

METALLURGY OF THE RARER METALS No. 3

MANGANESE

SULLY

MANGANESE

by

A. H. SULLY

PH.D., M.Sc., F.INST.P., F.I.M.

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PREFACE

THE author is grateful to Mr E. A. G. LIDDIARD, Director of Research, Fulmer Research Institute, for first stimulating the interest in manganese which led to the writing of this book and for library facilities without which it could not have been completed. He is especially grateful also to Miss I. E. PIMBLETT whose patient secretarial assistance was invaluable.

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A. H. SULLY

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INTRODUCTION

LIKE chromium, a metal with which it has much in common, the inclusion of manganese among the rarer metals is justified by the fact that until recently it was rarely encountered and little studied in a state of high purity. It occurs in large quantities in the earth's crust and, in the form of ferro-alloys readily and cheaply made from its ore, it is widely used as a scavenger and refining agent in the manufacture of steel, as much as 14 lb of manganese being used on an average in the production of one ton of steel.

In igneous rocks, which comprise 95 per cent of the earth's crust, the average percentage concentration of manganous oxide is 0.124. This is small compared with the content of alumina (15.34), $\text{FeO} + \text{Fe}_2\text{O}_3$ (6.88) and titania (1.05) but very much higher than the incidence of the well known metals copper (0.010), zinc (0.004) and lead (0.002).

The pure metal is however reactive, easily contaminated and not easily produced from its ores. Although it can be purified by distillation, pure manganese has been made by this method only in small quantities and within the last twenty five years so that the serious study of the properties of manganese and the constitution and properties of its alloys is comparatively recent. This study has been stimulated very considerably by the successful development in the U.S.A. of a commercial process for the production of manganese of over 99.9 per cent purity by electrolytic deposition from an electrolyte prepared directly from manganese ore. This material is now being produced on a scale of 7000 tons per annum and at a price which is competitive with that of manganese of much lower purity made by established methods.

It is, therefore, appropriate that at a time when manganese in a state of high purity is becoming available in commercially significant quantities a comprehensive summary should be made of the state of existing knowledge of the metal and of its alloys and of its commercial utilization. It is believed that the present book contains a description of all the more important contributions which have been made to the study of manganese and its alloys.

Within recent years a growing realization has been manifested that manganese is used wastefully in the iron and steel industry. Growing efforts are being made both in the U.S.A. and in Germany

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to improve the efficiency of the utilization of manganese in the steel industry and to recover manganese from steel-making slags and from low grade ores. Since this subject is of considerable importance to countries such as the U.S.A. and the United Kingdom which rely upon imports for the bulk of their requirements for manganese the subject of the conservation and recovery of manganese is exhaustively discussed in the early chapters of this book.

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THE HISTORY OF MANGANESE AND THE OCCURRENCE AND CLASSIFICATION OF ITS ORES

1.1. HISTORY

CREDIT for the establishment of manganese as a hitherto unrecognized metal is usually given to C. W. SCHEELE¹ in the year 1774. Some of its ores had, however, been known from times of antiquity and had been confused with ores of iron and magnesium. The history of its classification and of the gradual recognition of the differences between the various ores has been described by J. W. MELLOR² and by Sir ROBERT HADFIELD³. The commonest manganese mineral is pyrolusite. This, when added to glass, has the remarkable property of removing the greenish coloration produced in the glass by the oxides of iron, which are common impurities in silicate sands used for glass-making. This property was discovered in very ancient times and the mineral is to be recognized in early writings not so much by the names given to it, which were many and various, as by the association with it of this particular attribute. It was first described by Pliny as a variety of the magnetic oxide of iron, lodestone or *lapis magnes*. Although pyrolusite is non-magnetic and this fact was recognized by Pliny, he was still content to classify it as a *lapis magnes* on the grounds of its similar external appearance and to explain the difference from the other minerals in its lack of attraction for iron as due to a difference in sex, the manganiferous *lapis magnes* being female and consequently, in the view of the ancients and foreign to the view more commonly held today, less attractive. Pliny accounts for the use of the word *magnes* by ascribing to Magnes, a herdsman on Ida, the observation that his shoe nails and the iron ferrule of his staff were attracted to the ground beneath which lodestone was found. However, the term may also be derived from the fact that a further variant of *lapis magnes*, the white form now known to be magnesian earth or *magnesia alba*, was found in the Asian locality of Magnesia. Yet another hypothesis, advanced by L. DELÂTRE⁴, was that the term owed its origin to the Greek μάγανον, a delusion, deriving from the

brittle and unstable nature of the metal obtained from it, so different from iron which could be produced from ore of similar external appearance. It has also been suggested that the name derives from *Mangana*, which is in the East Indies.

The nomenclature had developed somewhat in the Middle Ages to the extent that the terms *lapis magnesius* or *lapis magnes* were applied to the magnetic lodes while the term *magnesia* was reserved for the non-magnetic ore of similar appearance. According to Mellor, who has ably summarized the medieval writings, Albertus Magnus, who wrote in the thirteenth century, states that *magnesia*, sometimes called *magnosiam*, is a black mineral frequently used in glass-making. It is referred to in much the same context by many medieval alchemists and natural philosophers, including Roger Bacon, Basilius Valentinus, G. Agricola, R. Boyle and M. Mercatus. Fourteenth-century MSS in the Sloane Collection in the British Museum refer to both *magnesia ferrea* and to *magnesia*, the latter in connection with the making of violet glass. The term *Manganesis* occurs frequently in the writings of Albertus Magnus who lived from 1193 to 1280 A.D. The earliest reference to the alteration of the name of the mineral from 'magnesia' to 'manganese' appears to be that of V. BIRINGUCCIO⁵ who, writing in 1540, stated that the mineral of this name was found at Viterbo in Tuscany and in Germany. He described it as the colour of iron slag and remarked that it cleansed molten glass when the latter was green or yellow and imparted to it an azure coloration. He also noted that no metal could be obtained from it by fusion but that it gave off a vapour when heated and turned to ashes. According to E. KUHN⁶, by the beginning of the nineteenth century, the mineral had come to be designated in Germany, *Mangan*, a shortened form of *manganesium*. The first reference to *pyrolusite* is due to W. HAIDINGER⁷ in 1826, who derived the name, also with reference to its use in glass-making, from the Greek $\pi\upsilon\rho$ fire and $\lambda\upsilon\varepsilon\iota\nu$ to wash. The same trend of thought is obvious in its description by J. B. L. Romé de l'Isle as *le savon des verriers* or *sapo vitriorum*. The mineral was also described as *Braunstein* by BASILIUS VALENTINUS⁸, as *manganaise gris* by S. A. FORSIUS⁹, and as *molybdenum magnesi* by C. VON LINNAEUS¹⁰, the latter obviously being in error in classifying the mineral with molybdenum ores.

The first clear demonstration that iron is present in the mineral only as a contaminant was made by J. H. POTT¹¹, a pupil of Stahl, who obtained salts which he did not recognize as novel. In common with other contemporary chemists he regarded the ore as an aluminous earth.

Although J. G. KAIM¹² was able to extract a regulus by heating together pyrolusite and black flux, it was not until 1774 that it was realized by Scheele that the ore and its extracts were those of a metal hitherto unrecognized. Although Scheele made this discovery he did not succeed in isolating the metal. This was first achieved by J. G. GAHN who did not publish a report of his investigations but whose work is mentioned by T. BERGMAN¹³ who also achieved the reduction a little later. Scheele and Gahn were in correspondence at this time and there is evidence in the shape of letters that Scheele supplied Gahn with samples of pyrolusite (Braunstein) ore. Gahn mixed the oxide with oil in balls and heated them in a crucible lined with charcoal. A number of small metallic globules were obtained equal in weight to one third of the mineral used. It has also been suggested that Gahn proposed that the new substance should be known as manganese but claims to this distinction have also been advanced on behalf of Bergman and the French chemist G. de Morveau.

Confusion about the name of the element continued for some time after its isolation, the names *Braunstein metal*, *Braunstein regulus* and *Braunsteinkönig* all having been used. The word manganese was, however, common in English translations and its use became general early in the nineteenth century.

1.2. THE OCCURRENCE AND ORES OF MANGANESE

Manganese occurs widely in crystalline rocks whence, like iron, it is dissolved out and is re-deposited as the oxide, hydroxide or carbonate. The primary occurrence as silicate minerals is important only when these are decomposed by water during weathering, especially in the tropics.

There are some manganese mines in Brazil and in India and horizontal beds are sometimes mined by adits in hill sides, but most manganese ore which is worked on a large scale is won by open cast methods.

The major ores of manganese are the oxides in hydrated or dehydrated forms and to a lesser extent the silicates and carbonates. They are as follows:

Pyrolusite MnO_2 —This is a relatively soft grey to black ore. Its manganese content when pure is 63.2 per cent. Its specific gravity is 4.8.

Psilomelane—This contains 45–60 per cent manganese and is thought to be a colloidal form of MnO_2 which has adsorbed impurities which are water and the oxides of sodium, potassium and

barium. It is relatively hard and occurs in massive forms. Its specific gravity is 3.7–4.7.

Manganite $\text{Mn}_2\text{O}_3 \cdot \text{H}_2\text{O}$ —This contains 62.4 per cent manganese when pure. It is dark grey to black in colour and of medium hardness with specific gravity 4.2–4.4.

Braunite $3\text{Mn}_2\text{O}_3 \cdot \text{MnSiO}_3$ —This contains 62 per cent of manganese and the silica content may be as high as 8–10 per cent. It is hard and has a specific gravity of 4.8.

Hausmannite Mn_3O_4 —This is of primary origin and occurs as veins in igneous rocks. It is brown to black in colour, hard and with a specific gravity of 4.8.

Rhodochrosite or *dialogite*—This is manganese carbonate with variable amounts of iron, calcium and magnesium carbonates. The manganese content can be considerably enriched by roasting to decompose the carbonates.

Rhodonite is manganese silicate MnSiO_3 and contains 42 per cent manganese.

Bementite is a hydrated silicate containing 31 per cent manganese and 5 per cent silica.

In addition to these ores of relatively well-defined composition, there are others of very variable composition, notably:

Manganiferous iron ores—These are variable mixtures of manganese and iron oxides usually containing upwards of 40 per cent iron and with a manganese content which may be as low as 5 per cent.

Wad or '*bog manganese*'—This is an earthy and amorphous mixture consisting of manganese oxide, iron oxide, water and other substances. It is usually soft and light with a specific gravity of only 3.0–4.2.

Finally manganiferous zinc and silver ores are of not insignificant importance and a considerable quantity of manganese in the form of ferro-alloys is produced in the U.S.A. from manganiferous zinc residuum which is the product which remains when the zinc has been distilled from the manganiferous zinc ore, franklinite $(\text{Fe}, \text{Zn}, \text{Mn})\text{O} \cdot (\text{Fe}, \text{Mn})_2\text{O}_3$. This residuum contains 14–15 per cent manganese and about 40 per cent iron and is well suited to the production of spiegeleisen.

1.2.1. Classification of manganese ores

Manganese ores exhibit a wide variability in composition, particularly in the balance of the manganese and iron contents, and since 95 per cent of the total manganese ore which is mined is used for

metallurgical purposes the ores are classified on the basis of the manganese content and the type of ferro-alloy for the manufacture of which they are to be used.

The normal classification is the following :

Manganese ores, containing more than 35 per cent manganese. These are suitable for the manufacture of high or low grade ferro-manganese.

Ferruginous manganese ores or spiegel ores containing 10-35 per cent manganese which are used for the manufacture of spiegeleisen.

Manganiferous iron ores, containing 5-10 per cent manganese, are used for the manufacture of manganiferous pig iron.

1.2.2. *Mode of occurrence, mining and concentration*

Most manganese ore is found in the form of secondary deposits, the manganese having been dissolved out of crystalline rocks and re-deposited as the carbonate, oxide or hydroxide. These secondary deposits are sedimentary or residual and the most common mode of occurrence is as wad, braunite, manganite, pyrolusite or psilomelane.

There are some primary occurrences of manganese ore. These, of course, are silicate minerals. They become of economic importance when, as in India, Brazil and the Gold Coast, the silicates are decomposed by surface water during tropical weathering.

Mining is usually carried out by open cast methods, although in the Caucasus working is carried out by adits in hill-sides and there is some underground mining in India and Brazil.

The ore is usually marketed in the crude state after only little hand picking. Some ores, however, require to be crushed and classified and washing is often necessary to remove earthy matter. This is particularly true of low grade ores. *Figure 1* shows Joplin jigs in use for washing and classifying ore in the Bhandara district of the Central Provinces of India.

In the U.S.A. concentration of low grade ore by flotation methods has been practised for carbonate and oxide ores. According to R. S. DEAN, F. D. DE VANEY and W. H. COGHILL¹⁴, the Anaconda Copper Mining Co. produced by flotation low phosphorus concentrates from the low grade ore of the Butte district of Montana. This, after sintering, contained 60-62 per cent manganese and about 7 per cent of silica. According to N. B. MELCHER¹⁵ the average manganese content of processed ore from this district in 1950 was 58.9 per cent. The methods used to treat low grade ores in the U.S.A. by conventional means such as washing and concentration have been described and discussed in some detail by W. R. CRANE¹⁶.

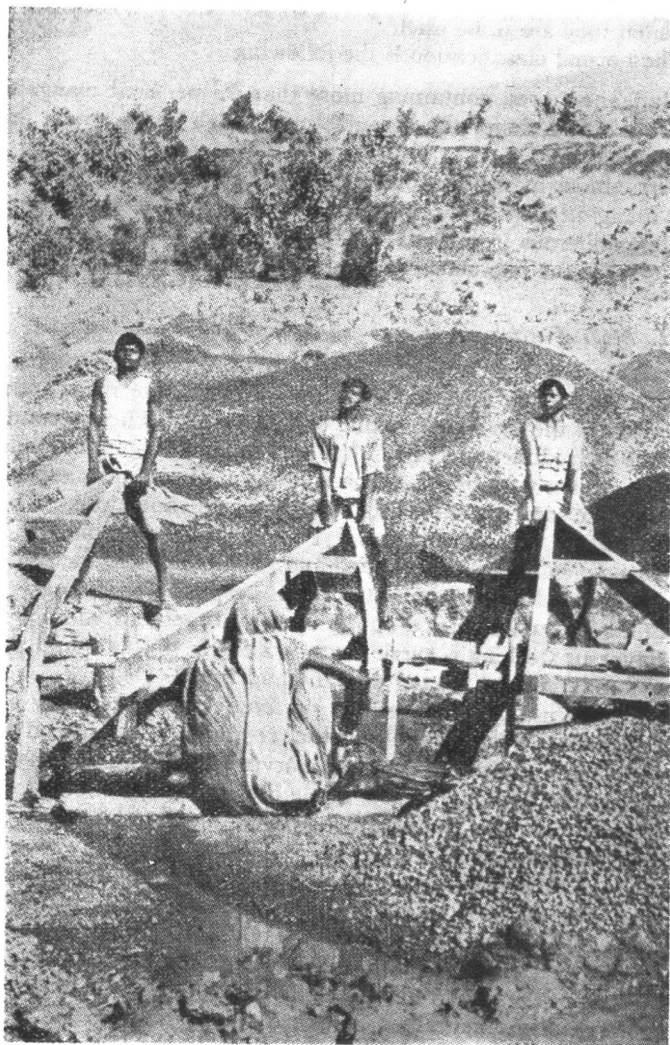


Figure 1. Hand jigging of manganese ore with Joplin jigs at the Dongri Buzurg mine in the Bhandara District of the Indian Central Provinces (Central Provinces Manganese Ore Company Ltd)