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http://dx.medra.org/10.17374/CI.2025.107.2.72

MANGANESE PERSPECTIVES

Manganese, a transition metal with particular physico-chemical properties, is a key critical element playing an essential role in steel-making and with a growing importance in the global decarbonization process with regard to batteries. The present article aims at a concise update concerning main current and future uses, production, reserves, and recycling prospects.

Manganese has been employed in pigments since prehistory and today plays a fundamental role in industrial economies: it ranks fourth among the most used metals in terms of tonnage [1].
The element is abundant and widely distributed in the Earth's crust with an average content of approximately 0.1%. The metal is brittle, very hard, silvery-gray and exhibits four allotropes (α, β, γ, δ) with specific physical properties and transition temperatures at 700, 1088 and 1139 °C, respectively, and a melting point at 1246 °C [2]. It belongs to the group VIIB of the periodic table and the electronic configuration of the atom ground state is $[Ar]3d^5 4s^2$. Its ions can have up to 10 oxidation states, while divalent Mn(II) is the most important and stable, forming complex compounds with different ligands. At room temperature, pure manganese metal oxidizes superficially in air and is not attacked by nitrogen or hydrogen; at high temperature, it reacts with oxygen to give Mn_3O_4 and also with sulfur and phosphorous: for these reasons it is widely used in metallurgy [3]. Manganese forms many stable oxides such as MnO, Mn_3O_4, Mn_2O_3, MnO_2, with different crystal structures and morphologies associated with specific properties and structural parameters. All the oxides and hydroxides - when heated in air at about 1000 °C - form Mn_3O_4 with a spinel structure having Mn^{3+} in the octahedral positions and Mn^{2+} in the tetrahedral positions [4].
Manganese is a non-homogeneous commodity and demand is highly price inelastic. Two reference prices normalized to the manganese content (44% Mn and 38% Mn respectively for high- and low-grade ores) are weekly published in the spot market and sales negotiations depend upon many factors such as grade, size, taxes, location, iron ore, and steel market. Spot prices are used as a benchmark, but the absence of a central exchange and the vertical integration of the value chain may cause opacity [5].
The International Manganese Institute (IMnI), with head office in Paris, is a non-profit association founded in the 1970s representing the production chain with over 120 member companies and providing databases, studies, and specialized information [6].
The present note aims at a concise update about uses, production, market, and reserves.

Uses

The global market for manganese was estimated at 23.9 million metric tons in the year 2022 and the demand is expected to outpace supply by 2030 due to absence of additional capacity and projections in electric mobility leading to a slight shortage. In 2022, steel and alloys industries took 96% of the share; the battery industry (*e.g.*, electric vehicles -EV-) was in expansion with a slice of 2.5%; agricul-

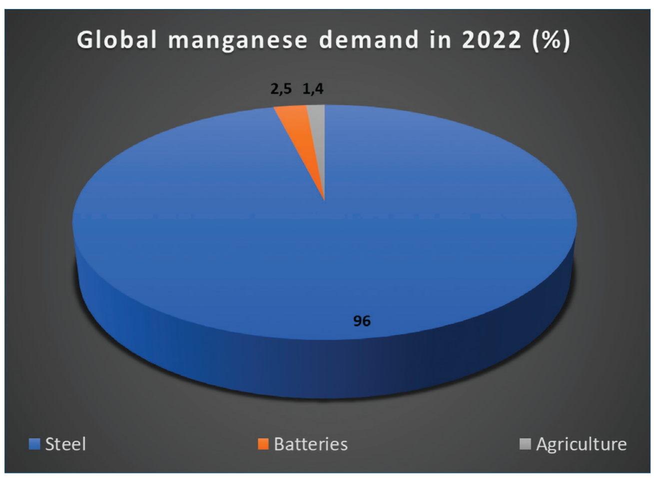

Fig. 1 - Global manganese demand, in % (from IMnI Annual Review 2022, International Manganese Institute, 2023)

tural additives to fertilizers were limited to 1.4% (Fig. 1) [7]. Overall demand is driven by construction, machinery, and transportation industries: according to the megatrends, consumption is expected to expand significantly with steelmaking the principal sector and EVs in a rising cycle associated with the emerging economies [8].

Long-established use in steelmaking is due to unique properties of Mn to provide several crucial characteristics, such as improved strength and hardness with removal of unwanted oxygen and sulfur. In almost all types of steel Mn has a concentration lower than 1 wt% but in high-strength steels its content exceeds 10 wt%. There are no known alternatives in the steelmaking process and Mn is the most cost-effective hardenability intensifier [9].

Manganese is also a key element to produce disposable and rechargeable batteries, which can be found in electric vehicles (EVs), energy storage systems (ESS) - *e.g.*, from solar and wind renewables - and portable consumer electronics. With a market share of 60% in 2022, the most popular battery type for EVs use is the lithium-ion nickel manganese cobalt oxide battery (NMC), where Mn enhances the structural and thermal stability of the cathode [10].

The chemical compound used in rechargeable batteries is manganese sulphate monohydrate (MSM), which is produced either from electrolytic manganese metal (EMM) or from manganese ore. For such applications, the purity is of the utmost importance due to safety and performance considerations, and exclusively high purity chemicals are required. Batteries typically account for 30% to 40% of the value of an EV, but MSM is estimated to contribute approximately 1-2% of NMC cathode cost: therefore, lithium-ion batteries (LIB) are not sensitive to the price of manganese. It is remarked that since technological and compositional advancements are steadily ongoing, sectorial long-term forecasts are to be treated with caution [11].

Manganese catalytic activity is mainly displayed as a co-catalyst with cobalt in homogeneous catalysis for the synthesis of terephtalic acid (TPA) and isophtalic acid (IPA), both with similar syntheses and connected end-uses. TPA is a precursor in the production of polyester for textiles, recyclable plastic bottles, and packaging: in 2021 the total output was 78 million metric tons [12]. IPA is a component of polyethylene terephthalate (PET) copolymer to reduce its crystallinity and production nearly reached 1.2 million metric tons in 2022 [13]. Direct liquid phase catalytic oxidation respectively of *p*-xylene (TPA) or *m*-xylene (IPA) with air in presence of cobalt and manganese acetates is the prevailing industrial process. Operating temperatures and oxygen pressures are 190-205 °C and 15-30 bar with xylene conversion higher than 98% and selectivity at 95% [14]. Manganese acts as a promoter increasing the reaction rate by up to five times, although its function is still to be clarified: it probably intervenes in the intermediate step of the aldehyde oxidation with a reducing role due to its lower oxidation potential than cobalt:

$$\mathrm{Co(III) + Mn(II) \rightarrow Co(II) + Mn(III)}$$

Catalyst recovery rates are higher than 99% and it can be estimated that manganese consumption in homogeneous catalysis was over 500 metric tons in 2022.

In heterogeneous catalysis the element gives a major contribution as a promoter: *e.g.*, in Fischer-Tropsch cobalt catalysts its presence helps to reduce methane selectivity and increase olefins [15]. Fast redox reactions occurring within manganese oxides are essential for the catalytic activity and Mn is used to improve selectivity and activity of oxide catalysts: for example, in mixed manganese-copper oxides Mn stabilizes the spinel towards reduction of Cu^{II} to Cu^{0} by occupation of tetrahedral sites. Such systems act as catalysts in the oxidation of CO to CO_2 for use in personal respiratory protective equipment and in environmental catalysis, exhibiting a selectivity which reflects the availability of the lattice oxide ions [16].

Production & Market

In 2022 few multinational companies mined globally around 21.1 million metric tons of manganese, with a modest contraction on a yearly basis due to the world geopolitical status and an overall increase by around 25% in the last decade. The market size is estimated at 23.2 million metric tons in 2024 and is expected to reach 28.1 million metric tons by 2029, growing at a CAGR of 3.9% during the forecast period (2024-2029) [17].

High-grade Mn ore production (>44% Mn) now represents 40% of total output, while mid-grade ore (>30% and <44% Mn) accounts for 50%, and low-grade ore (<30% Mn) makes up for the remaining

Fig. 2 - Pyrolusite crystals from New Mexico (USA). Photograph by R.M. Lavinsky, distributed under a CC-BY 3.0 license

10%: however, trends show current depletion of high-grade sources [7].

Manganese is not found as a free element in nature: it shows both lithophile and siderophile characteristics and, out of a large array, only about a dozen minerals containing Mn as the essential constituent are commonly found. The most important are oxides such as pyrolusite (MnO_2, tetragonal) (Fig. 2), hausmannite (Mn_3O_4, tetragonal), and jacobsite ($MnFe_2O_4$, cubic); hydroxides such as manganite (γ-MnOOH, monoclinic); carbonates such as rhodochrosite ($MnCO_3$, trigonal) and kutnahorite ($CaMn(CO_3)_2$); silicates such as braunite (Mn_7SiO_{12}, tetragonal); and sulfides such as alabandite (MnS, cubic). Psilomelane, a hydrous manganese oxide with various amounts of oxides of Ba, K and Na, and cryptomelane, a potassium-bearing manganese mineral, constitute other valuable ores [18].

Exploited deposits are usually sedimentary and contain oxide-type minerals. Besides the ore grade, also mineral hardness, and the presence of other elements such as copper, cobalt, phosphorus, sulfur, and arsenic determine the viability of economic development. For example, the presence of phosphorus in high quantities makes manganese ore unsuitable for ferromanganese production, while high phosphorus and iron contents prevent application in batteries industry. Both open-pit and underground mining operations are active: the first are most common and underground mining is used when high enough grades balance investment and operative costs [19].

The manganese value chain consists of three main segments: production of ore, smelting, and specialty processing to make chemicals. Ores are generally beneficiated by crushing, washing, and screening. Most manganese is acquired from the oxide pyrolusite with roasting and reduction to increase the manganese oxide content. Ferromanganese (85 wt% maximum Mn content) and silicomanganese (68 wt% maximum Mn content) are raw materials for the steel industry, manufactured by smelting the ores in blast or electric arc furnaces with carbon or aluminium as reducing agents. The metal is produced by hydrometallurgical treatment with sulphuric acid to extract manganese from ores and final electrolytic processes of $MnSO_4$ to reach manganese concentration up to 99.5%. From high purity manganese, three compounds are synthesized for the fabrication of alkaline batteries and LIB cathodes: electrolytic manganese metal (EMM), manganese sulphate monohydrate (MSM), and electrolytic manganese dioxide (EMD) [20].

South Africa is the top producer with 40% of output in 2022. The world's biggest land-based manganese ore body is concentrated in the Kalahari Manganese Field (KMF) in the Northern Cape Province, where operations started in the 1930´s and today cover an area around 425 km^2 [21]. The country is also considered to hold the greatest share (around 37%) of land-based Mn reserves, with over 90% of high-grade ore suitable for advanced applications [22]. Hence, innovative sectors such as high-quality steel and batteries might become locally prominent, depending on development of efficient transport and electric power infrastructures (Fig. 3) [23].

In 2022 other two main production countries were Gabon and Australia with shares at 22% and 14% respectively [24]: in the case of the African country, it is estimated that the production of Mn contributes to over 5% of national GDP in direct value and represents the second-largest economic activity.

China is a dominant player in the market, and the national construction field is a factor affecting glob-

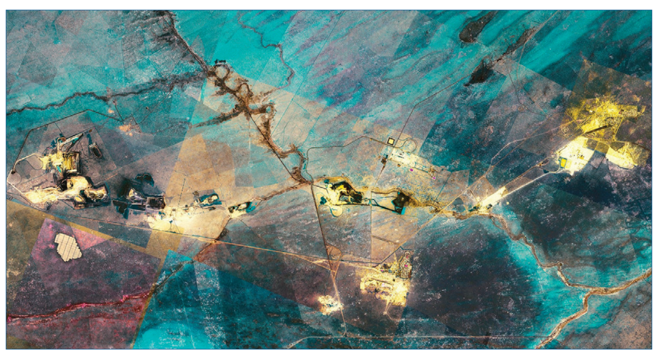

Fig. 3 - The Tshipi Borwa mine in the Kalahari Manganese Field (South Africa). Ultradistancia Mines series Ultradistancia.com, @ultradistancia ©Federico Winer

al demand and price of the metal. The country is the largest Mn consumer, the fourth major producer, the chief importer of ore with a share reaching nearly 60% in 2021 and is responsible for 90% of manganese refining [25].

China, Australia, and Brazil contribute to the reserves with a portion around 16% each out of a total around 1,700 million metric tons (Fig. 4) [22]. Vast areas of ocean floors are covered by metal-bearing nodules primarily containing manganese and iron, but also nickel, cobalt, and copper. Although several countries and companies are intensively investigating their distribution, the exploitation remains unaccomplished and debatable [26, 27]. In Europe, important extractive activity is present in Ukraine; in Italy, the abandoned Gambatesa mine in Liguria (now a touristic mine) was once the greatest on the continent and dismissed deposits are present in Sardinia.

A burn-off time of around 80 years (defined as the ratio between known reserves and average annual mining rate at the current consumption rates) is longer with respect to most critical elements: hence, criticality is not determined by geologic scarcity and new ores could be potentially developed from unexploited resources. However, a blend of factors such as importance, mines concentration, and possible supply disruptions makes the commodity highly strategic and industrialized countries such as Japan (1984), the US (2018), and the European Union (2023) included the metal within the respective critical materials lists [28].

Since predominant demand is accounted by a historical sector, prices between 2010-2020 were relatively stable and the recent spike in 2022 was attributed to post-pandemic rebound from traditional end-users and the growing EV business.

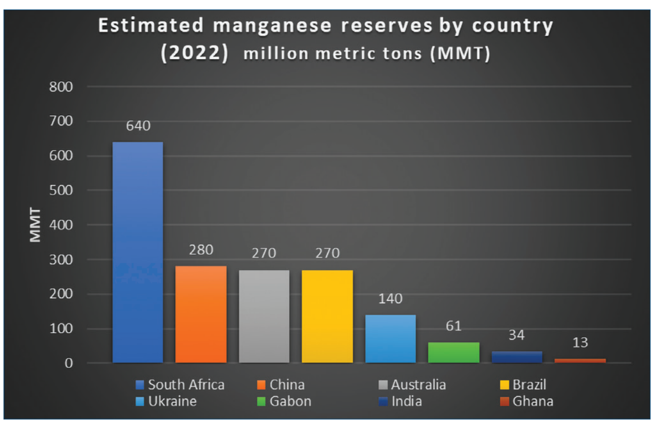

Fig. 4 - Manganese reserves in million metric tons (from U.S. Geological Survey, Manganese, Mineral Commodity Summaries, January 2023)

Recovery & Sustainability

No specific manganese recovery systems exist, and secondary production is associated with the recycling of steel, a well-established network supported by a functional system of collectors and companies utilizing the scrap as a valuable raw material [29]. Steel recycling rates are high, with over an estimated 85% of end-of-life (EOL) recycling and about one-third coming from primary production. Therefore, unlike many metals, manganese recycling is comparatively efficient: the end-of-life recycling rate (EOL-RR), defined as the fraction of metal in discarded products that is reused retaining its functional properties, is greater than 50% [30]. The EOL-RR depends on the collection rate and the efficiency of the subsequent separation and processing steps: the economic and technological feasibility of manganese recycling is assured by use in large quantities and occurrence in a relatively pure form in alloys, making it easier to remelt and recover. Mn is also recovered with aluminum alloys (*e.g.*, in the case of cans) with necessary distinctions: for example, manganese, contained around 1% in the 3000 series of aluminum alloys, is retained in the metal phase during remelting, producing a melt that would be unsuitable for reuse in any other Al-based system [31]. With the exclusion of alloys, the other manganese EOL products lack a recycling process, and the industrial chain does not form a closed loop: however, the set-up of a recycling system to be applied in other industries deserves proper attention. The lithium-ion batteries have a great recovery potential and the technical recovery rate of manganese from these products could exceed 90%. If NCM will continue to be the preferred choice of lithium-ion battery cathode materials, demand for manganese in batteries might rapidly increase at rates sensibly faster than those of the steelmaking industry: this factor stresses the necessity of a separate recycling process due to the purity required for batteries applications. Appeal is currently limited by low economic benefits: significant amounts of recycled metals available from EOL vehicles will be available only after 2035 due to a decade-long expected lifespan and "second life" reutilizations [32, 33].

Alternative ways are under evaluation and manganese-based catalysts were successfully synthesized from spent ternary lithium-ion batteries [34]: only an end-user related recycling phase will be able to support its new role in a sustainable society.

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Manganese: prospettive

Il manganese, metallo di transizione dalle particolari proprietà fisico-chimiche, è un elemento chiave critico nella manifattura dell'acciaio e con una crescente importanza nel processo globale di decarbonizzazione riguardo alla produzione di batterie. Il presente articolo si propone di fornire un sintetico aggiornamento sui principali usi attuali e futuri, produzione, riserve e prospettive di riciclo.