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Materials Flow of Tungsten in the United States

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MATERIALS FLOW OF TUNGSTEN IN THE UNITED STATES

By Gerald R. Smith[1]

ABSTRACT

Because of continuing concerns regarding the effects of cumulative quantities of materials in the environment, the Bureau of Mines has initiated a series of studies to evaluate, to the fullest extent possible, all aspects of the materials flow sequence for selected commodities. Although tungsten and its compounds do not pose a significant health hazard to the environment, they do represent valuable resource materials to which appropriate conservation considerations must be given. The present study includes a description of recent trends in the consumption, loss, and recycling of tungsten-containing materials in the United States during the period 1974 to 1991 and an estimation of the cumulative loss of tungsten to the environment since 1910. Obsolete tungsten is recycled primarily as cemented tungsten carbide components that have been used in cutting and wear-resistant applications. The quantity recycled, as a percentage of annual U.S. consumption of tungsten, was estimated to have increased from 10% in 1974 to 34% in 1991. An estimated 58% of the 348,000 metric tons of primary tungsten consumed since 1910 was lost to the environment through means such as dissipation, discard, and dilution.

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INTRODUCTION

The various components of the U.S. tungsten materials flow are discussed in this report with emphasis directed toward identifying as many factors as possible affecting the total available domestic supply of tungsten and the ultimate direction and disposition taken by that supply. Certain geologic information and environmental and health considerations pertaining to tungsten are also discussed.

Historical data for the tungsten materials flow relating to production, supply, and consumption were obtained from the U.S. Geological Survey and U.S. Bureau of Mines annual publications on minerals (*1*)[2] and the Bureau of Mines Mineral Facts and Problems (*2*) and Mineral Commodity Summaries (*3*). Estimates for tungsten lost and discarded or recycled prior to 1974 were based upon information reported in the annual mineral publications (*1*). Since 1974, these estimates were based mainly upon information contained in several other U.S. Government and industry reports (*4-10*).

The data and discussions presented in this initial report for tungsten are intended to provide a base upon which further understanding of the materials flow of tungsten can be realized. As the concept of sustainable development gains ever-increasing importance in the world's future, it correspondingly implies that more efficient and economical recovery and reuse of the world's finite resources of tungsten be achieved.

Tungsten's strategic importance in the world continues as its unique high-temperature properties are utilized in the production of numerous end-use items. The high melting point, high density, good corrosion resistance, good thermal and electrical conductivity properties of tungsten and its alloys, and the excellent cutting and wear-resistant properties of its carbide serve to provide important end-use products for both domestic and military consumption.

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GLOBAL GEOLOGIC OCCURRENCE OF TUNGSTEN

Mineral deposits containing tungsten are found on all continents. Tungsten appears in nature as the oxide and is combined principally with calcium (scheelite group) and with iron and manganese (wolframite group). Tungsten is a relatively rare element, constituting only about 0.00013% of the Earth's crust and ranking 18th in quantity among the metallic elements (*11*). An estimated 42% of the world's reserves of tungsten are in China. Other significant deposits are in Australia, Austria, Bolivia, Brazil, Burma, Canada, North Korea, the Republic of Korea, Peru, Portugal, Spain, Thailand, Turkey, the former U.S.S.R., and the United States.

The tungsten minerals occur in three main types of deposit, including hydrothermal, skarn, and stratiform (*11*). More than 60% of the world's resources of tungsten minerals is found in hydrothermal deposits, existing chiefly as wolframites and occurring in quartz veins. A significant portion of the remaining resources is found in skarn or tactite deposits, which are formed by high-temperature replacement and recrystallization of limestone near contacts with intrusive igneous rocks. The main tungsten mineral form in these deposits is scheelite, occurring in conjunction with sulfides of iron, copper, and zinc. Lesser quantities of tungsten minerals can be found in volcanic-sedimentary stratiform deposits resulting from underwater volcanic activity. Lastly, tungsten has been found in certain natural brines.

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[2] Italic numbers in parentheses refer to items in the list of references at the end of this report.

GLOBAL DISTRIBUTION AND ENVIRONMENTAL EFFECTS OF TUNGSTEN

A summary of several works describing the distribution of tungsten and its compounds in the environment has been reported by Hartung (*12*). Researchers in the United Kingdom indicated that only about 0.1 microgram per liter of tungsten was evident in Northern Atlantic seawater. Japanese researchers showed that the concentration of tungsten in Northern Pacific seawater also was quite low at about 0.008 microgram per liter. The low levels in seawater were considered attributable to tungsten's ability to rapidly adsorb onto ocean minerals such as iron hydroxide, manganese oxide, and clay. The researchers in the United Kingdom further determined that the level of tungsten in the atmosphere over the United Kingdom was only about 1.5 micrograms per cubic meter. Consistent with the findings of the latter researchers, the results of air sampling studies conducted over six U.S. cities indicated levels of tungsten in the atmosphere in the range of 0.1 to 2.0 micrograms per cubic meter (*13*).

On the basis of information provided by Morgan and Stumm (*14*), some approximations of the relative movement of tungsten in the atmosphere were able to be made. According to their summary, the atmospheric importance of the anthropogenic (human-caused) flux for a number of metals, relative to the natural mobilization of these metals, can be described by a numerical value termed the atmospheric interference factor (IF). The IF is calculated as the total anthropogenic emissions to the atmosphere (industrial particulate emissions plus fossil fuel flux) divided by the total natural mobilization to the atmosphere (continental and volcanic dust and gas fluxes) times 100. According to this formula, metals that fall into the category of lithophiles (those metals that exhibit mass transport to oceans and streams greater than transport to the atmosphere) exhibit IF values in the range of 15 to 820. Although insufficient data were available for them to calculate an IF for tungsten, it logically could be grouped with other known lithophile-type elements such as manganese, cobalt, chromium, vanadium, and nickel. Using this criteria, one can assume that tungsten is likely to have an IF in the aforementioned range. In contrast, metals classified in the category of atmophiles (those metals that exhibit mass transport to the atmosphere greater than that to oceans and streams) exhibit IF values in the range of approximately 1,400 to 35,000. Many atmophilic elements are, thus, characteristically volatile or have oxides with a low boiling point or form compounds that are readily vaporized.

Considering tungsten's probable lithophilic nature, there is evidence of limited tungsten enrichment on a global and regional scale, relative to its abundance on the Earth's crust, but this enrichment is believed unlikely to be caused anthropogenically. On a local scale, a greater enrichment is evident mostly through processes whereby the tungsten is solubilized, but in neither case are there specific data available on the degree of this enrichment.

Hartung (*12*), in summarizing certain environmental and health factors related to tungsten, indicated that tungsten accumulates on the leaves of certain plantlife both on land and in water. In one instance, it was reported that the spraying of various types of grapes with a dilute solution of sodium tungstate enhanced the yield and sugar content of the grapes.

Individual human intake of tungsten from food was estimated to be up to 13 micrograms per day. Studies with animals revealed, however, that ingested tungsten was either nonabsorbed and excreted in the feces or absorbed but rapidly excreted in the urine. Of the small quantities that remained absorbed in the animal's biological system, deposition occurred in several locations including the spleen, liver, kidneys, lungs, muscles, testes, bones, and the bloodstream. Results of embryo-larval bioassays performed on a number of fish species revealed that tungsten was the least toxic element of all coal components.

A report summarizing further health, safety, and toxicity information for tungsten indicated that there have been no documented cases of tungsten poisoning in humans (*15*). According to the results of several toxicity studies with animals included in this summary, soluble tungsten compounds represent the most significant threat to human health. The lethal dose (LD_{50}) for soluble sodium tungstate injected subcutaneously in adult rats was quite high, however, at 140 to 160 milligrams of tungsten per kilogram weight of test subject. Results of a separate study showed that guinea pigs treated orally or intravenously with sodium tungstate suffered anorexia, colic, lack of coordination, and trembling. In a related study in which three different soluble compounds were fed orally to rats, the decreasing order of toxicity was sodium tungstate, then tungsten trioxide, and finally ammonium paratungstate.

Exposure limits have been established in the United States for both soluble and insoluble tungsten compounds (*16*). A threshold limit of 1 milligram of tungsten per cubic meter of air, as a time weighted average (TWA), has been set for soluble compounds, and a limit of 5 milligrams of tungsten per cubic meter of air, as a TWA, has been set for insoluble compounds.

Occupational exposure to tungsten carbide powder in the preparation of cemented carbides may cause respiratory diseases such as bronchial asthma and progressive interstitial fibrosis. However, studies conducted with both animals and humans suggest that these diseases are not caused directly by the tungsten carbide but rather by the cobalt powder contained in the cemented carbide product (*16, 17*).

No tungsten compounds have been included in the U.S. Environmental Protection Agency (EPA) toxic release inventory (TRI) list since it was first published in 1987. Preparation of the list and subsequent annual publication of toxic release data provided by industry for the list were mandated in the Emergency Planning and Community Right to Know Programs section of the Superfund Amendments and Reauthorization Act of 1986, signed into law on October 17, 1986. The TRI list covers a very broad spectrum of toxicity concerns, from acutely lethal to mildly toxic, and is based upon considerations of the amount produced or used in the United States, present regulatory status, known levels in the environment, and professional judgment as to potential hazards. Criteria were applied to two existing toxicity data bases, the Registry of Toxic Effects of Chemical Substances and the Toxic Substances Control Act Inventory, to formulate the original TRI list of 402 substances. The TRI list is being updated continuously by EPA.

U.S. TUNGSTEN MATERIALS FLOW

GENERAL DISCUSSION

Figure 1 provides a general flow diagram of the U.S. tungsten industry from initial feedstock to end-use consumption. Most tungsten concentrate is converted to ammonium paratungstate (APT), metal powder, carbide powder, ferrotungsten, or other intermediate materials before being consumed in the fabrication and manufacture of the various end-use products. Some high-purity scheelite is added directly in steelmaking and may be consumed in either natural or synthetic form. The synthetic scheelite may, in some instances, be produced from tungsten carbide scrap.

As indicated in figure 1, the normal flow of tungsten can be divided into four stages. These include milling and concentrating of tungsten ores and byproduct tungsten, processing from tungsten concentrates to tungsten products, fabrication and manufacture of tungsten end-use items, and embodiment of such tungsten items in industrial and consumer products. A simplified diagram showing the utilization of tungsten scrap, as it relates to the various tungsten stages, is shown in figure 2.

The consideration of factors related to tungsten losses and scrap flows in the four tungsten stages are discussed in the following sections. Industry facts and statistics pertinent to this discussion were obtained mainly from a U.S. Government study that assessed technical options for conserving tungsten (*5*) and from a tungsten industry report that presented significant information on the recycling of tungsten carbide and tungsten mill products scrap (*7*).

MILLING AND CONCENTRATING OF TUNGSTEN ORES AND BYPRODUCTS

Tungsten recovery in the United States has been principally from tactite deposits. A significant quantity also has been recovered as a byproduct of the mining of a molybdenum porphyry ore body. As a result of their high density, tungsten minerals are concentrated primarily by physical methods such as gravity and flotation. In addition, magnetic separation procedures are used to beneficiate tungsten by removing magnetic impurities from scheelite minerals and by concentrating the magnetic wolframite fraction from associated nonmagnetic minerals. Fines or slimes created in the beneficiation of tungsten ores are not amenable to treatment by these physical methods. Consequently, some fines are processed chemically to produce synthetic scheelite or APT. Depending upon the type of ore body and the sophistication of the beneficiation procedures used, between 70% and 90% of the contained tungsten is recovered in the milling and concentrating of tungsten ores.

PROCESSING FROM TUNGSTEN CONCENTRATES TO TUNGSTEN PRODUCTS

Tungsten losses are generally fairly low in these tungsten processing stages. In the manufacture of APT from concentrate, for example, a minimum 96% recovery of tungsten is achieved in the industry. Similar or greater recoveries are attained for concentrates consumed directly

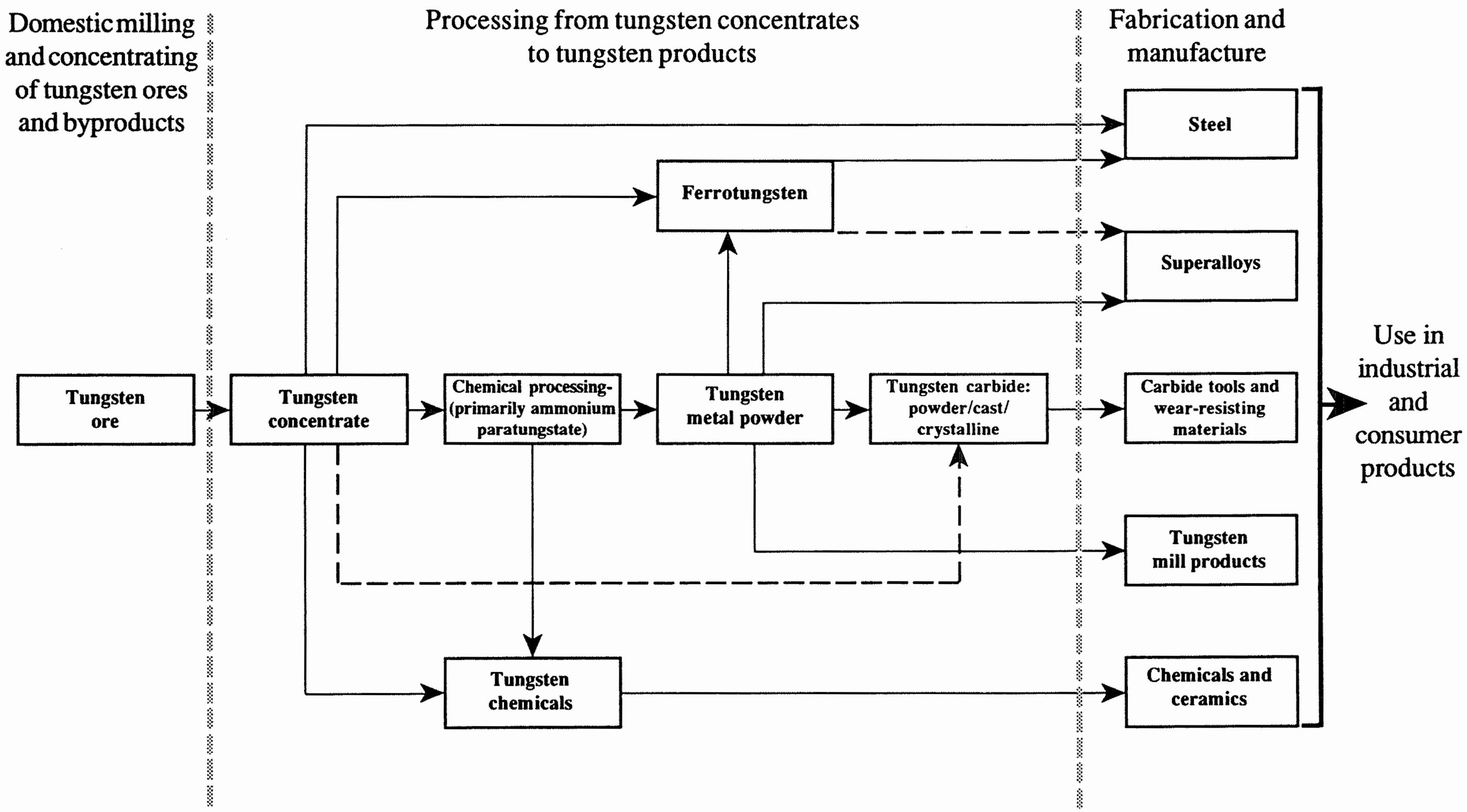

Figure 1.—General tungsten flow diagram.

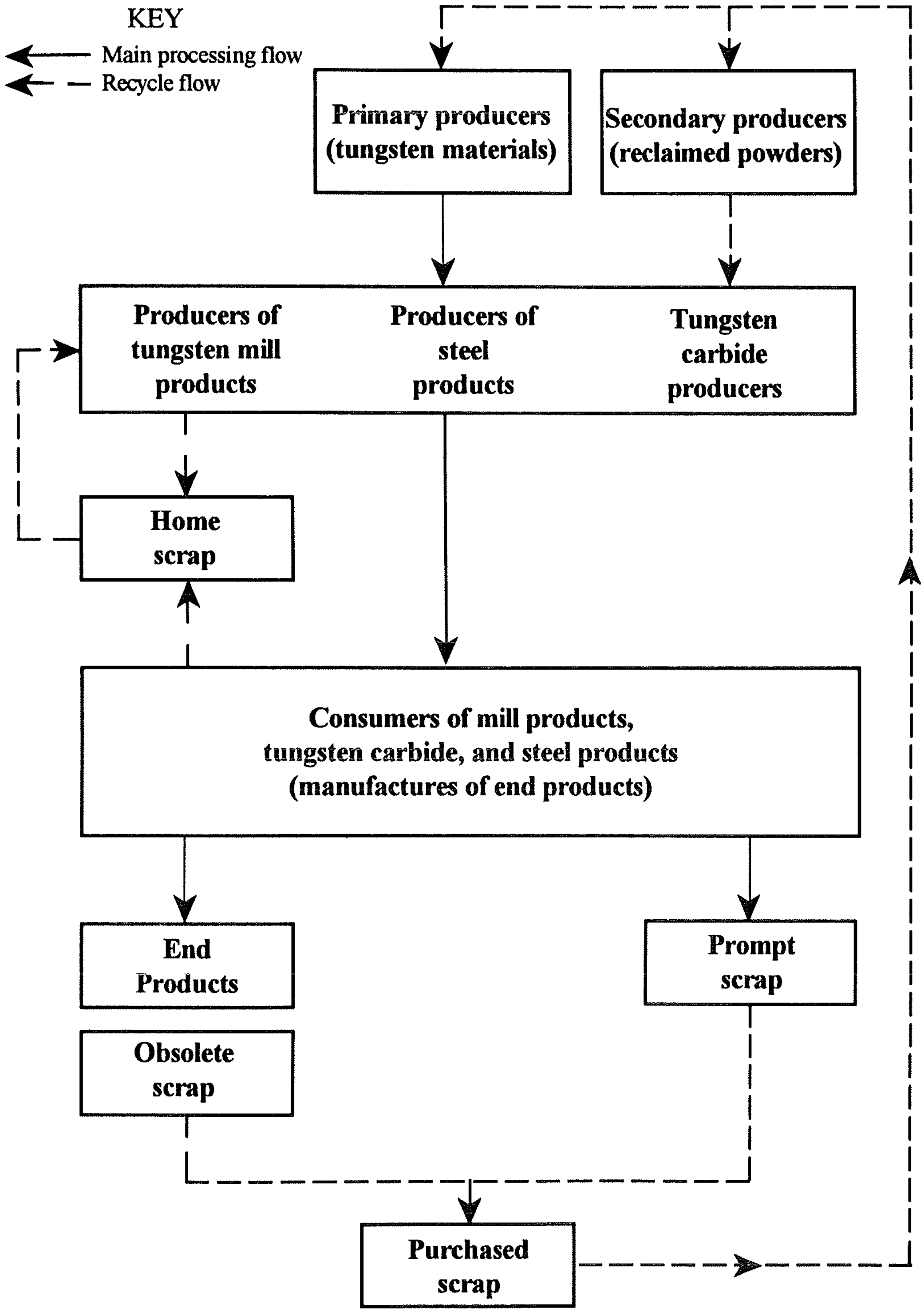

Figure 2.—Tungsten scrap flow diagram.

in the manufacturing of tungsten chemicals, in the producing of certain steels, and in the processing to wear-resistant tungsten materials. Losses incurred in the conversion of APT to tungsten oxides and in the subsequent reduction to tungsten metal powder are less than 1%. Further conversion of metal powder to tungsten carbide (WC) powder may result in a loss of about 1% of the contained tungsten. Metal losses are kept to a minimum during the preceding steps as a result of the efficient reuse of the "home" scrap or "prompt" scrap noted in figure 2. Home scrap, as the name implies, is a runaround scrap that is continuously recovered within an integrated processing and end-product manufacturing facility. Prompt scrap is defined as new scrap that is generated by the tungsten consumers in the production of end-use products.

FABRICATION AND MANUFACTURE

Tungsten losses associated with the manufacture of components for consumer products are considered to be negligible insofar as much of this manufacturing is via well-controlled powder metallurgy processing procedures. The inherent value of the tungsten materials being used essentially requires that the manufacturing procedures be conducted efficiently in order to recover most of the reject parts and scrap. This "prompt" or industrial scrap (fig. 2), generally consists of misruns, wire ends, trimmings, grindings, and sludges that are metal, alloy, or carbide in nature. Although fabrication and manufacture is a highly efficient stage in the tungsten cycle, some instances of low tungsten recovery rates at this stage have been known to exist in the industry (*5*). For example, tungsten losses of up to 15% may occur in the production of tool steels, superalloys, and other steels and nonferrous alloys where the source of tungsten for these alloys is low-grade ferrotungsten (tungsten melting base). The relatively high rate of loss occurs largely because of the impractical and uneconomic segregation of the diverse product mixes used in the preparation of the steels and alloys.

CONSUMER END-PRODUCT USE

Tungsten and tungsten products are consumed by the end-product manufacturing industry in four major sectors. Included are tungsten's use as the cemented carbide for cutting and wear-resistant purposes, as the relatively pure metal powder to produce numerous mill product shapes, as a metallic addition agent in the production of alloys, and as a chemical in the production of reagents for a variety of nonmetallurgical applications.

All industrial and consumer tungsten end products entering the flow each year in the above sectors may, for convenience sake, be considered as entering the "tungsten product reservoir." The tungsten embodied in these products each year is equivalent to the annual apparent consumption of tungsten. Apparent consumption is defined as the total domestic supply of tungsten material plus imports minus exports minus changes in industrially held stocks. The length of time a tungsten-containing product remains in the "reservoir" varies depending upon the product and also may be sensitive to changes in technology or conditions of use. There is assumed to be a net zero change in the quantity of tungsten in the reservoir resulting from imported and exported tungsten products.

Tungsten may be lost from the products in the reservoir in essentially three different ways. These include dissipation, discard, and dilution (downgrading). Dissipation losses, those occurring during use or as a result of use, are best exemplified by the inherent wear loss of carbide tool bit inserts, dies, mining and petroleum drill bits, and hard-facing materials. Other losses broadly covered in this category are wear and arc erosion of electrical contacts, oxidation losses of high-temperature alloys, and chemical dissipation losses. Tungsten losses through discard of used, obsolete tungsten-containing products or the tungsten components thereof may occur with essentially any of the products in the reservoir. Economics of the tungsten recycling processes as well as the practicality of collecting and recovering the tungsten-containing components significantly influence the quantity of tungsten that ultimately is lost through disposal. Examples of such losses may include uncollectible tool bit inserts, burned-out lamp and lighting fixtures, electrical contact stubs, welding rods, and carbide hard-facing materials. Losses in the dilution category occur in numerous products where the amount of tungsten, the degree of its dispersion, or the difficulty in separating it from the product make it impractical to recover the tungsten and return it to the tungsten cycle. Such losses may occur with certain tool steels, carbides, and nonferrous alloys incorporated in industrial and commercial machines and other manufacturing items. Because these items are not recognized for their tungsten value, they are often recycled to the steel industry, where the tungsten is diluted to a trace impurity.

RECYCLE IN THE DOMESTIC TUNGSTEN FLOW

RECYCLE METHODS

In the recovery of tungsten scrap, whether it be home, prompt, or obsolete, the industry employs several recycling methods to return the tungsten to the cemented carbide, mill product, and alloy sectors. Figures 3 through 7 and related discussions, extracted from the paper by Kieffer and Baroch (*7*), provide excellent illustrations of the important features of these recycling methods and descriptions of the sequential steps involved in the two most significant physical methods.

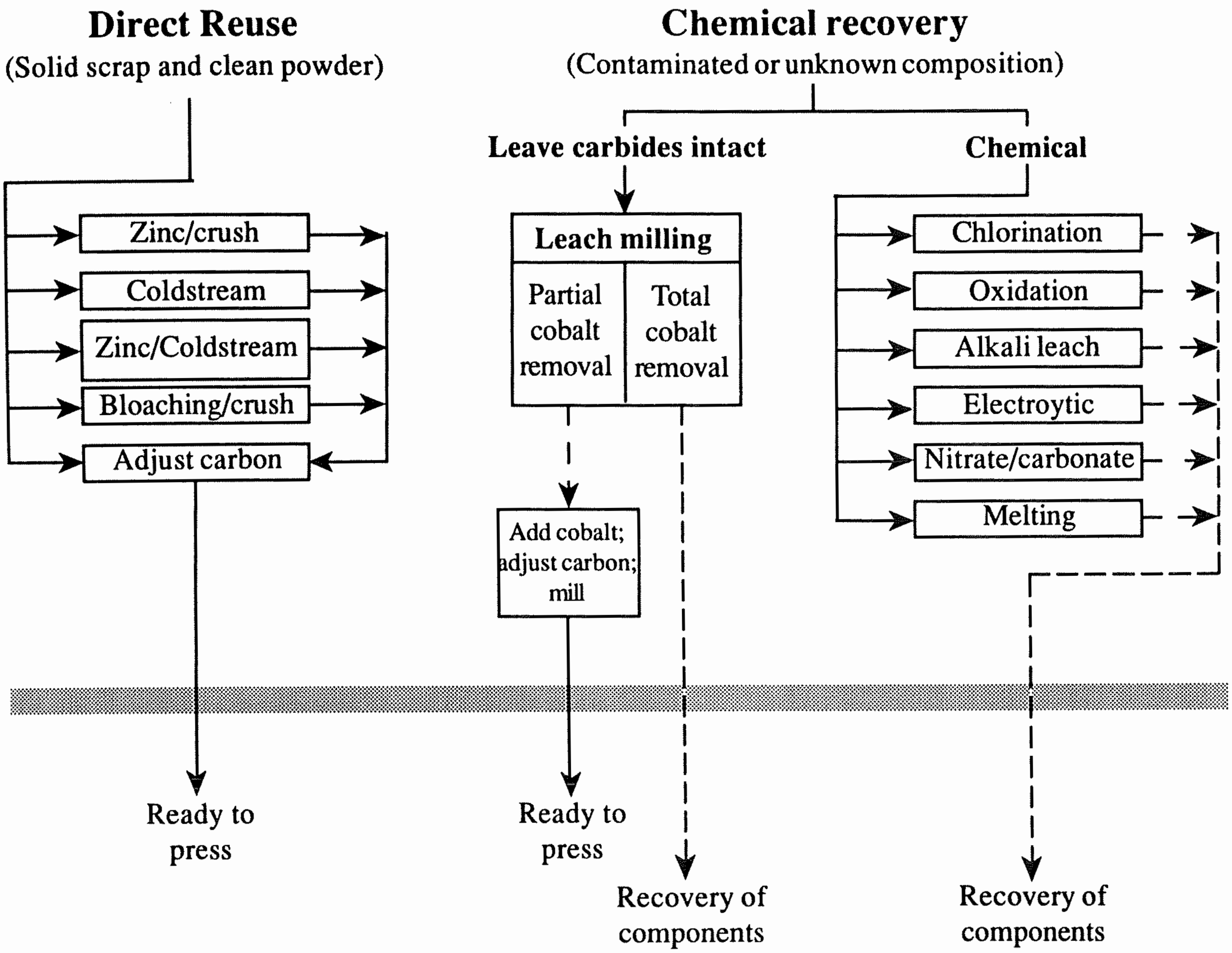

Figure 3.—Recycling cemented carbide scrap.

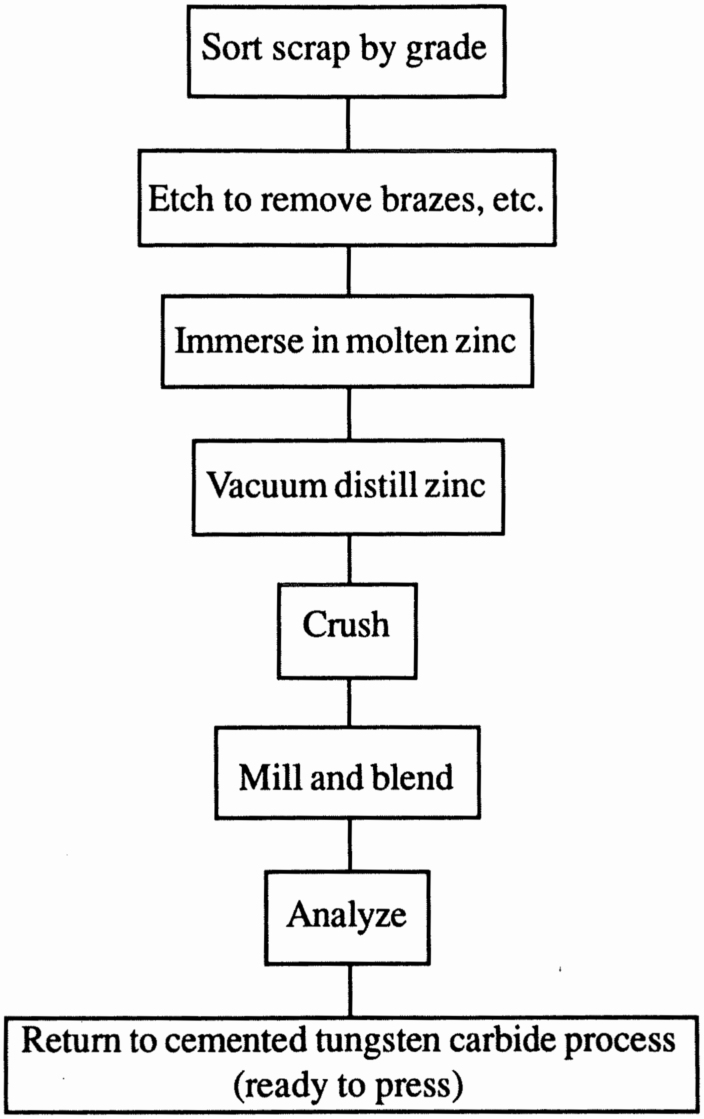

Figure 4.—Recovery of carbides containing cobalt: Zinc Process.

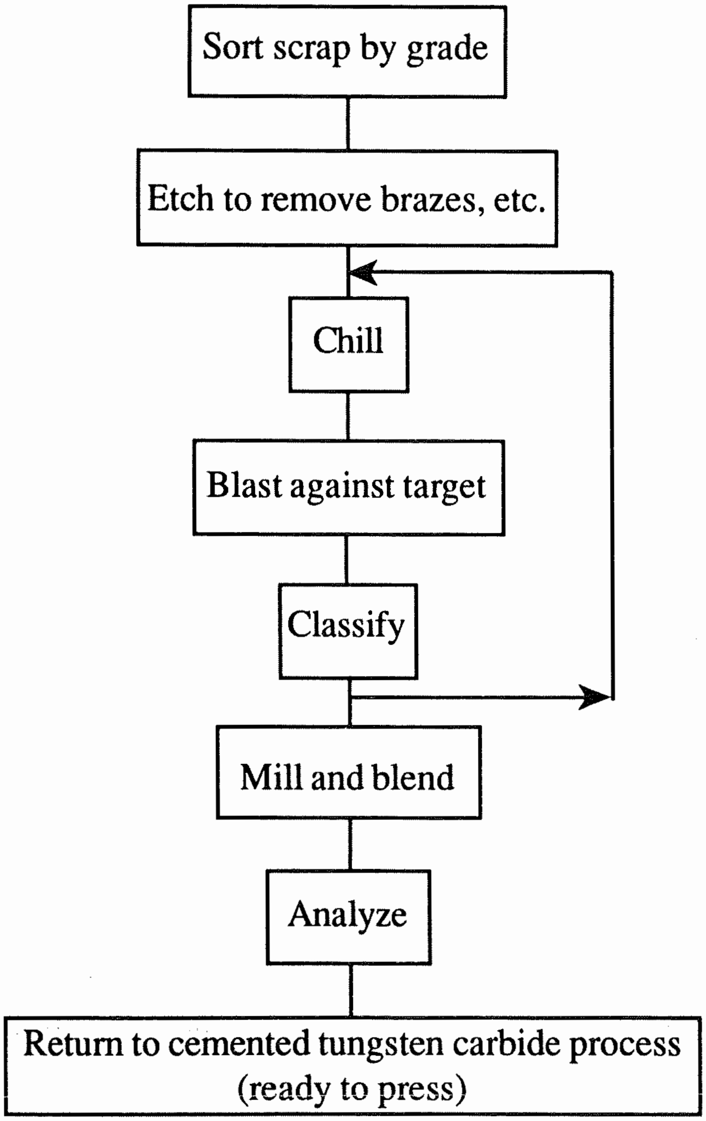

Figure 5.—Recovery of cemented carbides: Coldstream Process.

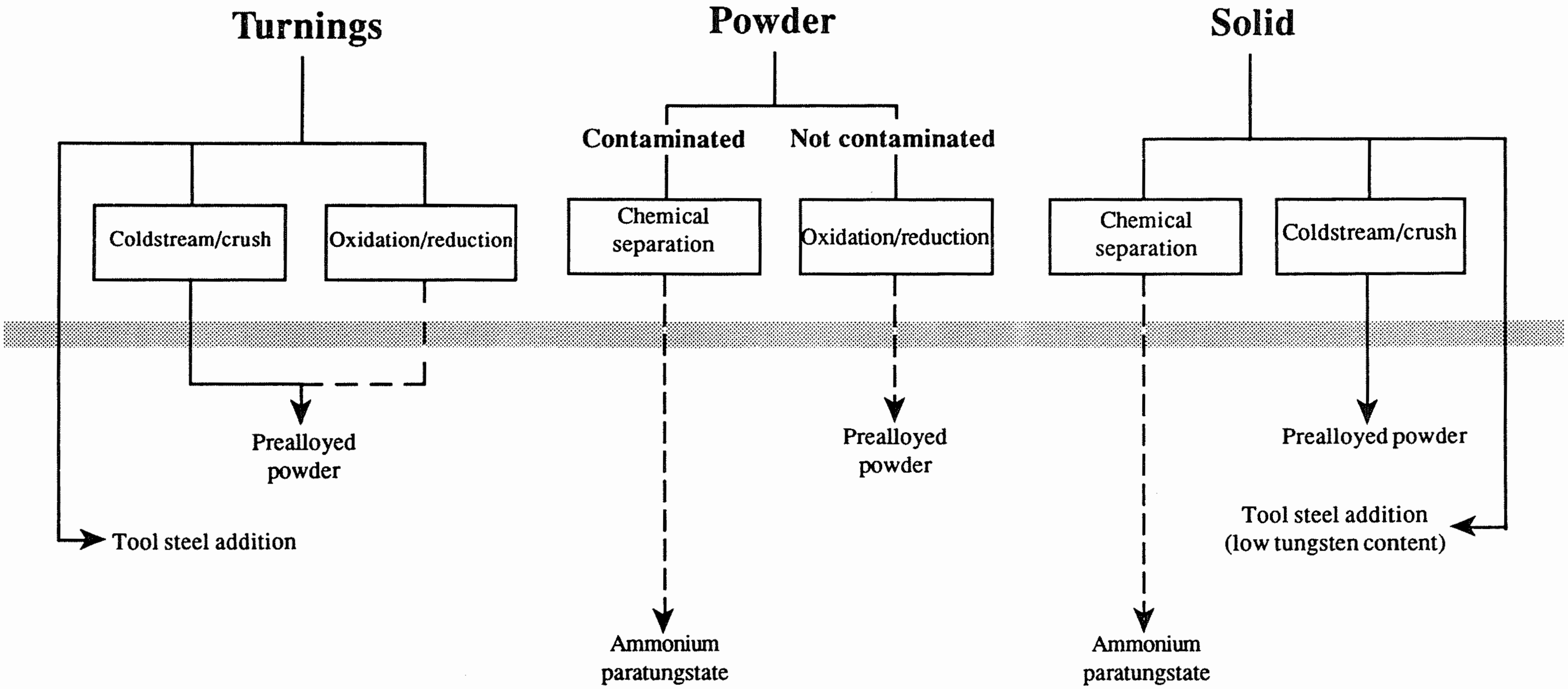

Figure 6.—Recycling heavy-metal scrap.

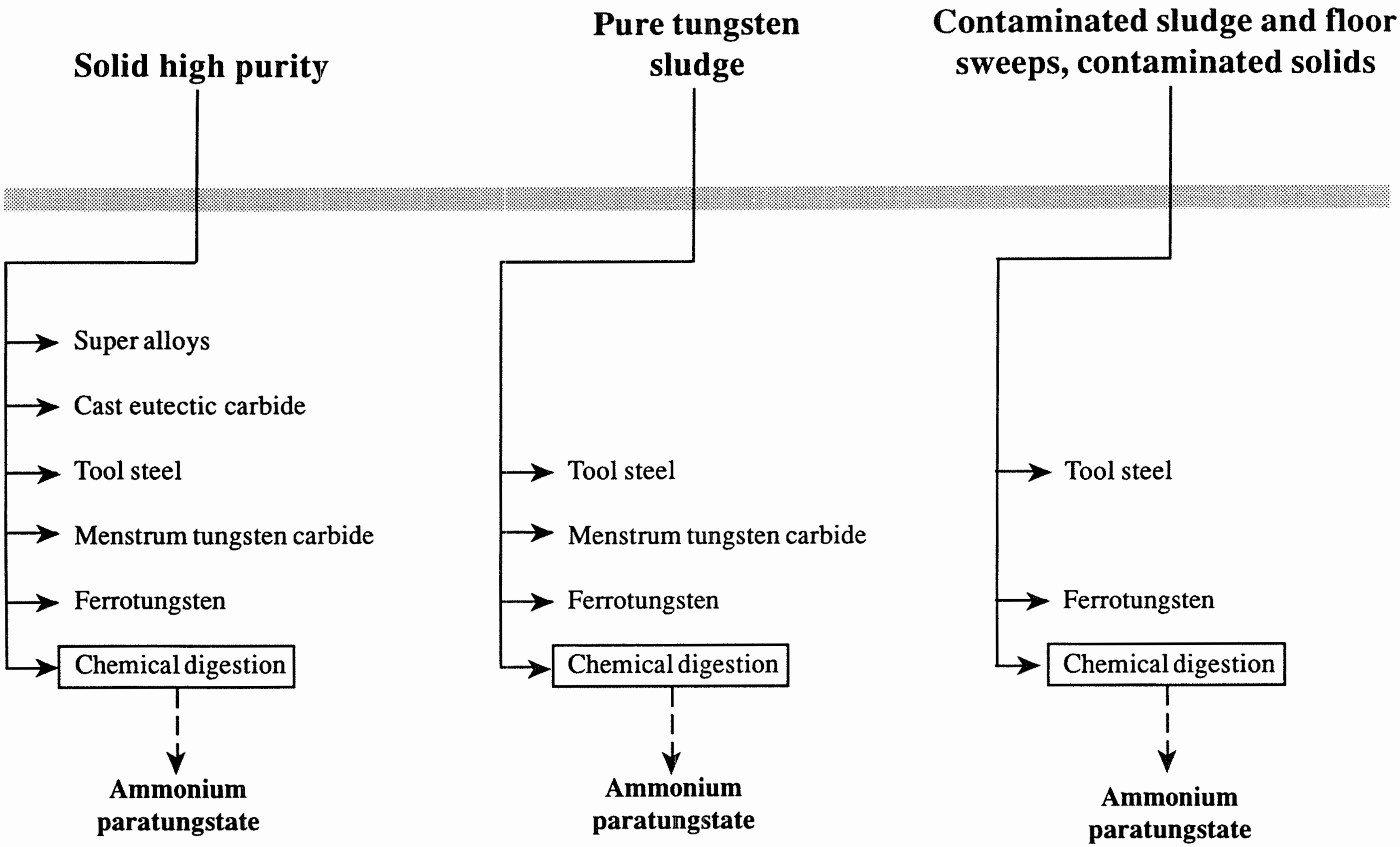

Figure 7.—Recycling pure tungsten metal scrap.

In figures 3, 6, and 7, the lines showing the flow of the various scraps through the recycle systems are depicted as dashed lines to indicate those stages in recycling where the original scrap has been chemically altered. The broad horizontal line in these figures shows where the recycled tungsten reenters the tungsten flow scheme. The closer proximity of the reentry arrows to the broad horizontal line indicates relatively greater contained tungsten in the final recycled product.

Recycle of Cemented Carbides

The extreme hardness of cemented carbides (WC powder compacted and sintered generally with a cobalt powder binder) makes them preferred materials for metalworking and metalforming purposes. The mining and petroleum industries also use significant quantities of cemented carbide in drill bits, in the cutting edges of earth-moving equipment, and in crushing machinery. Carbide surfaces also are used to provide wear resistance to certain engine components, to wear parts such as valves and bearings, and to electrical and electronic contact surfaces. The extensive use of cemented carbides for cutting and wear-resistant applications since the 1950's has generated large amounts of used carbides for potential recycling. Carbides for cutting and wear-resistant purposes presently represent about 64% of U.S. tungsten consumption.

In figure 3 is shown the recycle sequence for the various forms of cemented carbides. Direct and indirect, physical and chemical methods are used to recover tungsten carbide, with or without the removal of the cobalt binder. In addition, chemical methods are used extensively to recover the individual components of the cemented carbide. The chemical methods are best exemplified by an oxidation roasting of the cemented carbide, followed by a chemical digestion that converts the tungsten to a sodium tungstate solution. Once in this form, the sodium tungstate can be treated to produce pure metal powder or tungsten carbide powder using conventional tungsten processing methods. Economic recovery of the byproduct cobalt and, in some instances, tantalum in the cemented carbides is essential to the chemical processes. The two most frequently used physical methods for recycling cemented carbides are the Zinc Process and the Coldstream Process, both of which provide for direct reuse of the cemented carbide. In the Zinc Process (*18*), illustrated in figure 4, molten zinc is initially alloyed with the cobalt-rich phase of the cemented carbide. Upon subsequent removal and recovery of the zinc by distillation, a porous tungsten carbide-cobalt cake remains. The cake is then broken apart, reground, and blended for pressing and sintering into new cemented carbide parts. In the Coldstream Process (*7, 8*), shown in figure 5, the carbide scrap is entrained in a high-speed flow of air, accelerating the scrap against a carbide target with sufficient energy to cause fracture of the scrap material. The resulting shattered material is air classified to recover the finer particles, and the process is repeated as necessary to shatter the remaining larger particles to the desired size. As in the Zinc Process, the final material is reprocessed into new cemented carbide parts. A third recycling procedure uses a combination of the Zinc and Coldstream Processes to produce the recyclable tungsten carbide-cobalt powder. In this combined method, the porous cake produced by the Zinc Process is shattered using the Coldstream Process, thereby decreasing the energy expenditure required to produce the desired particle size compared with the individual processes.

Recycle of Mill Products

Mill products fabricated from relatively pure tungsten are employed in a number of products wherein the tungsten used represents approximately 24% of present U.S. consumption of tungsten. Its unique properties of high melting point, high density, good corrosion resistance, good thermal and electrical conductivity, low coefficient of expansion, and high tensile strength at elevated temperatures make tungsten and its alloys materials of choice in many end-use applications. Tungsten mill products may be used as filaments and electrodes in lamp and lighting products; as contact surfaces in electrical and electronic equipment; as heavy-metal alloys for kinetic energy penetrators, radiation shielding, aircraft counterweights, and competition darts; as sheet material for heat-shielding applications; as electrodes for inert gas welding; as electrodes in X-ray and cathode ray tubes; as target material in X-ray equipment; and as resistance coils for high-temperature furnace heating elements.

In figures 6 and 7 are shown the recycle sequences for the various forms of tungsten mill product scrap recovered from heavy-metal alloy and relatively pure tungsten metal sources. Heavy-metal alloys constitute a group of alloys containing 90% or more tungsten and varying quantities of iron, nickel, and copper. Typically, most of the heavy-metal scrap is internally generated (home scrap) and is recycled within its particular product sector as prealloyed powder through use of the Coldstream Process or an oxidation and reduction procedure. That which is not recycled in this manner is either added directly in tool steel production or chemically converted to the APT intermediate for further processing. Subsequently, this tungsten is fabricated (manufactured) into parts for use in most other end-product sectors.

As with heavy-metal scrap, the source of the relatively pure tungsten metal scrap is generally not that of used, obsolete items, but rather that of material generated in the course of fabricating tungsten parts. This material includes sinter-bar ends, rod and wire trim, sludge from cutoff wheels, floor sweeps, and rejected parts. In general, there are no simple methods for directly using this scrap material to manufacture pure tungsten metal products. Instead, the material is used to manufacture alloys, such as superalloys and tool steels in which tungsten represents a relatively minor constituent. It may also be used quite effectively as a starting material in the production of coarse carbides for hard facing, including the cast eutectic carbides as well as those made by the Menstrum Process. The coarse carbide product made by the latter method, a melting process, is recovered in, and then chemically separated from, an iron matrix (menstrum) prior to its use. The lower purity tungsten metal scrap is used to produce ferrotungsten. Metal scrap that cannot be used effectively in any of the preceding ways is reprocessed chemically to produce APT.

Recycle of Ferrous and Nonferrous Alloys

As an alloy constituent, tungsten is used primarily in the production of high-speed steels and tool and die steels. Hardness and oxidation resistance at elevated temperature are the most important properties of these steels that find use in machinery and equipment for the metalworking, construction, and mining industries. Tungsten is also a constituent of certain stainless and other alloy steels for the purpose of improving wear and abrasion resistance, shock resistance, corrosion resistance, and/or strength at high temperatures. Tungsten is an important constituent in certain superalloys where these alloys are used for their strength and oxidation resistance at high temperatures. Tungsten-copper and tungsten-silver products manufactured by powder metallurgy techniques are employed as electrical contacts, welding electrodes, and components in electrical machining procedures. Nonferrous alloys of tungsten with thoria, molybdenum, rhenium, platinum, or iridium are used in a variety of ways that include electrical contacts in discharge lamps, rods for inert-gas welding, thermocouples for high-temperature furnaces, heaters for electronic tubes, electrodes for spark plugs in aerospace engines, and hard tips for ballpoint pens.

Prior to the 1940-50 period when the significant shift from steels to cemented carbides for cutting and wear-resistant applications occurred, the tungsten alloy steels were the major tungsten consumption sector. Presently, about 9% of the U.S. annual consumption of tungsten can be attributed to its use in the aforementioned various alloy forms. Of the tungsten recycled from this end-product sector, it is likely that the greatest portion falls into the dilution category, that is, ferrous alloys returned to the steel industry with consequent dilution of the contained tungsten. Nonferrous tungsten alloys represent a relatively small fraction of tungsten consumption in this sector and correspondingly generate proportionately less scrap. The quantity of tungsten that is recovered from this scrap is uncertain. However, the types containing thoria cannot presently be recycled economically because of the additional costs associated with the generation of radioactive byproduct.

Recycle of Nonmetallurgical End-Use Forms

Nonmetallurgical applications of tungsten include chemicals used in textile dyes, paints, enamels, toners, and coloring glass. Certain tungsten compounds are luminescent and are thus used as phosphors in pigments, X-ray screens, television picture tubes, and fluorescent lighting. Sodium tungstate is employed as a corrosion inhibitor and a fireproofing agent in textiles. APT is used directly in the manufacture of catalysts for the refining of petroleum. Among other chemical applications, tungsten compounds are used to chemically vapor-deposit thin films of tungsten.

Nonmetallurgical end uses, historically, have accounted for only a small portion of U.S. consumption of tungsten. Presently, these chemical uses constitute about 3% of annual consumption. Little, if any, of this tungsten is recycled owing mainly to the significant dispersion of the tungsten in the end product.

RECYCLE STATISTICS (1974-91)

U.S. industry statistics and estimates of tungsten-containing material lost and recycled in the tungsten flow are shown in figures 8 through 11. The flow cycle information contained in these figures is intended to illustrate certain trends in the recycling of tungsten-containing products, using the years 1974, 1978, 1984, and 1991 as examples.

The individual tungsten flow schemes were developed from data published in several Government and industry reports (*1-10*). Collectively, these reports provided significant details on the tungsten cycle for estimating the total quantities of obsolete tungsten material available in a particular year and the various quantities lost, discarded, recycled, or diluted in that year. A summary of relevant information descriptive of the methods used to arrive at such quantities (materials flow components A through Q in figures 8 through 11) is presented in table 1.

On the basis of the data shown in figures 8 through 11, the estimated recycling of tungsten, contained in obsolete cemented tungsten carbide, as a percentage of apparent consumption of tungsten (Q/C), increased from 10% in 1974 to 34% in 1991 (fig. 12). If diluted tungsten, contained in steels and other alloys (M_1), also is included in the amount of tungsten recycled, the total quantity recycled as a percentage of apparent consumption ($Q+M_1/C$) is estimated to have increased from 22% in 1974 to 39% in 1991.

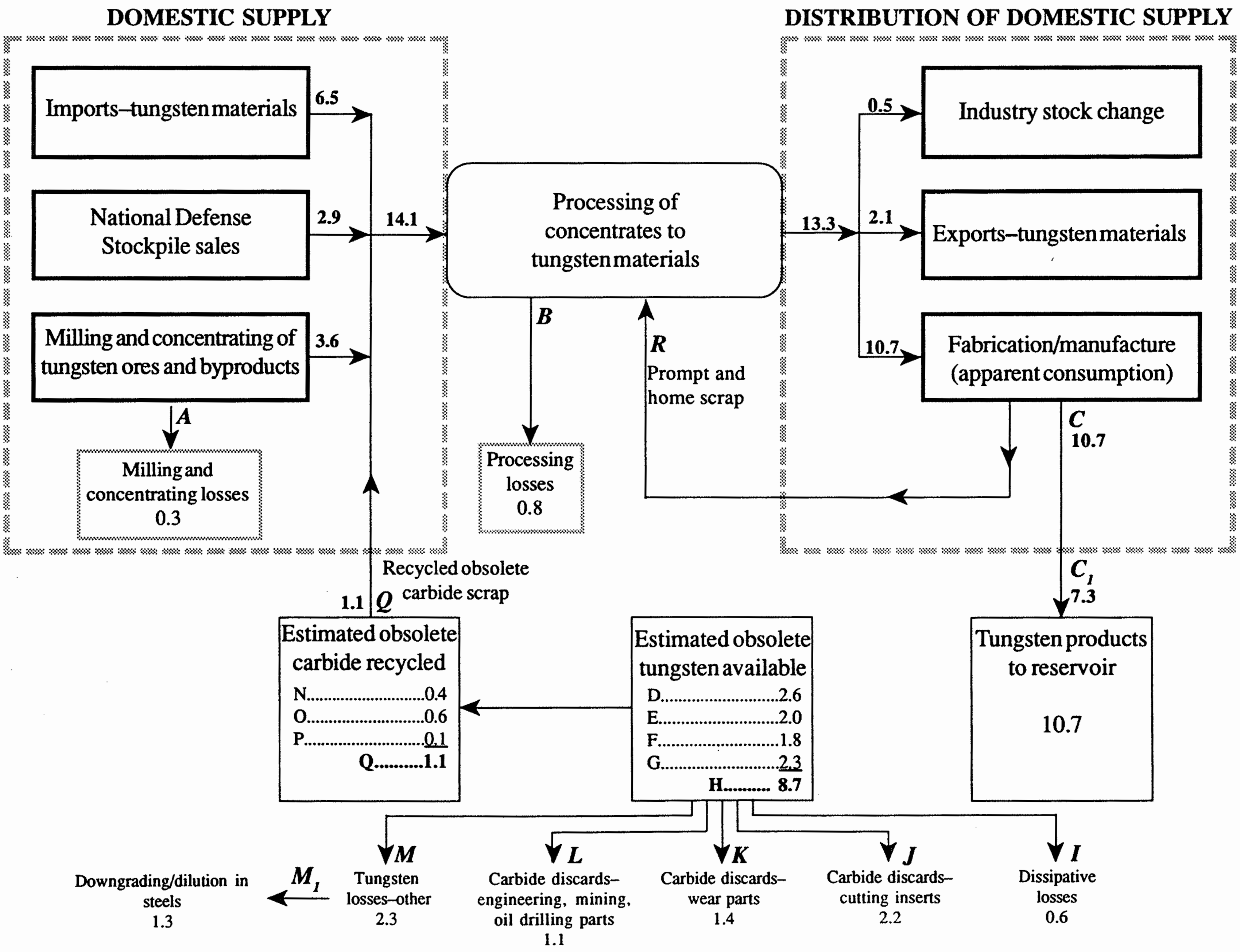

Figure 8.–Tungsten materials flow, 1974; data in thousand metric tons of contained tungsten. See table 1 for key.

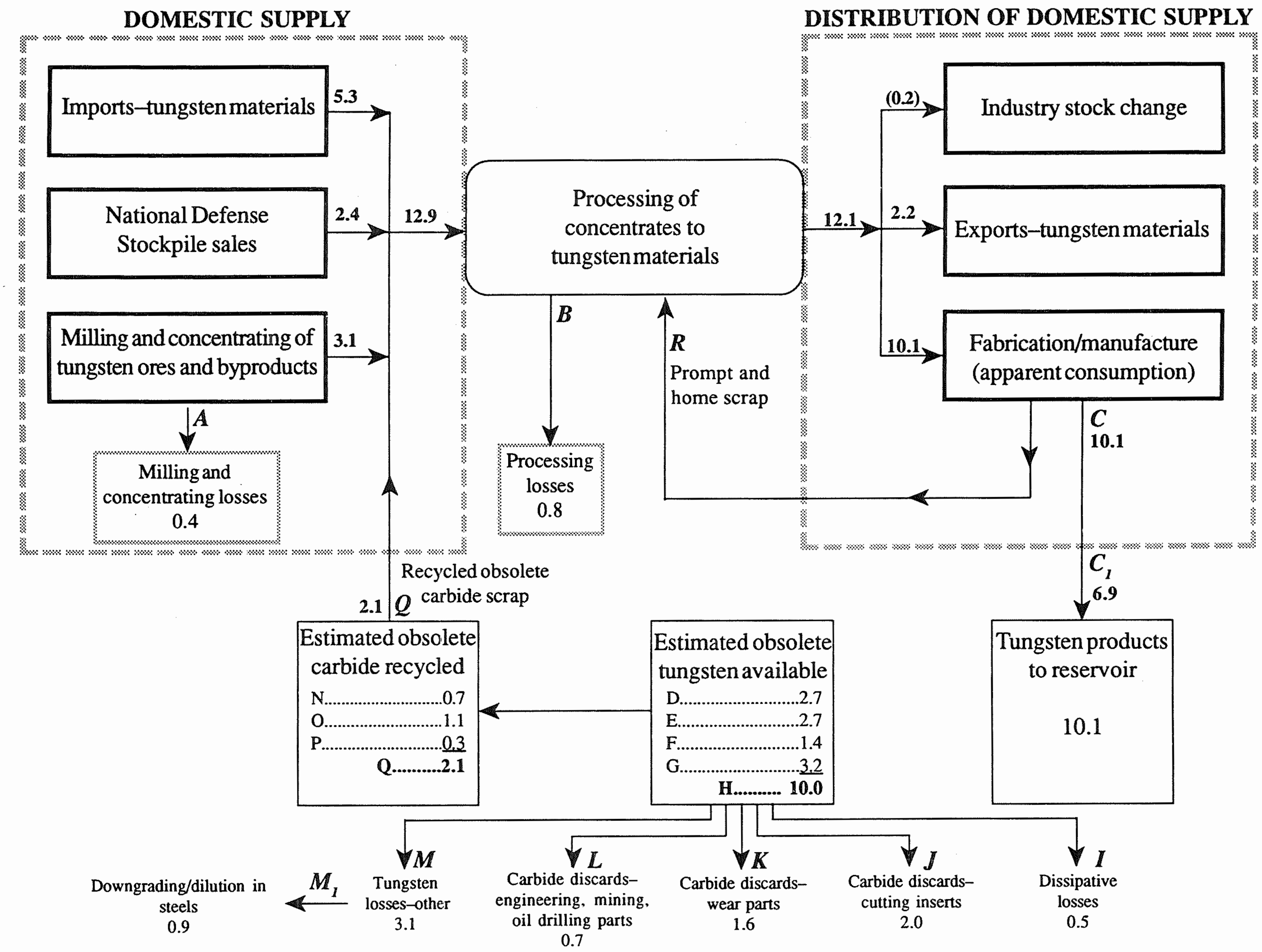

Figure 9.—Tungsten materials flow, 1978; data in thousand metric tons of contained tungsten. See table 1 for key.

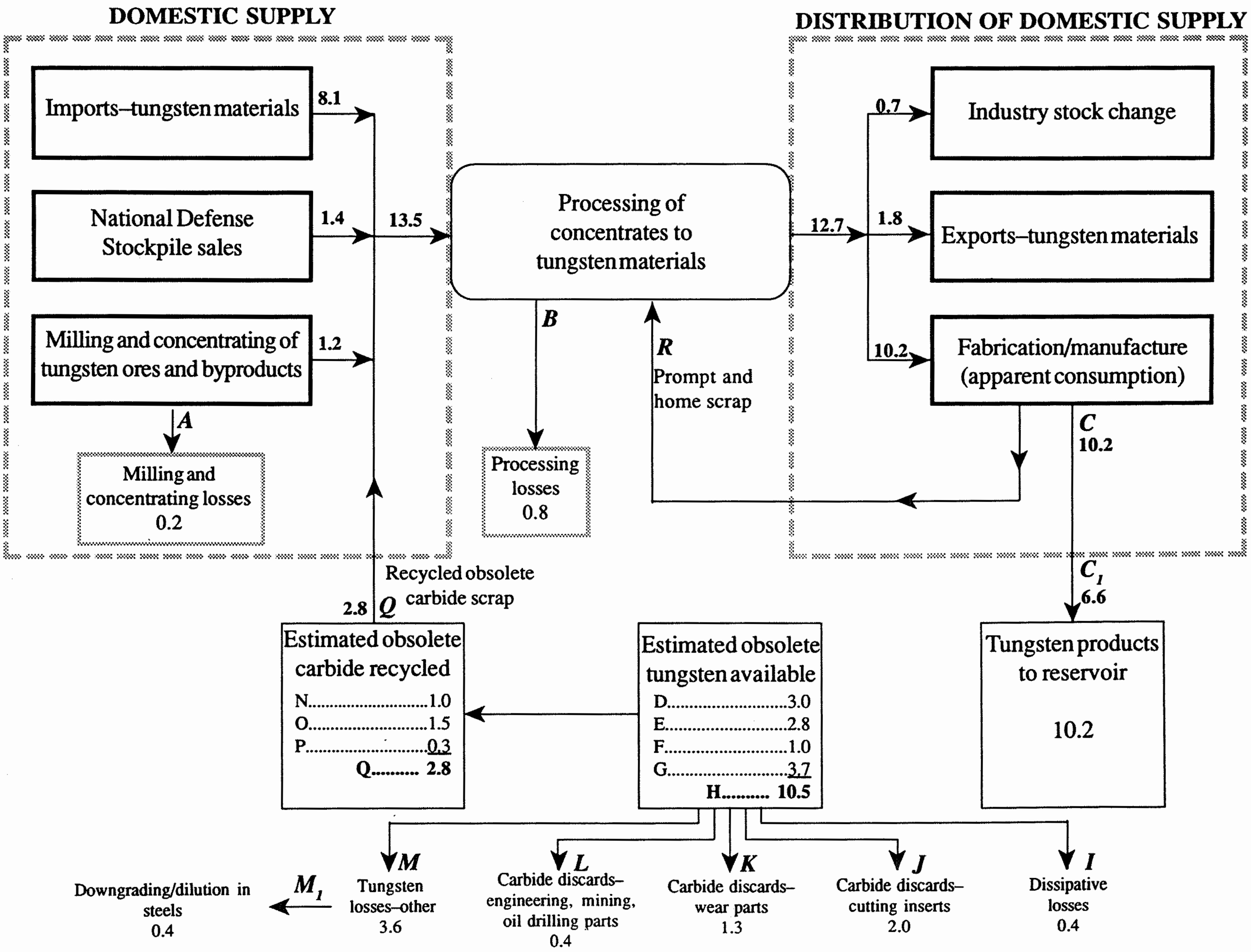

Figure 10.—Tungsten materials flow, 1984; data in thousand metric tons of contained tungsten. See table 1 for key.

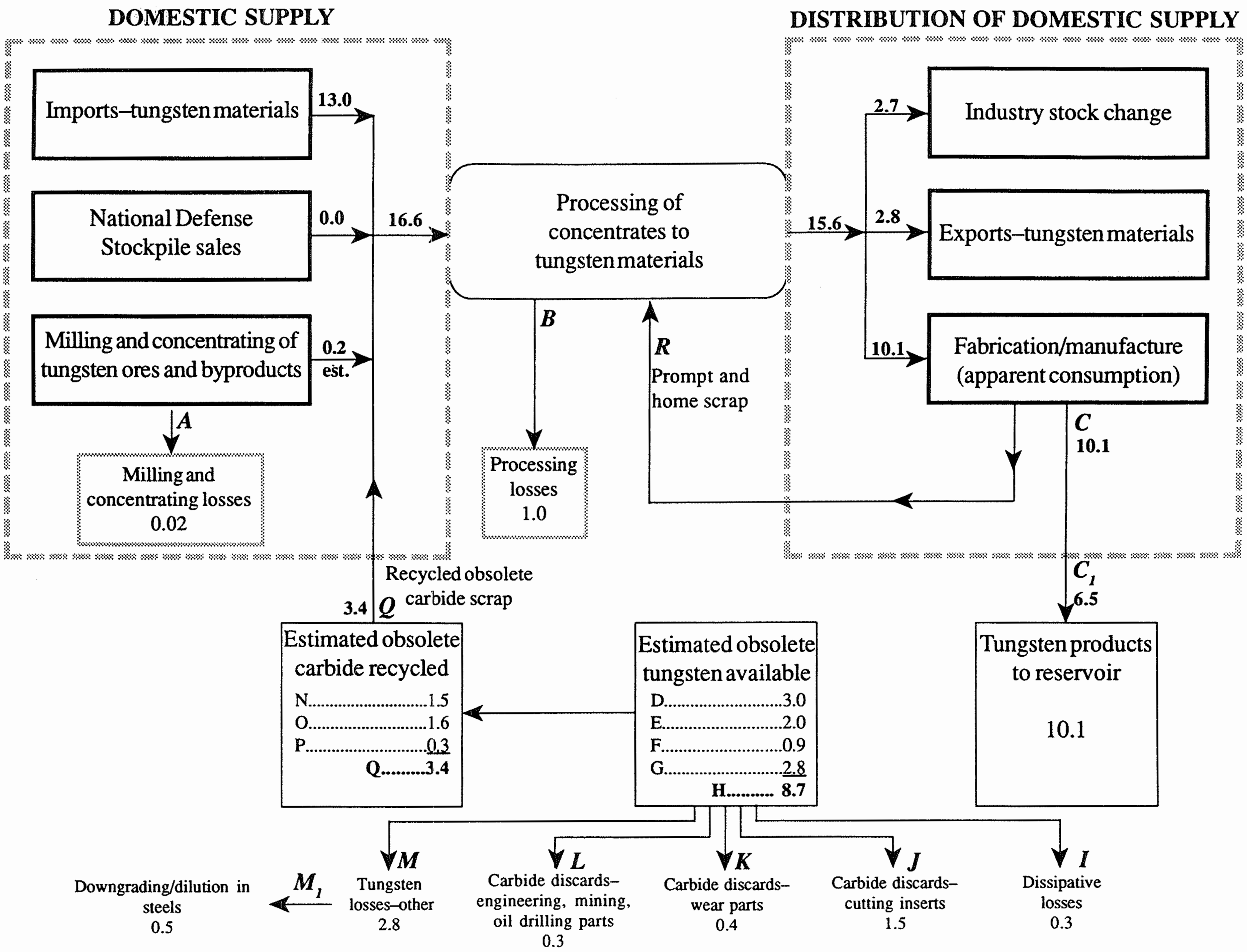

Figure 11.—Tungsten materials flow, 1991; data in thousand metric tons of contained tungsten. See table 1 for key.

Table 1.—Tungsten materials flow—consumption, loss, discard, and recycle factors

Flow component[1]	Description	Year			
		1974	1978	1984	1991
A	Milling, concentrating ores	10% Loss	10% Loss	10% Loss	10% Loss.
B	Processing total tungsten supply.	6% Loss	6% Loss	6% Loss	6% Loss.
C	U.S. apparent consumption of tungsten.	Post processing supply less exports less industry stock changes			
C_1	U.S. apparent consumption of cemented carbides.	68% C	68% C	65% C	64% C.
D	Cutting tools obsolete in 1 year	36% C_1	40% C_1	45% C_1	47% C_1.
E	Wear parts obsolete in 5 years	40% C_1	40% C_1	40% C_1	40% C_1.
F	Mining, engineering, oil drilling tools obsolete in 1 year.	24% C_1	20% C_1	15% C_1	13% C_1.
G	Other tungsten obsolete in 5 years.	32% C	32% C	35% C	36% C.
H	Total obsolete tungsten	Sum of D through G.	Sum of D through G.	Sum of D through G.	Sum of D through G.
I	Dissipative losses	Sum of 1% D, 1% E, & 30% F.	Sum of 1% D, 1% E, & 30% F.	Sum of 1% D, 1% E, & 30% F.	Sum of 1% D, 1% E, & 30% F.
J	Cutting tool discards	85% × net undissipated (99% D).	75% × net undissipated (99% D).	65% × net undissipated (99% D).	50% × net undissipated (99% D).
K	Wear parts discards	70% × net undissipated (99% E).	60% × net undissipated (99% E).	45% × net undissipated (99% E).	20% × net undissipated (99% E).
L	Mining, engineering, oil drilling tool discards.	90% × net undissipated (70% F).	70% × net undissipated (70% F).	60% × net undissipated (70% F).	50% × net undissipated (70% F).
M	Other tungsten losses	100% G	100% G	100% G	100% G.
M_1	Dilution in steels	17% C × 70%	13% C × 70%	6% C × 70%	7% C × 70%.
N	Recycled obsolete cutting tools	15% × net undissipated (99% D).	25% × net undissipated (99% D).	35% × net undissipated (99% D).	50% × net undissipated (99% D).
O	Recycled obsolete wear parts	30% × net undissipated (99% E).	40% × net undissipated (99% E).	55% × net undissipated (99% E).	80% × net undissipated (99% E).
P	Recycled obsolete mining, engineering, oil drilling tools.	10% × net undissipated (70% F).	30% × net undissipated (70% F).	40% × net undissipated (70% F).	50% × net undissipated (70% F).
Q	Total recycled obsolete carbides	Sum of N through P	Sum of N through P.	Sum of N through P	Sum of N through P.
R	Recycled home and prompt scrap.	5% C	5% C	5% C	5% C.

[1] Statistical significance of each flow component is illustrated in figures 8 through 11.

An additional estimate of the percentage (Q/C) recycled during this period was derived for the year 1980 based upon cobalt recycling data (*19*). The quantity of cobalt recycled directly from obsolete cemented carbide in 1980 was reported to be about 230 metric tons. Assuming that this recycled cobalt represented an average 10% of the total recycled cemented carbides, the corresponding Q/C for tungsten in 1980 was calculated to be 19%.

The data presented in figures 8 through 11 further showed that the estimated quantity of obsolete tungsten carbide recycled, as a percent of total obsolete tungsten available (Q/H) and as a percent of obsolete tungsten carbide available (Q/D+E+F), increased from 13% to 39% and from 17% to 58%, respectively, from 1974 to 1991.

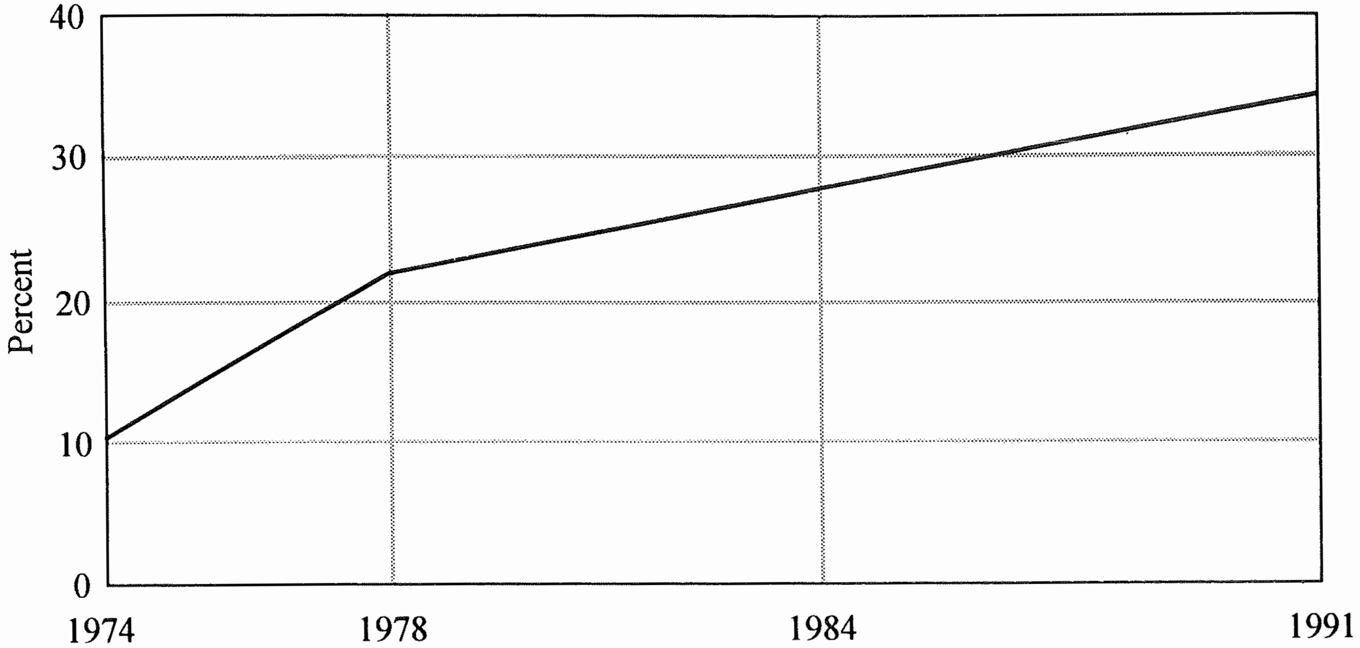

Figure 12.—Recycle of tungsten in carbides, percent of total U.S. consumption of tungsten, 1974-91.

CUMULATIVE CONSUMPTION, RECYCLING, LOSSES IN THE TUNGSTEN FLOW (1910-91)

Historical information on the U.S. pattern of tungsten recycled and the associated losses of tungsten to the environment prior to 1974 is very limited. However, a relatively complete series for U.S. consumption of tungsten could be derived from information in Bureau of Mines reports dating back to 1910 (*1*). Accordingly, this consumption data served as a basis for estimating the total amount recycled and, indirectly, the cumulative loss of tungsten to the environment for the entire period 1910 to 1991. Tungsten lost to the environment was considered to be that quantity that was not in use, in process, or recycled. Figure 13 illustrates the total consumption and the corresponding estimates of obsolete tungsten scrap recycled during several periods of time between 1910 and 1991. In the individual periods shown between 1910 and 1955, total consumption comprised the tungsten reported to be processed from primary sources plus that estimated to be recycled from obsolete high-speed and other tool steels and alloy steels. In order to estimate the quantities of scrap recycled in the various time periods, certain assumptions necessarily were applied. During the war years 1914-18 and 1940-45, all the tungsten from primary sources that was used to make the tungsten-containing steels, 90% and 78% of reported consumption, respectively, was considered to have been recycled for repeat use in steels. In the remaining three time periods through 1955, that is, 1910-13, 1919-39, and 1946-55, an estimated 90%, 80%, and 45%, respectively, of reported consumption from primary sources went into steels, but only a portion of this was considered to have been recycled during these periods. Available industry data suggests that an average of about 30% of the U.S. total annual consumption of tungsten during these periods was from steel scrap (*20, 21*). In the period 1956-73, following the major transition from high-speed steels to cemented tungsten carbide cutting tools, as well as the appearance of disposable carbide inserts on the cutting-tool market, the recycling pattern for tungsten accordingly began to shift. An estimated 16% of total consumption was derived from obsolete steels and an additional 10% from obsolete cemented carbide parts during this period. As the shift to use of cemented carbides continued from 1974 to 1991, the percentage of total consumption derived from cemented carbides increased from 15% to 24% to 30% in the periods 1974-77, 1978-83, and 1984-91, respectively. Conversely, the percentage of total consumption derived from tungsten in steels decreased from 10% to 7% to 5% in the same time periods. Figure 14 illustrates graphically the percentage of total obsolete tungsten scrap recycled as a function of the total U.S. consumption of tungsten for the nine periods described through 1991.

Estimation of the cumulative loss of tungsten to the environment from 1910 to 1991 was made by considering separately those losses occurring from 1910 to 1955 and

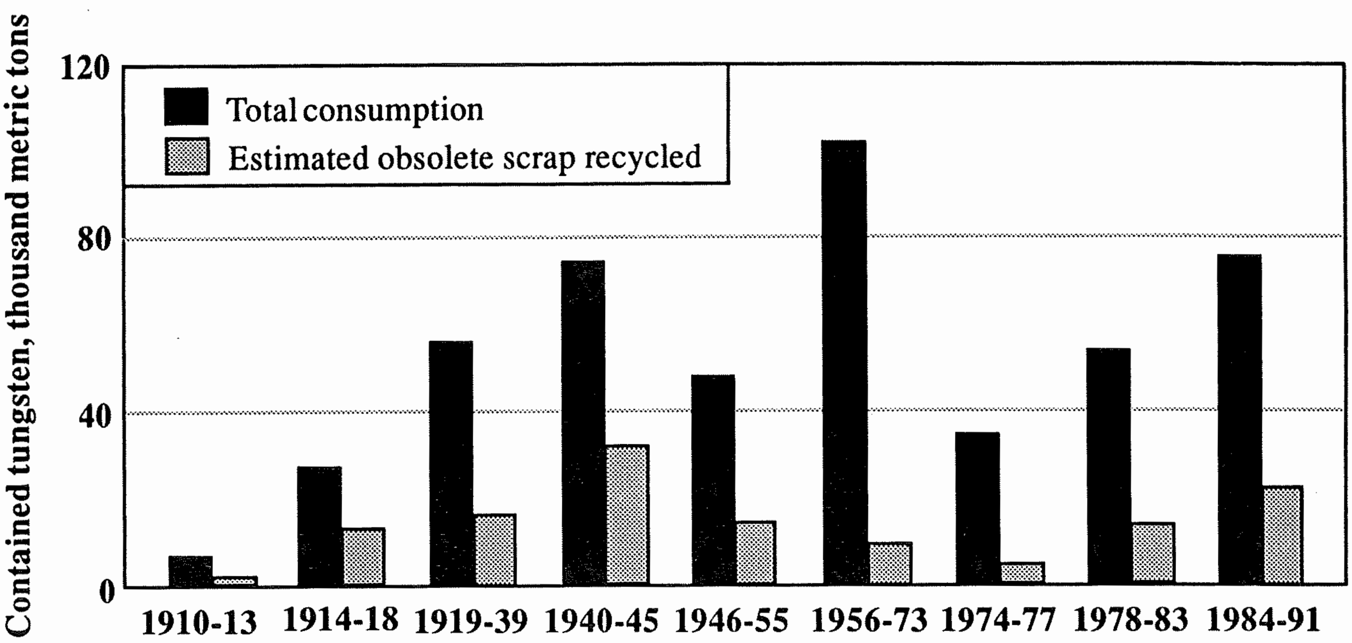

Figure 13.—U.S. scrap recycled and total consumption of tungsten, 1910-91.

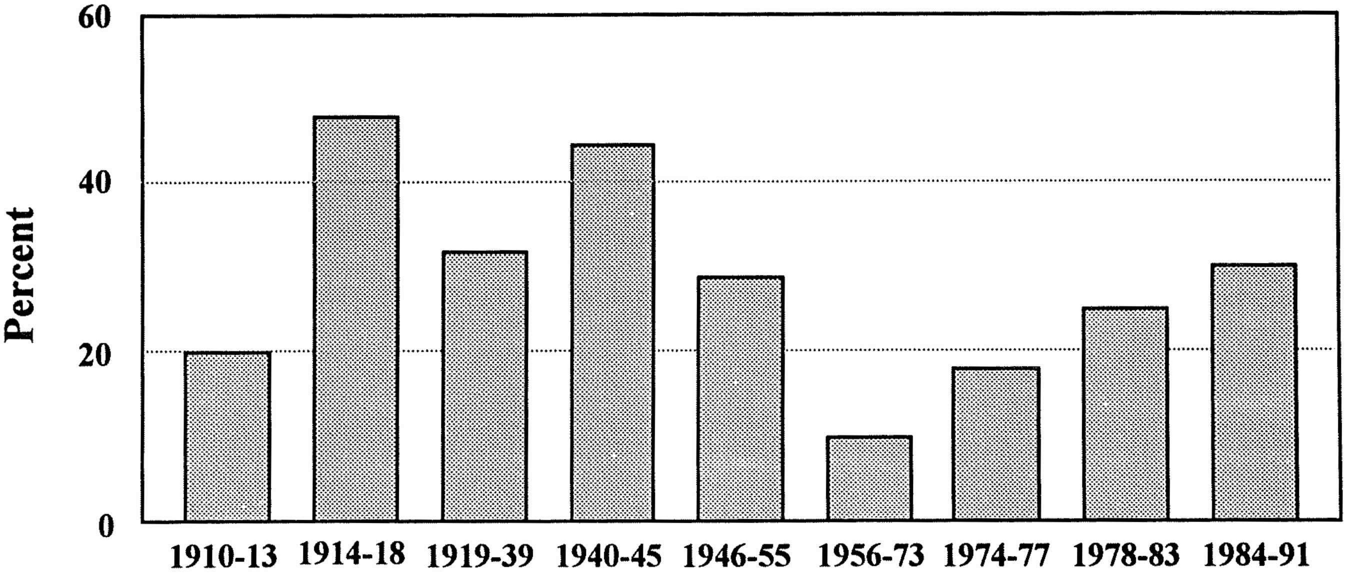

Figure 14.—Tungsten scrap recycled, percent of total U.S. consumption of tungsten, 1910-91.

those occurring from 1956 to 1991. According to the data shown in figure 13, the total U.S. consumption of tungsten, including obsolete scrap, from 1910 to 1955 was approximately 214,000 metric tons. Of this quantity consumed, an estimated 78,000 metric tons was from tungsten-containing steel scrap; that is, about 135,000 metric tons of tungsten in products was derived from primary tungsten material during this period. In evaluating the cumulative loss of tungsten from 1910 to 1955, it was assumed that an average 70% of the tungsten end-use items produced from the primary material were as tungsten-containing steels and that 70% of the tungsten in these items was ultimately diluted in steels and other alloys. On this basis, the cumulative loss of tungsten to the environment in the United States for the period 1910 to 1955 was determined to be about 66,000 metric tons. In the four, post-1955 periods shown in figure 13, total consumption of tungsten, including that recycled from obsolete cemented carbides, was about 264,000 metric tons. Of this quantity consumed, an estimated 51,000 metric tons was sourced from the obsolete carbide scrap, assuming recycling of the scrap at an average of 10%, 15%, 24%, and 30% of total consumption during the periods 1956-73, 1974-77, 1978-83, and 1984-91, respectively. The remaining 213,000 metric tons was sourced from primary and intermediate tungsten materials. On the basis of these recycling percentages, about 162,000 metric tons of tungsten, consumed in products derived from new primary and intermediate tungsten materials during these periods, was lost to the environment either through dissipation, discard, or dilution. In that portion potentially lost through dilution in steels from 1956 to 1991, it is estimated that 70% of the approximately 34,000 metric tons of tungsten consumed in this manner continues to be used in a variety of construction and manufacturing equipment and other items. As such, this tungsten has not been lost to the environment. According to the preceding statistics and assumptions, the maximum, total cumulative loss of tungsten to the environment from 1910 to 1991 was estimated to be about 204,000 metric tons. This corresponds to about 58% of the total 348,000 metric tons of tungsten from primary and intermediate tungsten materials consumed in end products during this time period.

Cumulative loss of tungsten to the environment is likely to be somewhat less than the maximum aforementioned figure because no consideration is given to that consumed in and recycled from heavy-metal alloys. Since most of this tungsten is used for defense-related purposes in kinetic energy penetrators, there are insufficient data available to evaluate the overall materials flow of tungsten in this sector.

SUMMARY

Most of the obsolete tungsten that is recycled in the United States is in the form of cemented carbide parts or related carbide materials. Recycling estimates presented in this report have shown the progressive increase in the quantity of carbides recycled since 1974. Since 1910, an estimated 42% of the cumulative U.S. consumption of tungsten from primary and intermediate sources was recycled, leaving the remainder as losses to the environment, either by discard, dissipation, or dilution.

Some anthropogenic disturbances to the tungsten geochemical cycle are evident as a result of the cumulative losses to the tungsten materials flow. This is particularly true on a local scale where tungsten enrichment relative to its abundance on the Earth's crust has been observed. This enrichment occurs through processes that solubilize a portion of the cumulative losses of tungsten to the environment. Studies indicate that, for animal and plantlife in general, the ecotoxicity of tungsten is minimal.

No tungsten compounds have been included in the TRI list since it was first published in 1987. The TRI list was mandated in 1986 as part of the Superfund Amendments and Reauthorization Act. The TRI list covers a very broad spectrum of toxicity concerns, from acutely lethal to mildly toxic. Considerations are based upon the amount produced or used in the United States, present regulatory status, known levels in the environment, and professional judgment as to potential hazards.

Because the concept of sustainable development is gaining ever-increasing importance in its implications to the world's future, it necessarily implies continued efforts toward more efficient and economical recovery and reuse of the world's finite tungsten resources. The quantity of obsolete tungsten scrap potentially available for recycling is certain to increase in the next 40 to 50 years. If a minimization of tungsten waste is to be achieved, it will require cooperative efforts among Government, industry, and the general public. Inherent in this effort should be a continuing education of the consumer to be aware of the tungsten values in their products and to avoid unnecessary waste of these values. There is, however, the realization that tungsten recycling may be faced with frequent economic challenges caused by competition from low-priced primary and intermediate tungsten materials on the world market.

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