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Sodium sulfide leaching of low-grade jamesonite concentrate in production of sodium pyroantimoniate①

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Abstract: Sodium sulfide leaching of a low-grade jamesonite concentrate in the production of sodium pyroantimoniate through the air oxidation process and the influencing factors on the leaching rate of antimony were investigated. In order to decrease the consumption of sodium sulfide and increase the concentration of antimony in the leaching solution, two-stage leaching of jamesonite concentrate and combination leaching of high-grade stibnite concentrate and jamesonite concentrate were used. The experimental results show that the consumptions of sodium sulfide for the two-stage leaching process and the combination leaching process are decreased by 20% and 60% compared to those of one-stage leaching process respectively. The final concentrations of antimony in the leaching solutions of both processes are above 100 g/L.

Key words: sodium sulfide; jamesonite concentrate; leaching; low-grade

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1 INTRODUCTION

There is a mine in Guangxi Chuang autonomous region that is rich in the lead and antimony resources. Up to 2001, the total geological reserves of antimony and lead in that mine are more than 400 kt and 500 kt, respectively. Antimony containing in the ore mainly exists in the form of jamesonite[1, 2]. From these jamesonite resources, two kinds of antimony concentrates are produced, in which one is a high-grade jamesonite concentrate with the total content of antimony and lead more than 58%(mass fraction), the other is a low-grade jamesonite concentrate, in which the total antimony and lead content is less than 45%. The annual output of the low-grade jamesonite concentrate is over 6 000 t (calculated by the net metal mass of antimony). Due to its low-grade of antimony and high content of impurities such as copper and bismuth etc, only Grade 2 antimony metals and lead-rich antimony could be produced by the traditional pyrometallurgical methods with high operation costs and environment pollution[3, 4]. In order to make the most of this low-grade jamesonite concentrate, other promising metallurgic processes such as chlorination - hydrolysis process[5, 6], chlorination - carbonization process[7, 8], slurry electrolysis technology[9, 10] and bath - smelting - continuous fuming process etc[11-13] have been developed. The production of sodium pyroantimoniate from the sodium sulfide leaching solution of the jamesonite concentrate has also been studied[14-16]. Using this process, the antimony resources could be comprehensively recovered. But the consumptions of sodium sulfide were relatively high and the concentration of antimony in the leaching solution was relatively low. In addition, too many reagents of beneficiation in the jamesonite concentrate made the over-swelling of the leaching solution happen frequently. In order to resolve the above-mentioned problems, a series of experiments were carried out using two-stage leaching process and combination leaching process, respectively.

2 EXPERIMENTAL

2.1 Principle

In the solution of sodium sulfide, antimony sulfide in jamesonite concentrate or stibnite concentrate will react with sodium sulfide, and the reaction can be described as follows[1]:

$$Sb_2S_3 + 3Na_2S = 2Na_3SbS_3 \qquad (1)$$

Then through air oxidation sodium antimonate can be precipitated from sodium thioantimonite solution, and the free sodium sulfide in the solution will also be oxidized to form sodium thiosulfate. The reactions are expressed as follows [13]:

$$2Na_3SbS_3 + 7O_2 + 2NaOH + 5H_2O = 2NaSb(OH)_6 \downarrow + 3Na_2S_2O_3 \qquad (2)$$

$$2Na_2S + 2O_2 + H_2O = Na_2S_2O_3 + 2NaOH \qquad (3)$$

2.2 Raw materials and reagents

The raw materials were low-grade jamesonite concentrate and high-grade stibnite concentrate.

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The chemical compositions are listed in Table 1.

Table 1 Chemical compositions of jamesonite concentrate and stibnite concentrate

(mass fraction, %)

Material	Pb	Sb	As	Bi	Cu	Fe
Jamesonite concentrate	24.91	16.67	0.8	0.3-0.4	0.6-0.8	9.64
Stibnite concentrate	3.10	62.0	<0.1	—	—	2.41

The main reagents used in the experiments were sodium sulfide (industrial grade, Changsha Jingshan Chemical Factory) and sodium hydroxide (industrial grade, Shantou Chemical Factory of Guangdong).

2.3 Experimental apparatus and procedure

A schematic diagram of the experimental apparatus is shown in Fig. 1. A beaker of 800 mL used as the reactor was put in an electric jacket to keep the leaching temperature constant. When the solution of sodium sulfide was heated to the given temperature, antimony concentrate was added into the solution and was subjected to leaching. After leaching, the pulp was filtrated, then the concentration of antimony in leaching solution was determined. The leaching residue was washed by tap water of 100 mL twice and was put into an oven to be dried. The content of antimony in it is assayed by the volumetric titration with cerium sulfate.

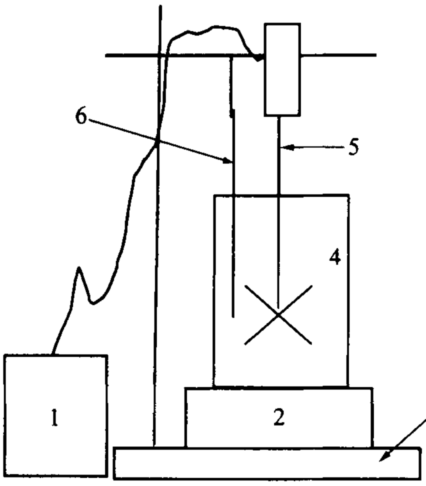

Fig. 1 Schematic diagram of experimental apparatus
1—Speed regulator; 2—Electric jacket; 3—Bracket; 4—800 mL beaker; 5—Agitator; 6—Thermometer

3 RESULTS AND DISCUSSION

The effects of liquid-solid ratio (i. e. volume of sodium sulfide solution to mass of concentrate, mL : g), leaching temperature, excess coefficient of sodium sulfide(mass ratio of actual consumption to theoretical consumption of Na_2S) and drying temperature of concentrate on the leaching rate of antimony contained in jamesonite concentrate were investigated, and the two-stage leaching of the jamesonite concentrate and the combination leaching of the jamesonite concentrate and high-grade stibnite concentrate were carried out.

3.1 Effect of liquid-solid ratio on leaching of antimony

Fig. 2 shows the relationship between liquid-solid ratio and leaching rate of antimony. The experimental conditions are as follows: jamesonite concentrate of 100 g, Na_2S concentration of 130 g/L, sodium hydroxide concentration of 40 g/L, leaching temperature of 95 ℃ and leaching time of 1 h. From Fig. 2, it can be seen that when the liquid-solid ratio changes from 2 to 4, the leaching rates of antimony maintain about 91%. This indicates that the liquid-solid ratio has little influences on the leaching rate of antimony. Due to the low-grade of the jamesonite concentrate, low liquid-solid ratio must be chosen so as to keep the concentration of antimony in the leaching solution as high as possible. On the other hand, too low liquid-solid ratio will lead to the increase of the viscosity of the leaching solution and the leaching of jamesonite concentrate will be difficult to be carried out, so liquid-solid ratio of 2.5 is chosen in the experiment. According to reaction (1), the excess coefficient of sodium sulfide under the experimental conditions chosen has arrived at 2.0.

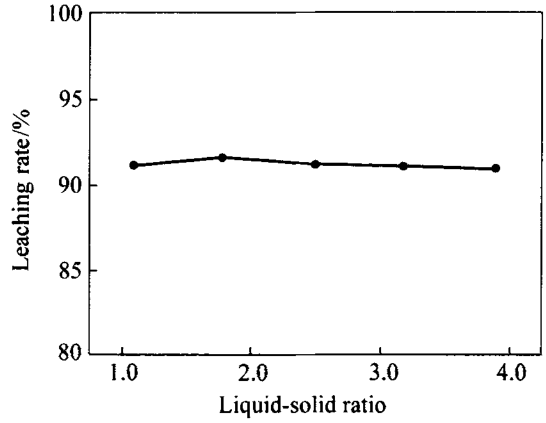

Fig. 2 Effect of liquid-solid ratio on leaching rate of antimony

3.2 Effect of leaching temperature on leaching of antimony

Fig. 3 shows the relationship between leaching temperature and leaching rate of antimony. It indicates that higher temperatures always respond to the higher leaching rate of antimony. At 75 ℃ only less than 50% of antimony is leached and a great majority of antimony remains in the residue. With the increase of leaching temperature, the leaching rate increases significantly. When the leaching temperature is raised to 95 ℃, the leaching rate reaches about 91%. The increase of leaching rate of antimony slows down when the leaching temperature is above 95 ℃. The leaching temperature of 95 ℃ is chosen in the experiment.

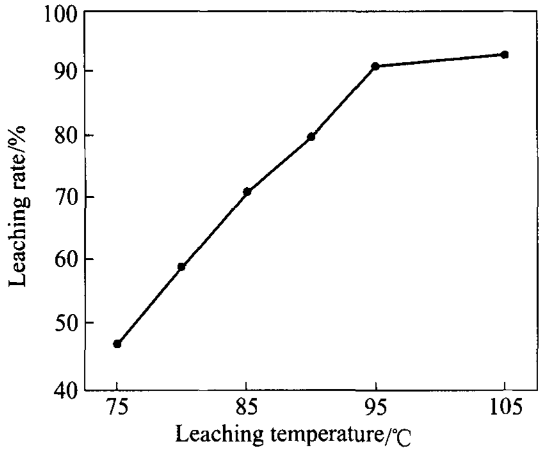

Fig. 3 Effect of leaching temperature on leaching rate of antimony

3. 3 Effect of excess coefficient of sodium sulfide on leaching of antimony

Fig. 4 demonstrates that the leaching rate of antimony increases with the increase of the excess coefficient of Na_2S. When the excess coefficient of Na_2S of 1. 4 is adopted, the leaching rate of antimony is only about 83%. While the excess coefficient of Na_2S of 2. 0 is used, the leaching rate of antimony is enhanced to about 91%. The leaching rate of antimony increases very slowly when the excess coefficient of Na_2S is above 2. 0, so the excess coefficient of 2. 0 is suitable for the leaching of jamesonite concentrate, which corresponds to the value in Ref. [1].

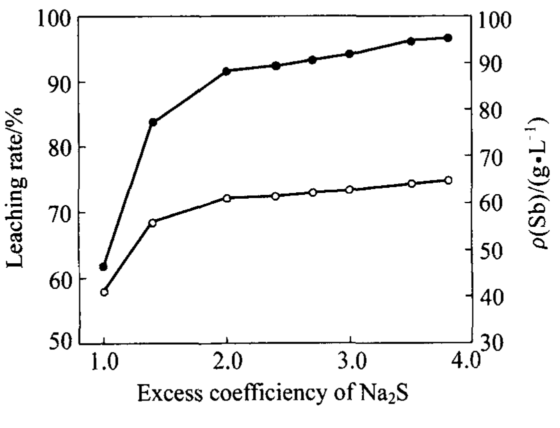

Fig. 4 Effects of excess coefficient of sodium sulfide on leching of antimony
●—Leaching rate of antimony;
○—Antimony concentration in leaching solution

3. 4 Effect of drying temperature on leaching rate of antimony

In the practical operation, a lot of foam is produced when the wet jamesonite concentrate is leached due to the high content of the reagents of beneficiation. In order to eliminate the effects of the reagents of beneficiation, the low-grade jamesonite concentrate is dried at different temperatures for 2 h before leaching. The effect of drying temperatures on the leaching rate of antimony is shown in Fig. 5. No foam emerges on the surface of the leaching solution for all the dried concentrates in the leaching procedure. Therefore, drying of concentrate is an effective method to remove the reagents of beneficiation. From Fig. 5, it can be seen that when the drying temperature is between 40 ℃ and 160 ℃, the leaching rates of drying concentrate are higher. When the drying temperature is above 160 ℃, the leaching rates decrease with the increase of drying temperatures which may be caused by the hardened and low-dispersible concentrate at high drying temperature. So the optimum drying temperature is 100 ℃.

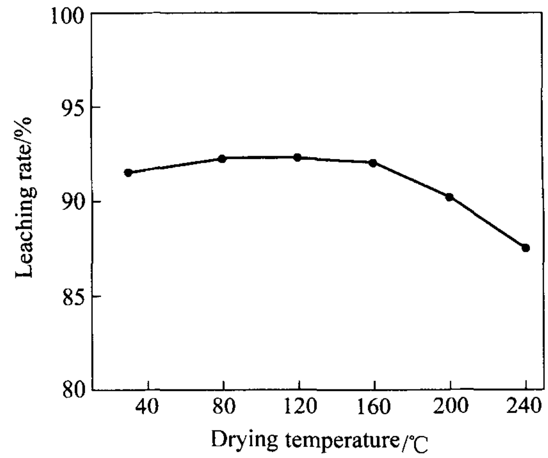

Fig. 5 Effect of drying temperature on leaching rate of antimony

3. 5 Two-stage leaching process of jamesonite concentrate

Fig. 4 shows that the concentration of antimony in the leaching solution for one-stage leaching is below 70 g/L when liquid-solid ratio is 2. 5 and the consumption of sodium sulfide is relatively high. In production of sodium pyroantimoniate, the optimum concentration of antimony required is above 100 g/L. In order to decrease the consumption of sodium sulfide and increase the concentration of antimony in the leaching solution, two-stage leaching is carried out and the leaching conditions for the first leaching stage are as follows: jamesonite concentrate of 100 g, sodium hydroxide concentration of 40 g/L, liquid-solid ratio of 2. 5, leaching temperature of 95 ℃ and leaching time of 1 h. The average excess coefficients of Na_2S in the two-stage leaching process are shown in Fig. 6. The leaching solution of the first stage are then used as the leaching agents of the second stage without addition of sodium sulfide and sodium hydroxide, and other leaching conditions are the same as those of the first-stage. From Fig. 6, it demonstrates that the highest leaching rate of antimony for the first stage is about 96% and the corresponding leaching rate for the second stage is about 87%. The average leaching rate of antimony with the two-stage leaching arrives at about 92% and the average sodium sulfide excess coefficient is 1. 8. From Fig. 4, it can be seen that the sodium sulfide excess coefficient for one-stage leaching is 2. 4 with the same leaching rate. The sodium sulfide consumption of the two-stage leaching decreases by about 20% and the utilization factor of sodium sulfide is increased significantly. Simultaneously, the volume of the leaching solution of the two-stage leaching is reduced to about 50% that of one-stage leaching when the same amount of concentrate is leached, so the energy consumption of heating the leaching solution decreases greatly. The highest final concentration of antimony in the leaching solution reaches above 120 g/L, which increases by about twice compared to that of one-stage leaching. With the rapid increase of the concentration of antimony in the leaching solution, the energy consumption in the air oxidation step and condensation and crystallization step decrease greatly.

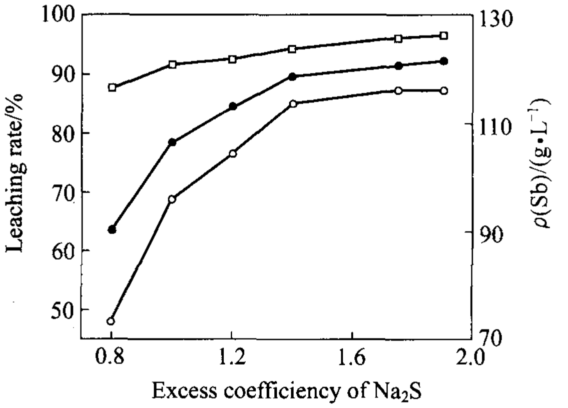

Fig. 6 Effects of average excess coefficient of Na_2S on leaching of antimony with two-stage leaching process of jamesonite concentrate

○—Leaching rate for the second stage;
□—Leaching rate for the first stage;
●—Final concentration of antimony

3. 6 Combination leaching of jamesonite concentrate and high-grade stibnite concentrate

From the above experimental results, it can be found that the sodium sulfide consumption for two-stage leaching is still relatively high although it decreases greatly in comparison with the one-stage leaching. In order to lessen the consumption of sodium sulfide further and increase the antimony concentration in the leaching solution, the combination leaching of jamesonite concentrate and high-grade stibnite concentrate is carried out, i. e. the difficultly leached jamesonite concentrate is leached first by appropriate concentration of sodium sulfide and then the stibnite concentrate is added into the filtrate of the first stage to consume the superfluous sodium sulfide.

For the first stage excess coefficient of the Na_2S of 2. 4 is used and other leaching conditions are the same as those used in the first stage of two-stage leaching process. Different amounts of stibnite concentrate are leached by the filtrate of first stage to find out the optimum addition, and the leaching conditions for the second leaching stage are as follows: leaching temperature of 95 ℃, leaching time of 30 min. Fig. 7 shows that when appropriate amount of stibnite concentrate is leached, the leaching rate of antimony in the stibnite concentrate reaches above 99%, and the optimum mass ratio of jamesonite concentrate to stibnite concentrate is 10 : 3 when the excess coefficient of sodium sulfide is 2. 4. The corresponding antimony leaching rates of the jamesonite concentrate and the stibnite concentrate are 92. 4% and 99. 8%, respectively. The average leaching rate of antimony is about 96%, the average excess coefficient of sodium sulfide is 1. 2, the utilization factor of Na_2S arrives at 80%, and its consumption decreases by about 60% compared to that of one-stage leaching. The final concentration of antimony reaches about 130 g/L, which increases by about twice compared to that of one-stage leaching.

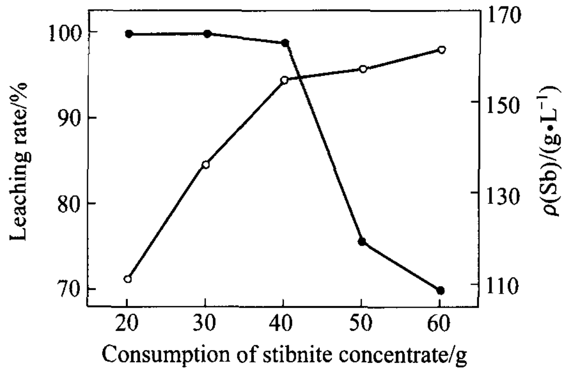

Fig. 7 Effects of consumption of stibnite concentrate on leaching of antimony with combination leaching of jamesonite concentrate and high-grade stibnite concentrate

●—Leaching rate of antimony containing in stibnite concentrate;
○—Final concentration of antimony in leaching solution

4 CONCLUSIONS

1) The low-grade jamesonite concentrate is leached by Na_2S solution, and the optimum leaching conditions are as follows: leaching temperature of 95 ℃, excess coefficient of Na_2S of 2.0, sodium hydroxide concentration of 40 g/L, liquid-solid ratio of 2.5 and leaching time of 1 h. The leaching rate of antimony reaches above 91%, and the concentration of antimony in the leaching solution is about 70 g/L.

2) In two-stage leaching process of jamesonite concentrate, the optimum leaching conditions are as follows: average excess coefficient of Na_2S of 1.8, liquid-solid ratio of 2.5, sodium hydroxide concentration of 40 g/L (the first stage), leaching temperature of 95 ℃. The average leaching rate of antimony is about 92%.

3) In the combination leaching process of jamesonite concentrate and high-grade stibnite concentrate, when the excess coefficient of Na_2S is 2.4, the optimal mass ratio of jamesonite concentrate to stibnite concentrate is 10 : 3, and the average leaching rate of antimony arrives at 96%. The sodium sulfide consumptions of the two-stage leaching process and the combination leaching process are decreased by 20% and 60% compared to those of one-stage leaching process respectively. The concentrations of antimony in the leaching solutions for both processes are above 100 g/L.

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