Alberto Cremona, Gerhard Mestl
Clariant Prodotti (Italia) SpA, Novara
alberto.cremona@clariant.com

http://dx.medra.org/10.17374/CI.2023.105.4.46

SILVER PERSPECTIVES

Silver, a precious metal with unique physico-chemical properties, is a key element playing an important role in heterogeneous catalysis and in the global decarbonization process, with particular regard to photovoltaic power and electric vehicles. The present article aims at a concise update concerning main current and future uses, production, reserves, and recycling prospects.

Silver is one of the seven metals known since antiquity and plays a major role in human evolution [1]. Its contemporary importance is growing, and catalysis constitutes a major industrial use: global silver catalyst market was estimated to be US$ 3.1 billion in 2021 and is expected to reach US$ 6 billion by 2028 at an annual growth rate over 6% [2].

Among the rarest elements in the continental crust with a concentration around 75 parts per billion (ppb), it can occur naturally in a native form although is more frequently associated with gold, lead, copper and zinc ores [3]. It is a soft and lustrous metal with the highest electrical and thermal conductivity; values of melting point (962 °C) and density (10.5 g/cm^3) are the lowest among the precious metals. It has high photosensitivity to visible, X-ray and γ-ray wavelengths and is stable in air and water, except when it reacts with sulfur compounds to form silver sulfide Ag_2S, producing a black tarnish on the surface. Pure silver can be alloyed with other metals (*e.g.*, copper) to make it stronger while preserving ductility and increasing resistance to tarnish.

Silver belongs to group IB transition metals with a $Kr4d^{10}5s^1$ electronic structure. The $5s^1$ shell is the principal valence orbital, which accounts for the preference for oxidation state +1 and the 4d shell can also act as a valence orbital, resulting in oxidation states 2 and 3. Due to the contribution from the inner valence orbital and the small differences between the energies of the valence electrons, silver exhibits the typical catalytic activity of a transition metal [4].

It shares, together with platinum group elements and gold, the application of a specific weight unit, the troy ounce, and the gold/silver ratio, *i.e.* the ratio of gold and silver prices, is reported in historical charts reflecting the market strength of the respective metals [5].

Its most important markets today are the New York Commodities Exchange (COMEX), the Tokyo Commodity Exchange (TOCOM), the Chicago Board of Trade, the London Bullion Market, the Multi Commodity Exchange of India, and the Shanghai Futures Exchange (SHFE). Silver prices traditionally react to macroeconomic trends with more volatility than gold and a high market fragmentation does not prevent its prices from being target of intensive financial speculations [6].

Different governmental, industrial, and financial organizations represent an invaluable source of specialized information: most notably, the Silver Institute (Washington, DC) a nonprofit international association of mining houses, refiners, bullion suppliers, manufacturers, and investment traders [7].

The present note aims at a concise update concerning uses, market, and resources.

Uses

Today, silver plays a relevant role in different advanced sectors and 508 million ounces (Moz) were destined for industrial uses in 2021, equivalent to 48% of total physical demand (a 9.3% rise on a yearly basis). Photography, jewelry, and silverware accounted for 24% of demand, with the rest related to investment (Fig. 1) [8].

Current changes in the energy and automotive industries strongly contribute to industrial demand as a result of the ongoing decarbonization process. In particular, photovoltaic (PV) power is under expansion among the renewable energy so-

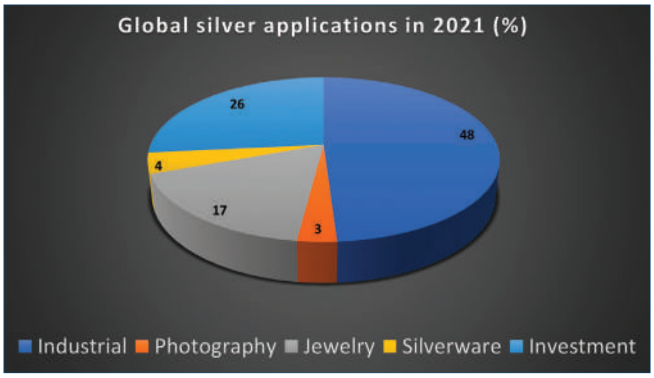

Fig. 1 - Global silver applications, in % (from World Silver Survey 2022, The Silver Institute, April 2022)

lutions and in 2021 record high PV installations required 113.7 Moz (3,536 t) of silver, close to 11% of total demand and to be compared to only 50.5 Moz in 2013. Silver is used in solar cells to conduct the electric charge out of the cell and into the system. Each module requires only a few milligrams of precious metal but at the current growth rate solar manufacturers would require over 20% of the current annual silver supply by 2027.
The green revolution is also affecting its demand in the automotive industry since the metal is extensively used for contacts and circuitry and an increasing number of advanced electronic control units has been introduced in the last few years. Additional demand is linked to the diffusion of electric vehicles (EV) and their sophisticated energy management systems. As a result, silver demand in the automotive segment was estimated over 60 Moz in 2021 and will raise to 88 Moz by 2025 [9, 10].
In 2022 demand for silver is expected to have reached a new high of 1.21 billion ounces, up 16% from the previous year and driven by increase in industrial use to 539 Moz, linked to vehicle electrification, green infrastructures, and diffusion of 5G broadband cellular networks.
Among the industrial uses, silver catalysts are especially important for the production of two primary building-block chemicals, ethylene oxide and formaldehyde.
Ethylene oxide (EO) is a precursor compound for ethylene glycol, which in turn is used for the production of antifreeze coolants and polyethylene terephthalate (PET), a resin of the polyester family used in fibres for clothing, plastic bottles, and food containers. Global EO capacity exceeded 41 million metric tons in 2021 with respect to 26 million metric tons in 2012 [11].
Formaldehyde (FA) is used for glues and resins, dyes, textiles, disinfectants, building materials and automotive parts and constitutes with acetylene the starting material to produce 1,4-butanediol (BDO), an intermediate for synthetic biodegradable plastics. Global FA production was around 17.5 million metric tons (FA 100%) in 2020 and is set to increase steadily in the next years [12].
Considering the global megatrends for population, energy consumption, and transportation, it is expected that demand for the mentioned products will significantly rise, and therefore the quoted processes will be briefly described [13].
The catalytic properties of silver towards ethylene epoxidation are known since 1931 and today industrial production takes place on a 15 wt% silver catalyst supported on low surface area α-alumina [14-16].
Reaction is performed in fixed-bed tubular reactors at 230-270 °C and 10-25 bar and selectivity is the most important catalytic parameter because the desired selective epoxidation (mildly exothermic) is accompanied by the thermodynamically favored total combustion of ethylene and ethylene oxide. There are currently two types of industrial catalysts: supported Re/Cs/Ag/Al_2O_3 and alkaline-metal (Na, Cs)-promoted supported Ag/Al_2O_3 catalysts, operating respectively in excess C_2H_4/O_2 and in excess O_2/C_2H_4 with an EO selectivity over 90%.
From a mechanistic point of view, ethylene interacts with oxygen atoms pre-adsorbed on silver: the metal catalyzes the selective addition of an oxygen atom from O_2 across the carbon-carbon double bond in ethylene and the high selectivity derives from the electrophilic nature of a particular surface oxygen species. As commonly observed in heterogeneous catalysis, the performance in terms of activity and selectivity of nanoparticles is strongly affected by their size. However, the structure sensitivity is usually evidenced for many catalytic reactions with particles smaller than 10 nm, whereas optimum silver particles for EO formation are in the range of 100-1000 nm, where a bulk silver type behavior is to be expected [17].
Catalyst life is typically three years with several regenerations, and it can be estimated that 148 Moz

of silver (4,600 tons) resided across over 400 EO plants around the world in 2021, an amount close to the world's entire demand for jewelry in the previous year. Around 60 Moz (1,840 t) are treated each year globally from EO spent catalysts in a closed-loop recycling process.

The reaction of oxidehydrogenation of methanol to formaldehyde over Ag is one of the oldest industrial catalytic technologies (use of a silver catalyst was patented in 1910) and the first non-Pt based catalytic industrial process. Since the 1950s the Ag process is being gradually replaced in modern plants by the selective oxidation with Fe-Mo catalysts, which nowadays accounts with significant geographical differentiations for more than 50% of world's production [18-21].

Polycrystalline silver (crystals of high purity electrolytic Ag) with very low surface area and different size distribution is the preferred catalyst of choice. The catalytic beds are shallow - only few centimeters deep - in order to minimize the contact time between process gas and catalyst and to avoid FA decomposition reactions. Process conditions involve methanol inlet concentration higher than 40% in an excess relative to air, temperatures between 600 °C to 720 °C and ambient pressure. Yields range from 82 to 92% and other carbon by-products mainly include CO_2 and CO.

Three different oxygen species O_α, O_β and O_γ are assumed to form during the reaction and show different stability regions according to temperature. Oxygen may dissolve in the silver lattice forming a reservoir of oxygen atoms and a strongly bound oxygen species O_γ is generated from O_β, when the latter segregates from the bulk to the surface: it exists predominantly in the uppermost layer and tends to be highly selective towards the dehydrogenation of methanol.

Particles restructuring takes place in the catalytic system and their morphology changes strongly during the reaction. Generally, sintering occurs due to high temperatures, which results in high pressure drop decreasing the performance of catalyst.

Use losses of the catalyst are small (2-3%) and depending on the operating conditions and poisons presence (*e.g.*, iron in methanol must be lower than 0.005 ppm) the lifetime varies between a few months to a year: it can be assumed that around 1,250 tons of silver are yearly employed in the specific sector.

Fig. 2 - Native silver mineral from Kongsberg (Norway) (Photograph by R.M. Lavinsky, distributed under a CC-BY 2.0 license)

Both epoxidation and dehydrogenation processes display that the presence of oxygen in the reactive atmosphere donates the silver metal unique catalytic properties, making it suitable also for nitrogen monoxide (NO) reduction in oxygen rich environment [22]. However, the poor thermal stability of supported Ag-based catalysts restricts their use in the environmental sector, due to sintering phenomena caused by a low Tamman temperature (481 °C).

Concerning future applications, classical use of silver in the manufacture of jewelry and silverware will remain relevant but mid-to-long term supply might become critical due to unprecedented major importance of industrial use [23].

Production & market

The metal occurs free in nature as a native element (Fig. 2) also in the form of nuggets sometimes alloyed in various percentage with gold as electrum (AgAu, cubic). Due to its strong geochemical affinity for sulfur (*i.e.*, a chalcophilic element) it is often found in a combined form in sulfide ores and the most common silver-containing minerals are acanthite and argentite (Ag_2S), pyrargyrite (Ag_3SbS_3), proustite (Ag_3AsS_3), tetrahedrite-tennantite [$(Cu,Fe,Ag)_{12}(Sb,As)_4S_{13}$], chlorargyrite (AgCl), and argentojarosite [$AgFe_3(SO_4)_2(OH)_6$]). The minerals are associated with lead, copper, gold, and zinc and the ores of these elements, where silver only occurs as a trace impurity, are its main primary commercial sources. Ores in which silver is the only valuable metal are located in Mexico and to a small extent in the United States (Utah) and depending on price it can be profitable to process materials containing 0.01% (100 ppmw) precious metal **[24, 25]**.

In 2021 over 70% of all silver extraction was as by-product of other metallurgies, with exclusive mining accounting for 28% of global production: the proportion explains the relative slowness of mining activity response to price variations and the higher impact of prices on the revenues of companies focused on primary silver production.

The extraction level is mainly related to actual demand: in 2021, global mine production increased by 5.3% y/y to 822.6 Moz (25,587 t). This was the biggest annual rise in silver output since 2013 and was largely the result of a recovery following the pandemic. Output from primary silver mines increased by 10.2% y/y to 229.9 Moz (7,152 t) and by-product silver output from lead-zinc and gold mines were respectively 252.8 Moz (7,862 t, 31% of the total) and 127.6 Moz (3,967 t, 16% of the total) (Fig. 3) **[8]**.

Fig. 3 - Aerial view of Cerro de Pasco city (Peru) with the open-pit mine (http://cerropasco.blogspot.com/)

The silver-containing base metal ores are initially crushed and concentrated by flotation methods to achieve mineral concentrations 30-40 times higher than natural occurrences. In this process, the hydrophobic sulphide particles adhere preferentially to a froth of oily bubbles that floats to the surface and is skimmed off. The specific methods for precious metal recovery are different for ores of copper, lead, zinc, and gold. As a by-product of copper, silver is separated with copper by smelting and then recovered as silver (so called doré due to a typical content of gold around 0.5-5%) in the anode slimes after electrolysis. As a by-product of lead or lead-zinc ores, silver is recovered with the lead bullion and removed by a liquid-liquid extraction with zinc added to a molten lead/silver mixture. Cyanide leaching can be used to recover both gold and silver from the respective ores. Silver metallurgy is complicated because of the relatively low concentrations in ores, the large number of minerals existing also within the same deposit

Fig. 4 - The Fresnillo complex (Mexico) in a painting dated 1846 by P. Gualdi. Silver ore amalgamation with mercury in the grey circles

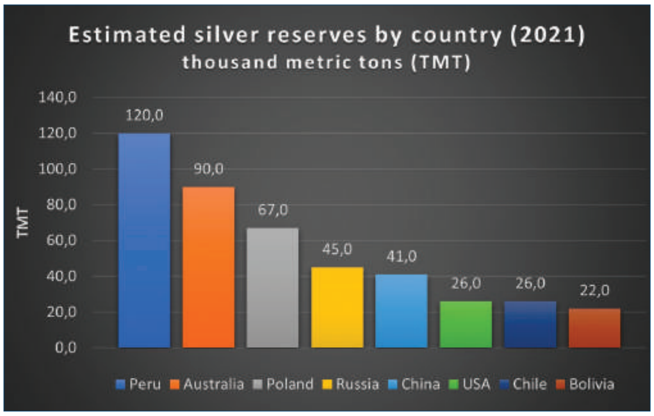

Fig. 5 - Silver reserves in thousand metric tons (from Silver, Mineral Commodity Summaries, U.S. Geological Survey, January 2022)

and the substitution of silver for copper and other elements in many minerals. Because of such complexity, comprehensive general plans are not easily described (Fig. 4) [26].

Electrorefining is the most complete method for obtaining a high purity metal from the crude product. It involves electrolysis of a silver anode in silver nitrate to form pure silver crystals on the cathode and precious metals such as gold can be collected from the slime when the silver and base metals dissolve in the electrolyte bath [27].

Approximately 57% of the world's silver production takes place in the Americas, with Mexico, Peru, and Chile supplying 40%. In the rest of the world, China, Australia, and Russia combine to make up nearly 33% of the world's production. Mexico, China and Peru were in 2021 the top three producing countries with shares of 23%, 14% and 13% respectively. Global reserves amount to 530,000 tons with Peru (23%) and Australia (17%) the front runners in a widespread geographical distribution (Fig. 5) [28]. Geo-political issues concerning supply seem limited but a short burn-off time around 15 years (defined as the ratio between known reserves and average annual mining rate at the current consumption rates) can be calculated. Surprisingly, silver is not enclosed in the several lists of critical raw materials although it has historically been a limited resource even when its industrial use was null and the ore grades is steadily declining: for example, production from the mines of Fresnillo (Mexico) and Cannington (Australia) reduced from 38.6 Moz each in 2010 to 13.1 and 11.6 Moz in 2020 respectively. Therefore, the outlook of the long-term supply is unfavorable and the estimated average silver price in 2021 was US$ 25.00 per troy ounce, 22% higher than the average price in 2020. In 2022 mined silver production is estimated to rise by a limited 1% year-on-year to 830 Moz despite a market forecast to record a second consecutive annual deficit four times the level seen in 2021 (194 Moz) [29].

Recovery & sustainability

Silver was already classified as a potentially scarce resource nearly half a century ago [30] and recurrent deficits on the market are made up by recycling and release from above ground stocks. In 2021 around 17% of world's production was obtained by recycling of old scrap as a secondary resource with important sectorial differentiations: this figure yearly rose by almost 7% to an eight-year high of 5,382 t (173 Moz) and the most important driver was the jump in industrial scrap supply, displaying a quicker pace after the pandemic and higher pricing attraction [8].

The different recovery techniques from ores mentioned above can also be utilized for recycling from scrap including solar panels and electronic equipment.

Such as usual in the precious metals sector, the chemical industry is a forerunner in the efficiency of the recovery process. Recycling rates of the catalysts for EO and FA "closed-loop" processes approach 100% and the spent catalyst is reactivated by the same catalyst manufacturers. A small part of the deactivated catalyst needs replacement and is recycled to the general silver loop. Recovery of silver from the spent alumina supported EO catalysts is usually accomplished by hydrometallurgical treatment, in which silver and other minor elements are first leached using moderately concentrated nitric acid and polycrystalline bulk silver catalysts for FA may be electrolytically regenerated on site [31, 32].

Although the potential for recovering silver from photovoltaics modules is significant, the current low collection and recovery rates, coupled with an average 25-year module lifetime, mean that

recycled silver from PV modules can contribute only marginally to supply [33].
Another scenario is offered by the electronic sector, a case of "open-loop" where it is estimated that in 2019 globally the formal documented collection and recycling was 9.3 million metric tons (17.4% compared to e-waste generated), showing that recycling activities are not keeping pace with the global growth of e-waste. A large part of Waste Electric and Electronic Equipment (WEEE) is recycled by the informal sector, with a substantial proportion of end-of-life products traded to developing countries. Under the auspices of the EU WEEE Directive (2012/19/EU) with the aim to promote the recovery of electrical scrap in Europe, the e-waste documented to be collected and properly recycled was about 42.5% in 2019 from 30% in 2016 [34, 35]. The silver content in electronic scrap varies between 0.02% and 0.5% (*e.g.*, a cell phone contains on average around 1,340 ppmw Ag and a computer board 1,000 ppmw), a concentration significantly higher than most ores. Few specialized companies take care for global recycling activities and silver, although constituting on average less than 1% of the metal mix volume - comprising both precious and transition metals -, makes up for over 25% of the value. In the case of WEEE industrial recovery, a difficulty is generated by losses of precious metals in the dust and ferrous fractions due to mechanical treatment (silver and palladium, especially). For instance, cell phones and circuit-boards are complex with respect to metals distribution and sorting of the shredded parts by traditional separation techniques (magnetic, etc.) can lead to substantial losses [36-38].
Silver is becoming one of the most demanded metals of the current decade: even for the ancestral metal with the alchemical symbol of the moon time has come to work towards a sustainable life cycle.

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Argento: prospettive

L'argento, metallo prezioso con proprietà fisico-chimiche uniche, è un elemento chiave che svolge un ruolo importante in catalisi eterogenea e nel processo globale di decarbonizzazione, con particolare riguardo all'energia fotovoltaica e ai veicoli elettrici. Il presente articolo si propone di fornire un sintetico aggiornamento sui principali utilizzi attuali e futuri, produzione, riserve e prospettive di riciclo.