Kirk-Othmer Encyclopedia of Chemical Technology.

SILVER AND SILVER ALLOYS

1. Silver and Silver Alloys

Silver [7440-22-4], is indispensable for today's technology because of its unique combination of exceptional physical, electrical, optical, and bactericidal properties. It is considered a noble metal because of its resistance to oxidation; thus it finds special use in oxygen-rich environments. It is a powerful oxidant and because it is chemically active, will tarnish in polluted atmospheres. Tarnish affects only the optical properties of silver.

In its physical properties, silver possesses the highest known electrical and thermal conductivity and the second highest thermal reflectivity of any metal. Its halide salts are unusually sensitive to light. Only gold exceeds silver in ductility and malleability.

In its optical properties, silver has the highest visual light reflectivity of any metal and is therefore used to reflect solar energy into collecting systems. It has been used for mirrors since ancient times. Silver has become the preeminent material for coating glass for energy-saving, transparent, thermally reflective windows. Its long-wavelength infrared radiation reflectivity is second only to that of gold.

Silver chemistry is almost entirely in the univalent state. However, in the presence of a strong oxidizer, silver can be prepared in a trivalent state with markedly increased chemical avtivity.

Silver was among the earliest metals worked by human because it is found in its native state. Archaeologists have found evidence that by about 3000 BC a form of cupellation (a bath of molten metal mixture subject to a stream of air which oxidizes the base metals into dross) was in use in Asia Minor, providing nearly pure silver (1).

Analysis of Greenland ice shows that lead levels in the Northern Hemisphere rose hundreds of times beginning about 500 BC and continued at that level for the next 800 years, confirming substantial smelting of silver-rich ores found at Laurium, Greece (2). These mines are still active. The rarity and beauty of the metal led to its becoming trade metal. By 560 BC, silver coins were standardized by weight to become a working medium of exchange. Silver coins instead of paper currency continues to be preferable for transactions especially in less developed countries.

Historical records show that the bactericidal value has long been recognized. Herodotus reports that Cyrus the Great, King of Persia (550–529 BC), who established a board of health and a medical dispensary for his citizens), had water drawn from a designated stream, then "boiled, and very many four wheeled wagons drawn by mules carry it in silver vessels, following the king whithersoever he goes at any time" (3). Pliny the Elder reported in his *Natural History* (78 AD) that the slag of silver "...has healing properties as an ingredient in plasters, being extremely effective in causing wounds to close up..." (4).

Since ancient times silver vessels have been used in Mexico, the world's major producer of silver, to keep water and milk sweet. The application of silver nitrate to inhibit venereal disease attack on newborns eyes during birth 1881, became a legal requirement throughout the industrial world (5). The use of silver sulfadiazine to eliminate bacterial contamination in burn wounds has been universal since its introduction in 1970 (6, 7).

In today's world of electrical appliances and conveniences, silver provides reliable, safe, long lasting electrical switches and relays in the home, commercial buildings, automobiles, ships, airplanes, and keyboards of computers. The technological development of a country can be measured by its industrial consumption of silver.

The range of research in which silver plays a significant role as reported in the scientific literature may be reviewed in abstracts, numbering about a thousand each year, in *Silver Chemistry*, CA Selects, a bimonthly publication of the American Chemical Society, (8).

2. Occurrence

Silver is found in all continents, but its largest quantities are located along the cordillera of the western Americas from Alaska to Bolivia. Silver is associated with intrusive volcanic deposits of Tertiary age transported by hydrothermal action. The bonanza silver districts of Potosi in Bolivia, Guanajuato and Pachuca in Mexico, and the Comstock lode in Nevada fall in this region.

Native silver is rare, occurring notably in Kongsberg, Norway and Cobalt, Ontario, Canada, where great slabs of nearly pure silver are found. Silver is often associated with native gold, copper, and zinc ores. The principal ores of silver are the sulfides associated with lead, antimony, arsenic, and copper. Galena, a lead sulfide, is a common source of silver (9).

2.1. Silver Exploration

A direction of silver exploration focuses on, locations where silver-rich hydrothermal fluids may have spread far from a fault. This is called epithermal (lower temperatures and shallower deposition) silver mineralization. Traditional exploration has centered on the mesothermal (higher temperatures and deeper deposition) mineralization seen at the major fault zones as in the case of Coeur d'Alene, Idaho. Epithermal deposits, such as the Carlin type in Nevada are spread far away from the fault and have very low precious-metal values. A combination of modern open pit mining with low-cost heap or dump cyanide leaching has made working of these low grade deposits economically viable.

Potential epithermal silver deposits located in the American cordillera are being exploited in southern California, southern Arizona, Montana, and Nevada. In the early 1980s, the first significant open-pit silver-gold mine came into production in Delmar, Idaho, and what became the largest open-pit silver mine in the world was opened near Zacatecas, Mexico. Opportunities to explore the "epithermal model" also exist in British Columbia and Quebec, Canada; El Indio, Chile; Caracoles and Charnacillo, Peru; and Nicaragua (10).

2.2. Silver Reserves

The known economically recoverable reserves of silver worldwide are located primarily along the American cordillera, in the Kazakhstan region of central Asia, and in Western Australia. The worldwide primary and by-product silver reserves in metric tons according to the U.S.G.S. (11) are listed in Table 1.

Approximately two-thirds of the world silver resources are associated with copper, lead, and zinc deposits. The remaining are either vein or epithermal deposits in which silver is a most valuable component.

2.3. Extraction

Economic extraction of silver from its ores is dependent upon the type and composition of the ore. Generally silver-bearing ores are milled, concentrated by froth flotation, then subjected to sodium cyanide leach followed by electrolytic refining.

Table 1. Worldwide Primary and by-product Silver Reserves, t

Country	Primary	Primary and by-product
United States	31,000	72,000
Australia	29,000	33,000
Canada	37,000	47,000
Mexico	37,000	40,000
Peru	25,000	37,000
Other countries	120,000	190,000
World total	*280,000*	*420,000*

Froth flotation mixes reagents that selectively float the silver-rich ore from the valuless fines. It enables economic separation of silver ore as a concentrate of high quality. An analysis of the chemical constitutiion of the ore is a requirement for the economical extraction of silver. For example, in some sedimentary ores an activated-type of carbon is present which tends to adsorb the silver or gold cyanide complex resulting in a loss of the metal in the tailings. In another example, the cyanidation of silver-bearing copper oxide ores is uneconomical, therefore other chemical treatments are required.

Alternatives to sodium cyanide, such as dimethyl sulfoxide and thiourea have been proposed, but their economics in the field have not been favorable to their use (12).

Some 60 silver minerals are known. The most important economically are argentite (Ag_2S) [1332-04-3], chloragyrite (AgCl) [14358-96-4], the telluride hessite (Ag_2 Te), polybasite (Ag_2SbS_6) [53810-31-4], prostite (Ag_3AsS_3) [15152-58-4], pyrargyrite (Ag_3SbS_3) [15123-77-0], and stephanite (Ag_5SbS_4) [1302-12-1] (13).

3. Properties

It is silver's unique combination of properties that has placed it at the forefront of essential metals for today's technologies. Chemically, it is less active than copper and does not exhibit corrosion. It does, however, react with atmospheric sulfur and hydrogen sulfide to form a soft black tarnish on exposed surfaces. Silver dissolves in oxidizing acids (eg, HNO_3) and in cyanide solutions in the presence of oxygen or peroxide.

3.1. Sensitivity to Light

For photography (which is the largest industrial use of silver) the reaction of silver halides with light is unique. Its effect is one of reduction (14), the silver ion is reduced to metallic silver and the halogen atoms reacting with the emulsion to make the process irreversible. The commercial production of multilayer films incorporating tabular silver halide crystals introduced in 1983 by Eastman Kodak resulted in emulsions of superior speed, definition, color saturation, and decreased light scattering.

Silver halides melted in glass are likewise reduced by exposure to sunlight. The resulting metallic silver crystallites darken the glass. On removal of sunlight the halides trapped by copper ions in the glass recombine with the metallic silver to form the original transparency of the colorless halides, a reversible process. Such glass can be formulated to provide a reduction in light transmission from 85 to 22% in less then 60 s in direct sunlight. Ultraviolet transmission can be reduced up to 97% (15).

The development of lasers that project light in the three basic colors, red, blue, and green, made possible the color hologram. Essential to the quality of the color holographic image is an ultra-fine grain silver halide film required to precisely record the laser-light wavefront reflected from the object illuminated by the three different color lasers (16). Color holograms have boosted holography to the forefront of three-dimension display technology.

Whole-body x-ray holograms provide physicians with three-dimensional interior views of the body, enabling the visualization of internal problems prior to operation. Essential to the definition of the color holographic image is the use of ultra-fine grained silver halide film (17).

3.2. Electrical Conductivity

Electrical and electronic uses account for over half of the silver used in industrial applications. Silver is the primary metal used in electrical distribution systems for electrical contact points in switches and circuit breakers where low-resistance and noncorrodible contacts are essential. This property eliminates overheating and thus the potential for fire. Although silver tarnishes, the tarnish film is soft and does not affect its electrical performance under all but the most polluted atmospheres (18). The high-performance silvercadmium oxide contact material used for high voltage switch contacts is being replaced by silver-tin oxide to avoid the health hazards of cadmium.

3.3. Silver Migration

The conditions under which silver migrates, principally under DC current, is well known (9). The problem is aggrevated when silver is used in microcircuitry.

3.4. Oxidative Capacity

Silver and its compounds are powerful oxidizers, recognized since ancient times for their clinical value. Silver has been used as an oxidation catalyst in gaseous reactions in the chemical process industry for nearly a century. The oxidation of methanol to ethylene oxide (a major building block for plastics) over silver is unique (19). In a new device, silver plated on alumina particles exposed to flowing water showed a 99% bacteria kill in a single pass over the silver in oxygen-charged water and a 100% kill in ozone-charged water. In water, however, a very weak bond is formed between silver and oxygen (approximately 7 to 8 kcal/mol) allowing the readily available oxygen to attack anymaterial it contacts (20).

3.5. Corrosion Resistance

ln the electromotive force series of the elements, silver is only less noble than Pd, Hg, Pt, and Au, all providing high corrosion resistance. Silver is not converted into its oxide (corrosion) on exposure to air. However, its highly reactive character results in the formation of a tarnish of black silver sulfides and chlorides on exposure to atmospheres rich in those elements (21).

3.6. Magnetic Susceptibility

The magnetic susceptibility of silver is very small, ca 0.2×10^6 Cgs units. However, although silver and cobalt are mutually insoluble, when ground together and fused they exhibit “giant magnetoresistance.” Changes in resistance as great as 50% are observed when a magnetic field is applied. The cobalt-rich precipitates in an silver-rich matrix are used in magnetic-tape read heads, sensing magnetism devices, etc (22).

Recently discovered, the magnetic properties of multiple-layer silver/nickel-iron alloy films, each about a millionth of an inch thick, are candidates for next generation read-out heads for personal computer storage systems. Not only do these new silver alloys exhibit extremely high changes in electrical resistance in response to infinitesimally small magnetic signals (giant magnetoresistance), but the films retain their physical dimensions unchanged despite the rapidly changing magnetic fields. Thus there is no unwanted shift in the location of the sensing function of the read head held over the spinning magnetic field of a personal computer’s hard drive (23).

3.7. Superconducting Electricity Transmission

The property of silver to permit the free flow of oxygen at room and higher temperatures and block the flow of oxygen at liquid nitrogen temperatures, combined with its high malleability and high electrical conductivity, has made silver the ideal encapsulant for the new high-temperature superconductors. These friable materials, mixtures of copper, barium, yttrium, other rare earth oxides, etc, exhibit zero electrical resistance at the temperature of easy-to-use liquid nitrogen (−195°C) which can be kept liquid by efficient mechanical refrigerators. [The first superconductors function only at the temperature of liquid helium (−276°C), an expensive gas requiring cumbersome equipment both to use and maintain.] The rare earth oxides require encapsulation to be fabricated. As only silver, gold, and platinum are compatible with these oxides, silver is the practical choice (24). High-temperature superconducting cable, motors, transformers, and electric power storage devices are designed for commercial service.

3.8. Ignition Suppression

Silver (alone with gold) does not ignite under oxygen. (Conversion to silver oxide must be accomplished by chemical or electrolytical means.) The formation of its weak oxide produces so little heat (14 J/g) that silver will not sustain combustion even if ignited (25).

Thermodynamically, silver exists only in the metallic state over 200°C; its oxides cannot exist over this temperature. It is this inactivity that provides silver with superior sparking and combustion resistance. Oxygen moves freely within the silver lattice, but cannot leave the surface until two oxygen atoms connect to form O_2, making possible an oxygen gun (26). At ∼300°C there is sufficient energy to form the oxygen molecule. Below this temprature silver is an efficient catalyst for gaseous oxidative chemical reactions (19).

3.9. Reflectivity

Silver has the highest visual light reflection of any metal (97%) and is second only to gold in its reflectance of infrared radiation. The near infrared transmission (at 2000 nm) for double-silver coated glass is nearly zero, whereas for clear glass transmission it is nearly 80%. The ultraviolet transmission (315–400 nm) for double-silver coated glass is 25% as against clear glass which is 71%. Transparent double coatings of silver sputtered onto window glass (known as low-E squared glass) effectively reject solar thermal radiation and conserve internal heat. It is the preferred treatment for thermal insulating windows (27).

The reaction of silver to laser stimulation results in a reflected signal over a million times stronger than other metals. Known as surface-enhanced Raman spectroscopy, this effect has been shown to be useful in catalysis (28).

3.10. Bearings

Silver stands as the ultimate bearing material, for it possesses the highest fatigue resistance, the highest corrosion resistance, and the highest thermal conductivity. It is used in the primary bearings of large diesel engines, large reciprocating aircraft engines, and applications where conventional lubrication will fail (temperature extremes and corrosive environments) (9).

Silver is widely used to prevent galling in bearings as it acts as a dry film lubricant because of its tendency for interplanar shear. It is also widely used as a seizing preventive wherever bearings may remain idle for long periods of time. On start-up the low shear strength of the silver surface permits instant response (29).

3.11. Malleability and Workability

Pure silver, like its Group Ib neighbors on the periodic table, can be rolled and drawn into fine wire. This property has made the production of high-temperature superconductors economical (9). Cold working results in rapid increases in strength and hardness and decreases in ductility, which is especially useful in the production of jewelry and giftware (9, 30).

3.12. Sanitation

The usefulness of the silver ion to inactivate bacteria has long been known. Its use for sanitizing drinking water purification systems, in swimming pool sanitation systems (31), for sanitizing farm animals, and in commercial installations such as air-conditioning cooling system towers, is worldwide. In contact with liquids, silverware and silver holloware provide sufficient silver ions to make the liquids bactericidal (31). Several possible antibacterial actions are postulated (32). Research shows polyvalent silver oxide ($2\ Ag^{3+}\ 2\ Ag^{1+}\ 4\ O^{2+}$) to be a powerful antibacterial and antivirus agents (33).

The properties of silver are summarized in Table 2.

Table 2. Properties of Silver

Parameter	Value	Reference
atomic mass, amu	107.8682	30
melting point[a], °C	961.93	30
electron structure	[Kr] $4d^{10}\ 5s^{1}$	30
isotopic abundant %		
106.9051	51.84	30
108.9048	48.16	30
atomic diameter, pm	288.3	30
ionic radius, pm	126	
crystal structure	fcc, Fm3m	30
lattice spacing, a_0, at 20°C	0.4078 nm	30
ionization potentials, eV[b]		
$Ag \rightarrow Ag^{+} + e^{-}$	7.574	34
$Ag^{+} \rightarrow Ag^{2+} + e^{-}$	21.960	34
$Ag^{2+} \rightarrow Ag^{3+} + e^{-}$	36.10	34
electrochemical potential[c], V	0.798	34
density, at 20°C, g/cm^3		
annealed	10.492	30
hard drawn	10.43	30
at 0 K	10.63	30
boiling point, °C	2187	21
recrystallization temperatue[d], °C	20–200	
tensile strength, 5-mm dia wire, MPa[e]		
annealed at 600°C	125–186	30
50% cold worked	290	30
elongation, 5-mm dia wire, % in 5.08 cm at 20°C, annealed at 600°C	43–50	
50% cold worked	3–5	5
electrical resistivity[f], ρ, Ω/m		
20 K	0.00422×10^{-8}	36
273.15 K (=0°C)	1.467×10^{-8}	36
500 K	2.875×10^{-8}	36
1235.08 K, sold	8.415×10^{-8}	36
1235.08 K, liquid[g]	17.30×10^{-8}	36
vapor pressure, Pa[h]		
684°C	10^{-6}	37

Table 2. ***Continued***

Parameter	Value	Reference
828°C	10^{-4}	37
1028°C	10^{-2}	37
1330°C	1	7
1543°C	10^{1}	37
1825°C	10^{2}	7
hardness, Brinell, kg/mm^2[i]	25–30	35
elastic constants, 0°C, GPa[j]		
C_{11}	131.15	30
C_{12}	97.33	30
C_{44}	51.1	30
elastic properties[k]		
Young's modulus at 20°C, GPa[i]	91.3	30
modulus of rigidity at 20°C, GPa[j]	26.9–29.7	35
Poisson's ratio, at 293 K		
annealed	0.364	30
hard drawn	0.39	
viscosity, molten, at 1043°C, mPa·s (=cP)	3.697	21
thermal neutron capture cross section, m^2	63×10^{-28}	38
Fermi energy, eV	5.52	30
Fermi surface, spherical	necks at $\langle 111\rangle$	30
work function, electrons		
thermionic, eV	3.09–4.31	21
photoelectric, eV	3.67–4.81	21

[a] A partial pressure of 20 kPa (2.9 Psi) O_2 results in a freezing point of ca 950°C.
[b] Electron volts, 1 eV = 1.602×10^{-19} J.
[c] For the equation, $Ag^+ + e^- \rightarrow Ag$.
[d] Depends on amount of dissolved oxygen and trace elements in solid solution in silver, plus cold work.
[e] To convert MPa to psi, multiply by 145.
[f] Total electrical resistivity of 99.999% pure or purer bulk silver. Impurities increase resistivity.
[g] Liquid 99.95% pure or purer.
[h] To convert Pa to mm Hg, multiply by 0.0075.
[i] At 20°C, annealed at 600°C
[j] To convert GPa to psi, multiply by 145,000.
[k] 1 Pascal = 10 $dyne/cm^2 = 1.45\times10^{-4}$ $lbf/in.^2$.

3.13. Supplies and Sources

Silver is mined in over 60 countries. In the United States silver has been produced in 27 states with over 99% of its production has been in the western states (Tables 4 and 5).

Of the newly mined silver entering the world market in 1999, over 77% was generated as a coproduct or by-product of lead zinc, copper, gold, ands other primary metal mines (39). The low price for silver in the recent past resulted in production slowdowns or closings of many primary mines. This reduced output was offset by increased by-product output from base metal production and gold mining. The present rise in price encouraged increased production from primary mines in the United States and South America. In the US this increase was somewhat offset by decreased output from U.S. gold mines due to lower gold prices.

Beginning in 1995, silver mine producers have forecast mine production increases for every year through 2000 to meet escalating demand, which jumped 14% between 1989 and 1996. Mine production rose 4% in 1996 alone. Although the increased annual rate of production will decline over the next four years from 6% in 1997 to 3% by 2000, silver production is projected to rise by about 10% by the turn of the century (40).

Table 3. Thermal Properties of Silver

Parameter	Value	Reference
thermal conductivity[a] at 0°C, W/(m·K)	418.7	30
linear coefficient of thermal expansion, m/(m·K)		
av 0–100°C	19.68×10^{-6}	
at 500°C	20.61×10^{-6}	30
specific heat, mean, J/(kg·K)[b]		
solid at 0°C	234	30
at 100°C	238	30
at 527°C	282	30
at 961°C	297	30
liquid at 961–2227°C	310	30
latent heat of fusion, J/g[b]	104.2	21
latent heat of vaporization, kJ/g[b]	2.636	
heat capacity, C_p, at 0–800°C, J/(g·°C)[c]	$C_p = 0.2320 + 0.06035 \times 10^{-4}\, t - 0.67896 \times 10^{-8}\, t^2$	21
thermal electromotive force vs NBS Pt 27 (NBS Standard), mV		
at 100°C	+0.76	35
300°C	+3.20	35
500°C	+6.50	35
700°C	+10.80	35

[a] $1\ \mathrm{W/(m{\cdot}K)} = 2.39 \times 10^{-3}\ \mathrm{cal/(s{\cdot}cm{\cdot}{}^{\circ}C)} = 0.578\ \mathrm{(Btu{\cdot}in.)/(h{\cdot}ft^2{\cdot}{}^{\circ}F)}$.

[b] To convert J to cal, divide by 4.184.

[c] Temperature, t, in °C.

Table 4. The Top Ten Silver Producing Countries in 1999, t[a]

Mexico	2339
Peru	2218
United States	1956
Australia	1720
Chile	1393
CIS	1377
China	1375
Canada	1166
Poland	1113
Bolivia	383

[a] Ref. 39.

3.14. Above Ground Stocks

Above ground stocks are critical to make up the deficit between mine production and fabrication demand. This deficit is satisfied by the use of recycled silver from scrap and drawing down stocks of bullion and coins. Industry estimates that for 1999, some 5440 tons of silver recycled from scrapped products and nearly 5179 metric tons from silver bullion stocks entered the market (39).

Silver bullion is marketed by international trading houses, and is traded on Exchanges such as the London Bullion Market the New York Mercantile Exchange Commodity Trading Market (COMEX Division), the Chicago Board of Trade, and the Tokyo Commodity Exchange. It is estimated that investors controlled about 6,000 tons of near-market stocks of silver in 1999, a decrease of over 33,000 tons over the previous 10 years. In a world market of increased home building, automobile production, and the manufacture of electric

Table 5. World Silver Mine Production, 1999, t[a]

Europe	1658
North America	5462
Central and South America	4164
Asia	715
Africa	442
Oceania	1751
Total	*14,190*

[a] Ref. 39.

appliances, electronic equipment, and battery driven devices, there is a consequent increase in the consumption of silver.

The rise in the price of silver after World War II made recovery of silver from scrap economically attractive. The U.S. Government fostered a program to recover silver from spent film and scrapped military equipment. Publications were issued by the U.S. Bureau of Mines in support of this program. The Eastman Kodak Company has issued brochures on techniques to recover silver from scrap film and from spent fixing solutions (41). The *World Silver Survey 2000* estimates that the world total recycled silver from all scrap during 1999 amounted to ca 5440 tons. A survey conducted by the International Precious Metals Institute in 1994 shows exports from the United States of precious metal bearing (including silver) secondary scrap material amounted to some 51,000 metric tons having a value of $914 million (42).

3.15. Imports and Exports

Imports of refined silver bullion into the United States amounted to 2,580 metric tons in 1996 and 2,120 tons in 1997, which almost matched exports of 2,900 tons in 1996 and 2,980 tons in 1997 (U.S. Geological Survey).

Imports for ores and concentrates plus dore and precipitates for refining in the United States on the other hand, significantly exceeded exports. These imports for refining amounted to 434 metric tons in 1996 and 426 tons for 1997. The exports for refining outside the U.S. amounted to 45 tons for 1996 and 100 tons for 1997, indicating economic advantages of refining silver in the United States. Principal international refineries are to be found in Switzerland, the United Kingdom, Belgium, Germany, Japan, Mexico, France, Peru, and Russia.

Waste and scrap imports into the United States were 1,810 metric tons in 1996 and 1,530 tons in 1997. Exports were 1,280 tons in 1996 and 1,020 tons in 1997 (U.S. Geological Survey).

3.16. Manufacturing and Production

Smelting and electrolysis are the processes by which the impure silver from mine production or from scrap metal concentrations is brought to acceptable purity. In electrolytic refining, impure silver is used as the anode and pure silver is deposited on the cathode in an electrolyte solution. The pure silver deposited as crystals on the cathode is scraped off and washed to remove retained electrolyte and becomes the starting point for the production of silver chemicals, silver alloys, and bullion.

3.17. Silver Powder

Fine silver particles are used to prepare microelectronic circuitry (such as electrodes for transistors in cellular telephones, fax machines, etc) and for electromagnetic shielding (45). Powders may be produced mechanically or chemically and are widely used in conductive adhesives, low-temperature drying conductors (membrane switches and capacitors, and fired conductors and thick film integrated circuits). Fine powder sizes can be controlled by adjusting a high-velocity jet of air impacting molten silver poured over the jet. Very fine silver particles are also produced by chemical precipitation from silver nitrate using reducing agents such as formaldehyde, sugars, hydrazine, etc. Colloidal particles are also produced by electrolysis of silver wire.

A new laser technique prepares nanometer-sized angular silver particles with sharp interfaces. The system patented by The Pennsylvania State University, State College, Pennysylvania, uses a high-power laser beam that impacts a metallic block immersed in a silver salt solution in a blender (45). The blender rotates the block to a high speed exposing fresh solution to a laser which blasts molecular-sized particles of silver from the solution. The output can be adjusted to control the size from 1 to 100 nanometers with a 10% variation. The silver particles generated by this technique are blocky and tend to fit or lock together, a particular advantage in thin film circuitry for electronic products permitting a reduction in the size of transistors. Experimental batches are being introduced into the market.

3.18. Silver Flake

Flake silver is prepared by ball milling silver powder in an organic vehicle containing a small amount of a polar, long-chain aliphatic compound to prevent cold welding. Silver flake is used in conductive adhesives for connectors and to repair connections in electronic components.

3.19. Shipment

Silver and fine silver shapes are shipped in a bonded carrier under security procedures and, depending on the material, with sulfur-free packaging materials. Shipment of silver chemicals is individually defined in U.S. DOT Codes in 49 CFR Sections 100–185, and in the Table in section 172.101. For example, silver nitrate is covered under UN1493 and silver oxide is covered under UN1479; both compounds are classified as oxidants.

4. Processing

The dissolution of silver and its associated precious metals by dilute sodium cyanide became the principal means of winning silver from its ores following discovery of this reaction by John Stewart MacArthur in 1887. It replaced the hazardous chlorine gas and mercury amalgamation processes in commercial operations (46).

4.1. Flotation Separation

The cyanidation process superseded all other recovery processes until non sulfide silver ores were nearly exhausted (47). Current world production of primary silver ores is mainly by the froth flotation process, which allows the selective recovery of metal values from difficult-to-process sulfide minerals. Froth flotation works by adding specific chemical frothing reagents to a solution of finely ground ore particles. There is selective adherence of the precious metal values onto the bubbles which are separated from the flotation bath. The reagents chosen are ore specific (48). The resulting concentrates are smelted to remove nonmetallic material.

These concentrates are poured in large vats containing a 0.1% sodium cyanide solution for agitation and dissolution. This process recovers over 85% of the precious metal in the ore. The silver and other precious metal cyanides are filtered and zinc powder added to precipitate the silver. The raw precipitated silver was in the past, filtered and de-aerated by vacuum. Current practive is to pass precipitates through flow-through carbon columns to selectively adsorb the metal values.

4.2. Heap Leaching

Large quantities of low grade silver ore and mine wastes in the Western United States too low for recovery by standard methods were, beginning in 1969, subjected to heap/dump leaching by sodium cyanide solutions. The economic advantage of heap leaching (which recovers about 70% of the precious metal) is its lower capital cost than the standard metal recovery process, thus being economical for very low grade oxidized ores which contain under 4 g. It is particularly advantageous for silver because silver leaches more readily than gold.

The capital costs of heap leaching are a fraction of the standard milling, vat dissolution by sodium cyanide, and filtration (49). To heap leach, a relatively permeable ore is roughly broken up, dumped on impervious pads, and sprayed with dilute alkaline sodium cyanide. The dissolved precious metal-containing solution is collected on the impervious pad, collected, and circulated through activated carbon columns for recovery of the silver and recycling of the sodium cyanid (50).

By the 1990s heap/dump leaching had become the dominant process of precious metal recovery from low grade ores throughout the world. Commercial operations in the U.S., primarily in Nevada and California, range from 10 tons of ore per week to 10,000 tons per day.

4.3. Electrolytic Refining

The final purification of the raw metal from the mine smelters (the "doré" bar which is a mixture of silver, gold, and other metals) and the precious metal values in sodium cyanide solutions from heap leach operations is achieved by electrolytic purification in a precious metals refinery (9).

In the standard Wohlwill refining process the doré bullion is cast in the form of anodes with pure gold-leaf strips are the cathodes. The gold is deposited on the gold-leaf cathodes and the silver precipitates as an insoluble silver chloride sludge at the bottom of the tank. The silver sludge is filtered, washed, dried, fluxed, and reduced to bullion. The bullion is cast in the form of anodes with pure silver sheet as the cathodes in a solution of nitric acid and silver nitrate. The pure silver crystals deposited on the cathode are periodically scraped into a basket for removal and washing. Substantial variations in the refining process are required to eliminate impurities (9, 51).

Research at the South Dakota School of Mines and Technology, Rapid City, SD is determining the commercial viability of using ammoniacal solutions to recover gold and silver from ores (52).

5. Economic Aspects

In 1792, the U.S. government adopted a bimetallic monetary system, setting $1.29/oz as the ceiling price for purchasing silver. In 1873, the U.S. Gold Standard Act set "... the dollar, consisiting of 25.8 grains of gold nine-tenths fine... shall be the standard unit of value, and all forms of money issued or coined by the United States shall be maintained at a parity of value with this standard..." This effectively relegated silver to be merely a coinage metal along with nickel and copper, not a monetary metal.

Nonetheless, the U.S. Treasury reports show the purchase of large quantities of silver for coinage. Between 1934 and 1941 purchases totaled over 2×10^9 ounces. World War II fostered a burgeoning industrial demand for silver, which, when combined with Treasury's increasing coinage needs, outpaced mine production. During the 1950s, the increase in efficient methods for recycling silver helped fill this gap. However, by 1958 industrial consumption alone, excluding Treasury's coinage needs, exceeded mine production. By the 1960s it became clear that there simply was not enough silver in the world to satisfy both industrial and coinage needs (9). Congress responded with the Coinage Act of 1965, eliminating silver from quarters and dimes, with the half dollar being reduced to 40% silver.

Table 6. Impact of Silver Mining by U.S. States in 1995[a]

State	Silver production, $\times 10^6$ $	Employment, jobs
Arizona	28	2,010
California	2	5,602
Idaho	27	1,416
Missouri	7.6	178
Montana	13	4,553
Nevada	109	51,457
Utah	23	12,093
Other	56	5,683

[a] Data from U.S. Geological Survey (jobs include some gold miners).

The free market for silver began in 1967 at 1.29/troy oz. Since that date the price has continued to advance, and on January 21, 1980, COMEX accepted four futures contracts for silver at a price of $52.50 per ounce, the highest price ever listed for silver. This was the result of an attempt to corner the silver market (53). By March 1980, the spot price had dropped to $10.20.

The U.S. Treasury reports show that from 1933 to 1987 over 2×10^9 ounces of silver were processed into coins. By mid-1987, the Treasury's remaining stocks of silver amounted to 43.5 million ounces, which were expected to be exhausted by commemorative and half dollar coinage. In addition, during World War II, the Department of Defense had built up a strategic stockpile of silver amounting to 135.5 million ounces, which, in 1985, the National Security Council/OMB recommended be reduced to 87.5 million ounces. As this "overhang" threatened the stability of the silver market, legislation was introduced in 1986 to require the U.S. Mint to use this stockpile for commemorative coins and American Eagle Silver Bullion Coins. It is expected that these reserves will be exhausted by 2001.

Since 1965, with its monetary connection severed, the price of silver is a function of market demand. Its price per troy ounce, with the exception of two excursions in 1980 and 1983, has risen steadily from $1.29 in 1965 to over $5.90 in 2000. The value ratio of gold to silver in ancient times (53) fluctuated around 13:1, and during the depression years to nearly 70:1; in 2000 it was about 48:1.

Silver is a mineral commodity providing a significant economic asset. Silver has been and continues to be a significant contributor to the economic prosperity of the U.S. states as shown in Table 6.

Silver provides important economic assets to many countries, eg, Peru counts silver as the source of about half of its foreign exchange earnings (53). Mexico, which has long been the world's largest producer, contributed 14% of world's production in 1999, Peru followed with over 13% and United States 12% (39). Less developed countries enjoy significant foreign exchange earnings trading silver.

In India, private assets are reckoned in terms of silver jewelry, coins, tableware, and religious art. During the 17th and 18th centuries, India was the crossroads of the fabulously rich oriental trade, for which the numeraire was silver. Today, that monetary stature is retained and private silver holdings in India are estimated to be some 93×10^3 tons. Silver is considered to be a stable store of value as opposed to banks whose accounts are subject to changes in the value of the rupee. As there are no silver mines in India, all silver is imported; in 1999 this amounted to nearly 1200 metric tons (39).

Silver utilization is based on three primary sectors: industrial uses, photography, and silverware/jewelry. Because silver is the key metal for these applications, these markets provide silver with a broadly based infinitely longterm stable demand.

6. Grades and Specifications

The purchase of silver bullion in the international metal markets such as the London Bullion Market and the New York Mercantile Exchange, COMEX Division is essentially a contract between a purchaser and the seller underwritten by the precious metal refiner whose hallmark is stamped on the bar. The international bullion markets enter bullion bar for sale only from approved refiner/assayers. Individuals who wish to sell their silver in international metal markets must submit it to approved refiner–assayers for processing. To obtain physical delivery of the silver, shipment from the refiner to the purchaser is made by approved carriers.

Silver bullion bar to be traded in international bullion markets must meet the requirements of "London Good Delivery Bar,“ defined by the London Bullion Market Association. The specifications for Good Delivery Bar include a regular size, a minimum fineness of at least 999 parts per 1000 silver, weight between 500 and 1250 troy ounces, and must be stamped with a serial number and ingot mark of an approved refiner/assayer. Approvals are granted to refiner–assayers who have achieved an international reputation as a quality producer, of substantial net worth, and with long-term experience in refining 999-fine silver.

Specifications for commercial-grade silver bullion, brazing alloys, electrical contact alloys, and similar products are published by the American Society for Testing and Materials, the American Welding Society, Japanese Industrial Standards the Society of Automotive Engineers (SAE) (Aerospace Materials Specifications), and the U.S. Department of Defense (DOD). Voluntary specifications for silver bullion include

ASTM B413, grade 99.90 refined silver, Ag 99.90 minimum Ag + Cu 99.95 minimum, Bi 0.001 maximum, Cu 0.08 maximum, Fe 0.002 maximum, Pb 0.025 maximum (one of three grades) (55).

SAE/UNS P07931, sterling silver—silversmith's grade: Ag 92.10–93.50, Ca 0.05 maximum, Cu 6.50–7.90, Fe 0.05, Pb 0.03 maximum, Zn 0.06 maximum, other elements 0.06 maximum (see also P07932) (56).

6.1. Quality Control

The most reliable, quantitative method for determining the purity of silver is the fire assay" (57, 58), which for quality control systems is used as the reference standard. Quality-control systems for monitoring high-purity bullion for market certification use emission spectroscope (59). Crosef-checking is done by the fire assay.

Where high-purity (99.999% or better) silver is demanded for electronic applications, emission spectroscopy (59, 60), mass spectroscopy, and/or inductively coupled plasma (61) are used for quality control. The inductively coupled plasma method is preferred because of its fast results and simplicity of operation, and it does not require the interpretation of a photographic plate. Where trace elements need to be known in parts per billiion, the glow-discharge mass spectroscope is employed (62).

7. Analytical Methods

It is only with the "fire assay" that a total quantitative determination of the precious metal values of a sample can be made. It has been the standard reference assay method for precious metals since ancient times. Other methods are capable of determining only portions of a sample, such as its surface composition, but not its totality.

There are no ores, concentrates, alloys, or scrap samples that cannot be analyzed by the fire assay. Accurate determinations can be made of concentrations from 5 ppm gold to 100%. With today's refinements, a skilled analyst can achieve an accuracy in the amount of 0.05 part per 1000 within the same sample, an accuracy of 0.10 part per 1000 between samples, and 0.2 part per 1000 between laboratories. Because some losses of silver are inevitable in the fire assay, a high-purity silver control must be used with each group of samples to determine the proportion of these losses.

In the fire assay, a fluxing material is added to the sample which is wrapped in silver-free lead and heated to $>1000°C$ to oxidize and dissolve all base metals. The presence of silver (or a specified addition), completely oxidizes any remaining base metals which are then absorbed in the bone ash cup (cupel) leaving behind only the noble metal values for wet chemical analysis (57, 58, 63–65).

Wet chemical analytical methods may be used to avoid the expense of conducting a fire assay, but only if the sample contains no interfering base metals. Nitric acid dissolution of the silver and precipitation as AgCl, the volumetric-titration method, the dimethylaminobenzylidenerhodanine colorimetric, or dithizone extraction methods are used interchangeably (66).

Spectroscopic techniques are the most commonly used instrument methods for the quantitative determination of silver purity which is determined by difference. These methods include emission spectroscopy, atomic absorption, mass spectroscopy, inductively coupled plasma, and x-ray fluorescence. All of these measure the quantitative presence of minor or trace elements whose values are then deducted from the sample to determine the proportion of silver (67).

Emission spectroscopy identifies elements in volatilized samples by photographing the spectrum of their excitation at high temperature (68).

Atomic absorption spectroscopy measure the fractional decrease in intensity of radiation per number of atoms per unit area. It is fast, accurate, and economical. Silver is very sensitive to this analysis and consequently it is widely used to assay ores and concentrates down to ca 2–3% silver. It is also used to determine the presence of silver in solutions, such as swimming pool sanitation systems, measuring silver in the 100-ppb range (69).

Mass spectroscopy identifies elements by their reaction to a magnetic field. It is used with emission spectroscopy to quantitatively assay high-purity silver for trace elements. The purity of the silver is found by subtracting the proportion of the trace elements identified. The use of mass spectroscopy is a necessity for electronics applications where 999.99 fine silver or better is required. Where determination of the presence of elements in parts per billion is required, the glow-discharge mass spectroscope is used (62).

The inductively coupled plasma (ICP) technique functions on the same principle as emission spectroscopy, but uses solutions that are vaporized in a 8000 to 10,000 K plasma of argon. It is capable of analyzing many elements simultaneously, such as determining low levels of platinum group and other metals in scrap. It is fast, simple, and does not require an interpretation of photographic plates. It is used to assay for trace elements in 999.99 fine silver for electronics, photographic emulsions, and very high-tech applications (70). This instrument is also used to measure very small concentrations of silver in solution, such as in swimming pools where the silver ion is used for sanitation at concentration of 100 ppb. For concentrations on the order of 10 ppb, the high resolution ICP mass spectrometer is used. The combination with the mass spectroscope provides a powerful analytical tool.

X-ray fluorescence is another rapid and accurate method of identifying elements by their characteristic x-ray emission; the composition of the sample is obtained by converting the x-ray intensities into concentrations using appropriate algorithms. However, each type of sample must be individually calibrated (71).

8. Environmental Concerns

8.1. Ambient Water Limits

The Clean Water Act (Public Law 92-500) set limits for silver in stream, lake, river, and estuary waters, these values intended to protect aquatic wildlife, not humans. The EPA at one time had quality control criteria for the protection of human health under the Clean Water Act, but these were withdrawn (72). The maximum recommended total of analytically recoverable dissolved silver concentrations for freshwaters open to wildlife now is 3.4 ug/I (with modifications for salt content), and in salt and estuary water ($>1\%$ salt) is 1.9 ug/l. These

Table 7. Mortality of Fathead Minnows Exposed to Concentrations of Different Silver Compounds[a]

Compound	Total silver concentration	Free silver ion concentration	Mortality 24 h	Mortality 96 h
silver nitrate	0.065 mg/L	0.065 mg/L	100%	100%
	0.013	0.013	5	10
	0.0031	0.0031	0	0
silver thiosulfate complex	280	0.12×10^{-6}	5	10
	140	0.33×10^{-6}	0	0
silver sulfide	240	<10–11	0	0
silver chloride	4.6	1.03×10^{-4}	40	40
	0.38	1.01×10^{-4}	0	0

[a] Ref. 45.

recommendations factor in the free silver ion concentration which is dependent upon dissolution of a specific silver compound; see for example, Table 1.

These concentration limits stand as national recommendations or guidelines to the U.S. states which can apply these standard limits to whole streams or rivers, or to their segments. Within these limits the states can reasonably expect that wildlife aquatic organisms will be protected.

The EPA's recommended limits for silver for wildlife are based on a scientific assessment of the effect of silver on fish gills. The limits for fresh water are 3.5 ug/l in the presence of 100 mg/L $CaCO_3$, and in saltwater 1.9 ug/L (73). The reaction of silver with fish gills is distinctly different from that of bacteria. This reaction results in a marked change in the gills' gas exchange, ionic balance, and excretion of nitrogenous wastes. The action of silver ions in certain concentrations, as with other metals, may lead ultimately to expiration, see Table 7 (74, 75).

8.2. Swimming Pool Limits

Silver–copper ionization systems are commonly maintained at about 50 ug/L Ag. Certification of the output of commercial Ag–Cu ionization systems is undertaken by NSF International, Ann Arbor, Michigan, in terms of the specifications of ANSI/NSF Standard 50 on Circulation System Components and Related Materials for Swimming Pools, Spas/Hot Tubs, Section 16 on silver–copper ionization swimming pool sanitation systems (see Water, treatment of swimming pools, spas, and hot tubs).

8.3. Airborne Silver

The limits to the ingestion of airborne silver in the workplace adopted by the Occupational Safety and Health Administration in 1971 were those earlier proposed by the American Council of Governmental & Industrial Hygienists as being 0.1 mg/m^3 (76).

8.4. Effluent Silver

The presence of silver in the effluent from any industrial activity is evidence of an economic loss that is a signal for correction. Silver recovery systems are economic (See section on Recycling and Disposal).

Should the silver from a representative sample of effluent from a system exceed 5 mg/L, the Environmental Protection Agency under the authority of the Resource Conservation a Recovery Act, 40 CFR 261.24, Table 7, will consider the waste as hazardous (77). Local laws may be more stringent. However, in any case, the operators the system should discuss limits with the local water treatment authority. Commercial products are available to leach silver from effluent solutions.

9. Recycling and Recovery

Recycling of silver recovered from obsolete products and scrap material is essential to the silver market. During 1999, for example, output of the world's silver mines was on the order of 17,000 metric tons, and the consumption of silver for fabrication of products exceeded 27,000 tons. This deficit was met by the supply of recycled silver which amounted to over 5440 metric tons, or about 20% of that demand (39).

The recovery of silver from obsolete equipment and scrap is achieved in a variety of ways entailing processes similar to that of winning silver from its ores (78). The impure silver from primary recovery, similar to that of the raw silver from mine smelters, must be electrolytically refined to a marketable purity of 999-fine. This purification is usually the role of established precious metal refiners.

9.1. Discarded Jewelry, Silverware, and Coins

Silver-bearing metallic material is melted (usually in air to help oxidize any base-metal in the alloys) to obtain a mixed metal solid, similar to the impure bars produced by mine smelters (79, 80). The resulting metal is used as an anode for electrolytic refining.

9.2. Solid Silver-Containing Scrap

Scrap electrical and electronic equipment (81–83), electronic circuit boards (84), etc, with silver containing parts are hand separated, shredded, pyrolyzed to remove organic material, and further oxidized at ca 1200°C to produce a mixed metal residue. Solids such as sweeps, spent catalysts, slags, smelter slags, slimes, etc, are agglomeration-roasted and fed into a ca 1200°C furnace for concentration into a metal residue (85). The metal residue becomes an anode for electrolytic purification.

9.3. Scrap Photographic Sensitized Goods

It has been common practice to recover silver from scrap black and white and color film, photographic paper, etc, by ashing the material at a temperature above the melting point of silver (86). Ashing volatilizes all organic material, producing a silver-rich impure melt. The emergence of stringent EPA and OSHA emission requirements are making film washing to remove the emulsion for silver recovery a viable alternative, particularly in view of the profitable recycling of the plastic film base (87). Chemical methods to dissolve the silver from the emulsion, such as by sodium cyanide, are more expensive and hazardous than ashing or washing.

9.4. Sprays from Coating Processes

Scrapings and items from spray booths are hand concentrated and then soaked in sodium cyanide solutions to extract the silver.

9.5. Recovery from Silver-Bearing Solutions

A number of industries generate spent silver-rich solutions, such as photographic and graphic arts laboratories, mini-laboratories, hospitals, dental offices, silver plating plants, mirror manufacturers, cut flower florists (silver thiosulfate solutions), etc. As the limits for silver effluent in local municipal codes may vary anywhere between 0 and 10 mg/L, and silver in an effluent is money lost, recovery is just good business practice.

Recovery of silver from solutions may be accomplished within the recycling plant or shipped to concentrators or refiners (see www.silverinstitute.org). Equipment to remove silver in house is listed below with possible efficiency noted. The equipment must be continuously monitored and controlled to achieve these efficiencies.

9.6. Recovery by Metallic Replacement

This results from the reaction between silver and a more active metal. In the case of steel wool or iron sponge, silver replaces the iron and is deposited as silver metal on the steel wool or iron sponge. The silver-laden deposit may then be shipped to a precious metal refinery for the recovery of pure silver. Up to 95% of the silver can be removed by this method with exiting solution having a concentration of between 200 and 800 mg/L. A cascade of units can achieve existing levels below 50 mg/L (41).

9.7. Electrolytic Plating

This process used by precious metal refineries for the production of highly purified silver. For small photographic laboratories, the metallic replacement system is a better economic choice. Small electrolytic silver recovery units are available; for example, Eastman Kodak Company markets a 30-liter unit designed for mini-laboratory which recovers 93 to 99% of the silver from photographic solutions with a maximum of silver concentration in the exiting solution of beween 20 and 80 mg/L (41).

9.8. Chemical Precipitation

Though more economical in terms of silver recovered, it requires long settling times (days) for the complexed silver, with a resulting concentration of between 0.5 and 5.0 mg/L (41).

9.9. Ion Exchange

This systems use a resin which exchanges one of its ions for silver, which is retained by the resin. The resin is regenerated by an ammonium thiosulfate solution. This system, though requiring a significant capital investment, has the advantage of reducing silver in the effluent to 0.1 to 0.5 mg/L (89).

9.10. Membrane separation

This entails a waste water stream flowing over the surface of a selectively-permeable membrane. The relatively pure water flows through the membrane, and the other constituents, including silver, are contained for further purification. This method is advantageous for very dilute solutions as the high chemical content of most spent photographic solutions tends to quickly clog the membranes. It has been successful in removing up to 90% of the silver present, providing an effluent with a concentration of 200 to 800 mg/L of silver. Because of the greater capital investment and more chemical handling, it is seldom used (41).

9.11. Controlling Silver in Effluent

Combinations of the above achieve additional silver recovery and consequently reduce the silver in the effluent (87). For example, a combination of electrolytic silver recovery followed by metallic replacement can reduce the silver in the effluent to as low as 1 mg/L. The use of a cascade of two metallic replacement treatments can achieve similar results.

Silver is included as a toxic characeristic of hazardous waste under regulations issued by the Resource Conservation and Recovery Act in Table 1 (40 CFR 261.24) mandating a concentration limit of 5 mg/l (77).

9.12. Marketing Recycled Silver

The silver-containing concentrates from the above processes are subject to refining similar to that of concentrated silver ore. That refined silver must meet the same standards of bullion quality as that required of all metal submitted for trading in the international bullion markets (See: section on Grades, Specifications, and Quality Control).

9.13. Health and Safety Factors

It has been suggested that the use of silver to keep water and other liquids pure was probably humidity's first attempt to control the environment. Pliny the Elder (78 AD) reported that the slag of silver "... has healing properties as an ingredient in plasters, being extremely effective in causing wounds to close up..." (4). Silver has been known since ancient times as the healthy metal. Vessels for potable liquids, tableware, holloware, chalices, baby pacifiers, etc, have been made of silver since ancient times in preference to other metals or ceramics for its bacteria-resisting, rust-resisting performance.

Silver compounds when exposed to the lungs or intestinal tract are only slowly absorbed because of their limited solubility in body fluids. Retention apparently is greatest in the ingestive organs (90).

9.14. Natural Defenses

All vertebrates, invertebrates and microorganisms possess defenses against accumulation of the heavy metals. Metals not consumed for the healthy function of the organism are removed by proteins known as metallothioneins. These transport, store, and detoxify essential and non-essential trace metals (91). Metallothioneins encapsulating heavy metals are excreted mostly by the liver in the feces. Supersaturation of this protective system may result in the excess metals binding with available thiols, binding the silver ions as silver sulfide. When this accumulation becomes noticeable, the cosmetic effect is known as argyria. This result is not associated with any health effect (92–94). Removal of these silver deposits has proved not feasible.

Argyria is today an extremely rare condition because it requires long, acute exposure to silver fumes or sprays. Modern industrial practice, which requires reactions involving silver to be carried out with face masks, gloves and under hoods, finds no such result.

There is no evidence that silver causes cancer (95).

9.15. Drinking Water

Metallic silver is reported to dissolve in water to the extent of 10^{-5} grams per liter [10 ppb], sufficient to be toxic to *E. coli* and *B. typhosis* (31).

Silver has been used to sanitize drinking water throughout recorded history. Herodotus records that Cyrus the Great, King of Persia (550-529 B.C.), boiled his drinking water and had it carried throughout his campaigns in silver vessels (3). In the Americas the ancients in Mexico, the world's major producer of silver, used and continue to use silver vessels to keep water and milk sweet.

The Safe Drinking Water Act (Public Law 93-523) sets national drinking water standards for human consumption. Silver appears in the National Secondary Drinking Water Regulations list which recommends a nonenforceable contaminant level for silver of 0.1 mg/l (100 ppb) (86) in consideration of the fact that "there is little or no adverse health effect associated with [its] presence in drinking water" (54). The EPA requirements for Registration of Bacteriostatic Water Treatment Units for Home Use state: "...the pesticide and other chemical components which are incorporated in the unit are not released at levels which exceed the maximum permitted in the National Interim Primary Drinking Water Regulations" (96).

9.16. Silver Ions in Swimming pools

Extensive studies beginning in the early 1950s with a large public pool proved that silver and copper ions generated by very low electric currents effectively sanitize swimming pools with a minimum use of chlorine.

This combination has proved equally effective in sanitizing aquatic mammal exhibition pools eliminating chlorination. The animals proved healthier and small scratches and abrasions that did not heal well under chlorine healed rapidly, likewise eye problems are markedly reduced. When the animals gave birth, the environment has proved definitely safer for them (96).

9.17. Silver Ions in Clinical Applications

Decades of clinical experience have shown electrically-driven silver ions rapidly enhance the regeneration of normal human structures destroyed by episodes of severe wounding (98, 99).

With a patient in clinical care, a severe injury is covered with a silver coated dressing which is changed and the wound irrigated at regular intervals. A steady regeneration of the original dermal or bone structures proceed unimpeded by bacteria in the wound area (99, 100, 101). Success has also been achieved in promoting rapid bone growth in cases where bone had not healed under other treatment (102, 103).

Healing rates in wounds treated with electrically generated free silver ions are significantly accelerated and are accompanied by enhanced healing of bone, soft tissue, nerve, and skin, with replacement of missing tissues by histologically normal tissues. Explanation of granulation tissue from such wounds during healing phase into standard culture media results in the production of large number of new cells, all with characterisitcs of primitave or stem cells. It is believed that this in vitro process is the same as that ongoing in the silver-treated wound. The responsible agent for these cellular effects is believed to be the electrically generated silver ion, although some ancillary effect of the iontophoretic current itself cannot be ruled out at present (99, 103–105).

9.18. Silver-Coated Products

Silver-coated nylon thread in dressings has been shown to have bactericidal value against *E. coli*, and the *Pseudomonas, Klebsiella, Stapyhlococcus* and *Streptococcus* species. At room temperature, bacteria in the vicinity of the thread shows a rapid decrease in survival usually after a delay of about an hour, but at body temperature (37°C, 98.6°F) there was no delay in its bactericidal action (105, 106).

Sputtered-silver coatings on medical dressings have shown significant activity against, for example, *P. aeruginoisa*, as a infecting organism (107). Data show that the sputtered nanocrystalline-type structure provides bacteriocidal properties unique as related to other forms of silver coatings.

9.19. Workplace Air

Workplace airborne concentration limits for silver compounds in the U.S. range from 0.1 to 0.01 mg/m^3 depending on the form of silver compound (108). These limits were set to avoid argyria. The employment of exhaust hoods and face masks wherever silver is reacted to form compounds, where electronic parts are silvered, or where silver is polished have effectively eliminated argyria as a workplace hazard (109).

9.20. The Function of Silver to Aid Health

Silver disturbs the multiplication function of bacteria leading to their expiration (98). Mammalian cells, which differ in structure, are not affected by silver. No evidence of carcinogenicity, neurotoxicity, or reproductive abnormalities has been observed over the millennia of exposure to silver, nor has there been a development of resistance by disease-causing bacteria to silver (95).

Silver disturbs the transport of oxygen through gill membranes in fish. At low concentrations, metallothioniens present in fish will remove the silver, but when these and other protective systems are exhausted the fish will expire (110). With the removal of silver, the normal function of the gill appears to be restored (111). Silver has no detrimental effect on aquatic mammals (97).

9.21. Dental Restorations

The use of silver amalgams has been commonly used for tooth restorations for over 150 years. The National Institutes of Health, noting that most of the over 200 million tooth restorations placed each year are silver amalgam, stated that “there is no scientific evidence that currently used restorative materials cause significant side effects” (112).

Studies conducted by the American Dental Association Fellowship at the National Institute for Standards and Technology show that when naturally occurring silver oxides are removed from the surface of silver powder by dilute acid, it can be compacted with normal dental tools until they harden. The resulting pure silver fillings are 80% as dense and as least as strong as mercury silver amalgams. The silver is more resistant to wear-induced damage than amalgam (113, 114).

9.22. Silver colloids

Silver colloids, with a particle sizes of less than 0.2 micrometers, are a useful form for the delivery of silver ions. Definitive research is in prospect (115).

9.23. Spent Silver Catalysts

Silver is the most efficaceous catalyst for the oxidation and dehydrogenation of organic chemicals. The catalyst inventory of the world’s chemical process industry is about 1600 metric tons and use requires regular regeneration. Regeneration of spent catalysts removes the silver from the alumina carrier for recycling of the silver, but some silver is unrecoverable from the alumina carrier. The remaining silver is sufficient to provide an effective biocide (116).

10. Uses

10.1. Jewelry Silverware, and Occurance

Some 29% of worldwide silver consumption falls into this sector. The workability, polished brilliance, and healthful bacterial resistance have combined to make silver an exceptional metal for personal adornment, tableware, holloware, and many decorative products. The 1999 consumption of silver for this sector was ca 8110 metric tons (39).

10.2. Photography

Some 28% of the silver consumed worldwide during 1999 was used for manufacture of photographic products. Silver halides are unique in their sensitivity to light. Prepared as infinitely small crystals, they are essential for high-definition color photographs and holograms. Silver halides are used in x-ray film for clinical observations and industrial structure inspection. The newly developed internal x-ray holograms are aiding surgeons in difficult operations. Silver halide products are essential in the graphic arts and motion picture industries. World silver consumption for photographic uses in 1999 was over 7660 metric tons (39) (see also Photography).

Photochromic glass for ophthalmic lenses and sunglasses incorporates silver halides melted in optical glass. In sunlight the glass darkens reducing light transmission up to 22% and blocking 97% of uv rays. In the 20 years since this glass has been on the market, some 87 million pairs of sunglasses have been made consuming over 47 metric tons of silver.

10.3. Electrical and Electronic Components

The second largest industrial consumer of silver is the electrical industry, which in 1999 consumed over 4600 tons, some 17% of all silver consumption (39). Silver is the electrical contact of choice for it avoids the high resistance and corrosion which lead to overheating and cause fire. Although silver tarnishes, the film is soft and does not affect its performance (18). Motor control contacts make up the largest proportion (about 70%) of this market. The traditional silver-cadmium oxide contact material for these heavy duty contacts is being replaced by silver-tin oxide avoiding the use of hazardous cadmium. Switches and relays in both household and industrial units use contact rivets with about 0.001-inch thick silver. This amounts to hundreds of millions of units per year for electrical appliances, automobiles, motor controls, etc. The keyboard switches in computers, elevator controls, etc, use silver membrane contacts; over 20 million of such switch panels are manufactured per year (117). Silver provides safe, healthful electrodes for attachment to the skin for electrocardiograms and other measurments.

10.4. Heat Sink Uses

Silver surpasses all other substances in conductivity of heat. In the Space Shuttle, silver is added to the copper alloys in the main combustion chamber both to increase high-temperature strength and to dissipate heat. Silver is commonly used in electronic equipment to conduct heat away from sensitive circuitry.

10.5. Security Barrier

A grounded coating of silver ecapsulating an electronic device or an entire office (including gounded sputtered silver glazing) is widely used as an effective barrier to electromagnetic interference or survelliance.

10.6. Brazing Alloys and Solders

An advantageous property of silver is its outstanding ability to wet a wide variety of dissimilar metals and ceramics at temperatures considerably below their melting points. These joints are ductile and thus shock-resistant, and provide high electrical and heat conductivity. Applications (and use) include: air conditioning and refrigeration (piping), plumbing and heating (lead-free solder joints), automotive (radiator brazing), aircraft and aircraft engines (exhaust manifold brazing), electrical appliances (contacts and bus bar), shipbuilding (steam and water piping), motors and generators (contacts and connections), electronic assembly solders (surface mounting of components), spac and missiles (fuel pump piping), and silverware and jewelry (soldered joints) (118). The world market use exceeds 1200 metric tons.

10.7. Silver and Aluminum Alloys

The addition of about 0.4% silver to aluminum and magnesium alloys promotes an advantageous grain refinement resulting in the formation of fine grain metallic crystals. This addition results in the strongest cast (A 201) and wrought (Weldalite 049) aluminum alloys known. The Weldalite alloy has been used in the launch propellant tank since 1998 Space Shuttles (119) Aluminum and aluminum alloys).

10.8. Batteries

Silver oxide–zinc batteries are used wherever energy delivered per unit weight and space is of prime importance. The combination finds use as miniature batteries in watches and calculators (which contributes about 7% to the $2 billion battery market) and as full scale batteries in submarines, aircraft, and space vehicles. Silver-zinc portable batteries are widely used for power systems for portable tools, portable power pack for commercial

TV cameras, and they power launch vehicles such as the General Dynamics' Titan, Lockheed Space Systems' Trident, LTV's Scout, and McDonnell-Douglas' Delta. Silver-zinc batteries are used wherever high-energy density and reliability is required (120).

The 3M Maxion cordless surgical tools introduced by MMM Co., St. Paul, MN, powered by silver–zinc batteries made by Yardney, provide 12 times the power and 10 times the operating time of conventional batteries (121).

Varta Batteries, Elmsford, New York, use the high-temperature performance of silver batteries for monitoring deep oil well production where temperatures may reach 195°C (122). U.S. silver consumption for batteries is about 96 metric tons per year (39) (see also Batteries).

10.9. Catalyst

Silver is a dehydrogenating agent in the presence of oxygen. The oxygen atom fits almost perfectly into the silver lattice and its presence is critical for catalysis (if oxygen is not present, catalytic action is poor) making silver an essential dehydrogenating catalyst. For the chemical process industry its primary use is to oxidize methyl (wood) alcohol into formaldehyde, and ethylene gas into ethylene oxide, both important building blocks for plastics (19). The catalytic efficiency of silver can be improved by addition of other elements such as gold and palladium, or by substituting chlorine for oxygen. About 1600 metric tons of silver may be in the worldwide catalyst pool, with over 4% added each year to replace losses during the regeneration/renewal of the silver catalyst (123).

10.10. Florist's Aid

Silver thiosulfate effectively blocks the formation of ethylene gas, the regulator of plant growth and development. When cut flowers are treated with this silver salt, wilting is markedly retarded. Today the entire cut-flower industry depends on it. Silver thiosulfate has also been shown to be a powerful inducer of seed production an exhibits a marked reduction in the premature dropping of ripe fruit (124).

10.11. Superconductors

Silver plays at least three crucial roles in the successful operation of the high-temperature copper–barium–yttrium superconductors which operate at the temperatures of liquid nitrogen (−195°C). [The early superconductors operated only at the temperature of expensive liquid helium (−276°C)].

First, silver does not react with these oxides and at the same time being malleable to allow extreme draw-down as the superconducting friable oxides have no tensile strength of their own. Second, silver bonds together the superconductor particles allowing a continuous flow of electrons between particles, and third, at these temperatures silver itself will become nearly superconducting to provide an efficient switching contact material at the ends of the wire. Industry estimates a potential use of silver for this application could reach over 900 metric tons per year when superconductor products come into commercial production (24).

10.12. Bactericidal Action of Silver

The use of silver to allay putrefaction of liquids has been known since ancient times. This action of silver and its compounds on bacteria is not yet clear. The First International Conference on Gold and Silver in Medicine held in 1987 (125), spurred research to understand its action. Much research has focused on silver sulfadiazine (126) which has been especially useful in controlling bacteria, viruses, protozoa and funguses. The use of electrically-driven silver ions to promote healing of massive wounds has been proven in decades of use (127).

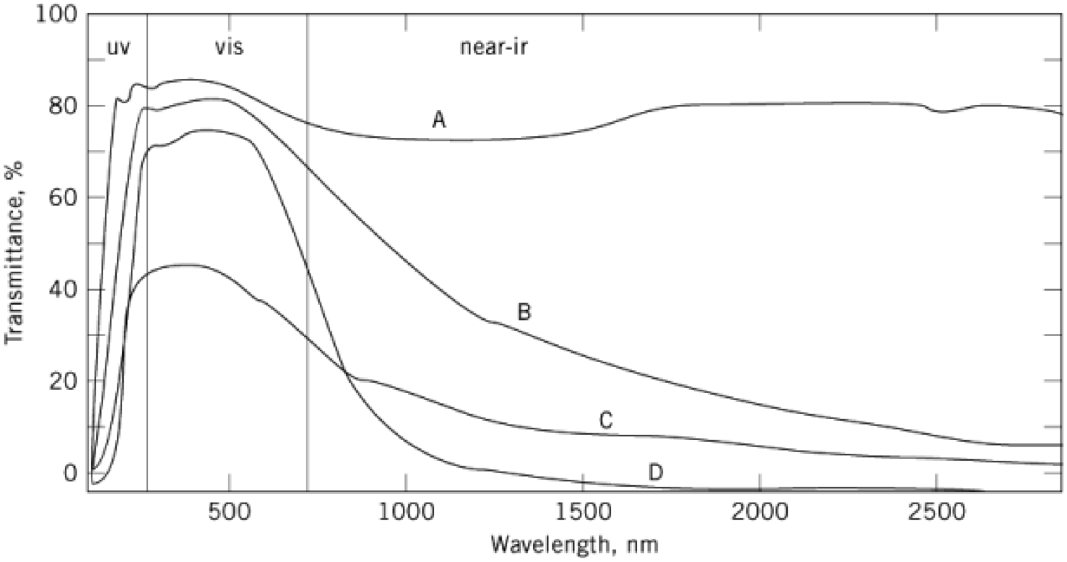

Fig. 1. Solar energy transmittance through glass and glass having sputtered silver coatings, where A corresponds to clear float glass; B, to LoE, one layer of sputtered silver in stack of oxides (prevents tarnishing and eliminates internal reflections) deposited on one interior surface of two layers of glass (an inert gas (argon) is placed between panes); C, to LoE_1, same as B except silver and oxide layer thicknesses selected to provide lower solar energy minimum transmission; and D, LoE_2, similar to B except that two separated layers of sputtered silver located in stack of oxides (27). Courtesy of Cardinal IG.

The value of silver ions for swimming pool sanitization has been confirmed by research conducted at the University of Arizona, Tucson, AZ (127). The use of silver for antibacterial applications now accounts for about 10% of the non-photographic uses of silver nitrat (39).

A unique antibacterial agent is silver chloride coated on titania particles. Inactive TiO_2 particles 3 to 5 microns in diameter are coated with about 20% by weight of silver chloride which in de-ionized water provides an equilibrium level of 20 to 40 ppm and 2 to 4 ppm in sea water. As free silver ions are removed from the water by microbes or other entities, silver ions are again released to regain their concentration. Field studies show effective sanitation is provided to clinical instruments, household products, industrial eqipment, and as a preservative for cosmetics, etc (128).

Since silver was removed from the EPA National Drinking Water Act's list of primary contaminants (129), the market has been expanding for use of silver as a drinking water sanitizing agent.

Silver impregnated activated carbon is widely used for drinking water filters. Industry estimates 53 metric tons of silver are used for this purpose each year. Silver-copper anodes are widely used to sanitize swimming pools, reducing or eliminating the use of chlorine, and polyvalent silver oxide (Ag_4O_4) sanitizes swimming pools without the need for chlorine (33) (silver consumption in this sector is ca 3 metric tons/yr).

10.13. Dental Amalgams

Silver amalgam for tooth restorations was introduced in Europe about 1830. A U.S. Public Health report (130) states that approximately half of the tooth restorations performed in 1990 used the silve–mercury amalgam; this would require well over 16 tons/yr of silver. As regards the mercury risk in tooth amalgams, The National Institutes of Health issued the statement: "The benefits of existing dental restorative procedures far outweight the currently documented risks" (131).

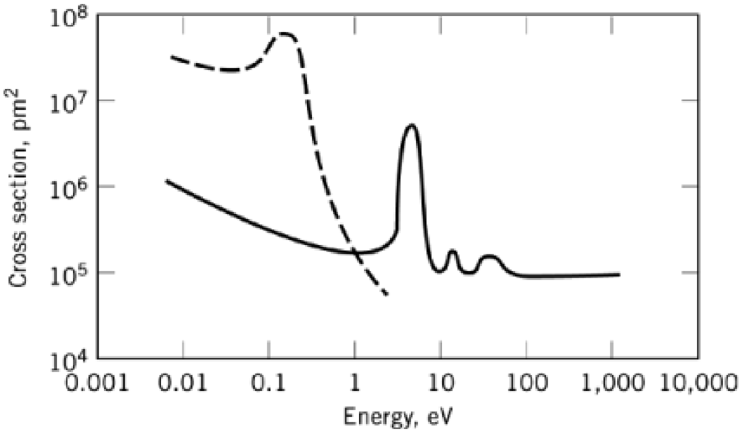

Fig. 2. Total neutron cross sections of silver (—) and cadmium (— — —) (10). To convert pm^2 to barns, multiply by 10^{-4} (9).

10.14. Silver in Medicine

Silver nitrate has been prescribed as a medicinal since ancient times and was listed in a pharmacopeia published in Rome in 69 BC. Its use as a powerful aid to clinical practice was further enhanced by the success achieved by the German Obstetrician, F. Crede, who in 1884 began to administer a silver nitrate solution to the eyes of newborns; this virtually eliminated venereal disease-induced blindness in newborns. The advent of synthetic antibiotics has overshadowed the use of silver in clinical practice, however, the evident increase in bacterial resistance to organic antibiotics has prompted new research into silver delivery systems.

10.15. Thermal Control

Transparent double coatings of silver sputtered onto window glass (low emissive square, Lo-E^{2TM} (27) reduce nearly 50% of thermal transmission and solar heat gain, and result in a dramatic reduction in damaging ultraviolet radiation that causes fading of fabrics and furnishings. This glass has high light transmission in the visible part of the solar spectrum so it appears to be very similar to standard clear glass (27). Production of Lo-E^2 glass has reached about 200 million sq ft per year. About 2.4 metric tons of silver are used per year in the U.S. in this application.

10.16. Mirrors

Solar Two near Barstow, California, uses 1,926 silver-coated mirrors to provide the intensity of 500 suns to heat black-coated stainless steel tubes atop a 300-foot tower containing nitrate salts to over 1050°F. The scalding hot salt is then piped to boilers which turn water to steam to drive turbines geared to electric generators (132).

10.17. Safety for Oxygen-Enriched Atmospheres

Silver is the most combustion- and spark-resistant metal. It will not ignite because of its virtual inertness toward oxygen (133). As a consequence, silver finds important use as a spark suppressor in oxygen-rich systems. In the Space Shuttle main engine, for example, sterling silver parts are used in the fuel delivery system and in the high pressure oxygen pumps where metal-to-metal friction would cause ignition exploding the Shuttle. Silver-coated metals are used to prevent explosion in oxygen-rich environments.

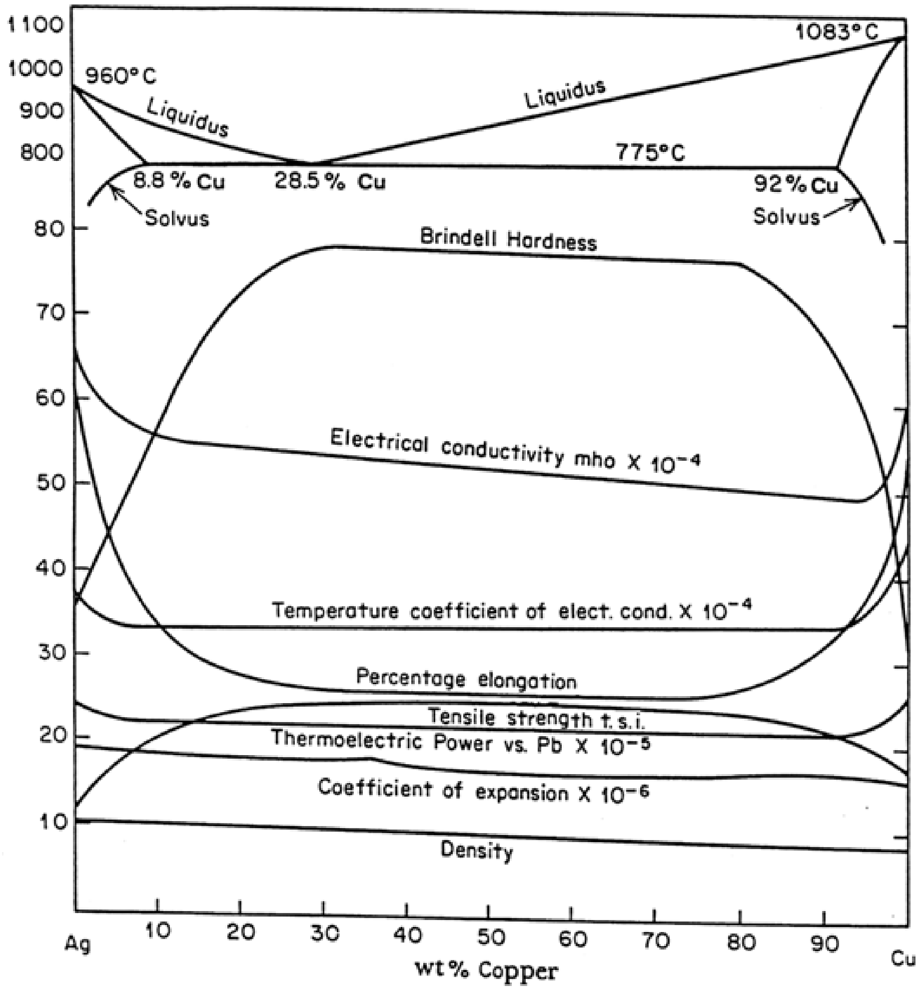

Fig. 3. Variation of properties with composition in the silver-copper system (43) Courtesy of McGraw Hill Book Co.

10.18. Bearings

As a bearing material silver is superior to that of all other materials. Thus its use on main shafts of railroad diesel engines and in reciprocating aircraft engines. A thin lead-tin overplate is usually applied to trap or hold particles that would score the rotating parts. This is due to the hardness of silver, which prevents embedding of hard particles that would wear down the silver bearing (8).

Some helicopter gears are plated with silver to provide smooth, easily lubricated engineering surfaces. Gears for high-speed compressors that inject gas into oil wells to stimulate output are silver-plated to prevent seizure should lubricants fail. The silver plating prevents galling that would otherwise occur during cold start ups when the lubricant is still cold, as in the oil pipeline pumps in Alaska (134).

10.19. Lubrication

Freedom from oxidation, the low shear strength of silver which starts to flow plastically very early, and the softness of the silver sulfide tarnish film make silver one of the most lubricative metals. It is especially useful wherever contacting metals would be inactive for long periods of time, yet be ready for immediate action. Silver prevents galling and fretting corrosion to develop in contacting surfaces where petroleum lubricants would be a pollutant in a chemical process, would carbonize at the operating temperature, or would freeze at low ambient temperatures. Silver coatings are widely used on cages of roller bearings, on gasketing, and on fasteners to prevent seizure or sticking between metals (135). Ion-plating of silver on contacting ceramic surfaces has been found to prevent friction at high-temperatures whose resulting stresses and strains lead to failure (136).

10.20. Coinage and Medals

Silver coins have been used as an acceptable medium of exchange since 600 BC. However, as a consequence of limited silver supplies, the The U.S. Treasury and Canadian Mint removed silver from circulating coinage in 1965. The use of silver for coinage is now limited to commemorative coins and bullion coins, such as the Silver Eagle, the Silver Maple Leaf, and the Mexican Libertad. Bullion coins though minted with a circulating value stamped on the face are sold in terms of their bullion value. Silver is a popular metal for medals ranging from incentive awards and collectable medallions to slot machine tokens.

The worldwide total use of silver for coins and medals in 1999 was ca 840 tons (1).

BIBLIOGRAPHY

“Silver and Silver Alloys” in *ECT* 1st ed., Vol. 12, pp. 426–438, by E. H. Konrad and F. A. Meier (Analysis), The American Platinum Works; in *ECT* 2nd ed., Vol. 18, pp. 279–294, by C. D. Coxe, Handy & Harman; in *ECT* 3rd ed., Vol. 21, pp. 1–15, by G. H. Sistare, Consultant; “Silver and Silver Alloys” in *ECT* 4th ed., Vol. 22, pp. 163–179, by Samuel F. Etris, The Silver Institute; “Silver and Silver Alloys” in *ECT* (online), posting date: December 4, 2000, by Samuel F. Etris, The Silver Institute.

Cited Publications

1. R. F. Tylecott, *History of Metallurgy*, The Metal Society, London, 1976.
2. C. Boutron, *Science* 1841 (Sept. 23, 1994).
3. *Herodotus*, Book I, Paragraph 188, transl. A. D. Godley, Harvard University Press, Cambridge, Mass. 1946.
4. Pliny the Elder, *Natural History*, Liber XXXIII, Part XXXV, transl. H. Rackham, Vol. IX, Harvard University Press, Cambridge, Mass., 1952.
5. V. Wahlberg, *Acta Paediat. Scand. (Stockholm)* Suppl. 295 (1982).
6. C. L. Fox, B. W. Rappole and W. Stanford, *Surg. Gynecolo. Obstet.* **128**, 1021 (May 1969).
7. H. Oka and co-workers, *Metal-Based Drugs* **1**(5–6), 511 (1994).
8. CA Selects, *Sliver Chemistry*, Chemical Abstracts Service, Columbus, Ohio.
9. A. Butts, *Silver Economics, Metallurgy, and Use*, D. Van Nostrand Co., Inc., Princeton, N.J., 1967.
10. P. I. Eimon, “Future New Primary Sources of Gold and Silver in the Western Hemisphere,” in *Precious Metals*, Pergamon Press, Willowdale, Canada, 1982, pp. 93–97.
11. U.S. Geological Survey, Mineral Commodity Summaries Washington, D.C., Jan. 1998.
12. L. Xinzhe and Z. Jian, “50 Years of the Extracting Gold and Silver by Thiourea—a Literature Review,” *1993 Proceedings*, International Precious Metals Institute, Pensacola, Fla., 1993, pp. 435–445.
13. C. S. Hurlbut and C. Klein, *Manual of Mineralogy*, J Wiley & Sons, Inc., New York, 1993.
14. C. E. K. Mees, *The Theory of the Photographic Process*, Prentice-Hall, Inc., New York, (1993).
15. R. J. Araujo, *Contemp. Phys.* **21**(1), 77–84 (1980).

16. T. H. Jeong and co-workers, *Appl. Optics* **36**(16) 3686–3688 (June 1, 1997).
17. D. D. Robertson and co-workers, *J. Computer Assisted Tomogr.* **19**(6), 967–974 (Nov./Dec. 1995).
18. W. H. Abbott, *Long Term Performace of Silver Electrical Contacts*, Battelle-Columbus Laboratories, Columbus, Ohio, 1987 et seq.
19. C. B. Wang, G. Deo, and I. E. Wacks, *J. Phys. Chem. B.* **103**, 645 (1999).
20. C. F. Heinig, *Ozone Sci Eng.* 533–546 (Dec. 1993).
21. L. Addicks, *Silver in Industry*, Reinhold Publishing Co., New York 1940.
22. A. P. Carey and co-workers, *F. Appl. Phy. Lett.* **61(24)**, 2935–2937 (Dec. 14, 1992).
23. Y. K. Kim and S. C. Sanders, *Appl. Phys. Lett.* **68(8)**, 1009–1011 (Feb. 20, 1995).
24. S. Jin and co-workers, *Appl. Phys. Lett.* **51(3)** (July 20, 1987).
25. J. G. Hust and A. F. Clark, *Cryogenics* **13(6)** 325–336 (June 1973).
26. R. A. Outlaw and M. R. Davidson, *Vacuum Sci. Technol. A.* **12**, (May-June 1994).
27. *Glass Products for Windows and Doors*, Cardinal IG, Minnetonka, Minn., 1998.
28. X. Bao and co-workers, *Berlin Bunsengs. Phys. Chem.* **97(3)**, 322–325 (1993).
29. K. G. Budinski, *Wear Characteristic of Industrial Coatings*, ASTM STP 769, American Society For Testing and Materials, Philadelphia, 1981, p. 118.
30. D. R. Smith and F. R. Fickett, *J. Research (NIST)* **100(2)**, 119–171 (Mar./Aprl. 1995).
31. G. V. James, *Water Treatment*, 4th ed., CRC Press, Cleveland, Ohio, 1971, p. 38 (The author states: “The activity of Silver is with its ion. Metallic silver, on exposure to water, will dissolve into ions in an amount of about 10^{-5} g/l which is toxic to *E. coli* and *Bacillus typhosis*”).
32. R. B. Thurman and C. P. Gerba, *CRC Crit. Rev. Environ. Control* **18(4)**, 295–315 (1989).
33. M. S. Antelman, *Soap/Cosmet./Chem. Specialties* 52–59 (March 1994); U.S. Pat. 5,676,977 (Oct. 14, 1997).
34. M. S. Antelman, *Encyclopedia of Chemical Electrode Potentials*, Plenum Press, New York, 1982, p. 87.
35. *Tech. Bull. (Engelhard Industries, Iselin, N.J.)* **10**(3), 80 (1970).
36. R. A. Matula, *J. Phys. Chem. Ref. Data* **8**, 4 (1979).
37. N. Nesyayanov, *Vapor Pressure of the Elements*, Acadamic Press, Inc., New York, 1963.
38. D. J. Hughes and R. B. Schartz, *Neutron Cross Section*, USAEC report BNL-325, U.S. Atomic Energy Commission, Washington, D.C., 1958.
39. *World Silver Survey 2000*, The Silver Institute, Washington, D. C.
40. *World Silver Production Forecast 1997–2000*, The Silver Institute, Washington, D.C., 1997.
41. *Technology of Silver Recovery for Photographic Processors*, J-212, Eastman Kodak Company, Rochester, NY, 1999.
42. “IPMI Industry Survey of Precious Metal-Bearing Secondary Material Exports from the United States—1994,” in *Precious Metals 1997*, International Precious Metal Institute, Pensacola, Fla., 1997, pp. 101–103.
43. F. N. Rines, *Phase Diagrams in Metallurgy*, McGraw-Hill Book Co., New York, 1956.
44. B. D. Rowan, “The Role of Precious Metal Powders in Electronics,” *Precious Metals*, Pergamon Press, Willowdale, Canada, 1982, pp. 254–268.
45. J. Singh, “New Techniques in Synthesis of Silver Nanoparticles by Laser-Liquid Interaction,” *Materials Science*, Vol. 33, p. 3471 (1998); and “Synthesis of Silver Nanoparticles by Laser-interaction Techniques,” *Journal of Materials Synthesis & Processing*, Vol. **6**, No. 2, p. 89 (1998).
46. F. Habashi, *CIM Bull. (Canadian Inst. Mining, Metallurgy and Petroleum)*, **80**(905), 108–114 (Sept. 1987).
47. F. W. McQuiston, Jr. and R. S. Shoemaker, *Gold and Silver Cyanidation Plant Practice*, Am. Inst. Mining Metallurgy and Petroleum Engineers, Vol. I, 1975; Vol. II, 1980, New York. P. F. Chamberlain and M. G. Pojar, *Gold and Silver Leaching Practices in the United States*, Bureau of Mines Information Circular, IC 8969, USDI, 1984.
48. R. R. Klimpel, *Introduction to Solid-Solid Separation of Fine Particles by Froth Flotation*, Society of Mining, Metallurgy, and Exploration, Littleton, Colo., 1998.
49. J. A. Eisele and co-workers, *Separ. Sci. Technol.* **18**, 1081–1094 (1983).
50. D. J. A. Van-Zyl and co-workers, *Introduction to Evaluation, Design and Operation of Precious Metal Heap Leaching Projects*, Society of Mining, Metallurgy & Exploration, Litteton, Colo. 1988.
51. C. W. Ammen, *Recovery and Refining of Precious Metals*, Chapman & Hall, Inc., New York, 1997.
52. D. Kang and co-workers, *Minerals Metallurg. Process.* **15(4)**, 53–59 (Nov, 1998).
53. T. P. Mohide, *Silver*, Ontario Mineral Policy Background Paper No. 20, Toronto, 1985.
54. T. P. Mohide, *The International Silver Trade*, Woodhead Publishing Ltd., Cambridge 1992.

55. "Standard Specification for Refined Silver" (B 413), in *Book of ASTM Standards*, ASTM, West Conshohocken, Pa.
56. *Metals and Alloys in the Unified Numbering System*, SAE HS 1086a, Society of Automotive Engineers, Inc., Warrendale, Pa.
57. *The Fire Assay for Gold*, The Gold Institute, Washington, D.C., 1985.
58. "Test Methods for Determination of Gold in Bullion by Cupellation" (E 1335), *Book of ASTM Standards*, American Society For Testing and Materials, West Conshohocken, Pa.
59. R. Payling and co-workers, *Glow Discharge Optical Emission Spectroscopy*, J. Wiley, New York, 1997.
60. "Spectrographic Analysis of Silver by the Powder Technique" (E 378), in *Book of ASTM Standards*, American Society For Testing and Materials, West Conshohocken, Pa.
61. A. Montaser, *Inductively Coupled Plasma Mass Spectroscopy*, J. Wiley, New York, (1998).
62. D. J. Hall and P. K. Robinson, *Am. Lab.*, (Aug. 1987).
63. E. E. Bugbee, *A Textbook on Fire Assaying*, John Wiley & Sons, Inc., New York, 1940.
64. O. C. Shepard and co-workers, *Fire Assaying*, McGraw-Hill Book Co., New York, (1940).
65. J. Ching and co-workers, "Complete Fire Assay by Microwave," in *Precious Metals 1994*, International Precious Metals Institute, Pensacola, Fla., 1994, pp. 401–413.
66. R. S. Young, *The Chemical Analysis of Silver*, The Silver Institute, Washington, D.C., 1983.
67. J. E. Paterson, "A Review of the Spectrographic Analysis of Precious Metals," in *Precious Metals 1982*, Pergamon Press, Willowdale, Canada, 1982, p. 367.
68. H. A. Liebhafsky and co-workers, *X-Ray Absorption and Emission in Analytical Chemistry*, J. Wiley & Sons, Inc., New York, 1960.
69. J. C. Van Loon, *Analytical Atomic Absorption Spectroscopy*, Academic Press, Inc., New York, 1980.
70. A. Montaser, *Inductively Coupled Plasma Mass Spectrometery*, J. Wiley & Sons, Inc., New York 1998.
71. B. D. Lass and co-workers, "The Use of X-Ray Fluorescence Equipment in the Process Environment," *42nd Annual Denver X-Ray Conference*, Metorex, Inc., Bend, Oregon, 1993.
72. *Fed. Reg.* **57**(246), 60910 (Dec. 22, 1992).
73. *Fed. Reg.* **60**(86), 22228, (May 4, 1995).
74. C. Hogstrand and C. M. Wood, *Environ. Toxicol. Chem.* **17(4)**, 547–561 (1998).
75. G. A. LeBlanc and co-workers, *Environ. Toxicol. Chem.* **3**, 37–46 (1984).
76. *Threshold Limit Values for Chemical Substances and Physical Agents*, Am. Conference of Governmental & Industrial Hygienists, Cincinnati, Ohio, 1980 et seq.
77. An extract from a representative sample of the waste, following filtration, may be tested using Method 1311, *Test Methods for Evaluting Solid Waste, Physical/Chemical Methods*, EPA Publication SW-846, Washington, D.C.
78. B. Keyworth, "The Role of Pyrometallurgy in the Recovery of Precious Metals from Secondary Materials," in *Precious Metals 1982*, International Precious Metals Institute, Pensacola, Fla., 1982, p. 509.
79. F. T. Embelton, "Secondary Refining of Gold and Silver," in *Precious Metals (1981)*, International Precious Metals Institute, Pensacola, Fla., 1981, p. 81.
80. E. G. Imperato and M. A. Pashelinsky, "Pyrometallurgical Processing of Precious Metals Scrap in an Electric Arc Furnace," in *1988 Proceedings*, International Precious Metals Institute, Pensacola, Fla., 1988, p. 159.
81. F. Ambrose and co-workers, "Mechanical Processing of Electronic Scrap to Recover Precious-Metals-Bearing Concentrates," in *Precious Metals 1980*, International Precious Metals Institute, Pensacola, Fla., 1980, p. 67.
82. S. Yarnes, "Pyrometallurgical Processing of Electronic Scrap," in *1995 Proceedings*, International Precious Metals Institute, Pensacola, Fla., 1995, p. 167.
83. A. Prior and co-workers, "Silver Scraps Recycling by Simultaneous Silver-Copper Electrolysis," in *1988 Proceedings*, International Precious Metals Institute, Pensacola. Fla., 1988, p. 473.
84. J. C. Bullock, "RCRA Classification of Circuit Boards," in *1997 Proceedings*, International Precious Metals Institute, Pensacola, Fla., 1997, p. 109.
85. S. Schneiter, "Precious Metal Waste Classifications—A View From Floor," *1997 Proceedings*, International Precious Metals Institute, Pensacola, Fla., p. 81.
86. W. Dahne, "Sampling and Treatment of Film Scrap," in *1988 Proceedings*, International Precious Metals Institute, Pensacola, Fla., 1998; C. McElroy, "Silver Reclamation from Photographic Films," in *1997 Proceedings*, International Precious Metals Institute, Pensacola, Fla., 1997, p. 141.

87. Code of Management Practice for Silver Dischargers, Association of Metropolitan Sewerage Agencies & The Silver Council, Chevy Chase, MD (1996); Water Quality Standards Handbook, 2nd Ed., U.S. Environmental Protection Agency, EPA-823-B-005a (1994); U.S. Code of Federal Regulations, 40 CFR 413.20 - Electroplating of Precious Metals, and also: #421.252 on effluent limitations guidelines.
88. *Fed. Reg.* **56**(20), 3597 (Jan. 30, 1991); Part 143, "National Secondary Drinking Water Regulations, Silver at 0.1 mg/l" (40 CFR 143).
89. S. C. Dhara, "The Applications of Ion Exchangers in the Precious Metals Technology," in *1993 Proceedings*, International Precious Metals Institute, Pensacola, Fla., 1993, p. 315.
90. J. C. Gammil and co-workers, *Proc. Soc. Exper. Biological Medi.* **74**, 691 (1950).
91. M. J. Stillman and co-workers, *Metal-Based Drugs* **1(5–6)**, 375 (1994).
92. D. R. Juberg, "A Review of Toxicity and Epidemiological Data for Silver in Animals and Humans," *Proceedings, Third International Conference on Transport, Fate, and Effects of Silver in the Environment*, University of Wisconsin, Madison, Wisconsin, 1996, pp. 126–132.
93. J. W. Pifer and co-workers, *Scand. J. Workplace Environ. Health* **15**, 210–221 (1989).
94. K. D. Rosenman and co-workers, *J. Occupat. Med.* **21(6)**, 530–535 (1979).
95. A. Furst and C. Schlaudr, *J. Enviorn. Pathology Toxicol.* **1**, 51–57 (1977).
96. *Fed. Reg.* **41(152)**, 32779 (Aug. 5, 1976).
97. S. F. Etris, "Sea Lions Thrive in Silver-Purified Water," *Silver News*, The Silver Institute, Washington, D.C. Dec 1995/Jan 1996.
98. R. O. Becker, *Electro- Magnetobiol.* **19(1)**, 1–19 (2000).
99. C. S. Chu, and co-workers, *J. Trauma, Injury, Infection Critical Care V.* **40**(5), 738–742 (1996).
100. D. A. Webster, J. A. Spadaro, R. O. Becker, and co-workers, *J. Clinical Othopaedic Related Res.* **161** 104–114 (1981).
101. R. O. Becker and J. A. Spadaro, C. T. Brighton, I. Blard, and S. Pollack, *Electrical Properties of Bond and Cartilage*, Grune and Stratton, 1979, 631–638.
102. R. O. Becker, Long Term Clinical Experiences in the Treatment of Local Infection with Free Silver ions, Fourth International Conference on Gold and Silver in Medicine, Univ. of Wisconsin, Milwaukee (1998), *Metal-Based Drugs*, **6** (1999).
103. U. S. Pat. 5,814,094 (Sept 29, 1998) R. O. Becker.
104. U.S. Pat. 4,528, 265 (July 9, 1985) R. O. Becker.
105. C. Mackeen and co-workers, *Antimicrobial Agents Chemotherapy*, 99 (Jan. 1987).
106. Chi-Sing Chu and co-workers, *J. Trauma, Injury, Infection Clinical Care* **39**(2), (1995).
107. R. E. Burrell and co-workers, *Wounds: A Compendium of Clinical Research and Practice* **11**(4), 64 (July/Aug. 1999).
108. *Threshold Limit Values for Chemical Substances and Physical Agents in the Workroom Environment*, ACGIH, Cincinnati, Ohio.
109. R. F. Davies, "OSHA Regulated Exposure to Airborne Silver, A Proposal for Change," *1995 Proceedings*, Precious Metals Institute, Pensacola, Fla. pp. 277–281.
110. C. Hogstand and C. M. Wood, *Environ. Toxicol. Chem.* **17**(4) (1998).
111. D. Morgan and co-workers, *Aquatic Toxicol.* **38** 145–163 (1997).
112. Effects and Side Effects of Dental Restorative Materials, *Technology Assessment Conference*, National Institutes of Health, Aug. 26–28, 1991.
113. F. C. Eichmiller and co-workers, *J. Res. Nat. Inst. Stds. Tech.* **103**, 511 (1998).
114. H. H. K. Xu and co-workers, *Quintessence International* **3(3)**, 199–208 (1999).
115. N. Grier, "Silver and Its Compunds," *Disinfection, Sterilization, and Preservation*, Lea & Febiger, Philadelphia, 1983.
116. U.S. Pat. 5,849,319 (Dec. 15, 1998) R. F. Davies.
117. Rapid Growth Seen for Silver Membrane Switches, *The Silver Institute Newsletter*, Feb/Mar 1992, p. 3, The Silver Institute, Washington, DC.
118. A. S. Cross, "Silver Brazing in the 1980s," *1981 Proceedings*, Int. Precious Metals Institute, Allentown, Pa, pp. 203–205.
119. C. Covalt, *Aviation Week Space Technol.* 56 (June 1, 1998).
120. Silver's High Performance Captures Battery Markets, *The Silver Institute News Letter*, Oct/Nov 1994, pp. 2–3.
121. "Maxion Brand Cordless Powered Instrument System for Ortheopedic Surgery Offers Sustainable Power," *3M News*, St. Paul, Minn., April 23, 1990.
122. Silver Batteries Withstand high Temperatures. *The Silver Institute Letter*, Oct/Nov. 1992, p. 4.

123. Silver Catalysts Critical to Plastics Industry, *The Silver Institute Newsletter*, Dec. 1994/Jan. 1995, p. 1.
124. Silver Keeps Your Cut Flowers Fresh and the Floral Industry Healthy, *Silver News*, The Silver Institute, Washington, D.C. April/May 1996.
125. Proceedings, *The First International Conference on Gold and Silver*, The Silver Institute, Washington, D.C., 1978.
126. C. L. Fox and S. M. Modak, *Antimicrobial Agents Chemotherapy* 582–588 (June 1974).
127. A. B. Flick, "Clinical Application of Electrical Silver Iontophoresis," *Proceedings, The First International Conference on Gold and Silver in Medicine*, The Silver Institute, Washington, D.C., 1987, p. 273.
128. M. T. Yahya, and co-workers, *J. Environ. Health* **51**(5), (May/June 1989).
129. R. J. Corbett, *Int. J. Cosmetic Sci.* **18** 151–165 (1996).
130. *Fed. Reg.* 1471 (Jan. 14, 1991).
131. NIDR Research News, National Institute of Dental Research, Bethesda, Md, Oct. 3, 1993.
132. *Effects and Side Effects of Dental Restorative Materials*, Nat. Inst. Of Health, Public Release, Washington, D.C., August 26–28, 1991.
133. S. F. Etris, "Solar Two, Relies on Silver Reflectors to Generate Electricity, *Silver News*, 1 (Oct/Nov 1997).
134. R. W. Monroe, "Metal Combustion in High-Pressure Flowing Oxygen," *Flammability and Sensitivity of Materials on Oxygen-Enriched Atmospheres ASTM STP 812*, Am. Soc. Testing Materials, West Conshohocken, Pa, 1983, pp 126–149.
135. "Silver for Lubrication," *The Silver Institute Letter*, June 1983, p. 2.
136. K. G. Budinski, *Thin Solid Films* **63** 379–363 (1979).
137. K. G. Budinski, "Wear Characteristic of Industrial Plantings," *Selection and Use of Wear Tests for Coatings*, ASTM STP 769, Am. Soc. Testing Materials, West Conshohocken, Pa, 1982, pp. 118–133.

SAMUEL F. ETRIS
The Silver Institute