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Tungsten Recycling in the United States in 2000

By Kim B. Shedd

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FLOW STUDIES FOR RECYCLING METAL COMMODITIES IN THE UNITED STATES

U.S. Department of the Interior
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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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TABLE

1. Salient statistics for U.S. tungsten scrap in 2000 R1

CONVERSION FACTORS

| Multiply | By | To obtain |
|--------------------------|-------------|--------------------------|
| | <i>Mass</i> | |
| kilogram (kg) | 2.205 | pound (lb) |
| metric ton (t, 1,000 kg) | 1.102 | short ton (2,000 pounds) |
| ton, short (2,000 lb) | 0.9072 | megagram (Mg) |

Temperature in degrees Celsius (°C) may be converted to degrees Fahrenheit (°F) as follows:

$$^{\circ}\text{F}=(1.8\times^{\circ}\text{C})+32$$

Temperature in degrees Fahrenheit (°F) may be converted to degrees Celsius (°C) as follows:

$$^{\circ}\text{C}=(^{\circ}\text{F}-32)/1.8$$

Tungsten Recycling in the United States in 2000

By Kim B. Shedd

ABSTRACT

This report, which is one of a series of reports on metals recycling, defines and quantifies the flow of tungsten-bearing materials in the United States from imports and stock releases through consumption and disposition in 2000, with particular emphasis on the recycling of industrial scrap (new scrap) and used products (old scrap). Because of tungsten's many diverse uses, numerous types of scrap were available for recycling by a wide variety of processes. In 2000, an estimated 46 percent of U.S. tungsten supply was derived from scrap. The ratio of tungsten consumed from new scrap to that consumed from old scrap was estimated to be 20:80. Of all the tungsten in old scrap available for recycling, an estimated 66 percent was either consumed in the United States or exported to be recycled.

INTRODUCTION

The purpose of this report is to define and quantify the recycling¹ of tungsten-bearing scrap, which represents an important component of total tungsten supply. Figure 1 illustrates the flow of tungsten in 2000. It shows sources and distribution of U.S. tungsten supply with particular emphasis on the flow of tungsten-bearing scrap. Table 1 lists salient tungsten scrap statistics for 2000.

Tungsten is a whitish-gray metal with a wide variety of commercial, industrial, and military uses that result from its unique mixture of properties—it is one of the heaviest metals and has the highest melting point of any element except carbon, excellent high-temperature mechanical properties, the lowest expansion coefficient of all metals, the lowest vapor pressure of all metals, very high moduli of compression and elasticity, very high thermal creep resistance, high thermal and electrical conductivity, and a very high coefficient of electron emission (International Tungsten Industry Association, 1997, p. 2).

¹Definitions for selected words are found in the appendix.

Table 1. Salient statistics for U.S. tungsten scrap in 2000.

[Values in metric tons of contained tungsten unless otherwise specified]

| | |
|---|--------------|
| Old scrap: | |
| Generated ¹ | 7,300 |
| Consumed ² | 6,200 |
| Consumption value ³ | \$35 million |
| Recycling efficiency ⁴ | 66 percent |
| Supply ⁵ | 9,700 |
| Unrecovered ⁶ | 3,300 |
| New scrap consumed ⁷ | 1,600 |
| New-to-old-scrap ratio ⁸ | 20:80 |
| Recycling rate ⁹ | 46 percent |
| U.S. net imports of scrap ¹⁰ | 2,940 |
| Value of U.S. net imports of scrap | \$15 million |

¹Old scrap generated is estimated to have been the tungsten content of products theoretically becoming obsolete in the United States in 2000.

²Old scrap consumed is estimated to have been the tungsten content of used products that were recycled in 2000.

³Value of tungsten contained in old scrap, which was based on estimated quantities and estimated values of cemented carbide and noncemented carbide scrap.

⁴Recycling efficiency is (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 stock increase).

⁵Old scrap supply is old scrap generated plus old scrap imported plus old scrap stock decrease.

⁶Old scrap unrecovered is old scrap supply minus old scrap consumed minus old scrap exported minus old scrap stock increase.

⁷New scrap consumption includes prompt industrial scrap but excludes home scrap.

⁸New-to-old-scrap ratio is the ratio of quantities consumed, expressed as a percentage.

⁹Recycling rate is the fraction of the apparent tungsten supply that is scrap, on an annual basis. It is defined as (consumption of old plus consumption of new scrap) divided by apparent supply; measured in weight and expressed as a percentage.

¹⁰Net imports of scrap are tungsten contained in imports minus tungsten contained in exports of scrap. Tungsten-bearing scrap imports are estimated to be approximately 25 percent new scrap and 75 percent old scrap; tungsten-bearing scrap exports are assumed to be principally old scrap.

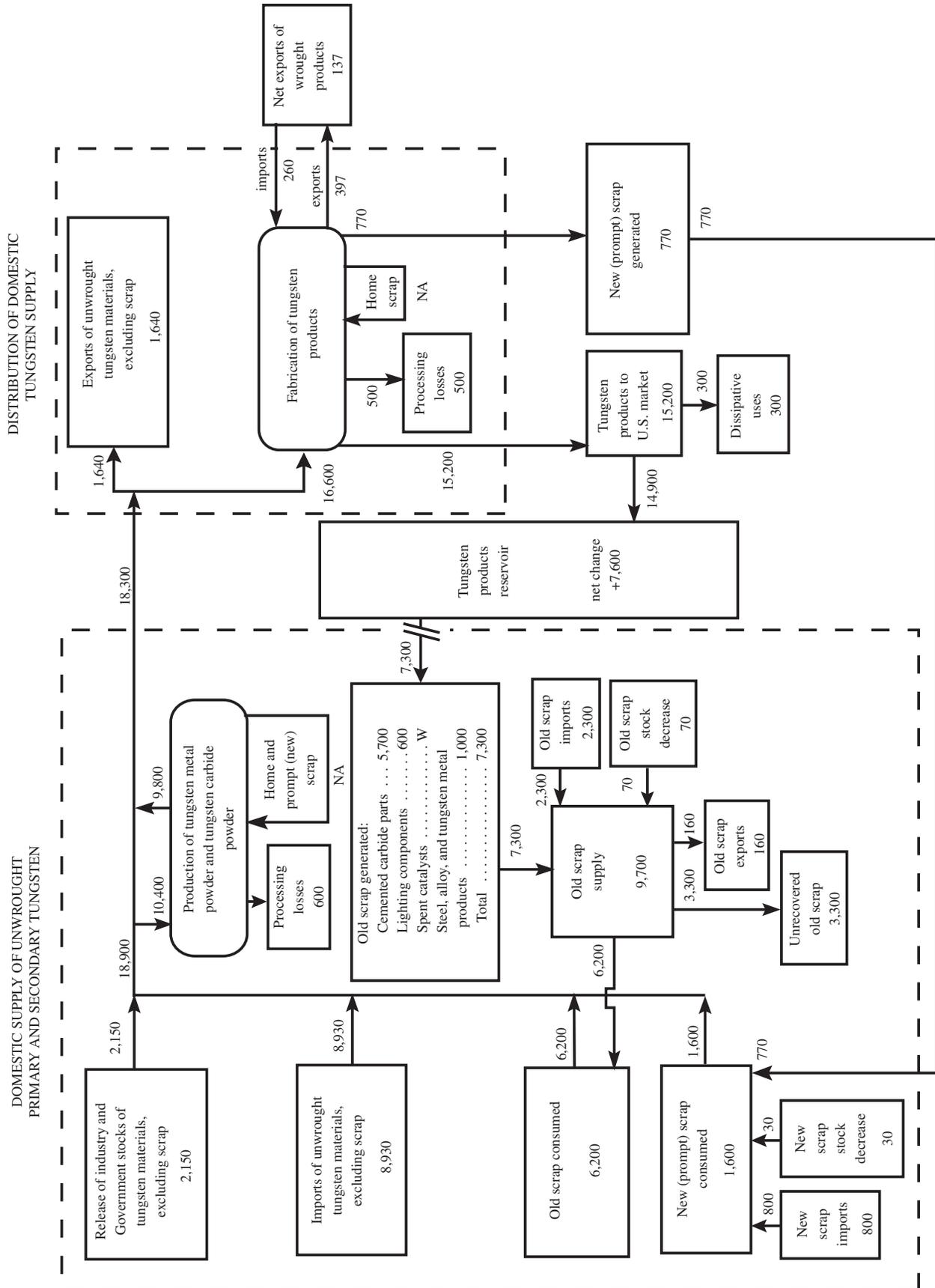


Figure 1. Flow diagram showing the U.S. tungsten materials flow in 2000. NA, not available; W, withheld to avoid disclosing company proprietary data. Values are in metric tons of contained tungsten, are rounded to no more than three significant digits, and may not add to totals shown.

GLOBAL GEOLOGIC OCCURRENCE OF TUNGSTEN

The average concentration of tungsten in the Earth's crust is estimated to be approximately 0.0001 percent (1 part per million). Although tungsten is present in more than 20 mineral species, only two are commercially important—scheelite and wolframite. Scheelite, which is sometimes referred to as “white ore,” is calcium tungstate (CaWO_4). Wolframite, which is sometimes referred to as “black ore,” is the name for a mineral and the mineral group to which it belongs. The wolframite group is a solid solution series of iron- and manganese-rich tungstates $[(\text{Fe},\text{Mn})\text{WO}_4]$. In this series, tungstates with more than 80 percent FeWO_4 are called ferberite; tungstates with more than 80 percent MnWO_4 , huebnerite; and tungstates with between 20 and 80 percent of each of FeWO_4 and MnWO_4 , wolframite (Hobbs and Elliott, 1973; Yih and Wang, 1979, p. 2–6, 22; Werner and others, 1998, p. 3; Lassner and Schubert, 1999, p. 65–70).

Tungsten deposits occur in a wide variety of geologic environments, which range from high-temperature deep-seated deposits associated with igneous intrusions to relatively low-temperature surface deposits associated with hot springs. Tungsten minerals can also be found in placer deposits, and tungsten-bearing brines and evaporites occur in certain arid regions. Because most tungsten deposits are associated with granitic igneous activity, many share common features, and as a result, there are several different ways of classifying them. One classification (Werner and others, 1998), which was used by an international committee convened to gather information on major sources of mineral raw materials, classifies most producing tungsten mines into the following four deposit types: vein/stockwork, skarn, porphyry, and strata-bound, which are listed in order of share of production from highest to lowest in the mid-1980s. The descriptions below were based on information from Hobbs and Elliott (1973), Yih and Wang (1979, p. 9–22, 49–50), Thalhammer and others (1989, p. 1153, 1158, 1160), and Werner and others (1998, p. 4–9).

Vein/stockwork deposits typically consist of tungsten-bearing quartz veins or vein stockworks that occur in or near granitic intrusions. The veins are tabular bodies that vary greatly in length, width, and depth and consist of quartz, scheelite and (or) wolframite, and minor amounts of other minerals. Most vein deposits are relatively small, on the order of a few hundred thousand metric tons of ore. Stockworks are three-dimensional networks of closely spaced veins, veinlets, or fracture-fillings that can be mined by bulk methods. In contrast to skarn deposits described below, the host rocks associated with this class of deposit usually contain little, if any, carbonates.

Skarn deposits are formed by high-temperature replacement and recrystallization of limestone or dolomite at or near contacts with granitic intrusions. The resulting

calcium silicate rocks are called skarns or tactites. When present in this type of deposit, tungsten is in scheelite or molybdenum-bearing scheelite, which can occur in veinlets or fractures or as disseminated grains. Skarn deposits range in size from hundreds to millions of metric tons of ore. This type of deposit is also called tactite, contact metamorphic, contact metasomatic, or pyrometasomatic.

Porphyry tungsten deposits are large equidimensional-to-irregular stockworks that occur in or near epizonal-to-subvolcanic felsic granitic intrusions. Tungsten occurs in wolframite and (or) scheelite in veins, veinlets, and fractures. Molybdenum is commonly present, sometimes in high enough concentrations to be a viable byproduct or coproduct. Mineralized breccia zones may be present. This type of deposit is generally large and contains tens to hundreds of millions of metric tons of ore but has a low average tungsten grade. Some of the specific deposits that fall into this category sometimes are classified as greisen deposits. As with porphyry tungsten deposits, greisen alteration is associated with granitic intrusions. It is distinguished by a given suite of alteration minerals, such as muscovite, quartz, topaz, and tourmaline. Tin and molybdenum can be present in economic concentrations.

Strata-bound deposits are those in which the distribution of tungsten minerals is strongly controlled by bedding in the host rock. They range in size from one to tens of millions of metric tons of ore. One example is the ore of the Mittersill Mine in Austria where scheelite occurs in quartz veins, lenses, and quartz-rich rocks that are parallel on the large scale to the planar texture of the metamorphosed host rocks. In this deposit, some of the tungsten-rich quartz veins also crosscut the texture of the host rocks.

In 2000, production of tungsten concentrates was not recorded in the United States. China, which was the world's leading producer, represented an estimated 84 percent of total concentrate production. Chinese tungsten production came from numerous mining areas that represented a wide variety of deposit types that contained scheelite, wolframite, and mixed scheelite-wolframite ores. A survey of 60 Chinese tungsten mines indicated that 95 percent of Chinese production was from Guangdong, Guangxi, Hunan, Jiangxi, and Yunnan Provinces. Russia contributed an estimated 8 percent of world tungsten concentrate production. This production was primarily scheelite from greisens and skarns at one mine in the Caucasus Mountains in western Russia and two mines in Primorskiy Krai in southeastern Russia. Other countries that produced more than 300 metric tons per year (t/yr) of tungsten in concentrates in 2000 included Austria where scheelite was mined from the Mittersill strata-bound deposit described above, Bolivia where wolframite was mined by small- and medium-scale mining entities and cooperatives from vein/stockwork and possibly other types of deposits, Portugal where wolframite was mined from a vein-type deposit, and possibly North Korea (Yih and Wang, 1979, p. 20, 49–51, 53;

Rabchevsky, 1988, p. 25–26, 38–39; Werner and others, 1998, p. 29–30, 32–35, 40, 44–45; Zhaoqing and Pugang, 1999; Zhaoqing and others, 2001; Velasco, 2002; Visser, 2002, p. 4, 15–16; Walser, 2002, p. 1–5; Shedd, 2003b, p. 80.18).

TUNGSTEN PRODUCTION PROCESSES

Most tungsten is mined from relatively small underground mines. A few tungsten mines have used open pit methods to access near-surface ores, but in most cases, these mines were later converted to underground mines to access deeper ores. Conventional underground mining methods, such as open stoping, shrinkage stoping, room-and-pillar stoping, sublevel stoping, sublevel caving, block caving, cut-and-fill, and square set, are used. The method used for a particular mine depends on the size, shape, and attitude of the ore body; the competence of the ore zone and wall rocks; and the continuity and grade of the ore body (Yih and Wang, 1979, p. 25; Rabchevsky, 1988, p. 11; Bernhardt, 1998, p. 1; Correa de Sá and Naique, 1998, p. 6–8). Tungsten ores are crushed, ground, and then concentrated by a combination of gravimetric, flotation, and (or) magnetic methods. Where necessary, preconcentration by ore sorting, the use of jigs, or heavy media separation; leaching; roasting; and high-tension (electrostatic) separation are also used in the beneficiation of tungsten ores (Yih and Wang, 1979, p. 55–57; Lassner and Schubert, 1999, p. 179–184).

Most tungsten ore concentrates are processed chemically to produce ammonium paratungstate (APT), which is the main tungsten raw material traded in the market. In modern tungsten conversion plants, scheelite concentrates, wolframite concentrates, and soft or hard tungsten scrap can be used as raw materials. Before processing, ore concentrates may need to be calcined, leached, roasted, and (or) ground to a smaller particle size. Soft scrap is heated in air or oxygen-enriched air to oxidize the tungsten to the hexavalent state so that it will dissolve easily under alkaline conditions. The oxidized scrap is then ground and screened before leaching. Hard scrap can be treated by one of two methods. It can be fused or roasted in the presence of an oxidizing agent and a diluent, then cooled, crushed, and dissolved in water, or it can be treated by electrolysis. Electrolysis uses the scrap as an anode in a solution of sodium hydroxide or sodium carbonate. It results in a solution of sodium tungstate and insoluble oxides or oxide hydrates of the other elements that were present in the scrap. The remaining steps to produce APT are outlined in figure 2 (Lassner and Schubert, 1999, p. 184–193).

The importance of scrap as a raw material in APT production was indicated by statistics compiled by the International Tungsten Industry Association. In 2001, an estimated 70 percent of the APT produced by companies that contributed data for Europe, Japan, and the United States was derived from scrap. The remaining 30 percent was derived from ore concentrates (Maby, 2002, p. 5).

APT can be calcined under reducing conditions to form tungsten blue oxide, which is a mixture of tungsten oxides and other constituents; calcined under oxidizing conditions to form tungsten trioxide; decomposed by hydrochloric acid to form tungstic acid; or subjected to partial thermal decomposition to form ammonium metatungstate. Tungsten blue oxide is the most commonly used starting material to make tungsten metal powder, which is used to make tungsten alloys, tungsten carbide powder, and tungsten metal. Tungsten trioxide can be used to make tungsten metal powder and is also used as a yellow pigment. Tungstic acid is used to make tungsten chemicals and ultrafine tungsten metal and tungsten carbide powders. Ammonium metatungstate is used to make tungsten chemicals and tungsten-bearing catalysts (Lassner and Schubert, 1999, p. 208–215).

Some tungsten ore concentrates are processed directly to tungsten carbide. In one process, which is alternatively referred to as the “macrocrystalline,” “macro,” or “thermit” process, a mixture of tungsten ore concentrates and iron oxide are reduced by aluminum metal and simultaneously carburized by calcium carbide or carbon. The reactants are proportioned and added at a rate to create a self-sustaining exothermic reaction. This process forms coarse macrocrystalline tungsten carbide, which can be used in hardfacing applications and diamond tool matrices and following milling to reduce particle size to make cemented carbide tips for mining tools (Smith, 1980).

Tungsten ore concentrates can also be used to make ferrotungsten, which is a master alloy used in the production of steel. Ferrotungsten can be made using either carbothermic or carbothermic-silicothermic reduction in an electric arc furnace (EAF) or metallothermic reduction. Artificial scheelite and soft tungsten scrap also can be used as raw materials to make ferrotungsten. Tungsten melting base, which is another master alloy used in steelmaking, is made by reducing tungsten-bearing scrap in an EAF (Lassner and Schubert, 1999, p. 309–312).

USES

In 2000, tungsten was used in many diverse commercial, industrial, and military applications. The leading use was as tungsten carbide in cemented carbides. These materials, which are also referred to as “hardmetals,” are sintered powder metallurgical parts that are used as cutting tools and wear-resistant components by the construction, metalworking, mining, and oil drilling industries. In making these parts, cobalt or nickel metal powder is used as a binder to hold together the tungsten carbide grains. Tungsten alloy or pure tungsten metal contacts, electrodes, and wires are used in electrical, electronic, heating, lighting, and welding applications. Tungsten is also used to make heavy metal alloys for armaments, heat sinks, radiation shielding, and weights and counterweights; superalloys for turbine parts; tool steels;

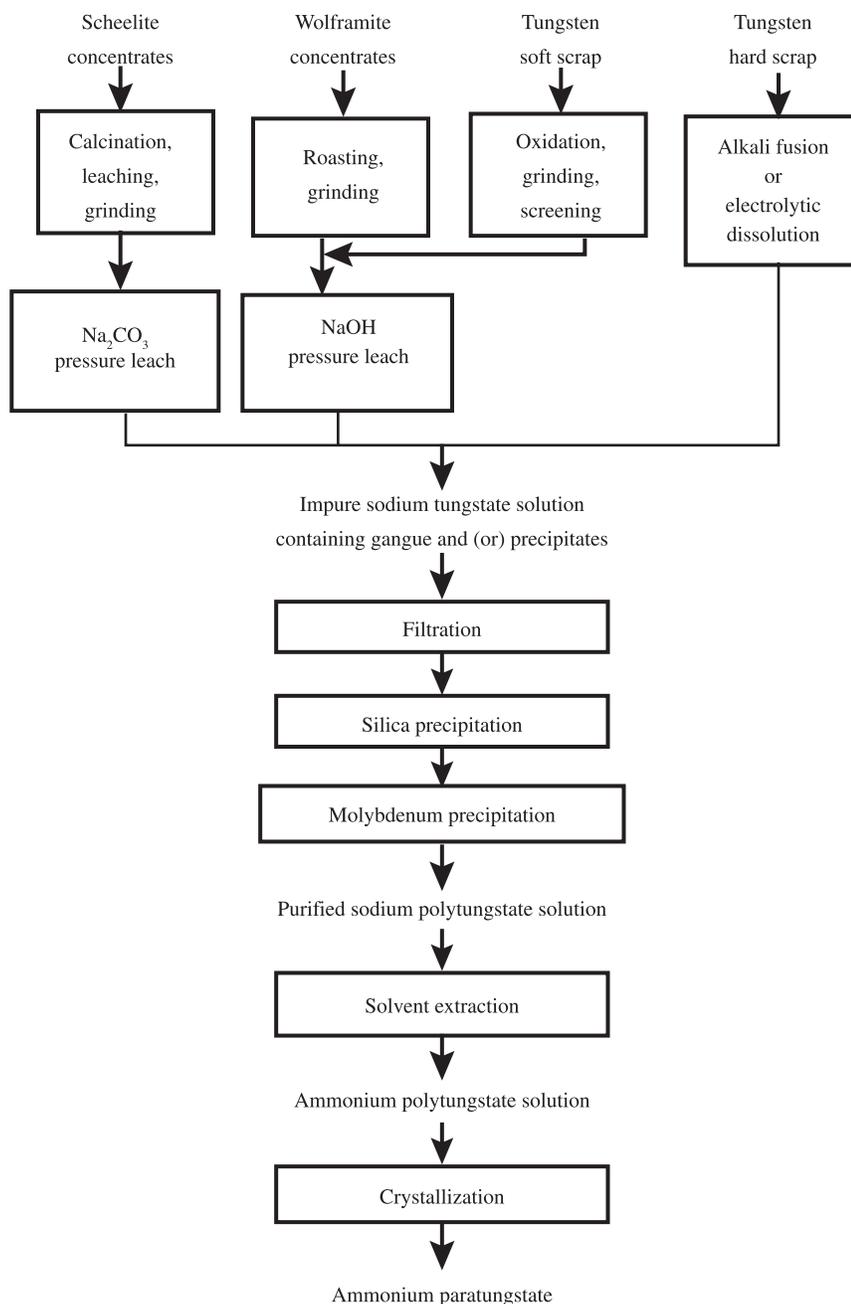


Figure 2. Simplified flow sheet for a modern tungsten conversion plant. Reprinted from Lassner and Schubert (1999) and published with permission from Kluwer Academic/Plenum Publishers.

and wear-resistant alloy parts and coatings. Tungsten alloys and tungsten composites are used as a substitute for lead in bullets and shot. Tungsten chemicals are used to make catalysts, corrosion-resistant coatings, dyes and pigments, fire-resistant compounds, high-temperature lubricants, and phosphors. They are used as chemical reagents and as a source of tungsten metal in the manufacture of semiconductor devices. Most of the chemical applications are considered

to be dissipative—the tungsten represents an important but very minor constituent of the final product, which is widely distributed during use. This makes tungsten reclamation or recycling impractical or impossible. One exception is the use of tungsten in catalysts, which are products that are sometimes recycled, as discussed in the section “Spent Catalysts.”

The United States is a significant consumer of tungsten materials. On the basis of data reported to the U.S. Geological

Survey (USGS), U.S. tungsten consumption in 2000 can be divided into the following end-use categories: cemented carbides (60–65 percent); steels and other alloys (15–20 percent); mill products, such as contacts, electrodes, and wires (15–20 percent); and chemical uses (approximately 1 percent). Actual consumption in chemical applications is likely to be higher than that reported to the USGS. Other estimates place U.S. tungsten use in chemical products at 3 to 4 percent of total U.S. tungsten consumption (International Tungsten Industry Association, 1997, p. 3; Payne, 2002, p. 8; Shedd, 2002, p. 81.8).

Figure 3 shows trends in U.S. consumption of tungsten by various industry sectors since 1980. Trends in total tungsten consumption are strongly influenced by general economic trends, industrial activity, and trends in cemented carbide production, which is the leading consuming industry sector. The cemented carbide industry is influenced by the performance of the following industries: aerospace, automotive, construction, electronics, general manufacturing, large equipment manufacturing, mining, and oil and gas drilling (Payne, 2002, p. 8–10). Consumption by the other industry sectors presented in figure 3 was relatively consistent during the past two decades. Some of the sudden changes in

consumption, either increases or decreases, are the result of changes in the number of companies that reported data to the U.S. Bureau of Mines (USBM) or the USGS.

PRICES

Prices of tungsten-bearing scrap are not published on a routine basis. Historically, the main reference price for tungsten was the price of tungsten concentrates. In the early 1990s, trade in tungsten concentrates decreased, and APT became the most widely traded primary tungsten material. As a result, the price of APT has become the reference price for upstream materials, such as tungsten ore concentrates, and downstream materials, such as tungsten metal powders and tungsten carbide powders (International Tungsten Industry Association, 1997, p. 32; Ross, 2001, p. 5). The price of APT is quoted in units of tungsten trioxide (WO_3). The short ton unit, which is used in the United States, is 1 percent of a short ton (20 pounds), and WO_3 contains 79.3 percent tungsten. Therefore, a short ton unit of WO_3 equals 20 pounds of WO_3 and contains 7.19 kilograms (kg) (15.86 pounds) of tungsten. The metric ton unit, which is used in most other countries, is

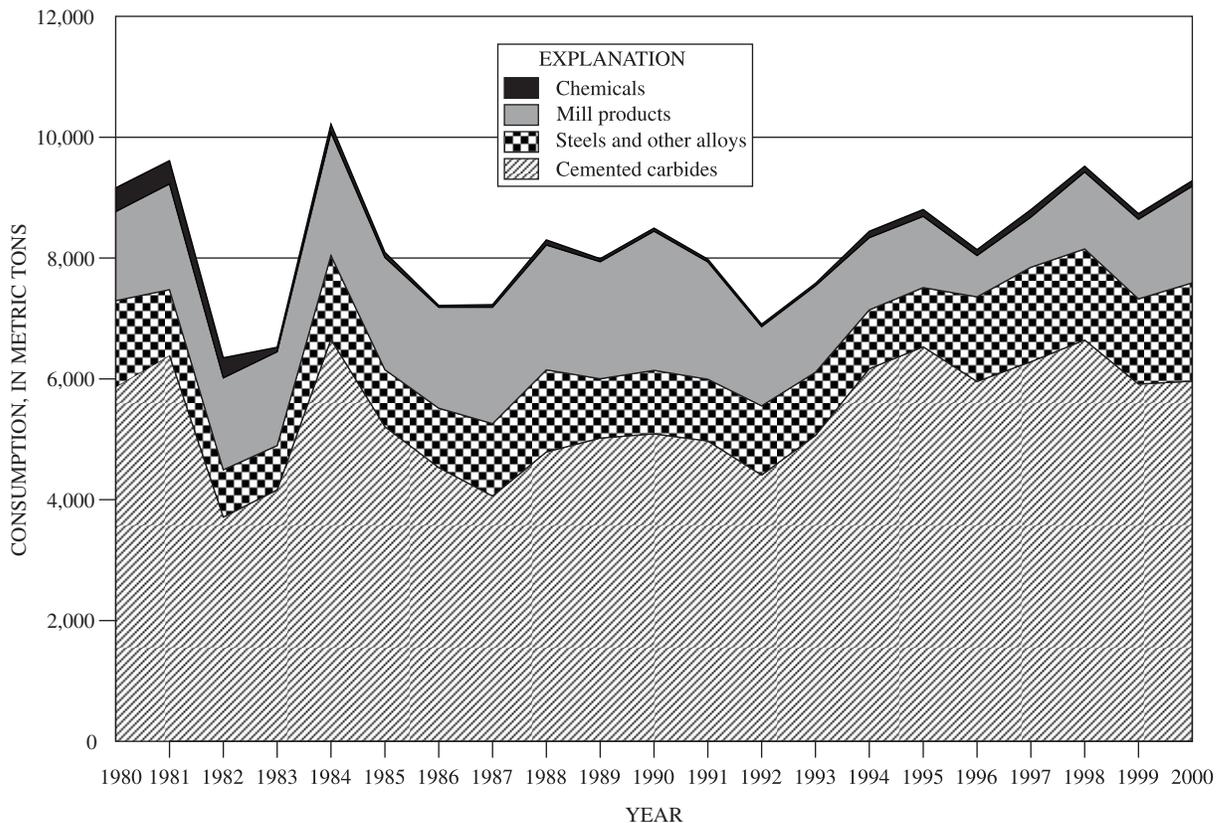


Figure 3. U.S. tungsten consumption by end-use sector from 1980 through 2000. Values are in metric tons of contained tungsten.

1 percent of a metric ton (10 kg). A metric ton unit of WO_3 contains 7.93 kg (17.48 pounds) of tungsten.

Historically, tungsten prices have fluctuated widely with the fluctuation of the market between periods of scarcity and oversupply (Shedd, 1999b). Figure 4 presents U.S. free market prices of APT for 1990 and European free market prices for 1991 through 2000 as reported in Metal Bulletin. During this time period, the price of APT fluctuated widely between a low of \$32 per metric ton unit (\$4 per kilogram of contained tungsten) and a high of \$100 per metric ton unit (\$13 per kilogram of contained tungsten). During the first half of 2000, the price reached a low of \$49 per metric ton unit (\$6 per kilogram of contained tungsten). During the second half of the year, the price rapidly increased to \$86 per metric ton unit (\$11 per kilogram of contained tungsten) as a result of efforts by China, which was the world's leading tungsten supplier, to reform its industry and control the exports of

tungsten materials from China (Shedd, 2002, p. 81.3–81.4).

To a certain extent, the price of cobalt influences the recycling rate of tungsten. Higher prices for cobalt encourage the recycling of cemented carbides, which contain cobalt and tungsten. During periods of low cobalt prices, recycling of cobalt-bearing scrap decreases, and more primary tungsten raw materials are consumed (Maby, 2002, p. 5). Since the late 1970s, free market prices for cobalt have varied considerably (Shedd, 1999a). During the 1990s, the U.S. spot price for cobalt cathode (minimum of 99.8 percent cobalt), as reported in Platt's Metals Week, fluctuated widely between a low of \$7.50 per pound (\$16.50 per kilogram) and a high of \$35 per pound (\$77 per kilogram) (fig. 5). Although this price varied significantly during the course of each year, the annual average price has trended downward from 1995 to 2000. During 2000, the U.S. spot cathode price fluctuated between \$13 and \$18 per pound (\$29 and \$40 per kilogram).

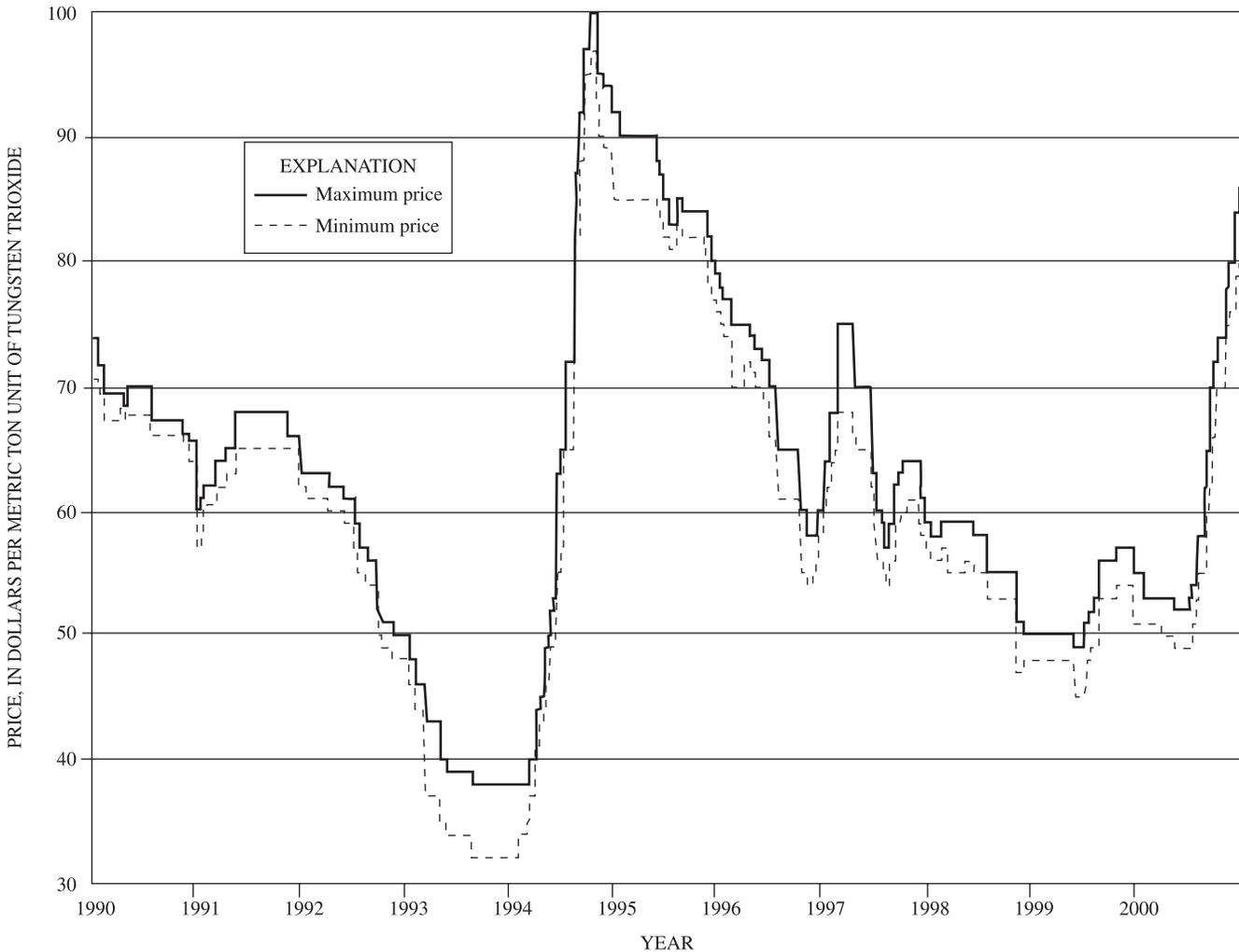


Figure 4. Free market ammonium paratungstate prices from 1990 through 2000. Data are from various issues of Metal Bulletin.



Figure 5. U.S. spot cobalt cathode prices from 1990 through 2000. Data are from various issues of Platt's Metals Week.

SOURCES OF TUNGSTEN SCRAP

Sources of tungsten scrap are key features of the U.S. tungsten materials flow shown in figure 1. Domestic scrap originates during manufacturing and following use of products in the United States. Scrap generated in foreign countries can enter the United States as imports.

OLD SCRAP GENERATED

Old scrap consists of tungsten-bearing products that are no longer being used. Some examples of used cemented carbide parts include metal cutting tools, such as burs, drill bits, end mills, form cutters, gundrills, inserts, reamers, saw tips, shim seats, and threading and grooving tools; metal forming tools, such as can tooling for aluminum and steel can manufacture, dies, and wire rod hot rolls; and other products, such as anvils, balls, bars, bits, blades, boring tools, circuit board drills and other micro tools, compacts, decommissioned

ammunition (piercers), grinding tools, high-pressure tools for manufacturing synthetic diamonds, honing tools, jet nozzles, knives, punches, mining bits, oil well drilling heads, rods, saw tips, seal rings and bearings, shanks, taps, wear-resistant parts, and woodworking cutters. Examples of used tungsten metal and tungsten alloy parts include decommissioned ammunition (piercers), electrical contacts, heating elements, protective shields, sputtering targets, switches, tips of sinter rods, and wires and filaments. Old superalloy scrap includes used turbine blades and other parts removed from jet engines. Tool steel components include blanking dies, boring tools, broaches, cutoff tools, drills, form tools, lathe and planer tools, milling cutters, punches, reamers, saw blades, and taps. Tungsten-bearing catalysts are used in the production of chemicals and petroleum and for cleaning power plant stack gases. Ideally catalysts are regenerated and reused, but eventually they are no longer effective and are considered spent (Kieffer and Lassner, 1987, p. 60; Froböse, 1995, p.

280; International Tungsten Industry Association, 1997, p. 16–19, 27–31; Carbide Recycling Co., undated; ELG Metals, Inc., undated; Martin Alloys Corp., undated a, b; Metal World, undated a-d; Recycler's World, undated).

To estimate the amount of tungsten that becomes available from old scrap (termed “old scrap generated”) in 2000, the following approach was used: For each tungsten-consuming industry in the United States, the average number of years the products would be in use was estimated. These product lifetimes were subtracted from 2000 to determine the year in which the product would have been manufactured. The amount of tungsten in the products was based on the amount of tungsten consumed by that industry sector during the year of manufacture minus the amount of tungsten that ended up as waste materials or new scrap. The amount of tungsten consumed by each industry sector in the year the products were manufactured was based on information collected by the USBM or the USGS. For some industry sectors, the percentage of tungsten consumed that ended up in final products was derived from information in a study by the National Research Council (1983).

This method of estimating old scrap generated is based entirely on tungsten consumed to make products in the United States and does not take into account the amount of tungsten in products imported into the country or exported out of the country. Although the net trade of tungsten in products could significantly alter the estimation of old scrap generated, the amount of tungsten in imported and exported products would be very difficult to quantify. Because of the lack of adequate information from which to make reliable estimates, no attempt was made to estimate the net trade of tungsten in products for this study.

As shown in figure 1 and table 1, 7,300 metric tons (t) of tungsten was contained in products that theoretically became available for recycling in 2000.

NEW SCRAP

New scrap is generated during the processing of tungsten concentrates, tungsten scrap, and tungsten chemicals to make tungsten metal powder, tungsten carbide powder, or tungsten chemicals, and during the fabrication of tungsten products from these materials. For the purpose of this study, new scrap does not include home scrap, which is generated and consumed within a single plant. As shown in the upper left part of figure 1, in 2000 an estimated 10,400 t of tungsten was processed to make tungsten carbide and tungsten metal powders in the United States. Production data for cast and crystalline tungsten carbide powders and tungsten compounds are withheld to avoid disclosing company proprietary data. In tungsten processing, recovery rates are high, and metal losses are kept to a minimum by recycling the home scrap generated. Losses from the domestic production of tungsten metal powder, tungsten carbide powder, and tungsten chemicals have been

estimated to equal approximately 6 percent of the tungsten in raw materials consumed (Smith, 1994, p. 4, 7, 18–19).

Tungsten in losses, new scrap generated, and products from U.S. industry sectors that produced alloys, parts, and other tungsten-bearing products are shown on the right-hand side of figure 1. Using material flows for individual industry sectors (National Research Council, 1983), the amount of tungsten lost during fabrication was estimated to be approximately 3 percent of the apparent supply, or approximately 500 t. The amount of tungsten generated as new scrap in 2000 was calculated from the estimated amount of tungsten consumed in new scrap minus imports of new scrap and releases of new scrap from stocks.

New scrap can be classified as either “hard” or “soft” scrap. Hard scrap consists of solid pieces, such as subspecification alloy parts, cemented carbide parts, and excess alloy generated during casting operations or removed during pressing and forging operations. Soft scrap consists of fine particles, such as baghouse dust from steel and alloy manufacturing, cutting or grinding sludges, loose powders generated during powder metallurgical processing, swarf, and turnings generated during machining of steel and alloy parts.

When used to produce near-net-shape parts, powder metallurgical processes generate less scrap than processes that require significant machining to produce finished parts. Powder metallurgical processes are used to make cemented carbide parts; heavy metal alloy components; mill products, such as lamp filaments and other tungsten metal parts; and some tool steels and superalloys.

Descriptions of the types of new scrap generated during the production of various tungsten end-use products follow. New cemented carbide scrap includes rejected finished products; tailings from pressing, presintering or sintering processes; and grinding residues, sludges, or powders that result from processing blanks or slugs (Froböse, 1995, p. 280).

Heavy metal alloys are alloys that contain high levels of tungsten with copper, iron, and (or) nickel. Although heavy metal alloy components are produced by powder metallurgical processes, large quantities of scrap are generated because of the milling and grinding steps necessary to produce parts with required dimensions. Most of the new scrap is in the form of high-quality turnings, but powders, floor sweeps, and solid scrap (rejected parts) are also generated (Kieffer, 1982; Asher and others, 1995).

Companies that manufacture mill products from tungsten metal powder generate hard and soft scrap. The hard scrap is in the form of sinter bar ends, rod and wire end trim, and rejected parts. The soft scrap includes sludge from cutoff wheels and floor sweeps (Kieffer and Baroch, 1981, p. 18).

Alloy industries that produce parts by cast or wrought processes typically generate large quantities of new scrap. The superalloy industry is one example. The buy-to-fly ratio,

which is the weight of metal purchased versus the weight of the finished parts, provides a measure of the amount of scrap generated in the production of aircraft engine parts. Depending on the part being made, these ratios can range from less than 5:1 to more than 20:1. In 1998, the average buy-to-fly ratio was about 7:1. This means that for every kilogram of aircraft engine parts produced, 7 kg of metal was purchased, and 6 kg of scrap was generated. New superalloy scrap can be in the form of grindings, solids, or turnings; by volume, turnings are the largest quantity generated (Lane, 1998; Schenk, 1998).

New scrap is also generated during the casting of corrosion-resistant alloys. In this industry sector, for every kilogram of alloy poured, only 0.4 to 0.6 kg of usable casting is produced. In other words, 40 to 60 percent of the melt becomes new scrap, which would be either recycled in-house or sold to be recycled elsewhere. The number of buyers of this tungsten-bearing scrap may be limited, however, by permissible levels of tungsten in the alloys a given melter produces (Spence and Stickle, 2002).

SCRAP IMPORTS

U.S. trade statistics are classified under the Harmonized Tariff Schedule of the United States Annotated (HTSA). The HTSA provides statistical categories and the applicable tariff rates for all merchandise imported into the United States. It is based on the international Harmonized System, which is the global classification system that is used to describe most world trade in goods.

The U.S. Census Bureau reported gross weight, tungsten content, and customs value of imports of tungsten waste and scrap under HTSA category 8101.91.1000, "Tungsten, waste and scrap." In 2000, the United States imported 993 t of tungsten in tungsten-bearing scrap valued at \$6.2 million under this category. On the basis of tungsten content, seven countries supplied 81 percent of these imports—China, 25 percent; the Republic of Korea and Russia, 15 percent each; Germany, 8 percent; and Japan, South Africa, and Uzbekistan, 6 percent each; the remainder was imported from 14 other countries (Shedd, 2002, p. 81.16–81.17).

Additional tungsten was likely to have been imported in scrap listed under other HTSA categories. One example would be cemented carbide scrap imported under HTSA category 8113.00.0000, "Cermets and articles thereof, including waste and scrap." In 2000, the portion of imports under this category that was estimated to be scrap was determined as follows: Gross weight and dollar value statistics were available on a country-by-country and month-by-month basis. In mid-2000, the price of cemented carbide scrap was reported to be approximately \$4.00 to \$5.50 per kilogram of contained tungsten (\$2.00 to \$2.50 per pound of contained tungsten), which was 20 to 30 percent less than scrap prices 1 year earlier (Metal Bulletin, 2000). The maximum amount

of tungsten carbide in cemented carbides is 97 percent, which would equate to a maximum tungsten content of 91 percent (Sandvik Hard Materials, undated). A maximum unit value of \$6.50 per kilogram, gross weight, was calculated using a maximum scrap price of \$7.15 per kilogram of contained tungsten ($\$5.50 \times 130$ percent) and a maximum tungsten content of 91 percent. Imports with a unit value equal to or less than \$6.50 per kilogram were assumed to be scrap, and imports with a unit value greater than \$6.50 per kilogram were assumed to be cermets and articles thereof. An average tungsten content of 80 percent was assumed, which results in estimated imports of 2,100 t of tungsten in scrap valued at \$10.8 million under this category. On the basis of estimated tungsten content, four countries supplied 99 percent of these imports—Canada, 49 percent; the United Kingdom, 36 percent; Japan, 9 percent; and Germany, 5 percent; the remainder was imported from five other countries. By adding the scrap imported under these two HTSA categories, the total tungsten content of imported scrap in 2000 was estimated to be 3,100 t. Specific information on the type of scrap imported under each category was not available. For the purposes of this study, scrap imports were estimated to be approximately 25 percent new scrap and 75 percent old scrap.

DISPOSITION OF TUNGSTEN SCRAP

Tungsten-bearing scrap can be consumed (by recycling or processing to recover the tungsten), discarded, dissipated, exported, or stocked. The influence of tungsten on living organisms depends on the type of organism, the type of tungsten compound, and the level of exposure. In general, tungsten and its compounds are less toxic than most other metals and their compounds and are considered to be relatively harmless to the environment. Thus, tungsten recycling is driven mainly by economic factors, although environmental factors are a consideration, as discussed in more detail in the "Outlook" section (International Tungsten Industry Association, 1997, p. 10; Lassner and Schubert, 1999, p. 377–378, 409–416).

SCRAP CONSUMPTION (RECYCLING AND RECOVERY)

Estimates of new and old scrap consumption were made using information from various sources, which included data reported to the USGS, import statistics, personal communications with industry representatives, and published reports. In 2000, U.S. industry consumed an estimated 1,600 t of tungsten in new scrap and 6,200 t of tungsten in old scrap. This resulted in a new-to-old-scrap ratio of 20:80 (table 1).

SCRAP EXPORTS

The Census Bureau reported the gross weight and free-alongside-ship (f.a.s.) value of exports of unwrought tungsten

and waste and scrap under HTSA category 8101.91.0000. An estimated 40 percent of these exports was assumed to be waste and scrap based on export statistics for 2002 and 2003 in which tungsten waste and scrap was reported separately from unwrought tungsten. The tungsten content of this scrap, which was assumed to be alloy scrap, was estimated as follows: An average unit value of approximately \$11.00 per kilogram of contained tungsten was assumed based on reported prices of \$9.00 to \$11.00 per kilogram of contained tungsten (\$4.00 to \$5.00 per pound of contained tungsten) for air-melt scrap and \$11.00 to \$13.00 per kilogram of contained tungsten (\$5.00 to \$6.00 per pound of contained tungsten) for vacuum-grade scrap (Metal Bulletin, 2000). The estimated f.a.s. value, in dollars, of the scrap exported in 2000 was divided by the average unit value, in dollars per kilogram of contained tungsten, to estimate the kilograms of tungsten in the scrap. This resulted in an estimated 160 t of contained tungsten valued at \$1.7 million under HTSA category 8101.91.0000. Additional tungsten-bearing scrap was likely to have been exported under other HTSA categories, but information was not adequate to make reliable estimates of the quantities. For example, on a month-by-month and country-by-country basis in 2000, most materials exported under the HTSA category called "Cermets and articles thereof, including waste and scrap" were assumed to be cermets because they had unit values that were too high for waste and scrap. For the purposes of this study, all scrap exports were assumed to be principally old scrap.

UNRECOVERED OLD SCRAP

Unrecovered old scrap represents tungsten in scrap that has not been recycled either in the United States or elsewhere. Examples of discarded tungsten-bearing products include burned-out lamps and lighting fixtures, electrical contact disks, landfilled spent catalysts and low-grade grinding swarfs, noncollectable carbide parts, tungsten carbide hardfacing materials, and welding electrode stubs. Generally, these materials are discarded because there is no efficient collection system to gather them or because they are not economic to recycle owing to contamination (Lassner and Schubert, 1999, p. 379; Oakes, 1999). An estimate of the amount of tungsten in unrecovered old scrap was derived by subtracting old scrap consumption and old scrap exports from old scrap supply. The magnitude of estimated unrecovered old scrap in figure 1 and table 1 appears to be reasonable considering that an estimated 35 percent of cemented carbide scrap is not recycled (Stjernberg and Johnson, 1998). If 5,700 t of tungsten was generated as old cemented carbide scrap in 2000, then approximately 2,000 t was not recycled. The following factors influence the accuracy of the estimated unrecovered old scrap: inaccuracies in the estimate of old scrap generated, either from products that were still being used or that had been exported or from imported products that

were not taken into account; any double counting between old scrap generated and old scrap imports that results from imported obsolete products that had been manufactured in the United States; and any inaccuracies in the estimates of old scrap consumed, stocked, or traded.

DISSIPATION

For the purpose of this study, all uses of tungsten in chemical applications, except for catalysts, were considered to be dissipative. Other sources of dissipated tungsten include material losses from wear during use of cemented carbide parts and hardfaced products, arc erosion of electrical contacts and electrodes, and the oxidation of alloys under high-temperature conditions (Smith, 1994, p. 7). A total of 300 t of tungsten was estimated to be the loss through dissipation from these industry sectors, as is indicated in the right-hand part of figure 1.

OLD SCRAP RECYCLING EFFICIENCY

Recycling efficiency shows the relation between the amount of tungsten in used products theoretically available for recycling and the amount that is recovered or recycled. By definition, this relation is the amount of tungsten in old scrap consumed and exported divided by the amount of tungsten in old scrap generated, imported, and released from stocks. The recycling efficiency for old scrap calculated for 2000 was 66 percent (table 1). The accuracy of this estimate is dependent on the accuracy of the individual estimates used in its calculation.

INFRASTRUCTURE OF TUNGSTEN SCRAP INDUSTRY

Although the United States is a major tungsten consumer, tungsten mine production has not been recorded since 1992. In 2000, approximately 10 companies in the United States processed tungsten concentrates, tungsten scrap, APT, and (or) tungsten oxide to make tungsten metal powders, tungsten carbide powders, and (or) tungsten chemicals. An undetermined number of additional companies recycled cemented carbide scrap using direct methods to break down the scrap into powders to make new cemented carbides or for use as hardfacing or abrasives. U.S. tungsten supply comprised imports, releases from industry stocks, sales of excess tungsten materials from the National Defense Stockpile, and the recycling of tungsten-bearing scrap.

The collection and processing of tungsten-bearing scrap depended on several factors, such as the quality, type, and volume of the scrap. A wide variety of collecting, sorting, preliminary processing, and recycling or metal reclamation systems was used. Some scrap was handled by brokers, dealers, or waste management companies. Certain companies

specialized in trading and (or) processing refractory metal scrap, which included tungsten carbide, tungsten metal, tool steel, and tungsten alloy scrap.

Scrap metal processors first hand sorted solid pieces of new and old metal and alloy scrap by alloy type. Skilled sorters did a preliminary sort on the basis of color, shape (object recognition), and weight of the scrap items. If necessary, the items were then tested with one or more of the following methods: analysis of the spark pattern generated when the alloy was ground on an abrasive wheel, chemical or physical analysis by various methods, or response to a magnet (Newell and others, 1982, p. 1–2; Riley, 1990, p. 576–577). Once the solids were sorted by alloy type, any attachments were removed and all assemblies were dismantled. Additional processing, such as chemical milling, cutting to size, degreasing, pickling, shot blasting, and washing, depended on the condition of the scrap and the customer's requirements (Meschter, 1990; Monico Alloys, Inc., undated).

Following collection, sorting, and preliminary processing, most of the tungsten-bearing scrap was processed and (or) consumed in the United States. Examples of scrap processing methods used in the United States are described in the section "Processing of Tungsten Scrap." The remaining tungsten-bearing scrap was exported to foreign smelters, refiners, processors, or consumers either directly or following some initial processing.

ALLOY SCRAP

This category includes new and old scrap of the following types: corrosion- and wear-resistant alloys, heavy metal alloys, specialty steels, superalloys, and other tungsten-bearing alloys. Scrap metal processors collected, sorted, and processed metal and alloy scrap and then returned it to scrap consumers for melting, recycling, or metal reclamation (Institute of Scrap Recycling Industries, Inc., 1996, p. 15).

Turbine engine parts from dismantled military aircraft are an example of tungsten-bearing old scrap. The Defense Reutilization and Marketing Service (DRMS) was the U.S. Department of Defense (DOD) agency that disposed of excess property received from the military services. The DRMS first offered excess military property for reuse within the DOD, transferred it to other Federal agencies, or donated it to State and local governments and certain nonprofit organizations. Property that was not reused, transferred, or donated was offered for sale to private companies and individuals (Defense Reutilization and Marketing Service, undated). The DRMS periodically held sealed bid sales with offers of high-temperature alloy scrap in the form of turbine engine parts. Scrap metal processors were potential buyers of this scrap.

CEMENTED CARBIDE SCRAP

In many cases, cemented carbide producers supplied scrap directly to converters, who returned recycled powders

to them for reuse. An increasing number of cemented carbide producers processed their home and purchased hard scrap using the zinc process, as described in the section "Processing of Tungsten Scrap—Cemented Carbide Scrap." Machine shops and manufacturers that use cemented carbide products collected their used inserts and other parts and sold them to dealers, scrap processors, or tungsten converters. The scrap processor's role was to sort, clean, and repackage the scrap for sale (Kieffer and Lassner, 1987; Payne, 2002, p. 7–8).

MILL PRODUCTS FROM METAL POWDER SCRAP

Refractory metals companies, such as Hi-Temp Specialty Metals, Inc. of Willingboro, N.J., processed such solid pieces of pure tungsten metal as bars, cuttings, and wire spool ends. These were analyzed, sorted, crushed, cleaned with acid, and then sold as a source of tungsten to manufacturers of air- and vacuum-melt alloys (Queneau, 2003, p. 37; Hi-Temp Specialty Metals, Inc., undated a, b).

PROCESSING OF TUNGSTEN SCRAP

In 2000, a wide variety of methods was used to process tungsten-bearing scrap in the United States. Lassner and Schubert (1999, p. 380–385) classified tungsten recycling methods into the following four groups: hydrometallurgy, melting metallurgy, direct recycling, and semidirect recycling. In hydrometallurgical recycling, chemical methods were used to reclaim tungsten from scrap; this reclaimed tungsten was used as a substitute for tungsten ore concentrates at conversion plants. This processing route, which is discussed in the section "Tungsten Production Processes," resulted in tungsten materials that were indistinguishable from those produced from ore concentrates. In melting metallurgical recycling, scrap was used as a source of tungsten in the production of alloys, such as steels, stellites, or superalloys; cast or menstroom tungsten carbide; or ferrotungsten or tungsten melting base. In direct recycling, the scrap was disaggregated into a powder by chemical and (or) physical means without changing its original composition. In semidirect recycling, one component of the scrap was dissolved chemically, which allowed the scrap to be broken down by physical means.

Additional information on the advantages and disadvantages of the many recycling methods is available from Kieffer (1982), Kieffer and Lassner (1987, 1994), Gries (1999, p. 1–5), Lassner and Schubert (1999, p. 380–385), and Oakes (1999). In general, the chemical processes had advantages, such as the ability to treat all scrap types and remove impurities, but tended to have higher costs, higher reagent and energy consumption, lower yields, and more waste products than the direct recycling methods. A balance between using chemical recycling and direct recycling processes allowed the tungsten industry to recycle soft and hard, contaminated and clean scrap; to reduce the

overall impurity levels in reclaimed materials; and to reduce recycling costs. The following discussion provides examples of the many methods used to process various types of tungsten-bearing scrap.

CEMENTED CARBIDE SCRAP

One of the simplest methods for recycling used cemented carbide inserts was to grind them into new shapes. For economic reasons, this was more commonly done in Asia than in Western countries, and only a small percentage of all scrapped inserts was treated this way. In the United States, an estimated 35 percent of cemented carbide scrap was recycled using chemical processes, 25 percent was recycled using the zinc process, 5 percent was recycled using other processes, and the remaining 35 percent was not recycled. The use of the zinc process to recycle hard cemented carbide scrap was increasing (Stjernberg and Johnson, 1998; Payne, 2002, p. 7–8).

A variety of chemical methods was available to treat cemented carbide scrap. The most common method involved oxidation followed by alkali leaching. Osram Sylvania Inc. was an example of a U.S. company that used this type of chemical process. Tungsten production at Osram's Towanda, Pa., conversion plant was from ore concentrates and tungsten-bearing scrap. The concentrates and oxidized scrap were leached with sodium hydroxide to produce a sodium tungstate solution, which was filtered to remove byproduct sludge that contained cobalt and other metals recovered from the scrap. The sodium tungstate solution was then purified and subjected to a liquid ion exchange process to separate the tungsten as an ammonium tungstate solution from which other tungsten products could be produced. Two other chemical methods used to treat cemented carbide scrap were chlorination by the Axel Johnson process and fusion at high temperature with sodium nitrite or sodium nitrate as an oxidizing agent and sodium carbonate as a diluent (Kieffer, 1982; Kieffer and Lassner, 1987, 1994; Stjernberg and Johnson, 1998; Gries, 1999, p. 4–5; Lassner and Schubert, 1999, p. 184–193, 381–384; GTE Products Corp., undated, p. 8–9).

In 1998, OMG Americas expanded its Apex hydrometallurgical plant in Saint George, Utah, to recycle hard and soft cemented carbide scrap. The plant used a chemical process to recover APT and cobalt compounds from the scrap (Magdics, 1998, p. 19, 22, 26, 31; OM Group, Inc., 2000, p. 3).

When treated by direct recycling methods, the powders from disaggregated cemented carbides contained tungsten carbide, cobalt, and any other carbides present in the original scrap. Coarser powders could be used as grit in hardfacing welding rods or to make abrasive discs, sheets, or saws and other tools edged with carbide grit. Finer powders were more or less ready to be used to make new cemented carbide parts. The zinc process was considered to be the most important direct process for recycling cemented carbide scrap. The scrap

was first carefully sorted by grade, cleaned to remove any brazing or impurities, crushed, and then immersed in molten zinc in the presence of argon gas. The molten zinc reacted with the cobalt binder, which caused the scrap to expand. The zinc was removed by vacuum distillation, which left a porous material that contained the tungsten carbide, cobalt, and any other carbides behind. This was crushed, milled, screened, and blended. Following chemical analysis and carbon adjustment, the reclaimed powder was then ready to press into new cemented carbide parts. Other examples of direct recycling processes included "bloating/crushing" in which the cemented carbide was embrittled by heating it to about 1,800°C followed by rapid quenching and the coldstream process, in which blasts of air were used to accelerate scrap towards a target with sufficient energy to cause fracture (Kieffer, 1982; Brookes, 1996, p. 73–74, 184–185; International Tungsten Industry Association, 1997, p. 10; Stjernberg and Johnson, 1998; Lassner and Schubert, 1999, p. 382–384).

Cemented carbide scrap could be recycled by semidirect methods, such as acid leaching, bloating followed by leaching, electrolysis, or leach milling. It could be recycled by melting to produce tungsten melting base, menstruum tungsten carbide, or specialty alloys, such as stellites (Kieffer, 1982; Kieffer and Lassner, 1987; Stjernberg and Johnson, 1998).

HEAVY METAL ALLOY SCRAP

The oxidation-reduction process was the preferred method for recycling tungsten heavy metal alloy turnings and powders. In this direct recycling process, the scrap was oxidized by heating it in air to a temperature of about 800°C, milled and screened, hydrogen reduced at a temperature of 900°C to 1,000°C, screened and blended, and then mixed with virgin heavy metal alloy powder to make a ready-to-press powder for the production of new products (Kieffer, 1982; Kieffer and Lassner, 1994; Lassner and Schubert, 1999, p. 381–384; Oakes, 1999).

Other methods for recycling hard or soft heavy metal alloy scrap included the following: the coldstream process for turnings and solids with binder contents of less than 3 percent; the menstruum process, which produced macrocrystalline tungsten carbide by dissolving sintered scrap in a carbon-saturated iron melt and then leaching the nickel, iron, and (or) copper with acid; melting, in which the scrap was used as a source of tungsten in the production of ferrotungsten, tool steels, or tungsten melting base; and chemical processing. Electrolysis, which uses the scrap as an anode in an electrolytic solution, could be used to dissolve the tungsten from hard heavy metal alloy scrap prior to chemical processing. Leach milling and leaching with an iron chloride solution to dissolve copper, nickel, and iron selectively were other possible methods for recycling heavy metal alloy scrap (Kieffer, 1982; Kieffer and Lassner, 1987, 1994; Lassner and Schubert, 1999, p. 193–194, 377, 380–384; Oakes, 1999).

In the process used by Metek Metal Technology, Ltd. in Ramat Hovav, Israel, tungsten-bearing scrap was mixed with sodium nitrate and sodium nitrite and fed into a preheated revolving furnace. The chemicals and scrap reacted exothermically to form soluble sodium tungstate; insoluble hydroxides of cobalt, iron, and nickel; and insoluble sodium tantalate and sodium titanate. As soon as the molten charge from the furnace was poured into water, the sodium tungstate dissolved. The resulting solution was filtered, the pH was increased, and calcium chloride was added to precipitate insoluble calcium tungstate. The calcium tungstate was suspended in water, and hydrochloric acid was added to produce insoluble tungstic acid, which could be treated by conventional methods to produce tungsten oxide, tungsten metal powder, or tungsten carbide powder (Asher and others, 1995).

MILL PRODUCTS FROM METAL POWDER SCRAP

The preferred use for hard pure tungsten scrap, in terms of economic value, was as a source of tungsten in the manufacture of superalloys. The scrap was analyzed, sorted, crushed, and then cleaned with acid before being sold to producers of air- or vacuum-melted alloys. The preferred use for pure tungsten scrap powder was as a source of tungsten in the production of cast or menstroom tungsten carbide. In addition, pure tungsten metal scrap could be recycled using the following methods: chemical processing; melting, in which the scrap was used as a source of tungsten in the production of ferrotungsten, stellites, tool steels, or tungsten melting base; oxidation-reduction; and the coldstream process. Electrolysis, which uses the scrap as an anode in an electrolytic solution, could be used to dissolve the tungsten prior to chemical processing (Kieffer, 1982; Kieffer and Lassner, 1987; Lassner and Schubert, 1999, p. 193–194, 377, 381; Queneau, 2003, p. 37; Hi-Temp Specialty Metals, Inc., undated a, b).

RESIDUES

Tungsten-bearing sludges, which often contained aluminum oxide or silicon carbide impurities, were generated during grinding of tungsten, tungsten alloy, and tungsten carbide products. Depending on their chemistry, these grinding residues were recycled by chemical methods or by melting to produce ferrotungsten, menstroom tungsten carbide, tool steels, or tungsten melting base (Kieffer, 1982; Kieffer and Lassner, 1987).

SPENT CATALYSTS

Processes for recovering metals from spent cobalt-bearing catalysts were well established (Shedd, 2003a, p. M11–M12). Although various metal recovery processes had been developed for spent nickel-tungsten hydrocracking

catalysts, most of this scrap was sent to nickel smelters or landfills. Some U.S. metal recovery facilities could not accept spent tungsten-bearing catalysts because they needed to avoid contaminating their molybdenum and vanadium products with tungsten. In addition, low tungsten prices can make recycling of spent catalysts uneconomical (Kieffer and Lassner, 1987; Berrebi and others, 1992; Case and others, 1995, p. 465; Llanos and Deering, 1995, p. 427; Sackett, 2003, p. 16; Eurecat S.A., undated).

STEEL AND SPECIALTY ALLOY SCRAP

Significant amounts of tungsten-bearing steel scrap were recycled by melting during steel production. Typical melts contained more than 60 to 70 percent scrap, which included home scrap (Kieffer, 1982).

Specialty alloy scrap included such alloys as stellites and superalloys. Turnings represented the largest quantity, by volume, of superalloy scrap generated. Scrap processors collected these turnings; qualitatively verified their chemical purity to remove materials that would contaminate a superalloy melt; crushed the turnings into chips; quantitatively assayed the chips; cleaned residual cutting fluids and dirt from the chips by kiln processing, detergent cleaning, or solvent cleaning; sampled and analyzed the scrap to certify that it met certain chemical specifications; prepared homogeneous lots if desired; densified the chips if desired; and then packaged the scrap for return to superalloy melters (Lane, 1998).

THORIATED TUNGSTEN SCRAP

Tungsten electrodes that contained about 2 percent thorium oxide were the most common type of electrode used for gas tungsten arc welding (also called tungsten inert gas welding) of carbon and stainless steels. Thoriated tungsten electrodes were also used in a variety of high-performance and special application lighting products, such as high-intensity discharge lamps. Because thorium is radioactive, thoriated tungsten scrap posed special environmental challenges when recycled (International Tungsten Industry Association, 1997, p. 27; Oakes, 1999; National Radiological Protection Board and Gesellschaft für Anlagen- und Reaktorsicherheit mbH, 2001, p. 9, 12; Smith, 2001).

In the mid-1990s, an estimated 80 t/yr of thoriated tungsten was produced in the United States. The powder input to make thoriated tungsten products was approximately 80 percent virgin material, 18 percent new scrap, and 2 percent old scrap. Of the raw materials used to produce thoriated tungsten products, 64 percent ended up in the final products, and 36 percent became scrap. Roughly one-half of this new scrap was impure, and one-half was clean. Impure thoriated tungsten scrap was processed by the following method: the scrap was oxidized in air and then either reduced with iron using a silicothermic or aluminothermic process to make ferrotungsten, tool steel, or tungsten melting base, or the scrap

was processed chemically to make APT. The thorium oxide, which ended up in the slag in the production of ferrotungsten or in the filter cake in the production of APT, was sent to a low-level radiation depository. Clean thoriated tungsten powders, solids, and turnings, which were generated as new scrap during the production of thoriated tungsten products or, in the case of solids, as old scrap by consumers, were processed using the oxidation-reduction method. The scrap was recrystallized, crushed, subjected to magnetic separation to remove iron-contaminated scrap, oxidized in air, hydrogen reduced, screened, blended, assayed, and then mixed with virgin thoriated tungsten to make a ready-to-press powder for the production of new products. The iron-contaminated scrap was then processed as impure scrap (Kieffer and Lassner, 1994; Lassner and Schubert, 1999, p. 377, 381–382).

OUTLOOK

The recycling of tungsten-bearing scrap and the recovery of tungsten from scrap materials are well-established practices for a number of reasons. The value of the tungsten and other metals present in the scrap, such as cobalt, columbium (niobium), copper, nickel, rhenium, silver, titanium, and tantalum, provides economic reasons to recycle. The use of scrap helps to improve process yields and to diversify the sources of raw materials for the production of tungsten chemicals, tungsten metal powders, and tungsten-bearing end products. This helps to reduce potential supply disruptions that could result from a high dependence on imports and to reduce price volatility. Other important factors that play a role in promoting tungsten recycling and recovery include environmental considerations (including regulations) and the desire to conserve resources and energy, to reduce environmental damage from mining, to reduce mining and processing wastes and the costs of disposing wastes and used products, and to portray an environmentally responsible image (Kieffer and Lassner, 1987, 1994; Stjernberg and Johnson, 1998; Oakes, 1999).

Increases in recycling since the mid-1970s have been attributed to the following factors: increased use of indexable inserts, which are easier to recycle than brazed tools; an increased appreciation of the value of tungsten through better communication and education; a better understanding of the value of other metals present in the scrap; improved scrap collection and separation at the places where it is generated; improved recycling methods; a steadily growing environmental awareness; and stricter regulations in industrialized countries. The primary reasons cited for discarding scrap rather than recycling it were the lack of efficient collection systems for certain scrap types and contamination, which makes some scrap recycling uneconomical. To a lesser extent, metal prices influence tungsten recycling. Higher metal prices and continued education of consumers on the value of their scrap could result in improved sorting of scrap in the places where

it is generated, improved collection systems, and higher recycling efficiencies. An increase in the share of recycling by direct methods was expected even though it would require consuming industries to learn how to modify production conditions to accommodate reclaimed materials (Kieffer and Lassner, 1994; Smith, 1994, p. 22; Lassner and Schubert, 1999, p. 384–385; Oakes, 1999).

World tungsten consumption is expected to continue to increase in the coming years. Because most tungsten products can be recycled, the availability of tungsten-bearing scrap also is expected to increase. The rate of increase may be dampened somewhat by improvements in products, such as coatings on cemented carbide parts, that increase their useful life. In addition to the types of scrap discussed in this report, a new source of tungsten-bearing scrap was expected to become available as the U.S. Army's "green bullet" program moved to full-scale production. Recycling used bullets from firing ranges was an integral part of the program, and large quantities of scrap were expected to be generated as the Army moved towards 100-percent replacement of lead in ammunition (Oakes, 1999; Middleton, 2000, p. 5, 7, 14, 20–22).

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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.

cast tungsten carbide. Tungsten carbide produced by melting tungsten and carbon in a vacuum arc furnace. The resulting carbide has a martensitic structure and eutectic two-phase composition (W_2C-WC) and is very hard and abrasion-resistant.

catalyst. A substance that changes the rate of a chemical reaction without being consumed in the reaction.

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

hard scrap. Scrap consisting of solid pieces. Examples of old hard scrap include used alloy or cemented carbide parts. Examples of new hard scrap include subspecification alloy or cemented carbide parts and excess alloy generated during casting operations or removed during pressing and forging operations. Compare with “soft scrap.”

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

menstruum tungsten carbide. Tungsten carbide produced by a menstruum process, in which macrocrystalline tungsten carbide grains are produced by dissolving sintered scrap in a carbon-saturated iron melt and then leaching the nickel, iron, and (or) copper with acid.

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, sintered cemented carbide parts, 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 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. Tungsten 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:

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

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

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

price. Prices for tungsten scrap are not published on a routine basis. The total value of old scrap consumed in 2000 was estimated using the unit values of imported tungsten-bearing scrap and prices from Metal Bulletin (2000).

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:

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

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

soft scrap. Scrap consisting of fine particles. Examples include cutting or grinding sludges, swarf, turnings generated during machining of steel and alloy parts,

baghouse dust from steel and alloy manufacturing, and loose powders generated from powder metallurgical processes (pressing, presintering, and sintering).

stellites. The word Stellite is a registered trademark of the Deloro Stellite Company. Stellites are a class of alloys containing cobalt, chromium, and tungsten, which are characterized by their ability to resist all types of wear,

particularly at elevated temperatures and under corrosive conditions.

superalloys. Alloys developed for high-temperature service where relatively high mechanical stress is encountered and where surface stability is frequently required.

swarf. Fine metallic particles and abrasive fragments removed by cutting or grinding tools.

