

rec

490
M3D2
x



BANCROFT
LIBRARY



THE LIBRARY
OF
THE UNIVERSITY
OF CALIFORNIA

DEPARTMENT OF THE INTERIOR
UNITED STATES GEOLOGICAL SURVEY
J. W. POWELL DIRECTOR

MANGANESE

BY

DAVID T. DAY

ABSTRACT FROM "MINERAL RESOURCES OF THE UNITED STATES,
CALENDAR YEARS 1883 AND 1884"—ALBERT WILLIAMS, JR.,
CHIEF OF DIVISION OF MINING STATISTICS



WASHINGTON
GOVERNMENT PRINTING OFFICE
1885

The Bancroft Library

No. 16726.

DEPARTMENT OF THE INTERIOR
UNITED STATES GEOLOGICAL SURVEY
J. W. POWELL DIRECTOR

MANGANESE

BY

DAVID T. DAY

ABSTRACT FROM "MINERAL RESOURCES OF THE UNITED STATES,
CALENDAR YEARS 1883 AND 1884"—ALBERT WILLIAMS, JR.,
CHIEF OF DIVISION OF MINING STATISTICS



WASHINGTON
GOVERNMENT PRINTING OFFICE
1885

Digitized by the Internet Archive
in 2007 with funding from
Microsoft Corporation



MANGANESE.

BY DAVID T. DAY.

Occurrence.—Manganese occurs as an essential constituent of several well known minerals, and it is also found in small quantity in many others, often giving them a characteristic color. Silicates frequently contain traces of manganese, and by their decomposition manganese passes into the soil and is taken up to a slight extent by plants. Further it may be stated as a general rule that where iron ores occur the ores of the closely allied metal manganese may also be found, sometimes in well defined masses, more frequently forming merely a small percentage of the iron ore. On the other hand all the manganese minerals are found to contain iron, though occasionally large beds of manganese ores are met with in such pure condition that iron can be found only as a trifling impurity, less in amount than that of other metals such as nickel and cobalt. The question whether a given mineral can be considered a practical ore of manganese is decided not merely by the amount of metallic manganese which it contains, but principally by the use to which it is put. It thus frequently happens that ores very poor in manganese find sale, while others containing three or four times the amount remain unmined. The two principal uses for manganese are (1) in the form of manganese dioxide as an oxidizing agent, and (2) as an addition to iron. For the first the richest ores obtainable are the only ones used. But frequently an ore containing only a small amount of manganese but comparatively rich in iron is used as a valuable source from which to obtain iron alloyed with the desired amount of manganese. It is to be borne in mind that in this last use—as an addition to iron—the richer ores would be valuable if it were not for the fact that they usually contain phosphorus in some form of combination.

Character of the ores.—Manganese is chiefly found as manganese dioxide or pyrolusite (MnO_2); it also occurs as braunite or brown oxide of manganese (Mn_2O_3); manganite (Mn_2O_3, H_2O); hausmannite (Mn_3O_4); and as psilomelane, which contains manganese dioxide together with compounds of barium or potassium and frequently iron, nickel, or cobalt. Manganese carbonate also occurs in quantity sufficient for its use as a valuable ore in Germany; and knebelite and manganiferous garnet, both silicates containing iron and manganese, have found special application in the manufacture of spiegel iron. Pyrolusite and braunite have been the important manganese ores of the United States until recently, when a hydrated variety of psilomelane called “wad” or “bog manganese” has become an article of commerce. The terms used by dealers to distinguish the various ores of manganese are frequently different from those given here, and much confusion exists. For a discussion of this

subject the reader is referred to "Mineral Resources of the United States, 1882," page 425.

Localities in the United States.—The extent of the manganese deposits in the United States is unusually great when compared with the deposits in other lands. They occur irregularly distributed through the eastern States from Maine to Georgia. Mines were formerly worked for bog manganese in several well known localities in Knox, Oxford; and Hancock counties, Maine. Bog manganese is again met with, though sparingly, in New Hampshire, Vermont, Massachusetts, Rhode Island, New York, and Pennsylvania. From Maryland to Georgia black oxide of manganese is much more common than bog manganese, although the latter is met with occasionally in Virginia and North Carolina. These deposits of black oxide are the important sources of American manganese. The most northern deposit is near Brookeville, Montgomery county, Maryland. This was formerly worked, but no manganese ore is now mined in Maryland.

Proceeding southward, the Crimora mine at Crimora station on the Shenandoah Valley railroad, Augusta county, Virginia, ranks as the most important mine in the United States. In 1867 a stock company bought the land containing this mine from Mr. Flannigan, of Charlottesville, for \$3,000; as soon as operations for mining were actually begun, the mine was valued at \$24,000. The stock company continued mining until 1869, when the total receipts showed a loss, owing to lack of experience in the managers. From May, 1869, to April, 1882, the mines were alternately either idle or worked by Mr. Samuel W. Donald in the interest of the stock company. On April 29, 1882, the mines were leased for five years to Messrs. James B. White & Co., of Pittsburgh, Pennsylvania, who have put in new machinery and increased the yearly product about fourfold. During the early years the ore was shipped to England and Belgium; lately it has been used in making spiegel iron in this country and for making bromine on the Ohio river. An analysis of the Crimora ore, made by Prof. Andrew S. McCreath, is given below. The analysis was apparently made from a particularly good specimen and cannot be said to represent the average value of the ore. It serves however to indicate the nature of the impurities met with in manganese ores.

Analysis of pyrolusite from the Crimora mine, Virginia.

	Per cent.
Manganese dioxide	81.70
Manganese oxide	7.28
Ferric oxide55
Cobalt oxide35
Nickel oxide09
Zinc oxide62
Alumina90
Baryta83
Lime88
Magnesia63
Phosphoric acid17
Alkalies47
Silica	2.13
Water	3.40
	100.00

Manganese is found at as many as thirteen other points in Wythe, Giles, Bland, Campbell, Louisa, Nelson, and other counties of Virginia. The mines in Pittsylvania and Nelson counties are especially large. At Goshen Bridge, Rockbridge county, mines have been opened from which 20 tons per day can be furnished.

In North Carolina manganese ores (pyrolusite and wad) are met with in Cherokee, Catawba, and Cabarrus counties, but not in large quantity and of a hard quality. As a rule these hard ores are coincident with poor ores, because pyrolusite is softer than the less valuable manganite and braunite. In South Carolina deposits have been found at Hard Labor creek, and a project is on foot to obtain manganese from the Dorris mine.

The chief rivals of the Virginia ores are those of the "Etowah region," Bartow county, Georgia. A Virginian named Ruckman discovered manganese at Cass station, Bartow county, and recognized a similarity between these ores and those of Virginia. In 1867 the property was bought for mining purposes by Mr. M. G. Dobbins, who has furnished the following information: In 1870 the mines were rented to a company of New York capitalists who extracted about 5,000 tons of ore from less than one-half acre of land, without going deeper than 40 feet. The property has now gone into the hands of the Bartow Manganese and Manufacturing Company, with \$30,000 paid stock. The company consists of M. G. Dobbins and others. Nearly the whole year has been spent in placing machinery in position and in other preparations for work. The indications are that the ore will find sale in Pittsburgh. A small quantity has been shipped to England. The following analyses give a fair idea of the average character of the ore. No. 1 is a sample analyzed in New York; No. 2 is taken from a lot of ore shipped to England.

Analyses of pyrolusite from the Etowah region, Georgia.

	No. 1.	No. 2.
	<i>Per cent.</i>	<i>Per cent.</i>
Manganese oxide.....	80.00	80.58
Iron peroxide.....	.54	15.72
Graphite.....	1.34
Silica.....	.60	1.32
Alumina.....	.13
Lime.....	.00
Magnesia.....	.15
Sulphur.....	.027
Phosphoric acid.....	.33
Water and carbonic acid.....	17.00	1.15
	99.677	100.11
Manganese available for chlorine.....	65.35

At Woodstock station, Calhoun county, Alabama, about 2,000 tons of manganiferous ore, containing 36 per cent. metallic iron and 23 per cent. manganese, were mined for the Woodstock Iron Company, of

Anniston, Alabama, for making spiegel iron. The production has ceased; no ore was mined in 1883 or 1884. The deposits at Candutchkee, Clay county, have never been mined. In Dixon county, Tennessee, there are more extensive deposits, but not rich enough to be used for the manganese alone.

Recently an effort has been made to obtain manganese from the deposits known to exist in Arkansas. The following history of these deposits is due to Mr. A. M. Evans, general superintendent of the White River Mining Company: The discovery of manganese ore in Arkansas was accidental. About thirty years ago a Colonel Martin, of Tennessee, bought lands in Independence county, and finding pieces of manganese ore, had them analyzed, and called the attention of the iron masters in England to the discovery. The civil war put a stop to further operations. The deposits lay untouched until three years ago, when Mr. E. H. Woodward began working them, and now several companies are engaged in the enterprise. The ore, which is black oxide of manganese, occurs in "pockets" in an elliptical belt of land, the major axis of which extends for 15 miles through Independence and IZard counties, beginning 3 miles from Batesville. Its minor axis is from 6 to 8 miles long. The ore is found resting upon Silurian limestone. Much of it is on the surface, and the cost of mining is said to be very small. The following are analyses, the first of a picked sample, the other three samples of carloads:

Analyses of manganese ore from Arkansas.

	No. 1.	No. 2.	No. 3.	No. 4.
	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>
Metallic manganese	62.00	49.06	52.26	55.02
Metallic iron.....	1.05	3.04	3.52	2.05
Silica.....	1.00	4.00	2.11	2.00
Phosphorus.....	.01	.12	.098	.15

Up to the present little has been done in sending the ore to market, but after an era of prospecting, several companies have been organized and mining operations have actually begun. It is probable that not more than 5,000 tons have ever been mined from these deposits. The Ferromanganese Company, of which Mr. E. H. Woodward is president, has mines about 12 miles from Batesville; it employs some twenty men, with eight or ten teams, and has shipped about 50 tons of ore. The Arkansas Manganese Mining Company, composed principally of Messrs. W. C. Whitthorne, John C. Brown, and Jerome Hill, all of Tennessee, has made some shipments of ore to Saint Louis, and is preparing for extensive operations. Mr. A. M. Evans represents a corporation known as the White River Mining Company. This company has shipped about 200 tons of ore. The White River Mining and Transportation Company controls a very large body of manganese lands, and has commenced operations. Besides the companies named, the firm of Hunton & Gibb, of Batesville, is making preparations for active work. The industry is

in the experimental stage, and many questions remain for decision by practical tests before the true importance of the new field can be determined.

There are many deposits in Virginia which once gave promise of great value but, for one or another slight objection, are not mined. Aside from the usual considerations of the percentage of manganese, amount of ore, cost of getting it out of the ground, freight to a manufacturing center, etc., is the one of whether the possible impurities will prevent its use in the manufacture of steel. For the other uses of manganese the supply from the eastern States fully equals the demand. But the attempt to use some of these eastern ores in steel making has not been markedly successful so far, because of the phosphorus which the ores contain. A small amount of this substance in steel renders it "cold short," that is, brittle when cold, and more than counteracts the beneficial effect of the manganese. Heretofore Spanish iron ore, containing small amounts of manganese and remarkably free from phosphorus, has been used for steel. The analyses given of the Arkansas ore indicate that it may not contain too much phosphorus to act as a valuable substitute for the imported ore. If this proves to be true it is probable that Arkansas will exert a powerful influence on the whole industry, whether the ore can be brought to market as cheaply as the Virginia ore or not. It is evident from the amount of capital invested that the necessary tests will soon be made.

Manganese minerals are again met with on the Pacific slope. The following information has been furnished by Mr. C. G. Yale: Manganese is found in heavy deposits in California and Nevada and occurs in greater or less quantity in the Rocky Mountain region. The only deposit that has been worked to any extent is on Red Rock island in the bay of San Francisco, concerning which nothing further is to be said than was given in "Mineral Resources of the United States, 1882," no ore having since been mined from this or any other manganese deposit on the Pacific coast. The following comprise the other localities in California where the mineral has been observed: Near Angel's Camp and at Railroad Flat, Calaveras county; abundantly at Corral Hollow, Contra Costa county; near Saucelito and Tomales, Marin county; Sweetland, Nevada county; Mount Saint Helena, Napa county; at Argentine and Mumford Hill, Plumas county; near Colton, San Bernardino county; Bernal Heights, near the city of San Francisco; at several places in Santa Clara and Sonoma counties; and near the town of Columbia, Tuolumne county, where pieces of ore weighing 100 pounds or more have been picked up on the surface of the ground.

Foreign sources.—The manganese ore occurring in Nova Scotia has an important bearing on American industries on account of its exceptional freedom from iron, which makes it valuable for neutralizing the green tint imparted to glass by iron. According to an article by Mr. Edwin Gilpin, read before the Royal Society at the Ottawa meeting, this pure pyrolusite is found in Hants, Colchester, Pictou, and Cape Breton coun-

ties, in quantities sufficient for profitable mining. Some of these ores are said to contain 95 per cent. manganese dioxide and mere traces of iron. Small amounts are regularly imported by glass manufacturers at prices quite out of proportion to native ores.

In Germany, Sweden, and Russia local deposits are used by iron manufacturers, but when particularly pure ores are desired all these countries import from the rich deposits in Spain and Portugal. Cartagena, Huelva, Marbella, and Bilbao are the principal shipping ports, and England particularly obtains large amounts of ore from these points.

Production.—The statistics from many of the small mines of Virginia and North Carolina are practically inaccessible. It is therefore impossible to determine exactly the total quantity mined, but the amount for 1883 and 1884 can be stated as 18,000 long tons to a very close approximation, of which 8,000 tons were mined in 1883 and 10,000 in 1884. Of this amount Virginia furnished fully three-fourths, Arkansas a fifth, and the balance was contributed by Georgia and North Carolina. In former years Virginia furnished nearly all the manganese mined in this country. The following table gives the actual number of tons obtained from the Crimora mine, which furnishes by far the largest part of the Virginia supply :

Production of the Crimora mine, Virginia.

	Quantity.
	<i>Long tons.</i>
Prior to 1869.....	5,684
May, 1869, to February, 1876.....	280
February, 1876, to December, 1878.....	2,326
December, 1878, to December, 1879.....	1,602
December, 1879, to December, 1880.....	2,353
December, 1880, to December, 1881.....	2,327
December, 1881, to April, 1882.....	165
April, 1882, to December, 1883.....	4,841
December, 1883, to November 19, 1884.....	8,473
Total.....	28,051

The production of manganese ores in foreign countries has always been much greater than in the United States. In 1874, the production in Germany was given as 18,725 long tons; in Austria, 4,937 long tons; the Huelva district, in Spain, 48,207 long tons; in England, 6,552 long tons. In the latter country the production has diminished markedly; thus in 1882, 1,548 long tons, with a value of £3,907, were mined in Great Britain. In 1881, Portugal produced 9,906 long tons. The production in Italy for three years ending 1879, as furnished by American Consul-General Richmond, was :

Production of manganese ore in Portugal.

Years.	Long tons.	Value.
1877.....	6,812	\$40,597
1878.....	6,655	48,256
1879.....	5,705	35,065

Value.—During the year 1883 the price of black oxide of manganese in the United States ranged from \$11 to \$16 per ton, according to the percentage of manganese. The total value of the year's production was about \$120,000. The price declined in 1884, and manganese ore containing 75 per cent. manganese dioxide is now worth \$12 per ton at the mines, or 27 cents per metallic unit delivered at Pittsburgh or Johnstown. The total product of 1884 may also be valued at \$120,000. The cost of mining varies from \$5 to \$10 per ton in the eastern States. It is claimed that the Arkansas deposits which occur near the surface can be mined for \$1.25 per ton.

Imports.—Manganese ores are imported from Nova Scotia, as already mentioned, for use in the manufacture of glass. Some manganese also finds its way into this country in the form of iron ore containing about 20 per cent. manganese. It is brought from Carthagena and Marbella as ballast by vessels seeking cargo. The importations from 1869 to 1884, inclusive, are given in the following table:

Oxide and ore of manganese imported and entered for consumption in the United States, 1869 to 1884 inclusive,

Fiscal years ending June 30—	Quantity.	Value.
	<i>Pounds.</i>	
1869.....		\$11,864
1870.....		10,685
1871.....		12,321
1872.....		9,768
1873.....	1,226,157	12,466
1874.....	1,507,448	16,992
1875.....	1,119,893	16,300
1876.....	386,408	5,805
1877.....	1,326,136	15,747
1878.....	3,068,634	31,571
1879.....	554,372	12,094
1880.....	1,864,968	19,825
1881.....	1,283,457	20,432
1882.....	2,225,936	38,879
1883.....	1,425,274	28,952
1884.....	1,151,531	24,326

The imports in 1884 were classified as—

	Pounds.	Value.
Ore.....	1,000,095	\$19,989
Oxide.....	151,436	4,337
Total.....	1,151,531	24,326

Exports.—England has been a consumer of American manganese ore since its mining was first commenced. The ore is used in the manufacture of chlorine. The following is the value of the exported ore from 1869, which was practically the beginning of manganese mining in this country, to the present time:

Value of manganese ore exported from the United States, 1869 to 1884 inclusive.

Fiscal years ending June 30—	Value.	Fiscal years ending June 30—	Value.
1869.....	\$43,382	1875.....	\$2,261
1870.....	56,125	1876.....	1,030
1871.....	7,760	1878.....	3,569
1873.....	41,075	1883.....	6,165
1874.....	9,939	1884.....	1,802

Utilization.—The uses for manganese ores may be grouped under two heads: (1) those in which the oxygen combined with the manganese is used, and (2) those in which manganese itself is sought. For the first group only ores which are rich in manganese dioxide are used. When heated strongly or treated with powerful acids, this substance serves as a convenient source of pure oxygen. More frequently it is used as an “oxidizing agent,” that is, to give up oxygen to some other substance, rather than to furnish oxygen in the elementary form. Thus chlorine and bromine are prepared by this oxidizing action of manganese dioxide in the following way: It is extremely difficult to separate these elements from others with which they are ordinarily in combination; it is comparatively easy, however, to obtain the compound of chlorine known as hydrochloric or “muriatic” acid from ordinary salt by treatment with sulphuric acid. When this substance is warmed with manganese dioxide, oxygen from the latter combines with the hydrogen of the acid, leaving part of the chlorine free. Large amounts of manganese are used annually for this purpose, in England particularly. The manganese is converted by this process into manganese chloride, which serves as a convenient substance from which all the other salts of manganese can be made. A brown and a black pigment can be obtained indirectly from it by heating it in contact with air. A green pigment is made by heating manganese carbonate, obtained from the chloride, in closed vessels. The beautiful violet color which manganese gives when fused with phosphoric acid salts led to the manufacture of a violet pigment called manganese or Nurnberg violet, from these same chlorine residues. “Rosenstiehl’s green,” obtained from this source, is used somewhat for printing on paper. It has been found that certain of the salts corresponding to manganese chloride hasten the oxidation of linseed oil. Thus when linseed oil is boiled with manganese dioxide, the addition of manganese borate aids in the desired oxidation. The most important use of these waste residues from the chlorine manufacture is in preparing potassium and sodium permanganates. Formerly native manganese dioxide was fused with potassium chlorate and potassium hydroxide, but the finely pulverized oxide obtained from manganese chloride is easier to convert into permanganates. This permanganate of potassium is used not only for purely chemical purposes, such as the preparation of specimens and the oxidation of various substances in analytic chemistry, but also for technical purposes in determining the value of

iron ores, in bleaching leather and textile fabrics, for the preparation of oxygen according to Motay's process, and for sanitary purposes as a powerful disinfectant. But these uses do not consume all the manganese chloride which continually results from the manufacture of chlorine. It is customary, therefore, to reconvert manganese chloride by Weldon's process into a substance capable of oxidizing hydrochloric acid. By this means the same manganese is used repeatedly. Were it not for this, the demand for manganese ores would probably be more than doubled. Bromine is made in a similar way, and about one-fifth of the manganese ore mined in the United States is used at Pomeroy and other places on the Ohio river, in the West Virginia and Ohio salt district, for making bromine. Thus far no attempt has been made to regenerate the manganese so used in America. Until recently nearly all the native ore was used for one or another oxidizing purpose in this country, or shipped, for similar use, to England. Meanwhile large amounts of manganese were imported to furnish manganese to the Bessemer steel works. There has been prejudice against American ores on account of the phosphorus they contain. Within the last few years, however, the manufacture of steel has consumed the greater part of the native ore. In just what way manganese proves advantageous in making steel has been an interesting subject of discussion, but one in which it is extremely difficult to obtain facts; partly because steel manufacturers are not ready to reveal the secrets of their industry, and also because there are great differences in the views held by authorities. The following will serve to indicate at least the main features of this subject; further information will be found in the treatises on metallurgy by Percy, and in "Steel, its History, Manufacture, and Uses," by J. S. Jeans, from which much of what follows has been taken:

It was known in quite early times that certain iron ores furnished pig iron from which particularly good steel could be made; it was shown, later, that this ore contained oxides of manganese, but it was barely suspected that it was the manganese which gave the improved character to steel, until, in 1839, Josiah M. Heath found as the result of many experiments that when a small amount of manganese is introduced into steel of poor quality in the melting pot, the steel is uniformly improved and can be welded to iron with facility. The enormous change which this discovery effected in the English manufacture of steel is sufficient testimony to the correctness of Heath's claim that the quality of poor steel is improved by the addition of small amounts of metallic manganese. It became possible by its aid to dispense with Russian and Swedish iron and use the inferior English iron. The use of manganese became general, and it has been calculated that a saving in the cost of steel amounting in all to \$10,000,000 had been effected by 1855. When the Bessemer process of making steel was introduced it was found that the finished metal contained as much phosphorus as the pig iron from which it had been made. It was "cold

short," and the effort was made to add some substance which would overcome this objection either by removing the phosphorus or by counteracting its effects. For several years Bessemer was unable to do this, and was obliged to use pure Swedish pig iron in his process. In 1856 Robert Mushet added to the iron made in a Bessemer converter a small quantity of cast iron containing manganese, and found that good steel could thus be made from very impure cast iron. He recommends adding from 1 to 5 per cent. manganese to the metal, according to the degree of hardness desired in the resulting steel. This process immediately became a general one, and now a certain amount of pig iron containing manganese is always introduced just before Bessemer steel is finished. In the manufacture of open-hearth steel also, manganese is used, so that at present manganese in the form of an alloy with iron is always added to Bessemer and open-hearth steels before these are finished. But as to the exact function of manganese many opinions have been expressed. Both Heath and Mushet proposed to add nearly 3 per cent. of manganese, but usually steel is found to contain less than 1 per cent.; it is therefore evident that the larger part finds its way out of the iron again, and if it produces any beneficial effect this must be sought in some reaction which it aids during its removal, by which the steel loses some impurity. It has been shown that sulphur can be removed to a considerable extent when manganese is introduced into a Bessemer converter. The majority of metallurgists believe, however, that the great benefit is due to the removal of oxygen from the finished steel. It is impossible to distribute the air of the blast perfectly through the molten metal, and hence some oxide of iron will be formed in one portion of the steel before all the carbon has been removed from another; the manganese introduced will oxidize more readily than iron, and will reduce any oxide of iron that is formed. The oxide of manganese is either blown out of the converter in a flocculent mass or unites with the slag, and thus leaves the steel in a more homogeneous condition. The amount of phosphorus in steel is not changed by the addition of manganese, but it seems that its deleterious effect is not so apparent when a small amount of manganese is present. According to Mushet nothing is gained by adding manganese to steel which contains no impurities. The present opinion seems, therefore, to be that manganese is valuable (1) in deoxidizing steel, (2) in aiding the removal of sulphur, and (3) in counteracting the effect of phosphorus. The best form in which to introduce manganese into steel would undoubtedly be that of the pure metal; but manganese is so difficultly fusible and oxidizes so readily that it is impracticable to reduce it from its ores; pure manganese, therefore, is never used. It is much easier to reduce a mixture of the oxides of manganese and iron and thus obtain an alloy of these metals, which is usually called "spiegel iron" when the manganese is less than 15 or 20 per cent., and "ferromanganese"

when it exceeds this percentage, though in practice the terms are sometimes used indiscriminately.

Manufacture of spiegel iron is carried on largely in Germany, France, and England, and lately has become a feature of American steel works. The following account of its manufacture is taken by Jeans from an article by Forbes in the *Journal of the British Iron and Steel Institute*: The ores used for making spiegel iron vary in the different countries. In Germany it is made entirely from manganiferous spathic carbonate of iron; in Russia it is reduced from ferruginous oxides of manganese; and in Sweden it is produced by smelting a mixture of knebelite and manganiferous garnet, both of which minerals are compound silicates of iron and manganese. In one point, however, the methods all agree; namely, that in all these ores the oxides of manganese and iron, if not in actual combination as compound silicates or carbonates, are at any rate in a very intimate admixture with one another, and therein lies one of the most important features connected with this manufacture. Until the year 1872, wherever true ores of manganese had been added to the usual charge of a blast furnace with the expectation of obtaining spiegel iron rich in manganese, it was found as a general rule that only a small fraction of the manganese combined with the iron, the major part being carried off in the slag. For this reason, when it was desired to produce a cast iron containing much manganese it was deemed requisite that this metal should be added to the charge in the shape of some strongly ferruginous compound, thereby facilitating the process of reduction, since a mixture of the two oxides (of manganese and iron) is much more easily reduced to the metallic state, and so enabled to unite with the iron, from the rest of the charge, than oxide of manganese alone, which, unless the heat is very intense and the reducing action of the furnace nearly perfect, is extremely apt to go into the slag in the state of silicate, from which it can subsequently be recovered only with great difficulty. The oxides of manganese are very much less easily reduced and require more time as well as a much higher temperature than the oxides of iron, and hence it follows that in making spiegel iron particular attention should be paid to the following points:

1. The mineral used as a source of manganese should be in itself highly charged with iron, so as to facilitate and insure the reduction of as large an amount of the manganese contained in it as possible.

2. The charge of the furnace should be highly basic, or, in other words, an excess of limestone, or preferably burnt lime, should be used.

3. The working of the furnace should be much slower than is usual in iron smelting, in order to allow more time for the reduction of the oxides of manganese.

4. The temperature of the blast furnace should be as high as possible, using as hot a blast as can be obtained, and as coke admits of the use of a sharper blast, and affords greater heat, it is to be preferred to charcoal in this manufacture.

Russian spiegel iron is smelted with charcoal and is known for its good quality. In order to increase the amount of manganese in gray pig iron which already contains 1.2 per cent. of manganese, so as to obtain spiegel iron, 12 to 15 per cent. of pure native oxide of manganese (pyrolusite) has been added, producing a low spiegel iron containing from 5 to 6 per cent. metallic manganese.

In Sweden spiegel iron is made by smelting a mixture of knebelite and mangiferous garnet containing an average of 42 per cent. iron and 13 per cent. manganese with equal parts charcoal and coke, the ore being fluxed with 30 per cent. limestone. The ore frequently contains visible particles of galena, pyrites, and zincblende, but it is stated that no sulphur is found in the spiegel iron, although the slag, which has a peculiar yellow-green color when the furnace is working well, is said to contain 4 per cent. sulphur, and up to as much as 16 per cent. oxide of manganese. The ordinary spiegel iron made at Schisshyttan, Dalecarlia, is superior to the average German product, and contains an average of 13 per cent. manganese, with about 4 per cent. carbon, or 5 per cent. carbon and silicon. Occasionally it has been as high as 17 per cent. Alexander Keiller, the manager of these works, informed Forbes that he was, in 1872, producing spiegel iron which averaged 15 per cent. manganese, with only 2.5 per cent. carbon, but that this metal was altogether different in appearance and could not be made to assume the crystallized, bladed, reflecting fracture peculiar to spiegel (specular) iron, and from which its name is derived. The characteristics of good spiegel iron are thus described: (1) A highly crystalline structure with large and smooth cleavage planes; (2) a tendency to iridescent tarnish, and (3) a chemical analysis showing 10 to 12 per cent. metallic manganese, which is quite sufficient for ordinary purposes, about 4 per cent. combined carbon, less than 1 per cent. silicon, not more than 1 per cent. phosphorus or copper, and only traces of sulphur and other elements. Uncombined carbon in the form of graphite should not be present.

The following analyses of spiegel iron represent the character of the best kinds imported into New York in 1868, 1869, and 1873:

Analyses of imported spiegel.

	1868.		1869.		1873.	
	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>
Iron	85.57	84.455	84.122	84.869
Manganese	9.142	10.625	10.568	10.223	11.130	10.22
Copper032	.034	.036	.031	.279	.20
Nickel and cobalt005	.005	.004	.002
Silicon068	.368	.268	.384
Carbon	5.048	4.304	4.907	4.461
Sulphur002001
Phosphorus037	.044	.104	.027	.039	.06
Aluminum082	.045	.032	.012
Calcium015	.016	.021
	99.999	99.898	100.062	100.010

Subjoined are some further analyses of spiegel iron given by Hackney in the "Proceedings of the Civil Engineers, April, 1875:"

Analyses of other foreign spiegels.

	No. 1.	No. 2.	No. 3.	No. 4.	No. 5.	No. 6.	No. 7.	No. 8.	No. 9.
	<i>Per ct.</i>	<i>Per ct.</i>	<i>Per ct.</i>	<i>Per ct.</i>	<i>Per ct.</i>	<i>Per ct.</i>	<i>Per ct.</i>	<i>Per ct.</i>	<i>Per ct.</i>
Iron.....	89.527	86.000	83.777	83.08	75.100	70.34	65.81
Manganese.....	5.619	8.500	11.782	12.000	12.30	18.870	20.350	23.48	28.70
Carbon.....	4.410	4.00	4.538	4.500	3.90	4.500	3.200	5.31	5.28
Silicon.....	.161	1.10	.041	.130	.54	1.050	.254	.09	.01
Phosphorus.....	.047	.288	.084	.075	.08	.102	.029	.37	.38
Sulphur.....	.017	.03	.010	.010	Trace.	Trace.	.010	Trace.	Trace.
Copper.....04	.015	.002063	Trace.	Trace.	Trace.
Arsenic.....	.288
	100.069	99.958	100.247	99.90	99.543	99.59	100.18

1. Swedish spiegel. Authority: G. J. Snelus, *Journal Iron and Steel Institute*, 1874, page 76.
2. Rhenish spiegel iron, from Spaeter and Wirth, Coblenz. Analyst: A. Willis.
3. Landore spiegel iron. Analyst: E. Riley.
4. Landore spiegel iron. Analyst: A. Willis.
5. West Cumberland spiegel iron. Authority: G. J. Snelus, *loc. cit.*, page 73. Analyst: G. J. Snelus.
6. Dowlais spiegel iron. Authority: G. J. Snelus, *loc. cit.* Analyst: W. Jenkins.
7. Spiegel iron made at Schisshyttan iron works, Sweden. Authority: D. Forbes, *Journal Iron and Steel Institute*, 1874, page 467.
8. No. 8 and 9. Spiegel iron from Illyria, Austria, made by the Krainischen Eisen-Industrie Gesellschaft. Authority: D. Forbes, *loc. cit.* Analysts: Of No. 8, M. Lill; of No. 9, H. Sturm.

The percentage of spiegel iron which is introduced into the Bessemer converter or into open-hearth steel varies between 1 and 5 per cent. according to the amount of manganese in the spiegel iron, and also according to the condition of the iron. If the elimination of carbon has been quite complete more spiegel iron will be necessary to combat oxidation and leave the desired quantity of manganese in the finished product. As has been said, a large part of the manganese is driven out of the iron into the slag, but usually about 0.25 per cent. (from 0.1 to 0.8 per cent.) remains in the iron. In an example by Mr. Snelus 251 pounds of spiegel iron containing 8.88 per cent. manganese was added to 72 cwts. of pig iron. If no manganese had been lost 22,288 pounds of this metal would have been found. But only 7.28 pounds were actually found, showing that 15 pounds, or about two-thirds, had been removed, leaving steel containing 0.104 per cent. manganese.

The following determinations of the quantity of manganese in various kinds of steel are given by Kessler in Dingler's *Polytechnische Journal*:

Amount of manganese in steel.

Steels.	Per cent.
Krupp's crucible cast steel (Essen).....	0.437 to 0.438
Bochum cast steel.....	0.312 to 0.317
Hasper steel.....	0.327 to 0.332
Manganese steel of Ludwig in Berlin.....	0.303
Fine piano wire.....	0.035
Hoerder steel.....	0.107 to 0.170
Cannon steel (Terre Noire).....	0.240
Common steel (Barroin).....	0.240
Rail steel (Creusot).....	0.550
Rail steel (Petit Gaudin).....	0.560
Rail steel (Terre Noire).....	0.860
Rail steel (Seraing).....	0.650

It has been found beneficial in making soft steel to add 1 per cent. of manganese; but as spiegel iron contains 4 to 5 per cent. carbon, too much of this latter substance would be introduced into the steel if spiegel iron were used to furnish the manganese. An alloy called "ferromanganese," containing a larger proportion of manganese and no more carbon, is therefore necessary.

Ferromanganese.—In general, when the amount of manganese in iron exceeds 20 per cent., it is no longer called spiegel iron, but ferromanganese; the distinction is due, however, not so much to the proportion of manganese to iron, but to the process of manufacture. Spiegel iron is made in the blast furnace, and this has been the method of preparing it since its first use in the iron industry. But no matter what proportion of manganese ore is used, it is extremely difficult to introduce more than 10 per cent. of manganese when a flux with considerable silica is used. When a greater proportion was desired it was the custom until recently to resort to one or another modification of a process originated by Bessemer, in which the desired reduction of manganese ores is effected in crucibles. This process, as first introduced on an industrial scale by Prieger, of Bonn, consists in heating a mixture of manganese dioxide, small lumps of cast iron, powder, lime, glass, and charcoal in a graphite crucible. The higher the temperature the richer is the resulting alloy in manganese, so that it is practicable at the highest temperature of a reverberatory furnace to obtain an alloy with 60 per cent. manganese. A process invented by W. Henderson, of Glasgow, and largely used at Terre Noire, dispenses with crucibles. An intimate mixture of manganese carbonate, iron oxide, and powdered charcoal is heated red hot for several hours in the reducing flame of a Siemens furnace. By this means a metallic sponge is obtained. By raising the temperature to white heat, the sponge melts, giving ferromanganese containing 20 to 30 per cent. manganese. Several patents obtained in late years contain only unimportant modifications of these processes. But since 1873 the use of coke in blast furnaces and a highly basic slag has made it possible to produce ferromanganese containing 60, and even 80, per cent. of manganese by the blast-furnace process. The use of coke aids in obtaining a temperature sufficiently high for the reduction of manganese, and the basic slag does not carry off much manganese with it. It was formerly the custom to use manganese dioxide in the blast furnace, but this is reduced to manganic oxide in the upper part of the furnace by carbon monoxide from the reduction going on below. This causes such overheating of the throat of the furnace that the gases cannot be collected. The manganese ores are therefore reduced to manganic oxide in a separate furnace.

The following analysis will show the constitution of ferromanganese: (a)

Analysis of ferromanganese.

	Per cent.
Manganese	69.64
Iron	23.45
Carbon	6.21
Silicon28
Copper14
Phosphorus06
Sulphur	Trace.
	99.78

The manufacture of spiegel iron and ferromanganese in the United States.—Up to the present time the greater part of the spiegel iron used in the Bessemer steel process in this country has been imported from Europe. The largest quantity imported in any one year was 25,000 tons. In 1870 the manufacture of spiegel iron was undertaken by the New Jersey Zinc Company, of Newark, New Jersey, which has furnaces each 20 by 7 feet, with a combined annual capacity of 5,000 long tons. The spiegel iron made by this company is said to be equal to the best that is imported, and is therefore readily sold. The following are two analyses of it:

Analyses of American spiegel iron.

	Per cent.	Per cent.
Iron	83.250	83.23
Manganese	11.586	11.67
Phosphorus196	.19
Silicon367	.99
Carbon	4.6.2	4.02
	100.031	100.10

It is said that pig iron quite rich in manganese is made at several furnaces in the United States, but not of a quality that will justify its use as spiegel iron. In 1875 the Bethlehem Iron Company and the Cambria Iron Company commenced to make spiegel iron from Spanish ores. In the same year the Woodstock Iron Company, of Anniston, Calhoun county, Alabama, undertook to make spiegel iron from the Alabama ores. The manganese ores which they used contained somewhat over 20 per cent. metallic manganese; these were smelted with iron ore containing 58.25 per cent. iron, 8.56 per cent. manganese, and 1.42 per cent. phosphorus. Samples of the product, taken for analysis on the following dates, were found to have the following composition:

Analyses of spiegel iron from Woodstock, Alabama.

	December 10, 1875.	January 6, 1876.	February 1, 1876.	February 3, 1876.
	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>
Iron.....	85.11	85.98	80.37	73.86
Manganese.....	10.18	8.14	14.33	20.69
Carbon.....	3.66	4.83	4.94	4.32
Silicon.....	.95	.88	.38	.93
Phosphorus.....	.10	.17	.18	.17
Total.....	100.00	100.00	100.20	99.97

The enterprise has not proved remunerative at this place; about 2,000 tons of manganese ore were used in all. No spiegel iron was made here in 1883 or 1884. A successful attempt to make spiegel iron was made at the Bessemer works, in Pueblo, Colorado, in 1883. At present the chief producers of spiegel iron are: The Edgar Thomson (Carnegie Brothers) Steel Works, the Bethlehem Iron Company, the Cambria Iron Company, the Brier Hill Iron and Coal Company, the Lehigh Zinc and Iron Company, and the Passaic Zinc Company.


The manufacture of ferromanganese was attempted some years ago at the Diamond furnace, in Georgia. It did not prove successful. The only other attempt to utilize native manganese ores in the production of ferromanganese was made in August, 1884, at the Edgar Thomson Steel Works, at Bessemer, Pennsylvania. At this time, blast furnace A began making ferromanganese instead of spiegel iron. The product is said to contain from 80 to 90 per cent. of metallic manganese, and 92 per cent. has been reached. The daily product is from 45 to 50 tons. Besides supplying their own steel plant, Carnegie Brothers are thus enabled to supply the open-hearth furnaces of neighboring steel works, and it is probable that this new departure will materially lessen, if not suppress, the importation of ferromanganese.

Hadfield's manganese steel.—In ordinary steel the proportion of manganese seldom exceeds 0.5 per cent., and 1.5 per cent. is the maximum which has been added in the ordinary processes of steel manufacture. Recently, however, Mr. Robert Hadfield, of the Hadfield Steel Foundry Company, Sheffield, England, has claimed that steel containing from 7 to 30 per cent. manganese is harder, stronger, denser, and tougher than ordinary steel, even when the latter has been forged and rolled, and in addition he believes this steel to possess properties which will make it exceedingly valuable for many purposes for which ordinary steel is not now used. In order to make this steel, melted ferromanganese (Mr. Hadfield recommends that containing 80 per cent. manganese, and as low as possible in carbon, silicon, and other foreign bodies) is added to iron which has been nearly or quite freed from carbon, or to molten steel. The manganese is thoroughly incorporated by stirring, and the steel is poured into ingots or other suitable molds. The percentage of ferromanganese to be used must be varied according to the use

to which it is to be put. No absolutely exact proportions can be given. To produce a steel suitable for armor plates, sufficient ferromanganese to give 10 per cent. of manganese in the steel should be added; for wheels, axles, or railroad plant, say 11 per cent.; edge tools, 12 per cent. It is claimed that the metal when melted is very thin and mobile, casts without misrunning, does not settle as much as ordinary castings, and does not draw, particularly at the junction of the thin and thick parts. The steel is said to be tough without forging, rolling, or hammering. An ingot with 9 per cent. manganese which had not been forged was bent $1\frac{1}{2}$ inches in $2\frac{1}{2}$ feet before breaking. Hammered samples from this ingot gave a tensile strength of 42 tons (94,080 pounds) and 20.85 per cent. elongation. Besides unusual toughness the steel is very hard; specimens containing 9 to 10 per cent. manganese can be drilled, etc., but not so readily as ordinary steel, while it is practically impossible to drill or turn those containing higher percentages. An ax made from 19 per cent. steel cut through $\frac{3}{8}$ -inch iron. If future investigation of such manganese steel shows that it can be made regularly with the properties claimed for it, there is little doubt that it will be a valuable addition to the varieties of hard steel now in use.

Other alloys of manganese.—Alloys of copper, such as brass and bronze, may be rendered denser and harder by the addition of manganese; if more than 8 per cent. of manganese is added its presence is indicated by the gray color of the alloy, which then becomes brittle. A beneficial effect is also observed when manganese is added to bronze or brass which is impure from the presence of copper oxide; manganese oxide is formed, which rises to the surface and may be removed. These alloys of manganese have received considerable attention in England in late years and have come into quite extensive use in the place of gun metal for main bearings, top and end brasses, crank pins, etc., on large steamers, and it is probable that the extension of the manganese interests will be in this direction during the next few years.



 Syracuse, N.Y.
Stockton, Calif.

