Concentrating and Dissolving Platinum Group Metals from Copper Anode Slime

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Abstract—The hydrometallurgy process of copper anode slime were studied in this study. Copper anode slime is a byproduct in electrorefining. PGMs in autocatalyst were concentrated by pyrometallurgy and were transformed into copper anode slime by electrorefining. In this work, sulfuric acid pressure leaching was employed to pretreat copper anode slime and the residue concentrated PGMs was dissolving with the mixture of hydrochloric acid and hydrogen peroxide. The optimum conditions for sulfuric acid pressure leaching were 1.0 M of the sulfuric acid concentration, 100 ml/g of liquid-solid ratio, 4 hr of reaction time, and 220 °C of leaching temperature; The optimum conditions for hydrochloric acid leaching with hydrogen peroxide were 6.0 M of hydrochloric acid concentration, 10 % of hydrogen peroxide concentration, 50 ml/g of liquid-solid ratio, 60 min of reaction time, and 70 °C of leaching temperature. Under the optimal parameters in the process, the recovery of PGMs were 97.1 % for Pd, 95.1 % for Pt, 75.6 % for Rh respectively.

Index Terms—Autocatalyst, copper anode slime, hydrometallurgy, platinum group metals, pretreatment.

I. INTRODUCTION

Nowadays, platinum group metals (PGMs) are applied in the field of various industries due to their distinct properties, such as autocatalysts, chemical process catalysts, specialty medical alloys, electronics, hydrogen fuel, and jewellery. PGM natural resource deposits are very limited, only 69,000 tons all over the world [1], and the demand for PGMs is increasing [2], so it is desirable to develop an efficient process to recover PGMs with high purity from secondary resources such as spent autocatalysts [3].

Autocatalysts account for large portions of the world consumption of palladium (Pd), platinum (Pt) and rhodium (Rh). To recover PGMs from spent autocatalysts, pyrometallurgical and hydrometallurgical processes are employed for the effective extraction and separation of metals [4]-[7]. In hydrometallurgical process, PGMs are recovered by dissolving in aqua regia and acids, such as hydrochloric acid, nitric acid and sulfuric acid, in the presence of oxygen, iodine, bromine, chlorine, hydrogen peroxide, etc. [8]-[10], and separate subsequently by various methods, such as ion exchange [11], [12] and solvent extractions [13]-[15]. In pyrometallurgical process, PGMs

are concentrated in the metal phase or converted to easilytreated compounds by relevant pyrometallurgical treatment, then followed by refining technology to recover PGM [16]-[19].

Copper anode slime is a byproduct in electrorefining of blister. PGMs in autocatalyst were concentrated by pyrometallurgy and were transformed into copper anode slime by electrorefining process. General, pretreatment, concentration and refining are three conventional process for the treatment of copper anode slime [20]. Particularly, pretreatment is the most vital to dominate the whole process, which can remove base metals to enrich precious metals. Therefore, it is necessary to research the pretreatment for removing base metals efficiently. In this work, sulfuric acid pressure leaching was employed to pretreat copper anode slime and the residue concentrated PGMs was dissolving with the mixture of hydrochloric acid and hydrogen peroxide. The effect of acid concentration, oxidant concentration, liquid-solid (L/S) ratio, reaction time and leaching temperature were investgated in this study. The experiment flowsheet was illustrated in Fig. 1.

II. MATERIALS AND METHODS

A. Materials and Reagents

The sample of copper anode slime used in the experiments was provided from a technology materials compapy. Before experiment, the original copper anode slime was washed and dried at 100 °C, and sieved with 200 mesh (0.074 mm) to eliminate large particle. The materials were analyzed by X-ray diffraction (XRD; Dandong DX-2700), and inductively coupled plasma optical emission spectrometry (ICP-OES; Varian, Vista-MPX). The XRD pattern of copper anode slime was given in Fig. 2. The chemical composition of copper anode slime was analyzed by ICP-OES and shown in Table I. All chemicals used were of analytical grade and were diluted with deionized water.

B. Experiments

Leaching procedures were carried out using standard laboratory leaching equipment. The leaching parameters, such as the acid concentration, liquid-solid ratio, reaction time and leaching temperature, were investigated. In the section of sulfuric acid pressure leaching, the acidity was set from 0.1 to 6 M, the L/S ratio was set from 10 to 500 ml/g, the reaction time was set from 1 to 8 hr and the leaching temperature was set from 140 to 220 °C. In the section of hydrochloric acid leaching with hydrogen peroxide, the acidity was set from 0.1 to 8 M, the oxidant concertration was set from 0 to 10 %, the L/S ratio was set from 20 to 500 ml/g, the reaction time was set from 30 to 120 min and the leaching

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temperature was set from 25 to 85 °C. The leaching percentage was calculated according to Equation (1):



where X_A is the leaching percentage, m_1 is the measured quantity of metal ion leached, and m_2 is the quantity of metal ion in the raw material.

III. RESULTS AND DISCUSSION

A. Sulfuric Acid Pressure Leaching

For concentrating PGMs in the material, the leaching percentage of the inpurities, such as Cu, Fe and P, in the material were emphasized in this section. The parameters, such as the acid concentration, L/S ratio, reaction time and leaching temperature, were invesigated.

1) Effect of sulfuric acid concentration

Fig. 3 showed the leaching efficiency of Cu, Fe and P in the material by sulfuric acid. The effect of sulfuric acid concentration was investigated by varing the sulfuric acid concentration from 0.1 M to 6 M. The results indicated that leaching percentage of Cu increased sharply from 58.7 % to 97.5 % as the sulfuric acid concentration increased up to 1.0 M, while Fe and P increased to 97.1% and 87.0% respectively. However, there was no apparent influence when sulfuric acid concentration was more than 1.0 M. Therefore, the optimum condition of sulfuric acid concentration was chosen as 1.0 M.

2) Effect of L/S ratio

Fig. 4 showed the effect of the L/S ratio on leaching efficiency. The L/S ratio was investigated by varing the L/S ratio from 10 ml/g to 500 ml/g. The leaching percentages of

Cu, Fe and P were generally increased, while the L/S ratio increased from 10 ml/g to 100 ml/g and percentages were increased to 97.5 % for Cu, 97.1 % for Fe, 87.0 % for P. The results indicated that when the L/S ratio was low, there was insufficient acid to react in the process. In other words, there was more acid readily able to react and available to obtain a higher leaching percentage. Hence, the optimum condition of the L/S ratio was chosen as 100 ml/g.



Fig. 3. Effect of the leaching percentage on H_2SO_4 concentration (reaction condition: 100 ml/g of L/S ratio, 3hr, and 220°C).



Fig. 4. Effect of the leaching percentage on L/S ratio (reaction condition: 1.0 M of H₂SO₄ concentration, 3 hr, and 220°C).

3) Effect of reaction time

The effect of the reaction time was shown in Fig. 5. The reaction time was investigated by varing the reaction time from 1 hr to 8 hr. The leaching percentages of Cu, Fe and P increased by about 87.3 %, 43.7 %, and 69.6 % when the reaction time was increased from 1 hr to 4 hr. The reason was that with the increase in the leaching time, a more andmore surface area of the unreacted particles cores could react with the sulfuric acid. For this reason, the optimum condition of the reaction time was chosen as 4 hr.

4) Effect of leaching temperature

Fig. 6 showed the effect of the leaching temperature on leaching efficiency. Leaching temperature was varied from 140 °C to 220 °C. The leaching percentage increased with the increasing temperature because the temperature no only can control the pressure in the pressure leaching also has a great effect on the leaching process. Thus, 220 °C of the leaching temperature was chosen as the optimum condition of the leaching temperature. the leaching percentages under the optimum condition were Cu: 99.3 %, Fe: 99.7 %, P 87.0 %, Pd: 0.9 %, Pt: 0.9 %, Rh: 16 %.

B. Hydrochloric Acid Leaching with Hydrogen Peroxide After sulfuric acid pressure leaching, the chemical composition of the residue was shown in Table II. For dissolving PGMs in the residue, the leaching percentage of Pd, Pt and Rh, in the residue were emphasized in this section. The parameters, such as the acid concentration, hydrogen peroxide concentration, L/S ratio, reaction time and leaching temperature, were invesigated. The leaching percentage of Pd, Pt and Rh in the residue would be emphasized in this section.



Fig. 5. Effect of the leaching percentage on reaction time (reaction condition: 1.0 M of H₂SO₄ concentration, 100 ml/g of L/S ratio, and 220°C).



Fig. 6. Effect of the leaching percentage on leaching temperature (reaction condition: 1.0 M of H_2SO_4 concentration, 100 ml/g of L/S ratio,and 4hr).

1) Effect of hydrochloric acid concentration

Fig. 7 showed the leaching efficiency of Pd, Pt and Rh in the residue by hydrochloric acid. The effect of hydrochloric acid concentration was investigated by varing the hydrochloric acid concentration from 0.1 M to 8 M. The results indicated that leaching percentage of Pd increased from 0.2 % to 98.0 % as the hydrochloric acid concentration increased up to 6.0 M, while Pt and Rh increased to 96.0 % and 90.3 % respectively. However, there was no apparent influence when hydrochloric acid concentration was more than 6.0 M. Therefore, the optimum condition of hydrochloric acid concentration was chosen as 6.0 M.

2) Effect of hydrogen peroxide concentration

Fig. 8 showed the leaching efficiency of Pd, Pt and Rh in the residue by hydrochloric acid. The effect of hydrogen peroxide concentration was investigated by varing the hydrochloric acid concentration from 0 % to 10 %. The results indicated that leaching percentage of Pd increased from 37.5 % to 96 % as the hydrochloric acid concentration increased up to 10 %, while Pt and Rh increased to 96 % and 90 % respectively. Therefore, the optimum condition of hydrogen peroxide concentration was chosen as 10 %.



Fig. 7. Effect of the leaching percentage on HCl concentration (reaction condition: 10% of hydrogen peroxide, 200 ml/g of L/S ratio, 240 min, and 85°C).



Fig. 8. Effect of the leaching percentage on hydrogen peroxide (reaction condition: 6.0 M of HCl concentration, 200 ml/g of L/S ratio, 240 min, and 85°C).

3) Effect of L/S ratio

Fig. 9 showed the effect of the L/S ratio on leaching efficiency. The L/S ratio was investigated by varing the L/S ratio from 20 ml/g to 500 ml/g. The leaching percentages of Pd, Pt and Rh were generally increased, while the L/S ratio increased from 20 ml/g to 50 ml/g and percentages were increased to 97.9 % for Pd, 95.8 % for Pt, 90 % for Rh. Hence, the optimum condition of the L/S ratio was chosen as 50 ml/g.

4) Effect of reaction time

The effect of the reaction time was shown in Fig. 10. The reaction time was investigated by varing the reaction time from 15 min to 240 min. The leaching percentages of Pd, Pt and Rh increased by about 6.2 %, 6.0 % and 6.3 % when the reaction time was increased from 15 min to 60 min. The optimum condition of the reaction time was chosen as 60 min.

5) Effect of leaching temperature

Fig. 11 showed the effect of the leaching temperature on leaching efficiency. Leaching temperature was varied from

25 °C to 85 °C. The leaching percentage increased with the increasing temperature because the temperature has a great effect on the leaching process. Thus, 70°C of the leaching temperature was chosen as the optimum condition of the leaching temperature. the leaching percentages under the optimum condition were Pd: 98.0 %, Pt: 96.0 %, Rh: 90.0 %.



Fig. 9. Effect of the leaching percentage on L/S ratio (reaction condition: 6.0 M of HCl concentration, 10% hydrogen peroxide, 240 min, and 85°C).



Fig. 10. Effect of the leaching percentage on reaction time (reaction condition: 6.0 M of HCl concentration, 10% hydrogen peroxide, 50 ml/g of L/S ratio, and 85°C).



Fig. 11. Effect of the leaching percentage on leaching temperature (reaction condition: 6.0 M of HCl concentration, 10% hydrogen peroxide, 50 ml/g of L/S ratio,and 60 min).

IV. CONCLUSION

In this work, a copper anode slime pretreatment for concentrating and dissolving PGMs in copper anode slime has been studied. In sulfuric acid pressure leaching section, Cu, Fe, and P were removed by 99.3 %, 99.7 %, and 87.0 % With the optimum condition of 1.0 M of the sulfuric acid

concentration, 100 ml/g of liquid-solid ratio, 4 hr of reaction time, and 220 °C of leaching temperature. Then in hydrochloric acid leaching with hydrogen peroxide, Pd, Pt, and Rh were dissolve by 98.0 %, 96.0 %, and 90.0 % with the optimum condition of 6.0 M of hydrochloric acid concentration, 10 % of hydrogen peroxide concentration, 50 ml/g of liquid-solid ratio, 60 min of reaction time, and 70 °C of leaching temperature. Finally, the recovery of PGMs in this process were 97.1 % for Pd, 95.1 % for Pt, 75.6 % for Rh respectively.

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