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METHODS FOR PROCESSING OF ANTIMONY-CONTAINING MATERIALS (REVIEW)

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ABSTRACT

The article presents the results of scientific developments in the field of pyro- and hydrometallurgical processing of antimony-containing mineral and technogenic raw materials. Important industrial antimony products are metallic antimony and antimony trioxide of various grades. Methods of reducing melting and sulfide-alkaline leaching of antimony sulfide concentrates to obtain metallic antimony and antimony trioxide are discussed, and methods of refining antimony from impurities are also analyzed.

Keywords: antimony, compounds, minerals, raw materials, alloys.

INTRODUCTION

Antimony is one of the most popular “small metals”, performs the function of a modifier that gives special properties to non-ferrous metal alloys, glasses, enamels, polymer materials, rubbers, paints, etc.

The role of oxide compounds is increasing in the overall balance of antimony consumption. The main sector of oxide compounds, the production of fire-resistant coatings and impregnations, the production of flame retardants, consumes about 90 % of the world production of antimony trioxide. Due to this, the demand for antimony trioxide is growing every year. In addition, the consumption of ultrapure antimony in new materials is increasing.

Currently, the world consumption of antimony is more than 120 thousand tons per year. Main consumers: USA 43 - 45 thousand tons/year, Japan 16 - 17 thousand tons/year, China 15 - 16 thousand tons/year, Western Europe - France, Great Britain, Germany for several thousand tons per year [1, 2].

The confirmed global antimony reserves are estimated by the USGS at 1.8 million tons. Almost half of the world’s antimony reserves are concentrated in China and the share of this country in the production of concentrates is over 90 %. That is why China is one of the leading antimony producers [3].

Antimony is mainly used in the form of Sb_2O_3 as a flame retardant in plastics, coatings and electronics due to its synergistic effect with halogenated flame retardants, which minimizes the amount of necessary halogenated flame retardant [4].

Reserves of antimony mineral raw materials are limited, as well as all ore sources of “small” metals. Today, secondary antimony production is mainly limited to the processing of antimony-containing lead alloys from lead-acid accumulator processing plants. Industrial interest is also represented by waste from the production of lead, gold, copper and antimony: enrichment tailings, man-made products, industrial scrap [5]. This article provides an overview of methods for processing antimony-containing mineral and technogenic raw materials, as well as methods for refining rough antimony, which is an important technological cycle for the production of commercial-grade antimony.

Methods of processing mineral raw materials

About 120 antimony minerals are known, and the most important of them are Sb_2S_3 (stibnite) (71.4 mass % Sb), native antimony, tetrahedrite $Cu_{12}Sb_4S_{13}$ (29.2 mass

% Sb), jamesonite $Pb_4FeSb_6S_{14}$ (about 30 mass % Sb), berthierite $FeSb_2S_4$ (mass % Sb), livingstonite $HgSb_4S_7$ (53.4 mass % Sb) and boulangerite $Pb_5Sb_4S_{11}$ (25.7 mass % Sb). Oxidized ores contain valentinite Sb_2O_3 (85.5 mass % Sb), senarmontite Sb_2O_3 (83.5 mass % Sb), cervantite Sb_2O_4 (79.2 mass % Sb), kermesite Sb_2S_{2O} (75 mass % Sb), etc. Along with their own ores, antimony-mercury, copper-antimony (tetrahedrite), gold-antimony and antimony–tungsten ores are used to produce antimony [6]. The industrially important source of ores for antimony production is mainly considered to be the mineral stibnite Sb_2S_3.

Antimony-containing ores extracted from the subsoil differ sharply in metal content, the antimony content in them can vary from 1 % to 60 %. In addition, mineral raw materials differ in the forms of antimony in them. These circumstances cause a wide variety of enrichment methods (manual sorting, gravity and flotation) and metallurgical processing (seigerization, distillation firing and firing “tightly”).

Ores containing up to 10 mass % antimony are sent to the processing of enrichment, since ores containing less than 10 mass % antimony are not rationally and economically profitable for metallurgical processing. Enrichment schemes make it possible to obtain concentrates with an antimony content of 10 % - 50 %.

The process of Seigern (seigerization) of antimony is one of the old methods and consists in heat treatment of ore to a temperature (600°C - 800°C) above the melting point of Sb_2S_3 stibnite, at which the molten crudum flows into the receiver. This process is applicable for ores containing 35 % - 40 % antimony and, if possible, free of arsenic, lead, copper and iron sulfides, as well as antimony oxides.

Distillation firing of antimony raw materials for the purpose of oxidation of antimonite/stibnite Sb_2S_3 to volatile antimony trioxide is used for raw materials containing 5 % - 25 % antimony. It is often used to remove antimony from ores and concentrates containing gold. The use of one or another method of processing antimony-containing ores and concentrates depends on the antimony content in them and its form of location (Table 1).

Antimony metallurgy is intended for the production of metallic antimony by pyrometallurgical and hydrometallurgical methods.

Table 1. The main methods of processing antimony raw materials [7].

Types of raw materials	Expedient processing methods	Basic chemical reactions
Poor oxidized and sulfide-oxidized raw materials; enrichment tailings; leaching keke; zeigerization residues	Distillation firing or sublime smelting	$(Sb_2O_3)s = (Sb_2O_3)_g$ $(Sb_2S_3)_s = (Sb_2S_3)_g$
Ordinary sulfide and sulfide-oxidized raw materials, oil contaminated with heavy metal impurities; mercury-antimony raw materials; arsenic-antimony raw materials	Oxidative firing	$2Sb_2S_3+9O_2 = 2Sb_2O_3+6SO_2$, $2Sb_2O_3+ O_2 = 2Sb_2O_4$
Ordinary and rich oxidized raw materials; burnt ores and concentrates; antimony dust and fumes; sodium antimonate	Restorative melting	Sb_2O_n+nC(CO) = 2Sb+nCO(CO_2)
Sulfide and sulfide-oxidized fusible raw materials	Sedimentary and sedimentary-restorative melting	$Sb_2S_3+3Fe = 2Sb+3FeS$, Sb_2O_n+nCO(CO)= 2Sb+nCO(CO_2),
Sulfide raw materials, refractory or heavily contaminated with heavy metal impurities; rich antimony matte; sodium antimonate	Sulfide-alkaline leaching	$Sb_2S_3+3Na_2S = 2Na_3SbS_3$, $Sb_2O_3+3Na_2S = Na_3SbS_3+ Na_3SbO_3$
Rich sulfide lumpy raw materials (ore)	Seigerization (melting of the crudum)	$(Sb_2S_3)_s = (Sb_2S_3)_l$

The production of metallic antimony from crudum and sulfide concentrates containing at least 30 % - 65 % antimony is carried out by precipitation melting at 1100°C - 1150°C by reaction:

$$Sb_2S_3 + 3\,Fe = 2Sb + 3FeS \qquad (1)$$

In the absence of iron scrap, sulfide ores and concentrates are converted into antimony oxide for subsequent melting with a carbon reducing agent. For this purpose, firing is used "tightly" at 400°C - 500°C to convert antimony sulfide into non-volatile tetraoxide Sb_2O_4. In these cases, the formation of antimony trioxide is unacceptable, since volatile trioxide leads to the loss of antimony from the concentrate. In these cases, the production of metallic antimony is realized through two stages. The above methods have been implemented on an industrial scale and have been providing the antimony products market for many years.

On a laboratory scale, a method has been developed for the direct production of metallic antimony from sulfide raw materials in one stage by microwave carbothermic reduction using ZnO as a sulfur fixing agent and carbon powder as a reducing agent. It is shown that the antimony reduction process proceeds according to the scheme: $Sb_2S_3 \rightarrow Sb_2O_3 \rightarrow Sb$, and sulfur was fixed in the form of ZnS. Under optimal firing conditions of 500°C and a duration of 90 minutes, the degree of extraction of antimony into metal was 90.1 mass % and sulfur into zinc sulfide was 95.3 mass % [8].

The production of metallic antimony from oxidized ores and antimony concentrates is realized by reducing melting in the presence of carbon:

$$Sb_2O_3 + 3C=2Sb +3CO \qquad (2)$$
$$2Sb_2O_3 + 3C=4Sb +3CO_2 \qquad (3)$$
$$Sb_2O_4 + 2C=2Sb +2CO_2 \qquad (4)$$
$$2Sb_2O_5 + 5C=4Sb +5CO_2 \qquad (5)$$

The recovery process is carried out at 800°C - 1000°C, low-melting salts are used as fluxes. In addition to antimony oxides, oxides of arsenic, lead and other metals are often present in the charge, which is also reduced to a metallic state and becomes part of the rough antimony. Next, the resulting rough antimony is refined from impurities and a vintage metal is obtained (Fig. 1). This technological scheme works at the enterprises of leading antimony manufacturers. Nevertheless, work continues on the study of the process of oxidative roasting of sulfide ores and reducing melting of oxidized ores and concentrates in order to improve the technical and economic indicators of the process.

Antimony concentrates, complex concentrates (copper-lead-antimony, silver-antimony), industrial products of pyrometallurgical processes, as well as antimony-containing waste and industrial products of

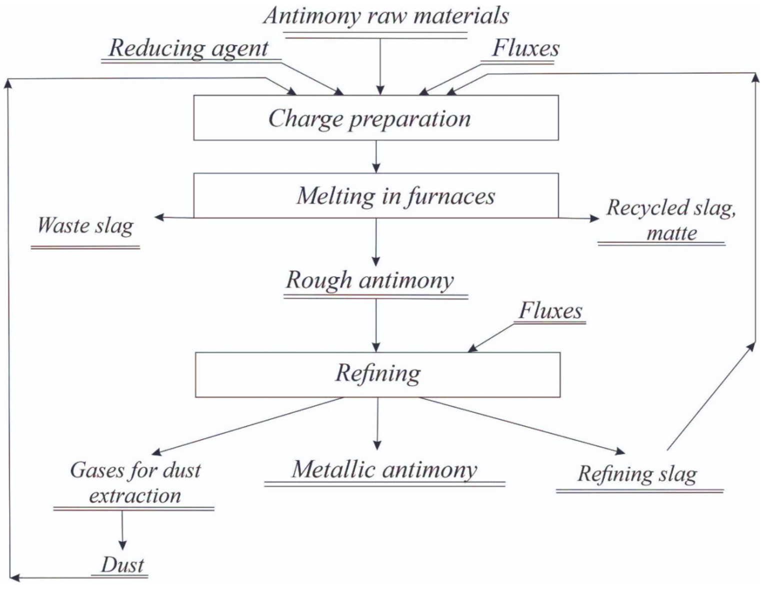

Fig. 1. Technological scheme of the pyrometallurgical method for obtaining metallic antimony.

the production of other non-ferrous metals are processed hydrometallurgically [9 - 13].

The hydrometallurgical process of obtaining metallic antimony consists of two stages: dissolution of antimony compounds in solvents and electrodeposition of metallic antimony on the cathode.

Solutions of alkaline sulfides and alkaline earth metals, as well as solutions of sodium hydroxide, hydrochloric acid, iron (III) chloride and others can be used as a solvent of antimony.

The hydrometallurgical process is based on the following reactions:

$$Sb_2S_3 + 3Na_2S = 2Na_3SbS_3 \qquad (6)$$
$$2Sb_2S_3 + 6CaS = 2Ca_3(Sb_2S_3)_2 \qquad (7)$$
$$Sb_2S_3 + 4NaOH = NaSbO_2 + Na_3SbS_3 + 2H_2O \qquad (8)$$
$$Sb_2S_3 + 6HCl = 2SbCl_3 + 3H_2S \qquad (9)$$
$$Sb_2S_3 + 6FeCl_3 = 6FeCl_2 + 2SbCl_2 \qquad (10)$$

Solutions of sodium hydroxide and sodium sulfide have been widely used in industry as a solvent.

The processes of leaching antimony concentrate with salt and chloride solutions are characterized by high speed, the ability to directly extract antimony in the form of commercial products and a closed cycle of repeated use of chloride solutions. Acid leaching is often proposed for hydrometallurgical treatment of sulfide concentrates of antimony-arsenic raw materials using $CaCl_2$ salt solutions, which reduces the acid concentration by five to seven times, reduces the ability to form Sb and As hydrides and allows to obtain oxides and sulfides of Sb without harmful additives [14].

A similar method is also proposed for the removal of antimony at the beginning of the process of processing antimony-gold concentrate with a high content of calcium and low content of antimony and gold (ore Ca–Sb–Au). The dissolved antimony can be directly electrodeposited at the cathode to produce metallic antimony, the sulfur present in the stibnite has been converted into elemental sulfur remaining in the residue, and the leaching residue can be used as a raw material for further gold extraction. Thus, the separation of antimony and gold in the "head" of the process was achieved [15 - 16].

The use of acidic solvents requires expensive acid-resistant equipment.

Electrolytic precipitation of antimony from leaching solutions is based on the following reaction:

$$2Na_3SbS_3 + 6NaOH = 2Sb + 6Na_2S + 3H_2O + 1.5O_2 \qquad (11)$$

Metallic antimony obtained by electrolysis contains an insignificant amount of impurities compared to rough antimony obtained by pyrometallurgical method, further production of commercial antimony is possible by fire refining with low reagent consumption. The generalized technological scheme of hydrometallurgical processing of obtaining metallic antimony is shown in (Fig. 2).

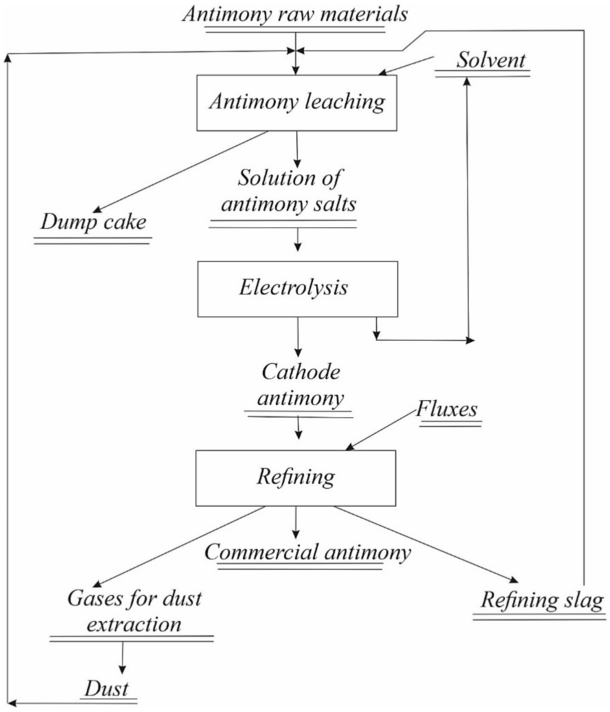

Fig. 2. Technological scheme of the hydrometallurgical method for obtaining metallic antimony.

Methods of processing technogenic formations

The reserves of the main mineral raw material of antimony - stibnite (Sb_2S_3) are limited [17, 18] and according to [19], the natural resources of antimony will be exhausted by 2050 if the rates of antimony production continue to increase at the current rate. There is a need to search for other industrially important sources of raw materials.

In the production processes of processing lead-zinc and copper ores and concentrates, where antimony is present, dust processing products, slurries, slags and other antimony-containing wastes are formed as impurities, but these wastes are also characterized by significant contents of other compounds of bismuth, lead, arsenic, tin, etc. These antimony-containing wastes are not yet processed on an industrial scale, their processing is at the stages of scientific development. The traditional technology for producing metallic antimony is the reduction melting of antimony oxide compounds in furnaces. If mineral raw materials containing antimony sulfide require oxidative firing to convert them into antimony oxides, then man-made waste contains antimony oxide compounds that does not require preliminary oxidative firing. When developing the technology of their processing, the content of antimony and harmful impurities interfering with production is important, which determines the technical and economic indicators of the technological scheme.

Zhong et al. proposed the extraction of antimony from dust formed during the reduction melting of non-ferrous metals by the restoration of a gaseous mixture of CO - CO_2 [20]. Dust of the following chemical composition, mass %: 36.28 As, 28.72 Sb and 22.35 O and consisting of the following phase compositions As_2O_3, Sb_2O_3, As_4O_6 and $(Sb, As)_2O_3$ is first subjected to oxidative firing in the presence of CuO copper oxide [21]. This solution is aimed at selective separation of antimony and arsenic and increasing the degree of their extraction in subsequent reduction firing. After oxidative firing, Sb_2O_4 and $Cu_3(AsO_4)$ are present in the stub. Next, the stub was subjected to reducing roasting in a gas atmosphere of a CO-CO_2 mixture. Under optimized firing temperature conditions of 800°C, partial pressure of 7.5 vol. CO % and firing time 120 min, the degree of arsenic extraction was 98.40 % and the degree of antimony extraction was 80.40 %. Arsenic in the form of As_2O_3 and antimony in the form of Sb_2O_3 were extracted into various cooling cylinders. Copper in the residual cinder is present in the form of Cu and Cu_2O and can be used for re-oxidation.

Binz et al. developed a pyrometallurgical process for obtaining antimony trioxide from lead refining slags by direct oxidation [22]. The raw material contains about 30 mass% Sb_2O_3 and 60 mass% PbO, as well as oxides of arsenic, tin and other elements. Antimony trioxide is a product for the plastic industry and must meet strict requirements for lead and arsenic content. Due to the high content of PbO in the slags formed in modern lead plants, PbO is a problematic compound in the firing process. Carbothermic reduction is proposed to obtain slags enriched with antimony oxide up to 75 %.

The method of processing antimony concentrates [23] formed as an intermediate product of lead production containing 47.77 mass % Sb and 0.17 mass % As is aimed at obtaining metallic antimony with a low arsenic content at the first stage of reduction melting. To do this, the authors suggest melting antimony concentrate with sodium Na^+ or lead oxide PbO.

The reduction of arsenic content in rough antimony is based on the maximum transfer of arsenic to slag by the following reactions:

$$2As+5Na_2PbO_2=2Na_3AsO_4+2Na_2O+5Pb \quad (12)$$

$$2As+3PbO=As_2O_3+3Pb \quad (13)$$

When reducing the antimony concentrate with coke without the addition of sodium plumbite or lead oxide, rough antimony with an arsenic content of 0.34 % was obtained. As a result of the reduction melting of the antimonate concentrate in the presence of sodium plumbite or lead oxide, rough antimony with an arsenic content of 0.07 % - 0.1 % was obtained.

As indicated in this article, when adding up to 3 % Na_2PbO_2 or PbO to the charge, the concentration of lead in rough antimony increases to 6 %, however, known methods of refining antimony from lead successfully reduce the concentration of lead to 0.015 % - 0.030 %. But the stage of refining rough antimony from arsenic is excluded, which leads to a reduction in the operating costs of the process as a whole.

Antimony raw materials are often processed into rough antimony, but schemes of hydrometallurgical processing with the production of antimony trioxide by leaching with hydrochloric acid are also proposed. To reduce acid consumption during the leaching of sodium antimonate, it is proposed to pre-wash the sodium antimonate from the sodium component with hot water, then the sodium antimonate is mixed with iron shavings at the rate of 5 % - 7 % by mass of sodium antimonate and leaching with hydrochloric acid is carried out at t = 65°C - 70°C and W:T=3:1. At the same time, the pentavalent antimony is reduced to trivalent, the leaching time is reduced from 3 hours to 0.5 - 1 hour, the extraction of antimony into the solution increases to 99 %.

Kershansky et al. also proposed to leach sodium antimonate in sulfide-alkaline solutions containing 150

- 180 g L^{-1} Na_2S at W:T = 6 - 8:1 and a temperature of 150°C - 170°C. In order to increase the extraction of antimony into the solution and reduce the consumption of Na_2S solvent, it is proposed to introduce elemental sulfur into the leaching charge at the rate of 0.1 - 0.2 parts per 1 part [24 - 26].

Antimony trioxide is obtained from solutions after hydrochloric acid leaching by hydrolysis, and antimony tartrates are subsequently obtained by reaction:

$$Sb_40_6 + 4KH\ (C_4H_4O_6) = 4K(SbO)C_4H_40_6 + 2H_2O \tag{14}$$

Extraction of antimony into a 95 % solution, extraction of 73.6 % into antimony trioxide [27].

The source for antimony extraction is also electrolytic sludge [28] of copper production containing 49 % Cu, 3.62 % Sb, 29.9 % As. Extraction of 95 % antimony and 89 % arsenic was achieved by leaching the sludge with 50 g L^{-1} solutions containing 200 g L^{-1} Na_2S and 20 g L^{-1} NaOH at 60°C for 24 hours [29]. The production of high-purity antimony chloride $SbCl_3$ with antimony extraction above 95 % was achieved by chlorinating leaching of anode slurries with simultaneous distillation [30]. Antimony extraction from anode slurries rich in bismuth and arsenic is realized by oxidative leaching under pressure. Sodium nitrate $NaNO_3$ was selected as the leaching reagent. The purpose of oxidative leaching is the transfer of antimony, arsenic and lead into solution and the concentration of bismuth, gold and silver in an insoluble residue.

Under optimized conditions, the recovery rates of arsenic, antimony and lead into the solution are 95.36 %, 79.98 %, 63.08 %, respectively. X-ray diffraction analysis showed that the leaching residue consists of Bi, Bi_2O_3, $Pb_2Sb_2O_7$ and trace amounts of $NaSb(OH)_6$. Arsenic, antimony and lead are thus separated from lead anode sludge in the form of $Na_3AsO_4 \cdot 10H_2O$ and $Pb_2Sb_2O_7$. It has been shown that the content of Pb (IV) and Sb (V) increases significantly with the addition of $NaNO_3$ [31].

Complex extraction of valuable components from flotation tailings and anode slurries was achieved as a result of three-stage vacuum distillation. Precious metals silver (95.4 %) and gold (96.9 %) were extracted into the distillation residue.; base metals lead (99.7 %), antimony (95.8 %) and bismuth (99.8 %) were removed and mainly concentrated in the first phases of ignition; rare metals selenium (90.9 %) and tellurium (92.2 %) were enriched in the second ascension. No additional waste was generated and the proposed technology ensures the completeness of the extraction of all components by vacuum distillation [32].

Thus, the developers of technology in the processing of technogenic raw materials offer various ways to extract antimony based firstly on the form of antimony and its content in the raw materials, as well as on the requirement of chemical purity of the resulting salt or antimony oxide.

Refining of antimony

Metal antimony for the production of lead alloys must comply with the Cu^+ grade according to GOST 1089 - 73. Metal of this quality can be obtained by fire refining of rough antimony obtained by reducing or precipitation melting containing 85 % - 90 % Sb and 10 % - 15 % impurities. But the main sector of metal antimony consumption - the production of trioxide as a feedstock - consumes the highest grades of antimony containing at least 99.65 % of the base metal and no more than 0.2 % lead, 0.002 % tin and 0.1 % arsenic. If we consider that the main producer of metallic antimony is China, then from the manufacturer's website you can see that the manufactured products contain trace amounts of impurities (Table 2).

Metal of the specified quality can be obtained by refining in several stages of fire (reagent) refining and electrolytic refining. Since the methods of fire refining are based on the difference in the affinity of the refined metal and impurities to oxygen and sulfur, it is impossible to carry out deep purification of antimony from lead and tin. For easily removable impurities, such as arsenic, the consumption of the reagent and refining stages is required in proportion to the arsenic content. Therefore, to obtain the highest grades of metallic antimony, cathode antimony with a low content of impurities was subjected to fire refining. There is a method of electrolytic refining of rough antimony from lead and tin. But this method is unprofitable in the absence of precious metals in the rough metal to produce sludge rich in gold and silver.

In practice, the removal of arsenic from rough antimony is carried out by refining the latter with molten sodium hydroxide and/or sodium carbonate in contact with air oxygen after the refining stage from iron.

Table 2. Quality indicators of metal antimony Hsikwangshan Twinkling Star Co., Ltd [33].

Stamp	Chemical composition, %								
	Sb≥	The content of impurities ≤							
		As	Fe	S	Cu	Se	Pb	Bi	Total impurities
Sb 99.90	99.9	0.02	0.015	0.008	0.01	0.003	0.03	0.003	0.1
Sb 99.85	99.85	0.05	0.02	0.04	0.015	–	–	0.005	0.15
Sb 99.65	99.65	0.1	0.03	0.06	0.05	–	–	–	0.35
Sb 99.50	99.5	0.15	0.05	0.08	0.08	–	–	–	0.5

Sodium hydroxide serves as a solvent for arsenic oxides to form sodium arsenite:

$$2As + 1{,}5O_2 + 6NaOH = 2Na_2AsO_3 + 3H_2O \qquad (15)$$
$$2As + 1{,}5O_2 + 6Na_2CO_3 = 2Na_3AsO_3 + 3CO \qquad (16)$$

This method has been widely used in the refining of antimony from arsenic and small amounts of iron since the advent of antimony production and is still used at existing refining plants [34 - 36], since this method can remove arsenic to a residual content of 0.05 % or Sb/As =1353. Simultaneously with arsenic, iron, sulfur and to some extent tin are removed from antimony by similar reactions (the latter up to a content not lower than 0.02 % - 0.05 %).

Hu et al. proposed a mixture of caustic soda with lead sulfide for refining antimony with a high arsenic content [37].

Thus, research on improving the refining of antimony from arsenic continues in the direction of deep purification from arsenic, so the reagents for removing arsenic do not change.

Refining from iron is carried out with a mixture of ore sulfide concentrate (antimony content more than 30 %, size up to 50 mm) and technical anhydrous sodium sulfate (base substance content 93 % - 97 %) at 1000°C - 1100°C and neutral atmosphere.

Refining from sodium is carried out, if necessary, after refining from arsenic and under approximately the same conditions. Quartz sand containing at least 95 % SiO_2 without visible foreign inclusions is loaded onto the surface of the liquid metal, and after 10 - 20 minutes of mixing the melt, the resulting slag is removed.
In this case, the reaction should proceed:

$$2Sb(Na) + 0{,}5O_2 + SiO_2 = Na_2SiO_3 + 2Sb \qquad (17)$$

Since lead and tin could not be removed to the required content by fire refining, an electrolytic method was used to refine antimony from lead [38].

Since the beginning of the 1990s, studies have been conducted on refining antimony from lead by fire refining. A special place in these studies is occupied by the works of scientists of the PRC. Phosphorus, boron and silicon oxides mixed with sodium salts (Na_2CO_3, NaCl) are proposed for lead removal.

The method claimed for refining from lead includes the treatment of antimony with a mixture of phosphorus oxy-acids and sulfuric acid with nitrogen purging at the melting point of antimony. When phosphorus oxy-acids (meta-, ortho-, pyrophosphoric acid) are melted in a mixture with sodium salts, phosphate polymerization reactions take place [39]. As a result, it achieves the refining of antimony to a residual lead content of 0.1 % - 0.2 %.

Phosphorus pentoxides mixed with sodium carbonate were also used [40]. Antimony refining was achieved at 800°C to a lead content of 0.015 % against its initial content in the rough metal – 4 %. At the same time, it is necessary to maintain the P_2O_5 ratio: Na_2CO_3 = 3:1. The consumption of the refining mixture is 20 % of the mass of the metal.

The processes of refining rough antimony from lead with ammonium dihydrogen phosphate have been studied. The thermal behavior of the mixture was studied by thermogravimetric TG/DTA analyses. The firing products of a mixture of $NH_4H_2PO_4$ and PbO of the following molar ratio of 2.5:3 obtained at 750°C for 30 minutes are $Pb_2P_2O_7$ and $Pb_5P_4O_{15}$.

Moreover, with a molar ratio of $NH_4H_2PO_4$:Sb_2O_3 = 2.5:1 at 750°C for 30 minutes, $SbPO_4$ was obtained. At 850°C, $Pb_{14.67}Sb_{1.33}(PO_4)_{12}$ is formed as a result of the interaction of $SbPO_4$ and PbO. This in turn proves that the complex compound $Pb_{14.67}Sb_{1.33}(PO_4)_{12}$ is more stable at high temperatures than $SbPO_4$. i.e., when refined with phosphate compounds, stable lead phosphate compounds are formed, easily separated from the metal phase [41]. In order to separate lead from antimony, the Wu Wen-wei,Wu Xue-hang and others of the above-mentioned works carried out various studies. They also studied the reactions of the interaction of BPO_4 with PbO and Sb_2O_3. As a result of sintering a mixture of BPO_4 and PbO at 850°C for 30 minutes, amorphous products were obtained, a product of $Pb_5(PO_4)_3Cl$ crystal structure was obtained by sintering the mixture in the presence of sodium chloride. During the interaction of BPO_4 with Sb_2O_3 at 850°C, compounds of the crystal structure $SbPO_4$ and $SbOPO_4$ were obtained. However, amorphous products were obtained in the presence of sodium. Thus, it can be argued that the composition and crystal structure of the obtained products depend on the consumption of BPO_4 [42]. Sodium metaphosphate was used to remove lead from antimony. The refining process was carried out at 700℃ - 1000°C to obtain a melt of antimony phosphate and lead [43].

In general, a mixture of phosphorus oxy-acids and metaboric acid with various sodium salts have been proposed as multifunctional refining agents for rough antimony from Fe, Pb, Sn, Cd, Cr and Ni [44].

Sodium tripolyphosphate, known as food stabilizer E451, was also used to refine antimony from lead in a mixture with phosphoric acid. At the same time, the composition of the refining agent consists of: 30 - 70 mass % phosphorus oxoacid, 20 - 60 mass % sodium tripolyphosphate and 2 - 10 mass % of the desiccant reagent. Sodium sulfate or sodium carbonate was used as a desiccant reagent. When refining 200 g of rough antimony with the addition of 35 g of refining mixture, 175 g of metal containing 0.1 % lead and 0.05 % iron was obtained [45].

All methods of refining antimony with phosphorus compounds are more aimed at the formation of stable lead phosphates than antimony. When refining antimony from lead with a mixture of phosphorus oxide (P_2O_5) and soda, the formation of sodium tripolyphosphate by reactions is also possible:

$$6H_3PO_4 + 5Na_2CO_3 = 2Na_5P_3O_{10} + 5CO_2 + 9H_2O \quad (18)$$

$$NaPO_3 + Na_4P_2O_7 = Na_5P_3O_{10} \quad (19)$$

$$Na_3P_3O_9 + 2NaOH = Na_5P_3O_{10} + H_2O \quad (20)$$

Therefore, the mechanism of separation of lead from antimony with the formation of lead phosphates in all the proposed methods, despite the type of reagent, should proceed with the same chemical process.

A method of fire refining of rough antimony has been developed to obtain a vintage metal with a content of at least 99.65 % Sb and no more than 2000 ppm Pb vs (1.4 - 2.6) x104 ppm, 1000 ppm As vs (1 - 3) x104 ppm, 20 ppm Sn vs (1.2 - 4) x 104 ppm and 50 ppm Fe vs (0.6 - 1.4) x104 ppm. According to the results of research experiments, it was found that the greater the ratio of P_2O_5/Na_2O, the higher the degree of purification of impurities. To obtain the proposed reagent for refining the melt, prepared with the preparation of sodium dihydrogen phosphate and phosphoric acid in a ratio of at least 0.64 and dehydrated at a temperature of 350°C. The required amount of phosphorus oxide (P_2O_5) in the mixture ensures the formation of stable phosphates of lead and tin, and a decrease in the sodium content in the mixture reduces antimony losses in the form of sodium antimonate compounds [46, 47].

It is also possible to dwell separately on the liquation separation of lead from antimony. At 4 - hour deposition, 80 % of the lead contained in antimony was deposited at the bottom of the antimony melt. The lead-enriched part of antimony is 40 % of the mass of the melt. Therefore, this method can still be considered unprofitable [48].

Vacuum distillation methods are suitable for cleaning antimony from lead, but for economic reasons they can only be used to obtain high-purity antimony. Methods of chlorination of impurities can also be used to remove lead and iron. But the residual content of impurities in the metal does not allow to obtain antimony of the highest grades. Thus, it still remains advisable to apply methods of fire or reagent refining of antimony.

The economic profitability and environmental safety of antimony production must be ensured by processing refining slags.

Solutions of potassium hydroxide KOH are also considered for leaching antimony from stibnite ore. Under optimal leaching conditions (KOH concentration 0.5 mol L^{-1}, temperature 25°C, S/L=100 g L^{-1} and duration 133 min), antimony extraction was 56.5 %. Antimony was extracted from the solution in the form of $KSb(OH)_6$. This research may pave the way for the development of new hydrometallurgical processes for the extraction of antimony from sulfide minerals [16].

Developments in the field of pyrometallurgical and hydrometallurgical methods for obtaining metallic antimony are continuing. The processes of reducing melting, alkaline-sulfite leaching are also being studied. No special changes in the reagent regime have been proposed, research continues in terms of adapting known technological schemes for complex antimony raw materials to involve them in production.

The proposed technological solutions depend on the composition of the ore and the quantitative content of antimony and its form of presence in the ore, the content of impurities having similar physicochemical properties with antimony minerals.

CONCLUSIONS

In order to obtain metallic antimony, recovery melting methods and to meet demand, it is necessary to switch attention to secondary sources and man-made waste. Developments in the field of pyrometallurgical and hydrometallurgical methods for obtaining metallic antimony are continuing. The processes of reducing melting, alkaline-sulfite leaching is also being studied. No special changes in the reagent regime have been proposed, research continues in terms of adapting known technological schemes for complex antimony raw materials to involve them in production. The proposed technological solutions depend on the composition of the ore and the quantitative content of antimony and its form of presence in the ore, the content of impurities having similar physicochemical properties with antimony minerals.

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