

Hydrometallurgical Processes of Antimony Extraction from Ores and Concentrates

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Abstract—Data concerning the preparation of antimony and complex ores by pyrometallurgical and hydrometallurgical methods, as well as results on developing a procedure for the hydrometallurgical processing of slime antimony concentrates using chloride dealcalization, have been presented.

Keywords: antimony, antimony ores, preparation, processing of the antimony ore

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INTRODUCTION

The article considers the methods of enriching and processing different types of antimony ores, as well as results of analysis made by the Institute of General and Inorganic Chemistry Russian Academy of Sciences concerning the development of a procedure for the hydrometallurgical processing of flotation antimonite concentrates using chloride leaching.

EXPERIMENTAL

Processing Antimony Ore [1–5, 8–10]

The gravity and flotation treatment process is a basic process for all industrial antimony ores. Combined schemes with gravity and flotation treatment and the subsequent extraction of the related compounds from the concentrates (Hg, Au, Ag, Pb, etc.) are used during the processing of the complex ores (fluorite–cinnabar–antimonite, gold–antimonite and berthierite–galena–antimonite) and oxidized ores (senarmontite–nadorite). Sulfide ores are usually processed by the flotation method and arsenic–antimony ores are processed based on the bulk-differential flotation. All sulfides are extracted into concentrate.

The concentrate is selected via the depression of pyrite (FeS_2) and arsenic pyrite (FeAsS) by cyanide and $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$. The selective flotation of sulfide ores containing Sb, As and Hg minerals is carried out using the sulfhydryl collectors. During flotation of the polymetallic ores over cyanide the FeAsS stays a tail along with the FeS_2 . Difference in speed and oxidation products of the minerals surface is used for their separation.

The O_2 air (aeration), permanganate, chromate, lime chloride and other oxidizing reagents are used as the oxidizing agent.

Boulangerite ($\text{Pb}_5\text{Sb}_4\text{S}_{11}$) and other compound minerals Sb-chalcostibite (CuSbS_2), tetrahedrite ($\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$), berthierite (FeSb_2S_4) float with xanthogenate and terpineol at pH8 without preliminary activation. Sb_2S_3 float with xanthogenates after the activation of $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$, Pb salts ($\text{Pb}(\text{CH}_3\text{COO})_2$, or $\text{Pb}(\text{NO}_3)_2$).

The application of antimony ores of the combination of xanthogenates, e.g., amyl with ethyl, during Sb_2S_3 flotation in sulfurous medium improves processing. In addition to xanthogenates, dithiophosphate, and wood-tar oil are also used as reagent collectors, which allows Sb processing to be improved by up to 95%. Sometimes it is expedient to apply a combination of collectors, as well as activators of Sb minerals. The use of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and amyl xanthogenate, flotation, pine oil, and NaCN during the antimony flotation cycle allowed 91–95% extraction to be achieved in the concentrate.

Xanthogenate mixtures with hydrocarbon oils, cation reagents, e.g., ANP-14, in the weak acid medium (pH 5–6), mixtures of the saponified sylvic oil with OP-7 and OP-10, and still residues of higher fatty acid are used for the reextraction of oxidated minerals (valentinite (Sb_2O_3), cervantite (Sb_2O_4), stibiconite ($\text{SbSb}_2\text{O}_6\text{OH}$)), etc., as well as minerals oxidated from the surface of the sulfide.

As a rule, since gravitational and flotation methods do not solve the problem of extracting Sb-oxidized minerals from ores, the segregated roasting of the oxidized antimony ore with CaCl_2 (5%) and coal (2%) at

950°C for 1 h is of some interest in their processing, which makes it possible to obtain 10–12% antimony concentrates during the extraction of Sb, and 90% within the next flotation using xanthogenate. This is 20% higher than with the application of flotation methods alone.

Gold antimony ores contain 1.5–2.0 g/t Au and 1–10% Sb (mainly Sb_2S_3); associates are FeAsS and FeS_2 . Schemes of the direct selective flotation and schemes with preliminary bulk flotation of antimony- and gold-bearing minerals, which obtained wide circulation, are used depending on the ratio of the forms of Sb minerals, the composition of the Fe sulfide in the ore, the forms of the Au location, and other factors.

Bulk flotation is carried out in neutral and soda medium (pH 7–8) using xanthogenates as the collector and their mixtures, as well as a combination of the xanthogenates with hydrocarbon oils and sylvic oil. $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ or lead salts are used as the Sb_2S_3 activator. Scheelite concentrate is obtained from the tails of sulfide flotation using Aerosoup reagent and liquid glass, which imparts makes the use of raw materials more complex.

The depression of Sb_2S_3 flotation during the separation of bulk concentrates is obtained by adding alkali and Na_2S at pH > 9 or by bichromate in sulfurous media. The flotation of gold-bearing iron sulfide (FeS_2 and FeAsS) may be activated by small additives of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, which have an additional depressing influence on Sb_2S_3 in the alkali medium.

The selection of bulk concentrate obtained during the flotation of antimony and gold-arsenic ores is carried out by the depression of either Sb_2S_3 or gold-bearing Fe sulfide. If Sb_2S_3 is flotated during the separation of the bulk concentrate, then NaCN and $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ are used for the depression of gold-bearing iron sulfide and salts of Pb, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, OP-7, Op-10, etc. are used to activate the Sb minerals. The method that involves drying, processing by an oxidizer, and the flotation of Sb minerals and obtaining antimony gold-bearing concentrate and pyrite product has been proposed to separate bulk antimony pyrite concentrate.

If ore contains big inclusions of gold or Sb_2S_3 lumps then sorting allows one to obtain concentrate with an Sb content of up to 50% at the preconcentration stage. Schemes that contain gravitational processes (separation in gravity solution, jigging etc.) flotation and cyanation of the floating tails that allow one to extract both Sb and Au may be more effective.

After the preliminary activation of $\text{Sb}_2\text{S}_3\text{Pb}(\text{NO}_3)_2$ or $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, xanthogenates are used during the flotation of mercury–antimony ores. NaCN additives considerably improve the Sb extraction into concentrate at $\text{Sb}_2\text{S}_3\text{Pb} \text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ activation. The use of Sp–Hg OP-10 ore instead of pine oil during flotation

allows one to improve the extraction of Sb and decrease the consumption of float reagent. During the flotation of the fluorite-bearing Hg–Sb ores, it is necessary to take into account that $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ activates CaF_2 and contributes to its transition into Hg–Sb concentrate. In these cases, $\text{Pb}(\text{NO}_3)_2$ is used as an activator of antimony minerals, which also provides higher CsFe₂ extraction into the Hg–Sb flotation tails. Furthermore, $\text{Pb}(\text{NO}_3)_2$ activates cinnabar (HgS), which improves the extraction of Hg into the bulk concentrate. During the flotation of Hg–Sb fluorite ores, it is necessary to avoid the excess consumption of liquid glass used for the CaF_2 depression, since the latter decreases the flotation ability of Sb_2S_3 and Hg. During the common application of liquid glass and $\text{Pb}(\text{NO}_3)_2$, a significant role is assigned to the charge sequence. If the liquid glass is charged first and only when $\text{Pb}(\text{NO}_3)_2$, xanthogenate is fixed more firmly on the surface of the HgS and Sb_2S_3 and in a larger amount. The maximum extraction of the floating minerals in the Hg–Sb flotation cycle with butyl xanthogenate is achieved at pH 7.8–8.0 and at a consumption of 200 g/t of liquid glass.

The separation of antimony–mercury concentrates is based on considerably higher oxidation by dichromate Sb_2S_3 compared to HgS. The depression of Sb_2S_3 by chrome salts is carried out over H_2SO_4 . Furthermore, chromate is delivered to the grinding cycle and H_2SO_4 is delivered to the conditioning tank before flotation as depression and HgS are observed during the joint delivery of both reagents. In order to avoid this, it is also recommended to use potassium dichromate mixed with hydrochloric acid (about 0.025 kg/t), which results in the formation of hydrophilic oxidized Sb compounds on the Sb_2S_3 surface. In combination with the potassium dichromate, H_2O_2 is an active oxidizer that does not influence the Hg flotation and provides effective Sb_2S_3 depression. Na_2S or lime, sometimes disodic phosphate or paraaminophenol, are also used to reinforce the Sb_2S_3 depression.

HgS is separated from Sb_2S_3 , FeAsS, and FeS_2 upon the joint availability of antimony, mercury, and arsenic minerals in ore (or bulk concentrate) originally in alkaline medium (lime or lime with Na_2S). After that, Sb_2S_3 is flotated over $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$. Liquid glass and NaCN are used for the FeAsS and FeS_2 depression. It was found that the Sb_2S_3 depression was only observed at an NaCN concentration >80 mg/L. In contrast, small additives of NaCN (30 mg/L) over $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ increase the activation of Sb_2S_3 . FeAsS is flotated at the end, after the activation of Na_2S .

Antimony Technology [2–4, 6–10]

Valuable (no less than 20–30% Sb), as-mined, and base (0.8 to 3–5% Sb, which are preliminary concentrated up to 35–50%) monometallic ores hold great

production interest for Sb extraction. As for complex ores, it is only economically attractive to develop them for Sb in rare cases, while for polymetallic ores, it is only effective to mine Sb simultaneously.

Pyrometallurgical processes are mainly used to get Sb-precipitation smelting with iron $\text{Sb}_2\text{S}_3 + 3\text{Fe} = 2\text{Sb} + \text{FeS}$ or oxidizing roasting with distillation Sb_2S_3 , which is further subjected to reduction smelting. In both cases, Na_2CO_3 , Na_2SO_4 , or NaCl are used as fluxes.

The following is also known: roast-reaction smelting $\text{Sb}_2\text{S}_3 + 2\text{Sb}_2\text{S}_3 = 6\text{Sb} + 3\text{SO}_2$, soda $2\text{Sb}_2\text{S}_3 + 6\text{Na}_2\text{CO}_3 = 3\text{C} = 4\text{Sb} + 6\text{Na}_2\text{S} + 9\text{CO}_2$, and also alkali.

The hydrometallurgical method of Sb preparation is based on the dealkalization of the antimony concentrates by $\text{Na}_2\text{S} + \text{NaOH}$ solution with subsequent electrolysis.

Bulk concentrate with the extraction of separate components in the process of metallurgical treatment, including Sb, is prepared from complex pure mineral ores presented, e.g., by livingstonite (HgSb_4S_8), jamesonite ($\text{Pb}_4\text{FeSb}_6\text{S}_{14}$), $\text{Pb}_5\text{Sb}_4\text{S}_{11}$, etc.

In complex polymineral fields, Sb forms independent forms of the mineral (mainly Sb_2S_3) or fahlores (minerals of isomorphous series tennantite $\text{Cu}_{12}\text{As}_4\text{S}_{13}$ – $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$) in association with the scheelite CaWO_4 ; wolframites (minerals of isomorphous series hubnerite–ferberite MnWO_4 – FeWO_4); HgS ; CaF_2 coarsely disseminated in quartz Au; etc. Mercury, fluorite, polymetallic, wolfram–scheelite, etc. or complex antimony-bearing (fahlore, polysulfide, gold–antimony, etc.) concentrate is obtained from ores of these fields, except antimony concentrate). Associated components are prepared from these concentrates by pyro and hydrometallurgical methods. Antimonite concentrate is processed based on the metallurgical scheme. For mercury–antimony ores, this is Hg extraction by the pyrometallurgical method with the subsequent Sb preparation by the pyro- and hydrometallurgical methods.

The processing scheme for gold–antimony ores is determined by the character of the Au bond with ore- and rock-forming minerals. If Au is directly connected with the Sb minerals the gold–antimony concentrate will be obtained. Without a clear bond, the ore is processed by the combined schemes with the Sb extraction and the part of the Au from tails by the methods of the gold-mining industry.

Different antimony compounds are obtained from lead, zinc, and copper concentrates by pyro and hydrometallurgical processes, including sintering; melting; fire or electrolytic refining; slag, matte, and fine treatments, etc.

The biochemical dealkalization is considered to be an advanced technique of the complex oxidized antimony ores, this is the method of the Sb, Au, Ag, Pb,

Zn, and Cu extraction based on the application of the ore matter as the nutrient source for microorganisms that develop in ore during dealkalization.

The rough Sb is subjected to fire refining, which provides the removal of Fe and Cu by the action of Sb_2S_3 or S; alkali cleaning from As and S; cleaning from Na by the action of SiO_2 and teeming under borax melt sheet or NaSbO_2 (asterial slag). Electrolytic refining using sulfide–fluoride potassium-alkaline solutions has been carried out to remove Au, Ag, and Pb, while high-purity Sb is obtained by SbCl_3 or SbH_3 carrier compounds cleaned by rectification. Electrolytic refining using glycerin–alkaline or xylite–alkaline electrolyte is also used. The final Sb cleaning is carried out by the crystal methods, in particular zone melting.

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Sb_2S_3 , Sb_2S_5 , and antimony halides, as well as sulfide antimony concentrate for the match industry and Schlippe's salt (sodium thioantimonate $\text{Na}_3[\text{SbS}_4]_9\text{H}_2\text{O}$), are the marketable products of the antimony industry, except for metallic Sb and Sb_2O_3 .

The specificity of the technogenic impact factors of the treatment of antimony ores is determined by flotation as the leading treatment method, as well as by the high toxic level of oxidation products of antimony-bearing ores; As, Hg, Pb, and Se as additives; etc. Sewage waters from Au dealkalization units are a significant ecological hazard, which requires a closed process with the maximum use of recycling water and subsequent waste burial.

Hydrometallurgical Treatment of the Flotation Antimony Concentrates

Dealkalization processes of antimony concentrates by muriatic and chloride solutions have not become widely used in industry. It appears that it is connected with the highly aggressive level of muriatic solutions and their ability to form antimony and arsenic hydrides during the dealkalization of ores that contain elementary As and Sb. These processes have a number of advantages, including a high level of decontamination, high velocity, and capacity for the direct extraction of Sb in the form of marketable products.

Physical and chemical modeling and experimental investigation of the processes of the selective dissolution and metallic sulfide precipitation (included in the antimony concentrates) in complex chloride solutions with due account for the impact of $p_{\text{H}_2\text{S}}$ was carried out at the Institute of General and Inorganic Chemistry, Russian Academy of Sciences in order to develop a hydrometallurgical treatment method for flotation

Table 1. Solubility of metal sulfides of antimony concentrates

| Sulfide | FeS | ZnS | SnS | PbS | SnS ₂ | Bi ₂ S ₃ | Sb ₂ S ₃ | As ₂ S ₃ |
|--------------------------|-------|------|-----|------|------------------|--------------------------------|--------------------------------|--------------------------------|
| C _{HCl} , mol/L | 0.001 | 0.01 | 0.1 | >1.0 | >2.0 | 3.0 | 4.0 | >12.0 |

antimony concentrates. Results of investigations are given in the Tables 1 and 2 and Fig. 1.

It has been found that the solubility of metallic sulfide decreases in the series FeS–ZnS–SnS–PbS–SnS₂–Bi₂S₃–Sb₂S₃–As₂S₃. The As₂S₃ solubility does not exceed 10⁻⁵ mol/L in solutions with almost any concentration of acid and chloride ions.

The fullest release of the Fe, Zn, Cu, Pb, and Bi sulfides from Sb and As sulfides are obtained in solutions with acid concentrations >5.5–5.7 mol/L. In these solutions, the Sb₂S₃ and As₂S₃ precipitate out and FeS, ZnS, SnS, PbS, SnS₂, and Bi₂S₃ pass into the solution. The separation of Sb and As sulfides takes place in solutions with an acid concentration >7.7–7.8 mol/L (Sb₂S₃ passes into the solution completely and As₂S₃ precipitates out (Fig. 1).

The solubility of Sb₂S₃ rises steeply in solutions with HCL concentrations higher than 7.2 mol/L at 25°C and *p*_{H₂S} = 2 atm. The decrease in *p*_{H₂S} enables the twofold decrease in the acid concentration required to solubilize Sb₂S₃ (Fig. 1).

The increase in the chloride-ion concentration in muriatic solutions with the addition of CaCl₂ significantly increases the selectivity of sulfide dissolution in an number of metals, which enables a decrease in the HCL concentration.

Equations (1)–(3) were obtained as a result of that analysis, which enables the contents of Sn, Bi and Sb to be calculated in solutions with different concentrations of HCL and CaCl₂ as follows:

$$C_{Sb} = -21.50 - 36.75C_{HCl} - 64.05C_{CaCl_2} + 2.51C_{HCl} + 14.33C_{HCl} \cdot C_{CaCl_2} + 0.036C_{HCl} \times t + 8.32C_{CaCl_2}^2 + 0.007C_{CaCl_2}t - 0.059t^2; \quad (1)$$

$$C_{Bi} = -56.96 + 1.66C_{HCl} + 9.78C_{HCl} \cdot C_{CaCl_2} + 0.38C_{HCl}t + 8.79C_{CaCl_2}^2 + 0.44C_{CaCl_2} - 0.01t^2; \quad (2)$$

$$C_{Sn} = [4.33 - 6.33C_{HCl} - 0.85C_{CaCl_2} + 1.78C_{HCl} \cdot C_{CaCl_2} + 1.45C_{HCl}](1/M_{Sn}), \quad (3)$$

Table 2. Solubility of Sb₂S₃ in muriatic solutions at 25°C and *p*_{H₂S} = 1 atm

| HCl _{equal} , mol/L | 4.93 | 6.74 | 6.92 | 7.25 | 7.36 | 7.40 |
|------------------------------|------|------|------|------|------|-------|
| Sb × 10 ² , mol/L | 0.0 | 0.09 | 2.09 | 6.11 | 7.28 | 11.61 |

where C_{HCl}, C_{CaCl₂} are the concentrations of HCL and CaCl₂ in the base solution, mol/L; *t* is the temperature of the solution, °C; *M*_{Sn} is the stannous molar weight; and C_{Sb}, C_{Bi}, and C_{Sn} are the concentrations of antimony, bismuth, and stannum in the dealcalization solutions, mol/L.

Equation (1) is true in the concentration ranges of 1.5–6.2 mol/L hydrochloric acid and 1.15–3.15 mol/L calcium chloride, at a solid-to-liquid ratio of 1 : 26, and dealcalization periods of 24 and 2 h at 25 and 75°C, correspondingly. Equation (2) is true at concentrations of 0.6–6.2 mol/L HCL and 0–3.15 mol/L CaCl₂ at 25–75°C for dealcalization period of 3 h. Equation (3) was obtained for concentrations of 1–4 mol/L HCL and 1.35–3.15 mol/L CaCl₂ at 25°C for 3 h.

It was found that the addition of CaCl₂ into the muriatic solutions enables the concentration of hydrochloric acid required for the Sb selective dealcalization to be decreased by a factor of five to seven. The selective dissolution of Pb, Sn, and Bi sulfides takes place at an acid concentration of 1.7–2.0 mol/L and CaCl₂ concentration of 2.2–2.7 mol/L, whereas Sb₂S₃ and As₂S₃ are nearly insoluble. A solution with concentrations of 3.5–4.0 mol/L HCL and CaCl₂ concentration of 2.2–2.7 mol/L is required to separate Sb₂S₃ from As₂S₃.

Data that characterize the dissolution of Bi₂S₃, Sb₂S₃, SnS₂, and As₂S₃ in the CaCl₂ in muriatic solutions are given in Table 3.

For the purpose of releasing of Sb³⁺ from chloride solutions, the process of its precipitation by the calcium hydroxide was studied. The formation of solid phases of different compositions is possible within the precipitation process depending on conditions. The following is formed under unbalanced conditions: SbOCl, Sb₄O₅Cl₂, SbO(OH), SbO(OH)₃, Sb₂O₃, Ca(SbO₂)₂, and Ca[Sb(OH)₄]₂. At low pH values, Sb³⁺ hydrolyzes in chloride solutions and Ca(OH)₂ : SbCl₃ in a 0.5 : 1 ratio, which leads to the formation of barely soluble oxychlorides. Without CaCl₂, fine-crystalline oxychlorides residuals are formed in solutions with a concentration of the muriatic acid in the range of 0.7–0.9 mol/L. With a decrease in the acid concentration in the mother solution, the possibility of the formation of amorphous precipitations increases. In the process of washing residues with hot water at 65–70°C, the oxychlorides degrade and form β-Sb₂O₃. With an increase in the Ca(OH)₂ : SbCl₂ ratio from 0.5 to 4.5, the Cl₂ content in residues formed in the process of hydrolytic precipitations of

Sb^{3+} decrease from 20 to 1%. The increase in the Sb concentration in the base solution shifts the pH of oxychloride, oxide, and hydroxide precipitations towards a more acid medium.

The almost complete precipitation of Sb^{3+} by calcium hydroxide in concentrated chloride solutions takes place at pH 7. It is recommended that the extraction of Sb from the process solutions be conducted at 75–100°C, a ratio of $\text{Ca}(\text{OH})_2 : \text{SbCl}_3 = 1.5\text{--}1.75$, and a concentration of Sb in the base solutions of no more than 0.2–0.3 mol/L. The almost complete precipitation of Sb is obtained at pH 7.

The obtained results were used to develop the chloride method for extracting antimony from sulfide concentrates received in the process of flotation by antimony–arsenic ores.

The average elemental and rational composition of the antimony concentrates is as follows: 48.8 wt % Sb(Sb_2S_3), 0.54 wt % Sn(SnO_2), 0.07 wt % Fe(FeAsS , 3.18 wt % FeS_2 , 0.07 wt % CuFeS_2 , 9.22 wt % Fe_2O_3), 0.1 wt % Zn(ZnS), 0.02 wt % Cu(CuFeS_2), 0.1 wt % Pb(PbS), 0.76 wt % Bi(Bi_2S_3), 0.1 wt % As(FeAsS , 0.57 wt % As_2S_3), 19.24 wt % S(Sb_2S_3), 0.04 wt % FeAsS , 0.36 wt % As_2S_3 , 3.64 wt % FeS_2 , 0.08 wt % CuFeS_2 , 0.05 wt % ZnS, 0.02 wt % PbS, 0.17 wt % Bi_2S_3 , 0.54 wt % $\text{O}_2(\text{SnO}_2)$, 0.26 wt % Fe_2O_3 , 1.4 wt % Al_2O_3 , 0.67 wt % CaO, and 8.0 wt % SiO.

The dealcalization of the concentrates is carried out in two stages. First, using muriatic solution with an HCl concentration of 50–70 g/L, it is converted into Zn, Fe, Pb, and Bi solutions and partially into Sn solution; then, with using a solution with a concentration of 120–140 g/L HCl, it is converted into Sb solution

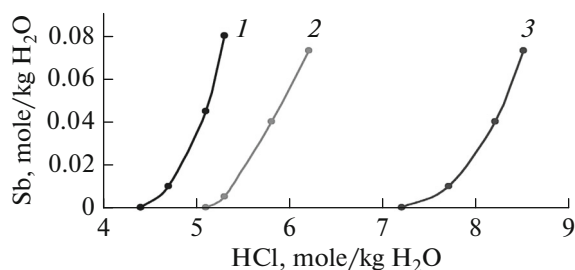


Fig. 1. Solubility of Sb_2S_3 in muriatic solutions at different values of $P_{\text{H}_2\text{S}}$, atm: 1. 0.01; 2. 0.1; 3. 1.0.

(Fig. 2). In these processes, the ratio of the solid to the liquid phase is within 1 : 4 (6).

At the first stage of dealcalization, Sb and As precipitate almost completely and Zn, Fe, Pb, Bi, and other metals pass in solution at 250–350 g/L of CaCl_2 and HCl concentrations in the base solution. At smaller concentrations of CaCl_2 and HCl, the extracting metals may partially stay in the antimony–arsenic agglomerated cake. Higher concentrations lead to the dissolution of Sb_2S_3 . The agglomeration cake is washed by an HCl solution of the same concentration and rinse waters are added to the main solution of the metal chlorides from which a sulfide solution mixture not containing As and Sb is precipitated.

At the second stage, the agglomerated cake of As and Sb sulfides is dealcalized by recycled muriatic solution with an HCl concentration of 120–140 g/L and CaCl_2 concentration of 250–350 g/L during heating and converted into Sb. The decrease in CaCl_2

Table 3. Dissolution of Sb, Sn, and As sulfide blends in CaCl_2 muriatic solutions

| In solution, g/L | | | | In residual matter, % from the base | | |
|------------------|-----------------|------|------|-------------------------------------|-------|-------|
| HCl | CaCl_2 | Sn | Sb | Sn | Sb | As |
| 43.0 | 350.0 | 4.11 | 0.0 | 10.3 | 100.0 | 100.0 |
| 56.0 | 250.0 | 2.51 | 0.0 | 45.3 | 100.0 | 100.0 |
| 56.0 | 350.0 | 4.58 | 0.0 | 0.0 | 100.0 | 100.0 |
| 70.0 | 250.0 | 4.33 | 0.0 | 5.4 | 100.0 | 100.0 |
| 70.0 | 350.0 | 4.58 | 0.06 | 0.0 | 99.0 | 100.0 |
| 100.0 | 250.0 | 4.58 | 0.12 | 0.0 | 98.0 | 100.0 |
| 90.0 | 350.0 | 4.58 | 3.23 | 0.0 | 30.1 | 100.0 |
| 140.0 | 250.0 | 4.58 | 4.71 | 0.0 | 0.0 | 100.0 |
| 140.0 | 0.0 | 0.35 | 0.0 | 92.3 | 100.0 | 100.0 |
| 180.0 | 0.0 | 4.58 | 0.0 | 0.0 | 100.0 | 100.0 |
| 220.0 | 0.0 | 4.58 | 0.38 | 0.0 | 92.0 | 100.0 |
| 245.0 | 0.0 | 4.58 | 1.30 | 0.0 | 72.5 | 100.0 |
| 270.0 | 0.0 | 4.58 | 4.51 | 0.0 | 4.2 | 100.0 |

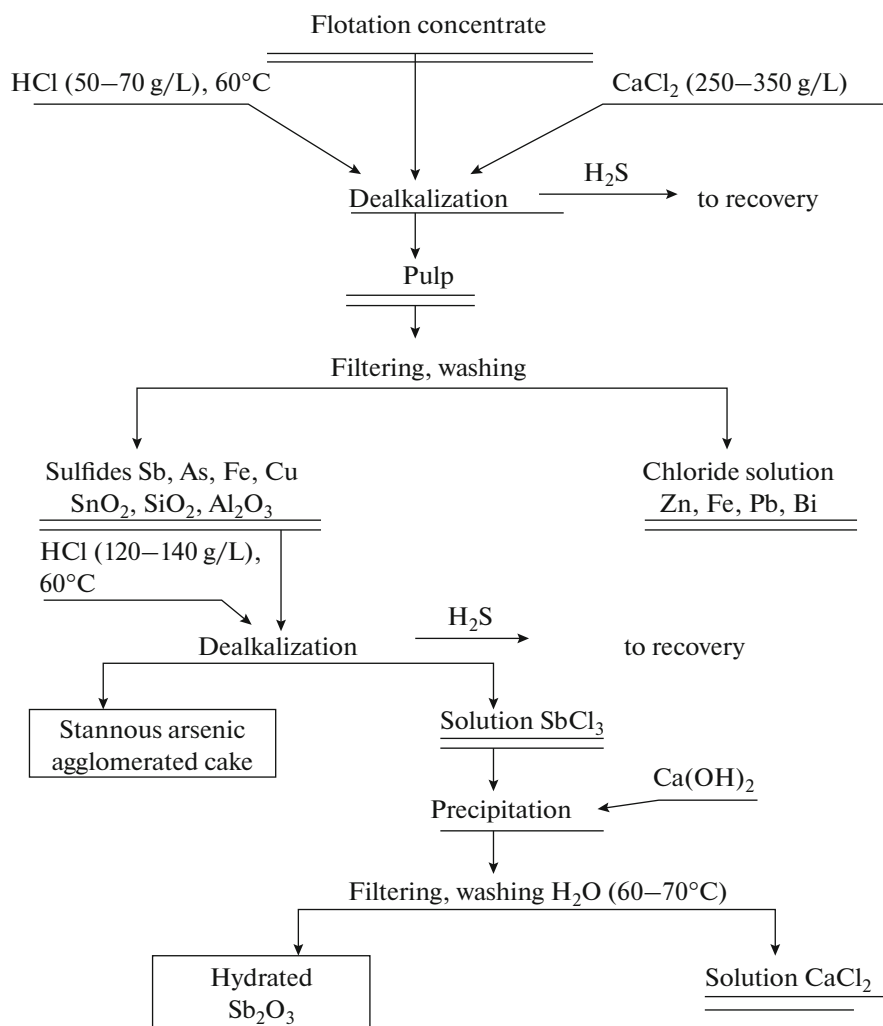


Fig. 2. Scheme of the process of treating antimony–arsenic raw material by CaCl₂ muriatic solutions.

and HCl concentrations may lead to Sb losses with arsenic agglomerated cake.

Agglomerated cake of arsenic sulfide after the second stage of dealkalization is washed by solution of same concentration. After this washing, the agglomerated cake may be processed with the resulting arsenic or its compounds. All solutions containing Sb are combined and oxide and hydroxide Sb compounds are precipitated by lime milk.

The best precipitation conditions for Sb³⁺ are provided by pH ≥ 3.0. The Sb extraction approaches 99% when the solution is neutralized by lime milk with a pH of 1.5–9.0. However, at low pH values and high CaCl₂ concentrations, the antimony is precipitated in the form of oxychlorides. In order to remove Cl₂, it is necessary to carry out multiple washes of the precipitations with water at 65–70°C, which results in the formation of β-Sb₂S₃ in residual matters. The percentage of Sb extraction is 92–95%.

Solutions with CaCl₂ concentrations of about 200 g/L are formed during the precipitation of Sb³⁺ oxides and hydroxides; they may be used to dealkalize the flotation concentrates.

CONCLUSIONS

The variety of methods and schemes of treatment processes for antimony ores is conditioned by their alternating compositions, large number of mineral forms, and the characteristic proximity of separated minerals.

Solving the problem of improving the modern metallurgical process for producing antimony from complex oxide–sulfide and tetrahedrite raw material, as well as its complex processing and the development of ecological technologies, is among the most important problems today for antimony production technology.

The dealcalization processes of the antimony concentrates by muriatic and chloride solutions are characterized by high velocity, capacity for direct Sb extraction in the form of marketable products and a closed cycle of reusable chloride solutions.

The proposed method for the hydrometallurgical treatment of sulfide concentrates of antimony–arsenic raw materials using muriatic solutions of CaCl_2 allows the acid concentration to be decreased by five to seven times, decreases the capacity to form Sb and As hydrides, and enables oxides and Sb sulfides to be prepared without harmful additives.

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