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COPPER PERSPECTIVES

Copper, a transition metal with unique physico-chemical properties, is a key element playing an important role in the global decarbonization process with particular regard to industrial equipment, electronics, communications, construction, and transports. The present article aims at a concise update concerning main current and future uses, production, reserves, and recycling prospects.

The history of civilization owes an enormous debt to the red metal, one of the first known elements still enjoying today a unique reputation as economic indicator. Its contemporary industrial importance is vital for many technologies enabling the transition to a climate neutral economy, and catalysis constitutes a remarkable use: the global nano copper oxide market was valued at US$ 39.1 million in 2021 [1].

Although ranking fourth after iron, aluminum, and chromium in terms of mined quantity, copper is a geochemically scarce element: while iron and aluminum are estimated to constitute respectively 5% and 8% of the earth's continental crust, copper content is around 0.006%. Furthermore, economically relevant iron ore deposits contain 20-65% iron, and bauxite deposits 22-29% aluminum, whereas concentrations of main copper mines are today generally lower than 0.5% [2].

Its utility is based both on physical and chemical properties: electrical and thermal conductivity, ductility, and corrosion resistance. Values of melting point and density are 1,083°C and 8.93 g/cm^3 respectively. The three traditional copper-based alloys, *i.e.*, brass (with zinc), bronze (with tin) and nickel-silver (zinc and nickel, with 52-80% Cu), contain no less than 40% copper. Hundreds copper alloys are classified under international standards and produced in all forms (wire, sheet, strip, plate, etc.) with a wide range of physical and mechanical properties [3].

Copper belongs to group IB transition metals with a [Ar]3d^{10}4s^1 electronic structure and a single valence electron. The element is low in the reactivity series and at room temperature in dry air slowly develops a thin protective film of copper (I) oxide. The presence of one electron in the s subshell above the filled d orbital makes copper ductile and conductive (thermally as well as electrically), whereas the characteristic color results from the electronic transition between the filled d orbital and the half-filled 4s orbital. Gold and silver, the other elements of the group IB, display physico-chemical properties similar to copper but availability and price differ by orders of magnitude [4].

Copper is a commodity metal, whose transactions are fixed at the London Metal Exchange (LME), the Commodity Exchange Division of the New York Mercantile Exchange (COMEX/NYMEX), and the Shanghai Futures Exchange (SHFE). These markets provide for the trading of futures, thus playing an important role in the global pricing mechanism; their exchanges account only for a fraction of the volume actually traded, the bulk takes place directly between producers and users [5].

The International Copper Association (ICA) - Washington, DC, USA - is a nonprofit organization of the copper industry and its stakeholders. Members represent the majority of the world's primary copper production, smelter/refiners, and fabricators, and more than 500 organizations are partners worldwide [6].

The International Copper Study Group (ICSG) is an intergovernmental organization of copper producing and consuming states functioning as an international commodity board. Member states represent approximately 85% of world mine production, refined production and usage and the main purpose is to promote international cooperation in the field [7].

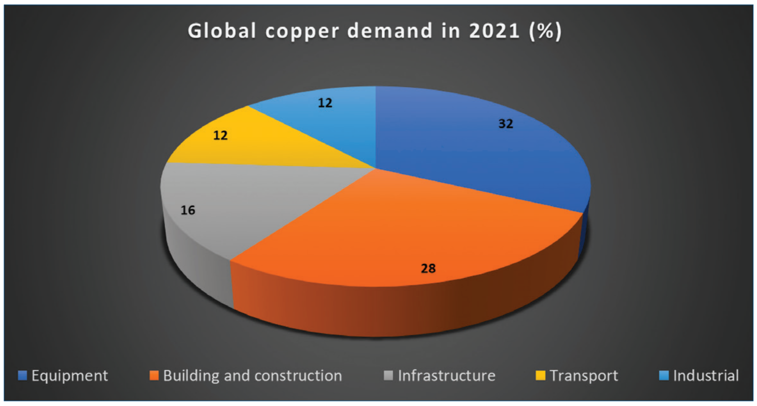

Fig. 1 - Global copper demand, in % (from The Pathway for Copper to 2030, RFC Ambrian, May 2022)

The present note aims at a concise update about uses, production, market, and reserves.

Uses

In 2022 refined copper usage stood at over 26 million metric tons and the market was balanced with a deficit amounting to less than 1% of global consumption: during the past decade strong growth in emerging economies and an increased use for innovative technologies led to significantly higher copper demand [8]. Copper consumption analysis can be related mainly to industry and product. In 2021 equipment accounted for about 32% of demand, building and construction 28%, infrastructure 16%, transport and industrial sectors 12% each (Fig. 1) [9]. Main product was wire, which represented about 60% of the share: for example, it represents 6-9% by weight (approximately 30 kg) of the content of a typical internal combustion engine (ICE) automobile, whereas an electric car would require up to three times more copper [10]. Proportion is even higher in the case of energy systems and new renewables contain even 12 times more copper than traditional ones. Considering the global megatrends for population, energy technologies, and transportation, the ability of copper to signal turning points in the economy will be reinforced: today, the new energy sector accounts for a small share but in the future around three-quarters of demand will come from solar photovoltaics, electric vehicles, wind turbines, batteries, and geothermal plants [11].
Copper's versatility is displayed in different fields of heterogeneous catalysis with particular importance for methanol and vinyl chloride synthesis [12, 13].
Methanol is one of the most common petrochemicals, accounting for roughly 16% of primary petrochemical consumption. It is an important building block to produce plastics, paints, cosmetics, pharmaceuticals, and pesticides. Derived chemicals include formaldehyde, acetic acid, olefins (via the methanol-to-olefins, MTO, and methanol-to-propylene, MTP processes), alternative fuels, and it provides an energy storage carrier for hydrogen. In 2022 methanol production was estimated over 111 million metric tons, an increase of nearly 4% compared to the previous year [14].
Vinyl chloride monomer (VCM) is a precursor compound for polyvinyl chloride (PVC), the second most widely consumed polymer 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 [15].
Methanol synthesis is a very exothermic reaction, and the conversion is equilibrium limited:

$$CO + 2H_2 \rightleftharpoons CH_3OH$$

The synthesis is conducted at 35-55 bar and 200-300 °C. In this temperature range, the maximum theoretical single pass conversion, which is limited by the reaction equilibrium, is 55-75%, although conversion is typically limited due to heat management. Selectivity can reach 99.9% with minor amounts of side products such as dimethyl ether and higher alcohols.
The current low-pressure technology came in use in 1970, though in principle copper catalysts had been known since the 1920s. The catalyst formulation is Cu/ZnO with a molar ratio of Cu/Zn in the range 2-3 and alumina acting as structural promoter to reduce the deactivation rate. Copper works as active element and ZnO is thought to function as a physical spacer between Cu nanoparticles. Before going into operation, the catalyst must be reduced converting copper oxide to the metallic form [16].
These catalysts are also active for the water gas shift reaction, which makes it possible to produce

methanol from CO_2. Capturing and converting greenhouse gases emissions is an advantageous technology for addressing global climate change and synthesizing methanol from CO_2 is a valuable approach. In practice, the composition of the synthesis gas employed for methanol synthesis contains a H_2:CO ratio larger than 2, partly to enable conversion of CO_2 in the syngas and partly to suppress side reactions.
The catalyst lifetime is several years, and deactivation can occur by Cu metal phase sintering and sulfur or halogenide poisoning [17]. It can be estimated that over 7,000 tons of copper are held up in industrial reactors for methanol production worldwide: since the operational cycle is up to 4 years, 1,800 tons of copper would be theoretically needed per year and metal price variations exert a high impact on cost.
Regarding the manufacture of VCM, ethylene oxidative hydrochlorination covered over 66% of global production in 2020, and the remainder was produced by the acetylene route in coal-based economies. The scheme of the strongly exothermic oxychlorination reaction of ethylene to ethylene dichloride (EDC) catalyzed by cupric chloride supported on γ-Al_2O_3 is the following:

$$CH_2{=}CH_2 + 1/2O_2 + 2HCl \rightarrow CH_2Cl\text{-}CH_2Cl + H_2O$$

The process, first commercialized in the mid-1960s, is executed in fluid or fixed bed reactors at 200-240 °C and 2-5 bar. Selectivities to EDC may be higher than 99%, with main by-products organochlorine compounds, CO and CO_2. The final step of the process is the thermal cracking of EDC at temperature around 500 °C to form VCM and HCl [18].
It is generally accepted that the reaction mechanism involves a three-step redox process: i) reduction of $CuCl_2$ to CuCl, ii) oxidation of CuCl to give an oxychloride, and iii) chlorination of copper oxychloride to $CuCl_2$ with HCl.
The competition between oxidation and chlorination processes depends on the operative conditions (mainly temperature and reactants partial pressures), which influence the catalyst surface composition. Promoters (*e.g.*, alkali earths metals and rare earth elements) can specifically increase the rate of the different steps and a high Cu^{2+} concentration is the key to high activity, selectivity, and stability of the catalysts [19].
The deposition of iron on the catalyst due to erosion in reactor walls leads to a yield increase of the total oxidation products and the main causes of deactivation are poisoning by impurities entering the reaction zone (*e.g.*, sulfur-containing compounds), particle agglomeration, and copper loss. It can be estimated that around 380 tons of copper are held up in industrial reactors for VCM production worldwide.
Other important and growing sectors for the metal in heterogenous catalysis concern hydrogenation, oxidation, and environmental reactions (*e.g.*, nitrogen oxides (NO_x) reduction) [20, 21].

Production & market

Total annual copper mine production increased by nearly 4% in 2022 to 21,922 thousand metric tons and growth rate in 2023 will be over 3%, benefiting from additional output of new and expanded mines: in 1990 it was slightly above 9,000 thousand metric tons. Major mining companies dominate the business, but rising prices and scarcity are kindling the development of artisanal mining, such as it happens from time immemorial for gold and silver [22].
Copper is seldom found in metallic form (Fig. 2) and out of more than 200 minerals with definable amounts only 20 are relevant as ores. Normally it is chemically combined with other elements and, as

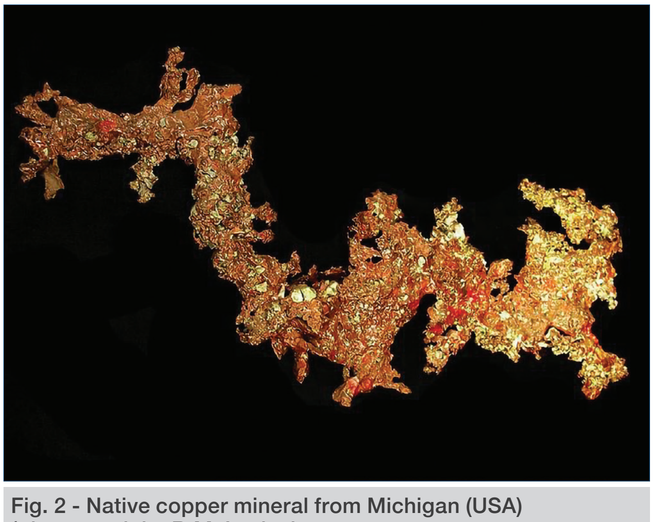

Fig. 2 - Native copper mineral from Michigan (USA) (photograph by R.M. Lavinsky, distributed under a CC-BY 3.0 license)

a typical chalcophilic element, sulfides are the principal class representing around 80% of the overall natural occurrence of the element. The most common is chalcopyrite $CuFeS_2$, a sulfide of copper containing nearly 35% copper and covering about half the world's deposits; bornite (Cu_5FeS_4) and chalcocite (Cu_2S) are prominent minerals. The other important class of industrial interest comprises the oxide minerals (*e.g.*, cuprite Cu_2O) **[23]**.
Metallic elements frequently found in copper ores are iron, lead, zinc, antimony, and others: for example, the Sudbury (Canada) mine contains also platinum group elements and Central African Copperbelt deposits are associated with cobalt. Indium, tellurium, selenium, and germanium are produced as by-product of copper metallurgy.
The major source of copper are porphyry deposits, where the primary economic mineral may be chalcopyrite or other sulfides minerals located along the west coasts of South and North America and in the South Pacific islands of Indonesia. These deposits have low grade (0.3-1.0% copper) and large tonnage (often greater than 1 billion tons): nowadays, high-grade mines (>2% Cu) are exhausted and the average copper content constitutes an essential economic factor. Mining and ore beneficiation contribute up to two-thirds of the final cost of copper and the extraction of precious metals and other elements can be decisive for the profitability. Primary copper predominantly comes from terrace-shaped open-pit mines, allowing economies of scale for the exploitation of low-grade ores: profitable production requires a minimum copper content in some cases as low as 0.3%, declining from the average copper grade of 1% in 2000 (Fig. 3) **[24]**.
Overall refining processes depend on the ore type. After crushing and grinding, the sulfidic ores can be concentrated from 0.3-1% to 20-40% copper content by froth flotation, and this concentrate is processed by pyrometallurgy and refined by electrolysis; according to another path, the less common oxidic ores are processed by hydrometallurgy and routed to leaching (solvent extraction) and electrowinning to recover a pure copper metallic cathode (SXEW process).
In the pyrometallurgical process, sulfide ore concentrate is roasted in air at 1,200-1,300 °C to give

Fig. 3 - Satellite image of the Escondida mine in Chile in 2000. Courtesy of NASA/METI/AIST/Japan Space Systems and U.S./Japan ASTER Science Team

a matte (primarily Cu_2S) with a copper content of about 50-70%. The matte is oxidized by dry air being flowed above the melt. Iron sulfide is oxidized and combines with the slag, while copper sulfide gives molten copper, called blister. The blister, which contains about 1% impurities, is melted in pure oxygen and cast into rectangular anodes and must be further electrorefined. A flash smelting process combining all the reaction phases - roasting, smelting, and converting - in a single step is generally adopted today.
Pure electrorefined copper cathodes (*i.e.*, at least 99.95 wt% Cu, with oxygen maximum 30 ppmw) are remelted in air or an inert atmosphere and cast formed, making commercial products (*e.g.*, bars, rods, ingots). Impurities must be reduced to a minimum of some parts per million, as even very small amounts can affect thermal and electrical conductivities.
In the hydrometallurgical process oxide ores and tailings are leached by a dilute sulfuric acid solu-

tion, producing a dilute copper sulfate aqueous solution. The mother liquor is then treated and transferred to an electrolytic cell. During electrolysis, copper metal electrodeposits at the cathode made from pure copper foil, while oxygen is evolved at the anode. During the electrolytic process, traces of precious metals (Ag, Au) and platinum group metals (Pt, Pd) can be recovered from the spent electrolytic bath. This process requires ten times as much electrical energy as classical electrolytic refining and established solvent extraction techniques do not work well on copper sulfide ores [25].

In 2021 Latin America was by far the largest producing region, with a total production volume that reached 8.7 million tons, representing 41% of the total. Chile, Peru, China, and Congo led the producing countries ranking with 5.6, 2.2, 1.8, and 1.8 million tons respectively. Mineral wealth greatly contributes to the regional economy: for the last two decades, for example, 10% of Chile's GDP came from copper mining. China dominates the smelter (almost 50%) and refining (42%) sectors: the country is the largest consumer of refined copper with apparent usage of around 13.9 million tons [8].

Global reserves are diversified across regions and reckoned to be around 890 million tons with Chile, Australia and Peru holding the main shares with 190 million tons (21%), 97 million tons (11%), and 81 million tons (9%) respectively. Over 50% of documented reserves are located in five countries: Chile, Australia, Peru, Mexico and the United States (Fig. 4) [26]. The burn-off time around 40 years (defined as the ratio between known reserves and average annual mining rate at the current consumption rates) remained unchanged since the 1960s: reserves have grown in parallel with increased demand, but trends display that needs will increase even faster in the future. Model curves for global copper production indicate that an output maximum is expected around 2030 and copper mining capacity is expected to hit 31.2 million tons by 2026. The price of copper is soaring and fluctuates between economic cycles and mining issues: in March 2022 the red metal hit its record level. It is difficult for producers to accommodate changes in consumer demand and spikes can cause temporary shortages, with consequent sudden price increase [27].

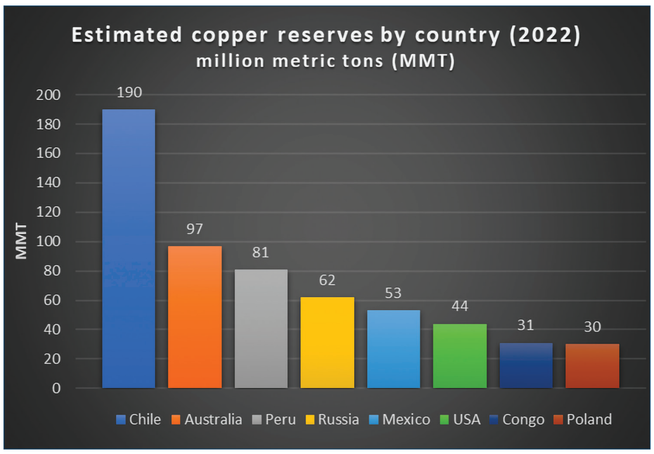

Fig. 4 - Copper reserves in million metric tons (from U.S. Geological Survey, Copper, Mineral Commodity Summaries, January 2023)

Therefore, supply restrictions could potentially threaten a long-term sustainable demand and in 2023 the EU added copper to the list of critical materials [28]. In Japan the metal isn't enclosed in the current stockpiling system relying on imported resources and in 2021 it didn't meet the US criteria of the revised critical mineral methodology, which considers the metal essential but with a low risk of supply restriction: a lobbying action for the classification as a critical material was ensued [29, 30].

Recovery & sustainability

Recycling extends the use of resources minimizing waste and it was estimated that 33% of the world's copper consumption came from recycling in 2021, a figure that has been constant during the last years although most applications stay in use for decades [31]. Copper scrap also reflects demand and prices: during periods of higher prices, recovery increases. With declining ore grades, higher energy requirements are requested for the same extractive amount, whereas secondary copper production requires only 20% of the energy used for primary production. Furthermore, the necessity of intensive investment and large infrastructures entails a high extraction cost and an intensive dialog with the local communities due to environmental issues [32, 33].

Copper maintains its chemical and physical properties after the recycling process: about 75% of copper produced since 1900 is still in use and it was estimated that approximately 440 million tons of copper were in use worldwide in 2015. Alternative materials, such as aluminum, display inferior electrical and thermal properties, thus permitting only a partial substitution potential [34].

There are large regional variations in recycling, which depend on collection efficiency and application: for example, copper grade is less critical in pipes and roofing, where each country adopts different solutions based on historical usage. In the EU, Japan, and China more than half of all copper is recycled after use. Market and customers play another important role; copper scrap is mainly produced in cities whereas copper smelters are often located in more remote areas [35].

It is important to distinguish the different sources, resulting from either metal discarded in fabrication or finished product manufacturing processes ("new" scrap) or end-of-life (EOL) products ("old" scrap). "New" scrap supply grows only with actual copper demand and is relatively insensitive to price. The most important driver is post-consumer "old" scrap, which is divided into several categories depending on concentration and enters the refining process at the different stages already described for the primary production cycle. Pure scrap >99% Cu is directly remelted; lightly contaminated scrap with >88% Cu must be refined. Shredder material containing around 60% Cu (*e.g.*, from vehicles) is treated in primary copper smelters, since it needs to be smelted, converted, and refined to remove impurities. Electronic scrap from waste electric and electronic equipment (WEEE) contains 5-30% copper and is another important source: printed circuit boards typically contain around 20% w/w copper, whereas smartphones content is around 13% w/w. Major companies operate state-of-the-art recovery techniques with integrated cycles and copper constitutes on average around 20 wt% of the metal mix volume, thus making up for an important share of the value at current price [36-38].

New methods for valorizing the e-waste are being approached and a copper-based heterogeneous catalyst obtained from treatment of smartphones and printed circuit boards via precipitation/deposition on a γ-alumina support displayed excellent hydrogenation properties [39].

The ubiquitous presence of copper in the journey of human society is destined to persist only by a closer synergy between all stakeholders and available resources.

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Rame: prospettive

Il rame, metallo di transizione dalle proprietà fisico-chimiche uniche, è un elemento chiave che svolge un ruolo importante nel processo globale di decarbonizzazione con particolare riguardo alle apparecchiature industriali, all'elettronica, alle comunicazioni, all'edilizia e ai trasporti. Il presente articolo si propone di fornire un sintetico aggiornamento sui principali usi attuali e futuri, produzione, riserve e prospettive di riciclo.