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MOLYBDENUM PERSPECTIVES

Molybdenum, a transition metal with particular physico-chemical properties, is a critical element playing an important role in the sectors of high-performance steels, special metal alloys, and catalysts. The present article aims at a concise update concerning main current and future uses, production, reserves, and recycling prospects.

Molybdenum is a refractory metal with a multiform utility as an alloying agent in steels, cast irons, and superalloys to enhance hardenability, strength, toughness, wear, heat, and corrosion resistance. The global molybdenum market reached US$ 5.3 billion in 2022 and is expected to reach US$ 6.7 billion by 2030 growing with a CAGR around 4.0% [1]. Its chemical versatility assured a significant role in numerous chemical applications, including catalysts, lubricants, and pigments: the hydrodesulfurization catalysts market alone was estimated at US$ 3.1 billion in 2023.

The abundance of the element is around 1.5 ppmw, thus ranking 54th as a rare element in earth's crust. It belongs to group 6 of the periodic table and the electronic configuration of the atom ground state is [Kr]4d^{5}5s^1: although the most common oxidation states are +4 and +6, it may assume valencies from -II to VI thus enabling participation in many redox reactions [2].

The metal is lustrous, silvery-white, hard, moderately dense, and can form alloys with many other elements. It is ductile, malleable, with high values concerning the melting point (2617 °C), the modulus of elasticity, the strength at elevated temperatures, the thermal conductivity, the resistance to corrosion, and low values in relation to specific heat and coefficient of expansion: physical properties also depend on the productive method. The element oxidizes only at elevated temperatures and is corrosion resistant at room temperature to halogens [3].

Since 2010 molybdenum prices are quoted as oxide (commercially designated as Roasted Molybdenum Concentrate or Technical Molybdenum Oxide) with 57% to 63% metal content at the London Metal Exchange (LME), where futures contracts are available.

The International Molybdenum Association (IMOA), based in London, is a trade association founded in 1989 representing currently around 95% of mine production and almost all conversion capacity outside China; the China Nonferrous Metals Industry Association, founded in 2001 and based in Beijing, has a Molybdenum Branch [4].

Growing importance is spurring institutional, scientific, technical, and economic literature: the present note aims at a concise update about uses, production, market, and resources.

Uses

In 2023 high-performance steel and specialty metal alloys represented the most important application (87%) with catalysts and specialty chemical products the second biggest market (13%): in the same year end-use demand for Mo reached a record high of 400,000 metric tons (Fig. 1) [5].

Molybdenum products commonly comprise ferromolybdenum, oxides, and metal pellets, each characterized by specific applications in metallurgy and chemistry. Ferromolybdenum is one of the

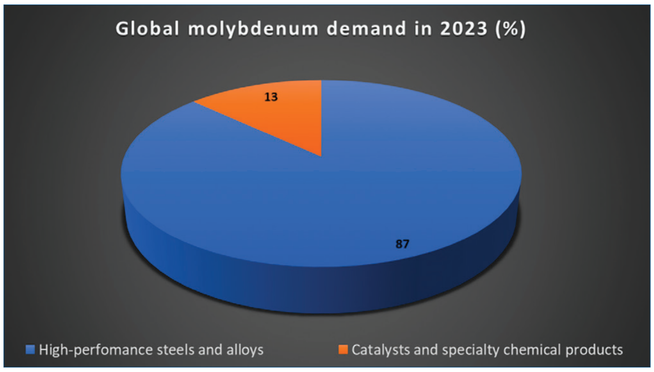

Fig. 1 - Global molybdenum demand in 2023, in % (from https://www.imoa.info/index.php)

most important iron-molybdenum alloys with a content of 60-75% of Mo and it is the main source for molybdenum alloying of high-strength low-alloy steel due to cheapness and easy dissolution in the steel melt. In special steels, where Mo content may range from 0.2% up to 8%, molybdenum increases the strength and hardness of cast iron by reducing the pearlite transformation temperature. Mo-containing high-chromium cast iron shows significant impact toughness and is ideal for applications under harsh abrasive conditions, such as in mining, milling, crushing, and other processes [6]. End use segments comprise machinery, electrical, transportation, automotive, chemical, oil and gas industries: according to the megatrends, consumption will expand significantly with steelmaking the principal sector and China the dominant region.

All green renewable energy generation, including wind, geothermal, solar, nuclear, and hydropower use molybdenum, thus being among the factors that will increase the global demand in the next decades along with the shift towards high performance steel and the rising content in Chinese steel manufacturing [7].

The exceptional catalytic properties of molybdenum relate to the ability of Mo ions to stabilize in different oxidation states from Mo^{6+} to Mo^0 [8]. Applications in hydroprocessing and oxidation will be briefly described: the first are catalyzed by molybdenum sulphide promoted by transition metal sulphides with molybdenum in the fourvalent state and the second by molybdenum oxide and transition metal molybdates, in which molybdenum is hexavalent.

Catalytic hydrotreating is a key process in the petroleum refining industry and the market is expected to expand despite the progress of electric mobility. It concerns the conversion and removal of organic sulfur, nitrogen, oxygen, and metals from petroleum crudes at high hydrogen pressures accompanied by hydrogenation of unsaturated as well as minor cracking of high molecular hydrocarbons. Sulfur is the most abundant heteroatom impurity: its content varies between 0.1 wt% and 4 wt% and must be reduced to a few parts per million. Hydrotreating industrial capacity has been growing steadily due to crude quality, downstream processing requirements, and environmental standards for fuels. Development started from the cracking and hydrogenation processes in the 1930s and a reaction scheme is the following:

$$R\text{-}SH + H_2 \rightarrow R\text{-}H + H_2S$$

where R represents a hydrocarbon chain. Main variables and process parameters are feedstock type, reaction temperature, pressure, liquid hourly space velocity, and H_2/Oil ratio, all differing according to the fraction. For example, temperature and pressure vary from 250 °C and 10 bar for naphtha up to 400 °C and 120 bar for vacuum gas oil. Catalysts choice is determined by specific activity, side reactions, pressure drop, and regeneration procedure: for some systems the optimum solution involves several types of catalysts in composite beds. In the case of hydrodenitrogenation, molybdenum and nickel are the preferred couple of active elements due to high hydrogenation activity; in the case of hydrodesulfurization molybdenum and cobalt are the most common couple of active elements and molybdenum content is around 8-16 wt% supported on γ-alumina. Deactivation factors are sintering and decomposition of the active phase, fouling, coking, and metal sulfides deposits. The lifetime is 1-3 years and the volume of spent hydrotreating catalyst is estimated to be 120,000 tons per year with a molybdenum content around 14,000 tons [9-11].

Regarding catalytic applications in oxidation reactions, ammoxidation to acrylonitrile and selective oxidation to formaldehyde will be briefly described: other important processes regard the acrolein production via propylene by a multicomponent molybdenum/bismuth/iron oxide promoted catalyst and the oxidation of acrolein to acrylic acid catalyzed by $(MoVW)_5O_{14}$-type oxides as the active and selective components [12].

Acrylonitrile is a leading commodity petrochemical whose applications include acrylic fibers, styrene copolymer resins, adiponitrile for the manufacture of hexamethylenediamine used in nylon 6,6 fibers and resins, and acrylamide for water treatment polymers. Global acrylonitrile production was around 6.4 million metric tons in 2022 and ammoxidation of propylene, developed and commercialized in the 1950's, accounts for about 90% of the market. In the process, chemical-grade propylene, fertilizer-grade ammonia, and air are combined in a fluidized-bed reactor at temperatures of 300-400 °C and pressures of 1.5-3 bar. The scheme of the highly exothermal primary reaction is the following:

$C_3H_6 + NH_3 + 1.5O_2 \rightarrow C_3H_3N + 3H_2O$

Catalysts vary according to adopted technology: first commercial compositions were based on Bi_2O_3. MoO_3 and numerous chemical formulations were successively patented. The multicomponent molybdates are one of the most fascinating systems in heterogeneous catalysis, characterized by multifunctionality and redox properties specifically designed due to precise knowledge of reaction mechanism. Yields can be improved by incorporating additional elements with redox properties (*e.g.* Fe, Cr, Ce) and a small excess of MoO_3, forming a molecular bridge between two cooperating catalytic phases and providing MoO_3 on a molecular level to partly depleted catalytic phases. Most employed catalysts also contain transition metals, such as Bi, Ni, Co and V, activated by alkali and rare-earth element. Acrylonitrile yields over 80% can be obtained and coproducts are hydrogen cyanide and acetonitrile, which are recovered and constitute a key economic parameter. Regular catalyst make-up must be executed during the industrial run to compensate for catalyst losses and molybdenum volatilization: expected lifetime is several years with an estimated Mo global installation in the specific sector over 1,500 tons [13-16].

Formaldehyde is used for resins, dyes, textiles, disinfectants, building materials, automotive parts and constitutes with acetylene the starting material to produce 1,4-butanediol (BDO), an intermediate for synthetic biodegradable plastics. Global formaldehyde production was around 18.8 million metric tons in 2022 and is set to increase in the next years. The reaction of selective oxidation of methanol to formaldehyde over Fe-Mo oxides catalysts was first patented in 1927, and since the 1950s the system began to replace industrially the Ag oxidehydrogenation process, thus accounting nowadays with significant geographical differentiations for more than 50% of world's production. The strongly exothermal reaction is represented by:

$CH_3OH + 1/2O_2 \rightarrow CH_2O + H_2O$

The process operates at temperatures between 300-380 °C and pressure 1.2-1.5 bar in tubular reactors surrounded by a heat-transfer fluid to which the heat of the reaction is transferred and recovered as steam. Typical commercial catalysts in the shape of cylindrical pellets contain $Fe_2(MoO4)_3$ with an excess molybdenum with respect to the stoichiometric value. MoO_3 exhibits high selectivity (almost 100%), but has poor activity, whereas Fe_2O_3 has poor selectivity to CH_2O: fine tuning of Mo/Fe atomic ratios leads to optimal performance. Formaldehyde molar yields higher than 90% can be achieved and catalysts are sensitive to thermal sintering and poisons such as sodium, sulfur, and chlorine compounds but the main deactivation cause is molybdenum volatilization. The lifetime around one year depends on the operative conditions and the estimated Mo global yearly utilization is lower than 1,000 tons [17-19].

Production & Market

The presence of molybdenum on earth is diffuse: however, mining and processing facilities for economic extraction are justified only where large ores occur. In 2023, the world primary molybdenum production was around 260,000 metric tons, increasing by 9% compared to 2022: around ten years earlier in 2014 the world's production of molybdenum reached a record high of more than 300,000 metric tons [6]. Active mines are more than 70, of which forty located in China and the Americas the second prominent geographic area.

The metal does not occur free in nature and its geochemical character is strongly chalcophile with molybdenite (MoS_2) the only mineral of commercial importance (Fig. 2). Only seven active Mo mining operations are primary, five in China and two in the US; in the other cases the metal is a by-product of copper mining, although out of the almost 700 copper mines around the world only 60 are also active in molybdenum production. Another source of molybdenum is represented by the tungsten ores, such as

Fig. 2 - Molybdenite crystal from New South Wales (Australia). Photograph by R.M. Lavinsky, distributed under a CC-BY 3.0 license

scheelite ($CaWO_4$), which is commonly associated with trace amounts of powellite ($CaMoO_4$), whence molybdenum is recovered as a by-product. The proportion of metal coming from by-product mines has been steady around 60% over the 2011-2021 decade and primary Mo ore accounts for around 40% of the world's molybdenum production: average molybdenite concentrations in primary porphyry deposits range from 0.01 to 0.25 wt%; in secondary copper porphyry deposits molybdenite concentrations are lower (0.01-0.05 wt%) [20].

Ore is mined by highly mechanized open-pit and underground block caving methods; artisanal mining was reported until several years ago in China, but the practice is unverified today. Processes depend on the ore type; molybdenite is recovered from the crushed and ground ore by flotation with over 95% of the unroasted molybdenite concentrate (about 85-92% MoS_2) roasted in air to MoO_3 and the remainder submitted to further grinding and flotation to produce lubricant grade MoS_2 with 99% purity. Roasting is executed in multiple hearth furnaces operating between 500 and 650 °C and producing MoO_3 with Mo content higher than 57 wt%. The output is known as roasted molybdenite concentrate: 30-40% is processed into ferromolybdenum and another 40% is directly used in steelmaking. The remainder undergoes additional processing to produce a high-grade molybdenum oxide suitable for use in catalysts, pharmaceuticals, fertilizers, and pigments [21].

Mo extraction can also occur by secondary resources such as waste rock and tailings, mill scale and dust from the steelmaking industries, fly ash from power stations, copper slag, spent acid from incandescent lamps industries, aqueous wastewater, and radioactive wastes.

Mo metallurgy also represents the main source of primary rhenium extraction by roasting of molybdenite and successive treatment of molybdenum concentrates [22].

In 2023 93% of the world's molybdenum production took place in five countries: China, Chile, Peru, the United States, and Mexico in decreasing order of productive volumes (Fig. 3). China was by far the largest producer with around 128,000 metric tons, up 13% from 113,000 metric tons in 2022 and more than twice as much as the next largest producer, Chile, but does not dominate the international market in terms of supply. In the same year South and North America were the second and third largest producing areas with 76,400 metric tons and 51,200 metric tons, both with a rise of 1% in the previous year. Data reflect the acceleration of exploration activity in China during the past decade following a 40-fold growth of Mo demand from 2000 to 2010 accompanied by a molybdenum national production increase from approximately 30,000 t in 1999 to 210,000 t in 2009 [23, 24]. On the other hand, since 2019 South America observed a decline of 10% in production due to rising environmental regulations and falling ore grades: declining output is generalized to all key Western producers [25].

Fig. 3 - Climax mine, Fremont Pass, Colorado (USA) in 2007. Photograph by J. and R. Klotz MD, distributed under a CC-BY 3.0 license

The Asia-Pacific region stands as the biggest end user, with Chinese consumption of Mo rising by 26% from around 100,000 metric tons in 2019 to 126,000 metric tons in 2023. During the same period Europe, the second largest user of the element, showed a fall of 8% and the rest of the world a rise of 3%. In 2023, Europe remained the second largest user at 56,600 metric tons, a rise of 1% with respect to the previous year, and the USA saw the largest yearly percentage rise in use (5%) to 29,211 metric tons. The contribution of the European Union to worldwide mine production of molybdenum is negligible: in 2021 Norway was reported to produce just 1 ton. The world reserves are estimated around 15 million metric tons, of which China provides about 40% and the USA 25% of the share, thus assuring supply in the near future for the two leading economic powers (Fig. 4) [26].

In most applications, molybdenum has no direct substitutes and potential alternatives such as vana-

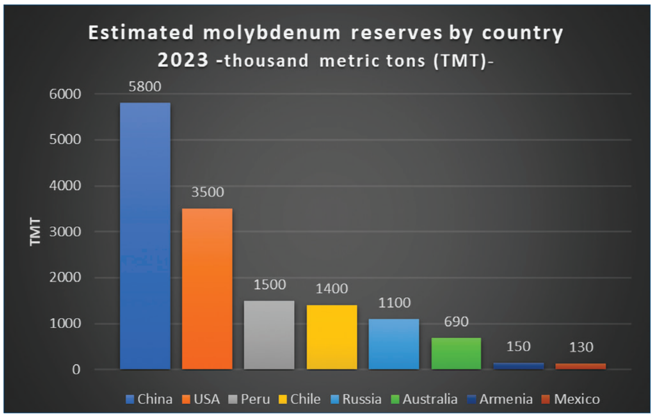

Fig. 4 - Molybdenum reserves in thousand metric tons (from U.S. Geological Survey, Molybdenum, Mineral Commodity Summaries, January 2024)

dium and chromium as a strengthening alloy in steel are not exercised because molybdenum has historically been plentiful and efficient: only meaningful market deficits (*e.g.* in 2022 around 20,000 metric tons) might change the practice. Molybdenum prices are mainly driven by the Chinese supply and demand, oil and gas prices, and stainless-steel market dynamics. Fluctuations in stocks are daily seen by LME and drops in stocks often result in speculative price increase and vice versa. Volatility was high from October 2022 until March 2023, when a supply shortage caused a deficit with prices rising steeply and declining only in March 2023 due to a reduced demand from downstream markets. Prominent reasons for the turbulence were a surge in copper prices, local discontinuities in supply, and the absence of significant additional secondary production from copper mines as well as of plans for new primary mines. Given the supply risks, molybdenum is listed as a critical element in China and Japan but, according to the privileged US point of view as a major producer, resources should be adequate to supply world needs for the foreseeable future albeit with a limited burn-off time around 60 years (defined as the ratio between proven reserves and average annual mining rate at the current consumption rates) [27].
The case of EU is special: the area is the second largest world user and the primary world importer but, although the current internal supply is much lower than 1%, molybdenum is not included inside the critical raw material list [28]. The approved Malmbjerg mining project (Greenland) might radically change the EU scenario with relevant mining volumes (potential supply of almost 25% of EU current demand) at a short distance from regional roasting facilities and off-take agreements were recently announced with a major European stainless-steel producer. However, such as for other critical elements, perspectives remain risky in the case of a bi-polar geographic concentration vulnerable to political factors: the point of view held by IMOA comparing the benchmark of a range of standardized materials stresses both a high degree of price volatility and a low degree of market concentration.

Recovery & Sustainability

Recycling is essential in the life cycle of resources: if in 2011 about 25% of yearly used molybdenum came from secondary production with shares approaching 40% in the case of stainless steel production [29], figures remain stable according to a recently calculated recycling input rate still around 27% [30] with Europe the region displaying the highest use of recovered molybdenum and around 60% of scrap use in stainless steel and constructional engineering steels.
Advantages are multiple: molybdenum content in scrap is usually higher than that of ores, thus reducing the extractive cost, requiring less energy and releasing fewer emissions than the productive process of new metal: even the shorter transportation routes linked to local sourcing play a significant role regarding cost and environmental benefits.
At present, methods for recycling molybdenum waste are mainly pyrometallurgical such as sublimation and molten zinc, supplemented by hydrometallurgical methods. Since waste sources might have different Mo concentrations, blending is executed by the use of programs able to provide values suitable to end product specifications.
About two-thirds of the secondary molybdenum comes from revert scraps produced during the steel making process and new scrap generated by steel fabrication. Therefore, its case resembles manganese and nickel, and secondary production is associated with the recycling of steel, a well-established network supported by a system of collectors and companies utilizing the scrap as a valuable raw material. Since molybdenum is by far one of the most expensive elements in stainless steel and special alloys, scrap prices reflect the trend of molybdenum prices and availability is affected by price elasticity. Steel recovery rates display around 85% of end-of-life recycling and therefore, unlike other metals, the main recycling chain might be considered already

efficient, and the recycling share is not expected to increase significantly if cheap primary molybdenum is available. Typical molybdenum content in the engineering steels does not exceed 1% and old scrap containing molybdenum is normally purchased and recycled for the sake of other metals, mostly iron. A common recycling method involves re-melting in an electric arc furnace after a pre-treatment to ensure suitable size, impurities removal and homogeneous composition [31].

Spent heterogeneous catalysts are treated for the recovery of base metals, but volumes are low with respect to the global business: in practice, recycling is part of a closed-loop process involving the stakeholders in the chemical sector of interest. Recovery processes of hydrotreatment catalysts comprise pretreatment (thermal, physical or by solvent extraction), roasting to eliminate oil, carbon and sulphur content (de-oiling and de-coking), leaching (by water, alkali, or acids), and final separation (via precipitation, solvent extraction, adsorption, or ion exchange). Many companies participate in the sector, each applying efficient proprietary techniques [32].

Molybdenum secondary production already plays an important part in meeting demand and contributing to sustainability, and its role should deserve the highest attention by any economic player with a role in the future.

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Molibdeno: prospettive

Il molibdeno, un metallo di transizione con particolari proprietà fisico-chimiche, è un elemento critico che svolge un ruolo importante nei settori degli acciai ad alte prestazioni, delle leghe metalliche speciali e dei catalizzatori. Il presente articolo mira a un aggiornamento conciso riguardante i principali usi attuali e futuri, la produzione, le riserve e le prospettive di riciclo.