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Mineral Commodity Profiles—Indium

By John D. Jorgenson and Micheal W. George

Overview

Indium, like gallium and thallium, is a highly volatile chalcophile element in subgroup IIIA of the periodic table. It is a malleable, silvery-white metal found primarily in ores, in order of descending importance, of zinc, copper, and tin. It has many uses, but the principal one, which accounts for about 65 percent of the indium consumed in industry, is as thin films of indium-tin oxide (ITO) for liquid crystal displays. Indium is also used in semiconductors, in the form of indium phosphide (InP).

The value of commercial grade indium consumed in the United States in 2001 is estimated to have been greater than \$8.5 million based on domestic consumption of 58 metric tons (t).

Indium is principally a byproduct of the electrolytic refining of zinc, although a small share is a byproduct of tin refining. Primary refined indium is produced in several countries which include, in descending order of quantity produced, China, France, Japan, Canada, Belgium, Russia, and Peru (Brown, 2002a). The United States produces only secondary material, and the quantity, which is the proprietary data of the only two producers, is not published. The world reserve base for indium is estimated to be about 5,700 t, which is far in excess of probable consumption over the next several decades; the United States has about 11 percent of this base. The sustainable production and consumption of indium appears to be no impediment in future years.

Historical Background

Indium was discovered by Ferdinand Reich and H.T. Richter Germany's of Freiberg School of Mines in 1863. They were studying zinc ores from a local polymetallic vein deposit looking for thallium when they discovered an unknown coating that gave a distinctive blue color on the spectrograph. This blue coloring led to their naming the material indium for the "indigo" spectral lines it developed. The metal itself is actually a lustrous silver-white color.

Although domestic U.S. production had begun in 1926, no real research with the material began until 1934 when the Indium Corporation of America identified the first practical applications for indium (White, 1977; Indium Corporation of America, undated). In 1933, small amounts of indium were added to certain gold dental alloys, but it was not until World War II that indium was used in its first large-scale application as a coating for bearings in high-performance aircraft engines (Carlin, 1985; Slattery, 1995). Indium increased hardness and helped prevent seizure and corrosion of the bearings.

Not until 1936 did the U.S. Bureau of Mines (USBM) begin to track indium as a metal commodity (Tyler, 1937, p. 767). One of the earliest uses was as a precious metal alloy that was used to enhance brightness and to retard tarnishing. In the 1940s, the use as a special bearing-metal alloy was established, but it was not until 1952, when it started to be used in semiconductor devices, that the demand for indium became established (Weeks, 1973).

Production gradually increased as new uses for indium as a component of electronics, fusible alloys, and solders were developed. Through 1980, demand continued to increase, especially for use in nuclear control rods. Orders for nuclear control rods dropped when nuclear power expansion decreased in the United States following the Three Mile Island accident on March 28, 1979.

In the middle and late 1980s, InP semiconductors and ITO thin films for liquid crystal displays (LCDs) were developed. By 1992, the thin-film application had become the largest end use of indium (Jasinski, 1993).

In the mid-1970s, the use of indium in the United States was almost equally distributed between the use in coatings and alloys and the use in electrical components and semiconductors. Changes in accounting by category have obscured some of the U.S. information since the mid-1970s. The percentage of end uses appears to have changed little since the mid-1970s other than a steady increase in the application for coatings since 1990 and a great reduction in the percentage used in research.

The Defense Logistics Agency included indium in the list of materials to be added to the National Defense Stockpile (NDS) in 1989 (Schmitt, 1989). The NDS had acquired its largest quantity of indium (1.56 t) by 1994, but this was sold by the end of 1998 (Brown, 2002a).

In 1995, a tight supply situation combined with strong demand led to the implementation of a more-efficient recycling process. Then, in 1998, indium demand slackened owing to lower LCD production and the introduction of new thin-film coating technology that required only one-third as much indium as the older process (Roskill Information Services Ltd., 1999, p. 3).

Although the introduction of indium can be traced to individual end uses, determining the tonnages of indium produced and consumed over time is much more difficult because statistics are incomplete. The USBM began publishing the annual series on indium refinery production in the United States in 1942. Production figures were made available for 1942 through 1951, 1956, and 1966 through 1969. During these years, some of the production figures were withheld as company proprietary data. From 1942 through 1951, the United States produced most of the world's refined indium; a sizable quantity of unwrought refined material at 99.8 percent purity, was imported from the La Oroya refinery in Peru (Mills and others, 1961, p. 221). The two U.S. zinc refiners that produced indium suspended their production in the early 1970s, when ASARCO Incorporated closed their production facilities in Perth Amboy, New Jersey, and Denver, Colorado, and Anaconda Copper Mining Co. shut down its facilities at Great Falls, Montana.

Estimated domestic consumption of indium, which has appeared in the USBM/U.S. Geological Survey (USGS) Mineral Commodity Summaries since 1979, has shown a progressive increase from approximately 20 t in 1979 to 55 t in 2000. The gap between the estimated domestic consumption of indium and the apparent consumption represented by the sum of domestic refining, imports, and the change in domestic stocks appears to be large. This 20- to 40-t difference represents the indium exported in "hi-tech" end products, which was a small portion of the estimated \$153.9 billion of U.S. exports of information technology (IT) manufactured goods (Pastore, 2002).

Description

Salient Facts

Indium is element number 49 in the periodic table of the elements. Its atomic weight is 114.82, its electron configuration is $[\text{Kr}]4d^{10}5s^25p^1$, and it is located in period 5, group 13 (the boron group). The top element in the group, boron, is semimetallic. All the rest of the elements in the group (aluminum, gallium, indium and thallium) are metallic (Greenwood and Earnshaw, 1997, p. 222). Indium's principal oxidation states are +1 (the most stable) and +3. The unit cell of indium's crystal structure is an unusual face-centered tetragon.

Sixty-seven isotopes and isomers of indium are now recognized; this is more than any other element. Natural indium contains two isotopes, one of which, In^{113} , is stable. The other, In^{115} , which comprises 95.7 percent of natural indium, is slightly radioactive with a very long half-life (Spectrum Laboratories, Inc., undated).

Indium's hardness is 1.2 on the Mohs scale, its specific gravity at 20° C is 6.25, and it melts at 156.6° C. It is a soft, lustrous, silver-white metal and the pure metal gives a high-pitched cry when bent (Mills and others, 1961, p. 225). Its most notable feature is its highly plastic property even at cryogenic temperatures. It is not oxidized by air at ordinary temperatures, dissolves in mineral acids, and is not affected by alkalis, boiling water, or most organic acids.

Principal Forms, Alloys, and Compounds

Indium metal is produced in various forms, which include foil and ribbon, ingot, plates, powder, shot and pellets, and wire. The varying sizes of the ingots [0.5, 1.0 and 10 kilograms (kg)] depend on the producer selected. Indium ribbons and foil are used for sealing and bonding; shot for alloying and evaporation; and shells for easy chemical dissolution.

Indium alloys with a significant number of metals and in a number of binary and ternary systems. Alloys with bismuth, cadmium, lead, and tin are often used in low-melting-point applications, such as fire door safety links, optical lens grinding, pattern making, sprinkler heads, turbine blade machining, and other fuse-type applications. An alloy of 5 percent indium, 15 percent silver, and 80 percent cadmium has been used for nuclear reactor control rods.

Soldering alloys with melting points in the 100°-to-300° C range are made of lead-silver-indium, lead-tin-indium, and tin-indium. These solders offer improved resistance to alkaline corrosion and thermal fatigue. The most important of these soldering alloys is ITO. Other indium alloys are used for ceramics and dental work and specialty brazing and wetting glass.

Indium's properties are similar to those of gallium, the element directly above it in the periodic table. Like gallium, it remains in the liquid state over a wide range of temperatures. Indium wets glass and can form a mirror surface that is more resistant to corrosion than silver, while reflecting just as well (Lagasse and others, 2000).

The significant commercial indium compounds, cited by Slattery (1995, p. 159), are the alkyls trimethyl indium [$\text{In}(\text{CH}_3)_3$], triethyl indium [$\text{In}(\text{C}_2\text{H}_5)_3$], and triphenyl indium [$\text{In}(\text{C}_6\text{H}_5)_3$], indium dichloride (InCl_2), indium hydroxide [$\text{In}(\text{OH})_3$], indium nitrate [$\text{In}(\text{NO}_3)_3$], indium oxides (In_2O_3 , In_2O , and InO), indium phosphate (InPO_4), indium sulfide (In_2S_3), indium trichloride (InCl_3), and indium trisulfate [$\text{In}_2(\text{SO}_4)_3$].

Of some importance are the intermetallic compounds, in which indium combines with alkali and precious metals, magnesium, the iron group, and rare earths. Indium also combines with metalloids and nonmetals. These form some of the most important semiconducting compounds of indium, such as, the antimonide (InSb), the arsenide (InAs), and the phosphide (InP).

Commercial Grades, Shapes, and Specifications

In the United States, producers determine their own indium product standards. Indium metal products produced by Indium Corporation of America include four products in the three-nines to five-nines range and an additional four products in the six-nines to seven-nines range; "nines" refers to the purity of an element or compound; for example, five-nines would refer to a product that is 99.999-percent pure. Sale pricing lots from the three major producers are as follows (Platts Metals, undated):

- 99.97-percent pure metal in 1-kg bars in lots of 10,000 troy ounces [free on board (f.o.b.), Utica, N.Y.],
- 99.97-percent pure metal in 100-troy-ounces bars in lots of 5,000 troy ounces (f.o.b., Providence, R.I.), and
- 99.99-percent pure metal in minimum lots of 50 kg (at warehouse, Rotterdam, Netherlands).

For pellets, typical commercial-grade metal varies from three-nines to six-nines indium with diameter by length sizing of as follows:

- 0.25 inch by 0.25 inch,
- 0.25 inch by 0.5 inch,
- 0.125 inch by 0.125 inch, and
- 0.125 inch by 0.25 inch.

Pellets are used for evaporation in deposition processes (Kurt J. Lesker Company, undated).

The principal uses for indium foil are as contact sheets with good thermal and electrical conductivity and as sealant material in high- and low-pressure and cryogenic applications. Foil purity is generally 99.99 percent with thicknesses that range from 50 microns (μm) to 2 millimeters (mm). It can be cut to customer's design specifications (Umicore Thin Film Products, undated).

Indium wire and ribbon is used in soldering and preparation of seals that will withstand cryogenic temperatures. The wire and ribbon come in varying shapes. For example, Indium Corporation offers several pure indium and indium alloys ribbons that vary as follows:

- Width—from 0.5 to greater than 25.4 mm,
- Thickness—from 0.025 to greater than 1.27 mm, and
- Length—from small strips for testing to large spools.

Powders of indium metal, indium oxide, indium hydroxide, and ITO are also sold. The metal is sold in -100- and -325-mesh size and in those sizes grades range from three-nines to five-nines by one producer (ESPICorp Inc., undated). Another producer sells indium oxide in grades of fine with 90 percent smaller than 15 μm and ultrafine with 100 percent less than 10 μm . That same producer sells indium hydroxide at a purity of up to five nines in grades of amorphous (90 percent less than 5 μm) or crystalline (90 percent less than 25 μm) for battery, catalytic, electrically conductive, and heat reflective applications (Teck Cominco Limited, 2002b).

Sources

Primary

Abundance

Indium is a rare element. It ranks 61st in abundance in the Earth's crust at an estimated 0.24 part per million (ppm) by weight. This makes it about three times more abundant than silver or mercury.

Indium, even in zinc concentrate, is a relatively minor proportion of the material. For example, in Kidd Creek, Ontario, Canada, concentrate, indium content represented 0.027 percent by weight, in Polaris, Northwest Territories, Canada, concentrate, 0.010 percent; and in Balmat, N.Y., concentrate, 0.004 percent (Rodier, 1990, p. 59-65).

Schwarz-Schampera and Herzig (2002, p.45-49, p. X-XII), gave an exhaustive discussion of indium levels in ore bodies around the world. For example, they showed 315 samples of ore from a volcanic-hosted massive sulfide deposit from the Kidd Creek Mine as ranging between 1 and 870 ppm indium with a mean of 106 ppm. They went on to state that the estimated bulk indium content of the ore deposit was 3,400 t.

Geochemistry and Geologic Occurrence

The geochemical properties of indium are such that it tends to occur with the base metals copper, lead, tin, and zinc and with bismuth, cadmium, and silver. It is a high-volatility, chalcophile element and tends to be associated with sulfide minerals of zinc, whose atom is of a similar size.

As described by Schwarz-Schampera and Herzig (2002, p. VII-IX), some of the major hosts for indium mineralization, include the following:

- Vein stockwork tin and tungsten deposits, as well as porphyry tin deposits;
- Volcanic-hosted massive sulfide (VMS) deposits;
- Sediment-hosted exhalative massive sulfide (SHMS) deposits;
- Polymetallic vein-type deposits;
- Epithermal deposits;
- Active magmatic systems;
- Porphyry copper deposits; and
- Skarn deposits.

Vein stockwork tin and tungsten deposits occur as individual veins, multiple-vein systems, vein and fracture stockworks, breccias, and altered wallrock adjacent to veins. The Mount Pleasant deposit, New Brunswick, Canada, is of this type and contains roughly 25 percent of the world's indium reserves. The economic potential of these deposits, in 2001, was difficult to determine because the complex mineralogy makes metallurgical recovery difficult.

The VMS deposits are important sources of base and precious metals. Strong partitioning into massive sphalerite in these deposits, as well as in the SHMS deposits, make them the major sources of indium from residues of zinc smelting. Examples of these deposits include Kidd Creek; Neves-Corvo, Portugal; Brunswick No. 12, New Brunswick, Canada; and Kuroko, Japan. The major example of the SHMS deposit is Rammelsberg, Germany, the ore from which indium was first separated and identified.

Polymetallic vein-type deposits are generally structurally controlled within fault systems and vein breccia zones. These deposits can contain high concentrations of indium and are among the world's most important indium producers. Several examples of these type deposits occur in Japan and in the Bolivian Cordillera.

Resources

No estimates are available for total resources of indium. Because most indium is recovered as a byproduct of zinc refining, known resources of indium can be inferred from the deposits of zinc being exploited in 2001, and the remainder, if any, is derived from the smelting and refining of tin ores.

The Soviet Union was a major source of indium production, but with its breakup, zinc mining and byproduct indium recovery has been significantly reduced. Over three-fourths of Commonwealth of Independent States (CIS) reserves are located in Russia. Russian reserves can cover their anticipated indium demand for several decades in spite of the fact that they have a low recovery (36 percent) from raw materials (Roskill Information Services Ltd., 1997).

Japan's Toyoha Mine, which has an average indium grade of 140 ppm, is among the leading producers of indium in the world. The contained indium in zinc concentrates is sufficient to produce 75 metric tons per year, or about one-third of the annual worldwide indium production. The Mount Pleasant deposit (New Brunswick, Canada) represents one of the largest indium deposits known with about 25 percent of the world reserves.

Almost all indium is produced from residues collected from zinc refining and recycling of flue dusts and gases generated during the smelting zinc. The remainder, if any, is derived from the smelting and refining of tin. Because of the heavy reliance on zinc as a source, the USGS bases its estimates of indium reserves and reserve base on the comparable figures for zinc. The estimates, shown in table 1, take into account that approximately one-half of the approximately 0.028 kg of indium per metric ton of zinc ore that is concentrated and later delivered for smelting is actually recovered.

Secondary

In 1996, the level of domestic recovery of secondary indium was unusually high. A \$12-per-troy-ounce price increase in 1995, which almost tripled the price, and which prompted concerns about lack of supply, encouraged the recycling of more old scrap. This recycling provided much of the domestic supply, and resulted in a decrease in imports of more than 50 percent (Fineberg, 1996).

Since then, recycled indium has remained low in the United States. In the year 2000, most of the secondary indium was recovered from new scrap, as is typical in the United States (Brown, 2002c). The quantity of secondary indium recovered is not known for 2000, but it was small.

In Japan, however, recycling has maintained its importance in recent years (McColloch, 2000). In 2000, Japanese indium demand reached a record 335 t. Slightly more than one-half of the material came from recycled scrap (Roskill's Letter from Japan, 2001).

Because most of the uses of indium are nondissipative, high tech, and short-lived in nature, scrap is generated from which secondary indium may be extracted. However, little was recovered in the United States in

Table 1. Indium reserves and reserve base, yearend 2001.

[In metric tons, recoverable indium. All data are rounded to two significant digits; because of independent rounding, they may not add to totals shown]

	Reserves	Reserve base
Canada	700	2,000
China	400	1,000
Japan	100	150
Russia	200	300
Peru	100	150
United States	300	600
Others	800	1,500
World total	2,600	5,700

Note: Estimate based on the indium content of zinc ores (Brown, 200b).

2001, but a large amount may be recovered in Japan and elsewhere from weld metal alloys, scrapped ITO, and indium phosphide in LCDs.

Production Technologies

The sources of indium material—alloys, dusts, fumes, residues, and slag from zinc and lead-zinc smelting—are leached by using hydrochloric (HCl) or sulfuric (H₂SO₄). The solutions are concentrated, and indium is recovered as 99+ percent metal. The low-grade indium is then refined to standard-grade (99.99 percent) and higher purity metal.

Early methods for indium recovery were very expensive because large quantities of indium-poor material had to be treated to obtain a small quantity of indium. The zinc industry had considered the recovery of indium and germanium as a marginal activity because they are difficult to separate from antimony, arsenic, copper, lead and tin.

While the pyrometallurgical processes are not conducive to the recovery of indium, roasting in a rotary furnace can be used for selectively fuming the metal. In the imperial smelting process (ISP), only a limited part of the indium is slagged off owing to its affinity for lead, absence of affinity for iron, and the strong reducing properties of the metal. About 50 percent of the indium is lost to lead bullion in ISP; the rest resides in the zinc residue, where it is recovered from those plants that operate a complete refinery unit.

In the electrolytic process for zinc refining, germanium and indium are concentrated in the neutral leach residue from the zinc plant. For zinc concentrates that contain high iron and silica, germanium and indium recovery is difficult if strong acid leaching is used to treat the neutral leach residue.

In the jarosite process for zinc refining where iron is always in the ferric state, a maximum of 60 percent of the germanium and indium can be dissolved from the neutral leach residue. The jarosite process plant will generally include reductive leaching and copper precipitation, two stages of neutralization, and iron removal as hematite by autoclave oxidation-precipitation. During the neutralization of the ferrous sulphate solution by calcium carbonate, gypsum is produced and later refined by several solvent extraction operations, and lastly indium is electrowon as a pure metal (Demarthe and others, 1990).

Traditionally only about 30 percent of the available indium is concentrated in flue dusts and treatable residues from which indium can be recovered. In the last few years, however, indium recoveries have improved to as high as 80 percent.

Production at Kidd Creek

Typical of the indium recovery process is the recovery from zinc concentrates in the zinc roasting and refining plant at Kidd Creek, where the indium grade of zinc concentrate has been estimated to be 0.027 percent. The concentrate is roasted to remove sulfur and passed through a two-stage leaching process. In the first stage, iron is removed as a jarosite residue, and in the second stage, Cottrell dust from the copper smelter is added to precipitate a silver-lead residue. The indium-containing liquor is then passed to a solvent extraction stage, as shown in figure 1, where refined indium metal is produced for sale (Falconbridge Limited, 2002).

Production From Tin

Indium is being recovered from tin concentrate that contains 0.01 percent indium into a 0.1 to 0.2 percent indium-lead-tin alloy by using a specialized vacuum refining apparatus. The indium alloy is then melted in a 20-t pot, and the raw indium metal is recovered in a special apparatus. The raw indium metal is then electrolytically refined in the melt. This apparatus also makes it possible to treat tailings with a primary indium content of 0.1 percent and higher (Novosibirsk City Guide, undated).

Production From Scrap

Small quantities of indium are recovered from the refining of new scrap, material generated in the production of indium-bearing products, and even smaller, from old scrap. Higher prices promote an increase

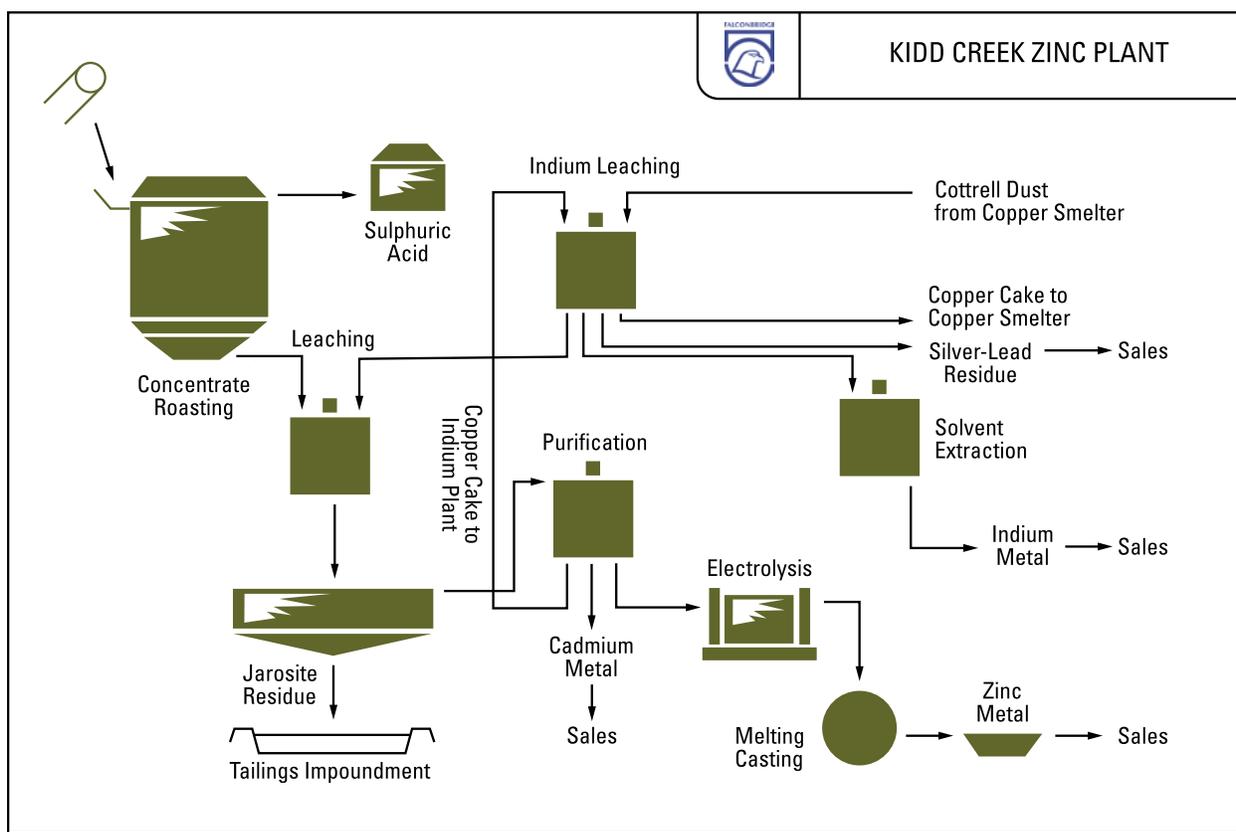


Figure 1. Flow diagram illustrating the process of zinc smelting at the Kidd Creek zinc plant. Source: Falconbridge Limited.

