



MINERAL COMMODITY PROFILES

Silver

By W.C. Buttermann and H.E. Hilliard

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Silver—Mineral Commodity Profiles

By W.C. Butterman¹ and H.E. Hilliard

Overview

Silver is one of the eight precious, or noble, metals; the others are gold and the six platinum-group metals (PGM). World mine production in 2001 was 18,700 metric tons (t) and came from mines in 60 countries; the 10 leading producing countries accounted for 86 percent of the total. The largest producer was Mexico, followed by Peru, Australia, and the United States. About 25 percent of the silver mined in the world in 2001 came from silver ores; 15 percent, from gold ores and the remaining 60 percent, from copper, lead, and zinc ores.

In the United States, 14 percent of the silver mined in 2001 came from silver ores; 39 percent, from gold ores; 10 percent, from copper and copper-molybdenum ores; and 37 percent, from lead, zinc, and lead-zinc ores. The precious metal ores (gold and silver) came from 30 lode mines and 10 placer mines; the base-metal ores (copper, lead, molybdenum, and zinc) came from 24 lode mines. Placer mines yielded less than 1 percent of the national silver production. Silver was mined in 12 States, of which Nevada was by far the largest producer; it accounted for nearly one-third of the national total. The production of silver at domestic mines generated employment for about 1,100 mine and mill workers. The value of mined domestic silver was estimated to be \$290 million.

Of the nearly 27,000 t of world silver that was fabricated in 2001, about one-third went into jewelry and silverware, one-fourth into the light-sensitive compounds used in photography, and nearly all the remainder went for industrial uses, of which there were 7 substantial uses and many other small-volume uses. By comparison, 85 percent of the silver used in the United States went to photography and industrial uses, 8 percent to jewelry and silverware, and 7 percent to coins and medals. The United States was the largest consumer of silver followed by India, Japan, and Italy; the 13 largest consuming countries accounted for nearly 90 percent of the world total. In the United States, about 30 companies accounted for more than 90 percent of the silver fabricated. The consumption of silver for all fabrication uses is expected to grow slowly through the decade ending in 2010 at about 1.3 percent per year for the world and 2.4 percent per year for the United States.

World and U.S. reserves and reserve bases are more than adequate to satisfy the demand for newly mined silver through 2010. The other components of supply will be silver recovered from scrap, silver from industrial stocks, and silver bullion that is sold into the market from commodity exchange and private stocks.

Historical Background

Silver and gold have been known and prized for at least six millennia. The two metals commonly are found together in nature and were almost certainly the first metals known to man. In streambed gravel deposits, from which they were first recovered, the gold invariably contains silver, sometimes enough to form the natural alloy “electrum,” in which the silver content can range from about 18 to 36 weight percent. The separation of silver from gold in these alloys probably was not achieved until about 2000 B.C. or later, but silver had been recovered as native silver and by charcoal reduction from certain silver minerals, such as cerargyrite (AgCl), as early as 4000 B.C. (Mohide, 1985, p. 4-5).

¹Retired.

Silver was valued by the ancients because of its color (it is the whitest of all metals), its brilliant luster, its noncorrodible nature, and the relative ease with which it can be worked. It still is valued for those same characteristics today, but in addition, several other useful properties have transformed it from being a decorative and monetary metal into a predominantly industrial metal.

Nonmonetary Uses

Like gold, silver is soft, malleable, and ductile; in fact, it is the most ductile of metals. These properties led to its being fashioned into items of personal adornment and decorative items of various kinds. Thus, silver belt buckles, bracelets, brooches, chain necklaces, neck rings, and other items of jewelry were developed early. Later, silver was used for such things as decorative handles for daggers and swords, and eventually, in relatively modern times, eating utensils and various items of tableware.

The industrial uses of silver (including photography), which today account for two-thirds of world silver consumption, did not arise until the 19th and 20th centuries. A short list of some of the important uses and the dates of their introduction follows:

- Silver and silver salts have been central to the development of photography since its origins in the 1820s.
- Silver-mercury dental amalgams have been used for tooth restorations since the late 1830s.
- Mirrors of polished silver were used by the Egyptians in the third millennium B.C., and “silvering” of mirrors with lead, tin, or mercury was practiced in Europe before and during the Renaissance. The large-scale production of silvered glass mirrors through the chemical reduction of silver nitrate dates from Justus von Liebig’s 1835 invention of the process.
- A patent for a process for the electroplating of silver was granted in 1840; it was the first patent for the electroplating of any metal.
- Although Alessandro Volta had used silver and zinc as the electrodes of his “electric pile,” or battery, at the beginning of the 19th century, it was not until military requirements in the 1940s created a demand for high-energy-density batteries that the first two types of practical silver batteries were developed.
- Silver sleeve bearings were developed in the 1940s for use in high-performance military aircraft engines.
- Silver catalysts for the large-scale production of formaldehyde and the oxidation of ethylene are developments of the second half of the 20th century.
- Although silver was known to be an excellent conductor of electricity in the 19th century, its widespread use in switch and relay contacts and in conductors arose gradually during the 20th century.

Silver as a Monetary Metal

After being used as money for more than two millennia, silver was removed from the world’s circulating coinage in the 1960s and 1970s. This was done out of necessity, because the burgeoning demand for silver for its many industrial uses and for coin-operated vending machines was rapidly outstripping the supply of silver. Because most silver is a byproduct of base-metal mining, the mine supply could not be quickly augmented, and national bullion stocks were rapidly approaching exhaustion. The situation was especially critical in the United States, which in 1965 coined 8,537 t of silver, which was nearly three-fourths of the silver used in coinage in the free world. In that year of peak coinage demand, U.S. Government bullion stocks totaled only about 25,000 t, of which 5,130 t was earmarked for the strategic stockpile and, thus, not available for coinage. The Government reacted by eliminating silver from dimes and quarters and reducing the silver content of half-dollars to 40 percent. Two years later it announced that all silver coins would be withdrawn from circulation, and in 1968, it ended the redemption of silver certificates, thus completing the demonetization of silver in the country (Hilliard, 1999).

Today, official silver coins are minted in several countries, but, as explained in the “Uses” section, they are bullion coins and commemorative issues not intended for use as circulating money.

Mine Production

Minable silver deposits were scattered across the ancient Mediterranean world in an east-west band from Spain through Sardinia, Tuscany, Yugoslavia, Greece, Romania, and Asia Minor and then beyond to Armenia and Afghanistan. The oldest sources of silver in the ancient world probably were gold-bearing stream gravels in Asia Minor, in which the silver was present in electrum. The first significant quantity of silver produced was mined in Cappadocia (central Turkey) sometime between 4000 and 3000 B.C. Perhaps the best known of the ancient lode silver deposits were the lead-silver deposits at Laurium, near Athens, Greece. These deposits had been worked since about 1000 B.C., but were not fully developed until 500 years later. They financed the rise of 5th century B.C. Athens as a political power, and during their lifetime are estimated to have yielded about 7,800 t of silver. Another important producing region was in Spain, where the indigenous Celtic inhabitants were mining silver-lead deposits. These mines were seized by Carthage in the years between 236 and 228 B.C., and then taken by Rome in 206 B.C. during the second Punic war. They remained in Roman hands for several hundred years. According to Mohide (1985, p. 15), “at the height of the Roman Empire, 127 A.D., [Rome] owned all the mine sources of gold and silver in the known world.”

During the Dark Ages, precious-metals mining continued in only a few places, and output was a small fraction of the output in Roman times. With the discovery of silver-bearing mineral deposits in Eastern Europe, silver production expanded in the later Middle Ages, and by the mid-14th century, was on the order of 50 metric tons per year (t/yr). European production then languished for several decades, but with the help of new technology in mining and refining, production picked up again around 1460 and had reached about 90 t/yr by 1530 (Green, 1999, p. 11, 13-14).

By the mid-16th century, silver began flowing from the Americas into Spain in appreciable quantities as new silver discoveries in Mexico augmented the South American sources. The slowness of the smelting process, however, limited the rate of production. In 1557, the extraction of silver by amalgamation with mercury was developed in Mexico; 10 years later, the Huancevalica mercury deposit in Peru was discovered, which enabled a rapid increase in silver output. By the last decade of the century, production in the Americas had risen to an average of about 270 t/yr; two-thirds came from Bolivia and Peru, and one-third from Mexico. In terms of weight not value,

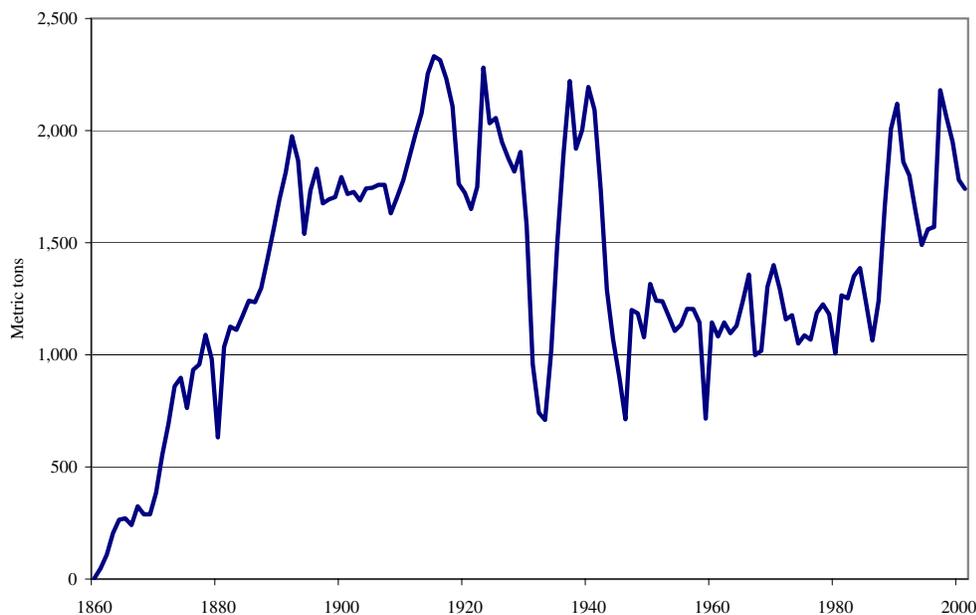


Figure 1. U.S. mine production of silver from 1860 to 2000. Total production prior to 1860 was estimated to be 25 metrics tons (t).

U.S. Bureau of Mines and U.S. Geological Survey Mineral Resources of the United States and Minerals Yearbook.

Table 1. Largest U.S. silver deposits/districts in terms of past production
[Modified from Long, DeYoung, and Ludington, 2000, p. 625]

Deposit/district	State	Production (metric tons)
Coeur d'Alene	Idaho	33,400
Butte	Montana	22,400
Tintic-East Tintic	Utah	8,500
Bingham Canyon	do.	8,300
Park City	do.	7,890
Leadville	Colorado	7,670
Comstock	Nevada	5,900
Tonopah	do.	5,420
Aspen	Colorado	3,110
Copper Queen	Arizona	2,830

98 percent of the precious metals shipped from the Americas was silver, and only 2 percent was gold (Green, 1999, p. 15; Jastram, 1981, p. 5).

By the mid-18th century, world silver production was about 530 t/yr, of which the Americas accounted for 90 percent; Mexico alone accounted for 62 percent. By the end of the century, world production had grown to 870 t/yr, of which 71 percent came from Mexico and 20 percent from South America. In 1858, the Comstock Lode was discovered in Nevada, and along with other deposits found in Nevada and other western States, it made the United States the world's largest silver producer from the early 1870s until nearly the end of the 19th century (fig. 1). By 1900, world production had risen to 5,400 t/yr.

Total world silver mine production from prehistory through 2001 is estimated by the U.S. Geological Survey (USGS) to have been about 1.26 million metric tons (Mt), one-half of which was mined in the last 62 years of the period. About 8 percent of the silver was mined before the discovery of the Americas, 22 percent from 1492 through 1900, 69 percent in the 20th century, and 1 percent in 2001.

U.S. silver mine production, which was negligible before 1861, totaled about 194,600 t through 2001; this is more than 15 percent of the world cumulative total. U.S. production has come from 32 States; nearly all, however, has come from Arizona, Colorado, Idaho, Montana, Nevada, and Utah. More than one-half of the total has come from the 10 largest domestic silver districts in terms of past production (table 1).

Description

Salient Facts

Silver, along with gold and the six PGMs, is one of the small group of elements known as the precious, or noble, metals. Chemically, silver is a 4d transition element, atomic number 47, atomic weight 107.87, and electron configuration $[\text{Kr}]4d^{10}5s^1$; it is located in period 5, group 11 (or IB) of the periodic table of the elements. Silver has four oxidation states; +1 is the common state, 0 and +2 are uncommon, and +3 can be induced only by the use of a powerful oxidizing agent and persists only when stabilized through the formation of a complex. Natural silver is a mixture of the two stable isotopes: Ag^{107} (51.82 percent) and Ag^{109} (48.18 percent). In addition, nine radioactive isotopes have been identified; these have half-lives that range from 24.6 seconds to 130 years (Cappel, 1997, p. 179; Silver Institute, 2000).

Silver crystallizes in a cubic face-centered structure, from which it melts at 961.93° C. Annealed silver has a density of 10.49 grams per cubic centimeter at room temperature (20° C), is soft and very ductile, and is exceeded in malleability only by gold. It possesses the highest electrical and thermal conductivities of any element. In

appearance, silver is a lustrous, very white metal; it is sometimes referred to as “the white metal.” It has the highest reflectivity in the visible spectrum of any metal (Butts, 1967, p. 104-105; Etris, 1997, p. 163-165).

Silver is essentially inert to atmospheric oxygen but is the most permeable of metals to atomic oxygen; molten silver dissolves almost 10 times its own volume of oxygen. Silver, however, readily reacts with sulfurous gases to form surface tarnish. Silver dissolves in oxidizing acids and in aqueous potassium or sodium cyanide solutions in the presence of oxygen (Chaston, 1967; Etris, 1997, p. 168).

The name silver derives from the Anglo-Saxon *siolfur*. The chemical symbol, Ag, represents *argentum*, the Latin name for the metal, which in turn derives from the Greek *argos*, meaning shining or white.

Principal Forms

Commercial (minimum 99.9 percent pure silver) or higher grade silver is used in metallic form for many applications and as the starting material for the production of silver compounds. More than one-half of the silver consumed in the United States each year goes into the production of compounds, mainly into the silver nitrate used as the starting material for photographic emulsions. For most of its metallic uses, silver is alloyed with other metals to achieve optimal metallurgical and chemical properties.

Metal, Alloys, and Composites

Fine (unalloyed) silver of commercial or higher grade is used for many purposes and is a standard, readily available metal. In many applications, however, alloying the silver with one or more other metals is desirable and sometimes necessary. With some exceptions, most of the commercially useful silver alloys are combinations of silver with 1 or more of 14 metals located in a block of the periodic table bounded by periods 3 and 6 and groups 10 and 14. The more important alloying metals are cadmium, copper, gold, indium, lead, mercury, palladium, platinum, tin, and zinc inside the block, and lithium, magnesium, and manganese outside the block. Of lesser importance are aluminum, germanium, nickel, and silicon inside the block and beryllium and titanium outside the block. The single most important binary alloy system is silver-copper in which useful alloys can be formed across the full range of composition. The commercially significant ternary and higher alloys of silver are based on additions to the binary systems silver-gold, silver-copper, and silver-palladium and on various combinations of silver with cadmium, indium, mercury, thorium, tin, and zinc (McDonald, Price, and Sistare, 1967a, p. 235-271, and 1967b, p. 272-303; Etris, 1997, p. 174).

Although a few silver alloys, such as sterling silver (silver 92.5 percent-copper 7.5 percent), the oldest standard silver alloy, and coin silver (silver 90 percent-copper 10 percent) are used in more than one end use, most silver alloys can be divided into groups, each of which is suited for a separate class of application. For example, yellow and green jewelry golds of 10 to 18 karats are alloys of gold, copper, silver, and minor amounts of zinc in which silver accounts for 4 to 35 weight percent of the alloy. Solders for these jewelry golds are alloys of gold, silver, copper, zinc, and sometimes cadmium.

Fine silver is used extensively in electrical switches and relays in low- and medium-current circuits, such as in home appliances and automotive uses. Where greater hardness and wear resistance are required, silver-based alloys are used, most of which are binary alloys with copper, cadmium, or palladium and a few with gold or platinum. To achieve even longer wear and/or to contend with arc erosion and welding in the more power-dense circuits, composite materials made of silver with semirefractory and refractory oxides or metals are used. The silver content of the electrical alloys and semirefractory composites is typically high and ranges from about 70 to 99 weight percent; the silver content of the refractory composites, however, is more nearly equal to the refractory component content and typically ranges from about 30 to 50 weight percent. A selection of four dozen electrical alloys and semirefractory and refractory composites is listed by Larsen and Imes (1967).

Nearly all silver brazing alloys (see “Uses” section) are based on the silver-copper system, and can be classified as binary silver-copper alloys, ternary silver-copper-zinc alloys, and quaternary silver-copper-zinc-cadmium

alloys. The silver content of the principal alloys of this type ranges from about 35 to 93 weight percent, and their melting points range from about 600° to 780° C. In addition, there are small families of copper-silver-phosphorus alloys and cadmium-based alloys in which silver is present in single-digit percentages; the cadmium-based alloys melt at temperatures below 450° C, and, thus, can be called solders. Some lead- and tin-based solders (see “Uses” section), which are used at lower temperatures than brazes, contain up to 6 weight percent silver to improve fluidity, wettability, and strength (Chamer, 1967, p. 386-390; Roskill Information Services Ltd., 1992, p. 293).

Dental alloys are formulated for use as casting alloys, precious metal solders, wrought alloys, or amalgam alloys. Dental casting alloys are essentially gold-silver-copper alloys with small additions of palladium, platinum, and zinc. Typical yellow gold casting alloys contain from about 3 to 26 weight percent silver; white golds contain as much as 30 percent silver. Dental solders are essentially gold-silver-copper alloys with silver contents of 3 to 35 weight percent. The wrought alloys are higher order alloys that contain, in approximate order of decreasing quantity, gold, platinum, palladium, silver, and copper, and with minor additions of nickel and zinc. Their silver contents range from single-digit percentages up to more than 40 percent. Amalgam alloy, which the dentist mixes with mercury in preparing an amalgam tooth filling, is “essentially epsilon silver-tin (Ag_3Sn) containing from 25 to 26.8 weight percent tin with small additions of copper and zinc, and the balance silver” (McDonald, Price, and Sistare, 1967b, p. 299). The composition of amalgam alloy has varied widely in past years—silver has ranged from 25 to 70 weight percent; copper and tin each, from 0 to 30 percent; and zinc, from 0 to 1 percent (Etris, 1997, p. 177).

Neutron-absorbing ternary silver-indium-cadmium alloys that contain from 80 to 90 weight percent silver have been used extensively in control rods for nuclear power reactors but have been largely, if not completely, replaced by boron carbide rods (McDonald, Price, and Sistare, 1967b, p. 301; Roskill Information Services Ltd., 1992, p. 302-304).

Compounds

Most silver compounds are based on silver (I), and most of them range from insoluble to at best moderately soluble in aqueous environments. Few silver (II) compounds are known, and no simple silver (III) compounds exist. Silver (I) and (II) also form complexes with ammonia, cyanide, halide ions, thiosulfate and thiourea and with many organic aromatics and olefins. The silver compounds of principal commercial interest are discussed below.

Silver nitrate (AgNO_3) is the intermediate chemical from which all other silver compounds are made and thus is, by far, the most important commercial compound. It is made by dissolving silver metal in hot nitric acid. The purified crystalline nitrate is not photosensitive, but it is easily reduced to metal by formaldehyde, glucose, and several other reagents.

Silver bromide (AgBr) is a yellow to green-yellow crystalline compound that is considerably more photosensitive than the chloride or iodide and, hence, is used extensively for photographic emulsions. Silver chloride (AgCl) is a white crystalline photosensitive material that is used widely in photographic papers. Silver iodide (AgI) is less photosensitive than the bromide or chloride, but is responsive to a wider span of the visible spectrum. It, too, is used extensively in photographic materials (Cappel, 1997, p. 180-186).

Silver chloride is also used in seawater-activated batteries. Silver oxide (Ag_2O) is used in standard silver batteries. The silver (II) tetroxide (Ag_4O_4) is an oxidizer used to kill bacteria in cooling system water and swimming pools (Etris, 1997, p. 164).

Commercial Grades, Forms, and Specifications

Doré bullion, which is unrefined silver that contains a variable but usually appreciable percentage of gold, is a common article of commerce and trade, of interest mainly to miners, smelters, and refiners.

Refined unwrought silver, or silver bullion, is most commonly available as 1,000-troy-ounce bars of 99.90 percent pure silver. Bars are also available in 99.95 and 99.99 percent purities. U.S. industry standards for these grades are listed in table 2.

Table 2. Chemical requirements for commercial refined silver
 [Composition is expressed as percentage of the total metal. --- Zero. Source:
 ASTM International standard B413-89 specification for silver]

Element	Limit	Grade and composition		
Silver	Minimum	99.9	99.95	99.99
Silver plus copper	do.	99.95	---	---
Bismuth	Maximum	0.001	0.001	0.000
Copper	do.	0.08	0.04	0.01
Iron	do.	0.002	0.002	0.001
Lead	do.	---	---	0.001
Palladium	do.	---	---	0.001
Selenium	do.	---	---	0.000
Tellurium	do.	---	---	0.000

The purity of silver, like that of gold, is often expressed in terms of “fineness,” or parts per thousand. For example, 100-percent-pure silver is 1,000 fine, and sterling silver, which is 92.5 percent silver, is 925 fine.

Refined silver is also produced as flake, foil, grain, powder, rod, sheet, strip, tubing, and wire. Rolled products can range downward from as much as 2 meters in width for heavy sheet to generally narrower widths for thinner sheet; foil can be rolled as thin as about 13 micrometers (μm). Silver rod and wire can range in diameter from about 5 centimeters (cm) down to about 125 μm . Silver tubing can range from capillary size to about 15 cm in diameter (Reese, 1985).

Several particulate forms of silver are made. Grain silver consists of irregularly shaped granules of less than 10 or 12 millimeters (mm) in diameter; it is made by pouring molten silver into water. Spherical powder, which is made by atomizing a stream of molten silver with a high-velocity jet of air or gas, is available in sizes that range from –325 mesh to more than 80 mesh. Galvanic, or cemented, powder consists of irregular, dendritic particles that have been precipitated from solution by ions of a more anodic metal. Chemical powders are irregular particles, which are commonly 0.5 to 2 μm in diameter that have been precipitated from solution by an organic reducing agent. Flake silver is made by ball milling silver powder in stearic acid or some similar organic vehicle that prevents the particles from cold welding together during milling and afterwards during storage and use (Coxe, 1967).

Reagent grades of several silver compounds, such as carbonate, cyanide, diethyldithiocarbamate, iodate, nitrate, oxide, phosphate, and sulfate, are marketed. Purified grades of the acetate, bromide, cyanide, and iodide are available, as is a grade of the nitrate intended for medicinal use (Cappel, 1967, p. 180).

Sources

Of the elements in Earth’s crust, silver, at 0.075 part per million [0.075 gram per metric ton (g/t)] ranks 65th in abundance, just below mercury and above selenium (Lide, 1999, p. 14). Its abundance in the crust is about 19 times that of gold. Its abundance in igneous rocks ranges from 0.05 g/t for ultramafic rocks and felsic granites to 0.07 g/t for rocks of intermediate composition and to 0.1 g/t for basalt (Heyl and others, 1973, p. 584). Its average concentration in seawater is 0.00004 g/t [0.00004 milligram per liter (mg/L)].

Silver tends to be associated with the sulfide ores of copper, lead, and zinc and sometimes with bismuth and antimony; it is always present in gold ores. In base-metal sulfide ores, silver typically is most concentrated in galena (PbS), less in chalcopyrite (CuFeS_2), and least in sphalerite (ZnS). In a few lead-zinc deposits, however, it is concentrated preferentially in ZnS. Silver is often highly enriched in the oxidized parts of sulfide deposits, sometimes forming bonanzas of limited extent that grade thousands of grams per metric ton (Heyl and others, 1973, p. 584-586). The concentration of silver in U.S. deposits from which silver is economically minable as the principal product at 2001 silver prices was typically about four orders of magnitude greater than the crustal average, or about 700 g/t.

Mineralogy

Silver forms a great many minerals; 55 of them are described in Ford (1932, p. 808-809). As many as 248 minerals, many of which are not primarily silver minerals, can have silver as a structural component (Jackson, 2002). Heyl and others (1973, p. 586) listed 33 principal silver minerals (table 3).

Payable quantities of silver may be carried in silver minerals that are associated with or form inclusions within base-metal minerals. Or, the silver may substitute for some of the base-metal atoms in the lattices of minerals. In gold-silver ores, the silver is usually alloyed with gold, as in electrum, or present in gold-silver minerals or in discrete silver minerals that accompany the gold-bearing minerals. Placer gold, when it contains any silver, contains much less than do the lode minerals from which the placer ore was derived.

Deposits

Heyl and others (1973, p. 587-596) discussed nine types of mineral deposits in which silver is a major constituent and a further nine classes in which it is a byproduct metal. Using somewhat different nomenclature, Long, DeYoung, and Ludington (2000, p. 640, 642) listed 37 types of silver-bearing deposits, of which 9 were considered to be the principal types in terms of U.S. past production and remaining resources. As the science of mineral deposits has evolved, the deposits themselves have been classified in various ways, some emphasizing genesis and others emphasizing characteristic combinations of chemical and mineralogical compositions, geochemical and geologic environments, host-rock associations, and morphology. In the past two decades, much work has gone into compiling mineral deposit models, each of which comprises “the systematically arranged information describing the essential attributes (properties) of a class of mineral deposits” (Cox and Singer, 1986, p. 2). Such models are modified or supplemented by new models as knowledge and understanding of the deposits grows. Collections of models of silver-bearing deposits and further explication of them may be found in Cox and Singer (1986, p. 109, 123-129, 143, 145-157, 189-197, 205-208) and Bliss (1992, p. 19-32). A good synopsis of silver-bearing deposits is given in Graybeal, Smith, and Vikre (1986, p. 1-184).

Table 3. Principal silver minerals

[Source: Heyl and others, 1973, p. 586]

Mineral	Composition	Mineral	Composition
Native element, alloy:		Sulfides, sulfosalts, selenides, tellurides--Continued:	
Electrum	(Ag,Au)	Pyargyrite	Ag ₃ SbS ₃
Silver	Ag	Stephanite	Ag ₅ SbS ₄
Carbonate, argentian cerussite	(Pb,Ag)CO ₃	Stromeyerite	CuAgS
Sulfides, sulfosalts, selenides, tellurides:		Sylvanite	Ag ₂ Au ₂ Te ₈
Andorite	PbAgSb ₃ S ₆	Argentian tennantite	(Cu,Fe,Ag) ₁₂ As ₄ S ₁₃
Acanthite	Ag ₂ S	Argentian tetrahedrite	(Cu,Fe,Ag) ₁₂ Sb ₄ S ₁₃
Argentite	Ag ₂ S	Halides:	
Diaphorite	Pb ₂ Ag ₃ Sb ₃ S ₈	Bromyrite	AgBr
Dyscrasite	Ag ₃ Sb	Cerargyrite	AgCl
Fizelyite	Pb ₅ Ag ₂ Sb ₈ S ₁₈	Embolite	Ag(Cl,Br)
Argentian galena	(Pb,Ag)S	Iodyrite	AgI
Hessite	Ag ₂ Te	Oxides:	
Matildite	AgBiS ₂	Aurorite	(Ag ₂ Ba,Ca,Pb,K ₂ CuMn ⁺²)Mn ⁺⁴ O ₇ •3H ₂ O
Miargyrite	AgSbS ₂	Argentian todorokite	(Ag ₂ K ₂ Ca,Ba,Na,Cu,Pb)Mn ⁺⁴ O ₉ •5H ₂ O
Naumannite	Ag ₂ Se	Ag-bearing Pb-Mn oxides	Variable
Pearcite	Ag ₁₆ As ₂ S ₁₁	Sulfates:	
Petzite	Ag ₃ AuTe ₂	Argentian anglesite	(Pb,Ag)SO ₄
Proustite	(Ag,Cu) ₁₆ Sb ₂ S ₁₁	Argentian plumbojarosite	(Pb,Ag)Fe ₆ (SO ₄) ₄ (OH) ₁₂
Polybasite	Ag ₇ AsA ₃	Argentojarosite	Ag ₂ Fe ₆ (SO ₄) ₄ (OH) ₁₂

In the United States, virtually all the silver produced to date and remaining in the ground as identified resources can be accounted for by large deposits, each of which originally contained at least 85 t of silver. Of these “significant” deposits, a very small number of the largest ones account for a disproportionately large share of the past production and remaining resources. The 10 largest deposits in terms of silver produced have accounted for about 60 percent of silver produced to date; the 10 largest deposits in terms of identified resources of silver remaining in the ground account for 56 percent of those resources (Long, DeYoung, and Ludington, 2000, p. 629).

In 2001, only about one-fourth of the silver mined in the world came from silver ores; the remainder was a byproduct of the mining of other metals. More specifically, the Silver Institute (2002, p. 26) estimates the breakdown by ore type as follows: silver ores, 25 percent of mined silver; gold ores, 15 percent; copper ores, 24 percent; lead, zinc, and lead-zinc ores, 35 percent; and other ores, 1 percent. For the United States, the breakdown by ore type in 2001 was silver ores, 14 percent; gold ores, 39 percent; copper and copper-molybdenum ores, 10 percent; and lead, zinc, and lead-zinc ores, 37 percent.

Reserves, Reserve Base, and Resources

Reserves and reserve base for several of the leading silver-producing countries are listed in table 4. More than two-thirds of world silver resources are estimated to be associated with copper, lead, and zinc resources, but a figure for the world total is not available. For the United States, the remaining silver resources have been estimated to total about 157,000 t (Long, DeYoung, and Ludington, 2000, p. 640). (See Appendix for definitions of reserves, reserve base, and resources.)

Secondary

Secondary silver (that is, silver recovered from scrap) is an important part of the total silver supply. Most of the scrap is generated by the manufacture and use of photographic materials, electrical switchgear, and catalysts. In the other uses of silver, the metal tends either to form such a small part of the product that its reclamation is uneconomical or it is locked into products, such as jewelry, sterlingware, and coins, that are infrequently recycled. Worldwide, an estimated 5,730 t of silver was recovered from scrap in 2001; this amounted to 21 percent of the silver market supply, a share that has held remarkably steady for at least the past decade (Silver Institute, 2002, p. 70). In the United States, 1,060 t of silver, or 15 percent of the U.S. market supply, was reclaimed from scrap in 2001. For most of the past decade, the amounts of secondary metal recovered were somewhat higher, typically forming about 20 percent of U.S. supply.

Production Technologies

Most (perhaps 80 to 85 percent) of the world’s silver is recovered from sulfide ores and oxidized sulfide ores. The other 15 to 20 percent is produced from gold and gold-silver ores, which are predominately oxide ores.

Table 4. Silver reserves and reserve base, yearend 2001

[In metric tons of contained silver. All data are rounded to two significant digits; because of independent rounding, the parts may not add to totals shown. Source: Hilliard, 2002]

	Reserves	Reserve base
United States	30,000	75,000
Australia	33,000	37,000
Canada	35,000	47,000
Mexico	37,000	40,000
Peru	25,000	37,000
Other countries	120,000	190,000
World total	280,000	430,000

In the United States and several other countries, the silver sulfide ores and the silver-bearing lead-zinc sulfide ores typically are mined from underground workings, whereas the silver-bearing copper ores and gold ores most often are produced at surface mines.

Ore Processing

Sulfide ores typically are crushed and then ground to free the sulfide ore minerals from the nonsulfide minerals with which they are physically associated in the ore; the nonsulfide minerals are of no commercial interest. The two kinds of minerals are then separated in an aqueous environment by froth flotation; in this process, the sulfide particles, which are hydrophobic, adhere preferentially to a froth of oily bubbles that floats to the surface of the flotation tank and is skimmed off and collected. The ore minerals are in this way concentrated to a degree that is contingent on the mix of minerals and other factors characteristic of the particular ore being processed. Copper concentrates that typically contain from 25 to 35 weight percent copper, for example, can be prepared from ore that contains less than 1 percent copper. The silver content of copper concentrate ranges widely, from about 0.06 to 3.1 kilograms per metric ton (kg/t) of concentrate (Schack and Clemmons, 1967, p. 68); the concentrate from silver-bearing lead ores may typically carry from 0.8 to 1 kg/t silver (Hilliard, 2003, p. 2). Base-metal ores and even some sulfidic refractory gold ores are routinely concentrated by froth flotation. Usually, however, gold ores, if they are concentrated at all, are concentrated by gravity separation devices, such as jigs, shaking tables, or spirals.

Metal Extraction

Copper and lead concentrates are smelted to produce crude metal that is suitable for further processing. Zinc concentrates are roasted to convert sulfide minerals to oxides; the silver-rich calcine residue is sent to a lead smelter for further processing. Gold-silver ores and concentrates are not usually smelted; rather they are leached. The silver-bearing product of each of these processes is doré.

When copper concentrate mixed with fluxes is smelted in a furnace, a layer of molten copper-iron sulfide, which is called “matte,” forms under a less dense cover of disposable silicate slag. The matte is tapped off periodically and, with the addition of more silicate flux, is charged hot into a reaction vessel, which is called a converter, where air is blown through the molten mass to oxidize iron, sulfur, and other impurities. The oxidized products leave the converter as fume, gases, and slag. The residual “blister” copper is then transferred to an anode furnace for further reduction in the level of impurities and is then cast into anodes that will be electrolytically refined. About 95 percent of the silver in the concentrate ends up in the anode copper (Schack and Clemmons, 1967, p. 67-68).

Copper, along with several base-metal and ferrous metal impurities, is released from the copper anode into the sulfuric acid electrolyte of the refining tank. Copper is deposited from the electrolyte onto the cathode, whereas most of the impurities remain in solution, and the precious metals, along with selenium, tellurium, and a few other rare metals, remain insoluble and collect in the anode mud at the bottom of the tank. The first step in recovery of the silver and other desired metals from the mud is the removal of copper by aerated leaching in sulfuric acid. The decopperized mud is mixed with fluxes and smelted to obtain doré (Johnson, 1967, p. 78-86).

Lead concentrates are agglomerated by sintering, mixed with fluxes and coke, and smelted in a blast furnace to yield crude lead bullion. The crude bullion then undergoes treatment to remove antimony, bismuth, copper and a number of other impurities; the result is silver-bearing lead suitable for refining. About 95 percent of the silver in the blast furnace feed is recoverable from the lead bullion.

To extract the silver, the lead is remelted, and zinc dust is added to the surface of a quantity of molten lead that partly fills an open kettle held at a temperature above the melting point of zinc. The lead and zinc are mixed by pouring additional molten lead through the thin layer of molten zinc floating on the surface. Copper, gold, and silver, which have greater affinity for zinc than for lead, alloy with the zinc to form a surface crust that is skimmed off at intervals. The collected crust is retorted and the zinc removed by vacuum distillation for reuse. Entrained lead and several other impurities are then removed from the molten retort residue by air-blast oxidation. The oxidized

products collect in a slag that is removed when the reaction is complete, leaving silver-gold doré (Schack and Clemmons, 1967, p. 68-71).

Zinc extraction is based on the reduction of the metal from oxides. Thus, as a first step in the electrolytic zinc process, silver-bearing zinc sulfide concentrates are roasted to convert the minerals to oxides and lesser amounts of sulfates. Zinc is extracted from the roasted concentrate, or calcine, by leaching with dilute sulfuric acid. Most of the silver and essentially all the lead remain in the calcine, which is then sent to a lead smelter for processing. The product is silver-bearing lead bullion from which doré can be extracted by the methods discussed above (Schack and Clemmons, 1967, p. 69-70).

Silver, along with gold from gold-silver ores, is extracted by leaching either the raw ore or a concentrate with aqueous alkali cyanide solutions. If too many sulfides are present, then the ore or concentrate must be oxidized, usually by roasting or pressure oxidation. Gold and silver are recovered from the pregnant cyanide solution either by precipitating them with zinc dust or by adsorbing the gold and silver complexes onto activated carbon, stripping a condensed pregnant solution from the carbon, and recovering gold and silver from the solution either by zinc precipitation or by electrolysis (Zadra, 1950, p. 29-32; Zadra and others, 1952, p. 7-10). The gold-silver precipitate from the zinc precipitation process or the loaded steel wool cathode from the electrolysis cell is smelted in a small furnace with borax fluxes, niter, and silica. The metal product is doré.

Refining

Silver is simultaneously refined to commercial grade and separated from gold and other impurities by electrolysis. The doré obtained by the processes outlined above is cast into anodes and placed in an aqueous electrolyte mixture of silver and copper nitrates plus a small amount of free nitric acid; the cathodes are stainless steel or sheet silver. The purified silver forms a crystalline deposit on the cathodes while the insoluble gold, palladium, and platinum collect under the anodes as a “gold mud” that will be processed further to recover the precious metal values. The silver crystals are scraped from the cathodes at intervals of several hours or daily, collected, washed free of electrolyte, melted, and cast into bars. These bars are remelted under a cover of charcoal to remove entrapped oxygen and other gases and cast into standard 1,000- or 1,100-troy-ounce bars for delivery to the market (Barker, 1967; Johnson, 1967, p. 79-81).

Recycling

More than 80 percent of the silver in old (postconsumer) scrap available for processing in the United States each year is contained in scrap and wastes from the photographic industry. Another 10 percent is in spent catalysts; 6 percent, in electronics and electrical scrap; and the remainder, in scrap from other products (Hilliard, 2003, p. 3).

Photographic Materials

About 70 percent of the silver recoverable from photographic scrap and wastes is derived from the processing of color films and color paper. During photographic developing and fixing, all the silver is removed from color films and papers and is transferred to the spent fixer-bleach solutions. The other 30 percent of recoverable silver is contained in spent fixer solutions used for black and white (B/W), or monochrome, films and paper and in exposed and unexposed B/W films and prints. The B/W films and prints are washed free of silver or silver emulsions in a heated solution of vegetable enzymes. A silver-bearing sludge is precipitated from the solution and is forwarded to the silver refinery for further electrolytic and pyrometallurgical processing. The fixer solutions, whether from color or B/W processing, are treated by one of three methods of silver recovery—electrolysis, metallic replacement, or precipitation.

The silver in spent fixer solutions is present as the silver thiosulfate complex $[\text{Ag}(\text{S}_2\text{O}_3)_2]^{-3}$. Electrolysis of the solution decomposes the complex and reduces ionic silver to metallic silver at the cathode. The cathode

silver is then upgraded to commercial grade at a silver refinery. The metallic replacement process is similar to the electrolytic process except that the reducing electrons are provided by metallic iron. A high-surface-area form, such as steel wool, is chopped and packed into a “metallic recovery cartridge” through which the spent fixer solution is passed. This method is capable of reducing the remnant silver in the solution to less than 5 mg/L. Silver can be precipitated from fixing solutions by one of the alkali sulfides, to give silver sulfide. Precipitation is less used than electrolysis or metallic replacement because it requires careful control to prevent discharge of toxic hydrogen sulfide gas. Ion exchange resins are also used, usually for removing silver from dilute process solutions, such as wash water, when very low regulatory limits for silver in waste water must be met (Hilliard, 2003b, p. 7-9).

Catalysts

Because the composition and structure of some catalysts are closely guarded trade secrets, the catalyst manufacturers commonly arrange to have spent catalysts returned to them for toll refining. Presumably, catalysts that are used for the production of ethylene oxide, which consist essentially of metallic silver coated on a silicate substrate, are processed chemically to separate the coating from the substrate, and then the recovered silver is re-refined. Formaldehyde catalysts, which are silver screens or silver crystals, are remelted and then electrolytically refined.

Electrical and Electronics Scrap

Electrical and electronic devices are sometimes dismantled if reusable components can be retrieved. After removal of reusable components, the remaining parts of the devices are shredded, ground, and then incinerated to remove nonmetallics. The resulting mixture of metallic bits and powdered ash is screened to separate the two fractions, each of which is a complex mixture of components, and usually sent to a precious-metals refiner for the extraction of gold, PGMs, and silver.

Uses

[Note: The classification of silver end uses that is used in the descriptive sections below is a blend of the 4-category scheme used by the Silver Institute and a slightly modified form of the 14-category scheme used by the U.S. Bureau of Mines for silver consumption in the United States from 1966 through 1987 and afterwards by CPM Group, which is a U.S. precious-metals consulting firm (Silver Institute, 2002a, p. 7). The 14-category scheme is used in table 5 for the United States. Because that degree of detail is not available for silver use in most countries, the 4-category scheme is used in figure 2.]

Silver, like gold, has been used in three principal ways—a fabricated product, an investment good, and, until the 1970s, a monetary metal. The first two are discussed in this section; monetary uses were discussed in the section “Historical Background.” Of the silver supplied to the world market yearly, more than 97 percent is destined for fabrication and the remainder, for investment and producer hedging (Silver Institute, 2002a, p. 7).

Although fabricated silver is used in the same products the world over, the pattern of use differs from country to country and region to region. In most countries, the industrial uses constitute an important sector of the market, often the most important sector. The two other prominent sectors—photography, and jewelry and silverware—vary greatly in relative importance, as shown by the charts for India and Japan in figure 2. Coins and medals constitute a very minor sector in most countries. Most silver, certainly most in the industrial uses and photography sectors, is consumed in the industrial countries. The use of silver for jewelry and silverware in a country appears to be determined more by social custom than by degree of economic development. The 13 largest silver-fabricating countries in 2001 are shown in figure 3.

Silver is used in the large majority of its commercially important end uses as an alloyed or unalloyed metal. It is prepared for many of these end uses through common metallurgical processes, such as alloying, annealing or

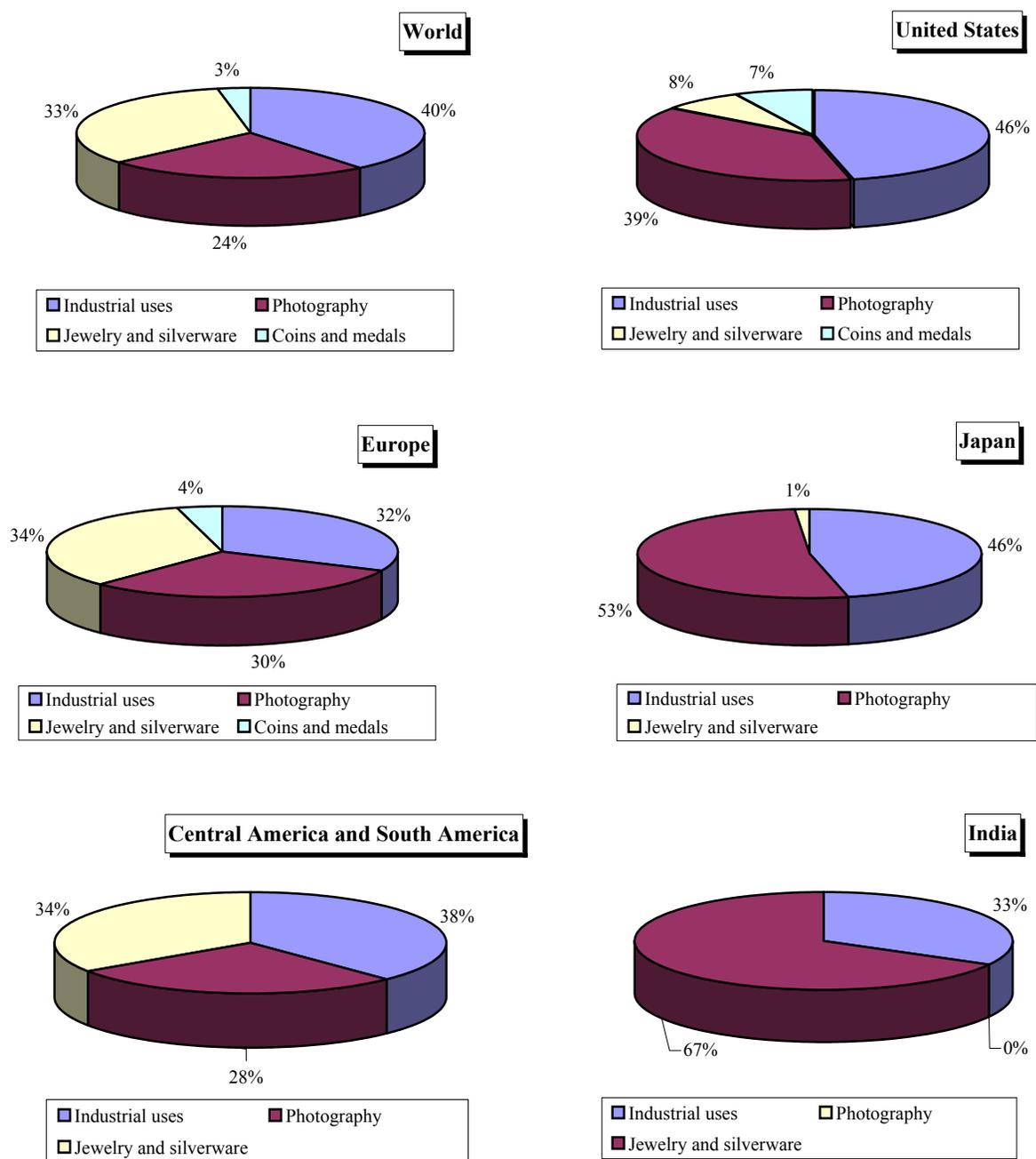


Figure 2. Selected end-use patterns for silver in 2001. Source: Silver Institute, 2002, p. 77-83.

hardening, rolling, cladding, brazing, and soldering. In a lesser number of the metallic products, such as catalysts, electroplated ware, or mirrors, it is prepared from an intermediate silver compound. In the largest single class of end-use products for silver, photographic materials, the silver remains in compound form until the photographic film or paper is exposed to light and chemical developers.

Table 5. U.S. supply and demand for unfabricated silver, and consumption pattern for fabricated silver
 [In metric tons of contained silver. NA, Not available. -----, Zero. Data include estimates. All data are rounded to three significant digits; because of independent rounding, they may not add to totals shown. Note change at 1995 from 5- to 1-year intervals. Data are from U.S. Bureau of Mines and U.S. Geological Survey Minerals Yearbooks]

	1965	1970	1975	1980	1985	1990	1995	1996	1997	1998	1999	2000	2001
Components of U.S. supply:													
Refined production:													
Primary (from ore, concentrate, and dore) ¹	2,700	2,530	1,870	1,220	1,670	1,940	NA	NA	2,200	2,300	2,000	2,780	2,640
Secondary (from scrap) ²	1,040	1,740	1,590	1,650	870	430	NA	NA	1,360	1,700	1,500	1,680	1,060
Total refined	3,740	4,270	3,460	2,880	2,540	2,370	NA	NA	3,560	4,000	3,500	4,460	3,700
Imports, refined bullion ³	215	921	2,090	2,020	4,270	2,700	2,630	2,580	2,120	2,800	2,660	3,810	2,940
Net deliveries from:													
U.S. Government stockpile						1,110	220	-----	230	190	252	320	437
U.S. Treasury stocks	13,000	2,460	93	3		157	362	118	-----	-----	-----	397	-----
Commodity Exchange stocks	12	-----	-----	-----	-----	4,110	1,740	1,120	1,070	-----	-----	-----	-----
Commercial stocks	NA	-----	457	-----	86	-----	NA	NA	NA	-----	NA	NA	NA
Total U.S. supply	7,650	6,100	4,900	6,340	7,320	4,440	7,030	8,060	6,410	8,990	8,990	7,080	7,080
Distribution of U.S. supply													
Net additions to:													
U.S. Government stockpile													
U.S. Treasury stocks	-----	-----	-----	-----	-----	-----	-----	-----	82	98	35	-----	-----
Commodity Exchange stocks	-----	460	1,150	384	1,100	841	-----	-----	-----	-----	130	430	330
Commercial stocks	NA	353	-----	39	-----	39	NA	NA	NA	5	NA	NA	NA
Exports, refined bullion ³	214	920	1,920	2,020	392	736	2,810	2,900	2,980	2,250	481	279	707
Exports, dore	NA	93	68	71	48	13	72	43	66	241	64	36	18
Consumption, industry, arts, coinage	13,800	4,370	4,990	3,880	3,700	4,300	4,090	4,200	4,530	4,840	5,110	5,264	4,970
Total distribution of supply		8,130	6,390	5,240	5,930	6,970	7,140	7,660	7,430	7,430	5,820	6,010	6,020
Apparent surplus (deficit in parentheses)		(2,030)	(1,490)	410	350	(2,700)	(630)	630	590	2,980	1,060	1,060	1,060
U.S. consumption pattern:⁴													
Batteries	317	199	132	187	77	93	128	140	149	152	156	162	165
Bearings	(5)	12	14	20	6	(5)	(5)	(5)	(5)	(5)	(5)	(5)	(5)
Brazes and solders	(5)	437	422	265	174	171	239	255	277	289	283	267	264
Catalysts	(5)	62	273	94	75	93	152	171	177	184	184	196	190
Coins, medallions, commemoratives	-----	-----	224	146	78	(5)	(5)	(5)	(5)	(5)	(5)	(5)	(5)
Contacts and conductors	886	783	846	865	856	709	650	694	824	883	908	1,020	918
Dental and medical uses	(5)	56	47	69	46	56	(5)	(5)	(5)	(5)	(5)	(5)	(5)
Electroplated ware	(6)	356	271	135	114	87	109	121	128	140	137	140	124
Jewelry and arts	180	159	396	183	180	62	128	137	152	171	177	190	152
Photographic materials	1,470	1,180	1,430	1,550	1,800	2,120	1,890	1,920	2,010	2,130	2,230	2,240	2,040
Mirrors	(5)	43	98	21	30	37	53	65	75	81	81	81	78

Table 5. U.S. supply and demand for unfabricated silver, and consumption pattern for fabricated silver—Continued

[In metric tons of contained silver. NA, Not available. -----, Zero. Data include estimates. All data are rounded to three significant digits; because of independent rounding, they may not add to totals shown. Note change at 1995 from 5- to 1-year intervals. Data are from U.S. Bureau of Mines and U.S. Geological Survey Minerals Yearbooks]

	1965	1970	1975	1980	1985	1990	1995	1996	1997	1998	1999	2000	2001
U.S. consumption pattern—Continued: ¹													
Sterlingware	1,500	595	738	282	110	109	137	149	159	177	180	174	143
Other uses	908	111	9	62	142	535	373	395	420	451	460	482	622
Consumption, industry and arts	5,260	3,990	4,900	3,880	3,690	4,070	3,860	4,050	4,370	4,660	4,800	4,950	4,700
Official coinage	8,540	22	85	2	11	236	233	156	165	174	311	335	384
Total consumption	13,800	4,010	4,990	3,880	3,700	4,310	4,090	4,200	4,540	4,830	5,110	5,280	5,080
U.S. consumption of primary silver ⁷	12,800	2,270	3,400	2,230	2,830	3,880	NA	NA	3,180	3,130	3,610	3,600	4,020

¹Includes imports.

²Includes imported scrap. Old scrap only, 1965-90; 1997 and later years include new scrap.

³The trade data shown in the table are unbalanced between imports and exports. Imported ores and concentrates, dore and precipitates, and waste and scrap are all assumed to be refinery feed materials, and that their silver content is accounted for in the output of refined silver. Exports of silver in ores and concentrates has, until about 1999, always been minor, and is not reported here. Data in the trade literature are insufficient to calculate the silver content of exported waste and scrap, so this category also is omitted here. In 1999, the U.S. Geological Survey began reporting several more trade categories, but they are omitted for the sake of continuity with earlier data and because they, too, like waste and scrap, are reported in gross weight. Monetary silver is excluded from both imports and exports.

⁴U.S. Bureau of Mines Minerals Yearbook, 1966-87; CPM Group, 1988-2001, except GFMS photographic materials, 1995 and 1997-2001.

⁵Included in "Other uses."

⁶Included in "Sterlingware."

⁷Total consumption less secondary metal produced from old scrap.

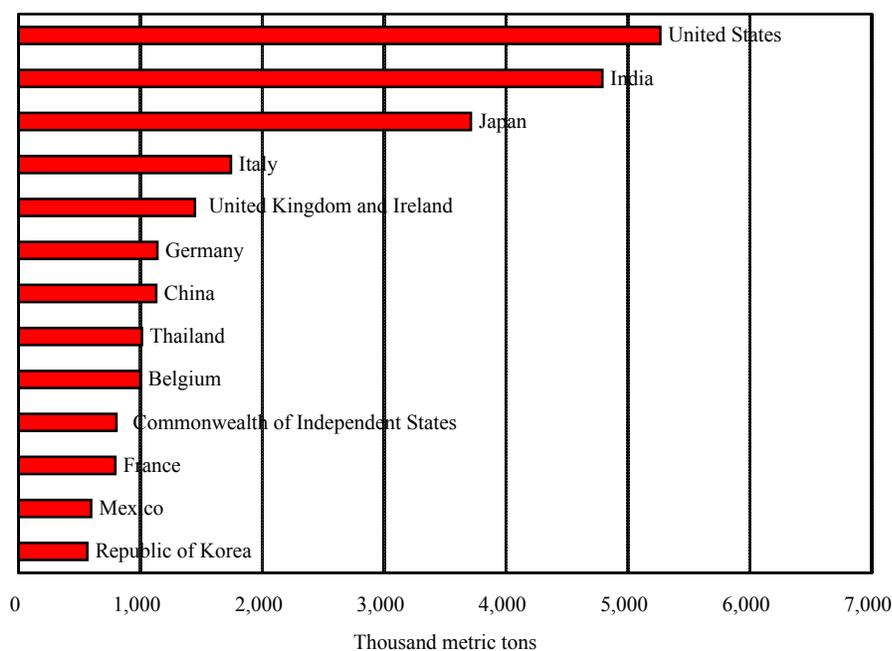


Figure 3. Leading silver-fabricating countries in 2001; these countries accounted to 89 percent of the world total. Source: Silver Institute, 2002, p. 75-76.

Properties That Determine Use

Photosensitivity to visible, x-ray, and gamma-ray wavelengths in the electromagnetic spectrum, very high electrical and thermal conductivity, chemical inertness to oxygen and many other gases and chemicals, workability, appearance, and cost are among the most important determinants of how and where silver is used as an industrial and decorative metal. For items of adornment or decoration, it is prized for its extraordinary whiteness, reflectivity, and luster. For industrial products, cost restricts silver to those uses for which it is uniquely suited, as in brazing, electrical circuitry, and photographic technology, or where reliable and safe functioning is of paramount or even crucial importance, as in seize-resistant sleeve bearings or as electrical contacts used in oxygen-rich environments in space vehicles. The ready workability of silver allows it to be used economically as, for example, silver inlays in base-metal electrical contacts and silver cladding on base metals in jewelry.

For most of the same reasons that suited it for use as money and as described in the “Historical Background” section, silver has long been considered by investors to be a good store of value.

Photographic Materials

Photography is the largest single use of silver and accounts for about one-fourth of world silver fabrication and even larger shares in those countries that are the largest manufacturers of photographic films and papers, such as Belgium, Japan, and the United States. Silver consumption for photographic materials fabrication ranges widely from country to country, as shown in figure 2; amounts consumed by the principal fabricating countries in 2001 are shown in figure 4. World consumption of silver for fabrication of photographic materials in 2001 was about 6,540 t, divided among markets as follows: consumer (amateur) photography, 42 percent; radiography, 35 percent; graphic arts (printing processes), 11 percent; and other uses (such as cinema, professional photography, and microfilming), 12 percent (Silver Institute, 2002, p. 61, 80).

Except for official coinage in the mid-1960s, the use in photographic materials has long been the largest use for fabricated silver in the United States. Since the late 1970s, photographic materials have accounted for between

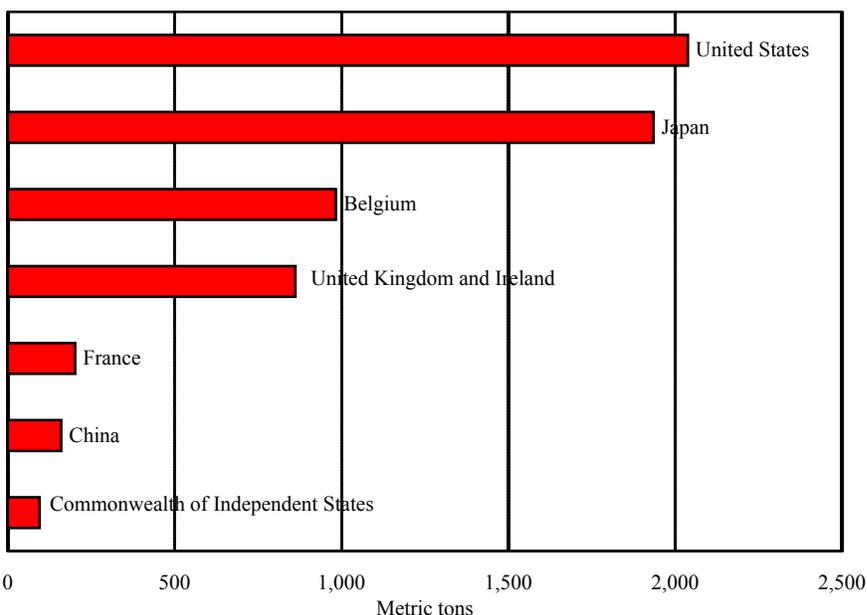


Figure 4. Silver used in photographic materials by principal operating countries in 2001; these countries accounted to 96 percent of the world total. Source: Silver Institute, 2002, p. 80.

40 and 50 percent of the silver consumed for fabricated products each year in the United States. In 2001, this use accounted for 2,040 t, or 41 percent of domestic silver fabrication (table 5). (The comparable number shown in figure 2, which was derived from a different set of U.S. statistics, is 39 percent).

Among the many different photographic processes that are used today, silver-based systems retain a very important place, especially for available-light applications, such as consumer and professional photography, and where the level of incident radiation must be kept low, as in medical x-ray applications. Silver-based systems are unmatched for sensitivity, resolution, and archival requirements, such as fade resistance and physical durability.

Basic Silver-Based Photography

Silver salts and, more specifically, the silver halides used in photographic films and papers are only a few of the many substances that are affected on the molecular or crystalline level by incident radiation. Some chemicals are far more sensitive to radiation than are the silver halides, and some are capable of capturing images with the aid of camera optics, but the light-induced changes are reversible and the images are, therefore, temporary. Silver halides are so important in photography not because they are particularly light sensitive, but because the light-induced changes formed in them can be amplified chemically by a factor of 10^{11} or more (MacWilliam, 1967, p. 200). Further, the continuous tone image thus formed of silver metal can be made permanent by dissolving and removing any unreacted halide salts from its vicinity.

The most common procedure for making a B/W photograph of an object may be outlined as follows:

- The lens system of a camera is made to focus an image of the object on the plane of a photographic film in the otherwise light-tight interior of the camera body. Light from the image is allowed to irradiate the film for some predetermined amount of time.
- The film consists of a strong but flexible base, usually a polyester such as polyethylene terephthalate (PET), onto which the active layer, or emulsion, is coated. The emulsion is a gel in which are dispersed microcrystals (or “grains”) of silver halide.

- Some of the incident light will be in the range of wavelengths that can be absorbed by the grains. Photons of the absorbed light disturb the crystalline structure of the silver halide in a grain; this promotes electrons from the valence band into the conduction band in which they move freely through the grain, and at the same time creates positively charged “holes,” which are also mobile. While irradiation continues, electron-hole pair creation competes with the reverse process of annihilation (Vincett, 1987, p. 465-466).
- The free electrons tend to become “trapped” intermittently at lower-energy sites associated with defects in the crystal structure. During residence at these sites, some of them will reduce nearby silver ions to atomic silver. As reduced atoms are formed at a site, they lower the site’s energy level; this tends to stabilize the cluster of atoms against oxidation. The presence of as few as three to five silver atoms can effectively stabilize a cluster.
- There may be multiple clusters (or “specks”) on the surface and in the interior of a grain, but one speck is sufficient to act as a nucleus for converting the whole grain to metallic silver. Concentrations of grains carrying specks of metallic silver form a latent image of the object being photographed.
- After exposure, the film is protected from further exposure and is then “developed”; that is, treated with a dilute aqueous solution of a mild organic reducing agent, such as hydroquinone, N-methyl-p-aminophenol sulfate, or one of the pyrazolidones, or a mixture of these. The nucleated grains are reduced very much more rapidly and extensively than grains that lack nuclei. The latent image is filled in with metallic silver; the density of metal at any point in the image is proportional to the degree of irradiation received at that point. In this way, a negative image is formed, the lightest parts of the object corresponding to the darkest (most metallic) parts of the “negative.” The latent image has been chemically amplified.
- Development is stopped when the image is complete and before reduction of nonnucleated grains can proceed enough to diminish contrast. The negative is washed free of developer and then treated in a complexing solvent, such as sodium thiosulfate, to remove unexposed silver halide and thus stabilize (“fix”) the image.
- After the negative is washed free of fixer and dried, light is shone through it to make a positive image on silver-halide-coated paper. The positive “print” is developed and fixed in the same manner as was the film.

Monochrome film can be processed in other ways also. For motion picture film, producing a positive directly is preferred. One way of doing this is to dissolve and wash away the silver image with a solvent that does not dissolve the unexposed silver halide grains, to expose the latter to light, and to develop and fix the positive image by the conventional means. This is called reversal processing, and films designed to be so processed are called reversal films (Vincett, 1987, p. 473-474).

Color photography is accomplished through the use of multilayer films. A typical color film has three layers of silver halide emulsions, each sensitized to absorb one of the primary colors (blue, green, or red). During developing, oxidation products of the developer react with chemicals called couplers, which may be introduced with the developer or embedded in the emulsion, to produce complementary-color dye images. Thus, a blue-light-absorbing yellow dye is formed in the blue-sensitive layer, a magenta dye in the green-sensitive layer, and a cyan dye in the red-sensitive layer. In each layer, the silver image, which is congruent with the dye image, is dissolved and removed completely so the transmission of light through the dye is not blocked. Color films may be designed for direct development and yield a color negative (for example, Kodacolor) or for reversal development and yield a positive (for example, Kodachrome). The actual construction and processing of color films is complex and exacting (MacWilliam, 1967, p. 211-214; Vincett, 1987, p. 474-476).

One-step, or instant, photography is another silver-halide-based system that uses complex multilayer film that contains within its layers (or in a rupture pod) developer, fixer, and other chemicals necessary to produce “instant” prints at the time of taking the picture.

The halides used in most photographic emulsions are AgBr, or the mixed crystals Ag(Br,I), and Ag(Br,I,Cl). These salts are sensitive to blue light [wavelengths 400 to 500 nanometers (nm)] but insensitive to green and red light (wavelengths 500 to 700 nm). AgCl alone does not absorb wavelengths longer than about 400 nm and, thus, is intrinsically insensitive to visible radiation. The response by silver halides to visible light is corrected by chemical sensitization (that is, treatment of the emulsion with certain gold- and sulfur-containing compounds that pass through the gelatin and are adsorbed onto the surfaces of the grains, thus reducing the intensity of blue light needed to form a latent image) and by spectral sensitization (which is the adsorption onto the grains’ surfaces of dyes that extend photosensitivity into the green and red regions of the spectrum) (Locker, 1996, p. 906-907).

The silver halide grains are precipitated from a mixed aqueous solution of silver nitrate and one or more alkali halide salts. Gelatin in low concentration is present as a peptizing agent to prevent agglomeration of the grains. The colloidal dispersion is cooled until it gels and is stored in the chilled state for further processing (Locker, 1996, p. 907). The average grain diameter in high-speed, low-resolution emulsions is on the order of 1 μm ; for an ultrahigh-resolution emulsion, it is about 0.05 μm . The thickness of a high-speed emulsion layer is typically about 7 μm , and the layer may hold 500 million grains per square centimeter of film surface (Vincett, 1987, p. 463).

Jewelry and Silverware

The jewelry and silverware sector accounted for one-third of the 8,944 t of silver consumed in the world in 2001. Consumption ranged widely from country to country, as shown in figure 2; consumption by the principal fabricating countries is shown in figure 5. Separate figures for consumption in each of the three subcategories (jewelry and arts, sterlingware, and electroplated ware) are available only for the United States (table 5). In 2001, the three subcategories accounted for approximately the same amounts of silver, each equivalent to 2 percent of U.S. total silver consumption.

Jewelry and Arts

Silver has several properties that make it a natural choice for a jewelry and decorative material. It has unmatched whiteness and luster and excellent workability and is highly resistant to corrosion. It alloys readily with gold, copper, and many other metals; this allows a variety of alloys from which to select the ones best suited to the mode of jewelry or artcraft manufacture, the desired degree of durability and chemical inertness, and the desired appearance of the manufactured item. Finally, it is a precious metal that possesses intrinsic market value in addition to the artistic value that is added to it in transforming it into an item of jewelry or decorative art. This last property is especially important in those parts of the world where jewelry is not only an item of adornment, but also a kind of portable wealth, convertible to money when desired.

Some jewelry is made from pure silver. The need for durability, however, usually dictates the use of an alloyed form of silver. The alloy most widely used in silver jewelry is sterling silver, which is 92.5 percent

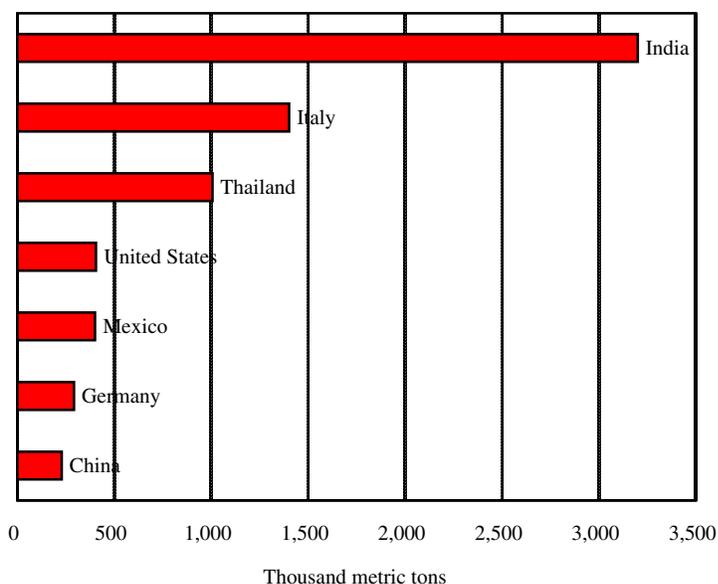


Figure 5. Silver used in jewelry and silverware by principal fabricating countries in 2001; these countries accounted to 78 percent of the world total. Source: Silver Institute, 2002, p. 81-82.

silver and 7.5 percent copper. Sterling silver has excellent working characteristics and yet is sufficiently hard and abrasion-resistant to be durable. The other alloys commonly used in jewelry making are silver-copper alloys—britannia silver (95.84 percent silver, 4.16 percent copper), coin silver (90 percent silver, 10 percent copper), and European silver (83 percent silver, 17 percent copper). The addition of copper, however, makes these alloys prone to react with sulfurous gases in the atmosphere to form a surface film of tarnish. The tarnish is easily removed by periodic cleaning and is not a major impediment to the appeal of silver items. In addition to the silver-based alloys, silver is an important component in several gold-based jewelry alloys. As mentioned in the “Description” section, some yellow and green golds contain as much as 35 percent silver, and the precious metal solders used in assembling jewelry pieces also contain silver.

Consumption of silver in jewelry and the arts in the United States in 2001 was 152 t.

Sterlingware

Sterlingware can be divided into flatware (that is, forks, spoons, and knives) and hollowware, such as bowls, coffee pots, and pitchers. Flatware is made through a combination of machine operations and hand craftsmanship. After a given item, a teaspoon for example, has been designed, craftspeople replicate the design in three dimensions and make the production dies. Spoon blanks are punched out of flat strips of sterling silver of the appropriate weight, thickness, and width. The blanks are thickened at desired points along the spoon by swedging and rolling. The blank is then annealed, and the pattern is impressed upon it. Excess silver squeezed out between punch and die is trimmed away, and the piece is finished and buffed by hand (MacFarlane, 1967, p. 322-330).

Much more handcrafting is involved in the manufacture of hollowware. Hollowware pieces are shaped by spinning, stamping, drawing, and casting operations. Parts are joined together by silver soldering. Much of the decoration is done by hand, involving such operations as embossing, chasing, etching, and oxidizing. As an example of the amount of work required to produce hollowware, Hallowell (1967) cited the 149 separate operations and 29 hours of skilled labor required to make a Renaissance style coffee pot.

Consumption of silver for sterlingware in the United States in 2001 was 143 t.

Electroplated Ware

Silverplate is an economical alternative to sterling flatware and hollowware. It possesses the beauty of sterling, but not its durability; its typical lifetime is sometimes given as 20 to 30 years of service, but the lifetime depends on frequency and conditions of use. Although silver can be electroplated on several metals, the commonly used substrates for tableware are brass, copper, and nickel silver.

Alkali cyanide plating baths are used for silver; these are almost always potassium cyanide, although sodium cyanide is used for silver strikes (very thin first-layer platings deposited on bare base-metal substrates under conditions of low silver ion concentration and high current density). The cyanide serves to complex the silver, thus restricting the silver ion concentration to levels conducive to the slow deposition of a smooth, continuous coating of non-granular silver. In making the bath, the required stoichiometric weight ratio is 2:1 silver cyanide to potassium cyanide. Cyanide in excess of the stoichiometric requirement, however, is usually used to prevent too-wide swings in silver ion concentration. Bath additives, such as potassium thiosulfate or carbon disulfide, which are called brighteners, help make the silver coating smoother and brighter. The silver anodes must be of high purity, better than 99.90 percent silver. Two grades are commonly used—99.90 plus (regular grade) and 99.95 plus (A.A. grade).

Product specifications for silver plate flatware are usually stated in terms of weight of silver for a set quantity of any given item. For example, Orr (1967) listed, in troy ounces of silver per gross of teaspoons, half plate (1 troy ounce), standard plate (2 troy ounces), double plate (4 troy ounces), triple plate (6 troy ounces), quadruple plate (8 troy ounces), and Federal specifications (9 troy ounces). These six grades cover a range of silver thickness from 3.8 to 32 μm (0.00015 to 0.00125 inch). In addition, many specifications require extra silver on wear spots, such as the tines of forks. He also listed hollowware hotel specifications, which are stated in terms of pennyweights

of silver per square foot, as follows: light plate, 2 pennyweights; medium plate, 5 pennyweights; heavy hotel plate, 10 pennyweights; extra heavy hotel plate, 15 pennyweights; and Federal specification plate, 20 pennyweights. These five grades cover a range of silver thickness from 3.2 to 32 μm (0.000125 to 0.00125 inch).

Consumption of silver for electroplated ware in the United States in 2001 was 124 t.

Coins and Medals

Coinage

Since the late 1970s, and even earlier in many countries, newly minted official silver coins have not been intended for use as circulating money. Some of them are intended for investment in silver in small increments; they are “bullion coins” whose intrinsic value in silver bullion equivalents can and often does depart significantly from the legal tender value. Others are commemoratives, minted to memorialize individual persons, sporting events, animals, or other objects or events of public interest. They are essentially medallions fabricated by or for national mints.

Since the mid-1980s, consumption of silver for U.S. official coinage has typically ranged from about 200 to 300 t/yr. In 2001, the United States and Germany accounted for well over one-half of the silver used for official coinage in the world (Silver Institute, 2002b, p. 69).

Coins, Medallions, and Commemoratives

The items in this category are typically intended as small investment items or as collectables. The subjects for collectables range widely; for example, wildlife to automobiles, guns, organizations, persons, places, and events. The “coins” referred to in this use category are not official coins and not legal tender; they are privately minted and are sometimes called rounds or medallions. Several silver refiners produce their own small fine silver bars or ingots in 1-, 5-, 10-, and 100-troy ounce sizes.

The U.S. Bureau of Mines Minerals Yearbook published consumption of silver in the United States for items in this category from 1971 through 1987. From 1988 through 1991, the Silver Institute included consumption for these items by country in its “Industrial Uses” category and after 1991 in its “Coins and Medals” category. As a counter to inflation, the items in this category were in demand as small investment goods by the U.S. public in the 1970s and early 1980s. U.S. consumption grew very rapidly in the early 1970s to 667 t in 1974; by the 1980s, it had subsided and fluctuated around the 100-t/yr level. In the 1990s, it ranged typically from about 40 to 50 t/yr.

Industrial Uses

This category includes all uses except photography, jewelry and silverware, and coins and medals. The 10 leading fabricating countries for industrial uses are shown in figure 6.

Bearings

Silver sleeve bearing liners were developed during World War II to cope with the high-stress loads encountered in high-performance military aircraft engines. The fatigue resistance of silver used as a bearing liner (that is, its ability “to withstand repeated applications of stress and strain without cracking, flaking, or otherwise being destroyed”) (De Bruyne, 1967, p. 446) is superior to that of other bearing metals. Its strength or load capacity also is excellent as are its thermal conductivity and corrosion resistance.

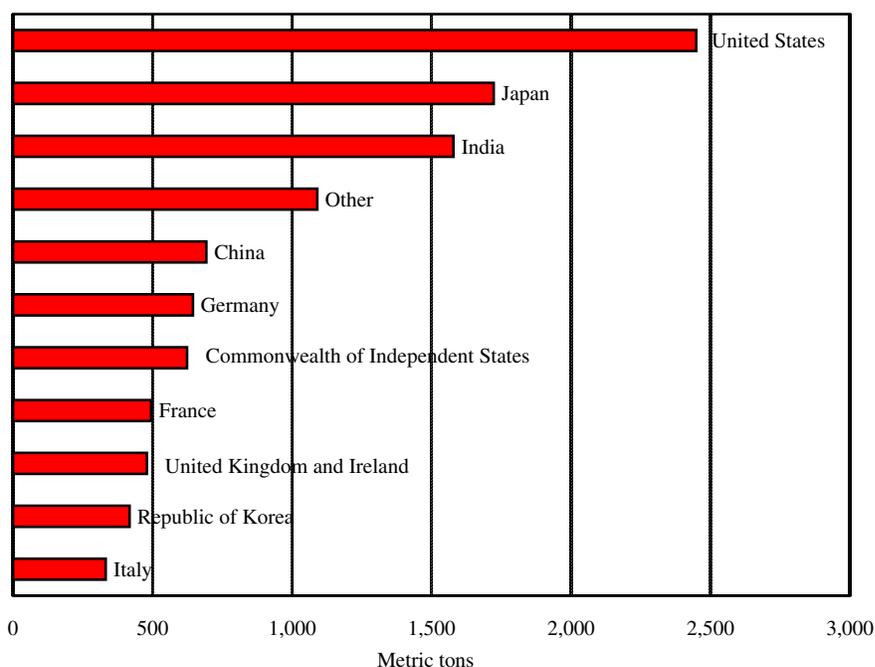


Figure 6. Silver used in industrial applications by principal fabricating countries in 2001; these countries accounted for 90 percent of the world total. Source: Silver Institute, 2002, p. 77-78.

In early trials, however, silver was not satisfactory when used alone as a bearing liner. The following reasons for this failure were identified: it failed to satisfactorily trap and embed dirt particles so that they did not score the journal or shaft, its ability to resist galling or seizing of bearing and shaft under dry start-up conditions was poor, and its ability to flow plastically and permit conformance between shaft and bearing contours was poor. Then it was discovered that a very thin overlay of lead-indium, lead-tin, or lead-tin-copper corrected these deficiencies and allowed the considerable advantages of silver to be realized. The silver/lead combination bearing became and remains the ultimate bearing for use in high-performance applications, such as in reciprocating aircraft engines, turbines, and heavy-duty diesel railroad engines. Silver has also been used as plating on bearing cages for roller or ball bearings for the main shafts of gas turbine engines (De Bruyne, 1967; Roskill Information Services Ltd., 1992, p. 307).

In manufacture, the silver layer of a sleeve bearing is sometimes bonded to the steel backing by heating under pressure or by casting but is usually deposited by electroplating. The steel is first plated with a microlayer (strike) of nickel, then silver of at least 99.75 percent purity is plated to a thickness of 0.5 to 0.75 μm (0.020 to 0.030 inch), and this, in turn, is plated with the lead alloy overlay to a thickness typically of about 0.025 μm (0.001 inch) (De Bruyne, 1967).

Current (2003) figures for the consumption of silver for bearings are not available. For the United States, figures from the 1970s and 1980s suggest that domestic consumption is in the range of 5 to 15 t/yr.

Brazes and Solders

Joining alloys that liquefy above 450° C are termed brazes; those that liquefy below 450° C are solders. In brazing and soldering, the joining metal must wet the metal pieces to be joined, but it is also required that it not alloy with them appreciably. Of the 20 or more metals with which silver forms solid solutions, several are used in brazes and solders for joining metals in which silver has only limited solubility. Thus, silver-containing brazing alloys and solders are used to join ferrous and several nonferrous metals, and boron, carbon (graphite), germanium, iridium,

magnesium, selenium, silicon, and tellurium. They also are used for joining powder-metal parts, ceramics, cermets, and dissimilar pairs, such as nonferrous to ferrous metals and metals to ceramics (Etris, 1997, p. 174).

Silver contributes ductility, wettability, high thermal conductivity, and tensile strength to brazing and soldering alloys. Silver brazes wet base metals at temperatures well below the melting points of the base metals and thus avoid overheating the parts being joined. The compositions of the silver alloys that are used as brazes and solders is discussed in the “Description” section. Silver is also present in smaller amounts in some lead- and tin-based low-temperature solders where it promotes fluidity and wettability (Chamer, 1967, p. 387-388).

World consumption of silver for brazing alloys and solders in 2001 was 1,128 t, of which the United States (258 t), China (215 t), and Japan (109 t), accounted for about one-half (Silver Institute, 2002b, p. 79).

Catalysts

Although silver metal and silver compounds are used as catalysts for a variety of oxidation, reduction, and polymerization reactions, most of the silver used for catalysts each year is accounted for by two large-scale industrial processes—the production of ethylene oxide and of formaldehyde.

Ethylene is oxidized by flowing a mixture of ethylene and oxygen (or air) over silver-coated ceramic granules or other large-surface-area forms, such as pumice, at 200° to 250° C. The product, ethylene oxide, is an intermediate petrochemical used to produce ethylene glycol and other organic compounds. The various products derived from ethylene oxide are used in automotive engine coolants (ethylene glycol), in the production of polyester resins, and in solvents and detergents.

Most formaldehyde is synthesized from methanol by using silver as a catalyst. In this process, a mixture of methanol and air is passed over the catalyst at 500° to 600° C. The catalyst is a silver screen, silver crystals, or a combination of the two forms. The gaseous products are absorbed in water and yield an aqueous solution of methanol and formaldehyde. The methanol is then removed by distillation and recycled. Formaldehyde is used in the production of various thermoset resins that are used for bonding plywood, particle board, and other wood products and for many other plastic products, such as computer cabinets and electric junction boxes (Pickhart, 1967; Cappel, 1997, p. 190-191; Etris, 1997, p. 168).

In the United States, about 190 t of silver went into catalysts in 2001. Figures for other countries or the world are not available.

Dental and Medical Uses

Between 1966 and 1990 (the only years for which separate U.S. silver consumption figures were published for this category), annual dental and medical uses showed a flat trend but fluctuating in a range of 45 to 90 t in the 1960s and 1970s and then in a narrower range, 45 to 55 t, in the 1980s. Nearly all of the silver probably was and is used for dental materials, especially amalgams, and that relatively little is used for medical purposes. No separate data are available for this category for other countries or the world.

Dental Uses

Most of the silver used in dental restorative work goes into the silver-mercury amalgams used to fill cavities in carious teeth. Dental amalgams have been used extensively since the late 1830s and remain the dominant material used for fillings (Etris, 1997, p. 177). In addition to having antibacterial properties, they are durable, able to withstand the strongly corrosive environment of the mouth, and the high stresses experienced by teeth in chewing. In clinical practice, the powdered amalgam alloy and the liquid mercury must react (amalgamate) quickly (3 minutes) to form a smooth plastic mass, remain plastic for the several minutes needed by the dentist to pack it into the cavity and express and remove excess mercury, and remain carveable for several more minutes while the dentist shapes and smooths the filling. It must then set up quickly, expand slightly as it solidifies so as to grip the cavity

wall securely, and within about 2 hours develop sufficient strength to withstand mild chewing forces (Tesk and others, 1993, p. 974). In service, it must not corrode appreciably or tarnish and must remain intact for several years.

Conventional dental amalgam alloys typically contain 66.7 to 75.5 percent silver, 25.3 to 27.0 percent tin, 0 to 6.0 percent copper, and 0 to 1.9 percent zinc. The packed amalgam, from which excess mercury has been squeezed, usually contains 50 percent or less mercury. One of the phases in these conventional amalgams—the tin-mercury phase ($\text{Sn}_{7.8}\text{Hg}$), which is called the gamma-two (γ_2) phase—is susceptible to corrosion. In the past two decades, a series of copper-rich amalgam alloys have been developed from which the γ_2 phase is absent or nearly so. In addition to being more corrosion resistant, the amalgams made from these non- γ_2 alloys, compared with conventional amalgams have appreciably higher compressive strength and low creep. The non- γ_2 alloys typically contain 42.2 to 70.3 percent silver, 17.7 to 30 percent tin, 12 to 27.8 percent copper, and 0 to 0.3 percent zinc (Tesk and others, 1993, p. 975).

Nearly all the dental alloys used in making bridges, crowns, orthodontic braces, and, in some countries false teeth, are gold-based. Silver, however, is an important component in most of them. The silver content of the group of cast alloys ranges from about 3 to 30 percent; that of the wrought alloys, from single digit percentages to more than 40 percent; and that of dental solders, from 3 to 35 percent (Roskill Information Services Ltd., 1992, p. 297).

Medical Uses

Silver serves several important functions in medicine, among which are the following:

- Silver nitrate and colloidal silver preparations are widely used as antiseptics, particularly for minor infections. The nitrate is effective but in strong solutions causes irritation of flesh. Colloidal forms are less harsh. Colloidal silver solutions consist of tiny particles of insoluble silver compounds, such as halides or the oxide, encased in protein protective colloids and suspended in a liquid medium. For example, one widely used silver halide preparation contains 18 to 22 percent colloidal silver iodide. Some protein colloids are “strong” formulations; one commercial preparation contains 7 to 8.5 percent silver in largely ionized form and is, therefore, quite active antiseptically. Typical of “mild” protein colloids is one that contains 19 to 23 percent silver as oxide particles in a gelatin colloid. Because only a small part of the silver is ionized, the preparation is not irritating and, in fact, is soothing. It is effective nonetheless and has the further advantage that the silver ion concentration remains nearly constant when the preparation is diluted by body fluids (Crannell, 1967).
- A one-time application of a 1-percent solution of silver nitrate to the eyes of newborn babies is routinely made, and in some countries mandated, to prevent neonatal ophthalmia, which is a conjunctivitis that occurs in the first few weeks of life and that can lead to blindness. Alternatively, either erythromycin or tetracycline may be used for this purpose (Canadian Paediatric Society, 2002).
- Sticks of fused silver nitrate, which has been known for centuries as “lunar caustic” and sometimes contains additions of potassium nitrate, are used for the removal of warts and the caustic treatment of surface ulcers. Alternatively, a 10- to 20- percent solution of silver nitrate is used.
- Silver sulfadiazine is a highly effective antiseptic and is used widely in the topical treatment of serious burn injuries (Silver Institute, 1997).

Electrical and Electronic Uses

The Silver Institute (2002b, p. 79) listed 21 countries in which silver was fabricated in 2001 for the uses in this category (in which batteries are grouped with contacts and conductors). Of the 4,123 t of silver fabricated, the United States accounted for 26 percent; it and the next largest fabricators in descending order, Japan, Germany, France, and China, accounted for 73 percent.

Batteries

Silver batteries, compared to many other batteries have the advantage of higher energy density but the disadvantages of higher cost and shorter life. They are used in satellites and spacecraft, and in military weapons,

such as missiles and torpedoes. The smallest ones are used extensively to power small electronic devices (Donahue, 1967, p. 155).

Most of the silver batteries in use are of the primary (nonrechargeable) type. Use of the secondary (rechargeable) silver oxide-zinc battery is largely limited to military and space applications. Primary silver batteries of several types are in service. Small silver oxide-zinc 1.5-volt button cells are used extensively in electronic devices, such as calculators, cameras, hearing aids, and watches. More than 1 billion silver button cells are manufactured each year, but each typically contains only 0.1 to 0.2 gram of silver. They are characterized by a higher energy density than mercury button cells, a very flat discharge voltage, good voltage regulation, good low temperature performance, good shock and vibration resistance, negligible leakage and salting, and good shelf life (Donahue, 1967, p. 169; Shimizu and Uetani, 1984).

The larger primary silver batteries tend to be used in military equipment in which they must be capable of being stored for long periods of time (years) in the inactive dry state and then activated very rapidly when required. The following silver-metal battery systems are used: silver oxide-zinc, silver oxide-cadmium, and silver chloride-magnesium. In batteries of the first two types, the electrolyte is stored in a separate chamber. The battery is activated remotely by very rapid pressurized flooding with electrolyte. For use in weapons, such as torpedoes, the battery must be fully operational within seconds. The silver oxide-cadmium batteries compared with silver oxide-zinc batteries have lower energy densities but longer life; they are used to a lesser extent than silver oxide-zinc batteries. The silver chloride-magnesium battery is activated by flooding it with either seawater or freshwater, which serves as the electrolyte. Water may be forced through the battery, as is done with torpedo batteries, by the rapid movement of the torpedo through water, or the battery plates may be immersed in water and kept there during operation; if the battery is constructed with highly absorbent plate separators, it can be removed from the water for use (Donahue, 1967, p. 165-179).

Other silver batteries are either restricted to highly specialized uses, such as the use of lithium/silver chromate batteries for pacemakers in Europe, or are still in the developmental stage. The U.S. Navy reportedly has tested silver-iron deep-discharge secondary batteries. Lithium/silver tungstate and sodium/silver tungstate batteries have also been developed. Lithium/silver selenate and lithium/silver tellurate batteries have been researched, but there has been little commercial interest (Roskill Information Services Ltd., 1992, p. 287-288).

Silver batteries are manufactured in several countries, but the United States and Japan are the two largest producers. U.S. consumption of silver in batteries in 2001 was about 165 t. A figure for world consumption is not available.

Contacts and Conductors

In the United States, the use of silver in this category is perhaps split about 50-50 between electrical and electronic uses. Electronic uses include not only contacts and conductors in the sense in which they are discussed below, but also the use as conductive layers in multilayer ceramic condensers.

Contacts, conductors, and connectors are used to connect electrical and electronic circuits and devices to one another. The term "conductor" is usually applied to such items as bus bars, cables, wires, or the conductive lines bonded to a printed circuit board. Connectors are junction devices that are assembled or disassembled when the circuits they are to join are inactive. They provide either a fixed connection where the separate components are soldered, brazed, welded, or crimped together or a separable connection where the components are held together by mechanical means and can be separated or connected with minimal effort. Examples of the separable connection type are cable clamp connectors for electrical circuits and pin connectors for electronic components. Contacts are the mating components in switches, relays, and circuit breakers—devices used to interrupt or to enable current flow in active circuits. The brushes and slip rings used in some types of electric motors and generators are also contacts (Antler, 1994, p. 38-60).

Copper and aluminum are the metals of choice for heavy current conductors because they are highly conductive, readily available, and relatively cheap. Silver is too expensive to use as a heavy current conductor and is sparingly used for small diameter wire but is widely used in the printed circuitry of electronics devices. The

conductive pathways of printed circuits are formed from thick-film pastes of mixed silver and glass powders in a liquid vehicle, screen-printed on the substrate, and then dried and fused.

Thick-film pastes are also used to form the conductive sheets of multilayer condensers. An estimated 40 percent of the silver used by the electronics industry goes into thick-film pastes (Etris, 1997, p. 176). Silver is also used on a small scale as the sheathing metal on so-called high temperature ceramic oxide superconductor cables, which are being installed in several test projects in the United States (Silver Institute, 1998, 2001).

The primary reason for the use of silver in connectors and contacts is its chemical inertness toward oxygen and other gases and chemicals in its working environment, and, hence, its resistance to corrosion and to the formation of poorly conductive or nonconductive oxide and sulfide surface films. Although silver alloys readily react with ambient sulfur to form a tarnish film, the film is readily pierced by the electric current and disrupted by the wiping motion of the contacts as they close. In addition to its excellent electrical and thermal conductivities, silver is valued for its suppression of arc erosion and welding (sticking) of contacts.

The main mechanical structures of circuit breakers, relays, and switches provide strength and/or springiness; they form the base onto which silver contacts are fastened or plated. The structural metals commonly used are copper and several of its alloys, iron and tin-plated steel, aluminum, and nickel. The contact metals, which are usually alloyed, are gold, indium, nickel, palladium, platinum, silver, and tin (Roskill Information Services Ltd., 1992, p. 277).

An estimated one-half of the silver used in contacts in the United States goes for use in the devices that control electric motors (Roskill Information Services Ltd., 1992, p. 278). Timers and thermostats are representative of the many other control devices in which silver contacts are used. Although it is not widely used for high-speed sliding contacts in electric motors, small amounts of silver may be added to copper contacts to improve conductivity. Silver-copper and silver-palladium alloys are used in some small motors.

The most widely used of the silver alloys and composites for electrical contacts are listed in table 6. The most widely used of these materials is the silver-cadmium oxide composite. Silver electrical alloys have been discussed in the "Description" section.

Along with several other metals, silver has been used as an electrically conductive filler material in plastics. These plastics have been used in electronic equipment for static charge drain and for electromagnetic shielding.

Because silver reacts so weakly with oxygen that little heat is generated by the reaction, silver will not sustain combustion. This spark-suppression property contributes to safety in electrical circuitry and machinery. Parts made of silver contribute to safety in oxygen-rich environments, such as in space vehicles, where friction between moving parts might tend to generate sparks (Etris, 1997, p. 168).

The consumption of silver in the fabrication of contacts and conductors in the United States in 2001 amounted to about 920 t. A figure for world consumption is not available, although silver probably constituted at least 90 percent of the 4,123 t attributed to the whole "Electrical and Electronics Uses" category.

Table 6. Widely used electrical contact alloys and composites

[---- Zero. Source: Roskill Information Services Ltd., 1992, p. 280]

Silver (weight percent)	Alloy material	
	Name	Content (weight percent)
100	None	----
96.5	Copper	3.5
96	Carbon	4
90	Nickel	10
90	Cadmium oxide	10
70	Palladium	30
60	Nickel	40
50	Tungsten	50

Mirrors

Silver's very high reflectivity and flat spectral response make it the reflector of choice for mirrors. Although some mirrors are made by metal vapor deposition in a vacuum, most silvered glass mirrors are made by a process that has remained fundamentally unchanged since its development in the mid-19th century. A dilute ammoniated aqueous solution of silver nitrate is brought together on the glass surface with an aqueous solution that contains a mild organic reducing agent, such as formaldehyde, hydrazine, invert sugar, or Rochelle salts. The ammonia in the silver solution serves to complex the silver, which keeps the concentration of free silver ions low to slow the reduction rate and thus avoid the deposition of granular silver.

Modern large-scale mirrormaking takes place on a conveyORIZED production line under carefully controlled conditions. The surface to be silvered is first cleaned thoroughly by polishing with a metal oxide rouge and then cleaned with deionized water and dried. Next, it is sprayed with a stannous chloride solution and then rinsed with deionized water and dried. This leaves a thin continuous layer of stannous ions adsorbed on the surface; their function is to initiate reduction of the silver at numerous points, which creates nuclei onto which the rest of the silver grows and forms a continuous sheet free of pin holes. Next, the silver solution and the reducer solution are sprayed onto the prepared surface from separate nozzles and mix on the surface. After deposition of the silver is complete, the surface is rinsed again with deionized water and then covered with a thin coat of copper precipitated from sprays of copper solution and a reducer that mix on the surface. The copper functions as a sacrificial protective coating. Additional protection is provided by one or several coats of a mirror-backing paint (Pohl, 1967; Venkateswaran, 1998).

Nearly 80 t of silver was used in the United States in 2001 for mirrors. Figures are not available for other countries or the world

Other Uses

In addition to the uses described above, silver has a number of other uses that are technologically important. Consumption statistics for the individual uses are not readily available, and individually, they account for relatively small quantities of metal. Collectively, however, they are significant. In the United States in 2001, other uses accounted for more than 600 t of silver, or 10 percent of total silver consumed (table 5). Three of these uses are described below.

- Silver-impregnated activated carbon filters are widely used to purify and improve the taste of drinking water at the point of use. These filters remove most of the chlorine from municipal drinking water, and the silver functions as an effective bactericide against several common disease-causing strains. Electrolytic systems that use silver-copper electrodes are used to treat swimming pool water. In the absence of these silver systems, swimming pool water must be heavily chlorinated, which results in discomfort to the swimmers and, in the case of indoor pools, corrosion (from exsolved chlorine gas) to building structures. Silver also competes effectively with chlorine in the treatment of the cooling water used in large-building air-conditioning systems; the treatment is used to suppress the organism that causes the type of pneumonia called legionnaires disease.
- Silver-coated glass is used in automotive vehicles to reflect the sun's rays, thus reducing the load on air-conditioning systems and reducing the fading of interior fabrics and finishes. Electrically heated coatings and conductive lines are also used to remove frost and condensation from windshields and rear windows. Silver-coated glass is also used in the windows of buildings to reduce heat loss in cold weather and the solar radiation heat load in warm weather.
- An 80 percent silver, 15 percent indium, and 5 percent cadmium alloy is one of the two most commonly used control rod materials in nuclear power reactors of the pressurized water type. A rough estimate put the amount of silver used in these reactors in 1991 at more than 400 t (Roskill Information Services Ltd., 1992, p. 302-304). As rods have been replaced routinely at the end of their service lives during the past two decades, the silver-indium-cadmium rods have tended to be replaced with boron carbide (B_4C) rods. Data are not published for the amount of silver, if any, still being required for replacement rods of the silver-indium-cadmium type.

Use as an Investment Good

Early in history, silver, like gold, was a durable store of wealth and was used as money. Since the 1970s, its monetary use has largely disappeared, and it has become almost entirely an industrial metal. Investment demand and producer hedging now absorb less than 3 percent of the world's supply of newly mined silver. Silver jewelry is regarded as an investment in some countries. Other small items of investment include the bullion coins, commemoratives, and small bars of fine silver discussed above in the subsection "Coins and Medals." World net investment in silver bullion in 2001 was estimated to be about 522 t, or about 1.9 percent of total market supply; this had been preceded, however, by 11 years of net disinvestments (Silver Institute, 2002b, p. 70).

Trends in Use

Projected growth and decline rates for the consumption of silver for individual end uses and groups of end uses from 2001 to 2010 are listed in table 7. These are straight-line extensions of regression lines drawn through the most recent distinct growth regimes, as nearly as these regimes can be identified from semilogarithmic plots of consumption over time.

The use of silver in photographic materials is subject to many influences in addition to the considerable overall influence of economic climate. Factors that favor the continued growth of silver consumption in photography include but are not limited to the following:

- High-resolution. A typical 35-mm slide frame contains about 20 million pixels (picture elements) compared with 6 million or 7 million pixels captured by high-end megapixel digital cameras.

Table 7. Projected consumption of silver for fabrication, by end use

[NA, not applicable. ~, approximately. Except in consumption trend line column, data are rounded to three significant digits; because of independent rounding, data may not add to totals shown. Based on data from U.S. Bureau of Mines and U.S. Geological Survey Minerals Yearbook]

	Regression data span (years)	Actual consumption in 2001 (metric tons)	Consumption trendline in 2001 (metric tons)	Projected consumption in 2010 (metric tons)	Annual growth rate for 2001-2010 (percentage)
United States:					
Batteries	1985-2001	165	164	218	4.9
Bearings	NA	⁽¹⁾	10	10	~0
Brazes and solders	1993-2001	264	285	343	2.3
Catalysts	1996-2001	190	194	233	2.2
Coins, medallions, commemoratives	1977-1987	⁽¹⁾	75	60	-1.8
Contacts and conductors	1988-2001	918	904	1,130	3.2
Dental and medical uses	1981-1990	⁽¹⁾	48	48	0
Electroplated ware	1984-2001	124	128	149	2
Jewelry and arts	1966-2001	152	129	112	-1.6
Photographic materials	1992-2001	2,038	2,250	2,840	3.1
Mirrors	1997-2001	78	71	76	0.9
Sterlingware	1984-2001	143	166	202	2.8
Other uses	1993-2000	622	501	679	4.2
Total, noncoinage uses		4,695	4,792	5,982	2.5
Official coins	1988-2001	275	247	250	0.1
Total, all fabrication uses		4,970	5,039	6,232	2.4
World:					
Industrial uses	1985-2001	10,529	10,604	12,320	2
Jewelry and silverware	1996-2001	8,944	8,842	10,075	1.5
Photography	1990-2001	6,539	6,837	7,218	0.6
Coins and medals	1986-2001	846	911	894	-0.2
Total, all fabrication uses		26,858	27,194	30,507	1.3

¹Included in "Other uses."

- Modestly priced conventional cameras yield photographs that are as good as or better than photographs produced by the far more expensive megapixel digital cameras.
- The great popularity during the past decade of one-time-use cameras and of the advanced photo system (APS) films and cameras.
- Excellent and proven archival quality of silver halide films and prints.
- Low power requirements for battery-powered conventional cameras, compared with power-hungry digital cameras.
- The growing use of silver printing processes to print the output of digital cameras.

Factors that can work against the continued growth of silver halide photography relate mostly to the fast-growing popularity of digital systems. Digital cameras are well suited for certain uses, such as in various graphics arts applications and in journalistic photography where rapid electronic transmission of digital image files from the scene of action to the point of use is important. Digital cameras are also favored by those photographers who process their pictures on a computer, select the ones they wish to keep, and print them on a color printer or store them on compact discs. Although rapid growth of digital imaging systems is expected, they are starting from a very small base; of the 1.6 billion cameras in use in 2001, only about 39 million, or 2.4 percent, were digital (Silver Institute, 2002b).

The consumption of silver for photography is projected to grow through 2010 at about 0.6 percent per year in the world and 3.1 percent per year in the United States.

World consumption of silver for jewelry and silverware was down around the 1,500-t/yr level during the years of high silver prices (1980 to 1984). It then climbed rapidly during the next 10 years, finally leveling off at from 8,000 to 9,000 t/yr in the mid-1990s. It is projected to grow slowly through 2010.

In the United States, consumption of silver for jewelry, as a separate category, has shown little, if any, evidence of having been influenced by the silver price; presumably it has been affected mainly by changes in fashion. During the past three decades, the price has ranged between about 60 and 400 t/yr and, despite doubling in the 1990s, it has shown a slow decline during the three-decade period as a whole. The slow decline is projected to continue through 2010.

After declining since the 1960s mainly because of competition from stainless steel flatware, the use of silver in electroplated ware in the United States leveled off in the early 1980s and began a slow climb. It is projected to continue to grow modestly through 2010. Sterlingware followed much the same course as electroplate but has been growing a little faster. It is projected to continue to grow through 2010.

World use of silver in coins and medallions climbed from lows of less than 100 t/yr in the early 1980s to the vicinity of 900 t/yr by the mid-1980s; in most of the years thereafter, it ranged between about 750 and 1,000 t/yr, trending downward very slightly. It is projected to decline a little through 2010. In the United States, silver consumption for the category Coins, Medallions, and Commemoratives was reported from 1971 through 1987 by the U.S. Bureau of Mines. The data points are scattered, but it appears to have slowly declined from 1977 through 1987; this decline has been projected, with low confidence, through 2010. After dropping precipitously from the mid-1960s to the late 1970s, the use of silver in official U.S. coinage climbed and then stabilized in a range of about 150 to 300 t/yr. It is projected to be essentially static through 2010.

Industrial uses of silver, which include all uses not discussed above in this subsection, is the largest use category in world silver statistics. World consumption for this category has followed a steady upward course since the mid-1980s, and growth is projected to continue through 2010. For the United States, seven of the uses in this category will be covered separately below.

Consumption of silver in batteries has been growing briskly since the mid-1980s.

It is expected to continue growing through 2010 as the volume of electronic devices grows.

Data on the use of silver in bearings, which are used primarily in high-performance aircraft and railroad engines, was published by the U.S. Bureau of Mines in its Minerals Yearbooks from 1966 through 1987. Silver consumption ranged between 5 and 20 t/yr during that period. In projecting consumption, it was assumed that this well-established niche market could still account for about 10 t/yr of silver in 2010.

After declining from about 600 t/yr in the 1960s, the consumption of silver in brazes and solders leveled off in the 1980s in the vicinity of 200 t/yr, and then began climbing in the 1990s. It is expected to continue to grow slowly through 2010.

Consumption of silver for catalysts was characterized by substantial swings in the 1960s and 1970s but stabilized in the early 1980s and began growing rapidly in the mid-1980s. The growth rate leveled off in the mid-1990s, and it is this flatter rate that is projected through 2010.

The use of silver in electrical contacts and conductors has ranged between about 600 and 1,200 t/yr since the 1960s. It was at the lower end of the range at the beginning of the 1990s but then began growing briskly. It is projected to grow at an intermediate rate of a little more than 3 percent per year through 2010.

Silver used for dental and medical purposes ranged between about 45 and 95 t/yr in the 1960s and 1970s and between about 45 and 55 t/yr in the 1980s; no data are available for the years after 1990. Consumption in this category appears to be essentially static. Zero growth is projected through 2010.

The consumption of silver for mirrors has ranged between about 20 and 140 t/yr since the 1960s. It was nearly flat during the 1980s at 30 to 35 t/yr, began climbing in the 1990s, and leveled off in the late 1990s at about 80 t/yr. It is projected to increase slowly through 2010.

The consumption of silver for the "Other Uses" category has been erratic since the 1960s because the uses content of the category has changed from time to time. From 1993 to 2000, however, the makeup of the category was stable, and the growth rate was also stable. Consumption through 2010 is projected at the 1993-2000 rate.

World consumption of silver for all fabrication uses, which includes official coinage, is projected to grow through 2010 at about 1.3 percent per year. Growth in the United States is projected to be a little faster at 2.5 percent per year.

Substitutes

Many nonsilver batteries can substitute for silver batteries, but not in all uses, and usually at a cost in performance or price. The same is true of brazes and solders, except that in some instances the substitution will be partial; that is, the substitute braze or solder will still contain silver but less of it. Copper, gold, platinum alloys, zinc, and other metals can be substituted for silver in coins and medals. Aluminum, copper, gold, palladium, platinum, and several refractory metals can replace silver completely or partially in electrical and electronic uses. Acrylic and other polymers and some of the newer amalgam alloys that contain less silver (the non- γ_2 alloys) can replace conventional silver-mercury amalgams as dental fillings. Tantalum can be used in place of silver for surgical pins, plates, and sutures. Stainless steel and silver electroplate can replace sterling silver in tableware. Silverless black and white film, film and papers with reduced silver content, and xerography can reduce silver use for some photographic applications. Aluminum and rhodium can replace silver in mirrors.

Industry and Market

About three-fourths of the world's mined silver, which amounted to 18,700 t in 2001, is a byproduct of base-metal and gold mining at several hundred mines. The other one-fourth of the total is produced at silver mines, that is, produced from silver ores. Of these silver mines in 2001, the 15 largest accounted for 86 percent, and the 2 largest, Cannington in Australia and Proano in Mexico, accounted for 40 percent of the silver recovered from silver ores. Of the companies that operate silver-producing mines of all kinds, the 20 largest producers accounted for 52 percent of silver mined in the world in 2001 (Silver Institute, 2002b, p. 19, 86).

In the United States in 2001, silver was produced from precious-metal ores at 30 lode mines and from base-metal ores at 24 lode mines. The majority of these mines are located in the Western States. Less than 1 percent of domestic silver was produced at placer mines. Only two domestic mines, Galena and Lucky Friday, both in Idaho, mined silver ores. A

third Idaho silver mine of long standing, the Sunshine, was closed permanently early in the year. The 32 leading domestic silver-producing mines listed by Hilliard (2002, p. 70.15) accounted for virtually all domestic production in 2001. Of these 32 mines, 2 mined silver ores, 15 mined gold ores, 7 mined copper and copper-molybdenum ores, 6 mined lead and lead-zinc ores, and 2 mined zinc ores. About 1,300 mine and mill workers were engaged in the production of domestic silver in 2001.

Silver is extracted from its ores and sometimes refined, at least partially, at base-metal smelter/refineries. At gold mines, gold-silver doré bullion is the usual product. The crude silver produced at these base-metals plants and at gold mines is usually shipped to precious-metals refineries for refining to commercial-grade silver bullion. In the United States, 22 principal refiners of commercial-grade silver operated in 2001 with an estimated output of 2,800 t of primary silver and 1,700 t of secondary silver. Most of these refineries were concentrated in the eastern and western seaboard States, which are nearer to the silver fabricating industries than to the silver mines.

Thousands of artisans and companies fabricate silver, but the bulk of silver consumption is accounted for by a relatively small number of companies. For example, in the United States, which uses about 20 percent of the world's silver, about 30 companies consume more than 90 percent of the silver. Extrapolation of those figures suggests that perhaps 100 to 150 large companies located in industrialized countries may consume 60 to 65 percent of the world's silver, while thousands of medium- and small-sized companies, shops, and individuals, mostly engaged in silversmithing, jewelry manufacture, and the decorative arts, consume the remainder.

Metal traders of the world lists 104 silver bullion traders worldwide (Moreno, 1997, p. 586-589). In addition, 70 firms trade in doré, and 39 trade in semimanufactured forms of silver, such as sheet, strip, tubing, and wire. These are overlapping lists because many traders deal in more than one form of silver. The number of separate companies is also a little smaller than might be inferred from the above numbers because some of the larger traders have subsidiaries in several countries. Because the international trade in precious metals is so extensive, most silver traders can be assumed to be importers/exporters as well.

Although there is a sizable international market in silver-containing raw materials, the movement of a large part of the contained silver is not documented in trade statistics. The trade recorded for the 60 percent of the world's silver derived from base-metal deposits is that of the silver carriers (the base-metal concentrates, copper matte, lead bullion, and anode slimes), but the silver content is seldom stated.

By contrast, the movement of silver through the markets for silver bullion, semifabricated forms, and fabricated products, which also are international, is well documented in trade statistics. The cost of transportation in these markets is no impediment to international trade, being small in relation to the value of silver. Like gold bullion, silver bullion is being traded somewhere in the world at virtually every hour of the day. Silver is purchased by buyers from banks, bullion dealers, mining companies and refiners. Some of the silver bullion is shipped to the buyers, but some remains in the seller's storage vault after the transfer of ownership is documented. Some of the stored bullion may be shipped on a predetermined schedule or as the need arises, but other bars may remain in the vaults indefinitely, sometimes passing through several changes in ownership. Principal silver trading centers include Bombay, Hong Kong, London, New York, Shanghai, Singapore, Tokyo, and Zurich.

Futures trading in silver bullion is active around the world at commodity exchanges in such cities as Chicago, Hong Kong, London, New York, Tokyo, and Toronto. Over-the-counter and Exchange silver options are also traded in several of these cities.

Silver and the Environment

Most silver compounds, aside from those containing toxic anions, such as arsenate or cyanide, are essentially nontoxic. Compounds that dissociate in solution and provide significant concentrations of free silver ions can be toxic to bacteria and to freshwater aquatic organisms, but compounds and complexes in which the silver is tightly bound, such as silver sulfide and thiosulfate complexes, are innocuous. Nonetheless, a few other silver compounds must be handled with care. Strong silver nitrate solutions, for example, are caustic and highly irritating to eyes, mucosa, and skin (Cappel, 1997, p. 188).

The presence of silver in payable quantities does not appreciably change the environmental issues associated with the mining and processing of silver-bearing base-metal ores. Its presence in gold ores, however, can significantly increase the quantity of cyanide required to leach the ores. Procedures for dealing with environmental issues in mining and metallurgical extraction are well known and used, at least in the developed world. Most of the silver released into the environment comes from the manufacture and use of silver-containing products, of which the most important by far in this respect are photographic materials.

For economic reasons, virtually all the silver in spent thiosulfate photographic processing solutions is routinely recovered. The waste-water effluent from the recovery processes typically contains only from 0.1 to 20 mg/L of complexed silver (Cappel, 1997, p. 189). Microorganisms at waste-water treatment plants convert more than 90 percent of this to silver sulfide with some metallic silver; these insoluble products settle into the treatment plant sludge. Most of the remainder, which is discharged from secondary waste-water treatment plants, is tightly bound to sediment particulates, and does not subsequently enter the ground water (Thailand Environment Institute, undated).

Silver has no known physiological function in humans (Faust, 1992, p. 1). Most of the silver that enters the human body is breathed in or ingested in foods; a lesser amount enters through the skin. Some health problems have been experienced in the past by chemical workers who manufacture silver compounds, such as silver nitrate and silver oxide, and are exposed to dust that contains high levels of these products. Their symptoms included breathing problems, irritation of throat and lungs, and stomach pain (Agency for Toxic Substances and Disease Registry, 1999). Chronic exposure to silver and silver compounds can lead to the deposition of silver-protein complexes in body tissues. When deposited in the skin, these cause a permanent bluish-gray discoloration, which is termed "argyria." This is viewed as a cosmetic problem only; it appears to have no other adverse effect on health. In a related condition, argyrosis, silver is deposited in the conjunctiva and cornea of the eye; in some cases, it may impair night vision (Faust, 1992, p. 2; Cappel, 1997, p. 188). Effective workplace hygiene has made occupational argyria and argyrosis uncommon today. "Tests in animals show that silver compounds are likely to be life-threatening to humans only when large amounts (that is, grams) are swallowed, and that skin contact with silver compounds is very unlikely to be life-threatening" (Agency for Toxic Substances and Disease Registry, 1992).

In the United States, the level of silver in drinking water is not regulated, but the U.S. Environmental Protection Agency recommends that to avoid possible skin discoloration, silver should not exceed 0.01 mg/L. The Occupational Safety and Health Administration limits silver in workplace air to 0.01 milligram per cubic meter (mg/m³) for an 8-hour workday, 40-hour workweek. The American Conference of Governmental Industrial Hygienists recommends that workplace air contain no more than 0.1 mg/m³ metallic silver and 0.01 mg/m³ soluble silver compounds (Agency for Toxic Substances and Disease Registry, 1999).

Supply, Demand, and Sustainability

World consumption (fabrication) of silver ordinarily outstrips what is sometimes termed "conventional" supply (mine production plus metal recycled from old scrap). The supply deficit is offset by sales of private and Governmental bullion stocks and by producer hedging. Individual countries may augment supply with net imports of silver. In the past decade, mine production has accounted for 60 to 67 percent of total annual world supply; secondary metal from old scrap, 19 to 23 percent; and bullion stocks and producer hedging, the remainder (Silver Institute, 2002b, p. 70).

The variable gap between conventional world supply and consumption for the past two decades is shown in figure 7. The record high silver prices of the late 1970s through the peak year of 1980 depressed consumption and increased the amount of scrap proffered to refiners, which led to surpluses during the 1980s. In the decade ending in 2001, the more usual supply deficits prevailed.

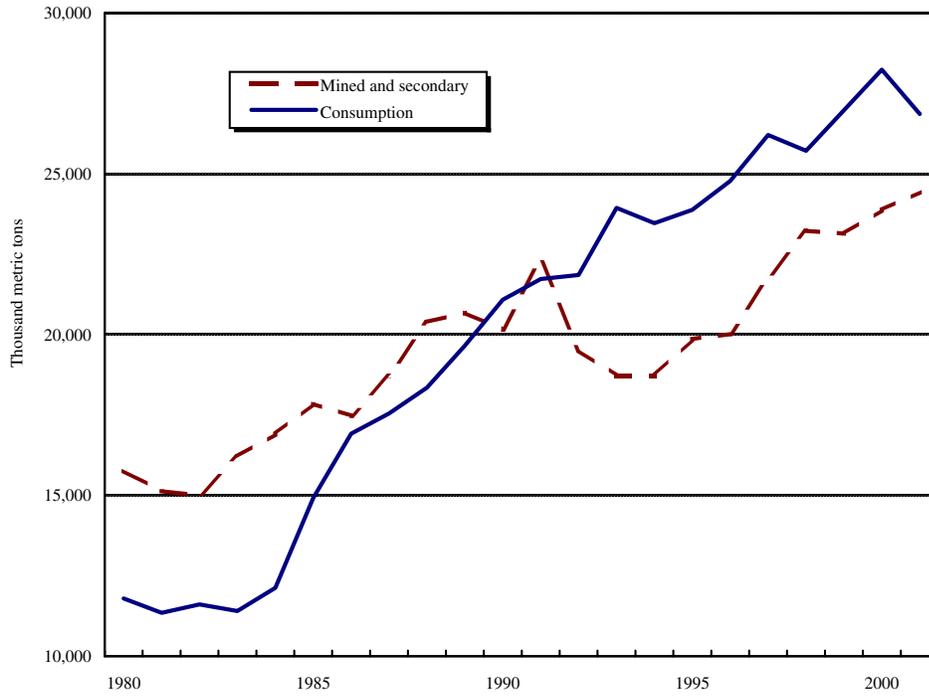


Figure 7. World silver supply and consumption from 1980 to 2000. Source: U.S. Bureau of Mines and U.S. Geological Survey Minerals Yearbook; Silver Institute World Silver Survey.

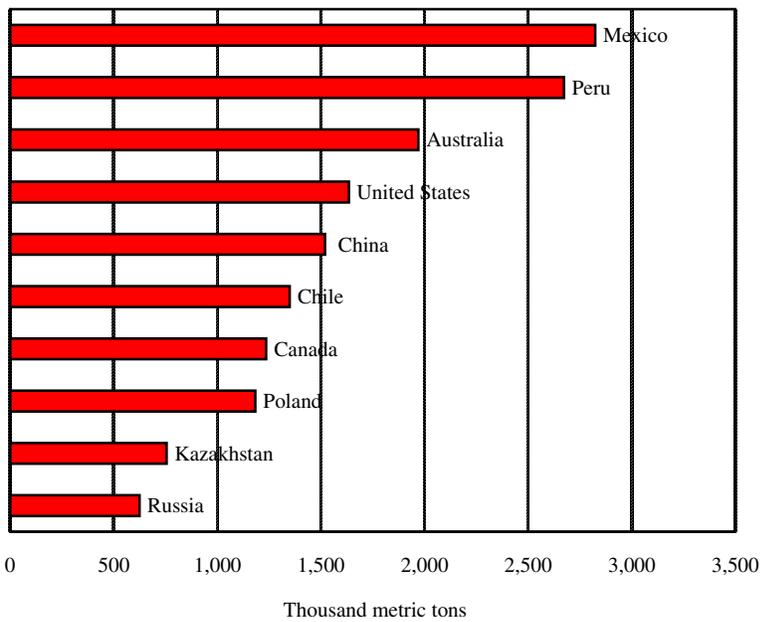


Figure 8. Ten leading silver mining countries in 2001; these countries accounted for 86 percent of world production. Source: Silver Institute, 2002, p. 71-72.

Current and Past Supply and Demand

According to the Silver Institute (2002b, p. 71-72), a total of 18,351 t of primary (newly mined) silver was mined in 47 countries in 2001; the USGS credits 18,700 t to 60 countries. The 10 leading producing countries accounted for 86 percent of the total (figure 8). At 1,635 t (USGS, 1,740 t), the United States was the fourth largest producer. World supply (27,381 t) comprised the 18,351 t mined plus 5,739 t from old scrap, 2,666 t from government sales of bullion, and 634 t from producer hedging. World demand, which is calculated to match the supply, consisted of 26,859 t of fabricated silver and an implied 522 t of bullion purchased by investors.

U.S. silver supply and demand for 2001 are shown in figure 9. U.S. supply and demand for selected years in the 36-year period ending in 2001 are listed in table 5.

Salient observations with respect to the United States include the following:

- Supply—Year-to-year fluctuations and lower levels in the 1980s notwithstanding, the overall trends in refined production and its primary and secondary components have been relatively flat. Both the primary and the secondary components of refined production were important throughout the period. Primary production ranged between 25 and 37 percent of total U.S. supply; secondary production ranged between 7 and 34 percent.
- Supply—Imports of refined bullion became an important component of silver supply in the early 1970s and

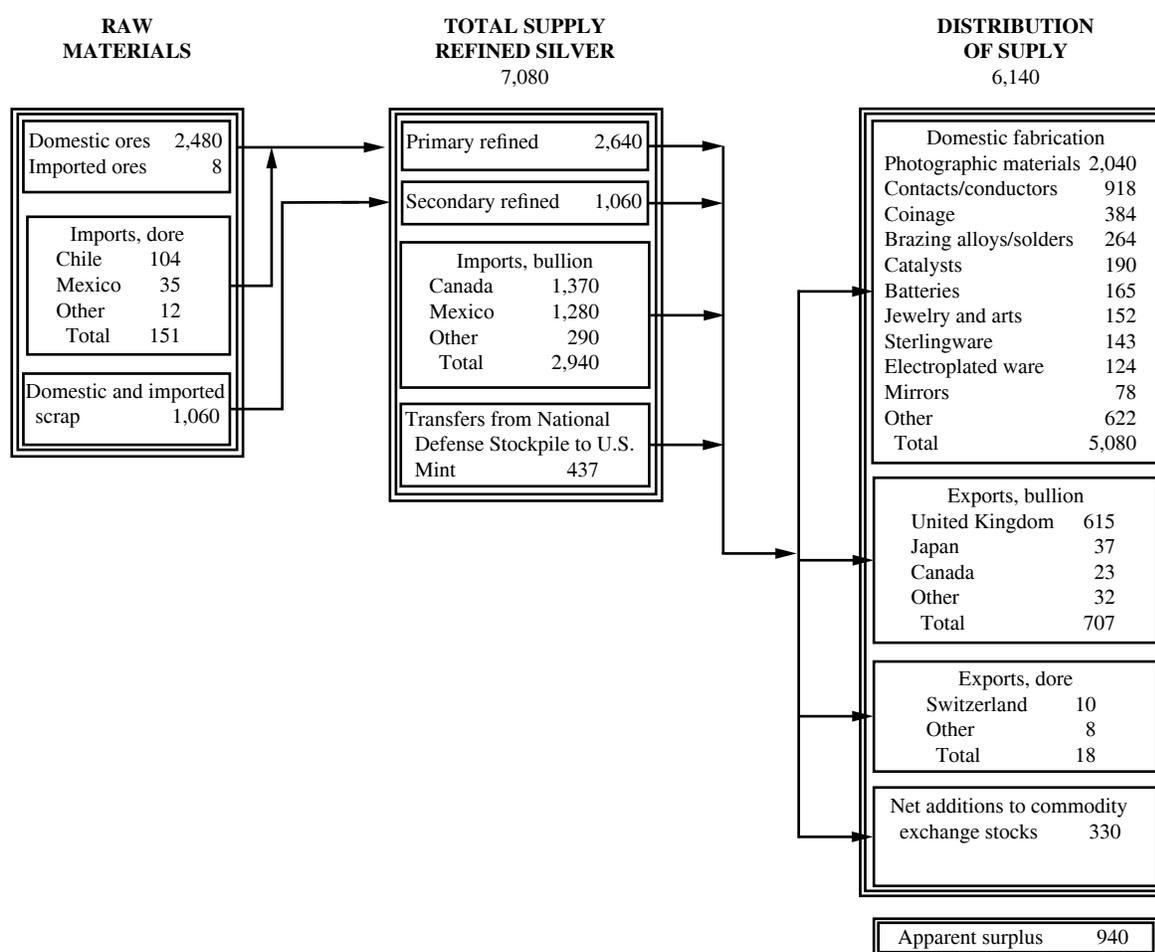


Figure 9. Supply and demand of silver in the United States in 2001. Figures are in metric tons of contained silver. Data on foreign trade in manufactured products are excluded, and other trade data are incomplete. All data are rounded to no more than three significant digits; because of independent rounding, components may not add to totals shown.

accounted for at least 30 percent of total supply thereafter. The United States has normally been a net importer of refined silver during the period covered in table 5.

- Supply—Deliveries of U.S Treasury stocks were very important in the years of peak coinage demand in the mid-1960s but relatively unimportant thereafter. Deliveries from the U.S. Government stockpile contributed little to supply in most years. Deliveries from Commodity Exchange stocks were substantial from 1993 through 1998.
- Distribution—After dropping precipitously from about 14,000 t/yr (at the time of the spike in coinage fabrication in the mid-1960s) down to about 4,000 t/yr in 1970, total consumption recovered partially in the early 1970s but then drifted downward to the vicinity of the 4,000-t/yr level where it remained through the 1980s. Beginning in 1994, consumption began climbing rapidly, at about 5.8 percent per year, through 2000.
- Distribution—Photographic materials have been the largest single component of silver consumption since 1967 and have accounted for 40 to 50 percent of the total since the late 1970s. Contacts and conductors have been the next largest component and have accounted for 16 to 23 percent of consumption each year through the 1990s. All other individual uses have accounted for single-digit percentages of consumption.
- Distribution—Net additions to Commodity Exchange stocks were substantial from the mid-1970s through 1992.
- Distribution—Exports of refined bullion have been a significant component of total distribution in most years and have ranged from single-digit percentages to as high as the 40-percent level in the mid-1990s. Exports of doré were always very small.

Potential Supply

The Silver Institute estimated that world identifiable silver bullion stocks at yearend 2001 were 18,444 t. This total comprised 9,207 t held by European dealers; 5,288 t, by world Governments; 3,266 t, by Comex; and 684 t, by “other” commercial entities. Unidentified, bullion stocks exist, but their size is not known. Also unquantified is the amount of silver in fabricated goods that would be offered on the market as scrap, in addition to what is already recycled routinely every year, in times of silver shortages or high prices. Presumably only silver in jewelry, sterlingware, coins, and medals would be readily available.

During the decade ending in 2001, identifiable bullion stocks declined by more than one-half. Government and Comex stocks each declined by about two-thirds. The seemingly imminent disappearance of some of these above-ground stocks has brought predictions by some market participants of higher silver prices in the not too distant future. The adequacy of mineral resources of silver in the United States and the world through 2010 is listed in table 8.

Strategic Considerations and Sustainability

Silver has so many industrial uses in which it is indispensable or at least difficult to substitute for, that it is essential to the U.S. economy and defense. In 2001, the United States relied on imports for about 44 percent of its silver requirements. In the event of a shortage, production increases at domestic silver mines could be made possible by higher silver prices; most domestically mined silver, however, is a byproduct of the mining of other metals and, thus, not very responsive to changes in the price of silver.

Sustainability of the production of silver is largely contingent on the sustainability of copper, gold, and

Table 8. Adequacy of silver resources, in metric tons through 2010

[In metric tons]	United States	World
Reserve base, yearend 2001	75,000	430,000
Reserves, yearend 2001	30,000	280,000
Projected fabrication demand for mined silver, 2001-2010 ¹	16,900	187,000

¹Newly mined silver is assumed to account for about 30 percent of the U.S. market supply and 65 percent of the world market supply as in the 1990s.

lead mining and processing. These activities appear to have no serious impediments to in the United States or most other countries. Likewise, the continued use of silver in all its applications will probably not cause any serious environmental or health problems.

Economic Factors

The yearly average silver price fell by 21 percent from 1998 to 2001, and this affected the profitability of silver mining. For 2001, the Silver Institute (2002b, p. 28) surveyed a representative sample of the world mining operations that accounted for the one-fourth of silver mined as a principal product, and for which mine production was costed on a per unit silver basis. It found that cash costs ranged from \$2.17 to \$5.14 per troy ounce, with a weighted average of \$3.10. With the average spot silver price for the year at \$4.37, about 1 in 10 of the mines in the sample had cash costs that were higher than the silver price. With respect to total production costs (taken from a different sample), about one-half of the mines had costs that were higher than the silver price.

The other three-fourths of world silver mine production was a byproduct of the mining of base metals and gold. The costs of finding ore deposits, developing mines, and producing this fraction of output are commingled with the costs of producing the principal metals and are not readily separable.

U.S. mine producers are granted a depletion allowance of 15 percent on their domestic operations and of 14 percent on their foreign operations. These allowances are percentages of income from mine production that are considered to be returns of capital and, thus, not subject to income tax, a recognition that ore deposits are depletable assets. Unwrought silver, whether refined or unrefined, may be imported into the United States duty free. About 1,100 mine and mill workers were employed in domestic silver production in 2001.

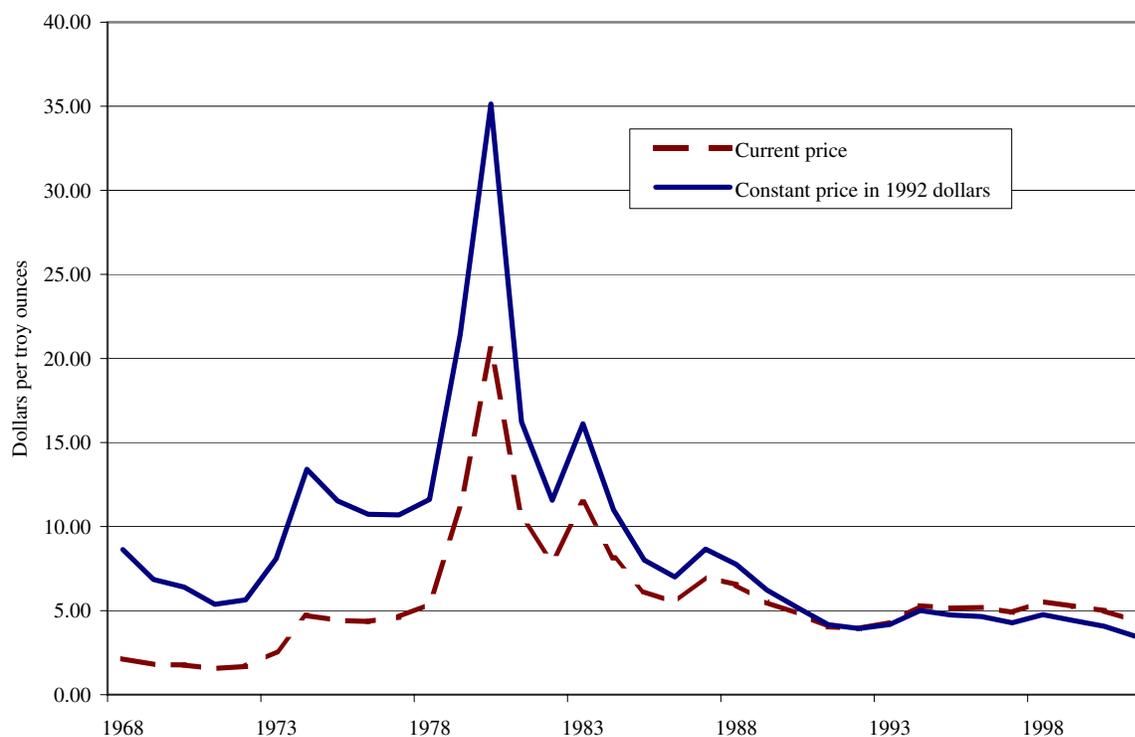


Figure 10. Annual average price of silver in the United States since the demonetization of silver. New York prices are for 99.9 percent-pure silver. Data from Hilliard, 1998, p. 142.

Silver is an expensive metal, and as such, is used only where there are significant advantages in doing so. In some applications, such as brazes and solders and electrical contacts and conductors, the cost of silver is an important component of the cost of the product. If the price goes too high, ways will be actively sought to economize on the use of silver. In other applications, such as jewelry (in the developed countries) or dentistry, quite a large price rise is required to elicit such a response. For the past decade, the price of silver has hovered between about \$4.00 and \$5.50 per ounce, and price movements within that range have probably had only a minor effect on demand. Annual average silver prices in the United States since the demonetization of silver are shown in figure 10.

Outlook

Total world consumption of silver is expected to continue to grow slowly, at a little more than 1 percent per year, through the first decade of the 21st century. Consumption for industrial uses will grow faster, at about 2 percent per year. Supply from mines, postconsumer scrap, and bullion stocks should be more than adequate to satisfy demand, although a higher silver price may be required to draw sufficient postconsumer scrap and unidentified bullion stocks into the market.

Total U.S. consumption of silver for fabrication is expected to grow at about 2.4 percent per year through 2010. Consumption for batteries, electrical contacts and conductors, photographic materials, sterlingware, and "other" (miscellaneous) uses are expected to grow faster than total consumption, whereas consumption in the nine other use categories will grow more slowly, and of these, coins, medallions, and commemoratives, and jewelry and arts may decline slowly. Supply from mines, old scrap, imports of bullion, and bullion stocks should be ample to satisfy demand.

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- Silver. *Mineral Industry Surveys*, monthly and annual
- Silver. Ch. in *Minerals Yearbook*, v. I, annual

Other Publications

- American Metal Market, daily
- Engineering and Mining Journal, monthly
- Metal Bulletin, weekly
- Metal Bulletin Monthly
- Mining Engineering, monthly
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- Mining Record, weekly
- Platts Metals Week, weekly
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Appendix

Definitions of Resources, Reserves, and Reserve Base

The term “resources,” as applied to metals, refers to those concentrations of metal-bearing minerals in the Earth’s crust that are currently or potentially amenable to the economic extraction of one or more metals from them. “Reserves” and “reserve base” are subcategories of resources. “Reserves” refers to the in-place metal content of ores that can be mined and processed at a profit given the metal prices, available technology, and economic conditions that prevail at the time the reserves estimate is made. “Reserve base” is a more inclusive term that encompasses not only reserves proper, but marginally economic reserves and a discretionary part of subeconomic resources—“those parts of the resources that have a reasonable potential for becoming economically available within planning horizons beyond those that assume proven technology and current economics” (U.S. Bureau of Mines and U.S. Geological Survey, 1980).