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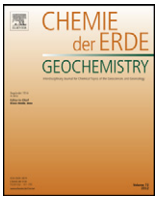

The metallurgy of antimony

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ABSTRACT

Globally, the primary production of antimony is now isolated to a few countries and is dominated by China. As such it is currently deemed a critical and strategic material for modern society. The metallurgical principles utilized in antimony production are wide ranging. This paper will outline the mineral processing, pyrometallurgical, hydrometallurgical and electrometallurgical concepts used in the industrial primary production of antimony. As well an overview of the occurrence, reserves, end uses, production, and quality will be provided.

1. Background

Antimony is a silvery, white, brittle, crystalline solid that exhibits poor conductivity of electricity and heat. It has an atomic number of 51, an atomic weight of 122 and a density of 6.697 kg/m^3 at 26 °C. Antimony metal, also known as 'regulus', melts at 630 °C and boils at 1380 °C. Antimony and the natural sulfide of antimony were known as early as 4000 BC. It was used as a coating for copper between 2500 BC and 2200 BC. The sulfide was used as eyebrow paint in early biblical times, and a vase found at Tello, Chaldea, was reported to be cast antimony. Antimony is seldom found in nature as a native metal because of its strong affinity for sulfur and metals such as copper, lead and silver. In fact, the word antimony (from the Greek *anti* plus *monos*) means "a metal not found alone". Metallic antimony is too brittle to be used alone and in most cases has to be incorporated in an alloy or compound. For this reason, its development was slow until military applications created new markets and the Russo-Japanese war of 1905 triggered demand. Antimony was widely used in that time and during the First World War as it was found to be the best alloying material for lead to produce munitions that capable of armor plate penetration. A variety of compounds containing antimony as the major constituents were also used for other ammunition types such as detonators, tracer bullets and armory. The start of mass production of automobiles gave a further boost to antimony, as it is a major constituent of lead-acid batteries. The major use for antimony is now as a trioxide for flame-retardants.

2. Occurrence and mineralogy

The abundance of antimony in the Earth's crust is approximately 0.2 mg/kg. Antimony is a chalcophile, occurring with sulfur and the heavy metals copper, lead and silver. More than 100 minerals of antimony are found in nature. Some of the more common ones, as summarized by the author, are listed in Table 1.

Industrially, stibnite (Sb_2S_3) is the predominant ore of interest and importance. Stibnite deposits are usually found in quartz veins. The deposits frequently contain minor amounts of gold, silver and mercury sulfides.

Antimony has been produced from ores in over 15 countries. As shown in Table 2 (Carlin, 2012), world reserves of antimony are estimated to about 1.8 million metric tonnes. As China, the leading producer, accounts for about 90% of the world's mined production and the vast majority of the reserve base (i.e. reserves consist of demonstrated resources that are currently economic. The reserve base consists of reserves plus marginally economic reserves and resources that are sub-economic). Moreover, China together with four three other minor producing countries, Bolivia, the Republic of South Africa, Tajikistan and Russia currently account for over 95% of the total world antimony production.

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Table 1
Common primary antimony minerals.

Horsfordite Cu_6Sb
Aurostibite $AuSb_2$
Ullmannite NiSbS
Stibiobismuthine $(Bi,Sb)_4S_7$
Freibergite $(Cu,Ag)_{12}Sb_4S_{13}$
Ramdohrite $Ag_2Pb_3Sb_3S_9$
Zinckenite $PbSb_2S_4$
Falkmanite $Pb_3Sb_2S_6$
Franckeite $Pb_5Sn_3Sb_2S_{14}$
Famatinite Cu_3SbS_4
Stibioenargite Cu_3 $(As,Sb)_4$
Gabrielite $Tl_6Ag_3Cu_6(As,Sb)_9S_{21}$
Romeite $5CaO_3 \cdot Sb_2O_5$
Cervantite Sb_2O_4
Dyscrasite Ag_3Sb
Breithauptite NiSb
Gudmundite FeSbS
Tetrahedrite $Cu_{12}Sb_4S_{13}$
Bournonite $PbCuSbS_3$
Andorite $AgPbSb_3S_6$
Jamesonite, $Pb_4FeSb_6S_{14}$
Meneghinite $Pb_4Sb_2S_7$
Livingstonite $HgSb_4S_7$
Stibioluzonite $Cu_3(Sb,As)S_4$
Gerstleyite $Na_2(Sb,As)_8S_{13} \cdot 2H_2O$
Stibiocolumbite $Sb(Nb,Ta)O_4$
Stibiconite $Sb_2O_4 \cdot H_2O$
Stibio-tellurobismutite $(Bi,Sb)_2Te_3$
Stibiodomeykite $Cu_3(As,Sb)$
Breithauptite NiSb
Stibnite Sb_2S_3
Annivite $Cu_{12}(Sb,Bi,As)_4S_{13}$
Stephanite Ag_5SbS_4
Geocronite $Pb_5(As,Sb)_{12}S_8$
Boulangerite $Pb_5Sb_4S_{11}$
Cylindrite $Pb_3Sn_4Sb_2S_{14}$
Berthierite $FeSb_2S_4$
Bournonite $PbCuSbS_3$
Kermesite Sb_2S_2O
Senarmontite Sb_2O_3
Stenhuggarite $CaFeSbAs_2O_7$
Valentinite Sb_2O_3

3. Uses and applications

Antimony trioxide, Sb_2O_3, is the most important antimony compound produced. Today, antimony trioxide is produced by volatilizing antimony metal in an oxidizing furnace. It is used in halogen compound flame retarding formulations for plastics, paints, textiles and rubber. Most commercial grades of antimony trioxide contain between 99.2% and 99.5% antimony trioxide with varying amounts of impurities such as arsenic, iron and lead. Commercial suppliers offer various grades of antimony trioxide based on the relative tinting strength of their product, which is a function of particle size. Antimony trioxide also finds growing use as a catalyst for PET production. Antimony pentoxide and sodium antimonate, $NaSb(OH)_6$, are also used as flame retardants. Antimony compounds, primarily sodium antimonate, are also used in decolorizing and refining agents for optical glass and CRT glass. In the electronics industry, Sb use grows for diodes. Antimony metal is also used for production of antimonial lead, which is an important product of the secondary lead smelter. A blast furnace charge containing used or discarded battery plates, type metal and bearing metal is reduced to lead bullion. The bullion is then refined in reverberatory furnaces to meet specifications. Lead–antimony alloys are used in starting-lighting-ignition batteries, ammunition, corrosion-resistant pumps and pipes, tank linings, roofing sheets, solder, cable sheaths and anti-friction bearings.

Currently, the major conservation practice within the antimony industry is the recycling of the metal in used lead acid storage batteries, type metal and babbit. Also, antimonial lead and antimony metal are recovered from intermediate smelter products such as slags, drosses, flue dusts and residues generated at copper and lead smelters. The supply of secondary antimony substantially exceeds that from primary sources for antimonial lead applications. In other minor uses, antimony oxides are used as white pigments in paints, whereas antimony trisulfide and pentasulfide yield black, vermillion, yellow and orange pigments. Camoflauge paints contain antimony trisulfide which reflects infrared radiation. Antimony trisulfide is also used in the liners of automobile brakes as well as in safety match compositions. In the production of red rubber, antimony pentasulfide is used as a vulcanizing agent. Antimony compounds are also used in catalysts, pesticides, ammunition, and medicines. As well, a variety of compounds containing antimony as the major constituent are also used for other ammunition such as detonators, tracer bullets and armory. Also, as previously noted, antimony was widely used during the First World War as it was found to be the best lead alloy material to use for penetrating armor plate.

Table 2
Annual world mine production and reserves by country (tonnes of contained antimony).

Country	Mine production		Reserves
	2010	2011	
Bolivia	5000	5000	310,000
China	150,000	150,000	950,000
Russia	3000	3000	350,000
South Africa	3000	3000	21,000
Tajikistan	2000	2000	50,000
Other countries	4000	6000	150,000
World total	167,000	169,000	1,800,000

Flame retardants continue to drive growth demand for antimony trioxide. The historic capacity of the world's major established producers as compiled by the author is listed in Table 3. Table 4 lists a recent compilation of production capacities of global mining operations (Roskill, 2011).

Overall, it is estimated that the distribution of antimony uses and consumption worldwide is flame retardants 72%, transportation including batteries 10%, chemicals 10%, ceramics and glass 4%, and other 4%. The USA, Japan and Western Europe which together account for around 70% of world demand dominate world consumption of antimony.

4. The mineral processing of antimony

Originally antimony was mined and hand sorted to effect concentration. Since the bulk of primary production is in China, where labor is plentiful and cheap, surprisingly, hand sorting still finds a large application. However, in recent years, many other unit operations are used in the mineral processing of antimony. These include primarily conventional crushing and grinding followed by combined gravity concentration and flotation. First, as stibnite is the predominant mineral and China is the predominant producer, the industrial mineral processing of a typical Chinese stibnite ore will be elucidated. As well, the historical flotation operation of a long term industrial North American silver bearing antimony tetrahedrite mining operation will also be discussed.

A typical stibnite deposit may contain the antimony sulfide along with pyrite and a gangue consisting of quartz, calcite, barite, kaolin and gypsum. The ore grading about 2.7% Sb is put to a combined treatment by hand-sorting, heavy medium separation and flotation (Xikuangshan, 1964; Chen, 1964; Huang et al., 1965; Xikuangshan, 1979). First, the ore is hand sorted on the feed belt to crushing for a finished concentrate of antimony lumps. Crushing takes place in two stage closed circuit consisting of a jaw and cone crusher. After crushing to −150 mm, a two stage hand sorting is carried out to give antimony lumps and tails that are −150 + 35 mm. The −35 + 10 mm fraction is heavy medium separated to discard a portion of gangue. Then the hand-selected low grade concentrate and the heavy product from the heavy media separation are ground to −10 mm. This is carried out in three separate sections. The first and second sections are combined into a

Table 3
Plant capacities of historic leading producers of refined antimony.

Company	Location	Total capacity and products (Sb tonne/year)
Hsikwangshan Mining Administration	China	30,000 (metal, trioxide, pentoxide, sodium antimonate)
Kadamjaisk Antimony Combine	Kyrgystan	20,000 (metal, trioxide)
Amspec Chemical Corp.	USA	15,000 (trioxide)
Laurel Industries Inc.	USA	12,500 (trioxide)
Societe Industrielle et Chimique de L'Aisne	France	12,000 (metal, trioxide)
Dachang Mining Administration	China	10,000 (metal)
Mines de la Lucette	France	9500 (metal)
Enal	Bolivia	9300 (trioxide)
Great Lakes Chemical (Anzon)	USA	6000 (trioxide)
Union Miniere	Belgium	6000 (sodium antimonate)
Guzhou Dushan Dongfeng	China	4000 (metal, trioxide)
Hubei Chongyang	China	4000 (metal, trioxide)
Sunshine Mining and Refining	USA	1000 (metal, sodium antimonate)
Total listed		138,300

closed circuit consisting of ball mills and spiral classifiers. The third section has a ball mill in conjunction with a spiral classifier, and provides the final ore feed of a fineness of 60% −200 mesh. Ore ranging −35 to +10 mm is fed to a drum H.M.S. separator. Separation density is regulated at 2.62–2.56 using ferrosilicon. The light product is used as backfill for the mine. The heavy product is sent to the grinding section where it is prepared for flotation. Bulk flotation is performed with natural pH on the ore ground to 60% −200 mesh. Flotation reagents used are butyl xanthate as a collector (100 g/tonne), sodium diethyldithiocarbamate as a collector (75 g/tonne), shale oil as a collector (300 g/tonne), lead nitrate as an activator (150 g/tonne), pine oil as a frother (100 g/tonne) and kerosene (65 g/tonne) as a collector. Scavenger tailings are combined and delivered to a separate bank of cells for final, tertiary scavenging. Rougher concentrate is thrice cleaned to make a pure stibnite concentrate. Overall 33% of the ore is treated by hand sorting, 7% by heavy media separation and 60% by flotation. The typical separation results are shown in Table 5 and detailed plant flowsheets and process descriptions may be found in the referenced literature (Xikuangshan Administration of Mines, 1979).

In the United States, the last primary producer of antimony was Sunshine Mining & Refining Company. The antimony bearing mineral in the mine was argentiferous tetrahedrite, or freibergite $(Cu,Ag)_{12}Sb_4S_{13}$. As this is the longest operating primary antimony mineral flotation circuit in the world, a detailed discussion flows. The principal vein minerals at Sunshine are siderite, quartz, pyrite, arsenopyrite, tetrahedrite, galena, chalcopyrite, and sphalerite. The only mineral of economic importance was tetrahedrite. Historically, tetrahedrite ore feed grades of 1000–1300 g/tonne silver was common and containing up to1% antimony. With little variation, silver to copper and antimony concentrate ratios were 50:1 and 63:1 respectively. The ore was crushed by staged gyratorys in closed circuit to minus 2 cm. Grinding was then carried out in three primary ball mills to 60% passing −200 mesh for optimum liberation. The combined throughput rate of the primary grinding mills is 45 tonnes/h.

Table 4
World mine capacity by main producing companies, mid 2011.

Country	Company	Total capacity (tonne/year as Sb)
Australia	Mandalay Resources	2705
Bolivia	Various	5460
Canada	Beaver Brook	6000
China	Hsikwangshan Twinkling Star	55,000
	Hunan Cheznu Mining	20,000
	China Tin Group	20,000
	Shenyang Huacheng Antimony	15,000
Kazakhstan	Kazzinc	1000
Kyrgyzstan	Kadamshai	500
Laos	SRS	500
Mexico	US Antimony	70
Myanmar	Various	6000
Russia	GeoPro Mining	6500
South Africa	Consolidated Murchison	6000
Tajikistan	Anzob	5500
Thailand	Various	600
Turkey	Cengiz & Ozdemir Antimuan Madenleri	2400
Total listed		143,280

Under these conditions, a 40,000 g/tonne silver bearing tetrahedrite concentrate containing 24% copper and 19% antimony was routinely produced. Overall, recoveries of the tetrahedrite ore were typically 97%.

The Sunshine mill saw its last major modification in the mid 1950s with added floor space and the incorporation of 30 new Fagergren 56 cells and 12 Galigher Agitair 36 cells which replaced old Denver cells. Additionally, a Denver regrind mill was installed. The purpose of these changes was to enhance production, whereby two concentrates would be produced. From the mid 1950s the Sunshine mill produced these two concentrates from the flotation process; the high-grade, 40,000 g/tonne tetrahedrite silver concentrate and a low-grade pyrite concentrate with 20,000 g/tonne silver with very little contained antimony. Distribution of the recovered silver was 92% to silver bearing tetrahedrite concentrates and 8% to pyrite concentrates while distribution of antimony was 97% to the tetrahedrite concentrates.

During the period between 1953 and early 1989, a bulk sulfide concentrate was produced in the first circuit utilizing Aerofloat 242 as the primary collector. Ninety-five percent of the silver bearing antimony tetrahedrite ore was recovered in this step. The recleaning of the first circuit cleaner concentrates as accomplished through the addition of zinc sulfate and sodium sulfite as a pyrite and galena depressant followed by flotation to a high-grade product at controlled conditions. Aero 3477 was used in the second circuit which scavenged any remaining recoverable silver mineral. Additionally, the tailings from the retreatment circuit and the second circuit cleaner concentrates reported to the regrind mill and were reground to passing 95% −325 mesh. This material was classified through a Krebs cyclone. The lower grade underflow was subjected

Table 5
Typical stibnite ore mineral processing results.

Operation	Ore grade (% Sb)	Con. grade (% Sb)	Tails grade (%)	Sb recovery (%)
Hand sorting	2.25	7.80	0.12	95.95
Heavy media	1.58	2.65	0.18	95.11
Flotation	3.19	47.58	0.21	93.97
Average	2.68	19.44	0.18	94.11

to roughing and cleaning. The higher grade overflow reported to the pyrite cleaner concentrates. Tailings from the pyrite roughers and pyrite cleaner cells reported to the second circuit roughers.

During early 1995, lead mineralization as galena and as antimony bearing bournonite began to show up in abundance in the mill feed. Hence, tetrahedrite concentrate dilution with lead became a growing problem. With zinc sulfate and sodium sulfite in use to depress pyrite and galena in the retreatment circuit, the galena would report to the regrind mill and was recycled as before. Galena and bournonite then refloated as a recirculating load in this arrangement and reported back to the first circuit to be recovered again in the first circuit cleaner concentrates. So, the recirculation of lead in the first, second, and retreatment circuits provided overloaded conditions as well as diluted the silver grade of our single concentrate.

The bank of four Agitair 36 cells removed from pyrite cleaning service during the initial single concentrate modification were brought back on line to serve as an intermediate process for the reground product (namely retreatment tails and second circuit cleaner concentrates), which had previously been split between the first and second circuit roughers. The Krebs cyclone used to split the reground product between the first and second circuit roughers was left in service with the higher grade overflow continuing to report to the first circuit roughers. The cyclone underflow became feed to these four Agitair flotation cells. Tailings from this new modification were directed to the new third circuit rougher head box. The disc filter which had previously been removed from service was placed on line. As lead values of concentrate produced rose to an acceptable level it was directed to this filter. The lead concentrates produced by this method proved to be an acceptable product for marketing. The referenced literature provides detailed flowsheets and process descriptions (Allen, 1998).

5. The pyrometallurgy of antimony

For primary production, the antimony content of the ore has traditionally determined the pyrometallurgical method of recovery. In general the lowest grades of sulfide ores containing 5–25% antimony are volatilized to antimony trioxide: 25–40% antimony ores are smelted in a blast furnace: and 45–60% antimony ores are treated by liquation or iron precipitation. A description of each of these as well as oxide reduction follows (Motoo, 1974; Vladislav, 1981; Yong-Fu and Wei-Tao, 1981).

Oxide volatilization: Removal of antimony as the volatilized trioxide is the only pyrometallurgical method suitable for low grade ores. Combustion of the sulfide components of the ore supplies some of the heat; hence fuel requirements are minor. There are many variations of the volatilization process, the principles employed being the same but the equipment differing. As shown in Eq. (1), the sulfur is burned away at about 1000 °C and removed as a waste gas, whereas the volatile antimony trioxide is recovered in flues, condensing pipes, a baghouse, a Cottrell precipitator or a combination of the above. Roasting and volatilization are affected almost simultaneously by heating the ore, mixed with coke or charcoal, under controlled conditions in equipment such as a shaft furnace, rotary kiln, converter or roaster. If the volatilization conditions are too oxidizing, the nonvolatile antimony tetroxide, Sb_2O_4 may form and the recovery of antimony, as antimony trioxide, is diminished. However, special attention to the choice of charge, volatilization conditions, and selection of product results in a high-grade oxide that is suitable for use in ceramics and other applications. Now, this is primarily accomplished by oxidation of antimony metal which is illustrated in Eq. (2).

$$2Sb_2S_3 + 9O_2 \rightarrow 2Sb_2O_3 + 6SO_2 \tag{1}$$

$$2Sb + 1.5O_2 \rightarrow Sb_2O_3 \tag{2}$$

Liquation: Antimony sulfide is readily but inefficiently separated from the gangue of comparatively rich sulfide ore by heating to 550–600 °C in perforated pots placed in a brick furnace. This is illustrated in Eq. (3). The molten sulfide is collected in lower containers. A more efficient method uses a reverberatory furnace and continuous liquation, however a reducing atmosphere must be provided to prevent oxidation of antimony sulfide and loss by volatilization. The oxide volatilization process to recover additional antimony usually treats the residue, containing 12–30% antimony. The liquated product, called crude, liquated or needle antimony, is sold as such for applications requiring antimony sulfide, or is converted to metallic antimony by iron precipitation or careful roasting to the oxide followed by reduction in a reverberatory furnace.

$$Sb_2S_{3(S)} \rightarrow Sb_2S_{3(L)} \tag{3}$$

Oxide reduction: The oxides of antimony are reduced to metal with charcoal in reverberatory furnaces at about 1200 °C. This is illustrated in Eqs. (4) and (5). An alkaline flux consisting of soda, potash and sodium sulfate, is commonly used to minimize volatilization and dissolve residual sulfides and gangue. Part of the slag is frequently reused. Loss of antimony from the charge by volatilization is high (12–20% or more), even with the use of ample slag and careful control. This necessitates the use of effective Cottrell precipitators or baghouses, and considerable recycling of oxide.

$$Sb_2O_3 + 3CO \rightarrow 2Sb + 3CO_2 \tag{4}$$

$$CO_2 + 3C \rightarrow 6CO \tag{5}$$

Iron precipitation: Rich sulfide ore or liquated antimony sulfide (crude antimony) is reduced to metal by iron precipitation This is illustrated in Eq. (6). This process consisting of heating molten antimony sulfide in crucibles with slightly more than the theoretical amount of fine iron scrap, depends on the ability of iron to displace antimony from molten antimony sulfide. Sodium sulfate and carbon are added to produce sodium sulfide, or slag is added to form a light fusible matte with iron sulfide and to facilitate separation of the metal. Because the metal so formed contains considerable iron and some sulfur, a second fusion with some liquated antimony sulfide and salt follows for purification.

$$Sb_2S_3 + 3Fe \rightarrow 2Sb + 3FeS \tag{6}$$

Blast furnace smelting: Intermediate grades of oxide or sulfide or mixed ores, liquation residues, mattes, rich slags, and briquetted fines or flue dusts are processed in water-jacketed blast furnaces at 1300–1400 °C. Theoretically, this process is illustrated in Eqs. (7) and (8). In general, the same blast-furnace practice used for lead is followed, employing a high smelting column, comparatively low air pressure, and a separation of slag and metal in a forehearth. It is the favored mode of smelting for all materials containing from 25% to 40% Sb, which can be mixed with fluxes to give a charge sufficiently poor in metal to hold down volatilization. As well, slag, usually running under 1% antimony, is desired because it tends to reduce volatilization losses.

$$Sb_2S_3 + 9O_2 \rightarrow 2Sb_2O_3 + 6SO_2 \tag{7}$$

$$2Sb_2O_3 + Sb_2S_3 \rightarrow 6Sb + 3SO_2 \tag{8}$$

Flowsheets and detailed process descriptions for a primary pyrometallurgical production May be found in the literature referenced (Vladislav, 1981; Xikuangshan Administration of Mines, 1964; Yong-Fu and Wei-Tao, 1981).

6. The hydrometallurgy of antimony

Hydrometallurgical methods can be employed for simple antimony materials as well as complex ones containing any number of metals. Normal industrial antimony hydrometallurgical practices call for a two step process of leaching followed by electrodeposition. In reality, there are only two solvent systems utilized in antimony hydrometallurgy. These are the alkaline sulfide system and the acidic chloride system and the alkaline sulfide system predominates. The alkaline sulfide system has been employed industrially in the former Soviet Union, China, Australia and the United States (Anderson et al., 1992, 1994; Anderson and Krys, 1993; Nordwick and Anderson, 1993). Essentially, the lixiviant is a mixture of sodium sulfide and sodium hydroxide and when it is applied to stibnite, a solution of sodium thioantimonite is formed. This can be illustrated as;

$$Na_2S + Sb_2S_3 \rightarrow +2NaSbS_2 \tag{9}$$

$$NaSbS_2 + Na_2S \rightarrow Na_3SbS_3 \tag{10}$$

However, dissolution of elemental sulfur in sodium hydroxide is also used as a lixiviant for alkaline sulfide leaching of antimony. The combination of sodium hydroxide and elemental sulfur results in the formation of species other than just sulfide (S^{2-}). Both sodium polysulfide (Na_2S_X) and sodium thiosulfate ($Na_2S_2O_3$) are created along with sulfide. This is illustrated simplistically in the following scenario;

$$4S^\circ + 6NaOH \rightarrow 2Na_2S + Na_2S_2O_3 + 3H_2O \tag{11}$$

$$(X-1)S^\circ + Na_2S \rightarrow Na_2S_X(\text{where}X = 2\text{–}5) \tag{12}$$

Due to the oxidizing power of polysulfide on sodium thioantimonite, the major species in solution is normally sodium thioantimonate (Na_3SbS_4). This can be viewed as follows;

$$Na_2S_X + (X-1)Na_3SbS_3 \rightarrow (X-1)Na_3SbS_4 + Na_2S \tag{13}$$

The electrodeposition of the antimony from the alkaline sulfide solution to cathode metal is normally carried out via electrowinning in either diaphragm or non-diaphragm cells.

The primary anode reactions are;

$$4OH^- \rightarrow 4e^- + 2H_2O + O_2 \tag{14}$$

$$S^{2-} \rightarrow 2e^- + S^\circ \tag{15}$$

The primary cathode reaction is;

$$SbS_3{}^{3-} + 3e^- \rightarrow Sb^\circ + 3S^{2-} \tag{16}$$

The cathodic metal antimony product may attain a grade over 99.5% pure after washing. This industrial alkaline sulfide hydrometallurgical plant ran successfully for about 60 years. Industrial alkaline sulfide hydrometallurgical leach plant flowsheets and more process details may be found in the referenced literature (Ackerman et al., 1993; Anderson et al., 1992).

The other methodology for antimony hydrometallurgy is the acidic chloride system. While the alkaline sulfide system predominates, much research and pilot scale work has been undertaken to utilize chloride-based technology (Kim Soo Sik et al., 1975; Su Guohi, 1981; Tang Motang et al., 1981; Li and Xu, 1984; Thibault et al., 1997).

In the acidic chloride hydrometallurgical antimony system, hydrochloric acid, HCl, often in conjunction with ferric chloride, $FeCl_3$, is commonly used as the solvent for sulfide mineral such as stibnite. This is illustrated as;

$$6FeCl_3 + Sb_2S_3 \rightarrow 2SbCl_3 + 6FeCl_2 + 3S^\circ \tag{17}$$

$$Sb_2S_3 + 6HCl \rightarrow 2SbCl_3 + 3H_2S \tag{18}$$

In the aqueous solution, $FeCl_3$ does the job of both an oxidizer and a chloridizing agent to convert the antimony of the sulfide mineral into a chloride complex while producing elemental sulfur.

In cases where the antimony is already oxidized, it may be leached directly with HCl without the need for $FeCl_3$. This is illustrated as;

$$Sb_2O_3 + 6HCl \rightarrow 2SbCl_3 + 3H_2O \tag{19}$$

As with the alkaline sulfide system, the solubilized antimony chloride can be produced by electrowinning from solution in diaphragm cells. This produces cathode antimony metal.

The primary cathode reaction is;

$$Sb^{3+} + 3e^- \rightarrow Sb \tag{20}$$

The primary anode reactions are;

$$Fe^{2+} \rightarrow e^- + Fe^{3+} \tag{21}$$

$$3Cl^- + Fe^{3+} \rightarrow FeCl_3 \tag{22}$$

Alternatively, the antimony chloride solution can be treated by hydrolysis precipitation of the antimony from solution as a solid oxychloride. Then, the precipitated solid is treated with ammonia to produce a pure antimony oxide. This is illustrated as;

$$SbCl_3 + H_2O \rightarrow SbOCl + 2HCl \tag{23}$$

$$SbOCl + H_2O \rightarrow Sb_4O_5Cl_2 + 2HCl \tag{24}$$

$$2SbOCl + 2NH_4OH \rightarrow Sb_2O_3 + NH_4Cl + H_2O \tag{25}$$

$$Sb_4O_5Cl_2 + 2NH_4OH \rightarrow Sb_2O_3 + NH_4Cl + H_2O \tag{26}$$

In summary, there are two predominant hydrometallurgical systems for antimony. Alkaline sulfide technology is by far the most utilized because of its inherent antimony selectivity and its ease of full scale application due to minimal corrosion issues that are associated with the chloride system. However, the chloride system is being applied with a greater degree of success and confidence.

7. Antimony product quality

In ancient times, in extracting antimony from sulfide ore by the addition of iron, a starlike fern shaped crystalline pattern appeared during the course of solidification. This was dubbed the “Philosopher’s Signet Star” in 1610 and until recently the shape of these stars had commonly served to indicate the grade of the metallic antimony. Indeed, when antimony metal contains impurities like sulfur, arsenic, lead or iron to any appreciable extent, its surface shows the presence of these foreign elements by specks, by a leaden appearance or by a poorly defined appearance of the crystalline pattern. This ‘starring’ phenomenon is also produced by cooling antimony metal, or so called ‘regulus’ under cover of a layer of a properly prepared starring mixture, or coverture (Wang, 1918), which is a slag that has a melting point lower than that of antimony metal. While starring was the original indicator of antimony quality, with enhanced analytical techniques available, specifications are now better defined. Tables 6–8 (Yong-Fu and Wei-Tao, 1981) indicate the typical quality and specifications for various antimony products.

Table 6
Analysis of typical impure antimony production products.

	Impure Sb from reduction smelting (%)	Impure Sb from precipitation smelting (%)	Hydrometallurgical cathode Sb metal (%)
Sb	96–97	80–90	98–98.5
As	0.2–0.3	0.2–0.3	0.02–0.1
Pb	0.1–0.25	0.1–5	–
C	0.001–0.01	0.03–0.2	0.004–0.005
Fe	0.01–0.5	3–15	0.005–0.01
Na	0.02–0.1	0.02–0.1	0.1–1.0
Sn	0.01–0.1	0.01–0.1	0.01–0.03
S	0.1–1.0	0.2–0.3	0.15–0.40

Table 7
Chinese national standards for antimony metal purity.

Grade classification	Sb (%)	As (%)	Fe (%)	S (%)	Cu (%)	Total impurities (%)
I	99.85	<0.05	<0.02	<0.04	<0.01	<0.15
II	99.65	<0.10	<0.03	<0.06	<0.05	<0.35
III	99.50	<0.15	<0.05	<0.08	<0.08	<0.50
IV	99.00	<0.25	<0.25	<0.20	<0.20	<1.00

Table 8
Typical quality of antimony trioxide.

Sb_2O_3 content (%)	As (%)	Pb (%)	Fe (%)	−325 mesh (%)
99.5	<0.03	<0.08	<0.01	99.99

8. Summary

Globally, the primary production of antimony is now isolated to a few countries and is dominated by China. As such antimony is currently deemed a critical and strategic material for modern society. The metallurgical principles utilized in production are wide ranging. This paper outlined the primary mineral processing, pyrometallurgical, hydrometallurgical and electrometallurgical concepts used in the industrial primary production of antimony. As well, an overview of the occurrence, reserves, end uses, production, and quality was provided.

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