# Manganese in rocks and as an alloying element

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*Abstract*- **Manganese is an essential element for modern industrial societies. Its principal use is in steelmaking, where it serves as a purifying agent in iron-ore refining and as an alloy that converts iron into steel Manganese resources in seabed deposits of ferromanganese nodules and crusts are larger than those on land and have not been fully quantified Manganese is the 12th most abundant element in Earth's crust. Its concentration varies among common types of rocks, mostly in the range of from 0.1 to 0.2 percent. The highest quality manganese ores contain from 40 to 45 percent manganese. The formation of these ores requires specialized geologic conditions that concentrate manganese at several hundred times its average crustal abundance. The dominant processes in forming the world's principal deposits take place in the oceans. As a result, most important manganese deposits occur in ancient marine sedimentary rocks**

## DESCRIPTION:

**Manganese is a hard, brittle, silvery white metal derived from the Latin word 'magnes', meaning magnet. Originally discovered in 1774, manganese is the fifth most abundant metal present on the Earth's crust. Pre-historic cave painters of the French's Lascaux region used this metal in the form of manganese dioxide or black ore pyrolusite some 30,000 years ago.** Manganese is the 12th most abundant element in Earth's crust. Its concentration varies among common types of rocks, mostly in the range of from 0.1 to 0.2 percent. The highest quality manganese ores contain from 40 to 45 percent manganese. The formation of these ores requires specialized geologic conditions that concentrate manganese at several hundred times its average crustal abundance. The dominant processes in forming the world's principal deposits take place in the oceans. As a result, most important manganese deposits occur in ancient marine sedimentary rocks that are now exposed on continents as a result of subsequent tectonic uplift and erosion. In many cases, other processes have further enriched these manganiferous sedimentary rocks to form some of today's highest grade ores. Modern seabed resources of ferromanganese nodules cover vast areas of the present ocean floor and are still forming by complex interactions of marine microorganisms, manganese dissolved in seawater, and chemical processes on the seabed.

Manganese is ubiquitous in soil, water, and air. It occurs most often in solid form but can become soluble under acidic conditions. Manganese mining, like any activity that disturbs large areas of Earth's surface, has the potential to produce increases in manganese concentrations that could be harmful to humans or the environment if not properly controlled. Although manganese is an essential nutrient for humans and most other organisms, overexposure can lead to neurotoxicity in humans. Workers at manganese mining and processing facilities have the greatest potential to inhale manganese-rich dust. Without proper protective equipment, these workers may develop a permanent neurological disorder known as manganism. Each manganese mine is unique and presents its own suite of potential hazards and preventative measures. Likewise, various nations have their own sets of standards to ensure safe mining, isolation of mine waste, treatment of mine waters, and mine closure and restoration. Interest in mining trace metals contained in ferromanganese nodules and crusts on the seabed has increased rapidly in the past decade. Prime areas for future research include overcoming the technological challenges presented by mining as deep as 6,500 meters below sea level and understanding and mitigating the potential impacts of seabed mining on marine ecosystems.

The Mn associated rocks in the study area are phyllite, schist, quartzite and limestone. The mineral assemblage in phyllite formed under greenschist facies metamorphism. Petrographic studies of various phyllite samples also reveal that porphyroblasts of biotite sat in the fine-grained micaceous matrix (Biotite, muscovite, chlorite) along with quartz, opaque and ore minerals. Petrographic studies of schist reveal its formation under prograde metamorphism. Mineral assemblages observed in schist are typical of greenschist to lower amphibolite facies. The various schist samples at places show clusters made up of perfect rhombshaped garnets which suggest the increase in the grade of metamorphism. The quartzites are disposed conformably with the phyllites, and are at times brecciated and re-cemented by secondary chert and manganese. These Mn-bearing quartzites are with sutured/serrated and straight grain boundaries. The quartzite samples are fully composed of quartz showing undulose extinction with subordinate feldspar, micas and carbonatic materials. The petrographic characteristics explain that mostly limestones are the dolomitic composition but some ferruginous varieties are also noticed at places. The purer variety of limestone consists of calcite, dolomite and some magnetite but tremolite, quartz and some minute flakes of biotite also occur in impure variety The surface of Mars has long been considered a relatively oxidizing environment, an idea supported by the abundance of ferric iron phases observed there. However, compared to iron, manganese is sensitive only to high redox potential oxidants, and when concentrated in rocks, it provides a more specific redox indicator of aqueous environments. Observations from the ChemCam instrument on the Curiosity rover indicate abundances of manganese in and on some rock targets that are 1–2 orders of magnitude higher than previously observed on Mars, suggesting the presence of an as-yet unidentified manganese-rich phase.

Berlin glass technologist Johann Heinrich Pott chemically studied the metal in 1740 and showed that it does not contain any iron as was previously believed. Several chemists have unsuccessfully attempted to separate the metal component in pyrolusite, but it was in 1774 that Swedish chemist Carl Wilhelm Scheele recognized the metal while working with the pyrolusite mineral. The same year, Scheele's associate and Swedish chemist and mineralogist, Johan Gottlieb Gahn successfully isolated the metal.

**Fig-1 Manganese Rock**

## Properties of Manganese

Manganese is similar to iron in its chemical and physical properties, but it is harder and more brittle. It is present in several significant deposits, and most major ores include manganese dioxide in the form of romanechite, pyrolusite, and wad. Among these, manganese dioxide is the most important compound.

Manganese is acquired either through the electrolysis of manganese sulfate, or by reducing the oxide with aluminum, magnesium, or sodium. Over 95% of the manganese created is employed in the form of ferromanganese and silicomanganese alloys for the production of steel and iron.

Natural manganese is a stable isotopemanganese-55 and occurs in four allotropic modifications. The metal oxidizes in air and corrodes in moist air. Similar to iron, manganese burns in oxygen/air at increased temperatures, and decomposes water gradually when cold but quickly on heating.

It instantly dissolves in dilute mineral acids, forming hydrogen and the corresponding salts. Manganese becomes ferromagnetic after suitable treatments. Also, the metal is relatively electropositive, dissolving instantly in dilute nonoxidizing acids. It reacts with many nonmetals at increased temperature but is unreactive at room temperature.

Manganese reacts with fluorine to produce manganese di- and trifluorides ($MnF_2$ and $MnF_3$), and burns in chlorine, nitrogen, and oxygen to give manganese dichloride ($MnCl_2$), trimanganese dinitride ($Mn_3N_2$), and trimanganese tetroxide ($Mn_3O_4$), respectively. Except for hydrogen, manganese directly combines with boron, phosphorus, carbon, silicon, and sulfur. The following table shows the element properties of manganese.

| Properties of Manganese | |
| --- | --- |
| Atomic number | 25 |
| Atomic weight | 54.938 |
| Melting point | 1,246°C (2,275°F) |
| Boiling point | 2,062°C (3,744°F) |
| Density | 7.21–7.44 gram/cm$^3$ at 20°C (68°F) |
| Oxidation states | +2, +3, +4, +6, +7 |
| Electron configuration | [Ar]3d$^5$4s$^2$ |



**Fig-2 Manganese ore**

**Properties of Manganese Alloys**

Manganese serves as an important alloying agent. Many different types of manganese alloys are available in the market today, including ferro manganese alloys, copper manganese alloys, high manganese alloys, and nickel manganese alloys, to name a few.



Fig-3 Mangnese nodular ore

Manganese is possibly the most flexible element that can be added to copper alloys. Small additions of manganese are used to deoxidize the alloy and enhance its mechanical strength and castability. In antimony and aluminum, the addition of manganese produces highly ferromagnetic compounds. In steels, manganese enhances strength, stiffness, hardness, toughness, hardenability, wear resistance as well as forging and rolling qualities

Manganese and iron are the main components of ferromanganese alloys. A ferroalloy containing approximately 80% manganese is used in steelmaking. Carbon ferromanganese, metallic manganese, metallic manganese, and purified, nitrided ferromanganese are some of the other types of ferromanganese alloys.

High-manganese alloys provides a favorable combination and balance of properties like ductility, formability, strain hardening, and strength level parameters, which enables reducing the weight of vehicles and at the same time improves resistance against the effects of automobile accidents.

Nickel manganese alloys have good corrosion resistance and are good thermal conductors. Nickel manganese alloys are often used in cables, Lead-in-Wire for electronic tube supports, lamps, and wire cloth. They are also widely used for filters and wire mesh for the petro-chemical and chemical industries.

The main product of the smelting process is a carbon-saturated ferroalloy consisting of 76 to 80% manganese, 12 to 15% of iron, 7.5% of carbon, and 1.2% of silicon. 70 to 80% of the manganese is recovered in the melt, and a slag consisting of 30 to 42% manganese is also achieved.

Silicomanganese alloy contains 65 to 68% manganese, 16 to 21% silicon, and 1.5 to 2% carbon, and is generated by the smelting of slag from manganese ore or high-carbon ferromanganese with a quartz flux and coke. The alloy's carbon content is reduced due to the presence of silicon. A silicomanganese with relatively lower carbon content can be achieved by resmelting silicomanganese with more quartz and coke. The product is used as a reducing agent in the production of low-carbon ferromanganese.

Medium- and low-carbon ferromanganese is a product of low carbon and silicon content is obtained by fusing manganese ore, coal, and lime flux in a furnace, thus forming a MnO-rich melt. This is later contacted with low-carbon silicomanganese or silicomanganese. These alloys contain silicon that reduces the MnO to manganese metal and get oxidized into the slag.

**Manganese as an Alloying Element:**



Fig-3Mangnese Coloured Nodules

Manganese is used as an alloying element for many different applications. Manganese is a key component of steel. In fact, this chemical element is present in all commercially available steels and is responsible for the steel's hardness and strength, but to less of an extent than carbon.

The effect of manganese in improving the mechanical properties of steel depends on its carbon content. Manganese also reduces the critical cooling rate during hardening, meaning it increases the hardenability of steel. Its effect on hardenability is higher than other alloying elements. Hadfield steel is recognized for its ability to be work-hardened due to the addition of 10% to 14% of manganese.

Manganese has similar effects like carbon, and steel producers use both of these elements to achieve a material with preferred properties. Manganese is required for the hot rolling process of steel by combining it with sulfur and oxygen. Steels often include 0.30% manganese, but certain carbon steels can include up to 1.5% of manganese.

Also, manganese is likely to boost the rate of carbon penetration during the carburizing process. Conversely, embrittlement sets in when too much manganese and too much carbon accompany one another. Manganese can form manganese sulfide (MnS) with sulfur, which is required for machining, and simultaneously counters the brittleness from sulfur, making it useful for the surface finish of carbon steel.

For welding purposes, 10 to 1 should be the ratio of manganese to sulfur. Less than 0.30% of manganese content can lead to cracking and internal porosity in the weld bead. If the content is more than 0.80%, it can promote cracking.

When manganese is added to aluminum, its strength is increased slightly through solution strengthening and its strain hardening is also improved. However, corrosion resistance or ductility is not considerably reduced. For instance, manganese (Mn) 3xxx is a moderate strength, non-heat-treatable material that retains strength at increased temperatures.

A large part of manganese is used as high-carbon ferromanganese and added to carbon steels. The low- and medium- carbon ferroalloy and electrolytic manganese are used in lower carbon content steels. Manganese, as a desulfurizer, forms stable, high-melting sulfide particles, and manganese as an alloying agent enhances hardness, strength, abrasion resistance, and hardenability.

After briquetting with aluminum shot, powdered electrolytic manganese is mixed with aluminum in up to 2% concentration. Such alloys have higher strength, corrosion resistance, and wear resistance compared to pure aluminum alone. The addition of manganese improves the properties of copper. Acting as a deoxidizer of the molten alloy, manganese lowers the solidus and liquidus, improving castability. It also has a general strengthening effect, and it is also possible to produce special alloys, for example, with high thermal expansion or high electrical resistivity.

A6063 alloy is a standard material that is lightweight yet has excellent strength. As a result, it is used in the construction of ships and boats. Conversely, its strength is lower than that of steel, so an enhancement of strength is required. Manganese element was added to the AA6063 alloy to enhance its tensile strength. Increased manganese content translates into an alloy with increased tensile strength.

The following are the key benefits of manganese as an alloying element:

- An active deoxidizer
- Less likely to separate than other alloying elements
- Enhances machinability by integrating with sulfur to form a soft inclusion in the steel, enabling a consistent built up edge along with a place for the chip to break
- Enhances yield at the steel mill by integrating with the sulfur in the steel and reducing the formation of iron pyrite, which can make the steel susceptible to crack and tear during high temperature rolling processes
- It boosts the tensile strength and hardenability, but reduces ductility
- It integrates with sulfur to form globular manganese sulfides, which are required in free cutting steels to ensure good machinability



**Fig-4**

## Manganese Ore and Alloy Producers

According to Research and Markets' recent report, the global manganese mining market is estimated to grow at a CAGR of 3.53% between the period 2016 and 2020. Manganese is produced by various countries, but the top 10 manganese-producing countries are:South Africa,China,Australia,Gabon,Brazil,India,Malaysia,Ghana,Kazakhstan.Ukraine

As such, the top five vendors in the global manganese mining market are Assmang, BHP Billiton, Consolidated Minerals, ERAMET, and Vale.

Established in 1935 and headquartered in Johannesburg, South Africa, Assmang is involved in the mining of manganese, iron ore, and chrome ores. The company also carries out mining, crushing, washing, and screening of ore through its manganese ore and alloys business division. It also deals with the smelting of ferromanganese minerals and produces refined ferromanganese.

BHP Billiton was founded in 1851 and is headquartered in Melbourne, Australia. The company develops natural resources throughout the globe and has projects in the Americas and Australia. It controls two iron ore mines in Australia and Brazil, and five copper mines in Chile, Australia, and Peru. In addition to these operations, BHP Billiton manages manganese mining operations in South Africa and Australia.

Established in 2004, Consolidated Minerals is a leading manganese ore producer with operations in Ghana and Australia. Its main activities are exploration, mining, processing, and sale of manganese ore.

Founded in 1880 and headquartered in Cedex, Paris, France, ERAMET is a mining and metallurgical company and develops alloys for a variety of markets. It produces high-grade manganese ore via its subsidiary, COMILOG. It extracts manganese ores and is also involved in recycling and reuse of industrial waste materials. Its product portfolio includes manganese alloys, high-grade manganese ore, and manganese chemistry.

Vale is a diversified mining and metal company that produces and sells nickel, copper, ferroalloys, cobalt, coal, cobalt, manganese, platinum group metals, iron ore and pellets, and fertilizer. Vale produces ferroalloys and manganese via its ferrous minerals segment. Manganese is the 12th most abundant element in Earth's crust. Its concentration varies among common types of rocks, mostly in the range of from 0.1 to 0.2 percent. The highest quality manganese ores contain from 40 to 45 percent manganese. The formation of these ores requires specialized geologic conditions that concentrate manganese at several hundred times its average crustal abundance. The dominant processes in forming the world's principal deposits take place in the oceans. As a result, most important manganese deposits occur in ancient marine sedimentary rocks that are now exposed on continents as a result of subsequent tectonic uplift and erosion. In many cases, other processes have further enriched these manganiferous sedimentary rocks to form some of today's highest grade ores. Modern seabed resources of ferromanganese nodules cover vast areas of the present ocean floor and are still forming by complex interactions of marine microorganisms, manganese dissolved in seawater, and chemical processes on the seabed.

Manganese is ubiquitous in soil, water, and air. It occurs most often in solid form but can become soluble under acidic conditions. Manganese mining, like any activity that disturbs large areas of Earth's surface, has the potential to produce increases in manganese concentrations that could be harmful to humans or the environment if not properly controlled. Although manganese is an essential nutrient for humans and most other organisms, overexposure can lead to neurotoxicity in humans. Workers at manganese mining and processing facilities have the greatest potential to inhale manganese-rich dust. Without proper protective equipment, these workers may develop a permanent neurological disorder known as manganism. Each manganese mine is unique and presents its own suite of potential hazards and preventative measures. Likewise, various nations have their own sets of standards to ensure safe mining, isolation of mine waste, treatment of mine waters, and mine closure and restoration. Interest in mining trace metals contained in ferromanganese nodules and crusts on the seabed has increased rapidly in the past decade. Prime areas for future research include overcoming the technological challenges presented by mining as deep as 6,500 meters below sea level and understanding and mitigating the potential impacts of seabed mining on marine ecosystems.

Manganese is an essential element for modern industrial societies. Its principal use is in steelmaking, where it serves as a purifying agent in iron-ore refining and as an alloy that converts iron into steel. Although the amount of manganese consumed to make a ton of steel is small, ranging from 6 to 9 kilograms, it is an irreplaceable component in the production of this fundamental material. The United States has been totally reliant on imports of manganese for many decades and will continue to be so for at least the near future. There are no domestic reserves, and although some large low-grade resources are known, they are far inferior to manganese ores readily available on the international market. World reserves of manganese are about 630 million metric tons, and annual global consumption is about 16 million metric tons. Current reserves are adequate to meet global demand for several decades. Global resources in traditional land-based deposits, including both reserves and rocks sufficiently enriched in manganese to be ores in the future, are much larger, at about 17 billion metric tons. Manganese resources in seabed deposits of ferromanganese nodules and crusts are larger than those on land and have not been fully quantified. No production from seabed deposits has yet been done, but current research and development activities are substantial and may bring parts of these seabed resources into production in the future. The advent of economically successful seabed mining could substantially alter the current scenario of manganese supply by providing a large new source of manganese in addition to traditional land-based deposits.

From a purely geologic perspective, there is no global shortage of proven ores and potential new ores that could be developed from the vast tonnage of identified resources. Reserves and resources are very unevenly distributed, however. The Kalahari manganese district in South Africa contains 70 percent of the world's identified resources and about 25 percent of its reserves. South Africa, Brazil, and Ukraine together accounted for nearly 65 percent of reserves in 2013. The combination of total import reliance for manganese, the mineral commodity's essential uses in our industrialized society, and the potential for supply disruptions because of the limited sources of the ore makes manganese among the most critical minerals for the United States.

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abundance. The dominant processes in forming the world's principal deposits take place in the oceans. As a result, most important manganese deposits occur in ancient marine sedimentary rocks that are now exposed on continents as a result of subsequent tectonic uplift and erosion. In many cases, other processes have further enriched these manganiferous sedimentary rocks to form some of today's highest grade ores. Modern seabed resources of ferromanganese nodules cover vast areas of the present ocean floor and are still forming by complex interactions of marine microorganisms, manganese dissolved in seawater, and chemical processes on the seabed.

Manganese is ubiquitous in soil, water, and air. It occurs most often in solid form but can become soluble under acidic conditions. Manganese mining, like any activity that disturbs large areas of Earth's surface, has the potential to produce increases in manganese concentrations that could be harmful to humans or the environment if not properly controlled. Although manganese is an essential nutrient for humans and most other organisms, overexposure can lead to neurotoxicity in humans. Workers at manganese mining and processing facilities have the greatest potential to inhale manganese-rich dust. Without proper protective equipment, these workers may develop a permanent neurological disorder known as manganism. Each manganese mine is unique and presents its own suite of potential hazards and preventative measures. Likewise, various nations have their own sets of standards to ensure safe mining, isolation of mine waste, treatment of mine waters, and mine closure and restoration. Interest in mining trace metals contained in ferromanganese nodules and crusts on the seabed has increased rapidly in the past decade. Prime areas for future research include overcoming the technological challenges presented by mining as deep as 6,500 meters below sea level and understanding and mitigating the potential impacts of seabed mining on marine ecosystems.

Table-1

| Type ofRock Sediment Type | Mineral Assembladge |
|---|---|
| Calcareous      Limestone | Calcite + Dolomite + Magnetite + Quartz + Chert + Opaque. |
| | Calcite + Dolomite + Quartz + Hematite + Opaque. |
| | Calcite + Dolomite + Tremolite + Biotite + Quartz + Opaque. |

Table-2

| Type ofMetamorphic Sediment equivalent | Mineral Assembladge |
|---|---|
| Psamite    Quartzite | Quartz + Plagioclase + Orthoclase + Sericite + + Calcite + Opaque. |
| | Quartz + Orthoclase + Sericite Calcite + Opaque. |
| | Quartz + Plagioclase + Orthoclase + Hematite + Muscovite Opaque. |
| | Quartz + Microcline + Muscovite + opaque |

Petrographic studies and modal analysis Table -3 suggest that the different rock types in the study area are Siliceous phyllite, Manganiferous phyllite, Muscovite phyllite, Chlorite-biotite phyllite, Garnetiferous-mica schist, Quartz-mica schist, Muscovite-chlorite schist, Limestone and Quartzite. In the light of above fact, it appears that regional metamorphism has played an important role in metamorphism of pelitic-psammitic and calcareous sediments which are the prominent Mn comprising rocks of the study area and finally metamorphosed to present

| Mineral | Mn phyllite | Siliceous phyllite | Chlorite biotite phyllite | Garnetiferous mica schist | Quartz mica schist | Muscovite chlorite schist | Limestone | Quartzite |
|---|---|---|---|---|---|---|---|---|
| Qtz | 22 | 39 | 24 | 23 | 39 | 21 | 5 | 80 |
| Mus | 31 | 31 | 12 | 34 | 28 | 41 | 1 | 2 |
| Bio | 3 | 4 | 29 | 3 | 5 | 2 | 1 | 1 |
| Chl | 14 | 7 | 22 | 7 | 7 | 20 | × | 1 |
| Feld | 2 | 2 | 1 | 3 | 4 | 1 | × | 4 |
| Gt | 3 | 2 | 3 | 21 | 4 | 4 | × | × |
| Op | 20 | 15 | 9 | 8 | 11 | 9 | 9 | 8 |
| Mg | 2 | × | × | × | × | × | 3 | × |
| He | 3 | × | × | × | × | × | 2 | 2 |
| Fa | × | × | × | 1 | 1 | 2 | 0 | × |
| Ca | × | × | × | × | × | × | 56 | 2 |
| Do | × | × | × | × | × | × | 22 | × |
| Total | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 |

Mineral percentage in Mn bearing rocks of study area.

Legend?Minerals in (%) Mus = Muscovite, Qtz = Quartz, Bio = Biotite, Chl = Chlorite, Gt = Garnet, Op = Opaque, Feld = Feldspar, Mg = Magnetite, He = Hematite Ca = Calcite, Do = Dolomite, × = None.

day rock types viz, phyllite, schist and quartzite. As the rocks of the study area have undergone metamorphism up to lower amphibolite facies, the deformation took place at relatively low temperature. The phyllite and schist samples mineral assemblages fall in greenschist to lower amphibolite facies and formed by prograde metamorphism of Aravalli metasediments. Quartzite is non-foliated and both medium to coarse grained (Granoblastic). The quartzites disposed conformably with phyllite and narrowly brecciated with re-cemented by secondary chert and manganese. The calcareous rock shows dolomitic composition with some impure ferruginous varieties. Thin sections studies suggest manganese ores in phyllite and schist rocks deposited along the mineral boundaries and the foliation plane. They are also found in form of dark colour patches in some thin sections. In garnet and quartz, manganese is found in both ways as inclusion or encrustation over them. In limestone manganese mineralisation in sporadic forms etc. In quartzite, manganese ores associated in form of patches and encrustation as well.



**Fig-5 Sea Floor Manganese ore**

**CONCLUSION:**
The Mn associated rocks in the study area are phyllite, schist, quartzite and limestone. Manganese is ubiquitous in soil, water, and air. It occurs most often in solid form but can become soluble under acidic conditions. Manganese mining, like any activity that disturbs large areas of Earth's surface, has the potential to produce increases in manganese concentrations that could be harmful to humans or the environment if not properly controlled. Modern seabed resources of ferromanganese nodules cover vast areas of the present ocean floor and are still forming by complex interactions of marine microorganisms, manganese dissolved in seawater, and chemical processes on the seabed.

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