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http://dx.medra.org/10.17374/CI.2023.105.6.57

GOLD PERSPECTIVES

Gold is a fascinating precious metal with unique physico-chemical properties exploited in important technological applications including heterogeneous catalysis. The present article aims at a concise update concerning main current and future uses, production, reserves, and recycling prospects.

Gold continues to fascinate across millennia by its unique beauty and properties [1]. Its contemporary industrial importance is growing, and catalysis constitutes a relevant use, although limited in quantitative terms: global gold catalysts market was estimated to be over US$ 430 million in 2020 and is expected to expand in the next years [2].

Among the rarest elements in the continental crust with a concentration around 5 parts per billion (ppb), it can occur naturally in a native form. It is soft, lustrous, and the most malleable and ductile of all metals; values of melting point and density are 1,064 °C and 19.3 g/cm^3 respectively. It does not oxidize nor reacts with water, ozone, and hydrogen. Alloys can be formed with different other metals: particularly mercury, zinc, lead, and copper act as collecting agents [3].

Gold belongs to group IB transition metals with a [Xe]$4f^{14}5d^{10}6s^1$ electronic structure. The $6s^1$ shell is the principal valence orbital, which accounts for the oxidation state +1 (aurous) and, less commonly, +3 (auric). The relatively high ionization energy of Au affords this metal little attraction in terms of molecular or complex chemistry and in the past it has conventionally been regarded as catalytically inert. In fact, dissociative adsorption of O_2 and H_2 on the surface of Au does not occur at temperatures below 473 K [4].

It shares, together with platinum group elements and silver, 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. Karats are a measure of fineness and refer to the gold percentage in an alloy: pure gold is 24 karats (1000/000 fine expressed in parts per thousand) [5].

The most important market is the London Bullion Market Association (LBMA), whose members are companies involved in trading, brokering, refining, mining, and assaying of precious metals. The LBMA issues the “Good Delivery Rules”, containing international regulative standards for gold and silver bars, and the ‘Good Delivery List’ including the refineries fulfilling the selection criteria. The rules contain requirements concerning the fineness, weight, dimensions, appearance, marks, and production of precious metals bars [6].

Gold represents a traditional refuge investment, and its price reacts to macroeconomic trends with less volatility than the sister metal silver and platinum group elements. The major central banks hold large reserves and the US Treasury detained more than 8,000 metric tons in 2022 [7].

Different governmental, industrial, and financial organizations offer a wide source of specialized information: most notably, the World Gold Council (London, UK) is an international association comprising the world’s leading gold mining companies [8].

The environmental and human issues of gold mining and metallurgy, associated with the important contribution of artisanal mining, favored the development of several non-governmental organizations with the goal to raise a sustainable awareness among the stakeholders. As a result, gold-related activities are subjected to several standards and certification programs as well as to the OECD Due Diligence Guidance for Responsible Supply Chains of Minerals.

The present note aims at a concise update about uses, production and market, providing such as usual specialized bibliographic references for further reading.

Uses

Consumer and investor purchases constitute over 90% of gold demand: in times of exceptional events, behavior changes especially concerning luxury goods, and statistics since 2020 do not give an adequate picture of global demand. Therefore, although in the last years jewelry has been confirmed by far the most important sector, numerous applications taking advantage of gold's unique physico-chemical properties make it an important industrial metal for the electronics, weapons, and aerospace industry (Fig. 1). Its reflective powers protect spacecraft and satellites from infrared solar radiation, and it is extensively used due to high corrosion resistance and electrical conductivity in the manufacture of connectors, printed circuits, semi-conductors, relays, and switches: products mainly involved are smartphones, personal computers, and light-emitting diodes [9].

In 2022, gold demand raised to 4,741 tons, the strongest over a decade and almost on a par with 2011, a time of extraordinary investment demand [10]. The technological sector contributed with 308.5 tons (around 6%), and electronics with 251.7 tons was the main driver.

Despite being a minor application, gold use in heterogeneous catalysis is a field particularly important for vinyl acetate and vinyl chloride production [11, 12].

Vinyl acetate monomer (VAM) can be polymerised to form polyvinyl acetate (PVA), or with other monomers to prepare copolymers such as ethylene-vinyl acetate (EVA), vinyl acetate-acrylic acid (VA/AA) and polyvinyl chloride acetate (PVCA). This makes VAM an important building block in a wide variety of products including construction, packaging, paints, coatings, adhesives, and textiles. Global VAM demand was 5.5 million metric tons in 2021 and is expected to evolve at an annual growth rate around 5% until 2030 [13].

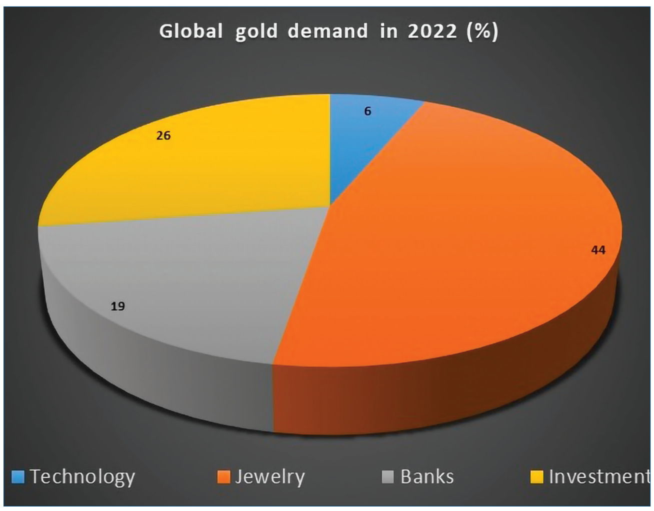

Fig. 1 - Global gold demand, in % (from Gold Demand Trends, World Gold Council, 31 January 2023)

Vinyl chloride monomer (VCM) is a precursor compound for polyvinyl chloride (PVC), one of the most important polymers used for production of pipes, fittings, profiles, cables, wires and sheets. In 2020, world VCM capacity amounted to 57.4 million metric tons, and China accounted for over 40% of the share [14].

Vinyl acetate monomer (VAM) is produced from acetic acid, ethylene and oxygen using palladium-gold catalysts in fixed/fluid bed processes according to the reaction:

$$C_2H_4 + CH_3COOH + 1/2O_2 \rightarrow C_2H_3OOCCH_3 + H_2O$$

The reaction is typically carried out at 130-200 °C and 5-12 bar pressure and proceeds with VAM selectivities as high as 95%.

Palladium exhibits a strong catalytic activity for the total combustion of ethylene and acetic acid and therefore has a low selectivity for VA synthesis: the addition of Au to a supported Pd catalyst significantly enhances selectivity and silica-supported Pd-Au bimetallic catalysts promoted with potassium acetate have been used as commercial catalysts for VA synthesis since the 1990s. The presence of gold as promoter leads to a strong increase in space time yield (STY) compared with the use of Pd alone and its role is probably linked to an electronic interaction, weakening the bonding strength of carbon monoxide (CO) and blocking the path to ethylene decomposition.

It is estimated that 4 tons of gold are held up in industrial reactors for VAM production worldwide: since the operational cycle is between 2 and 3 years, 2 tons of gold would be theoretically needed per year [15, 16].

Regarding the manufacture of VCM, there are two key routes: ethylene oxidative hydrochlorination and acetylene hydrochlorination. Over 66%

of global production in 2020 was via the ethylene route, and the remainder was acetylene-based. In the oil-based economies the ethylene route dominates, but the coal-based acetylene hydrochlorination process remains economically advantageous in China and India. This process uses mercuric chloride as a catalyst and is the second largest demand sector for mercury: direct replacement of mercuric chloride with an alternative catalyst represents an environmental breakthrough.
The scheme of the strongly exothermic reaction via acetylene is the following:

$CH{\equiv}CH + HCl \rightarrow CH_2{=}CHCl$

Different studies identified that active, carbon-supported gold (0.1-0.3 wt%) catalysts display at 180 °C up to three times more activity than commercial mercuric catalysts and the mechanism is influenced by the Au^{3+}/Au^{1+} redox couple. Deactivation phenomena concerning Au^{3+} reduction to Au^0 and oligomer formation can be minimized by operating at lower temperatures, high metal loadings and on-stream treatment with several reagents (*e.g.*, hydrogen chloride, chlorine, and nitrogen monoxide). Estimates suggest that, in case of widespread application of gold catalysts in the acetylene-based process, relevant amounts of precious metal could be required per manufacturing plant, but full commercial switch must still take place **[17, 18]**.
Other emerging sectors for gold use in heterogenous catalysis concern direct synthesis of hydrogen peroxide (H_2O_2) **[19]**, carbon monoxide (CO) oxidation **[20, 21]**, and nitrogen oxides (NO_x) reduction **[22]**. Gold increases efficiencies in the specific reactions while helping to thrift platinum group metals: however, price considerations are economically predominant and constitute the real hurdle to diffusion of the yellow metal also in homogeneous catalysis, where a relatively high loading is needed in gold-catalyzed reactions (1-10 mol %) **[23]**. Novel special applications of gold-based nanoparticles are also rising in medicine for antitumor diagnosis and therapy **[24]**.

Production & market

Total annual gold supply increased by 2% in 2022, to 4,755 tons and mine production increased to a four-year high of 3,612 tons **[10]**.

The metal occurs in nature as a native element also in the form of nuggets (Fig. 2) often alloyed in various percentage with silver as electrum (AgAu, cubic) and it is a constituent of various alloys containing mainly copper and platinum group elements **[25]**.
Quartz-pebble conglomerate deposits supply approximately 50% of the world's gold production and their erosion can lead to veins in rocks or deposits in rivers.
The following ores classification was proposed **[26]**:
- *native ores*, in which the precious metal can be removed by gravity separation, amalgamation, and/or cyanidation (*e.g.*, in placer deposits);
- *sulfides*, occurring either as free particles or disseminated in auriferous sulfides [*e.g.*, pyrite (FeS_2), chalcopyrite ($CuFeS_2$) or arsenopyrite (FeAsS)];
- *tellurides*, calaverite and krennerite [$AuTe_2$] contain about 40 wt% gold, sylvanite [$(Ag,Au)Te_2$] and petzite [Ag_3AuTe_2] about 25 wt%;
- *other minerals*, as with arsenic and/or antimony (*e.g.*, aurostibite, $AuSb_2$), with copper porphyries (as selenide and telluride), with lead and zinc minerals, and with carbonaceous materials.

Gold is one of the few metals for which artisanal small-scale mining (ASGM) is still practiced in secondary deposits (*e.g.*, alluvial) located in developing countries, providing a livelihood for millions of

Fig. 2 - Native gold mineral from Colorado (USA). Photograph by R.M. Lavinsky, distributed under a **CC-BY 2.0 license**

people predominantly in Africa, Latin America, and Asia. The specific production is difficult to quantify and may give rise to discrepancies in reported data: it is estimated that "dirty gold" represents around 20% of the world's annual newly mined supply. Many of these small-scale mining operations use amalgamation, a process reputed the largest source of mercury pollution [27-29].

In large-scale gold mining (LSGM) gold is mined both in open-pit and underground mines at depths up to 4 km, depending on the grade, size, and shape of the deposit. Better-quality underground mines contain around 8-10 g/t (*i.e.*, ppmw) gold, with some underground mines having averages of around 4-6 g/t; open-pit mines usually display lower grades from 1 g/t (or less) to 4 g/t [30, 31]. The ore can be transported by rail or conveyor belts to the processing plants, where gold is separated from the other minerals according to a site-specific process. First, mechanical steps and physical methods such as crushing, grinding, sieving, and gravity separation take place in a mill. When gold is associated with sulfides, it may be concentrated by froth flotation and cannot be processed by cyanide leaching directly because the sulfides hinder the leaching of gold. Therefore, the ore is pretreated by roasting at 600-800 °C to oxidize off sulphur and arsenic as their oxides. Bio-oxidation is another technology applied to reduce the environmental effect of cyanide consumption [32].

These steps are followed by chemical processes, which can be used to extract up to 99% of the gold. The most common chemical process used in LSGM is cyanide leaching followed by precipitation [33]. After milling, the ore containing 5-10 ppm gold is leached with a NaCN solution with formation of a $NaAu(CN)_2$ complex adsorbed on carbon. The loaded carbon particles with about 4-8 kg Au/t carbon are sieved off, and gold is removed from carbon using a concentrated cyanide solution that is subject to electrowinning (Fig. 3).

Usually, low-grade doré - a gold-silver bullion of variable composition - ingots are produced on site and transported to refining plants to produce high-purity gold by the long-established Miller and Wohlwill processes. The first one uses chlorine to separate gold from silver, copper, iron, zinc, and lead impurities. In the Wohlwill process raw gold cast as anode plates is placed in an electrolyte containing hydrochloric acid and tetrachloroauric $HAuCl_4$ acid to obtain the degree of purity necessary for advanced technological applications (99.999%) [34].

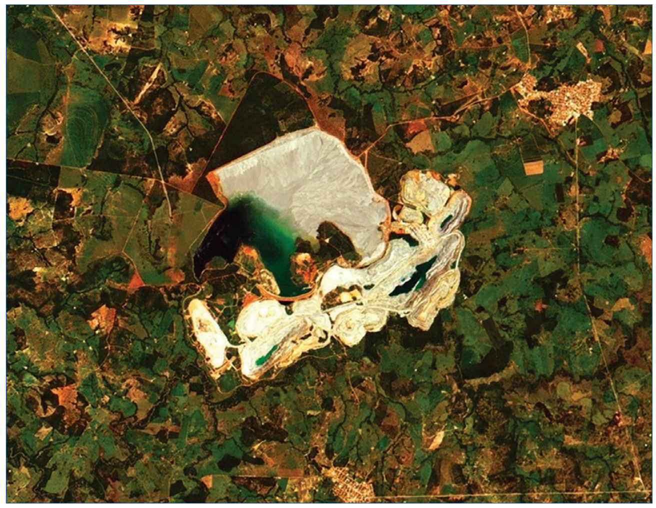

Fig. 3 - Aerial view of the Chapada mine at Goiás, Brasil's largest gold/copper mine, http://www.dsr.inpe.br

The Americas and Africa were the largest producing continents, with a total production volume that reached 1,049 tons and 981 tons respectively. China, Russia, and Australia led the producing countries ranking with 332 tons, 331 tons, and 315 tons each [35]. South Africa, until 2006 the world's major producer, lagged with 114 tons, although no country ever approached its peak production in the 1970s at more than 1,000 tons and around two-thirds of the world's total production [36].

Estimates indicate that around 200,000 tons of gold have been mined throughout history (of which around two-thirds since 1950) and almost all this metal is reputed still available due to its value, resistance to corrosion and oxidation, and consequent reuse [37].

Global mine reserves are well diversified across regions and are reckoned to be around 52,000 tons with Australia and Russia holding the main shares with 8,400 tons (16%) and 6,800 tons (13%) respectively (Fig. 4) [38]. Strikingly analogously to its sister metal silver, 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. Despite

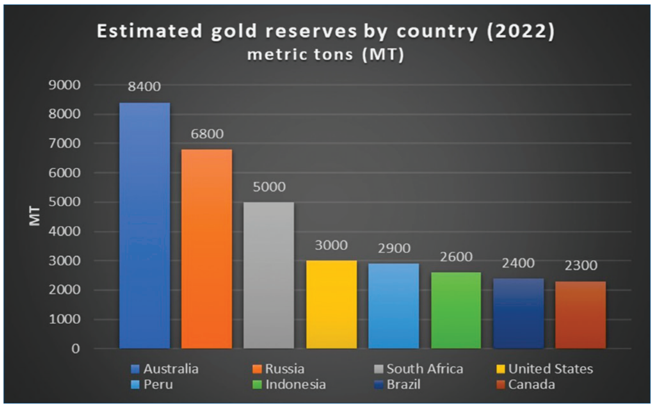

Fig. 4 - Gold reserves in metric tons (from Gold, Mineral Commodity Summaries, U.S. Geological Survey, January 2023)

several tipping points such as limited mining supply, low market potential for above-ground stocks, rising industrial applications and classification as a "conflict mineral", gold is not enclosed in any critical raw materials list.

Recovery & Sustainability

Over the last centuries the environmental price exacted for gold extraction and treatment was enormous especially in proportion to the low production volumes [39] and the issue persists today even in most developed countries. Substitution attempts are difficult to realize in high-tech applications due to unique physico-chemical properties and recycling assumes an essential role: social and environmental impacts of secondary production, also in relation to carbon footprints and slags, are minimal when compared to primary gold mining [40-42].
Total annual recycled gold increased by 1% in 2022 to 1,144 tons and constituted around 25% of global supply [10]: although it remains 30% below all-time highs reached in 2009, the recycled gold supply shows a raising trend over time, particularly swelling during economic crises in correlation to gold prices [43].
Precious metal recovery progresses also as mine deposits are shrinking and the market for consumer electronics continues to grow as well as the "urban" mines. For instance, typical gold concentrations are 300-350 g/t in smartphones and 200-250 g/t in personal computers circuit boards, approximately 100 times higher than that of the rich alluvial ores (2-4 g/t Au) [44].

Gold recycling industry includes two main sources [45]:
- high-value materials with a precious metal purity of at least 40% -mostly jewelry - account for over 95% of the total supply with end-of-life recycling rates over 90%.
- industrial materials contribute to the remaining 3-5% and consist primarily of gold recovered from Waste Electric and Electronic Equipment (WEEE).

High-value materials contain a significant proportion of gold alloyed with one or more metals and the separation processes are well-established physico-chemical procedures, such as heating and melting. Such methods are not adequate to reach the levels of purity often required by the hi-tech industry and further refining is executed by the Miller and Wohlwill processes [46].
The electronic sector is an "open-loop" where it was estimated that the formal documented collection and recycling was globally limited to 9.3 million metric tons (17.4% compared to e-waste generated) in 2019. Besides the arduous collection stage, reclaiming gold from WEEE, where it is used primarily in the form of thin wires and as a plating metal, is considerably complicated: these materials can contain up to 60 different elements and numerous complex chemicals. A pretreatment process involves washing, crushing, separation and incineration depending on the nature of scraps and the low purity metal obtained is converted into crude precious metal by dissolution, filtration, concentration, and reduction steps. Furthermore, typical difficulties are encountered, such as losses of precious metals in the dust and ferrous fractions during mechanical treatments [47, 48].
Similarly to primary production, unregulated recovery remains widely practiced by chemical leaching processes involving mercury, cyanide and aqua regia with pollution impact in developing countries, where a large share of WEEE is exported [49].
Few major companies operate state-of-the-art recovery techniques with integrated metals scrap cycles and gold, although constituting on average around 0.02 wt% of the metal mix volume, makes up for around 30% of the value, thus being a key enabler of the process economy [50]. In these

cases, the range of waste streams includes WEEE, spent catalytic convertors and chemical catalysts, industrial materials, and other manufacturing waste. Revenue figures are conceivable considering for example that only in 2021 over 1.4 bn smartphones were sold to end users worldwide.
Effective and original methods for valorizing the waste are becoming a priority and recently two gold (III) complexes obtained as recovery products from WEEE and their anion metathesis products were promisingly investigated as homogeneous catalysts in the first direct application in catalysis of gold sourced from e-waste [51].
After a long time, the principles of sustainability are showing the way for the most circular metal of mankind.

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Oro: prospettive

L'oro è un metallo prezioso affascinante con proprietà fisico-chimiche sfruttate in importanti applicazioni tecnologiche, tra cui la catalisi eterogenea. Il presente articolo mira ad un sintetico aggiornamento sui principali usi attuali e futuri, sulla produzione, sulle riserve e sulle prospettive di riciclo.