CHAPTER 12.3

Antimony Production and Commodities

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Globally, the primary production of antimony is now isolated to a few countries and continues to be dominated by China. As such, antimony is currently deemed a critical and strategic material for modern society.

BACKGROUND

Antimony is a silvery, white, brittle, crystalline solid classified as a metalloid that exhibits poor conductivity of electricity and heat. Alchemists were fascinated by a property of antimony to form a crystalline star (i.e., the star Regulus) under certain conditions. For alchemists, of course, that symbolized the quintessence of matter (Van der Krogt 2010). In the Western world, antimony was first isolated by Vannoccio Biringuccio and he first described it in 1540. In 1604, Basilius Valentinus (1893) wrote a monograph on antimony translated as *The Triumphal Chariot of Antimony*, regarded as the first monograph devoted to the chemistry of a single metal. Other authors have followed suit (Wang 1909, 1912; Zhao 1988; Anderson 2012). The formal chemical symbol for antimony is Sb, credited to Jöns Jakob Berzelius and taken from the Greek word *stibium*. Its alchemy elemental symbol is a circle with a cross above it, often depicted as ♁. It has an atomic number of 51, an atomic weight of 122 g/g-mol, and a density of 6.697 g/cm^3 at 26°C (Miller 1973). Antimony metal, also known as regulus, melts at 630°C and boils at 1,380°C. Molten antimony upon solidification expands. It does not readily oxidize and keeps its luster even in moist air and at elevated temperatures in the range of 100° to 250°C. At temperatures above its melting point, powdered antimony ignites and burns with a white-green flame. Antimony is resistant to attack by dilute hydrochloric acid and concentrated hydrofluoric acid. 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 a cast of 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* [opposed] plus *monos* [solitude]) means "a metal not found alone." Metallic antimony is too brittle to be used alone and, in most cases, must 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 at that time and during World War I because it was found to be the best alloying material for lead to produce munitions that were 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. In an analysis of strategic mineral supplies prior to World War II, it was stated that "Antimony has more uses of direct military character than other members of the strategic group and probably more important uses than any of the others except mercury" (Roush 1939). 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.

OCCURRENCE GEOLOGY 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 of copper, lead, and silver as a sulfosalt. It occurs as either a distinct antimony-bearing sulfide, such as stibnite; sulfosalt minerals, such as tetrahedrite; rare antimonides, such as aurostibite; or as minor or trace constituent in sulfides such as arsenopyrite and pyrite (Butterman and Carlin 2004). More than 100 minerals of antimony are found in nature. Some of the more common ones are listed in Table 1 (Anderson 2012). Industrially, stibnite is the predominant ore of interest and importance. Stibnite deposits are usually found in quartz veins. The most significant antimony mineral deposits occur in geologic environments with a thick sequence of siliciclastic sedimentary rocks in areas with significant fault and fracture systems. China has the bulk of the world's identified resources. Bolivia, Canada, Japan, Mexico, Russia, South Africa, Tajikistan, and Turkey also have demonstrated antimony resources. Antimony deposits frequently contain minor amounts of gold, silver, and mercury sulfides. Figure 1

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shows global antimony deposits and production locations (Seal et al. 2017). Most antimony deposits occur in orogenic gold provinces in collisional belts (Bliss and Orris 1992; Dail 2014; Seal et al. 1995). They can have linear zones parallel to sutures but are usually inboard of porphyry Cu and Sn-W. They are often found in distinct Sb-Au and Sb-Au-W belts such as the Murchison Range Antimony Line and the Bolivian Sb-Au belt. In several cases, there are also Carlin-like gold-bearing belts. The ultimate metal sources are assumed to be from subducted metal-enriched basinal shales assimilated into ascending reduced magmas under thick continental crustal contamination conditions. But some belts exhibit sedimentary exhalative (SedEx) deposits, distal volcanogenic massive sulfide (VMS), and high-temperature Mississippi Valley–type (MVT) basinal brine system characteristics or hybrids.

The host rocks are often platform or shelf carbonates, carbonaceous clastics, or silty calcareous units. There are few Archean deposits, but numerous Neoproterozoic and Paleozoic deposits. Antimony mobility is often controlled by alkaline hydrothermal solutions and antimony deposition by acidification and/or a drop in temperatures. Most common antimony deposits are Sb-Au-enriched low-temperature quartz veins but, based on contained metals, are insignificant. These vein deposits are strongly structurally controlled, narrow, and occur in discrete belts, with little wall rock alteration and are usually, but not always, small. This is attributed to orogenic processes inboard of subduction zones. Larger districts and deposits typically have higher-temperature assemblages, rock alteration, often with tungsten and likely magmatic input. Several larger deposits have an Sb-rich basinal brine context, including many Chinese and some Variscan and Andean deposits and could represent variants of MVT, Irish-style, or capital regional district.

By far, China dominates in antimony resources and reserves. The Southeast China orogenic belt is the world's dominant resource for antimony. It hosts more than 500 known deposits. It hosts the supergiant Xikuangshan antimony deposit in Xiangzhong Basin in Devonian carbonates. It also hosts numerous other large deposits in the Xuefeng Range with distinctive W-Au-Sb association. There is a country rock antimony endowment in region 20-40 X Clarke and at Xikuangshan on the order of 100,000 X Clarke concentration. These metals—likely sourced from older Proterozoic "basement" and genesis deposits uncertain in the Xiangzhong Basin but possibly variants of high-temperature MVT Xuefeng Range deposits—appear to be sourced from reduced W-Au-Sb–bearing granitic magmas and/or are orogenic Sb-Au (W) vein systems from remobilization.

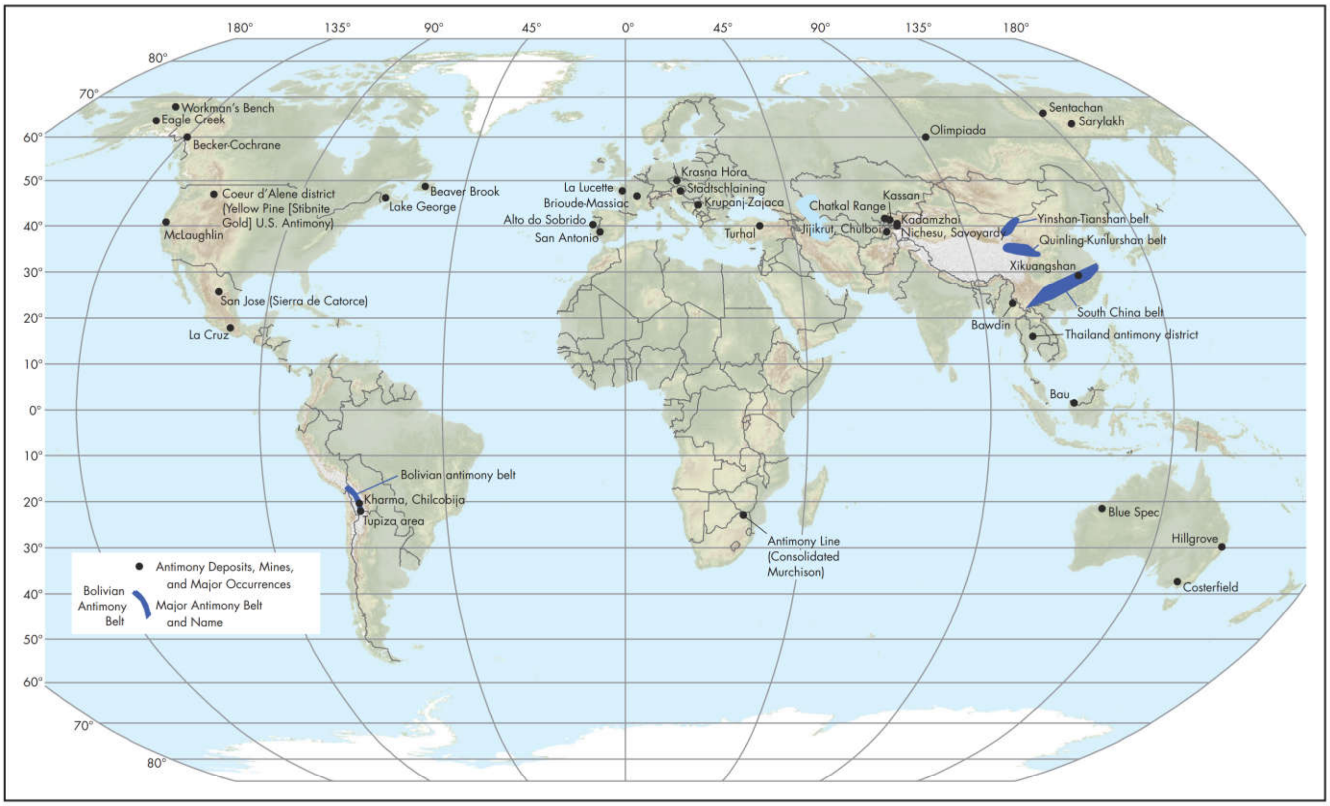
Table 1 Common primary antimony minerals

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

Source: Anderson 2012

The largest known deposit, Xikuangshan in Lengshuijiang, China, is a "Supergiant" antimony deposit (i.e., the world's largest past producer) with 801,000 t (metric tons) of antimony produced from 1897 to 1990. As of 2002, it hosted reserves of 570,000 t of antimony. These are now mostly depleted, and the mine has been shut down. It had four major deposits hosted in a series of antiforms in a 2 km wide × 9 km long belt. There are no igneous rocks for 25 km^2 around this ore field, except for a small ultramafic dike. The deposit is mostly stratiform, carbonate-hosted, and, to a lesser extent, black shale-hosted. It has collapsed breccias in limestones at shale contacts, important for lithologic control with silicification as the most common alteration. This has resulted in several prominent formations from early high temperature (200°–300°C) progressing to lower temperature (100°–200°C). These are classified as (1) quartz-stibnite, (2) calcite-stibnite, (3) barite-quartz-stibnite, and (4) fluorite-quartz-stibnite. They have many characteristics like some MVT or Irish-type Pb-Zn systems (but the metal is Sb vs. Pb-Zn).

Another major Chinese deposit is Woxi in Xiangxi District. It is a significant past producer of antimony since 1875 with estimated reserves of 94,600 t Sb in 1998. It is a series of deposits hosted in antiforms along the Woxi thrust. These are hosted in arkosic clastics, red and green shales, and slates—unconformity controls on fluid flow. It is mostly stratiform but also includes cross-cutting vein systems and



Source: Seal et al. 2017

Figure 1 Locations of selected antimony deposits, mines, and major mineral occurrences

replacement-style mineralization. There are no igneous rocks in the district. Likely fluids with deep crustal origin sourced the deposit in underlying basement, but with cryptic magmatic input. These are early high temperature (350°C) progressing to lower temperature (250°C). Typical deposit styles include (1) planar conformable quartz-stibnite veins, (2) sheeted quartz-scheelite veins, and (3) irregular quartz-scheelite-stibnite stockworks.

Other known Chinese deposits include Xujiashan, Songxi, and Qinling-Dabie. The Xujiashan deposit is in Hubei Province, South China. It has a genesis perhaps as a variant of an MVT. It is a carbonate-hosted stratiform located on the flank of a "basement" knob. It is hosted in dolomitized carbonates near lacustrine-dolomite transition with capping shales. Its isotopic signature is as a classic MVT and is very similar to the Dzhizhikrut deposit in Tajikistan and others in the Balkans and the Iberian Peninsula.

The Songxi deposit in Eastern Guangdong is an Ag-Sb association stratiform in black shale with high total organic carbon. There are volcanics, or sills, below the ore section. It is isotopic, and chemistry data suggest a hybrid nature. Its genesis could be as SedEx or possibly a distal VMS.

The Qinling-Dabie orogenic belt has more than 50 significant deposits. These are orogenic Au-Sb vein-hosted lodes in brittle-ductile shear zones. They have greenschist facies comprised of Devonian clastic rocks. It is a developing belt, but most antimony will be sacrificed to recovery of gold.

Antimony has been produced from ores in more than 15 countries. As shown in Table 2, world reserves of antimony are estimated to be about 1.5 Mt (million metric tons), and in 2017, global antimony production was estimated to be about 150,000 t (Guberman 2018). China, the leading global producer, accounts for over 70% of the world's mined production and most of the reserve base. (Reserves consist of demonstrated resources that are currently economic.) The reserve base consists of reserves plus marginally economic reserves and resources that are subeconomic. Moreover, China together with four other minor producing countries—Bolivia, the Republic of South Africa, Tajikistan, and Russia—currently account for more than 95% of total world antimony production. Table 3 lists domestic U.S. statistics including pricing for a recent seven-year period. As seen, the United States has a very high import reliance on antimony of more than 80% (Guberman 2017).

USES AND APPLICATIONS

Antimony compounds have been known since ancient times and were powdered for use as medicine and cosmetics, often known by the Arabic name, *kohl*. Antimony trioxide, Sb_2O_3, is now the most important antimony compound produced. Today, antimony trioxide is produced by controlled volatilization of antimony metal in an oxidizing furnace. It is used in halogen-compound flame-retarding formulations for adhesives, sealants, plastics, paints, textiles, and rubber. Major markets for flame retardants include electronics, plastics, and fabrics used in making children's clothing; aircraft and automotive seat covers; and bedding. During World War II, the fireproofing compound antimony trichloride ($SbCl_3$) saved the lives of many American troops when it was applied to tents and vehicle covers. In a fire, antimony and chlorine recombine to form unstable compounds that remove oxygen from the air, thereby smothering the flames (Gibson 1998; Eyi 2012).

Most commercial grades of antimony trioxide contain between 99.2% and 99.5% Sb_2O_3 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 products, which is a function of particle size. Antimony trioxide also finds growing use as a catalyst for PET (polyethylene terephthalate) 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 (cathode ray tube) glass. In the electronics industry, antimony 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 antifriction bearings. Antimony also has several pharmaceutical uses. Organic antimony compounds, such as antiprotozoal drugs, are used in the treatment of certain parasitic diseases. Potassium antimony tartrate ($K_2Sb_2(C_4H_2O_6)_2$) was formerly used as a nauseant and expectorant, although its use has been abandoned because of the compound's toxicity and because it is difficult to administer (Abdi et al. 2003).

Table 2 World mine production and reserves for antimony

Country	Mine Production, t			Estimated Mine Reserves, t
	2015	2016	2017	
United States	NA*	NA	NA	60,000
Australia	3,700	5,000	5,000	140,000
Bolivia	4,200	2,670	2,600	310,000
Burma	3,000	3,000	2,000	NA
China	110,000	108,000	110,000	480,000
Guatemala	NA	25	25	NA
Iran	NA	200	200	NA
Kazakhstan	NA	573	570	NA
Laos	NA	242	240	NA
Mexico	NA	196	200	18,000
Pakistan	NA	114	100	NA
Russia (recoverable)	9,000	8,000	8,000	350,000
South Africa	—	1,200	1,200	27,000
Tajikistan	8,000	14,000	14,000	50,000
Turkey	2,500	4,000	3,500	100,000
Vietnam	1,000	643	600	NA
World total (rounded)	**142,000**	**148,000**	**150,000**	**1,500,000**

Source: Guberman 2017, 2018
*NA = not available

Very high-purity antimony metal is used in the semiconductor industry in silicon wafers for making infrared detectors, diodes, and other devices. Antifriction bearings, type metal for mechanical type setting, and solder and decorative castings of Britannia metal and pewter also contain antimony. Graphite bearings are impregnated with antimony to increase heat tolerance. Antimony is used in nuclear reactors together with beryllium as start-up neutron sources. "Antimony black" is finely ground metallic antimony used in bronzing for metals and plaster casts.

Antimony sulfide will combust in the presence of oxygen. It is a key combustion-supporting ingredient in the manufacture of ammunition primers, detonators, smoke-screen generators, visual range-finding shells, tracer bullets, and the striking surface of safety matches. It is also used to provide the "glitter" effect in fireworks. The rubber industry uses antimony as a vulcanizing agent. Antimony is also used in ceramics and

Table 3 Annual salient antimony statistics for the United States

	2011	2012	2013	2014	2015	2016	2017 (estimated)
Production							
Mine	—*	—	—	—	—	—	—
Smelter							
Primary, t	W†	W	W	W	W	W	W
Secondary, t	2,860	3,050	4,410	4,230	3,850	3,780	3,700
Imports for consumption							
Ores and concentrates, t	NA‡	380	342	378	308	119	100
Oxide, and metal, t	23,500	22,300	24,300	23,800	22,500	23,300	24,000
Exports of metal, alloys, oxide, waste, and scrap, t	4,170	4,710	3,980	3,240	3,200	1,950	2,200
Apparent consumption, t	22,300	20,600	24,700	24,900	23,200	25,300	25,000
Price, U.S. cents/lb	650	565	463	425	327	335	401
Stocks, year-end, t	1,430	1,430	1,470	1,400	1,290	1,090	1,100
Plant employees, no.	24	24	24	27	27	27	27
Net import reliance, %	87	85	82	83	83	85	85

Source: Guberman 2017, 2018
*No domestic production.
†Information withheld.
‡NA = not available.

Table 4 Estimated plant capacities of historic leading producers of refined antimony

Company	Location	Total Capacity, t/yr as Sb	Products
Hsikwangshan Mining Administration	China	30,000	Metal, trioxide, pentoxide, sodium antimonate
Kadamjaisk Antimony Combine	Kyrgystan	20,000	Metal, trioxide
Amspec Chemical Corporation	United States	15,000	Trioxide
Laurel Industries Inc.	United States	12,500	Trioxide
Société Industrielle et Chimique de L'Aisne	France	12,000	Metal, trioxide
Campine	Belgium	10,000	Trioxide
Dachang Mining Administration	China	10,000	Metal
Mines de la Lucette	France	9,500	Metal
Enal	Bolivia	9,300	Trioxide
Great Lakes Chemical (Anzon)	United States	6,000	Trioxide
Union Minière	Belgium	6,000	Sodium antimonate
Guzhou Dushan Dongfeng	China	4,000	Metal, trioxide
Hubei Chongyang	China	4,000	Metal, trioxide
United States Antimony Corporation	Mexico and United States	1,500	Trioxide, sodium antimonate, metal
Sunshine Mining and Refining	United States	1,500	Metal, sodium antimonate
Total		**140,500 (estimated)**	

glassmaking. Sodium antimonate is used as a flame retardant as well as for removing bubbles from glass.

Currently, secondary production accounts for about 20% of total antimony production and takes place mainly through the recycling of lead–acid car batteries and, to a much smaller extent, through the valorization of antimony-containing residues from copper, lead, and gold production. These secondary sources of antimony are expected to become increasingly important because copper, lead, and gold processors must deal with lower-quality ores and tighter environmental regulations, making it more difficult simply to discard or stockpile antimony-containing residues (Dupont and Binnemans 2017). Accordingly, the major conservation practice within the antimony industry is the recycling of the metal in used lead–acid storage batteries, type metal, and Babbitt metal. 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. Camouflage 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.

Table 5 Estimated historic world mine capacity by main producing companies

Country	Company	Capacity, t/yr as Sb
Australia	Mandalay Resources	2,750
Bolivia	Various	5,460
Canada	Beaver Brook Antimony Mine	6,000
China	Hsikwangshan Twinkling Star	55,000
	Hunan Cheznu Mining	20,000
	China Tin Group	20,000
	Shenyang Huachang Antimony	15,000
Kazakhstan	Kazzinc	1,000
Kyrgyzstan	Kadamshai	500
Laos	SRS	500
Mexico	United States Antimony Mexico	500
Myanmar	Various	6,000
Russia	GeoProMining	6,500
South Africa	Consolidated Murchison	6,000
Tajikistan	Anzob	5,500
Thailand	Various	600
Turkey	Cengiz and Ozdemir Antimuan Madenleri	2,400
Total		**153,710 (estimated)**

Source: Roskill Consulting Group Limited 2011. Adapted courtesy of Roskill Information Services Limited.

Flame retardants continue to drive growth demand for antimony trioxide (Wintzer and Guberman 2015). The historic capacity of the world's major established antimony product producers is listed in Table 4. Table 5 lists a recent compilation of production capacities of global mining operations (Roskill Consulting Group Limited 2011). New production facilities are alleged to be under construction in Russia, Tajikistan, and Oman. According to their website, "Tri-Star [Resources] is a partner in the Oman Antimony Roaster Project, an antimony and gold production facility with capacity of up to 50,000 dry tonnes per annum of antimony concentrate, producing up to 20,000 tonnes of antimony and 60,000 ounces of gold" (Tri-Star Resources 2018). Overall, it is estimated that the distribution of antimony uses and consumption worldwide is flame retardants 72%, transportation including batteries 10%,

Table 6 Typical Chinese stibnite ore mineral processing results

Operation	Ore Grade, % Sb	Concentrate Grade, % Sb	Tailings Grade, % Sb	Sb Recovery, %
Hand sorting	2.25	7.80	0.12	95.95
Heavy media separation	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

Source: Xikuangshan Administration of Mines 1979

chemicals 10%, ceramics and glass 4%, and other 4%. The United States, Japan, and Western Europe, which together account for around 70% of world demand, dominate world consumption of antimony.

MINERAL PROCESSING

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 gravity concentration and flotation. Given that stibnite is the predominant mineral and China is the predominant producer, the industrial mineral processing of a typical Chinese stibnite ore will be elucidated.

A typical stibnite deposit may contain antimony sulfide along with pyrite and a gangue consisting of quartz, calcite, barite, kaolin, and gypsum. Ore grading about 2.7% Sb is treated by a combination of hand sorting, heavy medium separation, and flotation (Xikuangshan Administration of Mines 1964, 1979; Chen 1964; Huang et al. 1965). 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 treatment is carried out to give antimony lumps and tailings 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 in a closed circuit consisting of ball mills and spiral classifiers. The third section uses a ball mill in conjunction with a spiral classifier and provides the final ore feed to a fineness of 60% –200 mesh. Ore ranging from –35 to +10 mm is fed to a drum heavy media separator. Separation density is regulated at 2.62–2.56 g/cm^3 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/t), sodium diethyldithiocarbamate as a collector (75 g/t), shale oil as a collector (300 g/t), lead nitrate as an activator (150 g/t), pine oil as a frother (100 g/t), and kerosene (65 g/t) 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 given in Table 6 and a typical flow sheet is shown in Figure 2 (Xikuangshan Administration of Mines 1979).

PYROMETALLURGY

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% Sb are volatilized to antimony trioxide, 25%–40% Sb ores are smelted in a blast furnace, and 45%–60% Sb ores are treated by liquation or iron precipitation. A description of each of these, as well as oxide reduction, follows (Motoo 1974; Vladislav 1981; Xiao and Zhou 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 Equation 1, the sulfur is burned away at about 1,000°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 Equation 2.

$$2Sb_2S_3 + 9O_2 \rightarrow 2Sb_2O_3 + 6SO_2 \qquad \textbf{(EQ 1)}$$

$$2Sb + 1.5O_2 \rightarrow Sb_2O_3 \qquad \textbf{(EQ 2)}$$

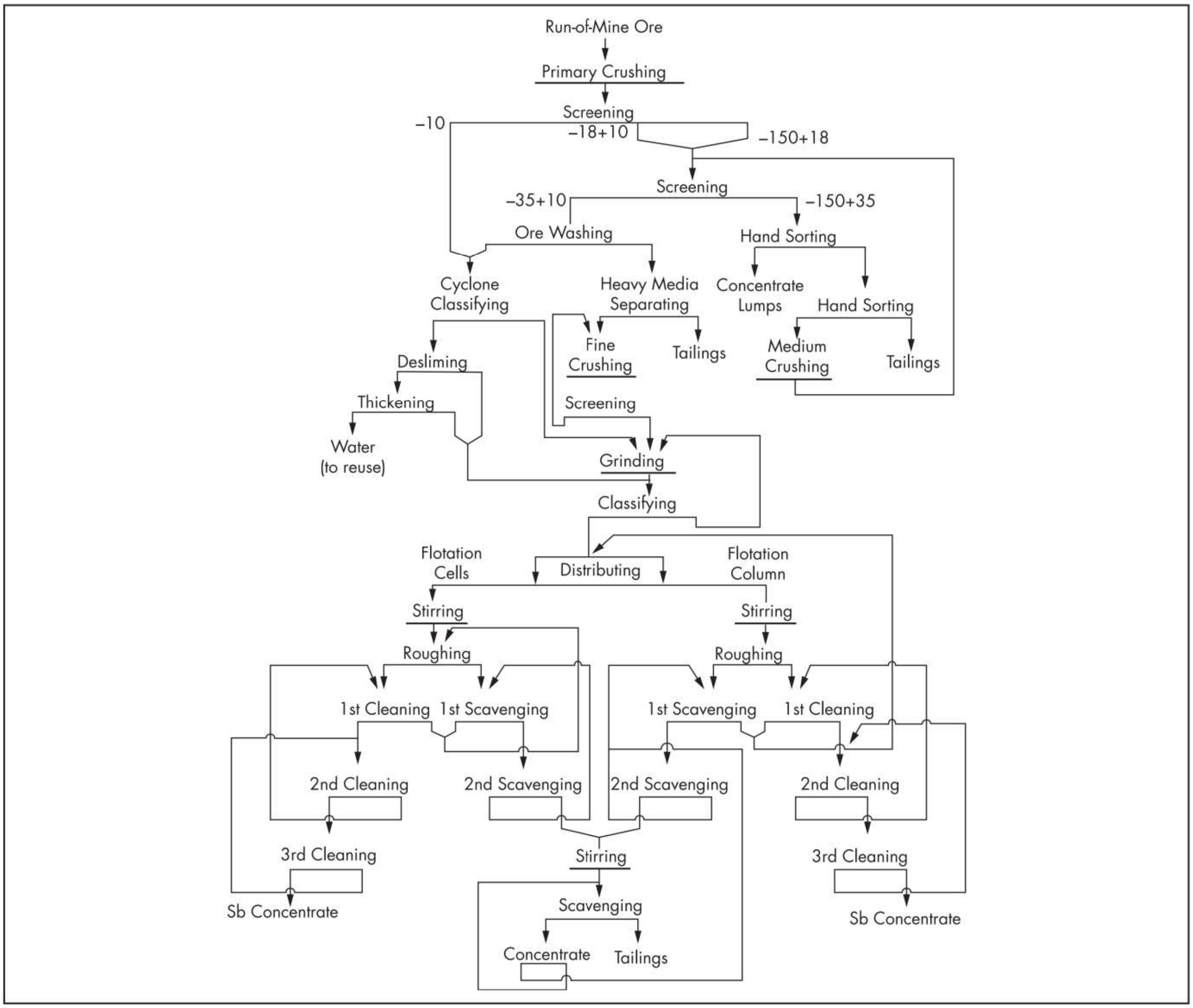
Liquation

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 Equation 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% Sb. 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.

$$Sb_2S_{3(s)} \rightarrow Sb_2S_{3(l)} \qquad \textbf{(EQ 3)}$$

Oxide Reduction

The oxides of antimony are reduced to metal with charcoal in reverberatory furnaces at about 1,200°C. This is illustrated in Equations 4 and 5. An alkaline flux consisting of soda, potash, and sodium sulfate is commonly used to minimize



Source: Xikuangshan Administration of Mines 1979

Figure 2 Typical Chinese antimony concentrator flow sheet

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.

$$Sb_2O_3 + 3CO \rightarrow 2Sb + 3CO_2 \qquad \textbf{(EQ 4)}$$

$$CO_2 + 3C \rightarrow 6CO \qquad \textbf{(EQ 5)}$$

Iron Precipitation

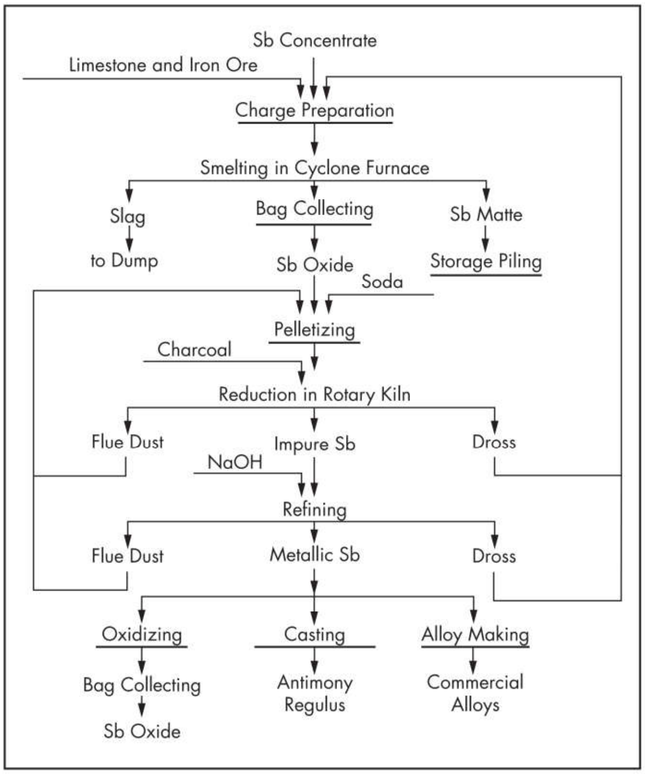
Rich sulfide ore or liquated antimony sulfide (crude antimony) is reduced to metal by iron precipitation. This is illustrated in the following equation:

$$Sb_2S_3 + 3Fe \rightarrow 2Sb + 3FeS \qquad \textbf{(EQ 6)}$$

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.

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 1,300°–1,400°C. Theoretically, this process is illustrated in Equations 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 25%–40% Sb that can be mixed with fluxes to give a charge sufficiently poor in metal to hold down



Source: Vladislav 1981

Figure 3 Flow sheet of the Bolivian Vinto antimony smelter

volatilization. As well, slag, usually running under 1% Sb, is desired because it tends to reduce volatilization losses.

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

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

A flow sheet for a primary pyrometallurgical production facility in Bolivia is shown in Figure 3 (Vladislav 1981). This facility was nationalized from Glencore by the Bolivian government.

HYDROMETALLURGY

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. There are only two solvent systems used in antimony hydrometallurgy. These are the alkaline sulfide system and the acidic chloride system. The alkaline sulfide system predominates.

Alkaline Sulfide System

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 through a complexation reaction. This can be illustrated as follows:

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

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

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 (all species in Equations 11–13 are aqueous species, except for elemental sulfur):

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

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

Because of 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:

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

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 as follows:

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

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

The primary cathode reaction is as follows:

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

The cathodic metal antimony product may attain a grade of more than 99.5% purity after washing. A typical industrial alkaline sulfide hydrometallurgical leach plant flow sheet is shown in Figure 4 (Ackerman et al. 1993). This industrial alkaline sulfide hydrometallurgical plant ran successfully for almost 60 years.

Acidic Chloride System

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 et al. 1975; Su 1981; Tang et al. 1988; 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 follows:

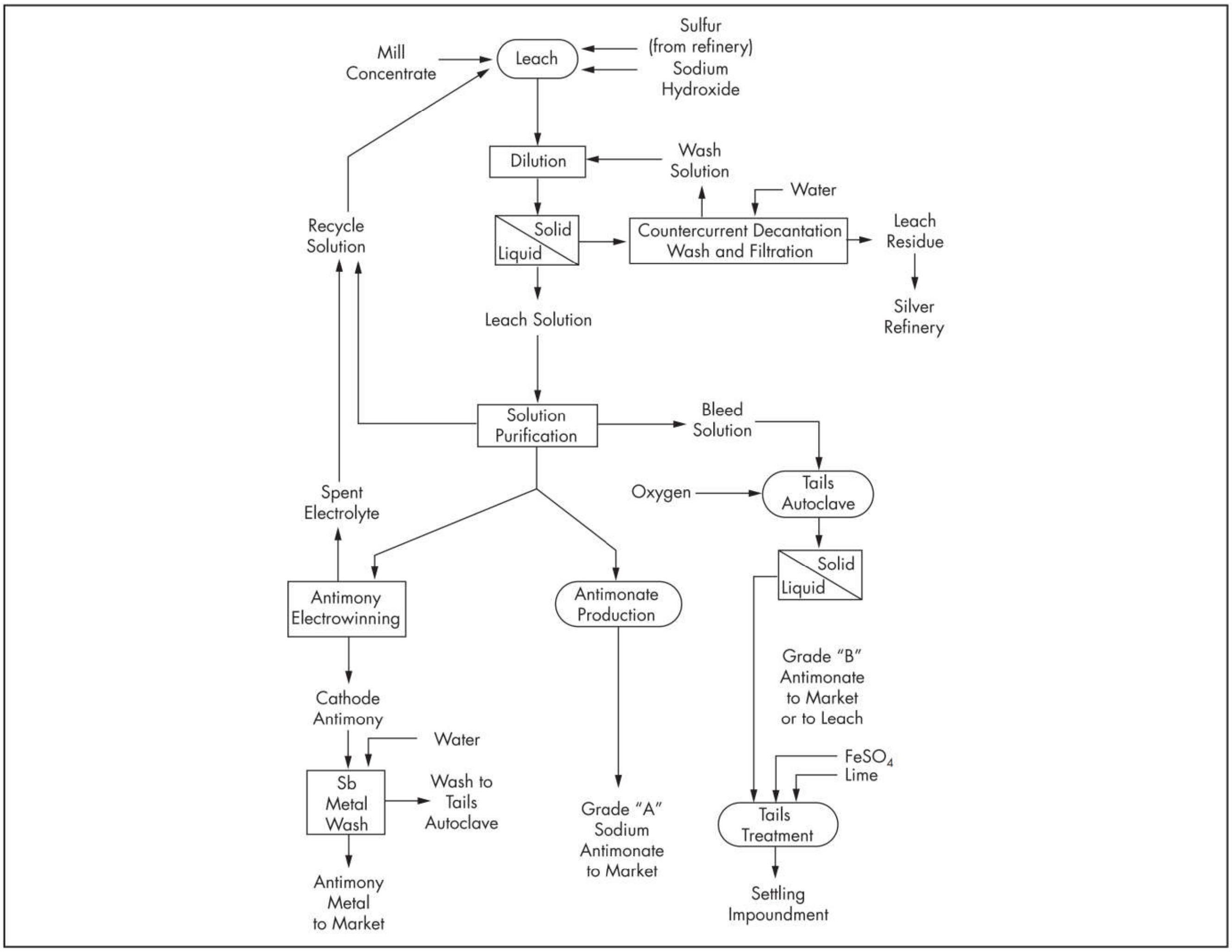
$$6FeCl_3 + Sb_2S_3 \rightarrow 2SbCl_3 + 6FeCl_2 + 3S^\circ \tag{EQ 17}$$

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

In the aqueous solution, $FeCl_3$ is 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

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

As with the alkaline sulfide system, the solubilized antimony chloride can be produced by electrowinning from



Source: Ackerman et al. 1993

Figure 4 Sunshine (Idaho) industrial hydrometallurgical alkaline sulfide antimony process

solution in diaphragm cells. This produces cathode antimony metal. The primary cathode reaction is

$$Sb^{+3} + 3e^- \rightarrow Sb \qquad \textbf{(EQ 20)}$$

The primary anode reactions are as follows:

$$Fe^{+2} \rightarrow e^- + Fe^{+3} \qquad \textbf{(EQ 21)}$$

$$3Cl^- + Fe^{+3} \rightarrow FeCl_3 \qquad \textbf{(EQ 22)}$$

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 in the following reactions:

$$SbCl_3 + H_2O \rightarrow SbOCl + 2HCl \qquad \textbf{(EQ 23)}$$

$$SbOCl + H_2O \rightarrow Sb_4O_5Cl_2 + 2HCl \qquad \textbf{(EQ 24)}$$

$$2SbOCl + 2NH_4OH \rightarrow Sb_2O_3 + NH_4Cl + H_2O \qquad \textbf{(EQ 25)}$$

$$Sb_4O_5Cl_2 + 2NH_4OH \rightarrow Sb_2O_3 + NH_4Cl + H_2O \qquad \textbf{(EQ 26)}$$

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 minimization of the corrosion issues that are associated with the chloride system.

PRODUCT QUALITY AND MARKETING

In ancient times, in extracting antimony from sulfide ore by the addition of iron, a starlike, fern-shaped crystalline pattern appeared during 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, a leaden appearance, or 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,

Table 7 Analysis of typical impure antimony production products

Element	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

Source: Xiao and Zhou 1981

Table 8 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

Source: Xiao and Zhou 1981

Table 9 Typical quality of antimony trioxide

Assay	Percentage
Sb_2O_3 content	99.5
As	<0.03
Pb	<0.08
F	<0.01
–325 Mesh	99.99

Source: Xiao and Zhou 1981

with the enhanced analytical techniques now available, specifications are now better defined. Tables 7, 8, and 9 (Xiao and Zhou 1981) indicate the typical quality and specifications for various antimony products.

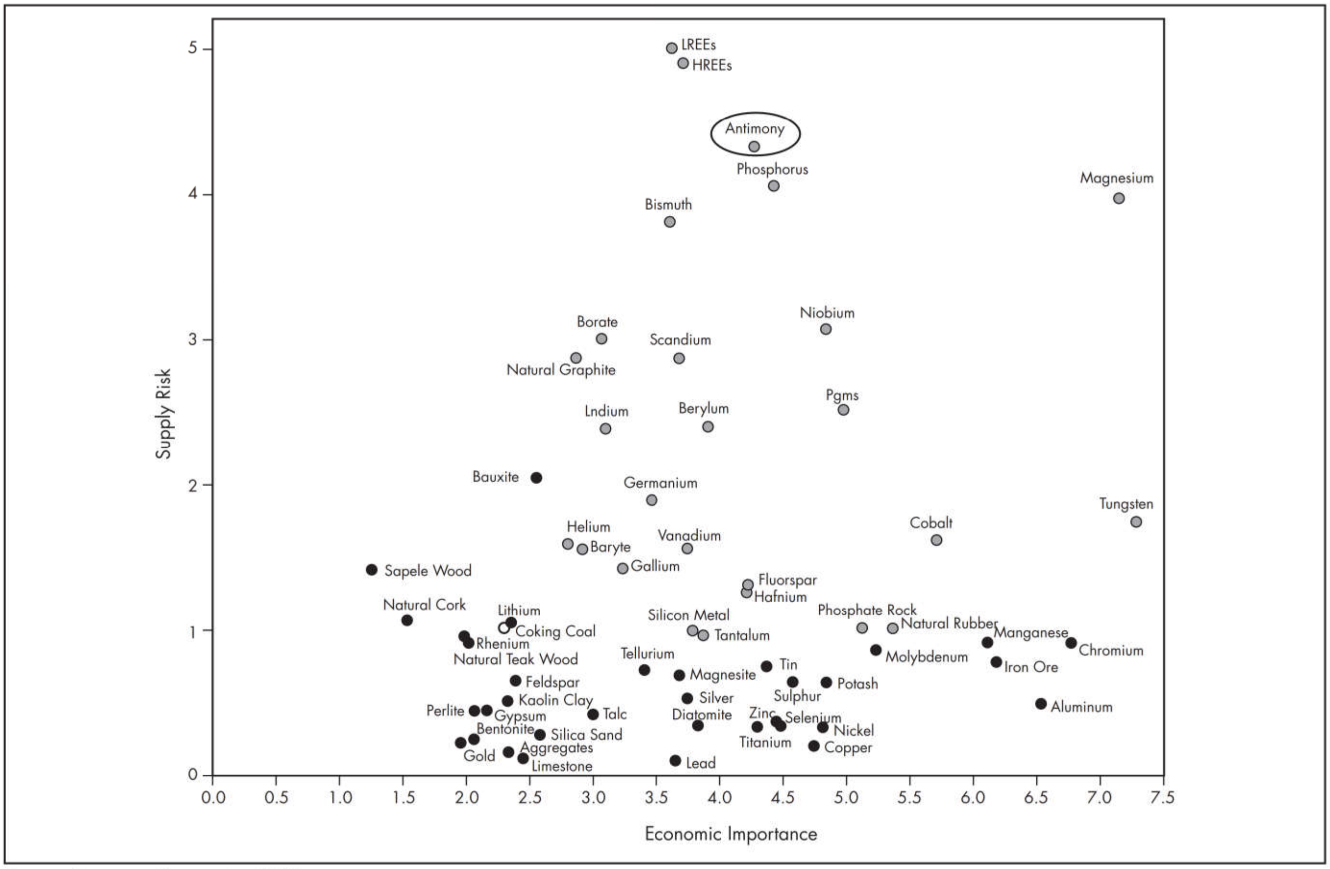
The marketing and sales of antimony metal and its compounds is subliminal. Entities such as the Chinese Fanya Metal Exchange were supposed to offer some insights, but the timeliness and reliability of the data have been suspect and called into question. According to Penfold World Trade, Metal Bulletin does publish a twice-weekly quotation for two metal grades, but there is no quotation for trioxide (B. Goldstein, personal communication). In China, several sources publish Chinese prices in local currency that may be indicative of pricing trends rather than of actual transactions. Unlike commodities such as copper or gold, there are no global exchanges for pricing and specifications. As such, the antimony market and its few entities are not transparent, and its trade aspects are generally closely held knowledge.

GLOBAL OUTLOOK

The European Union has studied and deemed antimony as a material of growing criticality, as illustrated in Figure 5 (European Commission 2018). In the figure, antimony is circled and it is near the top of the supply risk. This risk has grown in recent years.

Roskill (2018) provides a current projection of the imminent future for antimony:

> Antimony is mostly consumed in flame retardants and lead-acid batteries. Together these end uses accounted for 84% of antimony demand in 2017. Consumption trends in these two critical applications for antimony thus shape overall demand dynamics.
>
> In both cases, a similar situation prevails: while overall demand (for flame retardants and lead-acid batteries) has been steadily increasingly, the antimony loading within these applications has been reducing. In flame retardants, this is mainly because of high antimony prices prompting substitution of antimony, and legislative and requirements forcing changes to flame retardant formulas. In batteries, lead-calcium-tin alloys are increasingly being used instead of antimonial lead in battery grids for sealed-for-life maintenance-free automotive batteries, also called valve-regulated lead-acid (VRLA) batteries.
>
> Owing in part to these trends, demand for antimony in both non-metallurgical and metallurgical applications has stagnated in recent years. Consumption peaked in 2010 at around 201kt but has since declined year-on-year. Roskill expects that long-term demand for antimony in lead-acid batteries will continue to decline, with tin increasingly used instead of antimony, and lead-acid batteries themselves likely to fall victim to the EV boom over the longer term. While the outlook for construction and plastics is broadly positive, which suggests demand for flame retardants will increase, the future of antimony demand in flame retardants will remain highly sensitive to prices and the regulatory environment. Considering these factors, Roskill expects overall demand to grow at less than 1%py over the period to 2027.
>
> Importantly, Roskill believes the market may soon experience a fundamental shift. Antimony enters the supply chain in two ways: primary mine production, and secondary recovery of antimonial lead. In the mid-2020s, secondary supply from antimonial lead will be sufficient to meet metallurgical demand. As such, little or no primary supply will be required for metallurgical applications, making the metallurgical side of the market effectively "self-sufficient".
>
> With a modest growth in demand for antimony in non-metallurgical end uses expected, Roskill envisages that demand could start to outstrip current supply levels over the longer term. This would create a situation in which additional feedstock would be required, for supply to meet demand. This would need to be met from an increase in mine output from existing producers or new supply from potential producers. Alternatively, processors might look to utilize the growing surplus of secondary antimony available from antimonial lead although such recovery is not yet typical on a commercial scale.
>
> Global mine supply has been declining in recent years, mostly because of falling demand. However, there are considerable uncertainties over the future of mine production in China, with reports of dwindling reserves, falling grades and mine closures



Source: European Commission 2018

Figure 5 European commission critical raw materials matrix as of 2017

related to environmental inspections. Mine production has fallen from 115kt in 2010 to 80kt in 2017 according to Roskill estimates. Falling Chinese feedstock supply has been partially offset by increases in Tajikistan, Russia, and Australia. Environmental inspections and challenging market conditions have also led to a considerable reduction in Chinese smelter capacity. This could present an opportunity for new entrants into the market, although China will remain the dominant power in the antimony market for the foreseeable future.

SUMMARY

Globally, the primary production of antimony is now isolated to a few countries and is still dominated by China. Global resources and reserves are being depleted while demand is growing. Hence, antimony is currently deemed a critical and strategic material.

ACKNOWLEDGMENTS

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