the conventional sulfation roasting technique.

In this research, the conventional sulfation roasting technique was modified to recover selenium from copper anode slime with a lower temperature sulfation roasting method, decreasing the process temperature from 600-800 °C to ca. 247 °C, and also completing the process in single stage rather than three stages in conventional methods,, decreasing the gaseous and liquid effluents of the process, therefore, reducing the environmental drawbacks. The effects of the temperature and the L/S ratio on the process were investigated, and the parameters were optimized using a response surface methodology (RSM).

2- METHODS

2-1- Design of experiments

According to the preliminary experiments, the levels of the L/S ratio were selected between 1 and 2 mL/g. For the temperature, the levels were selected between 170 °C and 250 °C because the experiments revealed that below 170 °C, the vapor pressure of SeO2 is very low. Thus, selenium recovery decreases considerably. Also, the selenium recovery was more than 99.5% at temperatures below 250 °C. To determine the optimum condition of the sulfation roasting process and the effect of each parameter on the process, sixteen experiments were designed and analyzed statistically by a response surface methodology (RSM), D-optimal design. Design Expert 7 was used for the experimental design and statistical analysis.

2-2- Roasting

In each roasting experiment, 50 g of copper anode slime was mixed with sulfuric acid with the designed L/S ratio using a laboratory roasting setup. The setup consisted of 7 components (a. water reservoir, b. sand bath, c. condenser, d. acid resistant pump, e. slimes and acid container, f. rotator motor, and g. water pipe). The condenser was filled with a polyvinyl chloride-polyethylene-polypropylene-acrylonitrile butadiene styrene cooling tower packing to increase the interactions between the SeO_2 gas and water, with the purpose of producing selenium. The container was equipped with a three-blade agitator to mix the acid and the slimes. The sand bath in the container provides the required process temperature. The concentrated sulfuric acid and the copper anode slimes were mixed in a 500 mL container until the desired temperature was reached, then it was roasted for 1 h.

3- FINDINGS AND ARGUMENT

The designed experiments and the related results are summarized in Table 1.

According to the results of the experiments, an empirical model (Eq. (1)) is proposed as a function of temperature and L/S ratio to obtain optimum conditions for the roasting process, in order to maximize the recovery.

$$\text{Se Recovery} = +59.37+13.47\,A+32.01\,B \quad (1)$$

where A and B are the coded values of temperature and L/S ratio, respectively. The model illustrates that the temperature is more effective on the selenium recovery than the L/S ratio. An increase in the L/S ratio can improve SO_2 and SeO_2 generation, and therefore improves selenium recovery. By increasing the temperature, the SeO_2 vapor pressure will be enhanced resulting in more selenium recovery (Brebrick 2000)(Behrens et al. 1974).

Table 1. The designed experiments

Std	Run	L/S ratio (mL/g)	Temperature (°C)	Se Recovery (%)
1	7	1.74	250.00	95.84
2	16	1.00	250.00	81.1
3	10	2.00	170.00	54.40
4	14	1.00	170.00	13.60
5	13	2.00	223.00	75.77
6	6	1.44	204.00	46.93
7	2	1.37	249.00	92.57
8	8	1.86	195.00	68.34
9	9	1.52	170.00	36.8
10	3	1.00	210.00	46.24
11	4	1.25	187.00	27.49
12	11	1.00	170.00	11.37
13	5	2.00	170.00	24.26
14	15	1.00	250.00	76.90
15	12	2.00	223.00	84.21
16	1	1.74	250.00	96.61

The correlation coefficient of the model was calculated to be 0.93 for the selenium recovery, which shows a good agreement between the experimental and the predicted values of the fitted model.

Figure 1 illustrates the effect of the temperature and the L/S ratio on the recovery of selenium. The selenium recovery is clearly enhanced both at a higher temperature and L/S ratio, while the temperature has a greater effect than the L/S ratio on the selenium recovery.

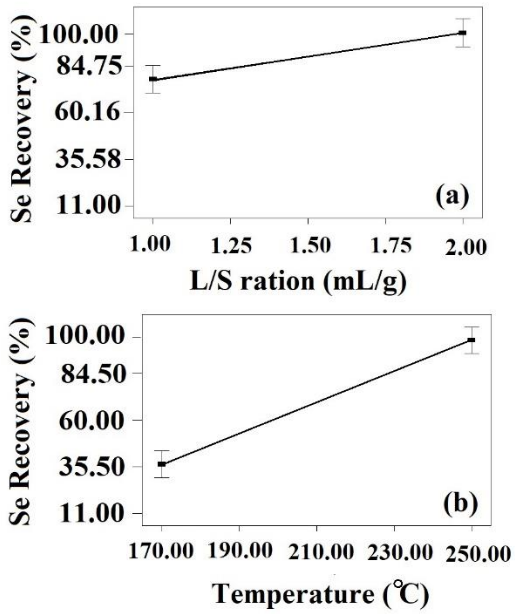

Figure 1. The effect of the L/S ratio (a) and the temperature (b) on the recovery of selenium.

The model predicted that at the temperature of 247.3 °C and the L/S ratio of 1.9 mL/g (optimum condition), 99.99% of the selenium would be recovered. Based on the confirmation experiments, the predicted optimum condition was repeated three times and the results of 99.93%, 99.97%, and 99.95% confirmed the model predicted condition.

4- CONCLUSIONS

In this study, a modified sulfation-roasting process was performed at a lower temperature than the traditional sulfation roasting technique to recover selenium from the copper anode slime. The optimized process reduced the conventional process temperature from 600-800 °C to ca. 247 °C, reducing energy consumption and the environmental drawbacks of the conventional process. At the optimum condition (temperature of 247.3 °C and L/S ratio of 1.9), the recovery of selenium was 99.99%.

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