

Silver processing

Silver processing, preparation of the ore for use in various products.

Silver has long been valued for its white metallic lustre, its ability to be readily worked, and its resistance to the corrosive effects of moisture and oxygen. The lustre of the pure metal is due to its electron configuration, which results in its reflecting all electromagnetic radiation of wavelengths longer than 3000 angstroms (3000 angstroms is in the ultraviolet range). Thus, all visible light (that is, light with wavelengths between 4000 and 7000 angstroms) is effectively reflected, conferring the white colour.

Silver (Ag), like gold, crystallizes in the face-centred cubic system. It melts when heated to 962 °C (1,764 °F). With a density of 10.49 grams per cubic centimetre, it is the lightest of the precious metals. It is also the least noble of the precious metals, reacting readily with many common reagents such as nitric acid and sulfuric acid. Metallic silver can be dissolved from gold alloys of less than 30 percent gold by boiling with 30-percent-strength nitric acid in a process referred to as parting. Boiling with concentrated sulfuric acid to separate silver and gold is called affination. Both these processes are used on a commercial scale for separating silver and gold.

History

Silver was discovered after gold and copper about 4000 BCE, when it was used in jewelry and as a medium of exchange. The earliest known workings of significant size were those of the pre-Hittites of Cappadocia in eastern Anatolia. Silver is generally found in the combined state in nature, usually in copper or lead mineralization, and by 2000 BCE mining and smelting of silver-bearing lead ores was under way. Lead ores were smelted to obtain an impure lead-silver alloy, which was then fire refined by cupellation. The best-known of the ancient mines were located at the Laurium silver-lead deposit in Greece; this was actively mined from 500 BCE to 100 CE. Spanish mines were also a major source.

By the 16th century, Spanish conquistadores had discovered and developed silver mines in Mexico, Bolivia, and Peru. These New World mines, much richer in silver, resulted in the rise of South and Central America as the largest silver-producing areas in the world. For the recovery

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of New World silver, the Patio process was employed. Silver-bearing ore was ground and then mixed with salt, roasted copper ore, and mercury. The mixing was accomplished by tethering mules to a central post on a paved patio (hence the name of the process) and compelling them to walk in a circle through the mixture. The silver was gradually converted to the elemental state in a very finely divided form, from which it was dissolved by the mercury. Periodically, the mercury was collected and distilled to recover the silver, and this was subsequently refined by cupellation. Cyanidation processes supplanted the Patio process in the late 19th century; by that time, the Moebius and Thum Balbach electrorefining processes had been introduced.

In the mid-19th century a large silver deposit was discovered in Nevada. This resulted in the United States becoming the world's largest silver producer until the 20th century, when it was surpassed by Mexico and South America (particularly Peru). By the early 21st century, Mexico, China, Peru, Australia, and Russia had become the world's leading silver producers.

Ores

Although some silver-bearing ores contain silver as their largest metal value, virtually none has silver as its main constituent. A typical ore might contain 0.085 percent silver, 0.5 percent lead, 0.5 percent copper, and 0.3 percent antimony. After flotation separation, the concentrate would contain 1.7 percent silver, 10 to 15 percent lead, 10 to 15 percent copper, and 6 percent antimony. Approximately 25 percent of the silver produced comes from ores actually mined for their silver value; the other 75 percent comes from ores that have as their major metal value either lead, copper, or zinc. All these ore minerals are sulfides; typically, lead is present as galena (PbS), zinc as sphalerite (ZnS), and copper as chalcopyrite (CuFeS₂). In addition, the mineralization usually includes large amounts of pyrite (FeS₂) and arsenopyrite (FeAsS). The silver mineralization is usually argentite (Ag₂S), proustite (Ag₃AsS₃), and polybasite [(Ag,Cu)₁₆Sb₂S₁₁].

Of the world's reserve base of silver mineralization, more than half is held by the United States, Canada, Mexico, Peru, Kazakhstan, and Russia.

Mining And Concentrating

Silver-bearing ores are mined by open-pit or underground methods and then are crushed and ground. Since virtually all the ores are sulfides, they are amenable to flotation separation,

by which a 30- to 40-fold concentration of mineral values is usually achieved. Of the three major types of mineralization, lead concentrates contain the most silver and zinc concentrates the least.

Extraction And Refining

The specific extractive metallurgy processes applied to a silver-bearing mineral concentrate depend on whether the major metal is copper, zinc, or lead.

From copper concentrates

The smelting and converting of copper sulfide concentrates result in a “blister” copper that contains 97 to 99 percent of the silver present in the original concentrate. Upon electrolytic refining of the copper, insoluble impurities, called slimes, gradually accumulate at the bottom of the refining tank. These contain the silver originally present in the concentrate but at a much higher concentration; for example, a silver content of 0.2 percent in the sulfide concentrate can result in a slime containing 20 percent silver. This is smelted in a small furnace to oxidize virtually all metals present except silver, gold, and platinum-group metals. The metal recovered, called doré, generally contains 0.5 to 5 percent gold, 0.1 to 1 percent platinum metals, and the balance silver. This metal is cast to form anodes and electrolyzed in a solution of silver-copper nitrate. Two different electrorefining techniques are employed, the Moebius and Thum Balbach systems. The chief difference between them is that the electrodes are disposed vertically in the Moebius system and horizontally in the Thum Balbach system. The silver obtained by electrolysis usually has a purity of three-nines fine; on occasion it may be four-nines fine, or 99.99 percent silver.

From lead concentrates

Lead concentrates are first roasted and then smelted to produce a lead bullion from which impurities such as antimony, arsenic, tin, and silver must be removed. Silver is removed by the Parkes process, which consists of adding zinc to the molten lead bullion. Zinc reacts rapidly and completely with gold and silver, forming very insoluble compounds that float to the top of the bullion. These are skimmed off and their zinc content recovered by vacuum retorting. The remaining lead-gold-silver residue is treated by cupellation, a process in which the residue is heated to a high temperature (about 800 °C, or 1,450 °F) under strongly

oxidizing conditions. The noble silver and gold remain in the elemental form, while the lead oxidizes and is removed. The gold and silver alloy thus produced is refined by the Moebius or Thum Balbach process. The residue from silver refining is treated by affination or parting to concentrate the gold content, which is refined by the Wohlwill process.

From zinc concentrates

Zinc concentrates are roasted and then leached with sulfuric acid to dissolve their zinc content, leaving a residue that contains lead, silver, and gold—along with 5 to 10 percent of the zinc content of the concentrates. This is processed by slag fuming, a process whereby the residue is melted to form a slag through which powdered coal or coke is blown along with air. The zinc is reduced to the metallic form and is vaporized from the slag, while the lead is converted to the metallic form and dissolves the silver and gold. This lead bullion is periodically collected and sent to lead refining, as described above.

From scrap

Approximately 60 percent of all silver produced is used in the photographic industry, and the metal can be recycled from spent photographic processing solutions and photographic film. The solutions are processed on-site electrolytically, while film is burned and the ashes leached to extract the silver content.

High-grade jewelry scrap is usually realloyed on-site rather than being refined. Jewelry sweeps, the fine dust generated in the polishing and grinding of precious metals, are usually smelted to form an impure silver, which is electrorefined. Because of the much lower value of silver scrap, recycling techniques applicable to gold (e.g., cyanidation of low-grade scrap) are uneconomic for silver. Low-grade silver scrap is instead returned to a smelter for processing.

Assaying

The fire assaying techniques described above for gold are equally applicable to silver. In order to determine the silver content of a fire assay bead, the bead is first weighed, then boiled with 35-percent-strength nitric acid to dissolve its silver content, and then weighed again. The weight loss defines the silver content, and the remaining residue contains the gold. In order to ensure complete dissolution of the silver, the silver content of the bead should be at least 60–70 percent. A process routinely employed in the fire assaying of gold ores is the

addition of silver prior to fusion of the ore in order to ensure that the silver content of the final bead is high enough to dissolve. This is called inquartation, and the separating of silver and gold by leaching with nitric acid is referred to as parting.

The Metal And Its Alloys

Even silver that has been fully work-hardened, either by rolling or forging, gradually recrystallizes, even at room temperature. This greatly softens the metal, making it susceptible to scratching and marring. To maintain hardness, therefore, other metals are added to form alloys that are harder, stronger, and less prone to fatigue.

The best-known copper-silver alloy is sterling, which is 92.5 percent silver and 7.5 percent copper. (In England sterling silver is traditionally identified by the hallmark of a lion passant.) Coin silver is an alloy of 90 percent silver and 10 percent copper. For jewelry and ornaments, 85–90 percent silver (and the balance copper) is frequently used. Dental alloys of 60–70 percent silver, 18–25 percent tin, 2–14 percent copper, and 0.5–2 percent zinc are amalgamated with varying quantities of mercury to form the filling materials for cavities in teeth.

Silver and alloys of silver and copper, although stable in air, tarnish in the presence of sulfur. In order to improve tarnish resistance, silver alloys with at least 40 percent palladium added are created for telephone relays, circuit breakers, and other electrical switching equipment. In order to obtain the lustre and corrosion resistance of silver on other metals and alloys, silver electroplating is practiced. Cyanide-based baths are most commonly employed.

Because silver has the highest electrical conductivity of all metals, it is used in alloyed form for electrical contacts. Palladium and nickel improve the metal's chemical resistance to oxidation and sulfidation as well as its resistance to corrosion.

Silver brazing fillers are the most frequently used precious-metal fillers. They are suitable for brazing nearly all steels and nonferrous metals except aluminum, magnesium, and titanium. A typical brazing alloy composition is 50 percent silver, 34 percent copper, and 16 percent zinc.

Chemical Compounds

Between 25 and 40 percent of industrial silver is consumed in the production of the photosensitive chemicals silver chloride and silver bromide. These silver salts are prepared by adding sodium chloride or sodium bromide to a very pure solution of silver nitrate. The highly insoluble silver chloride or silver bromide then precipitates from solution. All processing takes place in the absence of any light.

Silver oxides (both Ag_2O and AgO) serve as the cathodic materials in silver-zinc primary and secondary (i.e., rechargeable) batteries. The high energy density of the primary batteries (as measured by available electrical energy per unit weight) is responsible for their employment as miniature power cells for cameras and timepieces.

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