Removal of Copper and Enrichment of Precious Metals by Pressure Leaching Pretreatment of Copper Anode Slime in Sulfuric Acid Medium

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Abstract: The copper anode slime is a by-product of copper electrolytic refining. It is an important raw material for the recovery of precious metals. With air rather than oxygen as the pressurized gas, pressure leaching pretreatment of copper anode slime in sulfuric acid medium is studied systematically. Parameters studied included: concentration of sulfuric acid, partial pressure of air, leaching temperature, leaching time and liquor to solid ratio. The experimental results obtained showed that under optimal leaching conditions, the extraction percentage of copper is up to 98% and the dissolution of tellurium, selenium and silver are 49%, 13% and 1%, respectively. These values indicated that the pretreatment could be very effective for the selective separation of almost all of the copper and part of tellurium from precious metals, thus the precious metals can be enriched from the residue. The investigation of mechanism showed that the autocatalytic effect of variable valence copper ions in the raw copper anode slime can effectively accelerate the rate of copper dissolution.

Key words: copper anode slime; comprehensive recovery; pretreatment; pressure leaching; effective separation; autocatalytic effect.

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铜阳极泥加压酸浸预处理脱铜富集贵金属

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摘　要：铜阳极泥是铜电解精炼中的一种副产品，是回收贵金属的重要原料。以空气代替氧气为加压气体，系统研究了铜阳极泥加压酸浸预处理工艺。研究的影响因素包括硫酸浓度、空气分压、浸出温度、浸出时间和液固比等。结果表明，在最优工艺条件下，铜的浸出率高达 98%；碲、硒、银的浸出率分别为 49%、13%、1%。试验数据表明：铜阳极泥经过加压酸浸预处理，几乎所有的铜和部分的碲，能有效的从贵金属中分离出来，使贵金属得以富集。机理研究表明：充分利用阳极泥中水溶性铜离子的自催化氧化作用，能有效提高铜的溶解速度。

关键词：铜阳极泥；综合回收；预处理；加压浸出；有效分离；自催化效应

In the process of electrolytic copper refining, the undissolved metals, oxides and the other compounds deposit on the bottom of electrolytic cells and form anode slime. They are processed to recover their copper and precious metals. The value of the anode slimes is determined mainly by the noble metals

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content, but in certain processes the contributions of Ni, Se and other impurities are significant[1]. Therefore, there has been renewed interest in studying new approaches for the recovery of these metals from primary and secondary resources. A complete description of slimes processing is beyond the scope of this paper. Decopperizing of anode slimes is the first step which is called pretreatment, so a brief discussion of this technology is warranted. Various methods have been developed to recover copper from slags and anode slimes. These methods can be differentiated into: (a) pyrometallurgical processing which includes roasting in presence of an oxidizing agent, suflat-roasting and soda-ash processing[2-5]and (b) hydrometallurgical processing using different leaching agents namely chlorine, nitric acid and sulfuric acid[6-9]. The production of sulfuric acid is the troublesome aspect of a roasting process, as the marketability of sulfuric acid is highly dependent on site location. Furthermore, even if gas emission regulations are complied with, harmful SO_2 may be released. Hydrometallurgical processing of copper anode slimes has the following advantages: ① Capital costs are low compared to those for a smelter; ② It may be applied to small and large operations; ③ Air pollution by sulfur dioxide is eliminated; ④ The equipment may be designed and installed in modules[10]. In China, most of copper smelters generally use the suflat-roasting process pretreatment of copper anode slime. This bleed treatment presents many drawbacks, e.g. high-energy consumption, evolution of toxic gas and the formation of toxic deposits which have to be disposed of.

However, there have been few detailed studies on leaching pretreatment of raw copper anode slime with sulfuric acid under pressure. This process has a few advantages due to the higher dissolution rate of copper, non-polluting character, lower price of leaching reagents as well as the simplicity of the process itself. Sulfuric acid in pressure leaching improved copper and tellurium extraction from these slimes. The solid residues from the pressure acid leaching were collected for further processing to recover selenium and other noble metals such as gold, silver and platinum-group metals by a suitable method. The Cu-rich pregnant leach solution is first treated to precipitate Te as Cu_2Te, by adding copper metal shavings or granules. Filtered Te-free solution is then returned to the electrolyte purification section of the copper electro-refinery. In the present work, a study is conducted to determine optimum conditions for pretreatment of the raw copper anode slime. Optimization of five key parameters, namely sulfuric acid concentration, air partial pressure, temperature, time and liquor to solid ratio (L/S) were selected to examine the economic viability and the process performance. Experimental results confirmed that almost all of copper and parts of tellurium can be extracted effectively from the raw copper anode slime under certain conditions, selenium, silver and other noble metals were enriched in the leaching residue.

1 Experimental

1.1 Materials

The copper anode slime used in the present study was from Jiangxi Province of China. Tab.1 presents the particle size distribution of the raw copper anode slime used in this study. About 82.36% of the sample is below 200 mesh. The results of the chemical composition determined by inductively coupled plasma-atomic emission spectrometry (ICP-AES) are given in Tab.2. The analysis showed that the anodic slimes are characterized by high concentrations of copper, lead, silver, antimony, tellurium and selenium. In all the leaching experiments, the sulfuric acid used has a concentration of 96% w/w and a density of 1.84 g/mL; distilled water was also used.

Tab.1 Average particle size distribution of the sample

表 1 样品的平均粒度分布

Particle size / mesh	Distribution (mass fraction / %)
−16 +100	12.04
−100 +200	5.60
−200	82.36

Tab.2 Chemical composition of the copper anode slime

表 2 铜阳极泥化学成分 /%

Element	Cu	Ag	Au/(g/t)	Se	Te	Sb	Pb	As	S
Mass fraction	11.63	8.75	3532.6	5.26	2.58	4.69	7.24	4.13	6.85

1.2 Reactor and experimental procedure

The leaching experiments were conducted in a 2 liters titanium vertical autoclave. Temperature and agitation speed were controlled with a PID controller, manipulating both the power output of an external heating mantle and the flow in an internal cooling tube. The slurry was agitated by a four blade impeller driven by a variable speed motor. At the set temperature, the air was admitted continuously and the partial pressure of air was adjusted to the desired value, which was maintained constant for the duration of the experiment. At the end of the experiment, the air was shut down, the autoclave was rapidly water-cooled, the slurry was vacuum-filtered immediately; at the end of each filtration, washed leaching residue three times with 80 mL of 60℃ distilled water. Both the solids and the solution were retained and sent to Analysis and Testing Center of Jiangxi University of Science and Technology, Jiangxi, China, to determine the contents of Cu, Se, Te and Ag, for the calculation of copper, selenium, tellurium and silver extraction rate. In each test run, about 150 g raw anodic slime and sulfuric acid of required mass ratio diluted with distilled water were mixed thoroughly prior to each experiment.

2 Results and discussion

2.1 Comparative experiment

In the general pretreatment process of copper anode slime, first, washed raw copper anode slime with water, lotion was sent to electrolytic copper and solid residue after pulping was sent to leaching system. Under the same condition of sulfuric acid concentration 100 g/L, stirring rate 500 r/min, L/S 5:1, air pressure 0.6 MPa, temperature 120℃, comparative experiment between the raw copper anode slime and the copper anode slime was washed three times with 200 mL of 80℃ distilled water were carried out. The experimental results on the leaching rate of copper against time are presented in Fig.1.

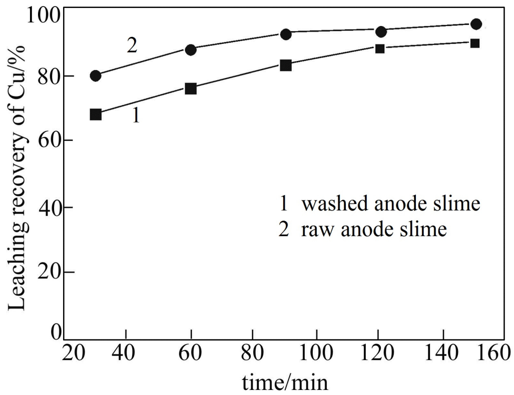

Fig.1 Effect of leaching time on recovery of Cu in comparative experiment

图 1 浸出时间对铜浸出率的影响的对比实验

As expressed in Fig.1, the leaching rate of copper in the raw anode slime was constantly higher than that of washed copper anode slime under the same condition. The reason is the autocatalytic effect of variable valence copper ions. The raw copper anode slime has not been washed and consequently contained a certain amount of copper and copper ions. There are three control-steps in the autocatalytic effect of variable valence metal ions, namely oxidation of copper from Cu and Cu (I) to Cu (II) and the reduction of copper from Cu (II) to Cu (I). It can be illustrated in the following reactions:

$$2Cu+4H^{+}+O_2 \rightarrow 2Cu^{2+}+2H_2O \quad (1)$$

$$Cu+Cu^{2+} \rightarrow 2Cu^{+} \quad (2)$$

$$4Cu^{+}+4H^{+}+O_2 \rightarrow 4Cu^{2+}+2H_2O \quad (3)$$

Cu(I) acts as a catalyst that can promote the transfer of dissolved oxygen to accelerate the oxidative leaching. Oxygen within air in pressure leaching is an indispensable and foremost oxidant directly participating in the oxidative leaching of copper anode slime, simultaneously oxidizing copper metal and cuprous ions released from the leaching system to copper ions that may in return act as oxidant to participate in the leaching of copper anode slime. Experimental results showed that during select directly leaching of raw copper anode slime in sulfuric acid medium, the leaching efficiency of copper was better than that of washed copper anode slime. Thus, the process could be shorten and choice of the raw copper anode slime is reasonable.

2.2 Effect of sulfuric acid concentration

The effect of sulfuric acid concentration on the extractions of copper, selenium, tellurium and silver from the raw copper anode slime was shown in Fig.2. Leaching conditions were: time, 90 min; temperature, 120℃; air pressure, 0.8 MPa; stirring rate, 600 r/min; liquid-to-solid ratio, 5:1.

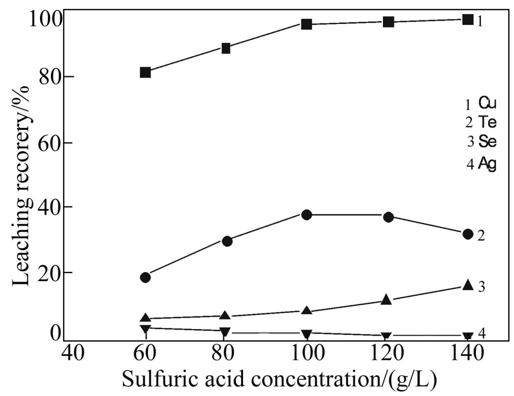

Fig.2 Effect of sulfuric acid concentration on leaching recovery

图 2 硫酸浓度对浸出率的影响

As expressed in Fig.2, the acid concentration affects the extraction of copper up to about 100 g/L, and this can also have a pronounced effect on selenium and tellurium dissolution. Especially, when sulfuric acid concentration is over 100 g/L, the dissolution percent of selenium increased significantly, and recovery yield of tellurium decreased when acidity reached a higher level. Silver leaching recovery kept a little invariable between sulfuric acid concentration 60 g/L and 140 g/L. The dissolution reactions of copper can be written as follows:

$$2Cu+2H_2SO_4+O_2 \rightarrow 2CuSO_4+2H_2O \quad (4)$$

$$2Cu_2S+2H_2SO_4+5O_2 \rightarrow 4CuSO_4+2H_2O \quad (5)$$

$$Cu_2Se+2H_2SO_4+O_2 \rightarrow 2CuSO_4+Se+2H_2O \quad (6)$$

$$2CuAgSe+2H_2SO_4+O_2 \rightarrow 2CuSO_4+Ag_2Se+Se+2H_2O \quad (7)$$

$$Cu_2Te+4H_2SO_4+5O_2+2H_2O \rightarrow 4CuSO_4+2H_6TeO_6 \quad (8)$$

The reason is that with the increased concentration of sulfuric acid, a variety of chemical reactions between elements or compounds of Cu, Se, Te, Ag with sulfuric acid become more thorough occurs, causing more copper and selenium to be extracted into the solution and leaving more silver into the leaching residue. However, the extraction of tellurium was increased with the increase of sulfuric acid concentration up to 100 g/L and afterwards dramatically become falling. This may be due to the reduction from hexavalent Te to negative divalent with the increased acid concentration:

$$H_6TeO_6+3H_2SO_4+5Cu \rightarrow Cu_2Te+3CuSO_4+6H_2O \quad (9)$$

Therefore, the optimum sulfuric acid concentration was 100 g/L and all the further experiments were carried out at this concentration.

2.3 Effect of temperature

Under the condition of sulfuric acid concentration100 g/L, stirring rate 600 r/min, L/S 5:1, air pressure 0.8 MPa, the raw copper anode slime is leached for 90 min at different temperatures. A plot of the percentages of leached copper, selenium, tellurium and silver against temperature was presented in Fig.3.

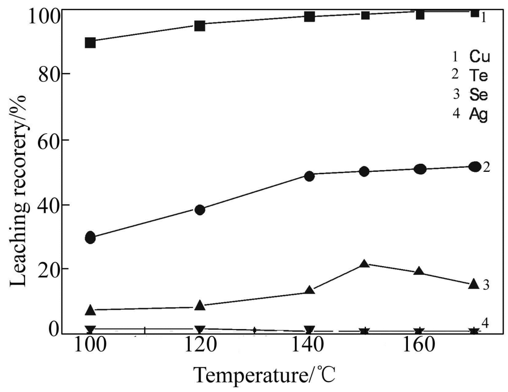

Fig.3 Effect of leaching temperature on leaching recovery

图 3 浸出温度对浸出率的影响

As expressed in Fig.3, recovery yields of copper, selenium and tellurium increased significantly with the increase of temperature from 100℃ to 140℃, but no significant effects were observed on leaching of copper and tellurium when temperature above 140℃. Experimental results also proved that the effect of leaching temperature on silver leaching recovery is indeed negligible. The reasons might be that the higher temperature has greatly improved kinetics and thermodynamic conditions of the dissolution of these metals. However, when leaching temperature is over 150℃, the dissolution percent of selenium decreased, this may be because according to Eqs. (6) and (7) selenium was re-oxidized to selenium dioxide under the conditions of more higher temperature and higher pressure, and selenium dioxide vapor is released from the exhaust valve in the vertical autoclave. The results demonstrated that the temperature of 140℃ is the optimum value.

2.4 Effect of time

The leaching recovery of metals from the raw copper anode slime was also examined against time when sulfuric acid concentration was 100 g/L, air pressure, 0.8 MPa, temperature, 140℃, stirring rate, 600 r/min and L/S, 5:1. The results plotted in Fig.4 indicated that within 30 min 86.13% copper and 27.76% tellurium were extracted then, after 90 min 98.25% copper and 49.23% tellurium were extracted, respectively. Especially, more than 90 min, there is no significant increase for copper and tellurium extraction. Selenium recovery increased and recovery of silver slightly decreased with prolonging time. Thus the holding time should be controlled in 90 min for lower energy consumption and higher productivity.

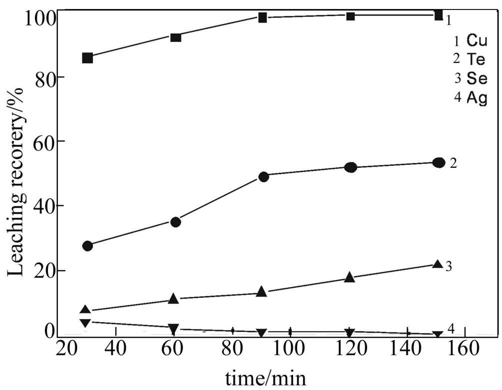

Fig.4 Effect of leaching time on leaching recovery

图 4 浸出时间对浸出率的影响

2.5 Effect of air partial pressure

Under the condition of sulfuric acid concentration was 100 g/L, stirring rate 600 r/min, L/S 5:1, the copper anode slime were leached for 90 min at 140℃. The leaching rates of copper, selenium, tellurium and silver were plotted in Fig.5 under different air partial pressure (0.6~1.4 MPa). These results showed that the copper leaching recovery increased from 91.57% to 98.25% when the air pressure was increased from 0.6 to 0.8 MPa. But there were no significant effect with the air pressure increased further. The dissolution of selenium increased with the increase of air partial pressure. It rises from 9.35% at pressure 0.6 MPa to 29.25% at pressure 1.4 MPa. Tellurium dissolution percentage increased from 21.25% to 61.67%. This result was similar to that obtained by Fernandez[11]. In Fernandez's work, the amount of selenium dissolved was strongly dependent on the degree of oxidation of the anode slimes. Silver leaching recovery is more or less constant in the air partial pressure range investigated. Higher air partial pressure is attributed to increasing the oxygen solubility and transfer of dissolved oxygen to speed up the oxidation reaction. So the dissolved oxygen was determined to be foremost responsible for the oxidative leaching of copper, selenium, tellurium and silver in raw copper anode slime. Therefore the optimum air partial pressure appears to be 0.8 MPa and all the further experiments were carried out at this pressure.

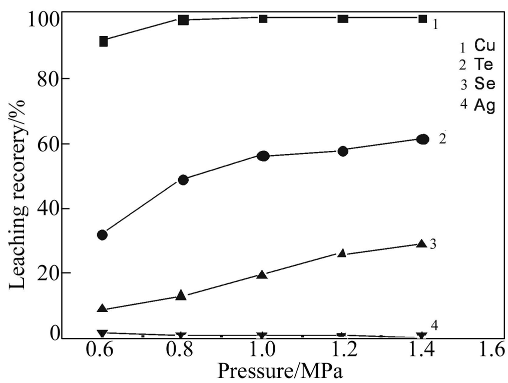

Fig.5 Effect of air partial pressure on leaching recovery

图 5 空气分压对浸出率的影响

2.6 Effect of liquor to solid ratio

On the condition of sulfuric acid concentration 100 g/L, air pressure 0.8 MPa, stirring rate 600 r/min, the copper anode slime was leached for 90 min at 140 ℃. The leaching rate of copper, selenium, tellurium and silver were plotted in Fig.6 at different L/S ratios (3~7).

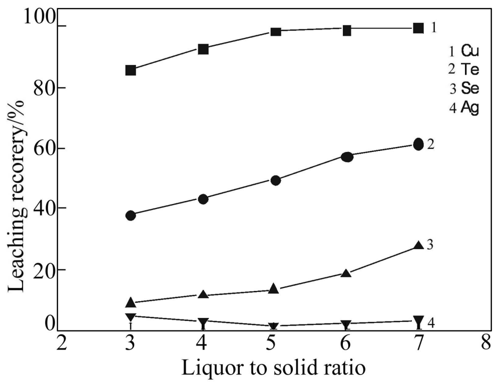

Fig.6 Effect of liquor to solid ratio (L/S) on leaching recovery

图 **6**　液固比对浸出率的影响

These results showed that copper, selenium and tellurium leaching recovery increased with the increase of L/S. The silver leaching recovery decreased with increased L/S up to 5 and afterwards becomes slightly rising. This is may be due to the acidity at the pressure leaching end would be raised when L/S increases and correspondingly improved the solubility of silver sulfate in acidic solution. The formation of silver sulfate can be described as follows:

$$2Ag_2Se+2H_2SO_4+3O_2 \rightarrow 2Ag_2SO_4+2H_2SeO_3 \quad (10)$$

When the ratio of liquor to solid is increased, the solid particles could be more easily mixed with sulfuric acid and hence copper, selenium and tellurium will be more extracted from the raw copper anode slime. Higher L/S ratio led to a dilute solution and expansion of the liquid volume which were unfriendly to the next technology. Consequently, liquor to solid ratio of 5:1 was chosen as a favorable value. In the leaching residue, the percentages of silver and gold were up to 18.1%, 1.3%, respectively. Thus, precious metals can be enriched by the pretreatment.

3　Conclusions

(1)　Using air as the pressurized gas, pressure leaching pretreatment of raw copper anode slime in sulfuric acid medium was studied. Based on the experimental results, the more favorable operating conditions for the pretreatment of raw copper anode slime can be summarized as follows: sulfuric acid concentration,100 g/L; air partial pressure, 0.8 MPa; leaching temperature, 140℃; leaching time, 90 min; liquor to solid ratio, 5:1; stirring rate, 600 r/min. Under these experimental conditions, the leaching rates of copper, tellurium, selenium and silver were about 98%, 49%, 13% and 1%, respectively. The result showed that acid pressure leaching pretreatment of raw copper anode slime is technologically feasible and was found to be very effective for the selective extraction of copper and tellurium over selenium, silver and other precious metals. The yield of the leaching residues is about 53% of the matte mass used in the experiments.

(2)　It is seen that the most important parameters affecting pressure leaching pretreatment of raw copper anode slime are sulfuric acid concentration, air partial pressure and liquor to solid ratio.

(3)　The raw copper anode slime needs not to washing in this pretreatment process and to make full use of the autocatalytic effect of variable valence copper ions which can be help to strengthen the leaching. It accordingly can shorten the process flow and improve the efficiency of production.

(4)　The pretreatment can ensured that almost all of copper as well as parts of tellurium in the raw anode slime were removed, and naturally the precious metals in the residue was enriched. The remainder solid would be processed economically to recover the valuable metals such as selenium, silver and gold.

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