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Removal of cobalt from zinc sulphate solution using rude antimony trioxide as additive①

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[Abstract] The process of cobalt removal from zinc sulphate solution using rude antimony trioxide as an additive was investigated. The rude antimony trioxide was produced in treatment of copper and lead anode mud and its main components are antimony trioxide, antimony arsenate and lead antimonate. Using the rude antimony trioxide as the additive of cobalt removal can not only decrease operation cost of purification but also find out a new way for utilization of the rude antimony trioxide. The effects of temperature, dosage of zinc dust, the rude antimony trioxide, copper ion and solution pH on removal of cobalt were studied. And experimental data using the rude Sb_2O_3 as additive were compared with those using Sb_2O_3. The results indicate that using rude Sb_2O_3 as additive, cobalt concentration in solution could be decreased from 24 mg/L to below 1 mg/L under about the same conditions as using Sb_2O_3.

[Key words] zinc sulphate solution; rude antimony trioxide; cobalt removal
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1 INTRODUCTION

Roast-leach-purification-electrowinning process is the most common method for zinc production in the world[1]. The removal of cobalt from zinc sulphate solution by cementation has been the focus of research for more than 20 years in the hydrometallurgy of zinc[1,2]. The presence of impurities in a zinc electrolyte is problematic for the electrowinning process[3]. Cobalt is one of the most harmful impurities and removal of cobalt is the most critical part of the purification processes. Co^{2+} is normally removed by cementation with zinc dust addition to the $ZnSO_4$ solution[2]. Co^{2+} cementation is troublesome because of extremely slow kinetics of the cementation reaction of cobalt on zinc and activators are in general required[3]. The activators can enhance the rate of cobalt cementation and make the cementation process viable. The main activation methods used in the process of cobalt removal from zinc sulphate solution are the addition of arsenic and copper or antimony and copper[1,3,4]. The research work about the activators has been carried out for many years[1,3,5]. This work is in search of the optimal process conditions for cobalt removal using rude antimony trioxide as an additive in order to obtain the target cobalt concentration below 1 mg/L.

According to the result of X-ray diffraction analysis of the rude Sb_2O_3(shown in Fig. 1), its main ingredient is antimony trioxide(Sb_2O_3) and the remains are antimony arsenate ($SbAsO_4$) and lead antimonate ($Pb(SbO_3)_2$). The function of antimony trioxide in the rude antimony trioxide during cobalt removal is forming a preferential substrate on the zinc dust surface for cobalt cementation in the same way as antimony white. According to thermodynamic analysis, antimony arsenate($SbAsO_4$) in the rude Sb_2O_3 can be reduced to arsenious acid and antimony trioxide by zinc dust in the cementation process as

$$2Zn + 2SbAsO_4 + 2H_2SO_4 = 2ZnSO_4 + 2HAsO_2 + Sb_2O_3\downarrow + H_2O \quad (1)$$

$$2Zn + Pb(SbO_3)_2 + 3H_2SO_4 = PbSO_4\downarrow + Sb_2O_3\downarrow + 2ZnSO_4 + 3H_2O \quad (2)$$

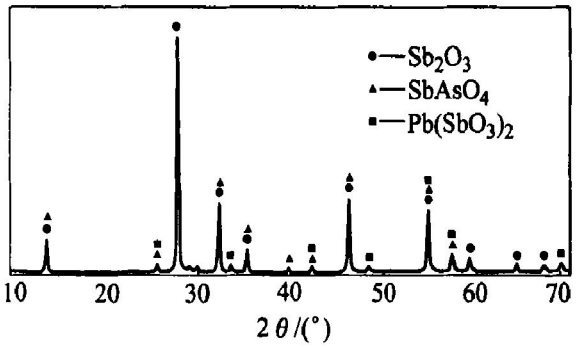

Fig. 1 XRD pattern of rude Sb_2O_3

Both $HAsO_2$ and Sb_2O_3 produced by reaction (1) and (2) can play the role of cobalt removal in purification process. That is to say, the rude antimony trioxide is a mixed additive. $PbSO_4$ produced by reaction (2) will enter into cobalt residue and be harmless to the process of cobalt removal. According to thermodynamic analysis[6], a little SeO_2 in the rude Sb_2O_3 will dissolve and then be reduced easily to metal selenium by zinc

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dust during the cementation. The selenium reduced enters finally into cobalt residue and cannot cause difficulty for zinc electrowinnig.

2 EXPERIMENTAL

Batch cementation tests were conducted in a two liter beaker which was sealed to prevent solution loss by evaporation. Agitation was achieved using an single blade mixer and stirring rate was fixed at 300 r/min. One liter of the neutral $ZnSO_4$ solution was used for each test and pH of the solution was manually adjusted to the desired value by the addition of sodium hydroxide or sulphuric acid solution. Each test was ran for 2.5 h and samples were taken at specific time intervals(every half an hour), approximately 10 mL aliquot of solution were removed and filtered with the conic funnel. Each 5 mL sample taken out of 10 mL solution was analyzed for cobalt concentration.

Analytical grade chemicals including H_2SO_4, NaOH and $CuSO_4 \cdot 5H_2O$ were used in the experiments. The neutral $ZnSO_4$ solution and the zinc dust were both obtained from the original Sherr-yang Smelter. Chemical composition of the neutral $ZnSO_4$ solution is given in Table 1. Total zinc content of the zinc dust is 95%, metal zinc content is 90% and the apparent particle size is 125~ 150 μm. Chemical analysis of the rude Sb_2O_3 is as(%): Sb 70.36, As 6.05, Pb 1.41, Fe 0.1, Cl 0.011, Se 0.26, Sn 0.012, F 0.014. Apparent particle size of the rude Sb_2O_3 is 175~ 200 μm.

Table 1 Chemical composition of neutral zinc sulphate solution (mg/L)

Zn	Cu	As	Co	Sb	Cd	Fe	Se
150*	164.50	0.25	24.00	0.55	694.60	8.00	0.02

* —g/L

3 RESULTS AND DISCUSSION

3.1 Effect of temperature

It is a known fact that increasing temperature has a beneficial effect on the rate of cobalt cementation[1, 7, 8] because cobalt cementation is a chemically or electrochemically controlled process[8]. To attain a higher efficiency of cobalt removal, high temperature of the solution is required. Experiments were conducted at 55, 65, 75, 85 and 95 ℃ respectively. The initial pH of solution is 4.5 and the dosage of zinc dust and activator was fixed at 5 g/L and 5 mg/L respectively. Fig. 2 is the cobalt concentration versus time curves in which the horizontal dashed line indicates the target cobalt concentration of 1 mg/L(the same as in the following figures). It can be seen from Fig. 2 that rate of cobalt removal increases significantly as the temperature rises from 55 ℃ to 85 ℃. When the operating temperature is up to 95 ℃, on the contrary, the cobalt removal rate decreases. It is also shown that the redissolution of cobalt deposited occurs evidently after 60 min when temperature is above 85 ℃. The redissolution of cobalt at high temperature may be attributed to the fact that hydrogen evolution becomes the most prominent reaction, rather than metal deposition[3, 8, 9]. It is also possible that at higher temperatures zinc deposition is inhibited as the zinc content in cements obtained at higher temperatures is lower[1]. To prevent cobalt deposited from redissolution, more zinc dust should be added during the purification. The other studies[7~ 11] also found that the optimum operating temperature using antimony white as additive was approximately 85 ℃, and that above this, the cobalt removal rate dropped significantly.

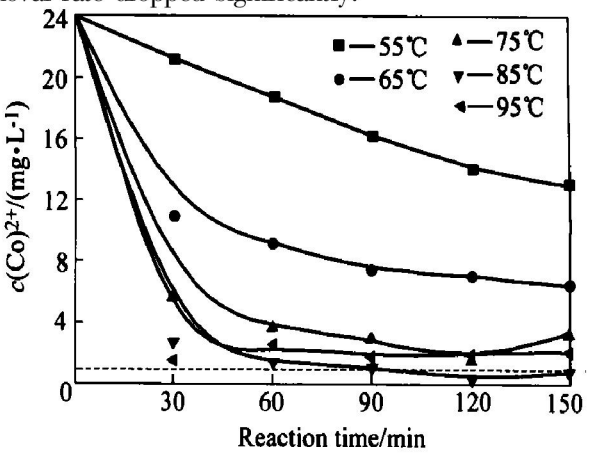

Fig. 2 Effect of temperature on Co removal

3.2 Effect of initial zinc dust dosage

In order to determine effect of zinc dust dosage on cobalt removal, tests were conducted under the conditions of 5 mg/L of the rude antimony trioxide, pH about 4.5 and 85 ℃, and the results are given in Fig. 3. Trina et al[3] reported the cobalt removal rate constant increased apparently with the dosage of zinc dust. This experimental results(shown in Fig. 3) are essentially in agreement with the mention above. The data in Fig. 3 indicate that when the dosage of zinc dust reach 5 g/L, the rate of cobalt removal enhances obviously and the target cobalt concentration of less than 1 mg/L is met after 120 min. The reason of slight high zinc dust consumption may be that the Cu^{2+}, Cd^{2+} concentration in the neutral $ZnSO_4$ solution used is a little higher[7]. What's more, the reduction of $SbAsO_4$ and $Pb(SbO_3)_2$ in the rude Sb_2O_3 can also result in increase of zinc dust consumption.

3.3 Effect of dosage of rude antimony trioxide

Tests for dosage of the rude Sb_2O_3 were conducted under the conditions of 85 ℃, 5 g/L zinc dust and pH about 4.5 and results are shown in Fig. 4. From these results, it can be seen that satisfactory cobalt removal is obtained when dosage of the rude antimony trioxide

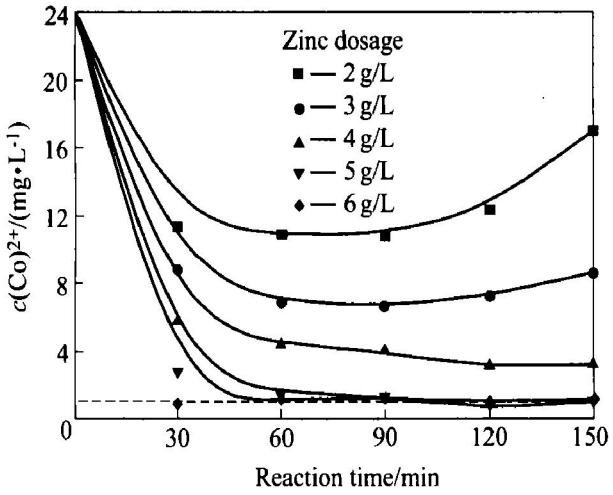

Fig. 3 Effect of zinc dosage on Co removal

reaches 4 mg/L and reaction time is 90 min. When the dosage of the rude Sb_2O_3 increases up to 6 mg/L, the rate of cobalt removal increases quickly before 60 min but after that redissolution of cobalt precipitated appears obviously. This may be due to lack of zinc dust, which is caused by the reduction of $SbAsO_4$ and $Pb(SbO_3)_2$ in the rude Sb_2O_3.

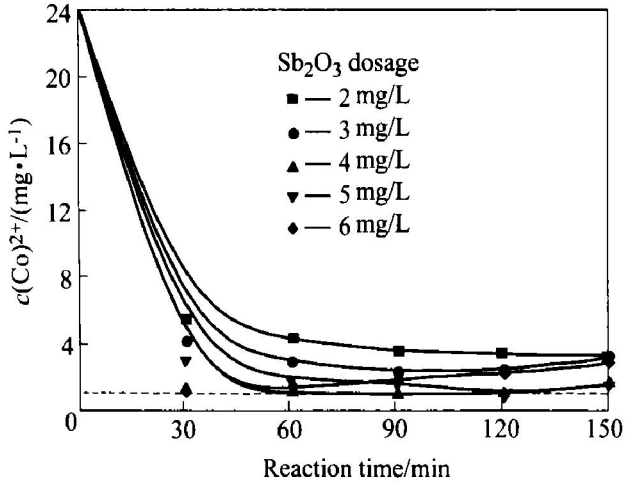

Fig. 4 Effect of rude Sb_2O_3 on Co removal

3.4 Effect of pH

pH of zinc sulphate solution plays an important role during cobalt removal[1]. If pH is too high (5.0 and above), the formation of basic zinc sulphate or zinc hydroxide retards the reaction kinetics by forming a passivating layer on the zinc dust[3, 7, 8]. At low pH (below 4), the hydrogen ion activity increases and hydrogen evolution enhances, therefore, zinc dust consumption increases[7]. Fig. 5 shows effect of solution initial pH value on cobalt removal under the conditions of 5 g/L zinc dust, 4 mg/L rude Sb_2O_3 and 85 ℃.

As shown in Fig. 5, lower pH (4.1 and below) or higher pH (above 5.2) of the initial solution is very harmful to cobalt removal. This result is in agreement with Refs. [1, 5, 8]. It is common practice in cobalt

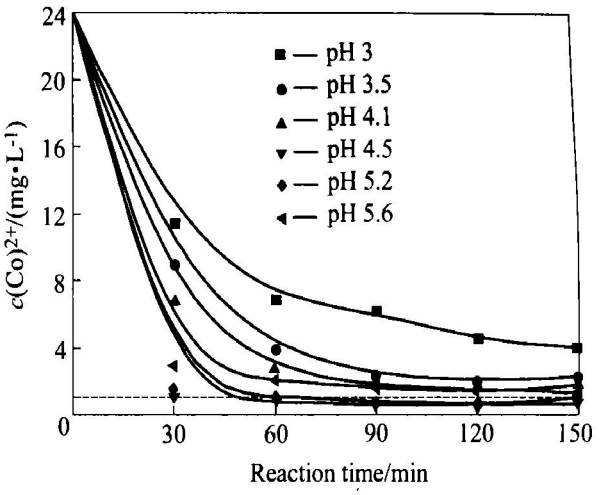

Fig. 5 Effect of pH on Co removal

removal that the optimum operating pH must balance reducing the hydrogen ion activity (by raising pH) and reducing the chance of forming solid precipitates (by lowering pH)[1].

3.5 Effect of copper dosage

Lew et al[1] suggested in their previous work that copper acted primarily as a substrate for cobalt cementation while antimony played a role in both maintaining a high overpotential for hydrogen evolution and providing a substrate for cobalt deposition. And this opinion was confirmed in the later work by van der Pas and Dreisinger[8]. To determine the effect of copper on cobalt removal using the rude Sb_2O_3, tests were performed under the experimental conditions of 85 ℃, 5 g/L zinc dust, 4 mg/L rude Sb_2O_3 and pH 4.5. The results with copper dosage of 20, 40, 60 and 80 mg/L are given in Fig. 6. It may be seen that none of the cobalt removal results attains to the target concentration of cobalt. Concentration of copper and cadmium in the neutral $ZnSO_4$ solution given in Table 1 is 164.5 and 694.6 mg/L, respectively. The reason for relatively poor results of cobalt removal may be the higher content of copper and cadmium in solution and thus zinc dust is not enough to cement cobalt from solution using rude Sb_2O_3 as the additive.

3.6 Comparative tests

In order to determine whether the rude antimony trioxide could be used as a substitute for antimony white, the comparative tests were conducted. In terms of the previous work[1, 8, 10], cobalt removal using Sb_2O_3 was performed under the temperature of 85 ℃, Sb_2O_3 4 mg/L, pH 4.5, zinc dust 4 g/L. Using the rude Sb_2O_3 as additive, the experimental conditions for cobalt removal were 85 ℃, zinc dust 5 g/L, rude Sb_2O_3 4 mg/L and pH 4.5. Fig. 7 presents the results for two additives tests. The results indicate that the rude Sb_2O_3 is superior to Sb_2O_3 before 90 min in point of cobalt removal, and

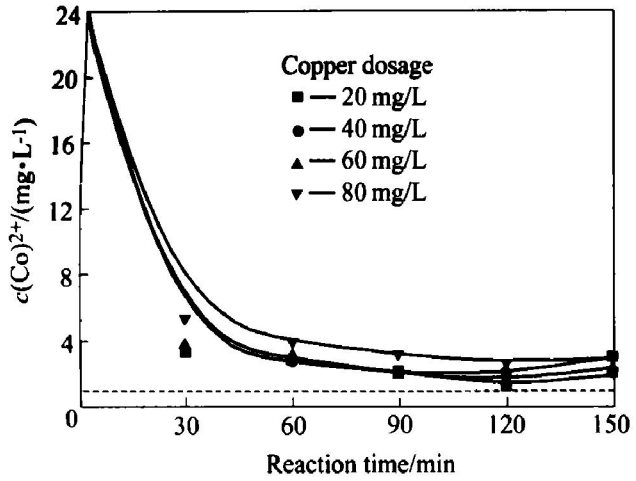

Fig. 6 Effect of copper concentration on Co removal

after 90 min, the two additives have the same results of cobalt removal.

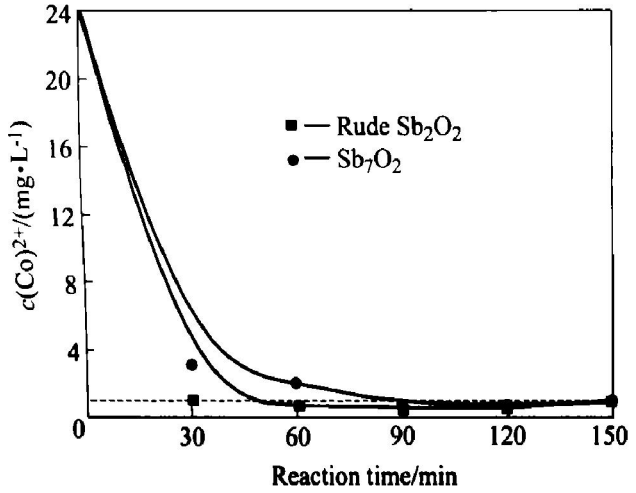

Fig. 7 Effect of two Sb additives on Co removal

The chemical compositions of the two purified zinc sulphate solutions by ICP are given in Table 2. Data in Table 2 show that the effects of two additives on removal of the other impurities are much the same, and Se in the rude Sb_2O_3 does not enter into purified solution during the cobalt removal.

Table 2 Chemical compositions of purified zinc sulphate solutions using two additives(mg/ L)

Additive	Zn	Cu	As	Co	Sb	Cd	Fe	Se
Rude Sb_2O_3	160.00*	0.11	0.04	0.54	0.11	15.37	7.50	0.03
Sb_2O_3	159.05*	0.15	0.03	0.78	0.23	16.87	6.50	0.02

* —g/ L

4 CONCLUSION

This research confirms that the rude antimony trioxide can be used as the additive for cobalt removal to replace antimony white. The results for cobalt removal using rude Sb_2O_3 reach the target cobalt concentration of below 1 mg/ L under the conditions about the same as using Sb_2O_3. The optimum operating conditions for the removal of cobalt from an industrial zinc sulphate solution are determined to be the addition of 5 g/ L zinc dust, 4 mg/ L rude Sb_2O_3, solution pH 4.5, temperature 85 ℃ and no addition of copper. Because the Cu^{2+}, Cd^{2+} concentration in the neutral $ZnSO_4$ used in this study is a slight higher and reduction of $SbAsO_4$ and $Pb(SbO_3)_2$ in the rude Sb_2O_3 can occur during the cementation, the dosage of zinc dust is not below 5 g/ L. The effects of the rude Sb_2O_3 and Sb_2O_3 on removal of the other impurities are basically the same in the process of cobalt removal.

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