

Mineralogy of Antimony Ores and Antimony Production

Subjects: **Others**

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Antimony is a metalloid element having common oxidation states of 5+ and 3+. It is a lustrous silvery-white solid, which is quite brittle and exhibits a flaky texture. Antimony is classified as a critical/strategic metal. Stibnite, jamesonite, and antimony-gold ores are the most common sources of antimony.

antimony

critical metals

extractive metallurgy

1. Introduction

Antimony is one of the medieval metals, and antimony-containing castings were found from 4000 BC in China. Metallic antimony was mistaken for stibnite until the early 17th century (1604) when Basilius Valentinus published a book titled “The Triumphal Chariot of Antimony” explaining antimony properties, applications, and winning methods. This is renowned as the beginning of human knowledge about antimony. Later in 1707, the French chemist Lémery published his “Traité de l’Antimoine”, which led to considerable acclaim for antimony.

The English word “antimony” is derived from the Greek words: anti [opposed] and monos [solitude], which means a metal that rarely occurs alone [1]. Native antimony has a strong affinity for sulfur and other metals such as copper, lead, and gold [2][3]. As a result, the development of extraction methods was very slow until the Japanese war in 1905. Its ability as an alloying element for lead, which could be used in the production of ammunitions that can penetrate armor plates, resulted in its wide usage during World Wars I and II, at which time China was the major producer by 30,000 to 40,000 tons of antimony per year [1]. Antimony use in military applications led to its classification as an important member of the “Strategic Metals” [4].

Antimony is a metalloid element having common oxidation states of 5+ and 3+. It is a lustrous silvery-white solid, which is quite brittle and exhibits a flaky texture. Natural antimony consists of a mixture of two stable isotopes that have atomic weights of 121 (57.25 wt%) and 123 (42.75 wt%); more than thirty radioactive isotopes of antimony are also known [3]. **Table 1** summarizes the important physicochemical and mechanical properties of antimony.

Table 1. Physicochemical and mechanical properties of antimony.

Properties/Characteristics	Value	Unit
Atomic number	51	N/A

Properties/Characteristics	Value	Unit
Atomic weight	121.76	u
Melting point	630.5	°C
Boiling point (at 101.3 kPa)	1325	°C
Density (at 20 °C)	6.688	g/cm ³
Tensile strength	10.8	N/mm ²
Mohs hardness	3.0-3.5	N/A
Modulus of elasticity	566	N/mm ²
Surface tension of solid (at 432 °C)	317.2	mN/m
Surface tension of liquid (at 1200 °C)	255	mN/m
Crystal structure	Rhombohedral	N/A
Lattice constant	$a = 0.437, c = 1.1273$	nm
Latent heat of fusion	10.49	kJ/mol
Latent heat of evaporation	195.10	kJ/mol
Coefficient of linear expansion (at 20 °C)	8-11	μm/m-°C
Electrical resistivity (at 0 °C)	37	μΩ.cm
Molar heat capacity of solid (at 630.5 °C)	30.446	J/mol-K
Molar heat capacity of liquid (at 630.5 °C)	31.401	J/mol-K
Thermal conductivity (at 0 °C)	25.9	W/m-K

2. Applications

Metallic antimony is brittle and has limited workability, but when alloyed in small amounts with other metals, it typically increases the hardness, resistance to wear, and improves castability. Historical applications of antimony included medicine and cosmetics (in powder form), battery grids, anti-friction bearing metals based on lead and tin, sheets and pipes [\[2\]](#), and type metals (60% Pb, ~25% Sb, and ~15% Sn), which is no longer the case because of off-set printing processes [\[5\]](#).

In World War II, antimony trichloride ($SbCl_3$) was widely used in tents and vehicle covers. In a fire, antimony and chlorine recombine to form unstable compounds that consume oxygen in the environment, leading to the flame suffocation. Later, antimony was significantly used in lead-acid batteries in automobiles to harden the lead from which the electrodes (grids) are made of. The hard lead contains 15–25% antimony [\[4\]](#). Lead-antimony alloys are used in starting-lighting-ignition batteries, ammunition, corrosion-resistant pumps and pipes, tank linings, and antifriction bearings [\[6\]](#). High-purity antimony is used in semi-conductors, infrared detectors, and diodes. Antimony

is also used in nuclear reactors together with beryllium [7] and pharmaceutical industry. Organic antimony compounds, such as antiprotozoal drugs, are used for certain parasitic diseases [6].

Antimony trioxide (ATO or antimony white) is now the most important antimony compound. Commercial grade is typically a fine and white powder, containing between 99.2% and 99.5% Sb_2O_3 and varying levels of other impurities (such as arsenic, lead, and iron) depending on the targeted application [4]. International Antimony Association provides the specifications required for the antimony trioxide products [8], provided in **Table 2**.

Table 2. Specifications of antimony trioxide products (adapted [8][9]).

Physical Form	Powder		
Particle size (μm)	0.2–44		
Constituents	Low PbO	Medium PbO	High PbO
Sb_2O_3 (wt%)	>98	>97.1 and \leq 99.6	>97 and \leq 99.6
PbO (wt%)	<0.25	>0.25 and <0.3	\geq 0.3 and <2.5
As_2O_3 (wt%)	<0.1	<0.1	<0.1
Other impurities (wt%)	<1.75	\leq 2.6	\leq 0.4

ATO is mainly used in flame-retardants, in conjunction with halogens for sealants, plastics, paints, rubber, fiberglass, aircraft, and automotive seat covers, children's clothing, textile goods, and electronic equipment [6]. Antimony trioxide is also used as a catalyst for polyethylene terephthalate (PET) production, polyester resins, phosphorescent agent in fluorescent light bulbs, and as an opacifier for porcelain [10].

Antimony pentoxide (Sb_2O_5) and sodium antimonate ($\text{NaSb}(\text{OH})_6$) are also used in flame retardants. Another application for sodium antimonate is in decolorizing and refining agents for optical and cathode ray tube glasses. Antimony trisulfide (Sb_2S_3) is used in the liners of automobile brakes and safety match compositions. Antimony pentasulfide (Sb_2S_5) is used as a vulcanizing agent in the production of red rubber [11][12]. The intermetallic compounds AsSb, GaSb, and InSb have found some applications in electronics as semiconductors [5][13][14].

3. Mineralogy of Antimony Ores

Antimony is not an abundant element, averaging ~0.2 g/tonne in the earth's crust, but it can be found in more than 100 different minerals [15]. Anderson [4] and Habashi [16] have provided detailed information on the occurrence, geology, and mineralogy of the antimony ores. Therefore, only antimony-containing minerals that are of higher industrial significance are listed in **Table 3**. These minerals have been categorized into three major groups, sulfides, oxides, and mixed minerals.

Table 3. Minerals of antimony with industrial significance.

Mineral		Chemical Formula	Sb (wt%)
Sulfides	Stibnite	Sb_2S_3	71.7
	Tetrahedrite	$\text{Cu}_6\text{Sb}_2\text{S}_6$	29.8
	Jamesonite	$\text{Pb}_4\text{FeSb}_6\text{S}_{14}$	35.4
Oxides	Zinckenite	PbSb_2S_4	42.1
	Senarmontite (cubic)	Sb_2O_3	83.5
	Valentinite (rhombohedral)	Sb_2O_3	83.5
Mixed	Cervantite (orthorhombic)	$\text{Sb}_2\text{O}_4/\text{Sb}_2\text{O}_3 \cdot \text{Sb}_2\text{O}_5$	79.2
	Stibiconite (antimony hydroxides)	$\text{Sb}_2\text{O}_4 \cdot \text{H}_2\text{O}$	74.8
Mixed	Kermesite	$2\text{Sb}_2\text{S}_3 \cdot \text{Sb}_2\text{O}_3$	83.5

Stibnite, jamesonite, and antimony-gold ores are the most common sources of antimony. The two formers are typically found with lead ores in nature [17]. Antimony-gold ores mostly consist of gold and antimony sulfide intergrowth and aurostibite (AuSb_2) [18]. Russia, Bolivia, Australia, and China have gold-antimony ore deposits [19]. Copper-rich sulfidic ores (e.g., tetrahedrite) have also received significant attention in recent years due to the depletion of richer ore bodies.

The most significant antimony-containing components that are present in different ore bodies, and intermediate or final products of the antimony production are listed in **Table 4**.

Table 4. Major antimony-containing compounds.

Element/ Compound	Sb	Sb_2S_3	Sb_2O_3	Sb_2S_5	Sb_2O_5	Sb_2O_4
Name(s)	<ul style="list-style-type: none"> • Antimony (Stibium) • Regulus (in product form) • Antimony Black 	<ul style="list-style-type: none"> • Antimony trisulfide (Rhombic) • Antimony Glance • Stibnite (mineral) 	<ul style="list-style-type: none"> • Antimony trioxide (ATO) • Valentinite (Cubic structure, chain allotrope mineral, 	<ul style="list-style-type: none"> • Antimony pentasulfide • Golden Antimony • mineral, 	<ul style="list-style-type: none"> • Antimony pentoxide 	<ul style="list-style-type: none"> • Antimony tetroxide • Carvantite (mineral)

Element/ Compound	Sb	Sb ₂ S ₃	Sb ₂ O ₃	Sb ₂ S ₅	Sb ₂ O ₅	Sb ₂ O ₄
(finely ground metal)	<ul style="list-style-type: none"> • Crudum (in molten form) • Senarmontite (Rhombic, cage allotrope mineral, stable >570 °C) • Needle Antimony (crystals after liquation) • Antimony Grey • Antimony white (powder product) 		stable <570 °C			
Melting point	630 °C	546–548 °C	656 °C	120–170 °C (decomposes to Sb ₂ S ₃ and S)	380 °C (decomposes)	930 °C (decomposes to ATO and oxygen)
Boiling point	1635 °C	1000–1150 °C	1425 °C (sublimes)	N/A	N/A	N/A

4. Antimony Production

In the '70s and '80s, Canada, Malaysia, Thailand, Japan, Italy, Spain, former Yugoslavia, and Czechoslovakia were among the main producers of antimony, but their production was ceased completely or reduced significantly. Canada, for example, was used to produce ~3000 tonnes/year of antimony in the late '70s, mainly using ores extracted from Consolidated Durham Mines and Resources Ltd., in New Brunswick, Canada. However, the mine operation was stopped in 1981. Teck's lead-smelter in Trail, British Columbia, was also used to produce antimony as a by-product, in small quantities [2], but the antimony metal is no longer among product lists of the operation [20].

According to U.S. Geological Survey 2022, almost 90% of the antimony mine production currently comes from three countries of China, Russia, and Tajikistan. The remaining 10% comes from other countries [21], shown in **Table 5**.

Secondary production accounts for ~20% of the total antimony production, and mainly originates from the recycling of lead-acid batteries and antimony-containing residues from lead-, copper- and gold-smelting processes [4].

China dominates mining of the raw materials and production of major antimony-bearing products (trioxide and metal). Antimony production in China is mainly concentrated in Hunan, Guangxi, Guizhou, Yunnan, and Gansu provinces [19]. China strictly controls the export rates and can put pressure on the market, which has led to an uncertain situation regarding the antimony price and availability for the demand of the western countries. Binz and

Friedrich [9] highlighted that this has been the main reason why the European Commission considered high supply risk and economic importance for antimony and listed it as one of the critical raw materials for the period 2015–2020. To manage the risk of dependence on foreign sources of antimony, the USA Government has stockpiled antimony for national defence purposes for several decades [3].

In addition to Europe and USA, Canada, Japan, and Australia also called antimony a critical metal due to its importance for transition to green energies (e.g., solar panels, windmills, and batteries), and the advance of the semiconductor industry and electronics [22][23][24].

Table 5. Main producers of antimony in the world.

Country	Mine Product. (t) [21]	Reserves (×1000 t) [21]	Main Producers [4]	Product [4]	Total Production Capacity (×1000 t/y Sb) [4]
USA	NA	60	Amspec Chemical Corporation Laurel Industries Inc. Great Lakes Chemical (Anzon) United States Antimony Corporation Sunshine Mining and Refining	Trioxide Trioxide Trioxide Metal, Trioxide, Na-antimonate Metal, Na-antimonate	15 12.5 6 1.5 1.5
Australia	3400	100			
Bolivia	2700	310	Enal	Trioxide	9.3
Burma	2000	140			
Canada	2	78			
China	60,000	480	Hsikwangshan Mining Administration Dachang Mining Administration Guzhou Dushan Dongfeng Hubei Chongyang Hunan Chenzhou Mining Co, Ltd., Guangxi China Tin Group Limited Yunnan Muli antimony industry Co., Ltd. Xikuangshan Flash-	Metal, Oxides, Na-antimonate Metal Metal, Trioxide Metal, Trioxide N/A N/A N/A Metal [25]	30 N/A 10 4 4 N/A N/A N/A 40

Country	Mine Product. (t) [21]	Reserves (x1000 t) [21]	Main Producers [4]	Product [4]	Total Production Capacity (x1000 t/y Sb) [4]
Antimony Industry Limited					
Guatemala	80	NA			
Iran	400	NA			
Kazakhstan	100	NA			
Kyrgyzstan	NA	260	Kadamjaisk Antimony Combine	Metal, Trioxide	20
Mexico	700	18			
Pakistan	20	26			
Russia (Recoverable)	25,000	350			
Tajikistan	13,000	50			
Turkey	1300	100			
Vietnam	400	NA			
France	NA		Société Industrielle et Chimique de L'Aisne	Metal, Trioxide	12
			Mines de la Lucette	Metal	9.5
Belgium	NA		AMG antimony [26]	Trioxide	10
			Campine	Na-antimonate	6
Oman			Union Minière/Umicore [5]		
			Strategic and Precious Metals Processing (SPMP) [10][28]	Metal, Trioxide	20 [27]
World Total (Rounded)	110,000	>2000		[13][29]	

on primary pyrometallurgical production routes.

Generally, the production of antimony can be via pyro- or hydro-metallurgical processes. More recently, bio-hydrometallurgical processes have also been proposed, but still at lab-scale [30][31]. Similar to lead, copper, and tin production, antimony is mainly extracted by pyrometallurgical methods. Hydrometallurgical routes, which are typically used for low-grade ores (<5% Sb) [32][33] and to minimize losses of precious metals (PMs), can be classified into two groups of alkaline leaching and acid leaching, followed by the electrodeposition of metallic antimony at the cathode or hydrolysis with NaOH or NaH₄OH to produce Sb₂O₃ [32][34][35][36][37][38][39][40][41][42][43][44][45][46][47][48]. An example is a process used at Sunshine Mining Co (between Kellogg and Wallace, ID, USA) [49]. Furthermore, the production of antimony based on electrolysis of Sb₂S₃ [50] have been recently developed in a lab

scale to mitigate SO₂ pollution and CO₂ emissions. More specifically, molten salt electrolysis of antimony smelting is a new development in the direction of antimony clean production [51][52].

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