

**U.S. Department of the Interior
U.S. Geological Survey**

Antimony Recycling in the United States in 2000

By James F. Carlin, Jr.

U.S. GEOLOGICAL SURVEY CIRCULAR 1196-Q

FOREWORD

As world population increases and the world economy expands, so does the demand for natural resources. An accurate assessment of the Nation's mineral resources must include not only the resources available in the ground but also those that become available through recycling. Supplying this information to decisionmakers is an essential part of the USGS commitment to providing the science that society needs to meet natural resource and environmental challenges.

The U.S. Geological Survey is authorized by Congress to collect, analyze, and disseminate data on the domestic and international supply of and demand for minerals essential to the U.S. economy and national security. This information on mineral occurrence, production, use, and recycling helps policymakers manage resources wisely.

USGS Circular 1196, "Flow Studies for Recycling Metal Commodities in the United States," presents the results of flow studies for recycling 26 metal commodities, from aluminum to zinc. These metals are a key component of the U.S. economy. Overall, recycling accounts for more than half of the U.S. metal supply by weight and roughly 40 percent by value.

Charles G. Groat
Director

CONTENTS

| | |
|---|-----|
| Foreword | III |
| Abstract | W1 |
| Introduction | 1 |
| Global Geologic Occurrence of Antimony | 1 |
| Production Technology | 3 |
| Sources of Secondary Antimony | 4 |
| Old Scrap Generated | 4 |
| New Scrap | 5 |
| Disposition of Antimony Scrap | 5 |
| Old Scrap Recycling Efficiency | 5 |
| Infrastructure of Antimony Scrap Recycling Industry | 5 |
| Processing of Antimony Scrap | 6 |
| Outlook | 7 |
| References Cited | 7 |
| Appendix—Definitions | 8 |

FIGURES

| | |
|--|----|
| 1. Flow diagram showing U.S. antimony materials flow in 2000 | W2 |
| 2. Graph showing U.S. consumption of antimony by end-use sector from 1980 through 2000 | 4 |

TABLE

| | |
|---|----|
| 1. Salient statistics for U.S. antimony scrap in 2000 | W4 |
|---|----|

CONVERSION FACTORS

| Multiply | By | To obtain |
|--|----------------|--|
| | <i>Length</i> | |
| meter (m) | 3.281 | foot (ft) |
| | <i>Volume</i> | |
| cubic meter (m ³) | 264.2 | gallon (gal) |
| cubic meter (m ³) | 35.31 | cubic foot (ft ³) |
| | <i>Mass</i> | |
| kilogram (kg) | 2.205 | pound avoirdupois (lb) |
| | <i>Density</i> | |
| gram per cubic centimeter (g/cm ³) | 62.4220 | pound per cubic foot (lb/ft ³) |

Antimony Recycling in the United States in 2000

By James F. Carlin, Jr.

ABSTRACT

The importance of recycling has become more obvious as concerns about the environment and import dependence have grown in recent years. When materials are recycled, fewer natural resources are consumed, and less waste products go to landfills or pollute the water and air. This study, one of a series of reports on metals recycling in 2000, discusses the flow of antimony from mining through its uses and disposal with emphasis on recycling. In 2000, the recycling efficiency for antimony was estimated to be 89 percent, and the recycling rate was about 20 percent.

INTRODUCTION

The materials flow chart of antimony, as shown in figure 1, is intended to depict the U.S. antimony recycling industry in 2000. It shows the extent of antimony recycling, consumption, losses, issues, trends, and other aspects of the domestic secondary antimony industry. Antimony recovered from scrap is an important part of total antimony supply in the United States, but one that has declined greatly during the last quarter century owing to declining usage in the automotive battery field. Since the 1920s, the largest source of secondary antimony by far has been scrapped lead-acid (LA) storage batteries, mostly automotive vehicle batteries.

Antimony (atomic number 51 and atomic weight 121.75) is located in period 5, group 11 in the periodic table of elements and appears to be a lustrous white metal. Although antimony is usually described as a metal, it possesses mixed metallic and non-metallic characteristics and is more properly described as a semi-metal or metalloid. Unlike typical metals, it is not malleable, but instead is hard and brittle and can be crushed to a powder. Compared with metals, antimony is a poor conductor of electricity and heat. Along with the other metalloids (arsenic, germanium, silicon, and tellurium), it is positioned in the periodic table along the boundary between metals and nonmetals. Its common oxidation states are +5, +3, 0, and -3, although other oxidation states have been recognized. Natural antimony consists of a mixture of two stable isotopes that have atomic weights 121 (57.25 percent by weight) and 123 (42.75 percent by weight); about three dozen radioactive isotopes of antimony are known. Antimony metal melts at 630.6° C, has a specific gravity that ranges from 6.62 to 6.69 depending on its method of preparation, and has a hardness

of 3 to 3.5 on the Mohs scale (about 55 on the Brinell scale). Antimony crystallizes in the rhombohedral class of the hexagonal system (Li and others, 1992; Anderson, 2001).

Nearly all antimony is consumed in one of the following four forms: antimony trioxide, which is used mostly for flame retardants and represents the largest market for antimony; antimonial lead alloys, which are used mostly in LA batteries; refined antimony metal, which is used in a variety of metallic products; and sodium antimonate, which is used for the clarification of specialty glasses.

In 2000, antimony mine output was dominated by a few countries. China, which has been the leading producer for 10 years, has accounted for more than 80 percent of world output since 1995. Domestic antimony and lead ores have never satisfied more than a small part of the U.S. antimony demand.

To offset the risk of dependence on foreign sources for its antimony, the U.S. Government has stockpiled antimony for national defense purposes for several decades. Such stockpiles have been maintained, along with other metals, at Government depots throughout the country, which are often located near plants that would require those materials for national defense. During the 1960s, the quantity of antimony stockpiled approached 50,000 metric tons (t) but declined steadily in subsequent decades as surplus metal was sold. In 1993, the stockpile goal for antimony was reduced to zero, and by year-end 2000, the inventory was down to about 8,300 t.

Antimony recycling has long been an important source of U.S. antimony supply. The contribution of recycled antimony to overall domestic supply has declined in recent years, and currently, no economic trends are seen to reverse that pattern. Indeed, with the possibility of newer forms of transportation batteries being introduced, the amount of recycled domestic antimony may decline further.

GLOBAL GEOLOGIC OCCURRENCE OF ANTIMONY

Antimony's abundance in the Earth's crust has been estimated to range from 0.2 to 0.5 part per million. Antimony is a chalcophile element that occurs with sulfur as well as copper, lead, and silver. More than a hundred minerals of antimony are found in nature. The uneven distribution of antimony resources throughout the world is a factor that causes variations in the availability of antimony and thereby affects global patterns of its recycling and its production. Antimony occurs in several types

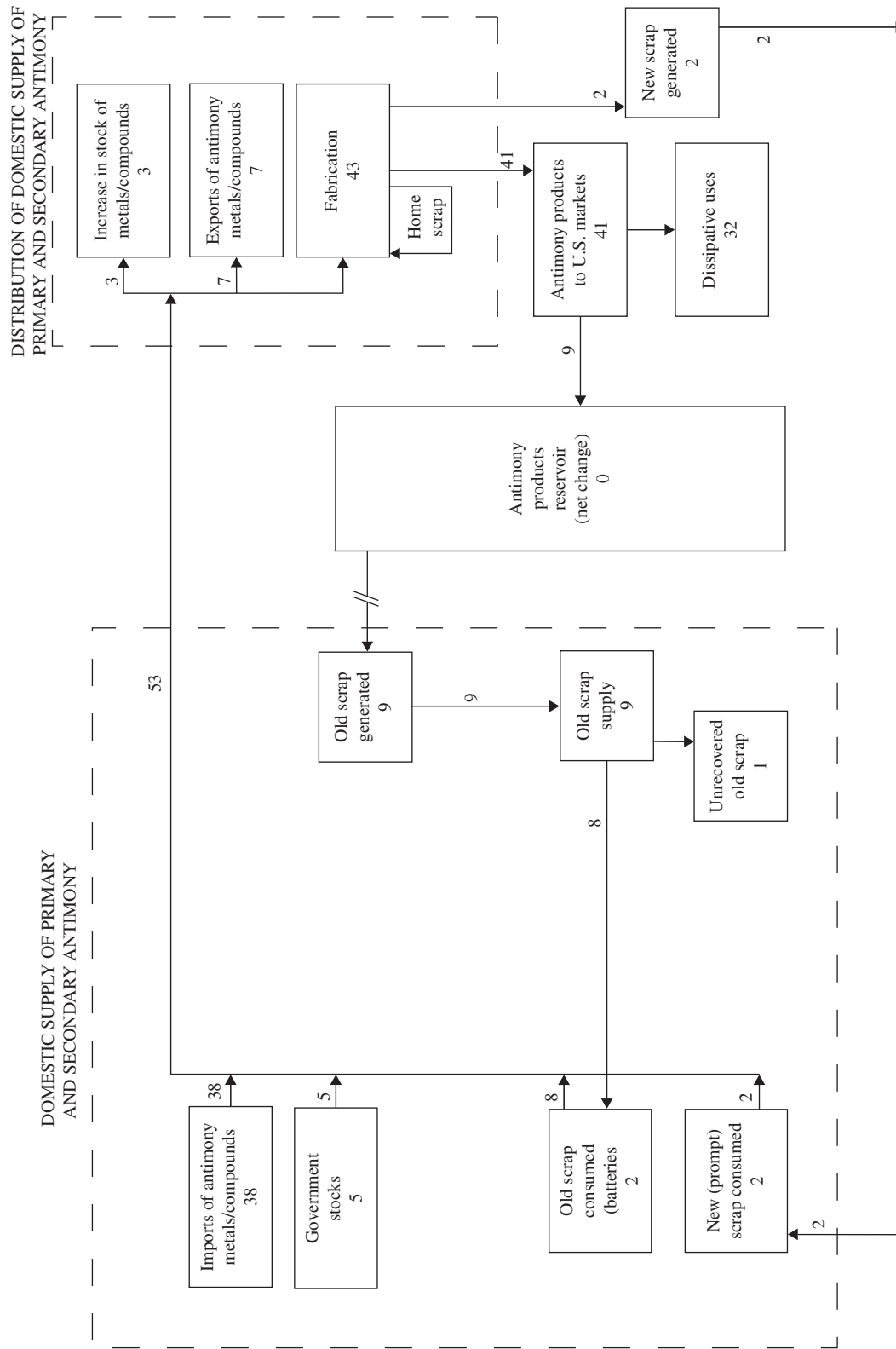


Figure 1. U.S. antimony materials flow, 2000. Values are in thousand metric tons of antimony.

of deposits—epithermal vein, pegmatite, replacement, and hot spring. Deposits of antimony range in age from Precambrian to Quaternary. Simple antimony deposits consist principally of stibnite or, rarely, native antimony in a siliceous gangue, commonly with some pyrite and in places a little gold and small amounts of other metal sulfides, principally silver and mercury. The “manto” deposits of Mexico are of the simple type and consist of selective replacements of favorable limestone beds, generally overlain by shale. Most stibnite of the hypogene deposits is oxidized to one or more of the antimony oxides. Most deposits of Bolivia, China, Mexico, and Peru are of the simple type (Miller, 1973).

Stibnite is the predominant ore mineral of antimony. In areas where stibnite has been exposed to the atmosphere, it is converted to an oxide. Important oxide minerals are bindheimite, kermesite, senarmontite, stibiconite, and valentinite. Complex antimony deposits consist of stibnite associated with arsenopyrite, cinnabar, pyrite, or scheelite. These deposits are usually mined primarily for gold, lead, silver, tungsten, or zinc and are the source of most antimony produced historically in the United States. Of the 18 countries that have produced primary antimony in the past decade, the most important have been, in order of decreasing production, China, South Africa, Russia, Bolivia, Tajikistan, and Australia (Carlin, 2002).

Until 2001, primary antimony was produced in the United States only by Sunshine Mining Co. (in the Coeur d’Alene District of Idaho), which recovered antimony-in-concentrate as a byproduct of the treatment of complex silver-copper-antimony sulfide ore.

PRODUCTION TECHNOLOGY

Many small mines contain irregular and scattered ore bodies that cannot be readily exploited by large-scale mining methods. These mines are entered by a shallow shaft or short adit, developed by drifting in the vein, and stoped by simple overhand methods between raises driven on the footwall of the ore. Mining methods used in mines that recover metalliferous ores, of which antimony is a minor constituent, are designed for producing the principal metals, such as gold, lead, or silver. One of the world’s major antimony-producing mines, the underground Consolidated Murchison Mine in South Africa, uses variations of shrinkage stoping. On the surface, the waste is separated from the high-grade ore, and lump ore is removed by hand-cobbing for direct sale; the remaining fines that contain antimony and gold are trucked to a mill for concentration (Plunkert, 1985).

As higher grade deposits become depleted, increasing emphasis is placed on beneficiation for treating low-grade ores. Flotation methods used to concentrate low-grade stibnite ores can produce a concentrate that contains more than 60 percent antimony with recovery rates of up to 95 percent. The particular combination of flotation reagents that is used depends on the physical characteristics of the ore being treated.

The antimony content of ores, which ranges from 5 to 60 percent, determines the method of recovery. In general, the lowest grades of sulfide ores, which have from 5 to 25 percent an-

timony content, are roasted to form antimony oxides; ores that have to 25 or 40 percent antimony content are smelted in a blast furnace; and ores that have 5 to 60 percent antimony content are melted and solidified under a reducing atmosphere to form needle or liquated antimony. The blast furnace also is used for mixed sulfide and oxide ores and for oxidized ores that contain up to about 40 percent antimony, direct reduction with iron scrap is used for rich oxide ores, and complex ores are treated by leaching and electrolysis (Wang, 1952, p. 10-20).

Roasting the ore to yield a volatile trioxide or the stable nonvolatile trioxide is the only pyrometallurgical procedure suitable for low-grade ores (5 to 25 percent antimony content). The method and equipment used can vary, but the principle remains the same. The sulfur is oxidized and removed from waste gases and then the volatilized antimony oxide is recovered in flues, condensing pipes, bag houses, precipitators, or a combination. The temperature and quantity of available oxygen determine the kind and relative quantity of the antimony oxide produced, which is generally impure but can be reduced to metal. Careful control of volatilization conditions, however, will produce a high-grade oxide that can be sold directly to consumers.

Water-jacketed blast furnaces are being used in several modern plants to reduce ores that contain 25 to 40 percent antimony. Oxides, sulfides or mixed ores, residues, mattes, slags, and briquetted fines or flue dusts can be used as blast furnace charges. The method employs a high smelting column and comparatively low air pressure, and slag and metal are separated in a forehearth. Considerable slag is formed, which is desired because it tends to reduce volatilization losses.

Ores that contain 45 to 60 percent antimony are melted in a crucible or reverberatory furnace with a reducing atmosphere to prevent oxidation and loss by volatilization. The melt is allowed to solidify and is called liquated, or needle, antimony. Rich sulfide ore or liquated antimony sulfide can be reduced to metal by precipitation with iron scrap; this process consists essentially of heating molten antimony sulfide in a crucible with fine iron scrap.

The metal produced by pyrometallurgical processes is normally not pure enough for a commercial product and must be further refined. The major impurities present are usually arsenic, copper, iron, lead, and sulfur. The iron and copper concentrations may be lowered by treating the metal with stibnite or a mixture of sodium sulfate and charcoal to form an iron-bearing matte, which is skimmed from the surface of the molten metal. The metal is then treated with an oxidizing flux that consists of caustic soda or sodium carbonate and sodium nitrate to remove the arsenic and sulfur. Lead cannot be readily removed from antimony, but material high in lead may be used in the production of antimony-bearing lead-base alloys.

Antimony metal is also recovered from the following: trioxide and tetroxide produced in volatilization and roasting, liquated sulfide, intermediate grades of ores by direct smelting, and slags and residues produced in refining other metals, such as lead. Oxides are generally reduced in reverberatory furnaces using coke and a suitable flux, such as soda ash.

Some complex ores can be treated by leaching and electrowinning to recover the antimony. A typical process uses an alkali hydroxide or sulfide as the solvent. The filtered leach solution, which contains sodium thioantimonate, is electrolyzed in a diaphragm cell by using an iron or lead anode and an iron or mild-steel cathode. The cathode metal obtained ranges from 93 to 99 percent antimony metal.

SOURCES OF SECONDARY ANTIMONY

OLD SCRAP GENERATED

Most secondary antimony is recovered by recycling used LA batteries. By 2000, an estimated 95 percent of secondary antimony resulted from used LA batteries. Old antimony scrap generated from recycled batteries ranged from 16,000 to 20,000 t in the 1970s. Recovery, however, gradually declined to the 8,000 t level in 2000 owing to the reduced use of antimony by the battery industry. Table 1 lists salient statistics derived from figures shown in figure 1.

Small amounts of old scrap are generated by the recycling of antimony alloys, especially some solders. Following the Federal ban on the use of solders that contain lead for joining pipes that carry potable water, an antimony-silver-tin solder was developed for that purpose. The new application served to boost antimony consumption.

Figure 2 shows how the share of various end uses of antimony has changed since 1980. Flame retardants have a larger

Table 1. Salient statistics for U.S. antimony scrap in 2000. [Values in metric tons, metal content, unless otherwise specified. --- zero]

| | |
|---|--------------|
| Old scrap: | |
| Generated ¹ | 9,000 |
| Consumed ² | 8,000 |
| Consumption value ³ | \$12 million |
| Recycling efficiency ⁴ | 89 percent |
| Supply ⁵ | 9,000 |
| Unrecovered ⁶ | 1,000 |
| New scrap consumed ⁷ | 2,000 |
| New-to-old-scrap ratio ⁸ | 20:80 |
| Recycling rate ⁹ | 20 percent |
| U.S. net imports of scrap ¹⁰ | --- |
| Value of U.S. net imports of scrap ³ | --- |

¹Antimony content of products theoretically becoming obsolete in the United States in 2000.

²Antimony content of products that were recycled in 2000.

³Value of antimony scrap based on primary antimony metal price.

⁴(Old scrap consumed plus old scrap exported) divided by (old scrap generated plus old scrap imported plus any old scrap stock decrease or minus any old scrap increase). Some elements of the equation were not available.

⁵Old scrap generated plus old scrap imported plus old scrap stock decrease. Only old scrap generated was available.

⁶Old scrap supply minus old scrap consumed minus old scrap exported; old scrap exported was not available.

⁷Including new (prompt) industrial scrap but excluding home scrap.

⁸Ratio of quantities consumed.

⁹Fraction of the apparent metal supply that is scrap on annual basis.

¹⁰Trade in scrap is assumed to be principally in old scrap. Net exports are exports of old scrap minus imports of old scrap are zero.

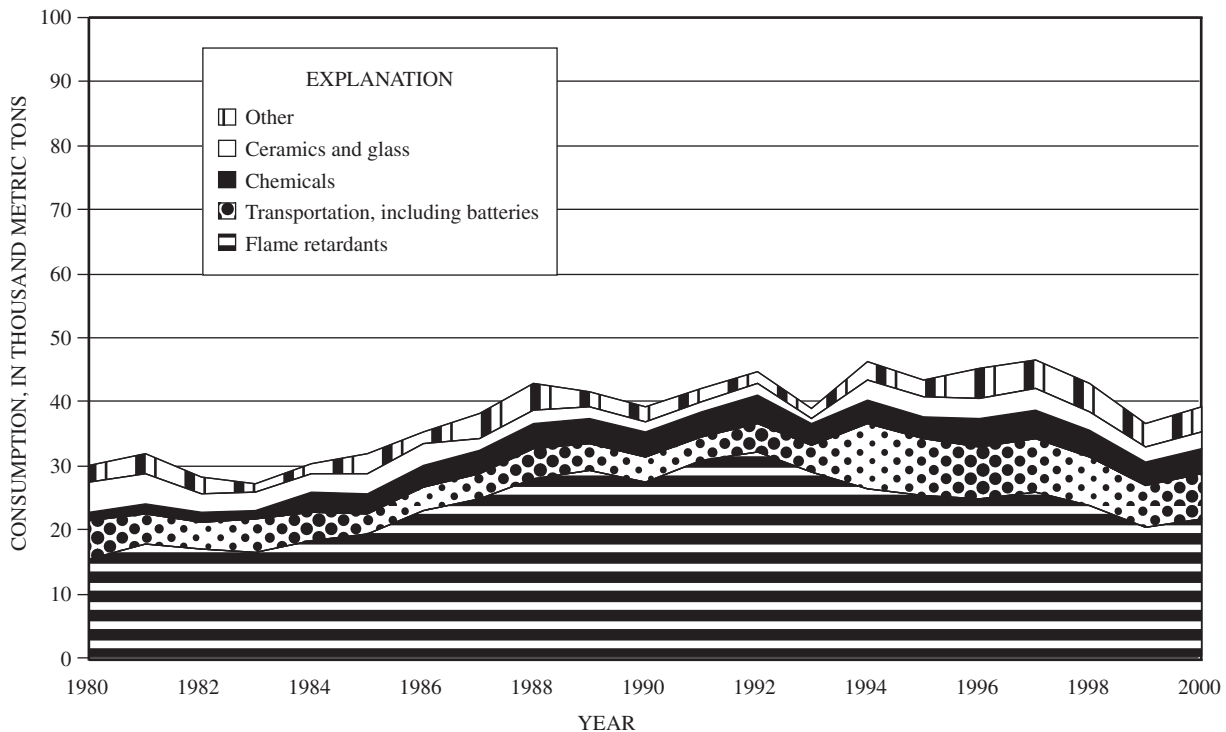


Figure 2. U.S. antimony consumption by end-use sector from 1980 through 2000.

share of the market, and other categories of consumption have changed little.

As shown in figure 2, flame retardants were the primary end-use for antimony and accounted for about 50 percent of all consumption in 2000; flame retardants had become a new market for antimony in the early 1970s. Flame retardants use antimony trioxide as an agent, along with bromine, to slow the spread of fire in applications such as automotive and aircraft seat covers, children's clothing, and toys. Virtually no antimony is recycled from flame retardant uses. Transportation applications in 2000, most of which are for LA batteries, account for about 15 percent of all antimony consumption. Aside from LA batteries, other transportation uses include babbitts, bearing metals, electrical cable covering, and solders. Almost no antimony from these applications, other than batteries, is thought to be recycled. Chemical applications in 2000 accounted for an estimated 12 percent of antimony consumption. These applications included white pigments for exterior paints and enamels and an antisolarant, or color stabilizer, where it is important to maintain color intensity. Some pigments made from antimony trisulfide and pentasulfide are used for coloring rubber black. Almost no antimony is recycled from antimony pigments.

Ceramics and glass accounted for an estimated 12 percent of antimony used in 2000. Most of this market comprises applications in glass where antimony is used as a fining agent, decolorant, and antisolarant for high-quality transparent glass. Antimony is not used in container glass. In ceramics, a mixture of antimony trioxide and tin oxide is used to produce a gray-to-blue color. Virtually no antimony is recovered from glass or ceramics, so it is virtually dissipated. The "Other" category was estimated to account for about 11 percent of antimony usage in 2000. These various applications included addition of antimony to some fluid lubricants to increase their chemical stability, antimony oxide used as a phosphor in fluorescent lamps, and antimony trichloride and pentachloride used as reactants in organic chemical reactions, notably in making freon. No antimony is believed to be recovered in these applications.

NEW SCRAP

New scrap is generated by manufacturers that use antimony, such as solder producers and other alloyers. New scrap is recycled through tolling arrangements with recyclers or between plants that may or may not be owned by the same company. Home (in-plant) scrap is included. Also, new scrap may be generated at fabrication plants that use alloyed forms of antimony to make end-use items, such as electronic components or household water-conducting pipe units. In addition, new scrap is produced as a result of sizing for meeting customer specifications and because of human error or equipment malfunction in the manufacturing processes. The amount of antimony produced from new scrap in 2000 was estimated to be 2,000 t.

DISPOSITION OF ANTIMONY SCRAP

Much of the scrap is recycled and reused in the same fabrication industries that generated it. Little or no antimony scrap is exported. At times, some antimony scrap may be imported, but none is recorded to have been imported for 2000.

Because the disposition and recycling of LA batteries is well controlled and regulated at the State and local government levels, essentially all antimony used for batteries ultimately ends up as scrap and is recovered for eventual reuse in batteries. The production-use-recycle loop is efficient largely owing to requirements for battery retailer-installers to collect used batteries.

OLD SCRAP RECYCLING EFFICIENCY

Antimony old scrap recycling efficiency has been estimated to be 89%. Given the maturity of the antimony recycling industry, that approximate level is expected to be maintained. Antimony is a moderately priced metal, and the requirement to recycle LA batteries will continue, thus justifying maintaining a recycling efficiency of near 90%.

INFRASTRUCTURE OF ANTIMONY SCRAP RECYCLING INDUSTRY

Since the LA battery was developed in the mid-19th century, it has been by far the most important rechargeable battery in use worldwide. LA batteries may be categorized either as starting, lighting, and ignition (SLI) batteries (used in motor vehicles) or as industrial batteries. Industrial batteries include motive power batteries, which are used in such vehicles as fork lifts, golf carts, and mine locomotives.

Stationary batteries are used, for example, as emergency power batteries, load-leveling batteries, and telephone exchange batteries. In the United States, more than 90 percent of LA batteries manufactured in recent years have been of the SLI type, about 5 percent have been motive power types, and 5 percent are stationary types. Within a few years of the development of the LA battery, manufacturers began alloying lead with antimony for certain parts of the battery that require corrosion resistance, creep resistance, and good strength. The largest of these parts is the plate grid, which is the inactive part of the battery plate that gives mechanical support to the active electrode materials (lead dioxide in the positive plate and lead in the negative plate) and provides a conductive path for the electric current. In addition to strengthening the lead, antimony simplifies and speeds up the casting of grids by enhancing the fluidity of the melt and minimizing shrinkage during cooling. After the battery goes into service, antimony leached slowly from the grid promotes recrystallization of the lead oxide, which keeps the plate grid firm and retards the progressive softening and spalling that can otherwise develop with service age (Siegmond and Prengaman, 2001).

Antimony has at least two disadvantages. It tends to migrate during discharge from the positive to the negative plate where it lowers hydrogen overvoltage; this augments the breakdown of water in the electrolyte and the evolution of hydrogen. To resolve this problem requires venting the battery case, and the consequent loss of water from the electrolyte necessitates battery "maintenance" (periodic addition of water to the electrolyte). The second is that it also deposits on the negative plate, which sets up local cells. These deposits cause self-discharge of the battery at rates of up to 1 percent per day of battery charge when the battery is standing idle.

More than 30 years ago, manufacturers of SLI batteries began to lessen the need for maintenance by decreasing the amount of antimony used in plate grids. They developed "low-maintenance" batteries and then "maintenance-free" batteries. The changeover was driven by convenience to the automobile owner; by the much higher under-the-hood temperatures typical of modern automobiles, which increased the corrosion rate of the positive grid; and by the trend towards a much larger electrical load, which required a larger number of plates in each cell. Because the outer dimensions of the battery were not allowed to increase, using more plates meant using thinner plates, which necessitated a change in the method of manufacture of the grids. The result was that calcium-lead, which has better electrical conductivity and lends itself to rapid automated casting of grids, largely replaced antimonial lead in grids in the United States where the modern automotive battery is a sealed unit that requires no maintenance during its lifetime (Rand and others, 1998, p. 166-170). Its use in plate grids in some batteries accounts for nearly all the antimonial lead still used in batteries, but a 3 percent antimony alloy is still used for the posts and cell connectors of virtually all types of LA batteries, which include maintenance-free automotive types (Prengaman, 1995, p. 116).

The LA battery is a well-known, widely used product with a long history of use. The regulations that prohibit its disposal and require recycling to avoid the toxic effects of lead are well established. Thus, a very high percentage of the batteries is recycled. They are taken to thousands of local automotive repair shops, car dealerships, and gasoline stations by the driving public. The LA battery recycling industry is organized regionally. Currently, there are 16 secondary lead smelters owned by 11 parent companies in the United States. Typically, a secondary lead smelter, such as Sanders Lead Co. (Troy, AL), will smelt old (used) batteries and ship the secondary lead and scrap antimony produced to a regional LA battery maker, such as Johnson Controls Co. (Winston-Salem, NC), to be used in the production of new batteries. The new batteries will be delivered to retail and wholesale automobile establishments, such as dealerships, manufacturing plants, repair shops, and service stations. As local distributors are making deliveries, they are also collecting used LA batteries that will be returned to the secondary lead smelter.

PROCESSING OF ANTIMONY SCRAP

A typical process to recover antimony (and lead) from recycled battery scrap also uses a system of battery wrecking to remove the acid-battery crushing, the separation and recovery of the plastic battery case, and the polypropylene separation and desulfurization of the chemical paste in the batteries.

Batteries are fed continuously to a dual wheel puncher that perforates the battery cells and releases the acid. The acid is collected in a pit beneath the puncher, filtered, neutralized, and sent to water treatment. The batteries move on a rubber belt through a cooling chamber that uses liquid nitrogen. The chilled batteries are fed to an enclosed single-roll crusher. The crusher contains teeth that shred the batteries against breaker bars. The shredded battery scrap is charged to a heavy-media separator. In the separator, the paste portion of the battery is agitated to form a slurry of about 1.4 grams per cubic centimeter density. The plastic, hard rubber, and separators float before they are removed by screws to the polypropylene recovery system. The grids, connectors, and paste portion sink before they are removed from the separator via a drag conveyor. The lead-bearing portion is washed on a perforated screw conveyor to separate the paste from the posts and grids.

The paste slurry is collected in a sump and pumped into one of two paste desulfurization tanks. There, sodium carbonate is added to the paste under controlled pH conditions to desulfurize the lead sulfate portion of the paste. The reaction takes place readily at room temperature and is completed within an hour. The paste slurry is filtered in a plate and frame filter press. The Na_2SO_4 solution is pumped to water treatment. The filter cake is washed to remove Na_2SO_4 . The sulfur content of the paste can be reduced to less than 0.5 percent from 6 percent sulfur.

The hard rubber and separators along with the contained lead are blended with the desulfurized drosses, fluxes, grids, paste, and reducing agents for charging to the reverberatory furnace. The furnace is fed by a front-end loader with a 2.50-cubic-meter capacity. The mixed charge is metered to the dryer by a steel pan conveyor, which fits beneath the feed hopper and removes material at a controlled rate, elevates the feed, and discharges it into a stainless steel rotary dryer 2 meters (m) wide by 10 m long. The dryer is gas fired and dries the charge to less than 1 percent total moisture. The dried battery scrap charge is fed continuously to the reverberatory furnace by means of a closed steel pan conveyor. The dryer and feed systems are operated under negative pressure to keep the gas-handling system sanitary.

The furnace, which is the key aspect of the process, is 2.4 m wide by 10 m long and is fired by two natural-gas burners. The mixed dried charge is fed to the furnace continuously by means of the steel pan conveyor from the dryer. In the reverberatory furnace, oxidizing and reducing conditions are produced simultaneously. The aluminum, antimony, arsenic, calcium, tin, and alloying elements in the grids and straps are oxidized to the slag, and the lead is reduced and recovered as a low-impurity bul-

lion. Refining of the recovered metals is the next and final stage of their recovery. The low-antimony bullion is refined in 160-t kettles. A typical refinery may contain about five 85- to 160-t kettles, in which the bullion is refined to pure lead. The bullion is drossed to remove copper, nickel, oxides, and sulfur by using an automatic dross skimmer. Antimony, arsenic, selenium, tellurium, and tin as well as other impurities are removed to reduce their presence to extremely low levels. The refined bullion is pumped to a clean casting kettle, given a final cleaning step to remove any suspended oxides, and cast into either 2,000-pound blocks or 30-kilogram ingots. The slag overflows the furnace continuously and is solidified on a continuous slag caster in a size suitable for optimum feed to the electric slag reduction furnace. The partial composition of the slag typically is as follows: lead oxide, 20 to 30 percent; silicon oxide, 7 to 17 percent; calcium oxide, 4 to 10 percent; antimony oxide, 4 to 8 percent; tin oxide, 0.5 to 2 percent; and arsenic oxide 0.5 to 1 percent.

The low-impurity bullion also flows continuously from the furnace via a siphon at a rate of 325 to 375 metric tons per day. The bullion is either delivered directly to a 160-t receiving-drossing kettle or is solidified into 3-t blocks. The furnace charging system, metal tapping, and slag caster are ventilated to the sanitary gas filtration system along with the dryer.

Fluxes, reducing agents, and slag, are blended in the reduction furnace. A conveyor discharges the blended slag charge to a 1.5 by 7 m rotary dryer fired by the hot exit gases from the furnace. The dried and heated slag is discharged into the furnace. In the furnace, antimony, arsenic, and tin are reduced from the slag. The carbon monoxide from the reduction process is burned as it exits the furnace to provide heat for the dryer. The furnace is operated on a batch basis. When the furnace is fully charged (about 30 t of slag), the slag is held at temperature for a period of time to reduce the metal content of the slag to the desired level to produce a nonhazardous slag and a metal bullion.

The typical bullion content is as follows: antimony, 13 to 18 percent; tin, 1 to 2 percent; arsenic, 0.5 to 1 percent; copper, 0.3 to 0.4 percent; and nickel, 0.05 to 0.1 percent.

The balance is deduced to be principally lead. The slag is batch-topped into a receiving room where it is cooled and broken up for disposal. The metal bullion is tapped from the furnace periodically via a siphon into 2-t cast iron molds.

Gasses from the feed system, furnace, metal, and slag are combined and fed to a 6-cell pulse bag house containing about 850 high-temperature Teflon bags. The dust from the electric furnace system is fed continuously back to the reverberatory furnace in a closed screw conveyor system.

Bullion from the electric furnace is combined with bullion from the reverberatory furnace to produce lead-antimony alloys with 0.75 to 10 percent antimony.

OUTLOOK

Antimony recovered from old scrap has been an important part of the total antimony supply, but its decline as a significant

source in the last quarter century will continue. Since the advent and subsequent success of the automobile in the early part of the 1900s, the largest source of secondary antimony by far has been scrapped LA batteries. Other sources have been bearing metal, cable coverings, solder, and type metal, mostly of which use lead-based alloys. Being lead-based, most antimony scrap is reprocessed at lead smelters into reconstituted lead, most of which returns for use in LA batteries. Owing to the limited life of LA batteries and the huge stock of them in use, however, the component of antimony scrap derived from old (post-consumer) scrap will remain much more important than that derived from new (manufacturing) scrap for the remainder of the first decade of the 21st century. Furthermore, since the advent in the 1970s of low-maintenance and maintenance-free automotive batteries, a typical car LA battery today has only about 0.6 percent antimony. Thus, modern LA batteries have either low levels of or no antimony. Industry sources believe the antimony level in LA batteries will reach zero by 2020.

The use of antimony as an ingredient in flame retardants is expected to remain as its principal consumption category (Roskill Information Services Ltd., 2001, p. 130-131). This is expected to be true for international as well as U.S. markets. Little or no antimony is recycled in that end-use category. Thus, LA batteries are expected to continue to be, for the foreseeable future, the main source of recycled antimony.

REFERENCES CITED

- Carlin, J.F., Jr., 2002, Antimony, *in* Metals and minerals: U.S. Geological Survey Minerals Yearbook 2000, v. I, 4 p.
- Li, T., Archer, G.F., and Carapella, S.C., Jr., 1992, Antimony and antimony alloys, *in* Kirk-Othmer encyclopedia of chemical technology (4th ed.): New York, John Wiley & Sons, v. 3, p. 367-381.
- Miller, M.H., 1973, Antimony, *in* Brobst, D.A., and Pratt, W.P., eds., United States mineral resources: U.S. Geological Survey Professional Paper 820, p. 45-50.
- Plunkert, P.A., 1985, Antimony, *in* Mineral facts and problems: U.S. Bureau of Mines Bulletin 675, p. 33-45.
- Pregaman, R.D., 1995, Lead alloys, *in* Kirk-Othmer encyclopedia of chemical technology (4th ed.): New York, John Wiley & Sons, v. 15, p. 113-132.
- Rand, D.A.J., Woods, R., and Dell, R.M., 1998, Batteries for electric vehicles: Taynton, United Kingdom, Research Studies Press, and New York, John Wiley & Sons, 577 p.
- Roskill Information Services Ltd., 2001, The economics of antimony (9th ed.): London, Roskill Information Services Ltd., 230 p. plus two appendices.
- Siegmund, Andreas, and Pregaman, R.D., 2001, Grid alloys for automobile batteries in the new millennium: JOM, v. 53, no. 1, January, p. 38-39.
- Wang, C.Y., 1952, Antimony—Its geology, metallurgy, industrial uses, and economics (3d ed., revised): London, Chas. Griffin and Co., 170 p.

APPENDIX—DEFINITIONS

apparent consumption. Primary plus secondary production (old scrap) plus imports minus exports plus adjustments for Government and industry stock changes.

apparent supply. Apparent consumption plus secondary production (new scrap).

calcinations. The heating of ores, concentrates, precipitates, or residues to decompose carbonates, hydrates, or other compounds.

dissipative use. A use in which the metal is dispersed or scattered, such as paints or fertilizer, making it exceptionally difficult and costly to recycle or recover the metal.

home scrap. Scrap generated as process scrap and consumed in the same plant where it is generated.

new scrap. Scrap produced during the manufacture of metals and articles for both intermediate and ultimate consumption, including all defective finished or semifinished articles that must be reworked. Examples of new scrap are borings, castings, clippings, drosses, skims, and turnings. New scrap includes scrap generated at facilities that consume old scrap. Included as new scrap is prompt industrial scrap—scrap obtained from a facility separate from the recycling refiner, smelter, or processor. Excluded from new scrap is home scrap that is generated as process scrap and used in the same plant.

new-to-old-scrap ratio. New scrap consumption compared with old scrap consumption, measured in weight and expressed as a percentage of new plus old scrap consumed (for example, 40:60).

old scrap. Scrap including (but not limited to) metal articles that have been discarded after serving a useful purpose. Typical examples of old scrap are electrical wiring, lead-acid batteries, silver from photographic materials, metals from shredded cars and appliances, used aluminum beverage cans, spent catalysts, and tool bits. This is also referred to as post-consumer scrap and may originate from industry or the general public. Expended or obsolete materials used dissipatively, such as paints and fertilizers, are not included.

old scrap generated. Metal content of products theoretically becoming obsolete in the United States in the year of consideration, excluding dissipative uses.

old scrap recycling efficiency. Amount of old scrap recovered and reused relative to the amount available to be recovered and reused. Defined as [consumption of old scrap (COS) plus exports of old scrap (OSE)] divided by [old scrap generated (OSG) plus imports of old scrap (OSI) plus a decrease in old

scrap stocks (OSS) or minus an increase in old scrap stocks], measured in weight and expressed as a percentage:

$$\frac{\text{COS} + \text{OSE}}{\text{OSG} + \text{OSI} + \text{decrease in OSS or - increase in OSS}} \times 100$$

old scrap supply. Old scrap generated plus old scrap imported plus a decrease in old scrap stocks or minus an increase in old scrap stocks.

old scrap unrecovered. Old scrap supply minus old scrap consumed minus old scrap exported.

price. The total value of old scrap consumed was estimated by adding the value of used beverage can scrap consumed to the value of other old scrap. The value of used beverage can scrap was calculated using the average annual transaction price for used aluminum beverage can scrap. The value of other old scrap was based on the average annual price for old aluminum cast and sheet scrap. The total value of net imports of aluminum scrap was derived from trade statistics reported by the U.S. Census Bureau as follows: total value of aluminum scrap imports minus total value of aluminum scrap exports.

recycling. Reclamation of a metal in useable form from scrap or waste. This includes recovery as the refined metal or as alloys, mixtures, or compounds that are useful. Examples of reclamation are recovery of alloying metals (or other base metals) in steel, recovery of antimony in battery lead, recovery of copper in copper sulfate, and even the recovery of a metal where it is not desired but can be tolerated—such as tin from tinplate scrap that is incorporated in small quantities (and accepted) in some steels only because the cost of removing it from tinplate scrap is too high and (or) tin stripping plants are too few. In all cases, what is consumed is the recoverable metal content of scrap.

recycling rate. Fraction of the apparent metal supply that is scrap on an annual basis. It is defined as [consumption of old scrap (COS) plus consumption of new scrap (CNS)] divided by apparent supply (AS); measured in weight and expressed as a percentage:

$$\frac{\text{COS} + \text{CNS}}{\text{AS}} \times 100$$

scrap consumption. Scrap added to the production flow of a metal or metal product.