Hydrometallurgically Treating Antimony-Bearing Industrial Wastes

C.G. Anderson

In many instances, by-products or wastes containing antimony are generated during metallurgical processes. Although these materials pose environmental, recycling, and marketing challenges worldwide, the use of antimony hydrometallurgical leaching principles and technologies may provide a remedy. This paper outlines techniques for treating antimony-containing wastes and offers examples of applications for those wastes and by-products.

INTRODUCTION

Antimony is a silvery, white, brittle, crystalline solid that is a poor conductor of electricity and heat.[1] 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 1,380°C. Antimony and the natural sulfide of antimony were known as early as 4000 B.C. Among the early uses of antimony or the sulfide were a coating for copper between 2500 B.C. and 2200 B.C., an eyebrow paint in early biblical times, and material for a vase found at Tello, Chaldea. Antimony is seldom found 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 into 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. Later, during World War I, it was found to be the best material for penetrating armor plate. A variety of compounds containing antimony as the major constituent were also used for ammunition such as detonators, tracer bullets, and armory. Mass production of automobiles gave a further boost to antimony, as it is a major constituent of lead-acid batteries used in cars. The major use for antimony is now as a trioxide for flame-retardants.

The abundance of antimony in the Earth's crust is approximately 0.2 g/t. 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. Industrially, stibnite (Sb_2S_3) is the pre-dominant ore of interest and importance. Stibnite deposits are usually small and found in quartose veins, which were products of intrusive igneous activity. The veins are usually found at shallow depths and frequently contain minor amounts of gold, silver, and mercury sulfides.

Antimony is produced from ore in more than 15 countries. World reserves of antimony are estimated to be from four to five million tonnes. China, the leading producer, accounts for about 80% of the world's mined production and the majority 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 sub-economic). China, together with the three other major producing countries, Bolivia, the Republic of South Africa, and the former countries of the Soviet Union, currently accounts for about 95% of the total world antimony production.

Antimony trioxide (Sb_2O_3), the most important antimony compound, is produced in an oxidizing furnace by volatilizing antimony metal. 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 their product's relative tinting strength, which is a function of particle size. Antimony trioxide is also a catalyst for polyethylene terephthalate production, while antimony pentoxide and sodium antimonate, $NaSb(OH)_6$, are used as flame retardants. Antimony compounds, primarily sodium antimonate, are used in decolorizing and refining agents for optical glass and cathode-ray tube glass.

Antimony metal also has a role in the 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 a lead bullion. The bullion is then refined in reverberatory furnaces to meet specifications. Lead-antimony alloys are used in starting-lighting-ignition batter-ies, ammunition, corrosion-resistant pumps and pipes, tank linings, roofing sheets, solder, cable sheaths, and anti-friction bearings.

Conservation efforts within the antimony industry include the recycling of the metal in used storage batteries, type metal, and babbit, and recovery of antimonial lead and antimony metal 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 serve as white pigments in paints, whereas antimony trisulfide and pentasulfide yield black, vermilion, yellow, and orange pigments. Antimony trisulfide, which reflects infrared radiation, is found in camouflage paints; antimony trisulfide is used in the liners of automobile brakes and in safety-match compositions; and antimony pentasulfide is used as a vulcanizing agent in the production of red rubber. Antimony compounds are also used in catalysts, pesticides, ammunition, and medicines.

Mine production, although lower than in recent years and considerably below refining capacity, remains more than sufficient to cover world demand. The largest refineries, such as HMA in China and KAC in Kyrgyzstan, are only running at about half capacity. Flame retardants continue to drive growth demand for antimony trioxide, with consumption forecast to rise by 3.6% annually. 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 United States, Japan, and Western Europe, which together account for around 70% of world demand, dominate world consumption of antimony.

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 leach-

Table I. Lead Smelter Speiss Treatment (Values in Percent Unless Otherwise Noted)										
	Cu	Ni	Sn	Cd	As	Sb	Pb	Fe	Zn	Au	Ag
Head Sample Assay	43.5	1.4	0.5	0.1	12.2	3.3	14.8	1.7	0.9	45.0 g/t	9 kg/t
Metal Leached	0.0	0.0	2.0	0.0	99.1	99.4	0.0	0.0	0.0	9.1	0.0

Leach Testing Conditions: Leach Time: 6 h; Percent Solids: 25%; Leach Temperature: 105°C; Total Sulfur Concentration: 100 g/L; Free Hydroxide Concentration: 25 g/L

ing followed by electrodeposition. In reality, only two solvent systems are utilized in antimony hydrometallurgy: alkaline sulfide and acidic chloride. Of the two, the alkaline-sulfide system predominates.

The alkaline-sulfide system is employed industrially in the Commonwealth of Independent States, China and the United States.[2] 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

$$Na_2S + Sb_2S_3 \rightarrow 2NaSbS_2 \qquad (1)$$

$$NaSbS_2 + Na_2S \rightarrow Na_3SbS_3 \qquad (2)$$
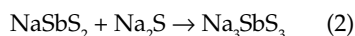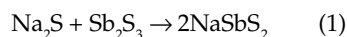
However, dissolution of elemental sulfur in sodium hydroxide is also used as a lixiviant for alkaline-sulfide leaching of antimony.[3] The combination of sodium hydroxide and elemental sulfur results in the formation of species other than just sulfide (S^{-2}); both sodium polysulfide (Na_2S_x) and sodium thiosulfate ($Na_2S_2O_3$) are created along with sulfide. This is illustrated simplistically in the following:

$$4S^O + 6NaOH \rightarrow 2Na_2S + Na_2S_2O_3 + 3H_2O \qquad (3)$$

$$(X–1)S^O + Na_2S \rightarrow Na_2S_x \\ \text{(where X= 2 to 5)} \qquad (4)$$
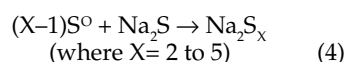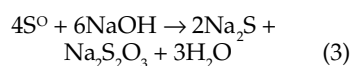
Due to the oxidizing power of polysulfide on sodium thioantimonite, the major species in solution is normally sodium thioantimonate (Na_3SbS_4). This can be viewed as follows:

$$Na_2S_x + (X–1)Na_3SbS_3 \rightarrow \\ (X–1)Na_3SbS_4 + Na_2S \qquad (5)$$
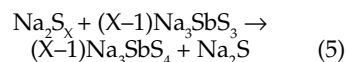
The electrodeposition of the antimony from the alkaline-sulfide solution to cathode metal is normally carried out via electrowinning in either diaphragm or non-diaphragm cells.[4,5] The cathodic-metal antimony product may attain a grade over 99.5% pure after washing.

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.[6–10]

In the acidic-chloride hydrometallurgical antimony system, hydrochloric acid, often in conjunction with ferric chloride, is commonly used as the solvent for a sulfide mineral such as stibnite. This is illustrated as
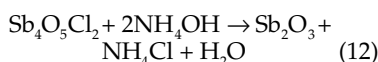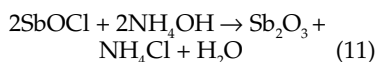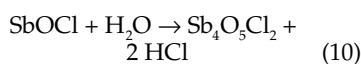
$$6FeCl_3 + Sb_2S_3 \rightarrow 2SbCl_3 + 6FeCl_2 + 3S^O \qquad (6)$$

$$Sb_2S_3 + 6HCl \rightarrow 2SbCl_3 + 3H_2S \qquad (7)$$
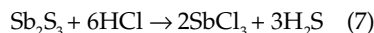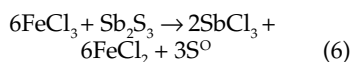
In the aqueous solution, $FeCl_3$ does the job of both an oxidizer and a chloridizing agent to convert the antimony of the sulfide mineral into a chloride complex while producing elemental sulfur.

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

$$Sb_2O_3 + 6HCl \rightarrow 2SbCl_3 + 3H_2O \qquad (8)$$
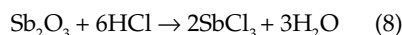
As with the alkaline-sulfide system, the solubilized antimony chloride can be eletrowon from solution in diaphragm cells. This produces cathode a pure antimony metal while regenerating the lixiviant at the anode.

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.[11] This is illustrated as

$$SbCl_3 + H_2O \rightarrow SbOCl + 2HCl \qquad (9)$$

$$SbOCl + H_2O \rightarrow Sb_4O_5Cl_2 + 2HCl \qquad (10)$$

$$2SbOCl + 2NH_4OH \rightarrow Sb_2O_3 + NH_4Cl + H_2O \qquad (11)$$

$$Sb_4O_5Cl_2 + 2NH_4OH \rightarrow Sb_2O_3 + NH_4Cl + H_2O \qquad (12)$$

In summary, of the 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.

SECONDARY PRODUCTS

The rest of this paper deals with the specific leaching application of the two hydrometallurgical systems to antimony secondary materials typically encountered in industry. As is the case in plant operations, the majority of the examples illustrate the alkaline-sulfide leaching system. And, due to space constraints, only the leach results are shown except for results of a novel, selective, gold-

recovery technique. The proven techniques and accompanying industrial flowsheets used to produce antimony products from the leach solutions is beyond the scope of this paper. However, they will be illustrated in future publications.

Lead-Smelter Speiss

The formation of speiss in lead smelters is a common occurrence and poses process problems because significant levels of precious metals are accumulated in the resultant arsenides and antimonides. An example of hydrometallurgical treatment is shown in Table I.

Lead-Softening Skims

The formation of arsenic and antimony skims is common in lead refining. An example of hydrometallurgical treatment is shown in Table II.

Lead-Smelter Copper-Dross Flue Dust

Arsenic- and antimony-laden dusts are commonly formed in lead processing. An example of hydrometallurgical treatment is shown in Table III.

Copper Electrorefining Slimes

In the electrorefining of copper anodes, slime formation and treatment is always a necessary challenge due to the presence of significant levels of precious metals. An example of hydrometallurgical treatment for antimony and arsenic removal from de-copperized and de-selenized slimes is shown in Table IV.

Pyrometallurgical-Antimony-Oxide Plant Residues

In the pyrometallurgical production of antimony trioxide from antimony metal, waste accretions and residues accumulate which contain precious and base metals in alloy form with antimony. An example of hydrometallurgical treatment is shown in Table V.

Table II. Lead Softening Skims Treatment (Values in Percent)			
	As	Sb	Pb
Head Sample Assay	3.3	31.7	52.9
Metal Leached	96.0	89.0	0.0

Leach Testing Conditions: Leach Time: 6 h; Percent Solids: 25%; Leach Temperature: 105°C; Sulfide Concentration: 100 g/L; Free Hydroxide Concentration: 10 g/L

Table III. Copper Dross Flue Dust Treatment (Values in Percent)					
	In	Pb	Sb	As	Zn
Head Sample Assay	0.3	46.0	9.0	12.0	11.0
Metal Leached	0.0	0.0	95.0	99.0	0.0

Leach Testing Conditions: Leach Time: 6 h; Percent Solids: 25%; Leach Temperature: 105°C; Sulfide Concentration: 100 g/L; Free Hydroxide Concentration: 10 g/L
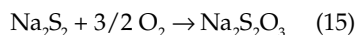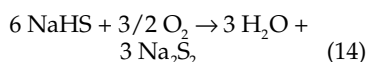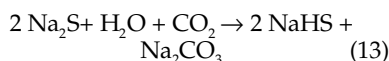
Table IV. Copper Electrorefining Slimes Treatment (Values in Percent Unless Otherwise Noted)

	Cu	Ni	Se	Te	As	Sb	Bi	Pb	Au	Ag	Pt	Pd
Head Sample Assay	1.0	1.0	0.2	0.2	2.0	8.3	2.0	35.7	16.5 kg/t	18.2	0.05	0.06
Metal Leached	0.0	0.0	0.3	0.0	99.3	99.5	0.0	0.0	7.2	0.0	0.0	0.0

Leach Testing Conditions: Leach Time: 6 h; Percent Solids: 25%; Leach Temperature: 105° C; Sulfide Concentration: 100 g/L; Free Hydroxide Concentration: 10 g/L

Table V. Pyrometallurgical Antimony Oxide Plant Reside Treatment (Values in Percent)

	Cu	Sb	Pb	Au	Ag
Head Sample Assay	12.0	63.0	18.0	2.4	3.1
Metal Leached	0.0	99.5	0.0	15.3	0.0

Leach Testing Conditions: Leach Time: 6 h; Percent Solids: 25%; Leach Temperature: 105° C; Total Sulfur Concentration: 100 g/L; Free Hydroxide Concentration: 25 g/L

Alkaline Sulfide Gold Recovery

In the examples cited, it is essential that any gold leached in the alkaline-sulfide solutions be recovered. Gold lixiviation is the result of leaching by polysulfides and thiosulfates. These are formed directly from the dissolution of sulfur in caustic, as previously illustrated in chemical Equations 3 and 4 or from pure sodium-sulfide solutions that are oxidized with air and carbon dioxide. This is illustrated as follows:

$$2\,Na_2S + H_2O + CO_2 \rightarrow 2\,NaHS + Na_2CO_3 \tag{13}$$

$$6\,NaHS + 3/2\,O_2 \rightarrow 3\,H_2O + 3\,Na_2S_2 \tag{14}$$

$$Na_2S_2 + 3/2\,O_2 \rightarrow Na_2S_2O_3 \tag{15}$$

$$Au^O + S_5^{-2} \rightarrow AuS_5^- + e^- \tag{16}$$

$$Au^O + S_2O_3^{-2} \rightarrow AuS_2O_3^- + e^- \tag{17}$$

Conventional methods of gold recovery such as zinc or aluminum cementation are not applicable to this type of solution because of the dangers associated with stibine- or arsine-gas generation. Also, the conventional method of direct collection of gold by activated carbon does not work in these solutions as it does for gold-cyanide solutions.

A novel gold-recovery practice[12] has been adopted to quantitatively and selectively recover gold from complex alkaline-sulfide solutions containing a mixture of metals such as arsenic, tin, mercury, and antimony. This is illustrated by selectively removing gold from an alkaline-sulfide leach solution containing these impurities. The overall results are presented in Table VI.

Further stages of gold-recovery treatment on this solution indicate that almost 100% of the gold can be selectively recovered from the mercury, arsenic, tin, and antimony in the solution. In addition, the substrate solids which have been employed to load the gold consist of several cheap and readily available

Table VI. Overall Gold Selectivity and Recovery (Values in Percent)

	Liquid	Solid
Au	16.5	83.5
Sb	100.0	0.0
As	100.0	0.0
Sn'	100.0	0.0
Hg	100.0	0.0

Table VII. Spent Antimony Catalyst (Values in Percent)

	Si	Sb
Head Sample Assay	2.3	39.3
Metal Leached	0.0	99.5

Leach Testing Conditions: Leach Time: 6 h; Percent Solids: 25%; Leach Temperature: 100° C; HCl Concentration: 2 Normal

materials. Direct processing of the material is probably the cheapest and most effective method of refining the gold.

Spent Antimony Catalyst

In the petrochemical industry, antimony is used as a catalyst for the direct oxidation of propylene to acrolein. Hydrometallurgically, the antimony catalyst is best recycled with the chloride system. Use of the alkaline system would solubilize the silica substrate causing downstream separation and product-quality issues. An example of this application is shown in Table VII.

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C.G. Anderson is with the Center for Advanced Mineral and Metallurgical Processing at Montana Tech of the University of Montana.

For more information, contact C.G. Anderson, Montana Tech of the University of Montana, the Center for Advanced Mineral and Metallurgical Processing, Room 221 ELC Building, Butte, Montana 59701; telephone/fax (406) 496-4794; e-mail: CAnderson@mtech.edu.