

U.S. DEPARTMENT OF THE INTERIOR  
U.S. GEOLOGICAL SURVEY

SILVER RECYCLING IN THE UNITED STATES IN 2000

By Henry E. Hilliard

Reston, VA

Open-File Report 03-33

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# CONTENTS

Abstract	1
Introduction	1
U.S. and World Geologic Occurrence of Silver	1
Mining and Processing Methods	1
Sources of Silver Scrap	2
Old Scrap Generated	4
Photographic Wastes	4
Electrical and Electronics Scrap	5
Jewelry and Silversmiths Scrap	6
Spent Catalysts	6
Home Scrap	6
Disposition of Silver Scrap	6
Old Scrap Recycling Efficiency	7
Infrastructure of Silver Scrap Recycling	7
Photographic Processing Facilities	7
Electrical and Electronics Scrap	7
Jewelry and Sterling ware	8
Catalysts	8
Manufacturing Wastes and Scrap	8
Processing of Silver Scrap	8
Photographic Wastes	8
Electrolysis	9
Metallic Replacement	9
Precipitation	9
Electrical and Electronics Scrap	9
Jewelry and Silversmith Scrap	10
Outlook	10
References Cited	10
Appendix—Definitions	12

## FIGURES

1. Flow diagram showing U.S. silver materials flow in 2000	3
2. Graph showing U.S. silver consumption, by end-use sector, from 1980 through 2000	5

## TABLES

1. Salient statistics for U.S. silver scrap in 2000	4
2. U.S. silver consumption in the photographic industry	5

## Silver Recycling in the United States in 2000

By Henry E. Hilliard

### ABSTRACT

In 2000, the global silver supply deficit (the difference between mine and scrap supply and silver demand) was more than 3,000 metric tons. U.S. silver demand for photographic applications alone was nearly equal to annual U.S. silver production. Until 1968, the U.S. silver deficit was filled by withdrawals from the U.S. Treasury reserves. In 2000, the deficit was filled by destocking, imports, and recycling. Photographic wastes, spent catalysts, and electronic scrap are the major sources of materials for silver recycling. Nearly 1,800 tons of silver contained in these materials were available for recycling in 2000. Other recyclable silver-bearing materials include dental alloys, jewelry, and silverware. In 2000, an estimated 1,700 tons of silver were recovered from secondary sources in the United States. The U.S. recycling efficiency for old scrap was calculated to have been 97 percent in 2000; the recycling rate was estimated to be 32 percent.

### INTRODUCTION

The use of silver dates from the earliest historic records, and it was usually extracted by melting silver-bearing lead ore (galena). Silver, which is the least expensive of the precious metals, is the whitest element and has the highest electrical and thermal conductivity of all the metals. Silver was once used primarily for coinage, decorative articles, jewelry, and silverware. Today, coinage has become an insignificant use and the aesthetic uses for silver have been surpassed by industrial and technical uses. Industrial and technical uses include brazing alloys, catalysts, electrical/electronics products, and photographic paper and film. Recycling<sup>1</sup> of silver from these uses is an important part of its supply.

### U.S. AND WORLD GEOLOGIC OCCURRENCE OF SILVER

Identified resources of silver in the United States comprise an estimated 33,000 metric tons (t) at 2000 prices and a reserve base of about 72,000 t (Hilliard, 2001). Only a small portion of these resources are silver ores that can yield silver as the main product (primary ores); the remainder can be economically recovered only as a byproduct of copper, gold, lead, or zinc production (U.S. Geological Survey, 2000, p. 10-12).

There are about 55 silver minerals, which include argentite ( $\text{Ag}_2\text{S}$ ), cerargyrite ( $\text{AgCl}$ ), native silver ( $\text{Ag}$ ), pearceite ( $\text{Ag}_{16}\text{As}_2\text{Sb}_{11}$ ), polybasite ( $\text{Ag}_{16}\text{Sb}_2\text{S}_{11}$ ), proustite ( $\text{Ag}_3\text{SbS}_3$ ), stephanite ( $\text{Ag}_5\text{SbS}_4$ ), stromeyerite ( $\text{AgCaS}$ ), and the tellurides. These minerals are commonly associated with lead, but they are also associated with copper, gold, and zinc. Ores in which silver is the main component are associated with igneous rocks of intermediate felsic composition. Examples include the McCoy/Cove Mine and the Comstock gold-silver deposit in Virginia City, NV, where almost 31,100 t was produced, and cobalt-silver ores in the Cobalt District of Ontario, Canada. The main silver-producing tetrahedrite vein deposits in the Coeur d'Alene district of Idaho occur in Precambrian quartzites and argillites. Silver-bearing base-metal ores are found in copper porphyries, massive sulfide ores, and copper-lead-zinc vein deposits (Heyl and others, 1973; Reese, 1983, p. 3).

In 2000, Mexico was the world's leading silver-producing country with a production of 2,620 tons. Peru (2,150 t) was second followed by Australia (2,060 t), the United States (1,980 t), and Chile (1,240 t). World production in 2000 was 18,300 t (Hilliard, 2002, p. 70.11).

### MINING AND PROCESSING METHODS

In the United States, silver ore is mined primarily by open-pit and subsurface shafts and drifts. The method used varies from one ore body to another depending on the ore grade, the steepness of the terrain, availability of transportation, reserves, ore body or vein shapes, depth of mining, character of host rock, and economic factors peculiar to the individual mine. At the Sunshine Mine in Coeur d'Alene, ID, the tetrahedrite silver ore is extracted through one main vertical shaft and several winzes and developmental drifts along the veins. Mining is principally by the cut-and-fill stoping method; explosives break the vein and host rock into pieces for transport by mine car and electric locomotive to the main shaft where the ore is hoisted to the surface. At the surface, the ore is subjected to crushing and fine grinding. Amalgamation, cyanidation, and leaching were first adapted to extract silver from high-grade ores. As these ores became less plentiful, processes for treating low-grade ores were developed, thus allowing amalgamation to be essentially discontinued. Improvements in the technique of cyanidation of low-grade gold-silver ores and the development of activated-carbon stripping of the pregnant solutions led to the use of cyanidation for these ores. For silver-bearing lead ores, a flotation process is used to separate the silver-bearing galena from waste rock particles (tailings) to form a concentrate. Ground-up

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<sup>1</sup>Definitions for selected words are found in the Appendix.

ore, water, and special chemicals are mixed together and constantly agitated in a bank of flotation cells. Air is blown through the mixture in each cell, and fine silver-bearing galena particles adhere to the bubbles that rise to form a froth on the surface of the cell. The tailings sink to the bottom of the cell and are removed. The froth is skimmed off, and the resulting silver-lead sulfide concentrate may assay from 0.8 to 1 kilogram per metric ton (kg/t) of silver (Heinen and others, 1979, p. 1-5; Hussey and others, 1979, p.1-6).

The concentrate produced in the flotation cell is sintered (partly melted) to combine the fine particles into lumps and to remove some of the sulfur as sulfur dioxide. It is then smelted in a blast furnace and drossed (removal of trace copper and impurities) to produce a crude lead metal that may contain as much as 2 kg/t of silver.

Silver is recovered when lead is refined to high purity. Crude lead is remelted, and antimony and other impurities are removed. The molten lead is then poured into a large upright container where it plunges through a molten zinc metal layer that floats on top of molten lead. The container is increasingly cooled toward its base so that as the incoming molten lead descends, the contained silver and any contained gold and copper combine with the molten zinc dragged down from the zinc layer and form crystals of copper-gold-silver-and zinc alloy (called doré). The crystals float to the surface and redissolve in the zinc layer. The zinc layer is periodically skimmed off. The doré is removed for further smelting. The final smelter product is cast into plates for the electrolytic removal of copper and separation of high-purity silver and gold bullion.

## **SOURCES OF SILVER SCRAP**

For analytical purposes, silver in circulation can be divided into three categories—products still in use (coins and medallions held for investment), items scrapped and/or recycled, and those irretrievably lost (figure 1; table 1). For example, of the 2,500 t of silver consumed in the United States in photographic applications in 2000, some of the metal is still in use (archived X-ray film, black and white photographs), another part has been recycled (silver recovered from fixer solutions), and some of it has been irretrievably lost (low-grade film disposed of in landfills and dilute solutions poured down drains) (World Silver Survey, 2001, p. 55).

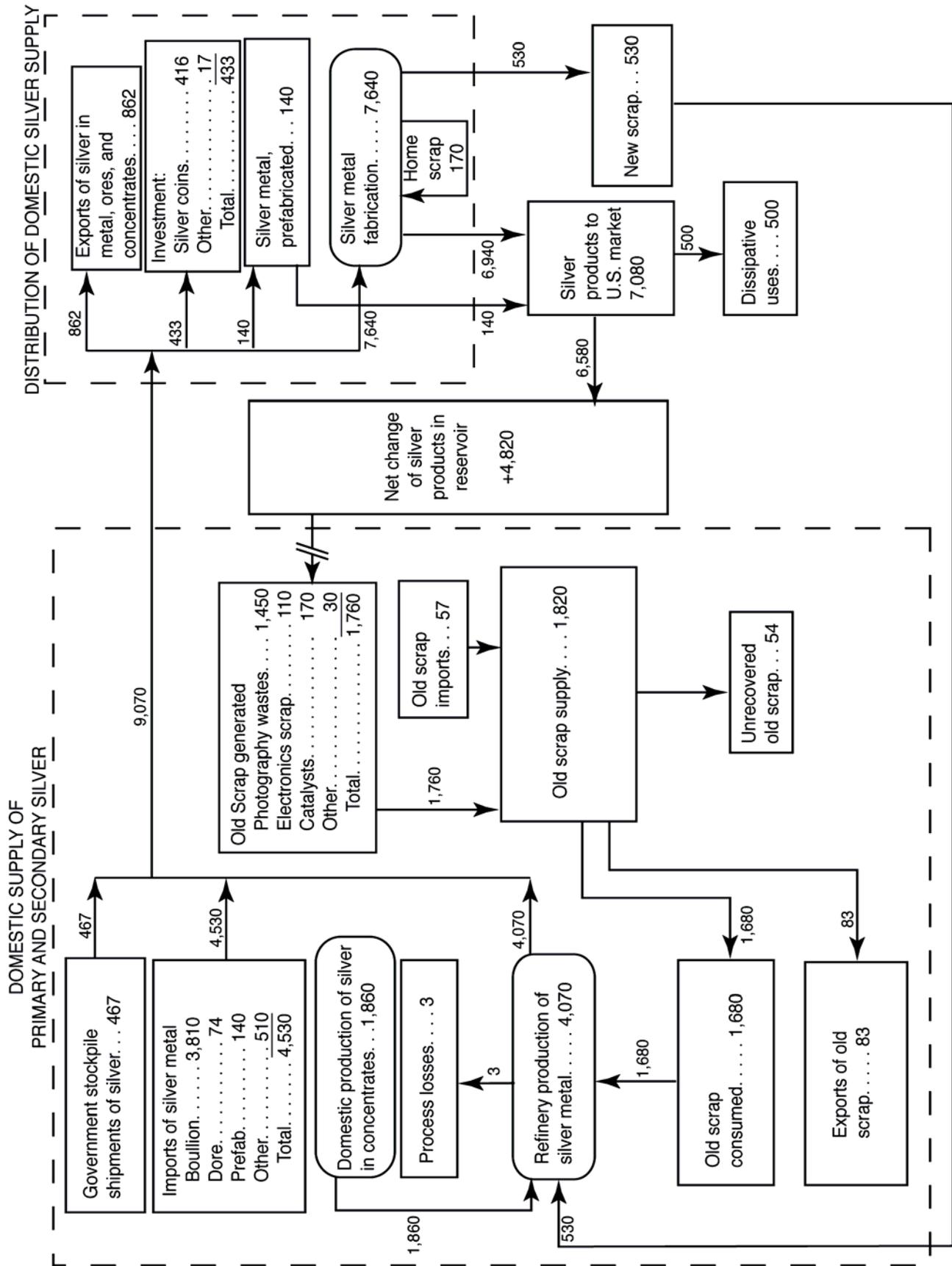


FIGURE 1. U.S. silver materials flow in 2000. Values are in metric tons of silver.

**Table 1.** Salient statistics for U.S. silver scrap in 2000.  
[Values in metric tons of contained silver, unless otherwise specified]

Old scrap:	
Generated <sup>1</sup> .....	1,760
Consumed <sup>2</sup> .....	1,680
Consumption value .....	\$270 million
Recycling efficiency <sup>3</sup> .....	97 percent
Supply <sup>4</sup> .....	1,820
Unrecovered <sup>5</sup> .....	54
New scrap consumed <sup>6</sup> .....	530
New-to-old scrap ratio <sup>7</sup> .....	24:76
Recycling rate <sup>8</sup> .....	32 percent
U.S. net exports of scrap <sup>9</sup> .....	26
Value of U.S. net imports of scrap .....	\$4.2 million

<sup>1</sup>Silver content of products theoretically becoming obsolete in the United States in 2000. Dissipative uses are excluded.

<sup>2</sup>Silver content of products that were recycled in 2000.

<sup>3</sup>(Old scrap consumed plus old scrap exported) divided by (old scrap generated plus old scrap imported minus old scrap stock increase).

<sup>4</sup>Old scrap generated plus old scrap imported plus old scrap stock decrease.

<sup>5</sup>Old scrap supply minus old scrap consumed minus old scrap exported minus old scrap stock increase.

<sup>6</sup>Including prompt industrial scrap but excluding home scrap.

<sup>7</sup>Ratio of quantities consumed, in percent (See Appendix–Definitions).

<sup>8</sup>Fraction of the metal apparent supply that is scrap, on an annual basis. It is defined as (consumption of old scrap plus consumption of new scrap) divided by apparent supply (see appendix), measured in weight and expressed as a percentage.

<sup>9</sup>Trade in scrap is assumed to be principally in old scrap. Net exports are exports of old scrap minus imports of old scrap.

### OLD SCRAP GENERATED

#### Photographic Wastes

Manufacturers of photographic materials are reluctant to provide accurate data about their silver consumption, how much silver was purchased, and how much was recycled from manufacturing wastes and captive film processing establishments. Nevertheless, the consumption of silver can be estimated by calculating the amount contained in the products used by consumers.

The silver content of photographic materials, which is called the coating weight, varies from less than 1 to 8 grams per square meter (g/m<sup>2</sup>). Generally, slow-speed, fine-grain emulsions have lower coating weights than high-speed coarse-grain emulsions; and films usually have higher speed and coarser grain emulsions than photographic papers. Normally, about 50 percent of the total silver incorporated in emulsions is used for the formation of continuous tone images; for example, chest X-rays, pictorial scenes, and portraits. Images of line drawings, documents, graphs, and half-tone images normally require about 20 percent of the available silver (positive image) to about 80 percent for negative images. The average coating weight of silver on paper is 2 ounces per 1,000 square feet (Eastman Kodak Company, 1998).

The calculation of the amount of silver available for recovery based on product usage requires two sets of data—the amount of films and paper consumed in square meters and the coating weight of each product type; that is, the silver concentration per square meter. To estimate the amount of recoverable silver based on U.S. silver consumption in color negative film in 2000, the following were assumed:

1. The average film mix was 70 percent with a coating weight of 5.4 g/m<sup>2</sup> and 30 percent with a coating weight of 8.0 g/m<sup>2</sup>.
2. The average roll of film was 24 exposures [0.041 square meter (m<sup>2</sup>)].

In 2000, U.S. consumption of color roll film, which included disk and one-time-use cameras, was 1,030 million rolls (Donald Franz, Photofinishing News, oral commun., 2002).

The average amount of silver available per roll of film was as follows:

$$\begin{aligned}
 5.4 \text{ g/m}^2 \times 70 \text{ percent} &= 3.8 \text{ g/m}^2 \\
 8.0 \text{ g/m}^2 \times 30 \text{ percent} &= 2.4 \text{ g/m}^2 \\
 \text{Total} &= 6.2 \text{ g/m}^2
 \end{aligned}$$

$$6.2 \text{ g/m}^2 \times 0.041 \text{ m}^2 \text{ per roll} = 0.254 \text{ gram (g) per roll.}$$

The amount of silver available for recovery from color films was as follows:

0.254 g per roll x 1,030 million rolls x 100 percent recoverable = 262 million grams, or about 260 t. Following this procedure for the other types of film, paper, and other photographic materials, U.S. consumption of silver by the photographic industry in 2000 was estimated to be 1,870 t; an estimated 1,450 t of silver was available for recycling from photographic wastes. The Silver Institute estimated the total U.S. demand for silver in photographic applications in 2000 to be about 2,500 t. On the basis of the above figures,

about 630 t of silver was contained in photographic products in the pipeline for delivery to consumers, on the shelf, or in the cameras of consumers. An estimated 420 t of silver was retained on negatives and photographic papers and was irretrievably lost.

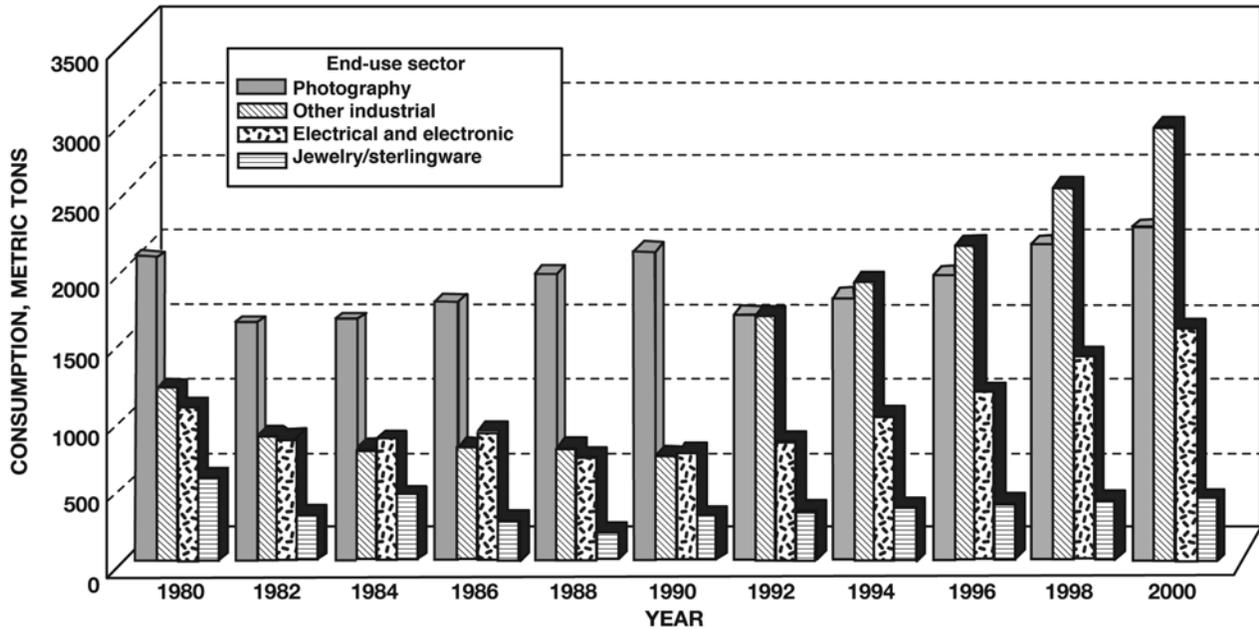


FIGURE 2. U.S. silver consumption, by end-use sector, from 1980 through 2000. Other industrial includes catalysts, electroplated wares, coins and medallions, dental and medical, and bearings.

Table 2. U.S. silver consumption in the photographic industry

Photographic material	Coating weight (grams per square meter)	U.S. consumption (millions)	Silver content (metric tons)	Recoverable silver		
				Percentage	Metric tons	
<b>Films</b>						
	Color negative	5-8	<sup>1</sup> 1,030	262	100	262
	Color reversal	4-6	<sup>1</sup> 51	11	100	11
	Black and White	5-7	<sup>1</sup> 40	10	40-50	4
	Motion picture	5-7	<sup>2</sup> 27.4	165	100	165
<b>Plates:</b>						
	X-ray(medical, industrial, dental)	4-6	<sup>2</sup> 110	550	40-50	248
	Graphic arts	3-5	<sup>2</sup> 53.1	212	20-80	138
<b>Paper:</b>						
	Black & white (C.T.)	1-5	<sup>2</sup> 14.1	56	40-60	28
	Black & white (line)	1-5	<sup>2</sup> 8.645	35	20-80	21
	Color	0.7-1/2	<sup>2</sup> 572	<u>572</u>	100	<u>572</u>
<b>Total</b>				<u>1,870</u>		<u>1,450</u>

<sup>1</sup>Rolls of film.

<sup>2</sup>Square meters of photographic film, paper, or plates.

### Electrical and Electronics Scrap

Electronics scrap can vary widely in physical aspect, metal content, and heterogeneity and only a weak infrastructure exists in the United States to capture electronics wastes. More than 20 million personal computers became obsolete in 2000. Most of these are in storage. Of the remainder, the bulk were disposed of; probably fewer than 6 percent were recycled. In 2000, the useful life of a computer was 3 to 5 years and shrinking. More than 63 million personal computers are projected to be retired in 2005 (U.S. Environmental Protection Agency, 2000).

Approximately 400 companies have been identified as having electronics recycling operations in the United States. The top 10

companies recycled approximately 65 percent of the total volume of available electronics scrap. The top five companies recycled about 43 percent. Among the top companies, 2 recycled more than 600 metric tons per year (t/yr), and the next 10 recycled between 300 and 600 t/yr. Most companies recycled less than 160 t/yr (International Association of Electronics Recyclers, 2001).

The scope of electronics recycling includes computer, telecommunications, military, and consumer electronics equipment. The total weight of electronics products recycling in 2000 was approximately 8,900 t. In addition, approximately 1,000 t of electronics parts, subassemblies, and materials were recycled (International Association of Electronics Recyclers, 2001). The silver content of computer and other electronics scrap can vary from 0.02 to 0.5 percent (Mid-Atlantic Consortium of Recycling and Economic Development Officials, 2000). The U.S. Geological Survey's estimate for silver recycled from this source was 90 t in 2000.

The Defense Reutilization and Marketing Service (DRMS) receives excess and obsolete electronics equipment from the U. S. Department of Defense (DOD). This property may be distributed to other parts of DOD or transferred to other Federal agencies, donated to State and local governments, sold by DRMS commercial venture agents, or demanufactured. In 2000, DRMS processed 334,500 t of military and other electronics scrap; 3,520 t of this material contained precious metals from which 334 kilograms (kg) of gold, 18 t of silver, 51 kg of palladium, and 9 kg of platinum were recovered (John Barrett, Demanufacturing Program Manager, Defense Reutilization and Marketing Service, oral commun., 2001).

### **Jewelry and Silversmith Scrap**

The silverware industry produces liquid and solid scrap. Most of the liquid waste is produced by the silver plating segment of the industry. Solid wastes are mostly from the production of sterling ware. No data are available on the amount of each type of waste that is processed for recovery.

### **Spent Catalysts**

Catalyst formulations are closely held proprietary technology. Silver-bearing scrap generated during the early stages of the catalyst production process is simply returned to the process. Scrap that is generated at a later stage of the process, such as end-of-life catalysts or a substrate that has already been coated with silver, is usually sent to a toll refiner for the recovery of silver. Catalyst manufacturers commonly take back spent catalysts from their customers and arrange for the recycling themselves. This is partly to protect proprietary catalyst formulations.

A typical use of a silver-based heterogeneous catalyst in a chemical process is the catalytic oxidation of ethylene to ethylene oxide over a silver catalyst. The catalyst is believed to be silver on a preformed alpha-alumina carrier. The catalyst for each process is somewhat different, and each manufacturer offers its own proprietary catalyst. Exact compositions and methods of manufacture of the catalyst are closely guarded secrets as are the quantities of catalyst used for each process (Hull & Co., 1990, p. 109).

The silver content of the catalysts has been estimated to fall in the range of 8 to 15 percent. Some ethylene oxide plants that use oxygen require an initial silver charge of about 1 kg per 1,200 kilograms per year (kg/yr) of ethylene oxide capacity; others are estimated to require an initial silver charge that is about 75 percent higher, or about 1 kg/700 kg/yr of ethylene oxide capacity. Catalyst life varies considerably, particularly for air process plants, depending on the purity of the air and ethylene feed (traces of chlorine can poison the catalyst). A good estimate of the average catalyst life for the air process is 2 to 3 years, although some catalyst charges have lasted as long as 12 years. Ethylene oxide plants that use an oxygen feed enjoy a longer catalyst life that has been estimated to be from 5 to 7 years (Hull & Co., 1990, p. 225). U.S. ethylene oxide output in 2000 was 3.9 million metric tons (Chemical & Engineering News, 2001). Assuming production at 95 percent of capacity and a 12-percent silver content of the catalyst, total silver content of the U.S. catalyst inventory in 2000 was estimated to be about 510 t.

## **HOME SCRAP**

Companies that manufacture semifinished and final products that contain silver and other precious metals reprocess virtually all scrap generated for precious-metals recovery. Casting scrap, such as croppings of castings, is recovered by simply adding it to melt charges. This material is not counted as scrap consumed because it is continuously recirculated and never leaves the plant. Grindings, ingot scalping, and machine chips are processed through toll refining.

## **DISPOSITION OF SILVER SCRAP**

Silver scrap is generated primarily in the industrialized countries, which indicates that demand for silver is skewed toward industrial nations. Also, silver-bearing scrap is mostly from electronics and photographic sources. Jewelry and silverware are less important as a source of recycled metal. This is important because despite strong growth in demand in developing countries, consumption of silver in electronics and photography in 2000 was still biased towards the United States, Europe, and Japan. By contrast, demand for silver in jewelry was dominated by Indian and other Asian markets where recycling rates are traditionally very high. The closure of the Handy & Harman facility in Attleboro, MA, in 1999 led to a substantial loss of capacity and to a temporary disruption in the scrap supply chain. Although other plants took up the slack, capacity constraints were still evident at times, which resulted in higher volumes of scrap being treated outside the United States. Nevertheless, the scrap supply increased in the United States in 2000 to 1,820 t. This was due to an increase in the recycling of photographic wastes, which has been growing for about 10 years, and an increase in the volume of spent catalysts; the volume of electronics scrap also seems to have risen.

## **OLD SCRAP RECYCLING EFFICIENCY**

Recycling efficiency shows the relation between old scrap materials theoretically available for recycling and old scrap that is actually recycled. Silver-bearing scrap materials consist mostly of electrical and electronics scrap, photographic wastes, scrap jewelry, silverware, and spent catalysts. The chemical industry recycled spent silver-bearing catalysts with recovery rates of more than 98 percent. The exact figure for recycling efficiency is uncertain owing to lack of data on stocks of silver-bearing material, but old scrap recycling efficiency was estimated to be 97 percent.

## **INFRASTRUCTURE OF SILVER SCRAP RECYCLING**

### **PHOTOGRAPHIC PROCESSING FACILITIES**

Silver-based photographic materials are made for many applications that require different photochemical and physical response characteristics and a wide variety of formats and sizes. All of these products are laminates that consist of a surface-treated support and bonded emulsions. Films have transparent or translucent plastic supports, which are mostly cellulose triacetate and polyester; papers have mostly a paper core coated with polyethylene resin layers on both sides. The front layer contains white titanium dioxide for high reflectivity, and the back layer contains a matting agent. Emulsions contain face-centered cubic silver bromide and silver chloride and may contain up to 10 weight-percent hexagonal silver iodide. A high degree of purity is required of the silver halides, the gelatin, and any other ingredients.

Silver, which is the material responsible for producing the photographic image, is found in a number of different materials in facilities that process photographic materials. The leading sources of silver for recycling are photographic films, processing solutions, and papers. Once processed, silver is retained on the film and paper or transferred to the photographic processing solution. Silver in the processing solutions may be collected by using silver-recovery equipment, or the solutions can be sent off-site for recovery and subsequent delivery to a refinery. Silver may also be recovered from unprocessed black-and-white film and paper. Black-and-white film and paper include graphic arts film; medical, dental, and industrial X-ray film; and micrographic film. With color film and paper, however, all the silver and unused silver halides are removed during processing and accumulate in the fixer or bleach-fix solution. Therefore, processed color photographic film and paper (negatives, transparencies, and prints) do not contain appreciable amounts of silver (Eastman Kodak Company, 1998).

### **ELECTRICAL AND ELECTRONICS SCRAP**

Electronics scrap, especially obsolete military electronics equipment, can be a fertile source of precious metals. The value is not always obvious because small quantities of precious metals are dispersed among large quantities of base metals, ceramics and plastics. Gold and silver can be found in anodes, diodes, grid wires, integrated circuits, printed circuit boards, relays and contact points, and waveguides. Precious metals may also be found in batteries, cable connectors, capacitors, laminates, lead frames, resistors, semiconductors, slip-ring assemblies, and transformers (Hilliard and others, 1983). The percentage of precious metals in electronics scrap is usually very small, but the value can be very high. Only small quantities of silver are consumed in individual items of electrical and electronics equipment, but the number of items in which it is consumed is very large. The National Electrical Manufacturers Association (2001) lists more than 50 categories of electrical components that incorporate silver as the contact material.

Electronics scrap includes nonrechargeable batteries that contain silver compounds. The silver oxide-zinc cell has a cathode of  $\text{Ag}_2\text{O}$  or  $\text{AgO}$ . These cells are characterized by a high-energy output per unit weight and a fairly constant voltage during discharge. Originally designed exclusively for the military, satellite applications, and space probes, these cells are now being used as power sources for calculators, cell phones, hearing aides, and wristwatches. Consumption of silver in batteries accounts for about 7 percent of total silver consumption by the electrical and electronics sectors (Roskill Information Services Ltd., 1992, p. 283-284).

Only a weak infrastructure exists in the United States to capture electronics waste. A few individuals and organizations have begun to realize the potential value of discarded electronics and have instituted procedures to reclaim valuable metals from these materials. The DOD and other Government agencies turn in most precious-metals-bearing scrap to the DRMS. Once gathered and accounted for, the material is sent to a refiner. The finished product, 0.999 percent pure refined metal, is sent to the Defense Industrial Supply Center. The DRMS recovers precious metals from scrap property only when it makes good business sense. In some cases, such as the metal found in used silver batteries, precious metals are too costly to recover (Defense Reutilization and Marketing Service, 2001).

### **JEWELRY AND STERLING WARE**

Products fabricated by jewelers and silversmiths consist largely of precious metals. Manufacturing scrap (new scrap) generated from these sources is, by its nature, of high value, and, therefore, intensive collection techniques are always practiced. Virtually everything is saved—clippings, fillings, lathe chips, production rejects, scrap from spinning sterling hollowware, and silver filled

blanking scrap, and grindings are swept up. Crucibles, dust filters, floor mats, and polishing cloths are collected. Also old scrap, which includes broken, used, and obsolete items of jewelry and sterlingware, are returned by users to dealers for salvage of metal values.

## **CATALYSTS**

A catalyst is a substance that changes the rate of a chemical reaction, but is itself not permanently changed in chemical form. A heterogeneous catalyst is one in which phase boundaries exist between the catalysts and the reacting substances; for example, a solid catalyst in a gas or liquid phase reaction. Heterogeneous catalysts that contain silver and silver compounds are widely used in research and industry for a variety of oxidation, reduction, and polymerization reactions. The products made by these processes, such as formaldehyde and ethylene oxide, have great economic value. Such catalysts can be deactivated by several different mechanisms, but deactivation is primarily the result of the accumulation of materials from the process stream onto the surface of the catalyst. This deposit results in substantial deterioration in catalyst performance. The catalyst activity or its ability to convert reactants is adversely affected by this deposition, and the catalyst is referred to as “spent” (Fung, 1993, p. 91-96).

The original performance of the spent catalyst can be restored by proper regeneration to remove accumulated surface materials (Kim and others, 1992, p. 39-46). Regeneration allows continued use of the same catalyst for several years. The number of times that a catalyst can be regenerated is limited, however, and eventually the catalyst must be replaced; catalysts may be regenerated two or more times. As a general rule, after a catalyst can no longer be regenerated to at least 75 percent of its original activity, it is reclaimed or discarded (Oil & Gas Journal, 1998, p. 49).

When catalysts are removed from service, they are sent to a toll refiner for recovery of the metal values. Toll refining is refining in which a fee, or toll, is charged to the owner of feedstock to be processed, to whom the refined product is returned for use or sale. The amount of silver used in catalysts for various chemical applications in 2000 was estimated to be 1,300 t. Each year a number of catalysts are taken out of service and recycled. The effect on silver demand, however, is limited to the metal lost in the recycling process. Because silver is valuable, great care is exercised in monitoring all streams that enter and leave catalyst manufacturing and recycling sites to ensure that no significant amount of metal is lost. In the United States, yearly overall materials recovery rates of more than 99 percent are attainable (World Silver Survey 2000, 2000, p. 43).

## **MANUFACTURING WASTES AND SCRAP**

Manufacturing wastes and scrap accounts for about 15 percent of silver consumption. The principal sources of such wastes are excess or rejected parts, experimental parts, material removed to eliminate defects or for testing, and above all, finishing waste consisting of cutting pattern losses, edge trim, and perforations. The silver content of these materials is almost always recovered by the manufacturer, and efficiency of recovery is better than 99 percent. Recovered silver is usually reused by the manufacturer in-house. Information on this aspect of operations is seldom released by the manufacturer.

## **PROCESSING OF SILVER SCRAP**

### **PHOTOGRAPHIC WASTES**

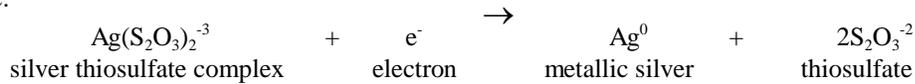
A number of techniques are available for removing silver from silver-rich photographic processing solutions. Of these, three are used in virtually all practical methods of silver recovery—electrolysis, metallic replacement, and precipitation.

Methods that are successfully used in other industries to recover silver, such as electrowinning, are not be applicable to photographic processing solutions because they tend to cause significant solution decomposition.

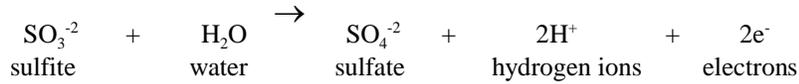
## Electrolysis

In electrolytic silver recovery, a direct current is passed through a silver-rich solution between a positive electrode (anode) and a negative electrode (cathode). During this electrolytic process, an electron is transferred from the cathode to the positively charged silver, thus reducing it to its metallic state, which adheres to the cathode. In a simultaneous reaction at the anode, an electron is taken from some species in solution. In most silver-rich solutions, this electron usually comes from sulfite. An overview of the reaction is as follows:

Cathode:



Anode:

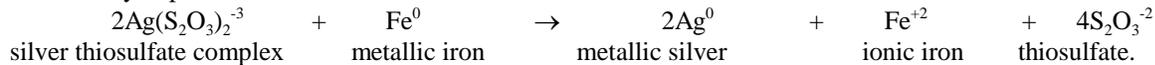


In solutions high in iron, such as bleach fixes, the silver plating proceeds more efficiently under slightly alkaline conditions.

Electrolysis produces a nearly pure metallic silver; any contamination by some surface reactions is slight. Purity of the plated silver is greater than 90 percent.

## Metallic Replacement

Metallic replacement, which is also called cementation, is the reduction of the silver thiosulfate in solution to metallic silver by metallic iron, which is usually present as a steel wool. Commercial equipment used for the process is referred to as “metallic recovery cartridges.” Steel wool was chosen as the reducing agent because of its large surface area. The steel wool is chopped and packed into a cartridge or wound on a core. Other sources of iron include iron particles glued to fiberglass, iron-impregnated resin blocks, or wound-iron screening materials (Eastman Kodak Company, 1999). The following metallic replacement process is similar to the above electrolytic process:



The final silver concentration is affected by flow rate, iron surface area, contact time, pH, original silver concentration, thiosulfate concentration, and the volume that passes through the cartridge. The silver concentration can be reduced to less than 5 milligrams per liter by using this method (Skoog and West, 1965, p. 425-439; Encyclopedia of Physical Science and Technology, 1987, p. 461-506).

## Precipitation

Precipitation can remove silver from silver-rich solutions, thus reducing silver concentrations to low parts-per-million levels. Common precipitating agents are alkali metal salts of sulfide (sodium sulfide, potassium sulfide, and so forth) which form silver sulfide in solution. The precipitation method is not widely used because the silver concentration in solution must be determined accurately so that only stoichiometric amounts of sulfide are added to the silver-rich solution to prevent overdosing. Excess sulfide leads to the discharge of toxic hydrogen sulfide gas.

Ion exchange, which refers to the substitution of an ion that is bound on a large polymer molecule, may also be used to remove silver from solutions. Ion exchange works best on such dilute solutions as wash-water. Typically, ion exchange, which requires large capital investments and technical expertise, is used only when wash-waters must meet very low silver regulatory limits.

## ELECTRICAL AND ELECTRONICS SCRAP

Precious metals in electronics scrap are usually mixed with base metals, organics, and plastics. When end-of-life electronics components enter a recycling facility, they are first checked for reuse potential. Assemblies that can be resold are repaired, refurbished, and sold. If resale is not practical, then the equipment is demanufactured, and individual parts are separated for resale. The remaining material is shredded, ground, and separated. The next step is to get rid of valueless nonmetallic bulk materials by burning. After the mixed scrap has been incinerated, an ash and bits of metal and plastic residues remain. The ash and bits of metal are pulverized in a ball mill, which is a large closed cylinder that contains steel balls. As the mill rotates, the balls pound the ash, thus crushing it to a fine powder. This powder is then separated from oversize metallics through a screening process. The powder undergoes a final blending operation to complete the homogenizing process and is sampled before being assayed. The metallic fraction is homogenized by simply melting it in an induction or gas-fired furnace.

## JEWELRY AND SILVERSMITH SCRAP

Jewelry scrap may contain manufacturing rejects, trimmings, grindings and sweeps, but usually does not contain plastics or organic materials. Treatment of this material is similar to that of electronics and electrical scrap. Jewelry scrap that is all metal can be sent directly to the melting furnace without an intermediate homogenizing operation. Grindings and sweeps are shipped to a refinery for silver recovery.

Silver-plated tableware is produced by electroplating silver onto preformed shapes. The silver wastes generated in this type of processing are spills of silver-rich electrolyte, dilute wash solutions, and spent electrolyte. Usually, these silver-bearing solutions are collected together as a mill waste and processed to precipitate the silver before discharge as plant waste. The typical silver-plating-mill waste solution may contain up to 250 parts per million silver. The solid wastes generated by the sterling silver industry are in many different forms and of widely different concentrations of impurities. The waste products include grinding and polishing dusts and abrasives, rejects, trimmings, turnings, and spillage and drosses from melting and casting. The different types of wastes are carefully segregated; any relatively pure materials are melted and assayed; and the composition adjusted for direct reuse. Wastes with low concentrations of silver are combined and melted, and the impure material is shipped to a refinery for processing (Butts and Cox, 1967, p. 74).

## OUTLOOK

The largest component of recycled silver comes from spent photographic film, paper, and solutions. These sources were increasing in 1999, and as photographic demand increased, the amount of silver recovered grew. The slight decline in the amount of silver used in photography in 2000 reflects the growing share of digital technology in the photographic market. The most significant impact of digital photography has been in the graphic arts and professional sector of the consumer market. The expected sizable growth of digital imaging will depend on a more-rapid acceptance of digital cameras by amateur photographers as well as a sizable switch by professional photographers from optical to digital cameras. The quality of images produced by digital cameras aimed at the amateur market improved steadily as the number of pixels in the charge-coupled device (CCD) sensors has increased to more than 1 million pixels by the end of 1999 from 300,000 pixels in 1995. A CCD is a type of semiconductor that is sensitive to light and consists of a two-dimensional (2-D) array of individual elements, each of which is, in essence, a capacitor. A capacitor is an electric circuit element used to store a charge. A CCD's charge is created when photons strike the semiconducting material and dislodge electrons. As more photons fall on the device, more electrons are liberated, thus creating a charge that is proportional to the light's intensity. With a 2-D array, an image can be captured. Digital images still have far inferior information capacity compared with a frame of 35-millimeter color negative film, which contains nearly 20 million pixels. Digital cameras also cost significantly more than the most widely used snapshot cameras and require considerable electric current for viewfinder, image processing, and display operations. It remains to be seen how well these disadvantages can be overcome in the short and long term.

Output of ethylene oxide and other chemicals that require silver-based catalysts has been adversely affected by high natural gas and electric power costs. Compounding the problem is the slowing economy with a gross-domestic-product growth of 1.5 percent in 2001. This will affect all catalyst application segments.

As discussed above, obsolete computers, telecommunications, and DOD-related scrap contain significant quantities of silver and other precious metals. Obsolete computer scrap, which is being reclaimed at the rate of tens of thousands of metric tons each year, is projected to fall within this decade. Although the number of computers sold in the future and the number of units scrapped will increase sharply, the precious metals content per unit will decrease. Further, because of the miniaturization of computers and electronic components of the future, this scrap source will become extremely dispersed. Thus, once the existing inventory of older computers to be scrapped is depleted, precious metals from this source are expected to become less important. DOD-related scrap, however, will remain a significant source for the short and long terms.

Overall, obsolete electronic scrap is diverse and contains materials other than precious metals. This diversity makes segregation and processing more difficult. New processing methods that could effectively segregate a wide range of electronics scrap into higher grade concentrates without losing too much of the precious metals in the process waste stream are in need of development.

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## 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 consumption of new scrap.

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

**downgraded scrap.** Scrap intended for use in making a metal product of lower value than the metal product from which the scrap was derived.

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

**new scrap.** Scrap produced during the manufacture of metals and articles for intermediate and ultimate consumption, which includes 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, which is scrap that is obtained from a facility separate from the processor, recycling refiner, or smelter. 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 in percent of new plus old scrap consumed; for example, 40:60.

**old scrap.** Scrap that includes but is not limited to metal articles which have been discarded after serving a useful purpose. Typical examples of old scrap are batteries, electrical wiring, metals from shredded cars and appliances, silver from photographic materials, spent catalysts, tool bits, and used aluminum beverage cans. This is also referred to as “postconsumer scrap” and may originate from industry or the general public. Expended or obsolete material used dissipatively, such as fertilizer and paints, is not included.

**old scrap generated.** Metal content of products theoretically becoming obsolete in the United States in the year of consideration; this excludes dissipative uses.

**old scrap recycling efficiency.** Amount of old scrap recovered and reused relative to the amount available to be recovered and reused. It is defined as [consumption of old scrap (COS) + 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 imports plus old scrap stock decrease.

**old scrap unrecovered.** Old scrap supply minus old scrap consumed minus old scrap exported minus old scrap stock increase.

**primary metal commodity.** Metal commodity produced or coproduced from metallic ore.

**recycling.** Reclamation of a metal in useable form from scrap or waste. This includes recovery as the refined metal or as alloys, compounds, or mixtures that are useful. Examples of reclamation are recovery of alloying (or other base metals) in steel; antimony in battery lead; copper in copper sulfate; and even 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 metal apparent supply that is scrap, on 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.

**secondary metal commodity.** Metal commodity derived from or contained in scrap.