Arsenic, Antimony, and Bismuth
Production

Arsenic, antimony, and bismuth are three metalloids that usually occur together in association with copper, lead, tin, and gold ores. Bolivia is the only country in the world where bismuth is found in sufficient concentration to justify mining for bismuth alone, while in Morocco both arsenic oxide and metallic cobalt are recovered from a unique deposit of cobalt arsenide mineral, skutterudite (Co,Fe)As₆.

These elements and many of their compounds were known to the alchemists of the Middle Ages. The reason may be the ease with which they can be obtained from their ores. For example, arsenic can be volatilized from arsenopyrite and loellingite when the minerals are heated in the absence of air:

\[
\text{FeAsS} \rightarrow \text{FeS} + \text{As} \\
\text{FeAs}₃ \rightarrow \text{FeAs} + \text{As}
\]

All three elements and their compounds are highly toxic. However, certain compounds are used under restricted conditions for medical purposes, e.g., Salvarsan is a derivative of arsenobenzene used for treating syphilis; tartar emetic, potassium antimonyl tartrate, is used as an emetic and for the treatment of some tropical diseases; and bismuth nitrte is used for treating intestinal disorders. Pertinent data on arsenic, antimony, and bismuth are given in Table 1. As metalloids, arsenic and antimony exist in different modifications; some have metallic character and some have nonmetallic character. The atoms in all three elements are united together by covalent bond forming a layered structure.

In nature, arsenic, antimony, and bismuth are present in an insoluble form, but during the pyrometallurgical treatment of their raw material, soluble compounds are formed, hence the danger of contaminating the environment. Further, during these operations, arsenic-bearing SO₃ is generated, which is used to produce H₂SO₄. The bulk of this acid is generally used to manufacture fertilizers, hence the danger that arsenic enters into the food chain. In addition, all metallurgical plants handling arsenic-containing material are faced with the problem of safe disposal of trace amounts of arsenic in solutions generated in disposal ponds. Some plants, however, prefer to dispose of small volumes of high concentrations of arsenic as hazardous waste instead of treating the material to get a marketable product and process the large volumes of waste solutions or residues for safe, long term disposal.

1. Compounds

While there are many similarities in the compounds of these elements, there are also remarkable differences.

1.1 Sulfides

(a) Arsenic sulfides. Arsenic sulfides occurring in nature are realgar, As₄S₄; orpiment, As₂S₃; arsenopyrite, FeAsS; and enargite, Cu₃AsS₄. Realgar can be distilled without decomposition while orpiment melts at 310°C and boils at 707°C without decomposition. Both are insoluble in water and acids, even in concentrated HCl, but dissolve readily in alkaline reagents, especially alkali sulfide solutions, forming thiosalts. For example:

\[
\text{As}_2\text{S}_3 + 3\text{S}^2- \rightarrow 2[\text{AsS}_3]^3-
\]

\[
\text{As}_2\text{S}_3 + 6\text{OH}^- \rightarrow [\text{AsS}_3]^3- + [\text{AsO}_3]^3- + 3\text{H}_2\text{O}
\]

Arsenic sulfides are precipitated from an acidified solution containing trivalent arsenic by H₂S:

\[
2\text{As}^{3+} + 3\text{H}_2\text{S} \rightarrow \text{As}_2\text{S}_3 + 6\text{H}^+
\]

(b) Antimony sulfides. Antimony sulfide occurring in nature is stibnite, Sb₂S₃, also known as antimonite. It is soluble in concentrated HCl and in alkali sulfide to form a thiosalt. For example:

\[
\text{Sb}_2\text{S}_3 + 3\text{S}^2- \rightarrow [\text{SbS}_3]^3-
\]

Antimony sulfides Sb₂S₃ and Sb₂S₅ can be obtained by melting the components together, or by precipitation by H₂S from acidified solutions containing trivalent or pentavalent antimony, respectively.

(c) Bismuth sulfide. Bismuth sulfide occurs in nature as bismuthite Bi₂S₃, also known as bismuth glance. It is a volatile compound and is insoluble in alkali sulfides. It is precipitated from an aqueous solution of a bismuth salt by H₂S:

\[
2\text{Bi}^{3+} + 3\text{H}_2\text{S} \rightarrow \text{Bi}_2\text{S}_3 + 6\text{H}^+
\]

1.2 Oxides

(a) Arsenic trioxide. Arsenic trioxide is obtained as a white smoke by roasting arsenopyrite or other native arsenides:

\[
2\text{FeAsS} + 5\text{O}_2 \rightarrow \text{Fe}_2\text{O}_3 + \text{As}_2\text{O}_3 + 2\text{SO}_4
\]

Two forms of oxide are known depending on the temperature of condensation. The vapor condenses in the form of glass above 310°C and as a mass of octahedral crystals below this temperature. The glassy form is more soluble in water than the crystalline form. The solubility of crystalline As₂O₃ in 100 ml water, is 1.2 g at 0°C, 2.1 g at 25°C, and 6.0 g at 75°C.
The solution is acidic and is referred to as arsenious acid:

\[ \text{As}_2\text{O}_3 + \text{H}_2\text{O} \rightarrow 2\text{HASO}_3 \]

\[ \text{As}_2\text{O}_3 + 2\text{H}_2\text{O} \rightarrow 2\text{H}_3\text{AsO}_3 \]

It can be oxidized by concentrated HNO\(_3\) or H\(_2\)O\(_2\) to form arsenic acid:

\[ \text{HASO}_3 + \frac{3}{2}\text{O}_2 + \text{H}_2\text{O} \rightarrow \text{H}_3\text{AsO}_4 \]

which separates after evaporating the solution as hydrated crystals. Arsenic acid is highly soluble in water: 630 g dissolves in 100 g water at 20°C. On dehydration it yields arsenic pentoxide, As\(_2\)O\(_5\).

(b) Antimony trioxide. Antimony trioxide is formed as a white smoke by roasting antimony sulfide in a limited supply of air:

\[ \text{Sb}_2\text{S}_3 + \frac{3}{2}\text{O}_2 \rightarrow \text{Sb}_2\text{O}_3 + 3\text{SO}_2 \]

When roasting is conducted in an excess air the nonvolatile tetroxide is formed:

\[ \text{Sb}_2\text{S}_3 + 5\text{O}_2 \rightarrow 2\text{Sb}_2\text{O}_5 + 3\text{SO}_2 \]

The tetroxide is a double oxide of Sb\(_2\)O\(_5\) and Sb\(_3\)O\(_6\), better represented as Sb\(_{11}\)Sb\(_5\)O\(_{15}\). Both Sb\(_2\)O\(_5\) and Sb\(_3\)O\(_6\) hydrate yield the tetroxide when heated in air at 800–900°C. The oxides and oxide hydrates are insoluble in water. Antimony trioxide is insoluble in dilute H\(_2\)SO\(_4\) and HNO\(_3\), but dissolves in HCl. It also dissolves in alkalis to form antimonates. The alkali antimonates, e.g., NaSb(OH)\(_4\), obtained by the oxidation of the antimonates, are insoluble in water.

(c) Bismuth trioxide. Bismuth trioxide is non-volatile, and is obtained as a powder by roasting the sulfide:

\[ \text{Bi}_2\text{S}_3 + \frac{3}{2}\text{O}_2 \rightarrow 2\text{Bi}_2\text{O}_3 + 3\text{SO}_2 \]

It is insoluble in water, dissolves in acids, but not in dilute alkali hydroxides. Bismuth hydroxide, Bi(OH)\(_3\), is precipitated by hydroxyl ions from bismuth salt solutions. Bismuth pentoxide, Bi\(_2\)O\(_3\), in hydrated form is obtained by oxidizing the hydroxide with HNO\(_3\). It is insoluble in water and decomposes when heated at 150°C.

1.3 Chlorides

(a) Arsenic trichloride. Arsenic trichloride, AsCl\(_3\), is the only known arsenic chloride. It is a colorless liquid, density 2.17, m.p. −16°C, b.p. 130.2°C. It is formed by reacting arsenic with chlorine, As\(_2\)O\(_3\), with HCl gas at 180–200°C, or by dissolving As\(_2\)O\(_3\) in concentrated hydrochloric acid and distilling off the formed chlorides.

(b) Antimony trichloride. Antimony trichloride, SbCl\(_3\), in best obtained by dissolving stibnite in hot concentrated HCl:

\[ \text{Sb}_2\text{S}_3 + 6\text{HCl} \rightarrow 2\text{SbCl}_3 + 3\text{H}_2\text{S} \]

(c) Antimony pentachloride. Antimony pentachloride, SbCl\(_5\), is obtained by treating the trichloride with chlorine.

(d) Bismuth trichloride. Bismuth trichloride, SbCl\(_3\), is the only bismuth chloride known. It is best prepared by dissolving Bi\(_2\)O\(_3\) in hydrochloric acid.
1.4 Hydrides
Arsenic, antimony, and bismuth form colorless gaseous hydrides, having the general formula MH₃, which are highly toxic. They are formed under certain conditions when arsenides, antimonides, and bismuthides react with acids. They may also form in metallurgical plants during electrowinning or cementation processes. Arsine decomposes when it is passed through a heated glass tube:

$$A_3H_3 \rightarrow As + \frac{3}{2}H_2$$

Arsenic is deposited just beyond the heated zone, in the form of a black metallic mirror. This is a test for arsenic known as Marsh’s test. Arsine precipitates metallic silver from silver nitrate solution (Gutzeit test):

$$ASH_3 + 6Ag^+ \rightarrow 6Ag + As^{3+} + 3H^+$$

2. Aqueous Chemistry

2.1 Arsenic in Solution

(a) Arsenious acid. Arsenious acid, H₃AsO₃ or H₂AsO₄, formed by the dissolution of As₂O₃ in water, behaves as a weak acid and a weak base:

$$H_2AsO_4 \rightarrow AsO_2^{2-} + 3H^+$$

$$H_3AsO_3 \rightarrow As(OH)_3 + As^{3+} + 3OH^-$$

Salts of arsenious acid are the arsenites. The alkali arsenites are water-soluble, formed by dissolving As₂O₃ in alkali:

$$As_2O_3 + 6OH^- \rightarrow 2[AsO_3]^{3-} + 3H_2O$$

The alkaline earth arsenites are insoluble in water. Copper arsenite, Cu₂(AsO₃)₃, known as Scheel’s green, was formerly used as a pigment.

(b) Arsenic acid. Arsenic acid, H₃AsO₄, formed by the oxidation of arsenous acid, forms arsenates. Only the alkali arsenates are soluble in water; other arsenates are precipitated from solution, e.g., calcium arsenate:

$$3Ca^{2+} + 2AsO_4^{3-} \rightarrow Ca_2(AsO_4)$$

2.2 Antimony in Solution
Antimony hydroxide, Sb(OH)₃, dissolves in acids forming antimony salts, SbX₃, and in alkalis forming antimonites, $M' [SbO_3]$. Antimonyl salts, [SbO]X, are more common than the normal salts. Thus antimony chloride dissolves to form a clear solution in a small quantity of water. On dilution, basic chlorides are precipitated, e.g., SbOCl.

2.3 Bismuth in Solution
Bismuth hydroxide, Bi(OH)₃, readily dissolves in acids forming salts, but does not dissolve in dilute alkalis. Basic salts are formed by hydrolysis.

3. Recovery

3.1 General
Nonferrous metal sulfide concentrates containing arsenic, antimony, and bismuth can be treated prior to smelting by either pyro- or hydrometallurgical routes to recover these elements as by-products. During the thermal treatment, however, a minor part of these elements will remain as an undesirable impurity in the raw nonferrous metal produced. Methods are available for removing or recovering these impurities and usually involve hydrometallurgical methods, e.g., solvent extraction.

3.2 Pyrometallurgical Route
Most arsenic, antimony, and bismuth can be volatilized as sulfides or oxides during the smelting of sulfide ores. The metallurgy of these elements is, therefore, mainly concerned with the treatment of dusts from smelters. In the case of lead smelters, however, the dust is usually recycled and therefore arsenic is eliminated as a spess while antimony and bismuth are enriched in the slimes of electrolytic refining. The metals are produced from the purified oxides by reduction with charcoal or hydrogen.

In copper smelting, volatilization of the sulfides or oxides takes place in the roasters, in the smelting furnace, and in the converter, but some of the arsenic, antimony, and bismuth still remain in the blister copper and are removed during electrolytic refining. The volatilized oxides may react with the mineral particles carried over mechanically with the vapors to form arsenates, antimonates, or bismuthate, thus complicating treatment of the dust. This, however, can be avoided by maintaining the first dust chamber at 350 °C to insure the vaporization of arsenic, antimony and bismuth sulfides and/or oxides, which are then collected in the next unit. The dust from the first unit, containing mainly material from the feed, can be returned to the furnace.

During electrorefining of copper, noble metals such as gold and platinum do not dissolve into solution and fall to the bottom of the cell as anode mud. Elements such as lead and tin dissolve but precipitate out as sulfates. Sulfur, tellurium, and selenium, present as
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sulfides, tellurides, and selenides, respectively, all fall into the anode mud. Metals less noble than copper dissolve at the anode but do not deposit at the cathode. They are recycled with the electrolyte, which leads to a concentration build-up of these impurities to the point that cathode contamination can take place. In practice, this is taken care of by diverting a bleed stream, which can then be treated in two ways:

(i) Recovery of copper by electrowinning followed by NiSO₄ crystallization. After this, what is left is a sludge that typically contains 50% copper, 20% arsenic, 5% antimony, and small amounts of bismuth, which is treated further to separate its components.

(ii) Recovery of copper by electrowinning followed by solvent extraction of arsenic, antimony, and bismuth, then the recovery of nickel sulfate.

(a) Factors enhancing volatilization. To enhance the volatilization of these elements the following factors should be taken into consideration:

(i) The oxidation of the sulfide concentrate should be conducted in a limited supply of air to favor the formation of the volatile lower oxides. For example:

$$\text{As}_2\text{S}_3 + 3\text{O}_2 \rightarrow \text{As}_2\text{O}_3 + 3\text{SO}_2$$

$$\text{Sb}_2\text{S}_3 + 3\text{O}_2 \rightarrow \text{Sb}_2\text{O}_3 + 3\text{SO}_2$$

(ii) The reaction should be preferably conducted to favor volatilization of sulfides and elemental sulfur derived from pyrite and these vapors are then oxidized in another reactor to form the oxides which are in turn captured in the dust collecting chambers.

(iii) High temperature of roasting is desirable but should not exceed 720°C, since above this, fusion in the bed may take place and inhibits volatilization.

(b) Purification of raw oxides. The oxides are generally purified by multiple sublimations or by wet methods. For example, raw As₂O₃ is slurried in water and aerated at 70°C with oxygen to dissolve it as arsenic acid. Any solids are separated by filtration, the clear solution is passed over a bed of active carbon, then reduced with SO₂ to precipitate pure As₂O₃:

$$2\text{H}_2\text{AsSO}_4 + 2\text{SO}_2 \rightarrow \text{As}_2\text{O}_3 + 2\text{H}_2\text{SO}_4 + \text{H}_2\text{O}$$

(c) Industrial examples. Arsenic oxide is recovered at El Indio plant in northern Chile from a copper concentrate under carefully controlled roasting conditions before shipping it to copper smelters. Arsenic oxide is recovered in Morocco by roasting cobalt arsenide concentrate under carefully controlled conditions:

$$2\text{CoAs}_2 + 6\text{O}_2 \rightarrow \text{Co}_2\text{O}_3 + 3\text{As}_2\text{O}_3$$

The cobalt oxide formed is then leached by H₂SO₄, the solution purified by solvent extraction, then electrolyzed to get pure metallic cobalt.

(d) Recovery during metal refining. During the electrorefining of copper, the small amounts of arsenic, antimony, and bismuth that are present in the blister copper are solubilized and accumulate in the electrolyte. A bleed solution is usually treated by organic solvents to remove or recover these elements.

3.3 Hydrometallurgical Route

(a) Sodium sulfide leaching. Arsenic, antimony, and bismuth can be leached from copper concentrates before smelting to improve the quality of the concentrate and to recover these elements. An alkaline solution of sodium sulfide is used, and the thiosalts formed are treated further for recovery or disposal. At Equity Silver Mines in Canada the solution was treated with oxygen at 145°C in an autoclave to precipitate sodium antimonate:

$$2\text{Na}_2\text{SbS}_3 + 13\text{O}_2 + 8\text{OH}^- + 2\text{H}_2\text{O} \rightarrow 2\text{NaSb(OH)}_6 + 6\text{SO}_4^{2-} + 4\text{Na}^+$$

while arsenic(III) is oxidized to arsenic(V) and remains in solution as sodium arsenate:

$$2\text{AsS}_3^{2-} + 13\text{O}_2 + 12\text{OH}^- \rightarrow 2\text{AsO}_4^{3-} + 6\text{SO}_4^{2-} + 6\text{H}_2\text{O}$$

Arsenic was then precipitated as calcium arsenate for disposal and the solution was then evaporated to crystallize sulfate.

(b) Reaction with nitric acid. Nitric acid can be used at room temperature to solubilize cobalt and other impurities from cobalt arsenide concentrates, leaving the major part of arsenic behind as white arsenic oxide.

(c) Reaction with copper sulfate. At Sumitomo Metal Mining Company in Japan the arsenic-containing slurry from the gas cleaning chambers was treated with H₂S to transform its components into sulfides, which were stockpiled. Since the early 1980s, the stockpile has been treated with CuSO₄ solution from the plant to solubilize the arsenic and precipitate CuS:

$$\text{As}_2\text{S}_3 + 3\text{Cu}^{2+} + 4\text{H}_2\text{O} \rightarrow 2\text{HAsO}_4^{2-} + 3\text{CuS} + 6\text{H}^+$$

After filtering off CuS, arsenic oxide is precipitated by cooling:

$$2\text{HAsO}_4^{2-} \rightarrow \text{As}_2\text{O}_3 + \text{H}_2\text{O}$$

Bibliography

Anonymous 1978 Effects of Arsenic in the Canadian Environment. National Research Council, Ottawa, Canada
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