

# Manganese: Its History and Properties

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**Abstract**—Manganese is a chemical element in the periodic table, with symbol Mn, and atomic number 25. It is a transitional element and is found in the first long cycle of the periodic table, where it is located between chromium and iron. Manganese has distinct properties with both of these elements. Despite what is known about it and its uses when it is in a pure state, manganese is of great importance from a practical point of view in the steel industry. Manganese is a chemical element with the symbol Mn. It is a silver-gray brittle metal, and it has many important uses in industry, especially in the steel industry. The atomic weight of manganese is 54,938, and its atomic number is 25. Manganese is an element that is found in abundance in many places in the earth's crust. However, it is only found in combination with other chemical elements. Minerals that contain significant amounts of manganese include bronite, hosmenite, manganite, psilmolene, and pyrolite. And all plants and animals need small amounts of manganese. Also, manganese deficiency in plants affects the production of chlorophyll (chlorophyll), which leads to yellowing of their leaves. In humans and other animals, manganese deficiency leads to impaired growth, resulting in many bone and central nervous system abnormalities.

**Keywords**— Manganese – chemical element – Manufacture – Uses - mining

## I. INTRODUCTION

A diet that includes beets, blueberries, whole wheat flour and wheat bran provides enough manganese. Manganese is also an essential human nutrient, important in macronutrient metabolism, bone formation, and free radical protection systems. It is a critical component of dozens of proteins and enzymes. It is found mostly in the bones, but also in the

liver, kidneys, and brain. In the human brain, manganese is bound to the protein mineral manganese, in particular the glutamine synthetase in astrocytes. Manganese was first isolated in 1774. It is familiar in the laboratory as potassium permanganate with a deep violet salt. It occurs at the active sites of some enzymes. Of particular interest is the use of mass Mn-O, an oxygen-extracting compound, in the production of oxygen by plants. Manganese is a silvery gray

metal that resembles iron. It is very hard and dry, and difficult to melt, but it is easy to oxidize. Manganese and its common ions are paramagnetic. Manganese slowly decays in air and oxidizes ("rusts") like iron in water containing dissolved oxygen.

Naturally occurring manganese consists of an isotope,  $^{55}\text{Mn}$ . Several radioactive isotopes have also been isolated and described, ranging in atomic weight from 44 u ( $^{44}\text{Mn}$ ) to 69 u ( $^{69}\text{Mn}$ ). The most stable are ( $^{53}\text{Mn}$ ) with a half-life of 3.7 million years,  $^{54}\text{Mn}$  with a half-life of 312.2 days, and  $^{52}\text{Mn}$  with a half-life of 5.591 days. All remaining radioactive isotopes have half-lives of less than three hours, and most of them are less than one minute. The primary decay mode in the lighter isotopes of the more abundant stable isotope,  $^{55}\text{Mn}$ , is electron trapping and the primary mode in the heavier isotopes is beta decay. Manganese also contains three nuclear isomers.

Manganese is part of the ferrous group of elements, which is believed to form in large stars shortly before a supernova explosion.  $^{53}\text{Mn}$  decays to  $^{53}\text{Cr}$  with a half-life of 3.7 million years. Due to its relatively short half-life,  $^{53}\text{Mn}$  is relatively rare, and is caused by the effect of cosmic rays on iron. The isotopic contents of manganese are often combined with those of chromium isotopes and have found application in isotope geology and radiometric dating. The Mn–Cr isotopic ratios bolster evidence from  $^{26}\text{Al}$  and  $^{107}\text{Pd}$  for the early history of the solar system. The differences in  $^{53}\text{Cr}/^{52}\text{Cr}$  and Mn/Cr from several meteorites suggest an initial value of  $^{53}\text{Mn}/^{55}\text{Mn}$ , which

indicates that the Mn–Cr isotopic composition must result from the "in situ" decay of  $^{53}\text{Mn}$  in dissimilar planetary bodies. Hence,  $^{53}\text{Mn}$  provides further evidence of nucleosynthesis processes just before the solar system merger.



## II. OXIDATION STATES

The most common oxidation states for manganese are +2, +3, +4, +6, and +7, although all oxidation states from  $-3$  to +7 are observed.  $\text{Mn}^{2+}$  often competes with  $\text{Mg}^{2+}$  in biological systems, with the ion also having similar properties to  $\text{Ca}^{2+}$  and  $\text{Zn}^{2+}$ . Manganese compounds where manganese is in a +7 oxidation state, which is mostly limited to the unstable oxide  $\text{Mn}_2\text{O}_7$ , intense purple permanganate anion compounds  $\text{MnO}_4^-$  and few oxides ( $\text{MnO}_3\text{F}$  and  $\text{MnO}_3\text{Cl}$ ) as strong oxidizing agents. Compounds with oxidation states +5 (blue) and +6 (green) are strong oxidizing agents and are prone to disproportionation.

The most stable oxidation state of manganese is +2, which has a faint pink color, and several manganese (II) compounds are known, such as manganese (II) sulfate ( $\text{MnSO}_4$ ) and manganese (II) chloride ( $\text{MnCl}_2$ ). This oxidation state also appears in the mineral rhodochrosite (manganese(II) carbonate). Mn(II) is commonly found with a high spin,  $S = 5/2$  ground state due to the high coupling energy of Mn(II). However, there are some examples of low spin,  $S = 1/2$  Mn(II). There are no d-d transitions allowed for spin in Mn(II), which explains why Mn(II) compounds are faint to colorless.

The +3 oxidation state is known in compounds such as manganese(III) acetate, but they are very strong oxidizing agents and are also prone to disproportion in solution, forming manganese(II) and manganese(IV). Solid compounds of manganese (III) are distinguished by their strong purplish-red color and the distorted octahedral coordination preference caused by the Jahn-Teller effect.

The +5 oxidation state can be produced by dissolving manganese dioxide in molten sodium nitrite. Manganese (VI) salts can be produced by dissolving manganese compounds, such as manganese dioxide, in molten alkali while exposed to air.

Permanganate compounds (+7 oxidation state) are purple and can give glass a violet colour. Potassium permanganate, sodium permanganate, and barium permanganate are all strong oxidizing agents. Potassium permanganate, also known as Condé crystals, is a commonly used laboratory

chemical reagent due to its oxidizing properties; It is used as a topical medicine (eg, in the treatment of fish diseases). Potassium permanganate solutions were among the first stains and fixatives used to prepare biological cells and tissues for electron microscopy.

The rare oxidation state of +1 is found in some organo-manganese compounds such as the  $\text{MnC}_5\text{H}_4\text{CH}_3(\text{CO})_3$  compound mentioned in the above table.



### III. USAGE

The huge consumption of manganese ore is related to the production of steel, which includes the huge iron industry and the industries of ferroalloys and silica alloys. Manganese compounds have many uses in industry. Manganese dioxide is used as a drying agent, or as a catalyst in dyes and varnishes, and as a color remover in the glass industry, and in dry batteries. Potassium permanganate is used for bleaching, as a color remover in oils, and as a catalyst for oxidation in analytical chemistry. Manganese is

also included in fertilizer components for agriculture, and animal food components.

### Date and Origin

The origin of the name manganese is complex. In antiquity, two black minerals were identified from the regions of the Magnets (either Magnesia, located within modern Greece, or Magnesia ad Sipylum, located within modern Turkey). Both were called magnets from their native land, but were considered different in sex. The "magnets" attracted the inner iron, and it was iron ore now known as magnetite or magnetite, which may have given us the term magnet. The female magnetite ore did not attract iron, but was used to decolor glass. This female magnesite was later called magnesia, and is now known in modern times as pyrolusite or quaternary manganese oxide.[citation needed] Neither this mineral nor manganese is magnetic. In the sixteenth century, glassmakers called manganese dioxide manganesum (note ns instead of one), possibly as a corruption and association of two words, as alchemists and glassmakers eventually had to distinguish black magnesia (black ore) from Magnesia alba (A white ore, also from Magnesia, also useful in the manufacture of glass). Michel Mercati called it Magnesia nigra "manganesa", and the mineral isolated from it eventually became known as manganese (German: Mangan). Ultimately, the name magnesia was used to refer only to the white Magnesia alba (magnesium oxide), which gave the name magnesium to the free element when it was later isolated.

Many colorful manganese oxides, for example manganese dioxide, are abundant in nature and have been used as pigments since the Stone Age. Cave drawings at Gargas between 30,000 and 24,000 years old contain manganese pigments.

Manganese compounds were used by Egyptian and Roman glassmakers, to either add or remove color from glass. The use of "glass-making soap" continued through the Middle Ages into the modern era and is evident in 14th century Venetian glass.

Because of its use in making glass, manganese dioxide was made available for experimentation by chemists, the first alchemists. Ignatius Gottfried Keim (1770) and Johann Glocker (17th century) discovered that manganese dioxide can be converted into permanganate, a useful laboratory reagent. By the mid-18th century, Swedish chemist Carl Wilhelm Scheele had used manganese dioxide to produce chlorine. First, hydrochloric acid, or a mixture of sulfuric acid and sodium chloride, was synthesized to react with manganese dioxide, after which hydrochloric acid from the Leblanc process was used and manganese dioxide was recycled by the Weldon process. The production of chlorine bleaching powder and hypochlorite agents has been a major consumer of manganese ores.

By the mid-18th century, Carl Wilhelm Scheele had used pyrolusite to produce chlorine. Schell and others were aware that pyrolusite (now known as manganese dioxide) contains a new element. Johann Gottlieb Gahn was the first to isolate

an impure sample of manganese in 1774, which he did by reducing the dioxide with carbon.

The manganese content in some of the iron ores used in Greece has led to speculation that steel produced from this ore contains additional manganese, making Spartan steel exceptionally hard. At the beginning of the 19th century, manganese was used to make steel and several patents were granted. In 1816, it was documented that alloying iron with manganese was harder but not more brittle. In 1837, British academic James Cooper noted an association between miners' extreme exposure to manganese and a form of Parkinson's disease. In 1912, U.S. patents were granted to protect firearms from rust and corrosion using electrochemical conversion coatings for manganese phosphate, and the process has seen widespread use ever since.

The invention of the Clanchante cell in 1866 and the subsequent improvement of batteries containing manganese dioxide as a depolarizing material increased the demand for manganese dioxide. Until the development of batteries using nickel-cadmium and lithium, most batteries contained manganese. Zinc-carbon batteries and alkaline batteries usually use industrially produced manganese dioxide because naturally occurring manganese dioxide contains impurities. In the twentieth century, manganese dioxide was widely used as the cathode drive for commercial dry disposable batteries of standard (zinc and carbon) and alkaline types.

#### IV. MATERIALS, AVAILABILITY AND PRODUCTION

The most important ore of manganese is pyrolusite ( $MnO_2$ ). Other economically important manganese ores usually show a close spatial relationship to iron ores, such as sphalerite. Wild resources are large but infrequently distributed. About 80% of the world's known manganese resources are in South Africa; Other important manganese deposits are found in Ukraine, Australia, India, China, Gabon and Brazil. According to a 1978 estimate, the ocean floor contains 500 billion tons of manganese nodules. Attempts to find economically viable methods for harvesting manganese nodules were abandoned in the 1970s.

In South Africa, most of the identified deposits are located near Hotazel in the Northern Cape Province, with a 2011 estimate of 15 billion tons. In 2011, South Africa produced 3.4 million tons, topping all other countries.

Manganese is mined mainly in South Africa, Australia, China, Gabon, Brazil, India, Kazakhstan, Ghana, Ukraine and Malaysia.

To produce ferromanganese, manganese ore is mixed with iron ore and carbon, and then reduced either in a blast furnace or in an electric arc furnace. The resulting ferromanganese contains 30 to 80% manganese.[6] The pure manganese used in the production of iron-free alloys is produced by leaching of manganese ore with sulfuric acid and subsequent electrolysis process.

A more advanced extraction process involves the direct reduction of manganese ore into a filter pile. This is done by filtering the natural gas through the bottom of the stack; Natural gas provides heat (must be at least 850°C) and reducing agent (carbon monoxide). This reduces all manganese ore to manganese oxide (MnO), a leached form. The ore is then moved through a grinding circuit to reduce the ore particle size to between 150 and 250 µm, increasing the surface area to aid filtration. The ore is then added to a filter tank consisting of sulfuric acid and solid iron (Fe<sup>2+</sup>) in a ratio of 1.6: 1. Iron reacts with manganese dioxide to form elemental iron and manganese hydroxide. This process results in the recovery of approximately 92% of the manganese. For further purification, the manganese can then be sent to an electrolytic extraction facility.

In 1972, the CIA's Project Azorian, through billionaire Howard Hughes, commissioned the Hughes Glomar Explorer with a cover story about harvesting manganese nodules from the sea floor. This led to a surge in activity to collect manganese nodules, which was not actually practical. The real mission of the Hughes Glomar Explorer was to raise a sunken Soviet submarine, K-129, with a view to retrieving Soviet code books.

An abundant manganese resource has been found in the form of manganese nodules on the ocean floor. These nodules, consisting of 29% manganese, lie along the ocean floor and the potential impact of mining these nodules is being investigated. Environmental, physical, chemical, and biological effects can be caused by this nodule mining

disturbing the sea floor and causing sediment plumes to form. This suspension contains inorganic minerals and nutrients, which can pollute the near-bottom water from toxic dissolved compounds. Manganese nodules are also abrasion areas, living quarters, and the protection of internal and collective systems. When these nodules are removed, these systems are directly affected. In general, this can cause species to leave the area or die out completely. Prior to the start of mining itself, research is being conducted by the United Nations affiliated agencies and state-sponsored companies in an effort to fully understand the environmental impacts in the hope of mitigating them.

### **Ocean environment**

Many of the ocean's trace elements come from mineral-rich hydrothermal particles from hydrothermal vents. Dissolved manganese (dMn) is found throughout the world's oceans, 90% of which comes from hydrothermal vents. Mn particles develop in floating plumes above an active vent source, while dMn behaves conservatively. Manganese concentrations vary among ocean water columns. At the surface, dMn rises due to input from external sources such as rivers, dust, and shelf sediments. Coastal sediments usually contain low concentrations of manganese, but they can increase due to anthropogenic discharges from industries such as mining and steel manufacturing, which enter the ocean from river inputs. Surface dMn concentrations can also be biologically increased through photosynthesis and physical from coastal upwelling and wind-driven surface currents. Internal cycling such as

reducing UV radiation can also raise levels by accelerating the breakdown of manganese oxides and oxidative scavenging, which prevents manganese from sinking into deeper waters. Elevated levels can occur in the central depths near mid-ocean ridges and hydrothermal vents. The hydrothermal vents release the dMn-enriched liquid into the water. The dMn can then travel up to 4,000 km due to the presence of microbial capsules, which prevents exchange with particulates, reducing sinking rates. Dissolved manganese concentrations are higher when oxygen levels are low. In general, dMn concentrations are usually higher in coastal areas and lower when moving offshore.

Most of the uses of manganese are in the manufacture of alloys and chemical compounds. Ferromanganese, an alloy containing 80% manganese and 20% iron, is used to make steel. Manganese removes oxygen and sulfur from the steel, thereby strengthening the metal. The presence of oxygen bubbles in the steel weakens it, and the presence of sulfur weakens the steel during the forging process, which is the process in which the iron is heated and formed. Other iron alloys, which contain a large proportion of manganese and are important in the manufacture of steel, include silicon manganese and Spiegel iron.

An alloy of steel known as manganese steel contains 14% manganese. It has many uses, as it is used in the manufacture of heavy-duty machines and safes. The uses of manganese, with the exception of the previously mentioned, include the electronics industry that uses manganese steel alloys to make a specific type of electromagnet, used in radar and

radio transmitters, and computer storage units called the magnetic core of memory.

Manganese is used in the manufacture of stainless steel, and in many alloys of aluminum, copper and magnesium, as adding manganese to these metals makes them strong and highly resistant to rust.

One of the most common manganese compounds used is manganese dioxide,  $MnO_2$ . Its importance comes from its use in the manufacture of dry batteries and many dyes. Paint producers and shoe polish dryers use large amounts of  $MnSO_4$  in their production processes. Manganese sulfate is also an essential component of some fertilizing fertilizers with certain uses.

Another manganese compound,  $KMnO_4$ , is used as a disinfectant and deodorizer, and in water purification. Other compounds, manganese nitrate  $Mn(NO_3)_2$  and manganese oxide  $MnO$ , are also used as catalysts in the production of a number of petrochemical compounds, plastics, and synthetic fibres. Catalysts are materials that help increase the speed of chemical reactions.

Most manganese is found with iron ore. The presence of large quantities of manganese makes the ore of great economic value. The ore that contains 5% to 10% of manganese is called manganese-containing ore, and the ore that contains 10% to 35% of manganese is called ferromanganese ore. The ore that contains 35% or more of manganese is called manganese ore. China and Ukraine are

at the forefront of the largest producers of the highest grades of manganese ore, followed by South Africa, Brazil and Australia.

The chemical composition of the high grade crude originating from Russia is as follows:-

Mn I 18.8 , Mn O<sub>2</sub> 62.4 , Fe<sub>2</sub> O<sub>3</sub> 1.3 , Si O<sub>2</sub> 6.9 , P<sub>2</sub> O<sub>5</sub> 0.33 , Al<sub>2</sub> O<sub>3</sub> 1.1 , Ca O 1.4 , H<sub>2</sub> O 5.5 .

This is equivalent to 53.97% Mn, 0.89% Fe, 0.15% P.

There are also large amounts of manganese deposits on the ocean floor in the form of round masses called nodules. Despite this, the high cost of mining these deposits limited their commercial use.

Manganese ore is purified in several different ways. In one of these methods, manganese ore is placed in an electric furnace with aluminum and sand, where it is reduced. Another way to purify manganese is by electrolysis of manganese sulfate solution. The electrolysis method is the most economical method and produces the purest form of manganese. Manganese ore can also be converted by heating to manganese oxides, which in turn are mixed with sulfuric acid to produce manganese sulfate. After purification, the manganese sulfate solution is subjected to electrolysis.

Manganese is an essential component in the massive wrought steel industry, and there is no equivalent substitute. It helps not to oxidize steel, and also, in combination with

sulfur, supports the properties necessary for hot use of steel. For this purpose, manganese is used in the form of ferro-manganese, which contains approximately (80%) manganese. It is used in high carbon grades of 6-7% and low carbon of 0.1% carbon or less. High carbon ferro-manganese is made by direct reduction of manganese ore with coke in combustion furnaces. Low silicon ores containing at least 40% manganese in a ratio of manganese to iron 10:9 are required for this purpose.

Low carbon ferromanganese is usually produced by reducing manganese ore by silico-manganese in an electric arc furnace.

Naturally, low-carbon ferromanganese is more expensive to produce than high-carbon alloys, but its primary use is to produce steel in which carbon must be low, such as some heat-resistant steels.

### **Pure manganese production**

Manganese with a purity of 97-98% is found at the commercial level by reducing aluminum ore with a high degree of manganese and a low iron content. High purity manganese is produced by electrolytic exchange between a solution of manganese (II) sulfate and ammonium sulfate in a cell in which a lead alloy (anode) and a steel alloy (cathode) are used, and this method, which is currently used on a commercial level, produces manganese with less than 0.1 % metal impurities at an acceptable cost by the method of producing low carbon ferro-manganese. Prior to this

method, high purity manganese was rarely produced metallurgically from commercially purified refractory aluminous manganese by distillation and condensation in a vacuum.

## V. CONCLUSION

Manganese is used as an additive to prevent oxidation or transformation into deoxidant and desulfurizing compounds in the steel industry. Therefore, all types of commercial steel contain manganese to a small degree, but it is basic and in the form of an alloy, and its presence affects the quality of steel and its ability to form with heat. A little manganese gives steel a high resistance to use, especially at low temperatures. Real steel contains 0.9-1.2% manganese, and other types of steel contain 1.3-1.6% manganese. This steel has a higher tensile strength compared to steel that contains carbon and manganese in the usual limits and is produced in large quantities.

The addition of manganese to iron lowers the transition temperature  $\gamma \leftrightarrow \alpha$  to iron, and by adding more than 12% manganese, the transition temperature is lower than room temperature. This stainless steel, manganese, non-magnetic has very important properties.

Manganese is also included in some types of stainless steel containing nickel-chromium, which has wide uses in corrosion- and heat-resistant applications. Well known types of steel contain 18% chromium, 8% nickel & 25% chromium, 20% nickel. Manganese can replace some nickel with the steel not losing any of its steel structure, heat resistance and corrosion properties.

Manganese has a limited use in non-ferrous alloys, as it is effective in preventing the oxidation of copper-based alloys, and the efficiency of its mechanical properties has been proven. When manganese is added to brass containing 40-45% zinc, it increases the tensile strength at a rate of 0.7 tons / inch<sup>2</sup>. Adding 1% manganese increases expansion by 5%. Further addition reduces ductility but continues to increase strength.

Brass contains 39% zinc, 1% manganese with small amounts of iron about 0.25%, and aluminum is known as manganese bronze, and it has a tensile strength of about 26.5 tons / inch<sup>2</sup>, and an expansion of 47%.

Both copper-manganese alloys, and copper-manganese-nickel alloys have important properties as the second type alloy contains about 84% copper, 4% nickel, 12% manganese. It is very well known for electrical purposes (Manganin) as it has a resistance of  $75 \times 10^{-6}$  ohms. cm and a heat coefficient of  $1 \times 10^{-5}$  at 20°C (68°F).

There are other alloys in this system that have more distinctive properties such as an alloy of 60% manganese, 20% each of copper and nickel, having an electrical resistance of  $190 \times 10^{-6}$  ohms. cm and has a thermal coefficient of stabilization that is at least as low as that characteristic of manganin.

This system of alloys also includes alloys with a very high coefficient of thermal expansion, as an alloy containing 72% manganese, 10% nickel, 18% copper has a maximum expansion coefficient of  $27 \times 10^{-6} / ^\circ\text{C}$  and is commercially offered as a high double metallic element Expansion as a

thermostat (thermal sensor to separate and connect the electric current). dolphin stands, and then re-rolled into huge coils. The cold rolling process increases the product's ability to stretch and form without any scratches. It also helps in thinning the thickness of the steel and making its surface smoother.

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