Research Article

Mechanical Activation of Antimony Sulfide Concentrates Combined with Pyrometallurgical Chlorination

Rakhimov Kh Sh[1], Anderson CG[2]*, Badalov AB[3], Eshov BB[4] and Kadirov AA[5]

[1]Senior Lecturer, Applicant, Faculty of Metallurgy, Mining and Metallurgical Institute of Tajikistan, Tajikistan

[2]Director, Kroll Institute for Extractive Metallurgy, Mining Engineering Department, Colorado School of Mines, Golden, Colorado, USA

[3]Doctor of Technical Sciences, Professor of the Department of General and Inorganic Chemistry, Avicenna Tajik Technical University M S Osimi, Corresponding Member NAST (National Academy of Sciences of Tajikistan), Tajikistan

[4]Doctor of Technical Sciences, Director - Center for Research of Innovative Technologies, NAST (National Academy of Sciences of Tajikistan), Tajikistan

[5]Candidate of Technical Sciences, Head of the Department of Metallurgy, Mining and Metallurgical Institute Buston, Tajikistan

Abstract

Research on a combined method of chlorination roasting of a mechanically activated antimony sulfide concentrate from the Anzob Mining and Processing Plant in the Republic of Tajikistan with sodium chloride was carried out. The influence of the main factors - temperature, processing time, charge composition – has been determined which allowed an almost twofold increase in the degree of antimony extraction and at lower process temperatures

Introduction

Antimony is an important and strategic material. The world annual consumption of primary antimony products is estimated at more than 120 thousand tons/year. Approximately 60-65% of all consumed antimony goes to the production of flame retardants as antimony trioxide. The next most common use is in the form of metal and alloys for the manufacture of battery grids, bearings (babbitt), typographic type, rubber vulcanization, and antimony trisulfide in match production and munitions. In recent years, the production of antimony oxide compounds has increased to provide fire-resistant, protective coatings. Ultrapure metal is also used to produce semiconductors [1-5]. Antimony is a critical element and there are many known antimony minerals. The estimated world reserves of antimony are 5.3 million/t, and Tajikistan ranks third after China and Thailand in Asia and first among the CIS countries [3]. The main and in most cases the only mineral of importance is stibnite, which is present in all genetic types of antimony deposits. Along with the traditional methods of pyro -, hydro - and electro - metallurgy, biochemical leaching can be used to liberate refractory ores and extract antimony, gold and other metals. This is predicated upon using the method of extracting antimony, gold, silver, lead, zinc, copper, based on the ore as a natural source of nutrition for microorganisms during leaching period [6].

A promising pyrometallurgical method for processing complex mineral ores and concentrates is chlorination roasting [7-13]. The processing of antimony sulfide concentrates from the Anzob GOK-a by chlorination roasting is of great socio-economic importance for the Republic of Tajikistan as there is a huge local supply of sodium chloride. For the processing of antimony sulfide gold-containing concentrates from the Anzob Mining and Processing Plant in Tajikistan, this paper proposes a method that combines preliminary mechanical activation of the concentrate [14] and its subsequent chlorination roasting with sodium chloride [15,16].

Experimental Results

The efficiency of traditional methods of processing minerals can increase with mechanical activation of the material [17-23]. Mechanical processing of mineral ores leads not only to "a decrease in the size of particles, ... but to the breaking of chemical bonds that hold it, and juvenile, i.e., "fresh" surface, rich in active centers…." [23]. Previously [14], we provided information on the results of mechanical activation of high-grade antimony sulfide concentrates from the Anzob mining and processing plant. Based upon XRD analysis, the initial sulfide-antimony concentrate had the following phase composition (% wt.) : stibnite, Sb_2S_3, - 49.78%; cinnabar HgS - 30.74%; antimony oxide sulfate $Sb_6O_7(SO_4)_2$ – 19.47% (Figure 1). To compare results, the original concentrate, pre-crushed to a particle size of passing 0.74 μm, was divided into two parts - (a) not mechanically activated and (b) subjected to mechanical activation.
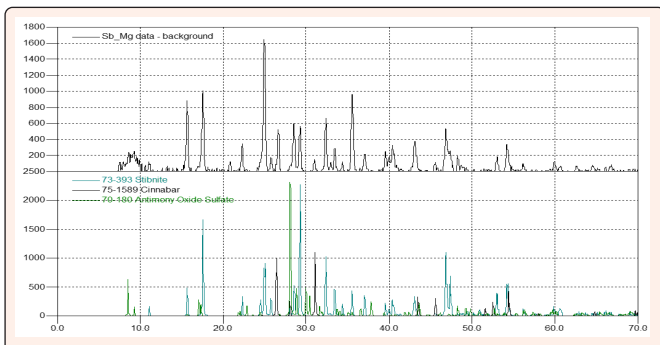
Figure 1: Concentrate X Ray diffraction analysis.

Mechanical activation of the concentrate (b) was carried out in a LAIR -015 activator mill. The influence of the following factors was studied; the degree of filling of the internal space (Z-volume) of the activator mill, the ratio of the mass of ball charge and concentrate (M_{Sh}:M_K), and the duration of mechanical treatment of the concentrate at room temperature. Hence, the following series of experiments were carried out:

a. determination of the optimal degree of volume fill (Z-volume) of the activator-mill with concentrate and balls;
b. different ratios of the mass of the concentrate (Mc) to the mass of the balls (Mm), designated M_c:M_m
c. different processing times for the process of mechanical activation of the concentrate (τa, min.);
d. use of the same ratio of M_c:M_{sh} and different processing times for the mechanical activation of the concentrate;
e. differing ratios of M_k:M_{sh} and the same processing time.

Upon completion of the mechanical activation process, the treated sulfide-antimony concentrate was sized on a sieve with an opening size of r=0.074 μm. The material passing through the sieve fraction of the concentrate was then dissolved in an aqueous solution of 25% NaOH for three hours at a temperature of T=90 ºC with the ratio of the mass of the concentrate (Mc) to the mass of the solution (M_r) equal to M_c:M_r=1:6. The content of antimony in the solution was then determined by the atomic absorption method. The optimal conditions for mechanical processing of the concentrate were determined, allowing achievement of a higher (almost twofold) degree of extraction (α(b)=22.5%) of antimony compared to the non-activated part (α(b)=13.1%) as shown in Figure 2.
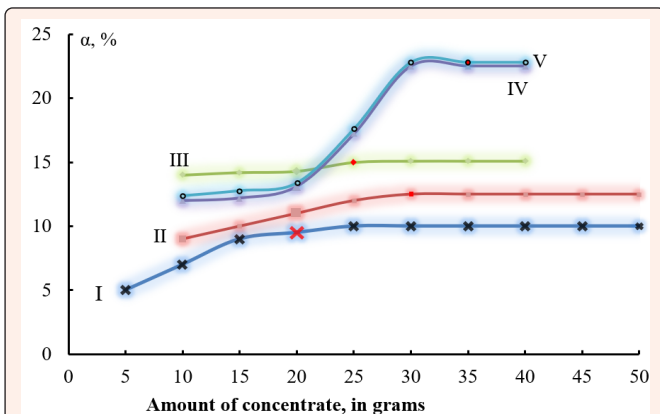

Figure 2: Dependence of the degree of extraction (α) of antimony on the amount of concentrate (M_c) at the time (τa, min.) of mechanical activation: I-0.5; II-1.5; III-2.5; IV-3.5; V-4.5.

Subsequently, a chlorination process was carried out in a Nabertherm RT 50-250/11/B410 tube furnace operating at temperatures up to 1100 °C. Specifically, this was an oxidation-chlorination roasting of sulfide antimony concentrates. This differed from a simple chlorination firing in that it is designed to allow oxygen air to flow through the chamber.

Under the conditions tested above, the process of oxidizing-chlorinating roasting occurred at significantly lower temperatures with the complete removal of sulfur and conversion of half of the antimony into the chloride form. From this, antimony can be easily extracted, and the remaining half is transformed into the oxide form, which is advantageous. To determine the material balance for the oxidation-chlorination roasting of sulfide antimony concentrates, a test configuration shown in Figure 3 was utilized which made it possible to capture any gaseous antimony-containing substances during the roasting process. The experimental configuration consists of a tube furnace, a reactor placed in it, in which a boat is placed, a condenser and absorbers. During the oxidation-chlorination roasting, part of the antimony is partially chlorinated in the composition of chlorides and gaseous oxychlorides and is deposited in the condenser and absorbers. As a result, several antimony-containing products are formed: a cinder form evaporated oxychlorides and chlorides from the condenser, and solutions through which the evaporated gases were passed to absorb them.
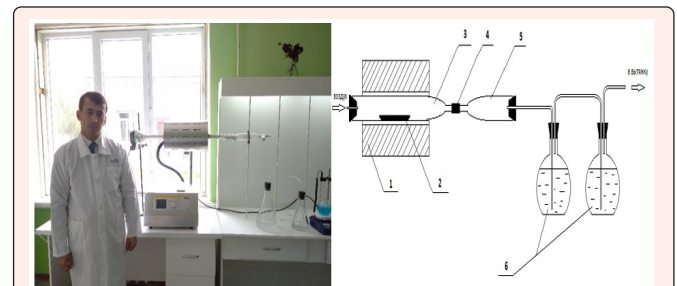

Figure 3: Installation for the oxidation-chlorination roasting of antimony concentrate: 1-turn tube furnace; 2-latochak with charge; 3-reactor for roasting; 4-connecting device; 5-dust chamber (condenser); 6 absorbers.

Further work on the resulting mixture was carried out under the following conditions:

i. at different temperatures of the sample in the range T=300 to 00 ºC (in increments of ΔT=50 ºC) and the ratio of mass of concentrate (m_1, g) and sodium chloride (m_2, g) equal to m_1/m_2=4/1 and the same time (τ=120 min.) exposure;
ii. at the same temperature (T=450 ºC) and a constant ratio of the mixture components (m_1/m_2=4/1), but with different exposure time of the sample firing (τ, in minutes) from 30 to 210 min., with a step of $\Delta\tau$=30 min .;
iii. at different ratios of the mixture components (m_1/m_2) and constant temperature (T=450 ºC) and exposure time (τ=120 min.).

In the experimentation, air was supplied to the system at a constant rate of 1 liter/hr. The evolution of antimony compounds formed consisted of antimony tri chlorides, $SbCl_3$, antimony oxides, Sb_2O_4 and $NaSb_5O_{13}$, antimony oxychlorides , Sb_3O_4Cl, and relic Na_2SO_4, which were deposited on the condenser tube. The condensate, which forms in the form of golden crystals, acquires a dark green color when cooled. Gaseous products of roasting (SO_2 and others) were captured in absorbers. The phase composition of the condensed product of the chlorinating roasting of the concentrate was established by X-ray Diffraction phase analysis and consisted of $SbCl_3$ at 49.55 wt.% and Sb_2O_4 at 25 wt.%, which are easily processed and technologically advantageous. The optimal mode of concentrate firing was determined to be T=450 ºC, t=120 min. and 25% NaCl in the mixture, which allowed the maximum transition from the sulfide - antimony to the chloride - antimony form.

Figure 4 shows an X Ray Diffraction analysis of the degree of formation of antimony chloride (α, %) based on a constant temperature and initial composition of the charge (m_1/m_2= 1/4) studied in the temperature range (100-450) ºC. Moreover, Figure 5 clearly shows that the process of extracting antimony from a mechanically activated concentrate consists of three distinct periods; - initial (I), main (II) and final (III). The initial period with up to 90 minutes of exposure time is accompanied by a slight increase in the extraction of antimony chloride within Δα=10%. The main period is accompanied by a significant yield of the product (Δα=30%) is achieved within 90-120 minutes. The proposed schematic flow diagram for the process of chlorination roasting of antimony sulfides is shown in Figure 6.
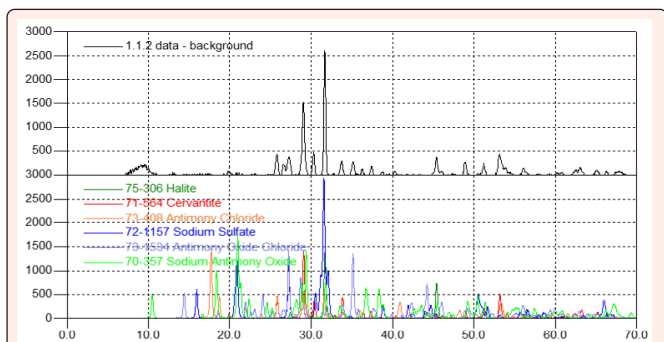
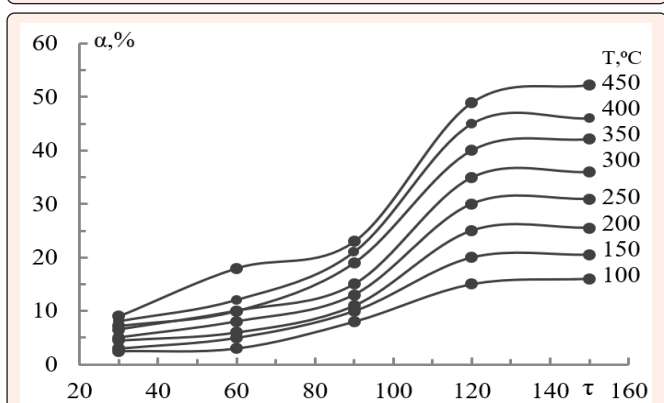**Figure 4:** X Ray diffraction analysis of a calcined antimony sulfide concentrate with sodium chloride addition.

Figure 5: Graph of the dependence of $SbCl_3$ formation on the time (τ) of holding the concentrate roasting at a constant temperature and composition of the charge.
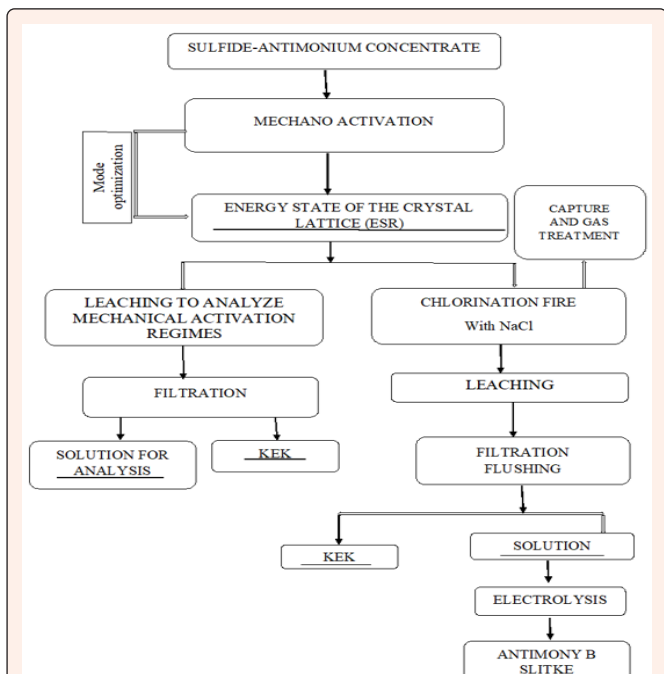

Figure 6: Schematic diagram of the oxidation-chlorination roasting of a pre-mechanically activated sulfide-antimony concentrate.

Overall, the process of oxidation-chlorination roasting of Sb_2S_3 in the mechanically activated sulfide-antimony concentrate in the presence of atmospheric oxygen can be simply expressed by equation 1.

$$Sb_2S_3 + 6NaCl + 6O_2 = 2SbCl_3 + 3Na_2SO_4 \quad (1)$$
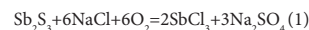
Conclusion

The optimal conditions for the combined method of mechanical activation and chlorination roasting of antimony sulfide from the Anzob Mining and Processing Plant with sodium chloride have been determined. The results obtained allowed the following important advantages with the developed process;

    a.   the use of locally available NaCl in the process of processing antimony sulfide concentrates;

    b.   the use of a lower temperature pyrometallurgical process with a high extraction of the antimony in the form of compounds that are easily processed during electrolysis;

    c.   minimization of environmental damage.

References

1. Anderson CG (2012) The metallurgy of antimony. Geochemistry 72(4): 3-8.

2. Anderson CG (2019) Antimony production and commodities. Chapter 9.22.2 SME Mineral Processing and Extractive Metallurgy Handbook, pp. 431-442.

3. Solozhenkin PM (2009) On the problem of physical and chemical geotechnology for the processing of antimony-containing materials in Tajikistan. Mining Journal 12: 144-147.

4. Solozhenkin PM (2011) Problems of heap leaching of complex gold-antimony and mercury-antimony ores. Non-Ferrous Metallurgy pp. 473-484.

5. Domracheva VA (2006) Extraction of metals from sewage and technogenic formations. Irkutsk: ISTU. p. 152.

6. Myazin VP, Baranov VV (2015) Bacterial leaching of refractory gold-bearing concentrate with evaluation of test sorption cyanidation of bio oxidation residues. Bulletin of ZabGU 1(116): 37-43.

7. Sik KS (1975) Leaching of antimony with ferric chloride. Daehan Gwangsan Hakoe Chi 12(4): 35-39.

8. Aleksandrov PV, Medvedev AS, Kadirov AA, Imideev VA (2014) Processing of molybdenite concentrates using low-temperature oxidation-chlorination roasting. Proceedings of Universities. Non-Ferrous Metallurgy 1: 12-16.

9. Aleksandrov PV, Medvedev AS, Kadirov AA (2012) Interaction of molybdenite with sodium chloride during heating. NUST MISIS, Non-Ferrous Metals 12: 73-77.

10. Medvedev AS, So T, Khamkhash A, Ptitsyn AM (2010) A variant of processing sulfide copper concentrate by a combined method. NUST MISIS, Non-Ferrous Metals 1: 33-36.

11. Medvedev AS, So T, Ptitsyn AM (2012) Combined processing of sulfide copper concentrate from the Udokan deposit. Izv Universities. Non-ferrous metallurgy 2: 17-20.

12. Chakravortty M, Srikanth S (2000) Kinetics of salt roasting of chalcopyrite using KC1. Thermochimica Acta 362(1/2): 25-35.

13. Chakravortty M, Srikanth S (2001) Non-isothermal thermoanalytical studies on the salt roasting of chalcopyrite using KC1. Ibid 370(1/2): 141-148.

14. Kodirov AA, Rakhimov KS, Badalov AB (2021) Mechanical activation of sulfide-antimony concentrates. Report NAST 64(7-8): 460-465.

15. Rakhimov KS, Kodirov AA, Badalov AB (2021) Chlorine roasting of mechanically activated antimony sulfide concentrates with sodium chloride. Report NAST 64(9-10): 583-587.

16. Rakhimov KS, Kodirov AA, Eshov BB, Badalov AB (2022) Rational method of processing sulfide-antimony concentrates. Mater 2nd Intl Scientific Conf, Innovative Development of Science, NAST (National Academy of Sciences of Tajikistan), Innovation Center, Technologies, Dushanbe, Tajikistan, pp. 46-49.

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17. Balaž P (2000) Extraction of antimony and arsenic from mechanically activated sulphide concentrates. Acta Montanistica Slovaca 5(3): 265-268.

18. Bogatyreva EV (2015) Development of the theory and practice of effective application of mechanical activation in the technology of hydrometallurgical opening of oxygen-containing rare-metal raw materials: p. 331.

19. Avvakumov EG (1986) Mechanical methods of activation of chemical processes. Novosibirsk: Nauka, p. 304.

20. Avakumov EG, Gusev AA (2009) Mechanical methods of activation in the processing of natural and technogenic raw materials. Novosibirsk: Academic Publishing House "Geo", p. 155.

21. Balaz P, Kamel R (1998) Mechanochemical leaching of refractory complex sulfide ores: from laboratory tests to pilot plant experiments. Chemistry for Sustainable Development 6: 259-261.

22. Bogomolov AM, Zakharchevny DI, Kalkov AA (1987) Chemical activity and structural features of molybdenum-containing products after mechanical and radiation exposure. Integrated Use of Mineral Raw Materials 9: 23-26.

23. Maltseva NN, Golovanova AI, Kedrova NS, Minaeva NA (1991) In: Mechanochemical synthesis in inorganic chemistry. Nauka M, Sibir Otd pp. 139-147.