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Selenium Recycling in the United States in 2004

By Micheal W. George and Lorie A. Wagner

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FLOW STUDIES FOR RECYCLING METAL COMMODITIES IN THE UNITED STATES

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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.

Marcia K. McNutt
Director

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CONVERSION FACTORS

Multiply	By	To obtain
	Mass	
metric ton (t, 1,000 kg)	1.102	short ton (2,000 pounds)

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ABSTRACT

The vast majority of selenium consumption in the United States is in dissipative uses, such as alloys, animal feeds, fertilizers, glass decolorizer, and pigments. The nondissipative use as a photoreceptor for xerographic copiers is declining. As a result of a lack of a substantial supply of selenium-containing scrap, there are no longer selenium recycling facilities in the United States. Selenium-containing materials collected for recycling, primarily selenium-containing photocopier drums, are exported for processing in other countries. Of the estimated 350 metric tons (t) of selenium products that went to the U.S. market in 2004, an estimated 300 t went to dissipative uses. An estimated 4 t was recovered from old scrap and exported for recycling.

INTRODUCTION

The purpose of this report is to discuss the flow of selenium within the U.S. economy and to show trends in consumption and recycling[1] of selenium in the United States. The selenium materials flow study presented in this paper provides a snapshot of the U.S. selenium recycling industry in 2004. As shown in figure 1 and table 1, there was no selenium recycling in the United States in 2004. The selenium-containing products that were captured for recycling were exported for recycling elsewhere. In the past, however, selenium-containing scrap was processed in the United States. In 1982, owing to the high cost of recovery and the decrease in the price of old scrap in 1981, domestic production of secondary selenium was discontinued (Jensen, 1987), and none has been produced since that date. As end-use technology changed (shift of selenium use in photocopier drums to the use of organic photoreceptor compounds), the selenium scrap source has diminished. Photocopier drums remain the main source of selenium containing scrap as 90 percent of selenium consumption goes into dissipative uses.

The data presented within this study are estimates because the amount of selenium that is produced, consumed, and recycled within the United States is difficult to estimate for a number of reasons. For example, ASARCO Incorporated (Asarco), Amarillo, Tex., was the only domestic producer of primary refined selenium in the United States in 2004, and its data are withheld to avoid disclosing company proprietary information. There were no dedicated selenium recyclers in the United States in 2004, and because trade statistics for selenium are an aggregation of selenium metal, waste and scrap, and

[1] Definitions for select words are found in the Appendix.

Table 1. Salient statistics of U.S. selenium scrap in 2004.

[In metric tons of selenium unless otherwise specified. XX, not applicable]

Old scrap:	
Generated[1]	XX
Consumed[2]	[3]
Value of old scrap consumed	XX
Recycling efficiency[4]	XX
Supply[5]	30
Unrecovered[6]	XX
New scrap consumed[7]	[3]
New-to-old-scrap ratio[8]	XX
Recycling rate[9]	XX
U.S. net exports of scrap[10]	4
Value of U.S. net exports of scrap[11]	$219,500

[1]Selenium content of products theoretically becoming obsolete in the United States in 2004. It excludes dissipative uses.

[2]Selenium content of products that were recycled in 2004 in the United States.

[3]Less than ½ metric ton.

[4]Old scrap consumed plus old scrap exported divided by old scrap generated plus old scrap imported.

[5]Old scrap generated plus old scrap imported.

[6]Old scrap generated plus old scrap imported minus old scrap consumed minus old scrap exported.

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

[8]Ratio of quantities consumed, in percent.

[9]Fraction of the apparent selenium supply that is scrap, on an annual basis.

[10]Trade in scrap is assumed to be principally old scrap.

[11]On the basis of average value in 2004, trade in scrap is assumed to be principally in old scrap.

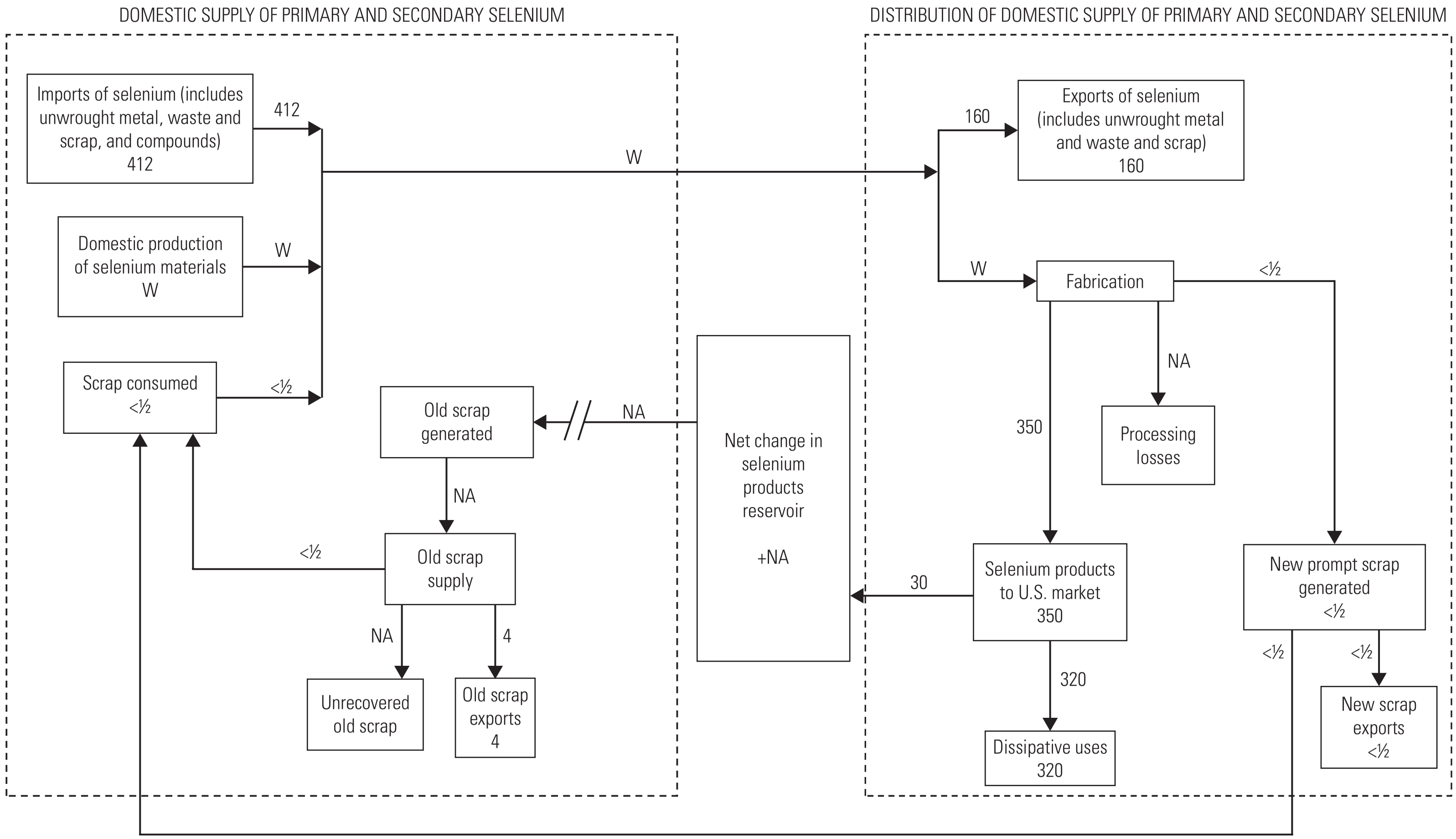

Figure 1. U.S. selenium materials flow in 2004. Values are in metric tons. NA, not available; W, withheld to avoid disclosing company proprietary information.

compounds, the estimation of the precise amount of selenium scrap leaving the United States for processing elsewhere was difficult. Therefore the data presented within this study should be viewed as estimated.

The global consumption of selenium during 2004 was estimated to have been about 2,700 t (George, 2006, p. 65.1). The U.S. Geological Survey (USGS) estimated that the 2004 consumption of selenium by end use was as follows: glass manufacturing, 37 percent; chemicals and pigments, 20 percent; electronics, 10 percent; and other, including agriculture and metallurgy, 33 percent (George, 2005, p. 146). Figure 2 illustrates the end-use patterns from 1975 through 2004. World refinery production of primary selenium (excluding U.S. production) was estimated to be 1,330 t for 2004 (George, 2006, p. 65.3). Belgium, Canada, and Japan accounted for more than 77 percent of the total world refinery production of selenium (excluding U.S. production) (George, 2006, p. 65.10). About 250 t of secondary selenium is produced worldwide each year (George, 2006, p. 65.3). Secondary selenium is recovered from scrapped xerographic copier drums and selenium rectifiers; the selenium in nearly all other uses is dissipated (not recoverable as waste or scrap).

Selenium, which is one of the chalcogen elements in group 16 (or 6A) of the periodic table, is a semiconductor that is chemically similar to sulfur for which it substitutes in many minerals and synthetic compounds. It is recovered as a byproduct of copper refining and, to a much lesser extent, lead refining. It is used in many applications, the major ones being a decolorizer for glass, a metallurgical additive to free-machining varieties of ferrous and nonferrous alloys, a constituent in cadmium sulfoselenide pigments, a photoreceptor in xerographic copiers, and a semiconductor in electrical rectifiers and photocells (Butterman and Brown, 2004, p. 4).

GLOBAL GEOLOGIC OCCURRENCE OF SELENIUM

Primary selenium is produced entirely as a byproduct of base-metal mining and processing. More than 90 percent of it is derived from copper ores, and most of the remaining 10 percent, from lead ores. There are no selenium ores or ore deposits, but selenium is present as a minor constituent in scores of minerals, most of them sulfides. Although selenium is a dispersed element, it is also capable of forming a substantial number of minerals in which it is a main component; thus, geochemically, it has aspects of being both a dispersed and a mineral-forming element (Butterman and Brown, 2004, p. 7). Sindeeva (1964, p. 35–37) provided chemical formulas for 36 minerals that can be called selenium minerals (minerals in which selenium is a main component). A few of the better known examples, all selenides, are calusthalite (PbSe), crookesite [$(Cu, Tl, Ag)_2$Se], eucairite (CuAgSe), and naumannite (Ag_2Se) (Stone and Caron, 1961).

The selenium reserves and reserve base figures published by the USGS are based solely on reserves and reserve base estimates for the main source of selenium—copper ores—in which selenium substitutes for sulfur in sulfide minerals. The world reserve base is expected to be able to satisfy demand for selenium for several decades without difficulty (Butterman and Brown, 2004, p. 4). The part of copper resources that appears likely to be processed by leaching/electrowinning is not included because these methods do not recover selenium. The selenium estimates take into account typical recoveries of selenium per metric ton of primary electrolytically refined copper; only a part of the selenium content of anode slimes from that process is recovered (Butterman and Brown, 2004, p. 7). The estimates are derived from the copper resource figures by using the recovery factor 0.215 kilogram of selenium per metric ton of primary electrolytic copper recoverable from the resources; for Canada, where the selenium contents of copper ores are higher, the factor 0.64 kilogram per metric ton is used (Brown, 1996, p. 731). No estimate is available for total selenium resources, but coal deposits have been estimated to contain from 80 to 90 times more selenium than do copper deposits. Economic recovery of selenium from coal is considered to be unlikely in the foreseeable future (Butterman and Brown, 2004, p. 7).

PRIMARY PRODUCTION AND PROCESSES

Only one U.S. copper refinery, located in Texas, reported domestic production of primary selenium in 2004. One producer exported semirefined selenium (90-percent-pure selenium content) for toll-refining in Asia, and two other companies generated selenium-containing slimes, which were exported for processing. Most of the selenium recovered in the United States in 2004 came from copper mines in Arizona and Utah. In 2004, despite an increase in the price for selenium as global demand for the metal increased, domestic production of primary selenium decreased because of a disruption in domestic copper production. With higher prices it was estimated that domestic producers would reduced their inventories of refined and semirefined selenium material. Most domestic selenium is produced as commercial-grade metal, averaging a minimum of 99.5-percent-pure selenium, and is available in various forms. Commercial-grade selenium may also be further refined to make minimum 99.999-percent-pure selenium for use in electronic applications (George, 2006, p. 65.1).

In the processing of copper ores, selenium follows the flow of copper sulfide minerals through beneficiation process (crushed, ground, and floated) where it is concentrated along with copper and other metals. During smelting (a pyrometallugical process to liberate the copper from the sulfur and iron) most of the selenium will reside in the copper anode, which is a semirefined copper material containing 99 percent copper and a minor amount of other metals including selenium. The copper anode is electrolyticlly refined to form a copper cathode containing about 99.99 percent copper. Electrolytic refining uses a sulfate-base electrolyte for its role in dissolving copper from the anode and absorbing copper ions on the cathode. This type of electrolyte does not dissolve precious and other base metals, allowing them to accumulate along with refractory components at the bottom of the electrolytic cell as slime. The quantities of metals present in the slimes, such as bismuth, gold, selenium, silver, and tellurium, are dependent on their initial content in the anode material and, therefore, on the ores from which the copper concentrate originated. Slimes resulting from copper metal refining can have average selenium concentrations of 10 percent and in a few cases as high as 40 percent. Much of the slimes are not processed to recover selenium (George, 2006, p. 65.1).

SOURCES OF SECONDARY SELENIUM

OLD SCRAP GENERATED

An estimated 412 t selenium products entered the U.S. market in 2004, of which 350 t was consumed domestically and the balance was exported (fig. 1). The estimated amounts of selenium consumed in each end-use sector were as follows: glass manufacturing, 130 t; chemicals and pigments, 70 t; electronics and photocopier components, 35 t; and other (including agricultural and metallurgical), 115 t (figure 2). Many of these end-use sectors are dissipative uses for selenium. The selenium contents of glass and free-machining alloys are too dispersive to be accounted for during recycling of those materials and are often volatilized during melting operations. Furthermore, during the recycling of these products, selenium-containing scrap is not segregated from other forms of scrap metal or glass, further diluting or dispersing these materials with low concentrations of selenium. Selenium pigments, fertilizers, animal feeds, chemicals, and pharmaceuticals are dissipated in the environment. Therefore, electronic uses are the principal source of old scrap and, in fact, a high percentage of the selenium used in document copiers and laser printers and possibly some of that used in rectifiers is recovered and reprocessed into secondary selenium (Butterman and Brown, 2004, p. 7–8). Photoreceptors on the drums of plain-paper copiers had been the leading single application for selenium during the 1970s and 1980s. However, organic photoreceptor compounds have replaced these high-purity selenium materials. Selenium rectifiers were invented in the 1930s to replace the vacuum tube; although they were more efficient, they had a shorter life span and were unreliable. They eventually were replaced by cheaper silicon rectifiers by the 1960s. In 2004, selenium was used to make replacement parts for older copiers and specialty made-to-order selenium rectifiers (George, 2006, p. 65.2).

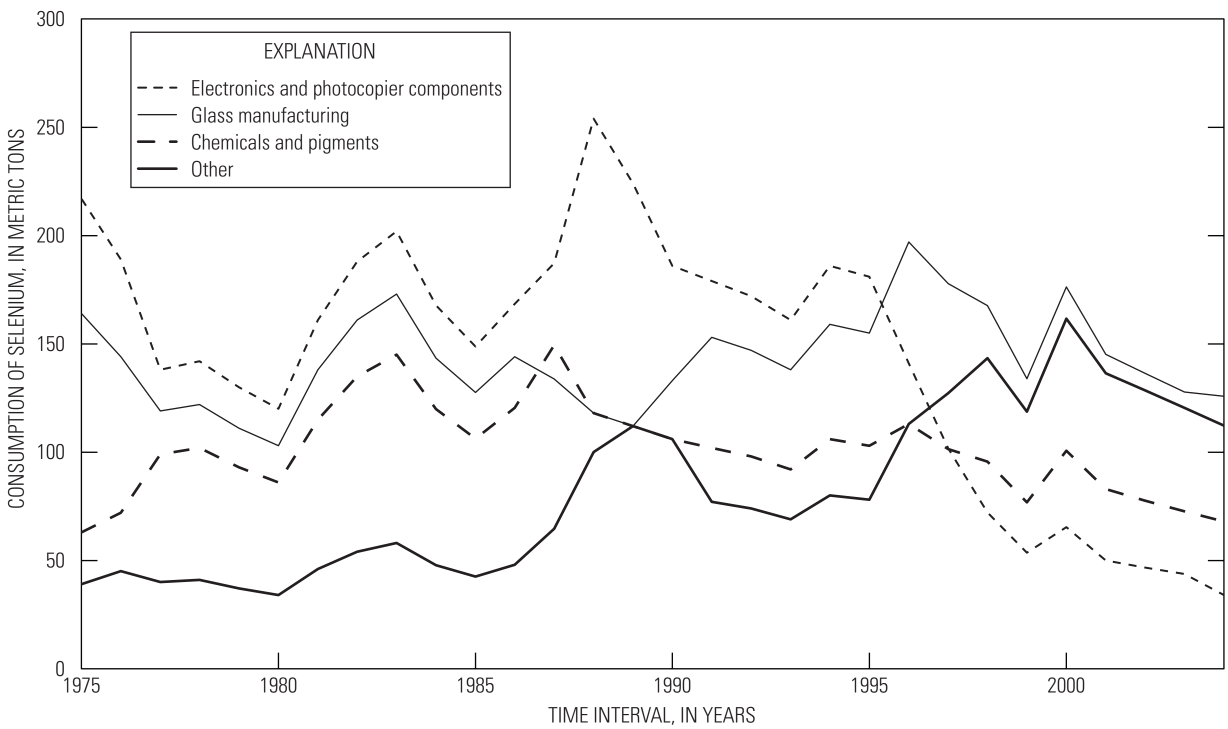

Figure 2. U.S. selenium end-use patterns from 1975 through 2004. Source: Matos and George, 2005.

The average life cycle of a photocopier is about 10 to 12 years, and in the United States, copiers are often replaced in one-half that time as a trade-in or for refurbishing. During the trade-in or refurbishing, the selenium-coated drum is sometimes replaced. In 1999, it was estimated that 40 t of selenium went into photocopiers. Five years later, much of the selenium in these photocopiers became available for recycling. However, many of these copiers that contain selenium are exported either as used copiers or as electronic scrap. This makes it difficult to determine how much of the selenium is recycled in a given year. In 2004, it was estimated that 4 t of selenium waste and scrap was collected and disseminated as selenium waste and scrap. However, much of the selenium-containing products would be exported as electronic scrap, office equipment, copiers, or other waste and scrap, with no information of quantity of contained selenium, and were therefore not included in import and export statistics.

NEW SCRAP GENERATED

A small amount of scrap was generated at plants that use selenium in fabrication and at electronics manufacturing assembly facilities, but the amount was difficult to estimate reliably.

DISPOSITION OF SELENIUM SCRAP

In 2004, an estimated 4 t of selenium in scrap was recovered from electronics and photocopier components. Since there are no selenium recyclers in the United States, all the scrap recovered (photocopier drums) was exported for processing elsewhere. The export of selenium material (unwrought metal, waste and scrap) in 2004 decreased by 36 percent compared with that of 2003. Reduced production and the export in 2003 by producers and consumers of most inventories to Southeast Asia left less material available for trade-in in 2004 (George, 2006, p. 65.3). Much of the selenium was exported to the Philippines for further processing and finally sold to China as refined material (George, 2005, p. 147).

OLD SCRAP RECYCLING EFFICIENCY

Recycling efficiency is the relation between what is theoretically available for recycling and what was recovered. This relation is defined as the amount of selenium recovered from old scrap domestically plus old scrap exports divided by the sum of old scrap generated and old scrap imports plus or minus old scrap stock changes, as applicable. For selenium, as there is no domestic recovery and no data on scrap stocks and scrap generated, it is impossible to calculate the recycling efficiency. All U.S. selenium scrap is exported for recycling.

INFRASTRUCTURE OF SELENIUM SCRAP RECYCLING

Many old photocopiers are either traded in for new ones, where they are refurbished for resale, sent for recycling, or they enter waste streams. Originally the drums were sent to the drum manufacturer for recycling, but now they are exported. Recycling of selenium from drums of photocopiers has been a practice in the copier industry, but is no longer practical. Information on the commercial scale of such recycling was proprietary, but some insight of what may be a commercial process, appears in two U.S. patents by S.S. Badesha of Xerox Corporation. Prior to the 1990s, Xerox recycled selenium from photoconductive scrap including arsenic, selenium, and tellurium. This is no longer practiced since its photocopiers contain much less selenium than in the past (Moskowitz and Zweibel, 1992, p. 11). In the early 1980s, changes in photoreceptor design enabled Xerox to replace arsenic and selenium with new organic materials (Xerox Corporation, 2000, p. 13). As of the early 1990s, domestic manufacturers sold their selenium scrap to selenium refiners, which was introduce their process stream and combine recycling with primary refining (Moskowitz and Zweibel, 1992, p. 11).

PROCESSING OF SELENIUM SCRAP

Nearly all secondary selenium, which may be as little as 100 metric tons per year worldwide, is recovered from xerographic photocopier drums. The selenium layer is either broken up mechanically, cleaned and remelted or dissolved in sodium sulfite or other solvents, which is recovered by precipitation (Roskill Information Services, 1988, p. 6).

OUTLOOK

Selenium supply is directly related to the production of copper, the main product from which it is derived, and to a lesser extent, by the production of lead. Selenium price is often inversely related to the supply of copper. For example, as a byproduct of copper refining, selenium prices typically fall during periods of high copper production, because of ore supply. In 2003 and 2004, however, the driving force behind the increased price was short supply brought on by a large growth in demand, as the production of copper grew only marginally. Since selenium price has little influence on copper production, an increase in selenium demand will not lead to an increase in the production of copper and its byproducts; however, an increase in selenium price does influence on its recovery rate from slimes (George, 2006, p. 65.4).

In 2005, domestic refined copper production, excluding leaching/electrowinning production, declined because of an extended strike and the bankruptcy filing by Asarco, the main domestic producer of selenium. In 2006, domestic copper refinery production in the United States recovered to 2003 levels; however, domestic selenium production was estimated to be lower in 2006 than in 2003 because of Asarco bankruptcy. World copper production increased during both 2005 and 2006, resulting in an increase in the global production of selenium. Many companies were investigating ways to increase selenium production or find untapped sources of selenium. However, many of the newer copper mines have lower selenium content than older mines. In addition, although the production of copper anodes increased in 2005 and 2006, an increasing share of the world's supply of refined copper came from the leaching and electrowinning of copper ores. This process does not provide for the recovery of contained selenium and will continue to constrain the future supply of selenium (George, 2006, p. 65.4).

Demand for selenium in photoreceptors is likely to continue to decline as the cost decreases for substituting organic compounds (George, 2006, p. 65.4). However, while the use of selenium in photoreceptors has been declining, other electronic uses for selenium, including a slight resurgence in rectifiers and new uses in photoelectric applications, have been increasing (George, 2006, p. 65.2). As electronics recycling continues to increase in the United States, a small amount of selenium could become available (George, 2007, p. 144).

Though there was promising prostate cancer research and other health benefits of selenium dosages taken directly for human consumption, these uses will not induce large increases in demand for the metal because only minute quantities are necessary for effective therapy. However, there could be an increase in selenium demand if selenium is increasingly applied to the soil for adsorption by crops grown for consumption by humans and livestock. Selenium could also be introduced to livestock as a supplement (George, 2006, p. 65.4). However, as this is a dissipative use it would be expected to lower the recycling rate.

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APPENDIX—DEFINITIONS

apparent consumption. Primary plus secondary production (old scrap) plus imports minus exports plus adjustments for U.S. 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 in paints or fertilizers, making it exceptionally difficult and costly to recover and recycle.

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 scarp is home scrap that is generated as process scrap and used in the same plant.

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 postconsumer 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], measure in weight and expressed as a percentage:

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

old scrap supply. Old scrap generated plus old scrap imported plus old scrap stock decrease.

recycling. Reclamation of a metal in usable 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.

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

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