



CORPUS PUBLISHERS

Journal of Mineral and Material Science (JMMS)

ISSN: 2833-3616

Volume 5 Issue 5, 2024

Article Information

Received date : November 02, 2024

Published date: November 18, 2024

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DOI: 10.54026/JMMS/1096

Key Words

Hydrometallurgy; Calcine Containing Antimony; Antimony Reserves; Sulfide-Antimony Concentrate; Chlorination Roasting; Metallic Antimony; Optimization

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Research Article

Hydrometallurgical Processing of Antimony Bearing Pyrometallurgical Calcines

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Abstract

The solid pyrometallurgical calcination product containing antimony was dissolved in H₂SO₄ under conditions that ensured a high extraction of the oxidized antimony compounds into the solution. The key conditions were [H₂SO₄]-180 g/l, duration - 2 hours, temperature - 80 °C, T: J = 1:6, and a rotation speed of 400-450 rpm. The study determined a high degree of antimony dissolution is possible and found the optimal points for the proposed process.

Introduction

Among the minerals in Tajikistan, antimony is one of the strategic and profitable metals of the mining industry and belongs to the group of rare metals. World antimony reserves vary from 1.87 to 5.33 million tons [1,2]. In Tajikistan, research in the field of antimony metallurgy is of high importance for the successful implementation of the strategic national goal of the industrialization of the country. This is the transition from an agricultural to an integrated industrial-agrarian economy. The presence of rich natural resources and multi-element mineral deposits plus an inexpensive and accessible source of electricity form a reliable basis for the development of the country's metallurgical industry.

Background

In recent years, significant research on the leaching of antimony sulfides with ferric chloride solutions has been carried out in the USA, China and the Russian Federation [3,4]. The hydrometallurgical method of processing antimony pyrometallurgical chlorination calcine makes it possible to obtain chlorine ion from the cinder, thereby freeing the antimony. To separate the chloride ion from the products of roasted antimony concentrate and transfer it into solution, as well as to separate the resulting compound into ions, a dissolution process was carried out. With the use of an acidic solution, heating and rapid stirring of the chloridized calcine, a rapid antimony leaching reaction occurs. Chloride antimony oxide is insoluble in cold water and precipitates, but when boiled it goes into solution as SbCl₃ is soluble in hydrochloric and sulfuric acids [5]. With continuous leaching with a circulating acidic solution, the chlorine-containing cinder quickly dissolves. Subsequent neutralization of acid also occurs quickly due to the large excess of antimony chloride calcine.

It was determined that after a chlorinating roasting of antimony sulfide concentrates at T = 450 °C, t = 120 minutes with the composition of the charge m₁/m₂ = ¼ (25% NaCl) there is a maximum extraction of antimony into the solution. This technology was first demonstrated by some previous research performed by the authors [6]. After the pyrometallurgical chlorination process, materials are formed that analyzed SbCl₃-49.55% and Sb₂O₄-25% by weight. At the same time, it was determined that the resulting pyrometallurgical products were best treated by hydrometallurgical processing. It is noted that some dissolution of the resulting material could also be carried out with water, since 25% of the resulting product is in the oxide form, which is readily dissolved [6].

Research Methods and Results

To carry out the experiments, calcine was prepared by using a mixture of 4 g of antimony concentrate with 1 g of NaCl (m₁/m₂=4/1). Roasting was then carried out in a Nabertherm RT 50-250/11/B410 tubular furnace operating at 1100 °C for 120 minutes. Diluted sulfuric acid was then used as a solvent to leach the calcine formed in the prior roasting step. The Table 1 below provides detailed information on each key hydrometallurgical factor studied. Antimony was extracted by leaching in a reactor immersed in an ultra-thermostatic UTU2/82 heating mantle. Mixing was carried out with a top mixer Ekros PE8100 using paddle stirrers in flasks, glasses, bottles and other containers.

Table 1: Hydrometallurgical sulfuric acid leaching experiments.

Experiment No. 1.	T, °C	Rotation Speed rpm	Solid to Liquid Ratio, T: F	t, min	H ₂ SO ₄ Concentration
1.2	30	250rpm	10 grconc/50mgr. (1:5)	30 minutes	120 g/l
1.3	40	300 rpm	8.33 g conc/50 mg po. (1:6)	60 minutes	140 g/l
1.4	50	350 rpm	7.14 g conc/50 mg po. (1:7)	90 minutes	160 g/l
1.5	60	400 rpm	6.25 g conc/50 mg po. (1:8)	120 minutes	180 g/l
1.8	70	450 rpm	5.55 g conc/50 mg po. (1:9)	150 minutes	200 g/l
1.9	80	500 rpm	5 g conc/50 mg po. (1:10)	180 minutes	220 g/l
1.10	90	550 rpm	4,54rp _{конц} /50Mr _{pac} . (1:11)	210 minutes	240 g/l
1.11	100	600 rpm	4,16rp _{конц} /50Mr _{pac} . (1:12)	240 minutes	260 g/l

After reaching the required temperature in the reactor filled with the acidic solvent, roasted calcine was placed into it. This is illustrated in Figure 1. From this moment, the time of extraction was monitored. The speed of rotation of the mixer was maintained constant and consisted of 400-450 rpm. The key lab equipment noted above are 1 - a tripod, 2 - a stirrer, 3 - a thermostat, 4 - a leaching vessel and 5 - a control block for the stirrer, 6 - cup with pulp. To separate the solution from the solids, a 55 Ft laboratory filter was used. The pulp was filtered on a Buchner funnel connected through a Bunsen flask to a vacuum pump. The volume of filtrate was measured using a measuring cup. The cake was washed with distilled water, dried at 80 °C and then weighed. After drying to constant weight, the cake was weighed. The pulp was subjected to filtration, the filtrate was neutralized to pH = 6-7 by adding NaOH in the presence of methyl orange, a red precipitate formed, and the mother liquor became purple.

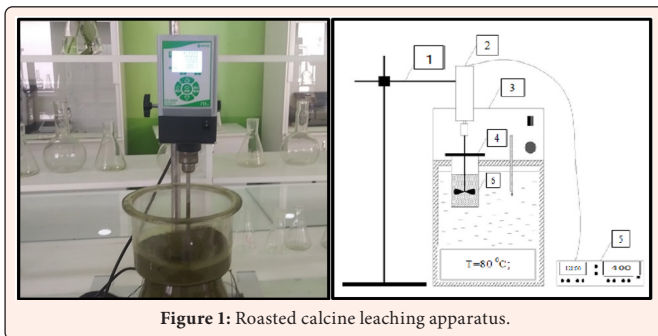


Figure 1: Roasted calcine leaching apparatus.

The filtrate, combined with the wash water, and the cake were analyzed for antimony, mercury and iron. The amount of antimony was determined by a photo colorimetric method. The amounts of the remaining elements were analyzed by ICP spectrometry. The pH of the solutions was also measured. The products obtained from process were in the form of a $[Sb_2(SO_4)_3]$ solution, which could then be treated by an electrolytic process to obtain pure antimony metal. As a result of analysis and research previously carried out [6,7], only 25% of antimony is in the form of oxides, and the rest is completely in the form of water-soluble chloride. Correspondingly, the solubility of the obtained cake using hydrochloric acid and distilled water was also determined using a magnetic stirrer with heating apparatus. This configuration is noted in Figure 2 below.

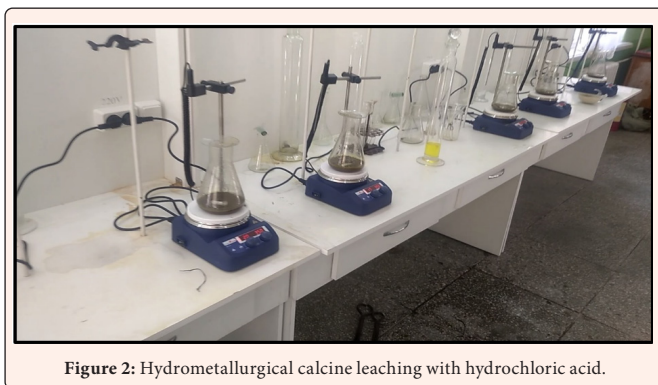


Figure 2: Hydrometallurgical calcine leaching with hydrochloric acid.

The comparative hydrometallurgical analysis determined that the recovery of antimony when leached in sulfuric acid is higher than when hydrochloric acid is used. Comparatively, the leaching recovery in water is 65%, in hydrochloric acid it is 75%, and in sulfuric acid it is more than 85%. It follows from the given data that practically all antimony can be extracted from the calcine by acid leaching. From a practical point of view, to minimize expensive acidic reagents, that ~65% of antimony is leached from the calcine with water is significant. Figure 3 shown below illustrates this comparison.

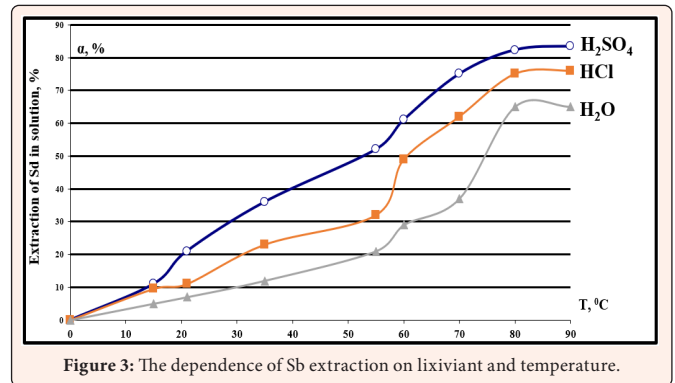


Figure 3: The dependence of Sb extraction on lixiviant and temperature.

In further research of the leaching process, five main factors were considered: temperature, speed of agitation, the ratio of solid to liquid, time and acid concentration. Again, from Figure 3, extraction increases exponentially to a critical point equal to $T = 80\text{ }^\circ\text{C}$, and then proceeds evenly [8].

Also, it was noted that:

- at different firing temperatures of the sample in the range $T = 10 \div 90\text{ }^\circ\text{C}$ (with varying steps $\Delta T = 10\text{ }^\circ\text{C}$), constant rotation speed revolutions/minute (400-450 rpm), solid to liquid ratio ($T:L = 1:6$), concentration $[H_2SO_4]$ - (180 g/l) and the same time ($\tau = 80\text{ min.}$) the process at this temperature, the recovery is 82% of Sb extraction into solution.
- 400-450 rpm of agitation is sufficient for the process and the recovery is an 82% extraction of Sb into the solution.
- the dependence of recovery on the solid to liquid, T:L, ratio shows that recovery increases exponentially to 83.2% at $T:L = 1:6$. When T:L increases by this amount, recovery to solution will decrease, for example, with $T:L = 1:13$, the recovery is 76%.
- at the same temperature ($T = 80\text{ }^\circ\text{C}$) and constant rotation speed (400-450 rpm), solid to liquid ratio ($T:L = 1:6$), concentration $[H_2SO_4]$ - (180 g/l) and exposure of the charge with different sample processing times (τ , in minutes) from 30 to 240 minutes, with a step of $\Delta\tau = 30$ minutes, the recovery at time $t = 120$ minutes is 82%. At the same time, it has been found that as time increases, recovery decreases.
- the recovery of antimony to solution strongly depends on the amount of the acid. If the amount of $[H_2SO_4]$ is below 180 g/l, recovery will decrease. In this regard, 180 g/l is sufficient for the process.

Based upon this research, a fundamental new flowsheet of the hydrometallurgical method for treating calcine from roasted antimony concentrates is shown in Figure 4.

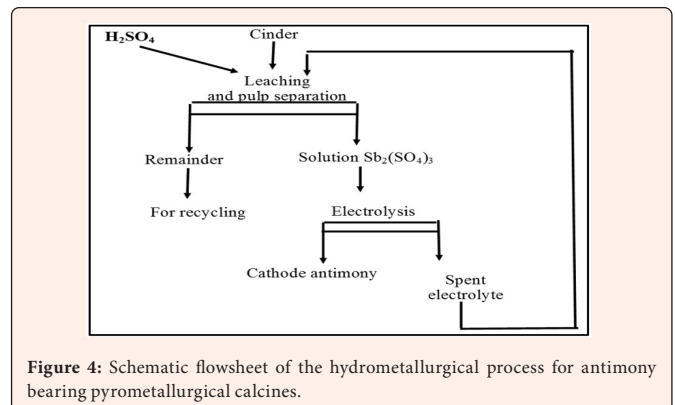


Figure 4: Schematic flowsheet of the hydrometallurgical process for antimony bearing pyrometallurgical calcines.



Summary

If chlorination roasting is carried out then the solid antimony compounds formed readily dissolve into a sulfuric acid solution. These studies have shown that at a process temperature of 80 °C, a stirrer rotation speed of 400-450 rpm, a solid to liquid ratio of 1:8, with a process time of $\tau = 120$ minutes, a concentration of $[H_2SO_4]$ 180 g/l, the technology for leaching antimony calcine is effective.

Acknowledgement

The authors the Mining and Metallurgical Institute of Tajikistan and the NAST (National Academy of Sciences of Tajikistan) for supporting this research.

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