BIBLIOGRAPHY


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MANGANESE

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There are four commercial sources of manganese in the United States, namely, manganese ores, manganiferous iron ores, manganiferous silver ores and manganiferous zinc residuum. The first three are ores; the fourth is a seridual product obtained after roasting zinc from an ore containing zinc, iron and manganese.

Although manganese forms a part of over one hundred minerals, and is a relatively widespread element, practically all the manganese in the United States occurring in nature in sufficient quantity to be of commercial value comes from the oxides, mainly psilomelane and pyrolusite. Other oxides are mined, but much less frequently. The carbonate of manganese, rhodochrosite, is not found in sufficient quantities in this country to be of commercial value, but is mined in several foreign countries, as Spain and Wales. The silicate of manganese, rhodonite, contains too much silica to be used for its manganese content, but is sometimes mined for ornamental purposes on account of its beautiful pink color. Other minerals of manganese are too rare to be of commercial importance.

Deposits of manganese ore occur in many parts of the United States, but are most abundant in the Appalachian and Piedmont regions, in the southern Mississippi Valley, and on the Pacific coast. Small deposits occur in the New England, Rocky Mountain, and Great Basin regions. The principal producing districts up to this time have been the James River Valley and Blue Ridge districts of Virginia, the Cave Springs and Cartersville districts of Georgia, the Batesville district in Arkansas, and the Livermore-Tesla district of California. Of minor importance is the New River region in Virginia, the northeastern Tennessee region, the McCormick area in South Carolina, and the Little Grande district in Utah. Besides these are many minor deposits in many parts of the country, which have been operated intermittently, producing small quantities of ore.
MANGANIFEROUS IRON ORES

Manganiferous iron ores consist of mixtures of manganese and iron oxides and hydrous oxides in various proportions. The amount of metallic manganese in these ores varies from less than one per cent to 40 per cent or more. The high and medium grades of ore are used in the manufacture of spiegeleisen and ferro-manganese, but the low grade ore is used for the iron content only.

In some deposits the iron and manganese oxides may occur together as a coarse mixture, easily separated; the manganese, however, seems to have penetrated into the mass, while the iron ore is nearer the surface. The various oxides may be so intermixed, however, that there seems to be no definite relation between them.

MANGANIFEROUS SILVER ORES

Manganiferous silver ores are found abundantly in the oxidized portions of many of the silver deposits of Western United States. They consist of manganese and iron oxides intimately associated, forming a black, amorphous ore carrying silver chloride and lead carbonate. The iron is usually in the form of limonite and as a rule predominates over the manganese, which is in the form of Wad.

Manganiferous silver ores may be classed under three heads with regard to their uses:

1. Ores high in silver and lead, and used for these metals only. The manganese and iron are valuable as fluxes, and ores containing considerable quantities of them are worth more than other silver ores with the same silver content.

2. Ores that are low in silver and lead, but contain iron and manganese in large quantities; these are used for the manufacture of spiegeleisen and ferro-manganese.

3. Ores having a low silver and lead content and a low iron and manganese content. These are sent to the smelters to be used as fluxes, the silver and lead being recovered dur-
ing the smelting, while the iron and manganese pass into the slag and are lost.

MANGANIFEROUS ZINC RESIDUE

Manganiferous zinc residuum is obtained from zinc oxidizing and volatilizing furnaces using New Jersey zinc ores. The crude ores consist of franklinite, zincite, and willmite. The zinc is removed by volatilizing and is collected as zinc oxide, leaving a residuum of iron and manganese oxide.

THE MANGANESE MINERALS

The minerals of manganese occurring in nature in sufficient quantity to be of commercial importance are the oxides, the carbonates and the silicates.

OXIDES

There are many varieties of oxides, but only five of them are important as ores—psilomelane, pyrolusite, braunite, manganeite, and wad.

PSILOMELANE:—BLACK HEMATITE

Composition: \( \text{MnO}_2 + (\text{H}_2\text{O},\text{K}_2\text{O},\text{BaO}) \) or \( \text{H}_4\text{MnO}_8 \), with replacement by Ba or K. The percentage of metallic manganese varies from 45 to 60 per cent; that of baryta from 0 to 17 per cent, that of potassa from 0 to 5 per cent; and that of water from 3 to 6 per cent.

General Description: A smooth, black, massive mineral, commonly botryoidal, i.e. having something of the appearance of a bunch of grapes, stalactitic or in layers with pyrolusite; has concentric structure and on fracture it appears rounded and curved like a shell.

Physical Characteristics: Moderately heavy and cannot be scratched with a knife.

Lustre, submetallic or dull.............................................................................Opaque
Streak, brownish black............................................................................Tenacity, brittle
Color, iron black to dark gray.
Qualitative Tests: Infusible. When heated in closed tube yields oxygen (the presence of which is detected by applying a flame to the mouth of the tube) and usually water, which collects on the sides of the tube. Soluble in hydrochloric acid, with the evolution of chlorine, which has a strong pungent odor. A drop of sulphuric acid added to the solution will usually produce a white precipitate of barium sulphate.

**PYROLUSITE:**—**BLACK OXIDE OF MANGANESE**

Composition: \( \text{MnO}_2 \) (Mn 63.2% when pure).

General Description: A soft black mineral of metallic lustre. Frequently composed of short, indistinct crystals or radiated needles, but also found compact, massive, stalactitic, as velvety crusts, and branching like a tree. Usually soils the fingers. It generally occurs in association with psilomelane, either lining or filling cavities in it, or occurring in alternate layers with it.


- Lustre, metallic or dull: Opaque
- Streak, black: Tenacity, brittle
- Color, black to steel gray.

Qualitative tests:—Infusible, becomes brown on heating. Usually yields oxygen and a little water when heated in closed tube. By looping a piece of platinum wire and fusing on it some of the powdered ore, with a little borax, the bead thus obtained is amethystine in color. Soluble in hydrochloric acid with evolution of chlorine.

**BRAUNITE**

Composition:—\( \text{Mn}_2\text{O}_3 \), but usually containing \( \text{MnSiO}_3 \). When pure, braunite contains 69 per cent metallic manganese, but it never occurs pure in nature.

General Description:—A heavy, slimy, brownish or grayish-black mineral, either massive or in minute tetragonal pyramids, almost isometric.

Lustre, submetallic. Opaque
Streak, brownish-black. Tenacity, brittle
Color, brownish to steel gray.

Qualitative tests:—Infusible. Gives an amethystine bead with borax. Soluble in hydrochloric acid, evolving chlorine and leaving gelatinous silica.

MANGANITE

Composition:—Mn₂O₂·H₂O. Theoretically, it contains 62.4 per cent of metallic manganese, 27.3 per cent of oxygen, and 10.3 per cent of water.

General Description:—A heavy, black mineral, massive or in long and short prismatic (orthorhombic) crystals, often grouped in bundles with fluted or rounded cross-section and undulating terminal surface. Rarely granular or stalactitic.


Lustre, submetallic. Opaque
Streak, reddish brown to black. Tenacity, brittle
Color, steel gray to iron black.

Qualitative Tests:—Like pyrolusite, but yields decided test for water and very little oxygen.

WAD:—BOG MANGANESE

Composition:—Mixture of manganese oxides, often with oxides of cobalt, copper and lead.

General Description:—Earthy to compact indefinite mixtures of different metallic oxides, in which those of manganese predominate. It is dark brown or black in color, often soft and loose, but sometimes hard and compact.

Lustre, dull.................................................................Opaque
Streak, brown. Often soils the fingers.
Color, brown to black.

Qualitative Tests:—Same for psilomelane, but often with strong cobalt or copper reactions.

The remaining oxides of manganese are of small importance as ores, and are rare in this country. They are hausmonite, polianite, franklinite, and pelazite.

CARBONATES
RHODOCHROSITE

Composition:—MnCO₃. Theoretically, it contains 47.56 per cent of metallic manganese.

General Description:—Rose pink to brownish-red rhombohedral crystals, usually small curved. Frequently massive cleavable, or granular or compact. Less frequently botryoidal or incrusting. Commonly occurs as gangue in association with rhodorite in veins traversing granitic rocks. On exposure, it becomes black by oxidation.

Lustre, vitreous to pearly. Transparent to opaque.
Streak, white.........................................................Tenacity, brittle
Color, light pink, rose red, brownish red and brown.
Cleavage, parallel to rhombohedron.

Qualitative Tests:—Infusible, but on heating decrepitates violently and becomes dark colored. On borax yields amethystine bead. Soluble in warm hydrochloric acid, with effervescence; slowly soluble in the cold acid.

Other manganiferous carbonates that occur sparingly are mangano-calcite (Ca,Mn)CO₃, mangano-siderite (Fe,Mn)CO₃ and aukerite (Ca Mg Fe Mn)CO₃.
SILICATES

Rhodonite is the only important silicate.
Composition:—MnSiO₃, with replacement by Fe, Zn, or Ca. It has a theoretical content of 41.9 per cent metallic manganese.

General Description:—A brownish red to light red mineral, occurring generally as gangue in ore or pegmatite veins in association with other minerals as quartz and rhodochrosite. It is usually found in fine grained or cleavable masses and disseminated grains, often coated with a black oxide. Sometimes in triclinic crystals. On exposure it becomes black. Commercially unimportant, on account of its high content of silica.


- Lustre—vitreous
- Transparent to opaque
- Streak—white
- Tenacity, brittle
- Color, brownish red to flesh red, bright red, greenish, yellowish, pinkish.
- Cleavage, prismatic.

Qualitative Tests:—Blackens and fuses easily with slight intumescence. With fluxes reacts for manganese and zinc. In powder is partially dissolved by hydrochloric acid leaving a white residue.

USES OF MANGANESE

The uses of manganese in the industries may be classified as follows: 1. Metallurgical, in the manufacture of alloys and as fluxes in reduction of copper, lead, and silver ores; 2. Chemical, as an oxidizer and as coloring material.

METALLURGICAL USES

a. Iron-Manganese alloys:—Ferro-manganese, spiegeleisen, silico-manganese and silicospiegel. The three sources of manganese, namely, manganese ores, manganiferous ores and
manganiferous zinc residuum are used in the manufacture of iron-manganese alloys.

Spiegeleisen includes all iron-manganese alloys containing less than 20 per cent manganese. Carbon in various amounts, silicon, phosphorous and sulphur may be present. However, more than 1 per cent of silicon and 0.1 per cent of phosphorous are not permissible for commercial use. Spiegeleisen is used for the manufacture of steel when only small amounts of manganese are required. When larger quantities are necessary, too much carbon and other injurious impurities would be introduced by using spiegelsien, and therefore some other alloy containing a higher percentage of manganese and a proportionately lower percentage of carbon and other impurities is required.

Ferro-manganese contains from 20 to 80 per cent of manganese, from 1 to 7 per cent carbon, from 1 to 1.6 per cent silica, and small amounts of sulphur and phosphorous, the latter not to exceed 0.22 per cent in ferro-manganese containing 80 per cent of manganese.

Silico-spiegel contains from 20 to 50 per cent manganese, from 40 to 70 per cent iron, from 4.2 to 4.9 per cent silicon, and from 2.5 to 3.5 per cent carbon. If the iron and silicon are decreased and the manganese increased, the alloy becomes silico-manganese.

All these alloys are used in the manufacture of steel, the use of each depending on the quality of steel desired.

b. Non-ferrous alloys:—Manganese is also used to form alloys with copper, zinc, aluminum, tin, lead, magnesium, and silicon, and with combinations of these elements. Manganese bronze, and silicon, which is the most important of the non-ferrous alloys, is used for steamboat propellers, and other alloys are used for coins, statuary and ornamental purposes.

c. Fluxes in reduction of copper, lead, and silver ores:—The manganese ores used as fluxes are necessarily those which are relatively impure or which contain metals of greater
value than the manganese, namely—low grade manganiferous iron ores and manganiferous silver ores.

CHEMICAL USES

a. Oxidizers:—
   1. Decolorizer of glass.
   2. Dry batteries.
   3. Drier of varnishes and paints.
   4. Preparation of oxygen.
   5. Manufacture of disinfectants.

b. Coloring materials:—
   1. Coloring glass, pottery, tiles and bricks.
   2. Calico printing and dyeing.
   3. Paints.
   4. Fertilizer.

Manganese ores are also used for gems and ornamental stones in the form of the minerals rhodonite and spessarite.

MANGANESE INDUSTRY IN THE UNITED STATES

Although manganese is relatively abundant in nature, there are not many deposits in the United States that are of commercial importance. This is largely due to the fact that manganese ores in this country generally occur in small discontinuous pockets which do not warrant the erection of expensive concentrating plants, and the mining is carried on on a small scale. A large proportion of the ore is of low grade variety, containing too many injurious impurities, such as silica and carbon. The eastern ores are embedded in clay and must be washed and sorted before they can be put on the market. In many instances the low price of manganese ores does not permit their working, due to the high cost of transportation to shipping centers.

By far the larger part of manganese ores consumed in the United States is imported from foreign countries, chiefly from India, Brazil, Cuba and the East Indies.
Manganese oxide is abundant in the oxidized ores of certain mines of the Tombstone district, Cochise County. The ore in these mines is principally pyrolusite and earthy black wad, with some psilomelane, and occurs in a calcareous or siliceous gangue. The ore is mined for its silver content only, the manganese oxides being of assistance as flux in smelting.

The rocks of the district consist of a series of limestones, quartzites and shales of probable lower Carboniferous age, associated with porphyritic and feldspathic dikes and granite. The ore deposits are in the form of veins and chimneys, and occur mainly in the limestones at the contact with the porphyry dikes. Pyrolusite is found in the Clifton-Morenci district, where it is mined for flux. Manganese claims are also located about 30 miles south of Wickenburg, at Salome in Yavapai County, and in the Mohawk Mountains, Yuma County. Some pyrolusite is found in Yavapai County, as secondary mineral in ores of the Bradshaw Mountains. It is, however, of small importance, and is not mined.

Due to the fact that the average grade of domestic ores is much lower than those imported, and at the same time could not be placed on the market at as low a price, the larger part of manganese or consumed in the United States has been imported from foreign countries, chiefly British India, Russia and Brazil. But at the present time importation from these countries is practically impossible, and the demand for domestic ores has greatly increased.

The reported ores of manganese in Arizona have been small, rather scattered, and few in number. Owing to their remoteness from railroad transportation, together with the low price of the ores and the high cost of transportation, the mining of these ores in Arizona has so far been prohibited. Under present conditions of transportation, the only manganese ores that are marketable are those of sufficient grade to be used as oxidizers, in the manufacture of chemicals, and for fluxes in local smelters.
In spite of the fact that the eastern steel companies have been energetically engaged in seeking deposits of this mineral, with a large amount of publicity relative to the rareness, the price has not gone up accordingly, and unless the deposits are close by railroad transportation, no profit could be made at the present prices. It is not unlikely, however, that deposits of the purer material may be found within the state.

**VALUE OF ORES**

The value of ores containing manganese depends upon their mineralogical nature as well as their purity. In the metallurgical industries the prices are governed according to the manganese content, and are based on ores which do not contain more than 8 per cent silica and 0.2 per cent phosphorous, and are subject to deductions as follows: For each per cent in excess of 8 per cent silica, there shall be a deduction of 15 cents per long ton, fraction in proportion. For each 0.02 per cent, or fraction thereof, in excess of 0.2 per cent of phosphorous, there shall be a deduction of 2 cents per unit of manganese per long ton.

Ores containing less than 40 per cent manganese or more than 12 per cent silica or 0.225 per cent phosphorous are subject to acceptance or refusal at the buyer's option.

Settlements are based on analysis of sample dried at 212 degrees F., the percentage of moisture in the sample as taken being reduced from the weight.

According to these specifications, the prices paid for the ores range from 4 to 6 cents per unit.

The value of an ore adapted to use as an oxidizer varies with its content of manganese dioxide, and does not depend, except incidentally, on its content of manganese metal. Prices range from $35 to $80 per ton.

As the manganese content of manganiferous iron ores and manganiferous silver ores is used only indirectly, the value
of these ores depends largely on local conditions in the metallurgical industries which consume them.

These ores are of value principally for their content of iron, silver, and metals other than manganese, which but rarely adds more than $3 per ton to their value. The more impure ores, such as would serve for coloring glass and pottery are sold at prices ranging from $2 to $6 per ton, F. O. B. works.