MANGANESE AND MANGANESE ALLOYS

1. Introduction

Manganese [7439-96-5], atomic number 25, atomic weight 54.94, belongs to Group 7 (VII) in the Periodic Table. Its isotopes are ^{51}Mn, ^{52}Mn, ^{54}Mn, ^{55}Mn, and ^{56}Mn, but ^{55}Mn is the only stable one. Manganese, a gray metal resembling iron, is hard and brittle and of little use alone. Its principal use in the metallic form is as an alloying element and cleansing agent for steel, cast iron, and nonferrous metals (see METAL SUYRFACE TREATMENTS, CASE HARDENING). Manganese is essential to the steel (qv) industry where it is used mostly as a ferroalloy. After iron (qv), aluminum (see ALUMINUM AND ALUMINUM ALLOYS), and copper (qv), manganese ranks along with zinc as the next most used metal (see also MANGANESE COMPOUNDS).

The name manganese is derived from the Latin *magnes*, meaning magnet. It was once thought that manganese ores were iron ores. Manganese, recognized as an element by the Swedish chemist Scheele in 1771, was isolated in 1774 by reduction of manganese dioxide with carbon. In the 1840s, manganese was used for the first time in crucible steels. The addition of manganese as spiegeleisen (20% manganese–iron alloy) made the Bessemer process a success (see STEEL). Ferromanganese as an additive to counteract the effects of sulfur and phosphorus in steel was patented in the late 1860s. The use of manganese as an alloying agent to produce a tough wear-resistant steel was discovered in 1882.

2. Properties

Tables 1 and 2, respectively, list the properties of manganese and its allotropic forms. The α- and β-forms are brittle. The ductile γ-form is unstable and quickly reverses to the α-form unless it is kept at low temperature. This form when quenched shows tensile strength 500 MPa (72,500 psi), yield strength 250 MPa (34,800 psi), elongation 40%, hardness 35 Rockwell C (see HARDNESS). The γ-phase may be stabilized using small amounts of copper and nickel. Additional compilations of properties and phase diagrams are given in References (1) and (2).

3. Minerals and Ores

Manganese, which occurs in many minerals widely distributed in the earth's crust, constitutes about 0.1% of the earth's crust and is the twelfth most abundant element (3–6). The principal sources of commercial grades of manganese ore for the world are found in Australia, Brazil, China, Gabon, India, the Republic of South Africa, Ukraine. The chief minerals of manganese are pyrolusite, romanechite, manganite, and hausmannite (Table 3). There is also wad, which is not a definite mineral but is a term used to describe an earthy manganese-bearing amorphous material of high moisture content.

Pyrolusite is a black, opaque mineral with a metallic luster and is frequently soft enough to soil the fingers. Most varieties contain several percent water. Pyrolusite is usually a secondary mineral formed by the oxidation of other manganese minerals. Romanechite, a newer name for what was once known as psilomelane [12322-95-1] (now a group name) (7), is an oxide of variable composition, usually containing several percent water. It is a hard, black amorphous material with a dull luster and commonly found in the massive form. When free of other oxide minerals, romanechite can be identified readily by its superior hardness and lack of crystallinity.

Manganite is an opaque mineral of medium hardness, ranging in color from steel gray to iron black, and having a dark, reddish brown streak. It also has a submetallic luster. Hausmannite is a black to brownish black opaque mineral, usually crystalline having a submetallic luster and a specific gravity of 4.73–4.86. It has a hardness of 5.0–5.5 (Mohs' scale) and a brownish black streak. A fresh fracture usually shows numerous bright shiny crystal faces. Rhodochrosite is the most common carbonate mineral of manganese and usually occurs with rhodonite. It is light rose in color, although other shades are not uncommon. It is a translucent mineral with a vitreous luster and a colorless streak. Cryptomelane is found in many manganese ores around the world, and may constitute as much as 50% of some ores. The K_2O content of manganese ores is usually associated with cryptomelane.

None of the natural sulfides of manganese are of any commercial importance. Some silicates have been mined. Rhodonite and braunite are of interest because these are frequently associated with the oxide and carbonate minerals. The chemical composition of some common manganese minerals are given in Table 3.

3.1. Manganese Ores. In general, only ores containing at least 35% manganese are classified as manganese ores. Ores having 10–35% Mn are known as ferruginous manganese ores, and ores containing 5–10% manganese are known as manganiferrous ores. Ores containing less than 5% manganese with the balance mostly iron are classified as iron ores.

Table 4 gives typical analyses of some of the commercial manganese ores available in the world market. Table 5 gives a breakdown of the world's total estimated manganese ore reserves that account for 98–99% of the known world reserves of economic significance. No manganese ores of commercial value are to be found in the United States.

Table 6 shows the production of manganese ores in the world by countries. In 1989, the world production represented about 89% of the rated production capacity, which in 1992 was reported to be 10.4 million metric tons of contained manganese. This percentage steadily decreased reaching 64% in 1992. Rated capacity is defined as the maximum quantity of product that can be produced in a period of time on a normally sustainable, long-term operating rate (9). This large decrease in manganese ore production is a reflection of the worldwide decline since 1979 in the volume of steel production coupled with improvements in steelmaking processes which use ferromanganese alloy additions more efficiently.

3.2. Deep-Sea Manganese Nodules. A potentially important future source of manganese is the deep-sea nodules found over wide areas of ocean bottom (see OCEAN RAW MATERIALS). At depths of 4–6 km, billions of metric tons of nodules are scattered over the ocean floor in concentrations of up to 100,000 t/km^2. Metal content varies widely. Higher grade nodules are found in the North Pacific Ocean (see Table 7). Although the prime interests in deep-sea nodules are the nickel, copper, and cobalt values, the large quantities of manganese could also be of future importance (11,12).

Several multinational private consortia were formed in the 1970s to explore and develop the mining and extraction processes for deep-sea nodules. Each of these consortia developed mining equipment deemed economically and technically feasible. However, by the mid-1980s, after collectively spending around $700 million, none of the consortia continued its development program. None has a near-term development plan. Private sector groups are maintaining leases for the future. There are active government funded mining programs in Japan, India, and Korea (12).

3.3. Impurities. Impurities usually found in manganese ore may be classified into metal oxides, eg, iron, zinc, and copper; gangue; volatile matter such as water, carbon dioxide, and organic matter; and other nonmetallics.

A good metallurgical grade of manganese ore for smelting ferromanganese meets the specifications given in Table 8. In practice, ores are blended to provide the most economical mixture consistent with the specifications for ferromanganese. Thus individual ores can exceed these specifications.

Gangue. Oxides such as silica, alumina, lime, and magnesia are considered gangue which form slag in the smelting process. Although slag removes impurities, excessive gangue results in larger slag volumes that require more energy for the smelting process. Furthermore, because the percentage of manganese in the slag is independent of slag volume, larger slag volumes result in greater loss of manganese to the slag.

Volatiles. Manganese may contain some chemically bonded water or carbon dioxide both of which can be removed by calcining or sintering. The Mexican Molango ore (Table 4) is an example of a low grade ore that is upgraded by calcination in a rotary kiln.

Nonmetallics. During smelting, arsenic and phosphorus pass into the ferromanganese alloy. Because these elements are undesirable in steel, their content in the ore and other raw materials in the furnace charge must be kept low. Sulfur in ferromanganese is usually at very low levels because sulfur remains in the slag as manganese sulfide. Table 9 shows specifications for manganese ferroalloys.

3.4. Ore Processing. *Ore Size.* The particle size of manganese ores is an important consideration for the smelting furnace. In general, the ore size for the furnace charge is −75 mm with a limit to the amount of fines (−6 mm) allowed. Neither electric furnaces nor blast furnaces operate satisfactorily when excessive amounts of fines are in the charge.

Large amounts of fines in the ores and other raw materials promote agglomeration or caking of the charge in the furnace. This is detrimental to efficient smelting because it inhibits the downward movement of the charge and the uniform distribution of reaction gases through the burden. Furnace operators refer to this as mix bridging. In the case of the electric furnace, this can result in a hazardous situation that could lead to violent eruption of the furnace contents. Thus many of the ferromanganese-smelting operations around the world that use electric furnaces limit the amount of −6 mm ore fines in the charge to a maximum of 15%.

Ore Sintering. Most of the principal producers of ferromanganese operate sintering plants as the means of agglomeration of manganese ore fines. A mixture of manganese ore fines, fine coke, and returned sinter fines are fed to a grate (moving or stationary) where the coke is ignited and, under suction, generates enough heat to fuse together the ore particles. During the process, the MnO_2 in the manganese ore is reduced to lower oxides, eg, Mn_2O_3 or Mn_3O_4. The amount of manganese ore sinter in the electric furnace smelting charge is in the range of about 20–35% of the ore blend. Higher amounts of sinter in the ore blend for the electric furnace result in somewhat greater electrical energy consumption (13).

Since 1988, a 500,000 t/yr sinter plant has been in operation in South Africa at the Mamatwan manganese ore mine (14). The sintering process removes the 15–17% CO_2 that is contained in the Mamatwan ore. With 35% sintered Mamatwan ore replacing an equivalent amount of the unsintered ore in the furnace charge, energy consumption in the electric smelting furnace is decreased by about 16%. This lower power consumption and accompanying increase in productivity is the result of the removal of CO_2 before smelting in the furnace (see also MINERALS RECOVERY AND PROCESSING).

4. Alloy Processing

4.1. Smelting. The greatest application of manganese is in ferrous metallurgy (qv). Manganese alloys such as those listed in Table 9 are employed as refining agents as well as alloying additions. The nature of manganese raw materials and the requirements of the iron and steel industry have created an interesting and varied extractive metallurgy for producing ferromanganese alloys (see EXTRACTIVE METALLURGY).

4.2. Process Chemistry. Manganese is combined with oxygen in its ores (see Table 3) and carbon is the most economical reducing agent for oxides. Therefore, the essential characteristics of manganese metallurgy is evident from examination of the interactions between manganese oxides and carbon (15). The highest oxide, MnO_2, decomposes to Mn_2O_3 at 507 °C, and Mn_2O_3 goes to Mn_3O_4 at 1240 °C. These oxides can be reduced exothermically by CO in the shaft of a furnace. This is analogous to the situation in the Fe–O–C system where Fe_2O_3 can be reduced by CO to FeO. However, the Mn and Fe systems differ in the conditions required for the final reactions:

$$FeO + C \xrightarrow{\text{air}} Fe + CO + CO_2 \;\; 670\,^\circ C$$

$$7\,MnO + 10C \xrightarrow{\text{air}} Mn_7C_3 + 7CO \;\; 1267\,^\circ C$$

Because of the relative instability of FeO, the reduction to metallic Fe occurs at a much lower temperature and appreciable CO_2 is present in the product gas.

The high temperature required for the reaction of MnO and C results in the formation of essentially pure CO; the partial pressures of CO_2 and Mn are <0.1 kPa (1×10^{-3} atm). The product of this reaction is manganese carbide (7:3) [12076-37-8], Mn_7C_3, containing 8.56% carbon. Assuming immiscibility of the metal and carbide, Mn should be obtainable by the reaction of MnO and Mn_7C_3 at 1607 °C. However, at this temperature and activity of Mn, the partial pressure of Mn vapor is approximately 10 kPa (0.1 atm) which would lead to large manganese losses.

This simplified picture must be modified to take into account the other constituents of the ore that include FeO, CaO, Al_2O_3, and SiO_2 (Table 4). In the presence of carbon at elevated temperatures, Fe is easily reduced and thus reports to the metallic phase; CaO and Al_2O_3 are unreactive with carbon under the conditions of Mn smelting and enter the slag. SiO_2 is also largely retained in the slag but under certain conditions can be reduced and contribute Si to the alloy.

Slag composition influences the amount of manganese recovered as metal (16). Basic slags, those containing CaO, increase the activity of MnO and therefore promote manganese reduction. Such slags also suppress the activity of SiO_2 thus limiting the introduction of silicon into the alloy. Although adjusting the slag composition by the addition of base can lead to higher activity of MnO, it can have a negative influence on recovery by increasing the slag volume. This latter should be kept to a minimum.

Slag volume is directly related to the SiO_2 content of the raw materials and to a lesser extent, Al_2O_3. Although the addition of base leads to higher activity of MnO, the melting point and viscosity of the slag must also be taken into consideration. The melting point of the slag increases as MnO in the slag is replaced by the CaO and MgO added to the charge mixture; therefore, complete replacement of MnO with CaO is impractical. For this reason high grade ores, ie, of high manganese content, are favored and slag chemistry is best adjusted by employing a blend of ores of different gangue compositions to attain the desired slag composition.

Increased temperature favors Mn reduction. A thermodynamic analysis of manganese smelting (17) showed that under conditions of carbon saturation on a typical smelting charge at 1400 °C, the recovery of manganese as metal was low, leaving high concentrations of manganese in the slag. At 1500 °C, 90% recovery of manganese as metal was predicted. However, at 1600 °C, the recovery in the metal did not improve. Appreciable silicon was present in the alloy and Mn vapor appeared in the gas phase.

The silicon content of the alloy is increased by smelting manganese bearing charges containing increasing amounts of SiO_2 and by increasing smelting temperature through slag composition. Manganese vaporization is not excessive but SiO losses become significant at Si levels of greater than 25% (18). Silicon and carbon in manganese alloys saturated with carbon have an inverse relationship, as shown in Figure 1, and therefore at high silicon concentrations carbon content is low (19,20).

Because of the limitations imposed by the presence of gangue and the relatively high volatility of manganese, the initial products obtained when reducing manganese ore with carbon are a carbon saturated alloy and a slag containing some manganese. Under suitable conditions the manganese recovery can be sufficiently high to justify discarding the slag. Otherwise, the slag is smelted carbothermically using SiO_2 additions at higher temperature to produce silicomanganese and a slag of low manganese content giving a high overall recovery of manganese.

Ferromanganese low in carbon cannot be produced directly from ore and carbon because of the Mn volatility or the co-smelting of gangue constituents. Refining the primary reduction products is required. Figure 2 shows the overall scheme of reducing Mn ore to a variety of products. High carbon ferromanganese can be made by three different practices, blast furnace, discard slag electric furnace, and high manganese slag electric furnace. Medium carbon ferromanganese can be made by decarburizing high carbon ferromanganese or by the oxidation–reduction reaction of silicon in silicomanganese with manganese ore. Silicomanganese and low carbon silicomanganese are made in an electric furnace. Low carbon ferromanganese is produced by the reaction of manganese ore and low carbon silicomanganese.

The blast furnace for ferromanganese is usually located in a steelworks and is owned and operated by the steel producer. Most of the electric furnaces for manganese ferroalloy products are located in ferroalloy plants where other manganese products are made. In addition to large tonnages of high carbon ferromanganese, silicomanganese and refined (medium and low carbon) ferromanganese are also produced. Manganese-rich slags from the various ferromanganese production steps are used as all or part of the manganese charge to the silicomanganese furnace.

4.3. High Carbon Ferromanganese. Ferromanganese, also known as high carbon ferromanganese, or in the United States as standard ferromanganese, is the largest tonnage manganese alloy used in the steel industry. Of the overall average usage of manganese in steel, 75% is supplied as ferromanganese. Specifications of the various grades of ferromanganese and other manganese ferroalloys are given in Table 9. Table 10 is a listing of the countries in the world that produce ferromanganese and silicomanganese.

Ferromanganese is produced in blast furnaces and electric smelting furnaces. Economics usually determine which smelting process is chosen for ferromanganese. Both methods require about the same amount of coke for reduction to metal, but in the case of the blast furnace, the thermal energy required for the smelting process is supplied by the combustion of additional coke, which in most countries is a more expensive form of energy than electricity.

Capital requirements for a new facility generally favor the electric furnace process. However, in some countries having integrated steel industries, the availability of excess ironmaking blast furnaces, metallurgical coke, and relatively high cost of electricity, the blast furnace is an attractive choice (21). There was a decline in blast furnace production during the 1060s and 1970. As of the start of the 1990s, however ~30% of world ferromanganese production was made by blast furnaces. Five European countries produced ferromanganese by blast furnace representing about half of the total European production (see Table 10). More recently, Germany and the U.K. have discontinued blast furnace production of ferromanganese. For a time in the early 1980s, there was one blast furnace producer of ferromanganese in Japan. China produces about two-thirds of its ferromanganese by the blast furnace.

Blast Furnace Production. High carbon ferromanganese is produced in blast furnaces in a process similar to the production of iron (21). Ferromanganese production in a blast furnace differs from pig iron production in that larger amounts of coke are required in the former. The reduction of MnO takes place at a higher temperature than the reduction of FeO necessitating a high blast temperature which results in a high top temperature (2).

Preheating the blast and oxygen enrichment are used to reduce coke requirement. Further increase in blast temperatures is obtained by using plasma heaters, and because of the substitution of electrical energy for coke, lower production costs are obtained (22). Dolomite or limestone added to the charge raises the activity of MnO. By careful control and a method for ensuring a more uniform charge mixture in the shaft, manganese recoveries of over 90% and coke rates of 1530 kg/t are reported (23) (see FURNACES, FUEL-FIRED).

Electric Furnace Production. Electric furnaces used for smelting ferromanganese range in size up to 40 MW. Important design parameters for electric furnaces are electrode diameter and spacing, hearth diameter, crucible depth, voltage range, and KVA capacity of the transformer. For furnaces larger than 15 MW, design parameters are specific for each ferroalloy product to be produced. Because the resistivity of the burden in the electric furnace production of ferromanganese is low, low voltages between the electrodes are necessary to maintain satisfactory penetration of the electrodes in the charge. To obtain the proper power loading for the furnace, higher currents are required. Therefore, to operate within the current carrying capacities of carbon electrodes, the diameter of the electrodes for ferromanganese furnaces is larger than for other ferroalloy furnaces (see FURNACES, ELECTRIC). Large electric smelting furnaces operate at low power factors. If the factor goes below ~0.90, a penalty may be imposed by the supplier, therefore capacitors are installed to maintain power requirements.

Most electric furnaces have sealed covers although some are open and have a hood for fume collection. Figure 3 shows a 40 MW covered furnace for ferromanganese. The furnace gasses are drawn off and wet scrubbed by high energy Venturi scrubbers or can be dry filtered through large bag collectors if the furnace is of the open type. The sealed cover is generally preferred because it allows better fume control at lower capital cost and lower energy requirement. The crucibles are steel shells lined with refractory oxide brick and an inner lining of carbon blocks. The hearth is similar, but has a thicker carbon lining. Electric energy is supplied to the smelting reaction through three carbon electrodes, of the Søderberg, ie, self-baking, type. The electrodes for large (>30 MW) furnaces are 1.9 m in diameter. Most large ferromanganese furnaces have separate tapholes for metal and slag (see Fig. 3).

An important consideration for a successful smelting operation is the slag composition, which is largely determined by the make-up of the gangue constituents of the ores. The composition of the slag has pronounced effects on furnace resistivity, smelting temperature, recovery of manganese, and the amount of silicon in the ferromanganese. Blending of ores or the addition of fluxing reagents is often necessary to produce the desired slag composition.

High Manganese Slag Practice. Table 11 gives typical ranges of operating data for a large ferromanganese furnace using the high manganese slag practice using no flux additions in the charge, ie, a self-fluxing system. The high manganese slag practice is used by most plants where high grade manganese ores are smelted and silicomanganese is also produced. Manganese content of this slag ranges from 30–42%. Small amounts of fluxes may be used, such as dolomite or limestone, depending on the manganese concentration desired in the slag. In a silicomanganese furnace, smoother operation and higher overall manganese recovery are obtained if a high manganese slag is used as the charge.

High grade ores without flux additions (self-fluxing) produce slags containing 36–42% manganese. The ratio of slag to alloy ranges from 0.4 to 0.7, depending on the gangue level of the ore and the manganese content of the slag. Recovery of Mn in the alloy ranges from 70–80%, depending again on the gangue concentration (principally SiO_2) and the amount of flux used.

An efficient electric furnace operation for ferromanganese consumes ca 2100 kWh/t alloy. Energy needs for less efficient furnaces or when smelting lower grade ores that produce excessive slag, range from ca 2400 to 2800 kWh/t. Unlike any other electric furnace ferroalloy process, a substantial portion of the gas produced in a ferromanganese smelter is carbon dioxide. Coke and energy consumption are minimized and the CO_2 content is maximized when the CO reduction of the manganese oxides is carried to completion. The gaseous reduction is affected by smelting conditions, the skill of the furnace operator, and the charge permeability. Ore-size distribution and coke size are important for charge permeability. In this regard, excessive amounts of ore fines (<6–8 mm) are undesirable and some smelters agglomerate manganese ore fines before using the smelting operation (14,24).

Discard Slag Practice. The discard slag practice is followed when the ore is of such low quality that a high degree of manganese extraction is required to achieve the alloy grade, or the ore contains base oxides, eg, CaO and MgO, which if smelted alone, leads naturally to low manganese slags. Manganese content of the slag from this practice ranges from 10 to 20% and manganese recovery in alloy ranges between 85 and 90%.

If the ores contain little CaO or MgO, the charge is made up of manganese ores, coke, and a basic flux such as limestone or dolomite. Better results are obtained when the required basic oxides (CaO or MgO) are contained in the manganese ores, eg, as in some of the South African manganese ores (see Table 4). Specific energy consumption for this practice ranges from ca 2600 to 3100 kWh/t alloy. Power consumption is higher than that for the high manganese slag practice because of the additional energy required to calcine dolomite or limestone in the charge and the greater amount of manganese extracted from the slag which results in higher CO content in the off-gas than in that of the high manganese practice.

In South Africa where most of the manganese ores contain $CaCO_3$ and $MgCO_3$, there is little choice but to smelt with the discard slag practice, resulting in higher energy consumption. The introduction of sintering of part of the carbonate ores mined in South Africa, where the CO_2 is removed in the sintering process, substantially improved the electric furnace smelting operation. Energy consumption was reduced 14.69% and production was increased by 17.37% (13).

4.4. Silicomanganese. Silicomanganese is an alloy of manganese and iron containing 12.5 to 18.5% silicon which provides the steel industry with a convenient source of the two most important alloying and deoxidizing elements (Mn,Si) consumed in the production of steel. The production process is similar to that of electric furnacing smelting of ferromanganese. It differs in the furnace charge which contains large amounts of quartz (SiO_2) and, if required to adjust slag composition, limestone or dolomite. Smelting temperature is higher and the off-gas is predominantly carbon monoxide. In a plant that produces high manganese slags from other ferromanganese products, these slags are blended with ore for smelting in the silicomanganese furnace. Power consumption ranges from ca 3.86 to 4.84 MWh/t alloy, depending on the quality of ores, slag volume, furnace efficiency and, more importantly, the silicon content of the alloy.

In plants or companies that also produce ferrosilicon products, off-grade silicon-bearing materials such as ferrosilicon fines, drosses, or ladle digouts may be available. The addition of these materials to the silicomanganese furnace charge provides a relatively inexpensive method for increasing the productivity of the silicomanganese operation because remelting such silicon materials uses less energy than smelting silicon.

A furnace designed specifically for silicomanganese has a smaller crucible, electrode diameter, and electrode spacing than required for ferromanganese at the same power loading. Provided the gas-cleaning system has the capacity, a furnace designed for ferromanganese can be operated at substantially higher power when producing silicomanganese because of higher electrical resistance. Silicomanganese contains less carbon than ferromanganese but, nevertheless, is carbon saturated. The relationship of carbon and silicon in manganese–iron–silicon alloys is an inverse one (Fig. 1).

Low Carbon Silicomanganese. A low carbon grade of silicomanganese containing 28–32% Si and <0.06% C is usually made by a two-stage process. In the first step, low iron silicomanganese containing 16 to 18% silicon and about 2% carbon is made by smelting quartz and ferromanganese slag which is depleted in iron. Subsequently, in a separate furnace process, a mixture containing the crushed low iron silicomanganese, quartz, and coal (qv) or coke is smelted in a slagless process where the quartz is reduced to silicon that displaces the carbon in the remelted silicomanganese.

This product is mainly used within the ferroalloy plant as the reducing agent in a silicothermic process to produce the low carbon grade of refined ferromanganese.

4.5. Refined Ferromanganese. Refined ferromanganese refers to alloys that are not carbon saturated and range from less than 0.10 to 1.50% maximum carbon. Medium carbon grades are used in special grades of steels where in final additions carbon control is important. The low carbon grades are used mainly in the production of certain grades of stainless steels.

In the past, all grades of refined ferromanganese were made by various modifications of multistep silicon reduction processes. Depending on the carbon content desired in the product, a manganese ore and lime mixture was allowed to react with the silicon in silicomanganese or low carbon silicomanganese in an open, electric-arc furnace. The equilibrium reaction is

$$2\text{MnO}_2 + \text{Si} \leftrightarrows 2\text{MnO} + \text{SiO}_2$$

$$\frac{2\text{MnO} + \text{Si} \leftrightarrows 2\text{Mn} + \text{SiO}_2}{\text{MnO}_2 + \text{Si} \leftrightarrows \text{Mn} + \text{SiO}_2}$$

Lime is added to the reaction to increase the activity of MnO and reduce the activity of SiO_2. This allows greater extraction of manganese in equilibrium with less than 2% Si in the alloy.

In later modifications the manganese ore was reduced to MnO in an ore–lime melt by carbon reduction. The reaction of molten ore–lime with the silicon in silicomanganese was conducted in large ladles. The advantage is the use of less expensive carbon before the final reduction of MnO by silicon. Because half as much silicon is required, less SiO_2 is generated, therefore requiring less lime and producing less slag, which allows the extraction of more manganese for better recovery.

In 1971, oxygen refining of high carbon ferromanganese was introduced as a method for producing medium carbon ferromanganese (25). This manganese oxygen refining (MOR) process is similar to that used by the steel industry to produce steel in the basic oxygen furnace (BOF) (see Fig. 4). The MOR process offers substantial savings in investment costs, production costs, and energy usage but is limited to the production of medium carbon ferromanganese. Other oxygen refining processes for ferromanganese have been developed that use different methods of introducing oxygen with and without inert gases to the refining vessel.

The low carbon grade of ferromanganese must still be made by the silicon reduction method. The process is essentially the same as the silicothermic process shown in Figure 4 but uses ferromanganese–silicon, the low carbon grade of silicomanganese, as the reducing agent.

4.6. Manganese Nitride.

Manganese nitride is an addition agent for steel where both manganese and nitrogen are required in certain grades of steel. Briquettes of comminuted medium carbon ferromanganese are nitrided in an annealing-type furnace in a nitrogen atmosphere. The reaction is exothermic and commences at 600 °C (26). Nitrogen content of over 4% is attained. The nitrogen content is influenced by the amount of iron, carbon, and silicon in the medium carbon ferromanganese.

5. Electrolytic Processes

5.1. Electrolysis of Aqueous Solutions.

The electrolytic process for manganese metal, pioneered by the U.S. Bureau of Mines (now the U.S. Geological Survey), is used in the Republic of South Africa, the United States, Japan, and beginning in 1989, Brazil, in decreasing order of production capacity. Electrolytic manganese metal is also produced in China and Georgia.

Manganese metal made by this process is 99.9% pure. It is in the form of irregular flakes (broken cathode deposits) about 3-mm thick, and because of its brittleness, has little use alone. Most of the electrolytic manganese that is used in the aluminum industry is ground to a fine size and compacted with granulated aluminum to form briquettes that typically contain 75% Mn and 25% Al.

Manganese ore is roasted to reduce the higher oxides to MnO which is acid soluble, or as practiced by Elkem Metals (Marietta, Ohio), the MnO is supplied from slag produced as a by-product from the ferromanganese smelting operation. The reduced ore or slag is then leached with sulfuric acid at pH 3 to give manganese(II) sulfate. The solution is neutralized with ammonia to pH 6–7 to precipitate iron and aluminum which are removed by filtration. After treatment with hydrogen sulfide gas, arsenic, copper, zinc, lead, cobalt, and molybdenum are removed as sulfides. Ferrous sulfide or ammonium sulfide plus air is then added to remove colloidal sulfur, colloidal metallic sulfides, and organic matter. The purified liquid is electrolyzed in a diaphragm cell. Table 12 gives the conditions of electrolysis.

The impurity levels in electrolytic manganese metal are listed in Table 13.

5.2. Fused-Salt Electrolysis. Fused-salt electrolysis in many ways is similar to the Hall process for producing aluminum (see ALUMINUM AND ALUMINUM ALLOYS). The process was developed and solely used by Chemetals Corp. (26). The plant using this process discontinued production in 1985. The starting material is manganese ore reduced to the manganese(II) level in the solid state by using a rotary kiln under reducing conditions. The reduced ore is charged to the electrolytic cell which contains molten calcium fluoride and lime. Because of the ore's gangue content, additional fluorspar and lime are required as the reaction proceeds, the fluorspar to maintain the desired fused-salt composition, and the lime to neutralize the silica contained in the ore. As the volume of fused electrolyte increases, excess fused electrolyte is periodically removed.

The cell for this process is unlike the cell for the electrolysis of aluminum which is made of carbon and also acts as the cathode. The cell for the fused-salt electrolysis is made of high temperature refractory oxide material because molten manganese readily dissolves carbon. The anode, like that for aluminum, is made of carbon. Cathode contact is made by water-cooled iron bars that are buried in the wall near the hearth of the refractory oxide cell.

The cell is operated above 1300°C so as to maintain the manganese in the molten state. Molten manganese metal is periodically removed from the cell, much like tapping an ordinary ferromanganese furnace, and is cast in cast-iron pots. The metal produced by this process contains 92–98% Mn with iron as the main impurity. Manganese ore, chemically pretreated to remove iron, is used as the cell feed for the 98% Mn grade. The metal is reduced to lumps <150 mm for sale to the steel industry. Electrical energy consumption is ca 8–9 kWh/kg product. In addition to the lump form of manganese metal, refined ferromanganese products such as medium and low carbon ferromanganese also were produced by the fused salt electrolysis process at this plant.

6. Economic Aspects

Steelmaking accounts for most of the manganese use in the United States. The level and nature of manganese use in the United States is expected to remain about the same in the near future. No practical technologies exist for replacing manganese with other materials or for using domestic deposits to reduce the complete dependence of the United States on foreign sources. The value of U.S. consumption based on foreign trade data was about $\$205 \times 10^6$.

Table 14 gives economic statistics for the United States for the period 1999–2003 (10).

7. Health and Safety Factors

7.1. Health and Environment. Manganese in trace amounts is an essential element for both plants and animals and is among the trace elements least toxic to mammals including humans. Exposure to abnormally high concentrations of manganese, particularly in the form of dust and fumes, is, however, known to have resulted in adverse effects to humans (27,28) (see MINERAL NUTRIENTS).

Two kinds of diseases owing to manganese are known in humans: manganic pneumonia and manganism. These diseases mainly concern workers occupied in manganese ore mills, smelting works, battery factories, and manganese mines. A risk also exists when welding (qv) if electrodes containing manganese are used. Short exposures to manganese dust or fume can result in manganic pneumonia, a form of lobar pneumonia that is unresponsive to antibiotic treatments.

Manganese poisoning can result in chronic manganism which is primarily a disease of the central nervous system often first manifested by disordered mentation similar to the symptoms of Parkinson's disease. Presymptomatic exposure periods have been known to range from three months to 16 years but usually cases of manganism develop after 1–3 years of exposure, although individual susceptibility plays a role in the development of the disease. Many symptoms of manganism regress or disappear quickly if the victim is removed from exposure, although disturbances in speech and gait may remain. Well-established manganism is a crippling disease with permanent disability, but is not fatal and is considered to be rare.

Airborne manganese concentrations in the United States range from 0.02 to 0.57 $\mu g/m^3$ in urban areas and 0.0017–0.047 $\mu g/m^3$ in nonurban areas. The ACGIH recommends a TLV of 5 mg/m^3.

7.2. Plant Safety. Of the many ferroalloy products produced in electric furnaces, ferromanganese has the greatest potential for furnace eruptions or the more serious furnace explosions. The severity of the explosions increases with the size of the furnace. Such incidents are infrequent, but can occur, and when they do are often disastrous. Explosions usually result in extensive damage to the furnace and surrounding area, and often severe injuries or death to personnel in the immediate area. An eruption is the sudden ejection of solids, liquids, or gases from the furnace interior. A more violent and instantaneous ejection of material, accompanied by rapid expansion of burning gas, is considered an explosion (29).

The higher oxides of manganese (MnO_2, Mn_2O_3) are strongly exothermic in the presence of carbon and CO. In a normal, well-running ferromanganese furnace, the charge travels downward at a steady rate while the CO gas formed deep in the furnace rises and reacts with the oxygen-rich ores quietly and at a steady rate. Thus the manganese ore in the charge is reduced to manganese(II) before entering the hot reaction zone of the furnace.

Most all the serious eruptions of manganese furnaces can be traced to a set of conditions that cause bridging or hang-up of the charge materials so that the normal downward movement through the furnace is disrupted or retarded. As electrical energy continues to be supplied to the furnace with little or no movement of charge owing to the bridging, a cavity forms under and around the electrodes particularly after tapping the furnace. When conditions change that allow the bridge to collapse, usually during or shortly after a tap, large quantities of unreacted mixture enter the superheated cavity and react rapidly with a sudden release of CO and the ejection of hot and molten materials.

Safe operation of ferromanganese furnaces requires careful control of raw material particle size, oxygen content of the ore blend, and charge stoichiometry (29).

Most modern furnaces are equipped with computers that log raw material usage and other operating data. Many of the larger furnaces have computer systems that are programmed to continually monitor operating data and to automatically make adjustments to obtain optimum performance. On the basis of the analysis of each tap of slag and metal, continuous analysis of furnace off-gas, electrode length and penetration, and electrical data (volts, amperes, resistance), the computer makes adjustments to the amount of carbon in the charge mixture and controls the movement of the electrode. The benefits of computer controlled electric smelting furnaces include safer and more efficient operation, as well as increased productivity and lower costs (30,31) (see PROCESS CONTROL).

8. Uses of Metallic Manganese

Manganese is essential to iron and steel production because of its sulfur-fixing, deoxidizing, and alloying properties. Steelmaking, including its ironmaking component, has accounted for most the U.S. manganese demand, presently in thge range of 85–90%. Relatively small amounts of manganese were used for alloying with nonferrous metals, chiefly in the aluminum industry. The most important use of aluminum-manganese alloys is in the production of soft-drink cans. Other uses include automobiles, cookware, radiators, and roofing (32).

Some small amounts of managese were used in the United States in animal feed, brick coloring, dry cell batteries, fertilizers, and manganese chemicals (32).

United States consumption of manganese ferroalloys and metal in 2002 is given in Table 15 (10).

8.1. Austenitic Manganese Steels.

The invention of a manganese-bearing steel in 1882 by Sir Robert Hadfield was the first of the austenitic group of steels. It contained 1.2% C and 12% Mn, and combined toughness and ductility with good resistance to wear. Austenitic manganese steels find use in crushing and grinding equipment and many applications that require toughness and wear resistance. The composition of the various grades of austenitic manganese steel castings all contain 11 to 14% Mn with carbon in the range of 0.7–1.35%.

Austenitic steels that are used for nonmagnetic and cryogenic applications have lower carbon content than Hadfield steels and range in composition from 15 to 29% manganese (33).

8.2. High Strength Low Alloy Steels. Steels low in carbon and containing 1 to 1.8% of manganese in combination with microalloying additions such as niobium or vanadium in amounts of around 0.10% are known as high strength low alloy steels. These steels take advantage of the effect of manganese on the austenitic transformation temperature to obtain ultrafine-grained ferrite and the increased strength obtained from the carbonitrides formed by the microalloy additions. By controlled rolling and rapid quenching, steels of high strength-to-weight ratios are obtained that are used in pipelines (qv), automobiles, and other transportation (qv) equipment, as well as structural applications (34,35).

8.3. Stainless Steels. In chromium–nickel stainless steels, 1–2% manganese improves the hot working and weldability characteristics. Since the 1950s, the 200 series of stainless steels have come into use as a partial substitute for the AISI 300 series. The 200 series consists, among others, of AISI types 201 and 202 which contain 5.5 to 7.5 and 7.5 to 10.0% manganese, respectively. The 200-series stainless steels were developed to obtain higher strength and more economical austenitic materials by using the less expensive manganese in place of nickel.

8.4. Nonferrous Uses. In the nonferrous metal industry, manganese is consumed in significant amounts for its effect on hot working and for modifying physical properties. The metals so treated include a number of aluminum and copper alloys and some nickel- and cobalt-base alloys. In the special cases of some bronzes, hardening alloys made from copper and ferromanganese are added to the molten bronze in order to add small amounts of iron that cannot be alloyed directly. Manganese has many beneficial effects when combined with copper-based alloys containing one or more of the alloying elements of aluminum, nickel, and zinc (36).

Manganese has been employed as an alloying element almost from the beginning of the aluminum industry. The amounts added are small and very seldom exceed 2% Mn and most often are in the range of 0.20 to 0.8%. In these amounts, the physical properties of aluminum are only slightly affected but the electrical properties are greatly affected, eg, resistivity increases threefold. Manganese in solution in aluminum has a strengthening effect accompanied by a small decrease in ductility (37).

Aluminum–manganese alloys are extensively used for food handling equipment, ranging from cooking utensils to frozen food trays, beverage cans, bottle caps, and any other application where good corrosion resistance and absence of food contaminants, together with strength and wear resistance higher than aluminum, are required. By far the most important use for this aluminum alloy is for beer (qv) and soft drink cans of which some 100 billion are produced annually. In the building industry the aluminum–manganese alloys are used mainly for siding and roofing for houses and buildings, sometimes painted or enameled for durability and low maintenance (36,38) (see BUILDING MATERIALS, SURVEY; CARBONATED BEVERAGES; FOOD PACKAGING).

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Table 1. **Properties of Manganese**[a]

Property	Value
melting point, °C	1244
boiling point, °C	2060
density at 20°C, g/cm^3	7.4
specific heat at 25.2°C, J/g[b]	0.48
latent heat of fusion, J/g[b]	244
linear coefficient of expansion, 0–100°C, °C^{-1}	22.8×10^{-6}
hardness, Mohs' scale	5.0
compressibility	8.4×10^{-7}
solidification shrinkage, %	1.7
latent heat of vaporization at bp, J/g[b]	4020
standard electrode potential, V	1.134
magnetic susceptibility, m^3/kg	1.21×10^{-7}

[a] Ref. 1.

[b] To convert J to cal, divide by 4.184.

Table 2. **Properties of Manganese Allotropes**[a]

Property	α	β	γ	δ
crystal structure	cubic	cubic	fcc	bcc
atoms per unit cube	58	20	4	2
lattice parameter, nm	0.89	0.63	0.387	0.309
transformation temp, °C	720[b]	1100[c]	1136[d]	1244[e]
latent heat of transformation, J/g[f]	36.4[b]	41.9[c]	32.8[d]	243.9[e]
density at 20°C, g/cm^3	7.43	7.29	7.18	6.3
electrical resistivity at 20°C, mW · cm	160	90	40	
thermal expansion, °C^{-1}	25.2×10^{-6}	43.0×10^{-6}	45.2×10^{-6}	41.6×10^{-6}
heat capacity, *Cp*, J/mol[f,g]				
298–980 K	$23.589 + 0.014T - 1.397 \times 10^5/T^2$			
980–1360 K		$32.715 + 0.0047T + 2.234 \times 10^5/T^2$		
1360–1410 K			$31.757 + 0.0084T$	
1410–1517 K				$34.221 + 0.0078T$

[a] Ref. 1.

[b] From α to β.

[c] From β to γ.

[d] From γ to δ.

[e] From δ to liquid.

[f] To convert J to cal, divide by 4.184.

[g] The heat capacity for liquid Mn from 1517–2000 K is $Cp = 46.024$.

Table 3. **Common Manganese Minerals**[a]

Mineral	CAS Registry number	Composition	Mn, %
bementite	[66733-93-5]	$Mn_8Si_6O_{15}(OH)_{10}$	43.2
braunite		$Mn_2Mn_6SiO_{12}$	66.6
cryptomelane	[12260-01-4]	KMn_8O_{16}	59.8
franklinite		$(Fe,Zn,Mn)\dot{O}(Fe,Mn)_2O_3$	10–20
hausmannite	[1309-55-3]	Mn_3O_4	72.0
manganite	[52019-58-6]	$Mn_2O_3\cdot H_2O$	62.5
manganoan calcite		$(Ca,Mn)CO_3$	35.4
romanechite		$BaMnMn_8O_{16}(OH)_4$	51.7
pyrolusite	[14854-26-3]	MnO_2	63.2
rhodochrosite	[598-62-9]	$MnCO_3$	47.8
rhodonite	[14567-57-8]	$MnSiO_3$	41.9
wad		hydrous mixture of oxides	variable

[a] Refs. 3–7.

Table 4. **Chemical Composition of Important Manganese Ores, wt % Dry Basis**[a]

Location	Typical moisture	Mn	Fe	SiO_2	Al_2O_3	CaO	MgO	BaO	P	As	K_2O	CO_2	Available oxygen[b]
Moanda, Gabon	8.8	50.2	2.8	5.0	5.9	0.05	0.06	0.25	0.101	0.003	0.81	0.03	13.9
Groote Eylandt, Australia	1.8	48.6	3.8	6.8	4.0	0.08	0.15	0.74	0.084	0.004	1.84		13.4
South Africa													
Mamatwan	1.4	38.8	4.7	4.8	0.3	13.9	4.6	0.25	0.003	0.00	0.22	13.7	4.4
Gloria	0.7	38.9	4.8	5.9	0.3	11.8	3.5	0.05	0.021		0.05	15.5	3.9
Associated 50	0.7	50.4	10.2	5.8	0.4	4.9	0.7	0.44	0.033	<0.002	0.01	1.20	6.0
Molango,[c] Mexico	1.1	38.4	7.7	15.6	3.7	9.9	9.4	0.02	0.072	<0.002	0.04	0.09	

[a] Ref. 8.

[b] Associated with Mn in excess of MnO.

[c] Calcined nodules.

Table 5. **World Manganese Production Reserves and Reserves Base, 10^3 t[a]**

	Mine production			
Region	2002	2003[b]	Reserves	Reserve base
Australia	983	990	32,000	82,000
Brazil	1,300[b]	950	23,000	51,000
China	900[b]	900	40,000	100,000
Gabon	810[b]	1,000	20,000	160,000
India	630[b]	630	15,000	33,000
Mexico	88	85	4,000	9,000
South Africa	1,504	1,630	32,000	4,000,000
Ukraine	940	830	140,000	520,000
other countries	955	985	small	small
World total (rounded)	*8,100*	*8,000*	*300,000*	*5,000,000*

[a] Ref. 9.

[b] Estimated.

Table 6. **World Production of Manganese Ore, 10^3 t**[a,b,]

Country[c]	Range percent Mn[b]	Gross weight					Metal content				
		1998	1999	2000	2001	2002	1998	1999	2000	2001	2002
Australia	37–53	1,500	1,892	1,614	2,069	2,187	729	926	787	948	983
Brazil	30–65	1,940	1,656	1,925	1,863	2,000[b]	1,261	1,076	1,250	1,210	1,300
China[b]	20–30	5,300	3,190	3,500	4,300	4,500	1,060	630	700	860	900
Gabon	45–53	2,092	1,908	1,743[b]	1,791	1,856	966	881	804	830[b]	810
Ghana	32–34	537	639	896	1,077	1,136	172	204	287[b]	344[b]	363
India[b]	10–54	1,557	1,500	1,550	1,600	1,700	592	570	590	600	630
Kazakhstan, crude ore	20–30	634	980	1,136	1,387	1,792	155	240[b]	280[b]	350[b]	440
Mexico	27–50	510	459	435	277	233	187	169	156	100	88
South Africa	30–48+	3,044	3,122	3,635	3,266	3,322	1,298	1,343	1,578	1,479	1,504
Ukraine	30–35	2,226	1,985	2,741	2,700	2,736	755[b]	675[b]	930[c]	930[b]	940
other[b,d,]	XX[e]	522	451	434	499	487	151	133	126	152	149
Total	XX[e]	*19,900*	*17,800*	*19,600*	*20,800*	*21,900*	7,330	6,850	7,490	*7,800*	8,110

[a] Ref. 10. World totals and estimates are rounded, data through July 25, 2003.

[b] Estimated.

[c] In addition to the countries listed, Cuba, Panama, and Sudan may have produced manganese ore and/or manganiferous ore, but available information is inadequate to make reliable estimates of output levels.

[d] Category represents the combined totals of Bosnia and Herzegovina, Bulgaria, Burkina Faso, Burma, Chile, Colombia, Egypt, Georgia, Hungary, Indonesia, Iran, Italy (from wastes), Morocco, Namibia, Romania, Russia (crude ore), Thailand, and Turkey.

[e] XX = not applicable.

Table 7. **Average Metal Content of Deep-Sea Nodules,[a] wt % Dry Basis**

Location	Mn	Fe	Ni	Cu	Co
North Atlantic					
Blake Plateau	14.5	13.7	0.50	0.08	0.42
red clay region[b]	13.9		0.36	0.24	0.35
seamount and mid-Atlantic ridge	13.5		0.39	0.14	0.36
South Atlantic	7.2		0.14	0.09	0.05
Indian Ocean	16.3		0.54	0.20	0.26
North Pacific					
red clay regions	18.2	11.5	0.76	0.49	0.25
siliceous ooze	24.6	8.2	1.28	1.16	0.23
South Pacific					
deep-water clay region	15.1		0.51	0.23	0.34
submarine highs on seamounts and plateaus	14.6		0.41	0.13	0.78

[a] Ref. 11.

[b] 1770 km east of Florida.

Table 8. **Specifications of Metallurgical-Grade Manganese Ore, wt %, Dry Basis**[a]

Assay	Composition	Assay	Composition
Mn[b]	48.0	As	0.18
Fe	6.0	P	0.19
Al_2O_3	7.0	Cu + Pb + Zn	0.30
$Al_2O_3 + SiO_2$	11.0		

[a] All values are maximum unless otherwise indicated.

[b] Value is minimum.

Table 9. **Compositions of Manganese Ferroalloys, wt %t**[a]

Alloy	Mn[b]	C	Si	P	S	As
ferromanganese						
high carbon	76–80	7.5	1.2	0.35	0.05	0.30
medium carbon	80–85	1.5	1.2	0.30	0.02	0.15
low carbon	85–90	<0.10–0.50	1.2	0.20	0.02	0.10
silicomanganese	65–78	2.00	16.0–18.5	0.20	0.04	0.10
low carbon silicomanganese	63–66	0.08	28–32	0.05	0.04	0.15

[a] Values given are maximum unless otherwise noted.

[b] Range represents minimum values.

Table 10. **World Production of Ferromanganese and Silicomanganese,[a] 10^3 t gross weight**

	2001					2002[c]				
	Ferromanganese					Ferromanganese				
Country[d]	Blast furnace	Electric furnace	Total	Silicomanganese	Grand total	Blast furnace	Electric furnace	Total	Silicomanganese	Grand total
Argentina				5	5				5	5
Australia[c]		115	115	135	250		115	115	135	250
Brazil		96	96	180	276		96	96	180	276
Chile		4	4	2[c]	6[c]		4	4	2	6
China[c]	500	670	1,170	1,170	2,340	500	700	1,200	1,300	2,500
Egypt[c]		30	30		30		30	30		30
France[c]	300	130	430	50	480	300	130	430	50	480
Georgia[c]		7	7	25	32		7	7	25	32
India[c]		165	165	150	315		165	165	150	315
Indonesia[c]		12	12	7	19		12	12	7	19
Italy		40	40	90	130		40	40	90	130
Japan[c]		368	368	62	431		357	357	71	428
Kazakhstan		5	5	141	147		2	2	164	166
Korea, North[c]		6	6		6		6	6		6
Korea, Republic of		144	144	102	245		146	146	105	251
Mexico		60	60	74	134		39	39	73	112
Norway[c]		240	240	230	470		240	240	230	470
Poland	1		1	20	21	1		1	20	21
Romania		[e]	[a]	72	72				89	89
Russia[c]	70		70		70	80		80		80

Table 10 (*Continued*)

	2001					2002[c]				
	Ferromanganese					Ferromanganese				
Country[d]	Blast furnace	Electric furnace	Total	Silicomanganese	Grand total	Blast furnace	Electric furnace	Total	Silicomanganese	Grand total
Slovakia[c]		20	20	35	55		20	20	35	55
South Africa		498	498	253	751		500	500	260	760
Spain[c]		10	10	100	110		10	10	100	110
Taiwan										
Ukraine	85	250	335	685	1,020	85	250	335	685	1,020
Venezuela		13	13	57	69		12	12	55	67
Total	*956*	*2,880*	*3,840*	*3,650*	*7,480*	*966*	*2,880*	*3,850*	*3,830*	*7,680*

[a] Ref. 10.

[b] Data through July 25, 2003.

[c] Estimated.

[d] In addition to the countries listed, Hungary is believed to have produced some blast furnace ferromanganese and Iran is believed to have produced ferromanganese and silicomanganese, but production figures are not reported; general information is inadequate for the formulation of reliable estimates of output levels. Data for United States production of manganese ferroalloys are not included to avoid disclosing company proprietary data.

[e] Less than 1/2 unit.

Table 11. **Operating Data for a Ferromanganese Electric Furnace**[a]

Parameter	Value
operating load, MW	30–35
apparent power, MV · A	58.9–61.6
power factor	0.51–0.57
electrode current, kA	130
single-phase resistance, mΩ	0.592–0.690
secondary voltage[b]	262–274
usage per ton alloy	
Mn ore, t[c]	1.969
coke, t[c]	0.417
electrode paste, kg	8.0
power, kWh	2200
ratio, slag:alloy	0.45
slag composition, wt %	
MnO	38.7
SiO_2	24.7
Al_2O_3	14.4
CaO	13.0
MgO	2.7
alloy composition, wt %	
Mn	79.0
Fe	13.0
Si	0.3
C	6.7
Mn recovery, %	
alloy	83.2
slag	13.8
fume, etc	3.0

[a] Using high manganese slag practice. Furnace has three 1.9-m Søderberg electrodes.

[b] Assuming single-phase reactance = 1.0 m Ω.

[c] Dry basis.

Table 12. **Electrolysis of Aqueous Solutions of Manganese**

Condition	Value
purified feed solution, catholyte	
Mn as $MnSO_4$, g/L	30–40
$(NH_4)_2SO_4$, g/L	125–150
SO_2, g/L	0.30–0.50
anolyte	
Mn as $MnSO_4$, g/L	10–20
H_2SO_4, g/L	25–40
$(NH_4)_2SO_4$, g/L	125–150
current density, mA/cm^2	43–65
catholyte pH	6–7.2
anode composition	Pb +1% Ag
cathode composition	Hastelloy, type 316 stainless steel, or Ti
cell voltage, V	5.1
diaphragm	acrylic[a]
current efficiency, %	60–70

[a] Usually specified as to porosity.

Table 13. **Impurity Levels in Electrolytic Manganese Metal**

Element	Quantity, wt %
Fe	0.0015
Cu	0.0010
As	0.0005
Co	0.0025
Ni	0.0025
Pb	0.0025
Mo	0.0010
S as sulfide	0.0170
S as sulfate	0.0140
C	0.0020
H_2	0.0150

Table 14. **U.S. Economic Statistics for Manganese**[a,b] **$\times 10^3$ t, Gross Weight**

Salient Statistics	1999	2000	2001	2002	2003
production, mine[c]	0	0	0	0	0
imports for consumption					
manganese ore	460	430	358	427	390
ferromanganese	312	312	249	275	240
silicomanganese[d]	301	378	269	247	200
exports					
manganese ore	4	10	9	15	9
ferromanganese	12	8	9	9	9
shipments from Government stockpile excesses					
manganese ore	76	63	37	56	44
ferromanganese	35	33	2	38	28
consumption, reported[e]					
manganese ore[f]	479	486	425	360	410
ferromanganese	281	300	266	253	266
consumption, apparent, manganese[g]	719	768	692	689	610
price, average value, 46% to 48% Mn metallurgical ore, dollars per mtu cont. Mn, c.i.f. U.S. ports	2.26	2.39	2.44	2.30	2.35
stocks, producer and consumer, yearend					
manganese ore[f]	172	226	138	148	127
ferromanganese	40	31	25	21	14
net import reliance[h] as a percentage of apparent consumption	100	100	100	100	100

[a] Ref. 9. Data for 2003 are estimated.

[b] Manganese content typically ranges from 35% to 54% for manganese ore and from 74% to 95% for ferromanganese.

[c] Excludes insignificant quantities of low-grade manganiferous ore.

[d] Imports more nearly represent amount consumed than does reported consumption: Internal evaluation indicates that reported consumption of silicomanganese is considerably understated.

[e] Total manganese consumption cannot be approximated from consumption of manganese ore and ferromanganese because the ore is used to produce manganese ferroalloys and metal.

[f] Exclusive of ore consumed at iron and steel plants.

[g] Thousand tons, manganese content; based on estimates of average content for all significant components except imports, for which content is reported.

[h] Defined as imports − exports + adjustments for Government and industry stock changes.

Table 15. **U.S. Consumption, By End Use, and Industry Stocks of Manganese Ferroalloys and Metal in 2002**[a]

	Ferromanganese				
End use	High carbon	Medium and low carbon	Total	Silicon-manganese	Manganese metal
steel					
carbon	108,000	82,500	190,000	53,300	220
high-strength, low-alloy	17,800	3,940	21,700	2,920	[b]
stainless and heat-resisting	11,800	[b]	11,800	8,680	1,350
full alloy	15,200	4,430	19,600	17,900	[b]
unspecified[c]	598	364	962	211	158
Total	*153,000*	*91,200*	*245,000*	*83,000*	*1,730*
cast irons	6,950	478	7,420	1,190	5
superalloys	[d]	[d]	[d]	0	[d]
alloys, excluding alloy steels and superalloys	823	484	1,310	[d]	17,100[e]
miscellaneous and unspecified	0	[d]	[d]	[d]	[d]
Total consumption	*161,000*	*92,200*	*253,000*	*84,200*[f]	*18,800*
total manganese content[g]	*125,000*	*73,500*	*200,000*	*59,000*	*18,800*
Stocks, December 31, consumers and producers	9,020	12,200	21,200	13,600	1,470

[a] Ref. 10. Data rounded.

[b] Withheld to avoid disclosing company proprietary data; included with “Steel: Unspecified.”

[c] Includes electrical and tool steel, and items indicated by footnote *b*.

[d] Withheld to avoid disclosing company proprietary data.

[e] Approximately 85% of this combined total was for consumption in aluminum alloys.

[f] Internal evaluation indicates that silicomanganese consumptioin is considerably understated.

[g] Estimated based on typical percent manganese content.

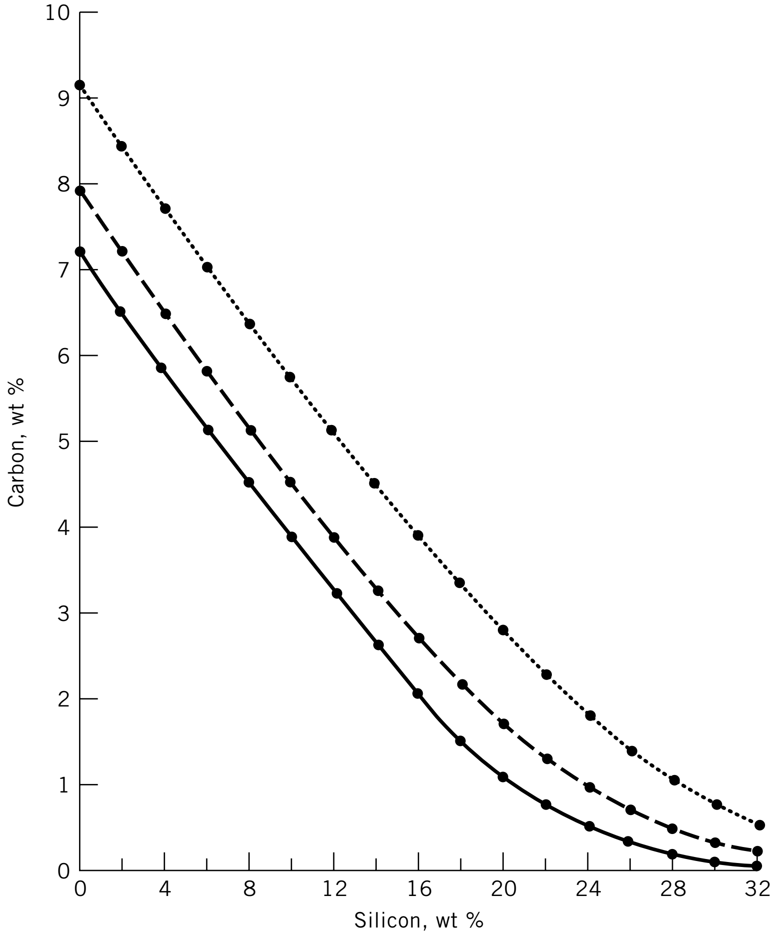

Fig. 1. Effect of silicon on carbon solubility in ferromanganese at (—) 1350°C, (– – –) 1500°C, and (····) 1800°C (20).

Fig. 2. Schematic diagram of manganese metallurgy where HCFeMn = high carbon ferromanganese; MCFeMn = medium carbon ferromanganese; SiMn = silicomanganese; LCFeMn = low carbon ferromanganese; LCSiMn = low carbon silicomanganese; FeMnN = nitrided ferromanganese; and Mn = electrolytic manganese.

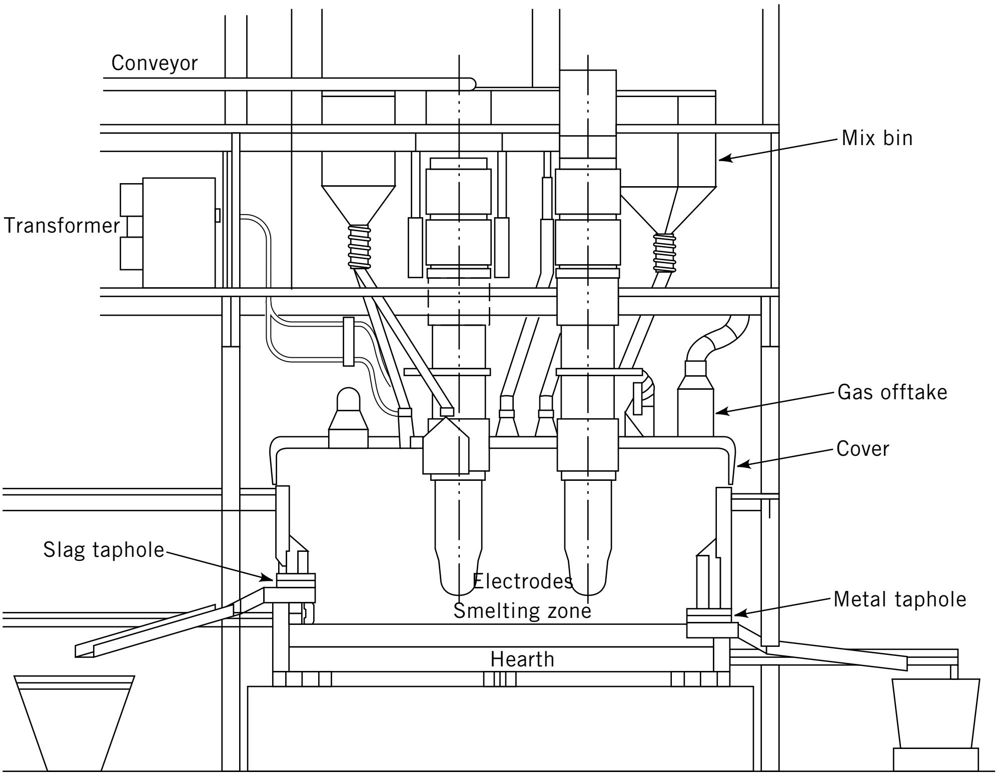

Fig. 3. Covered ferromanganese furnace.

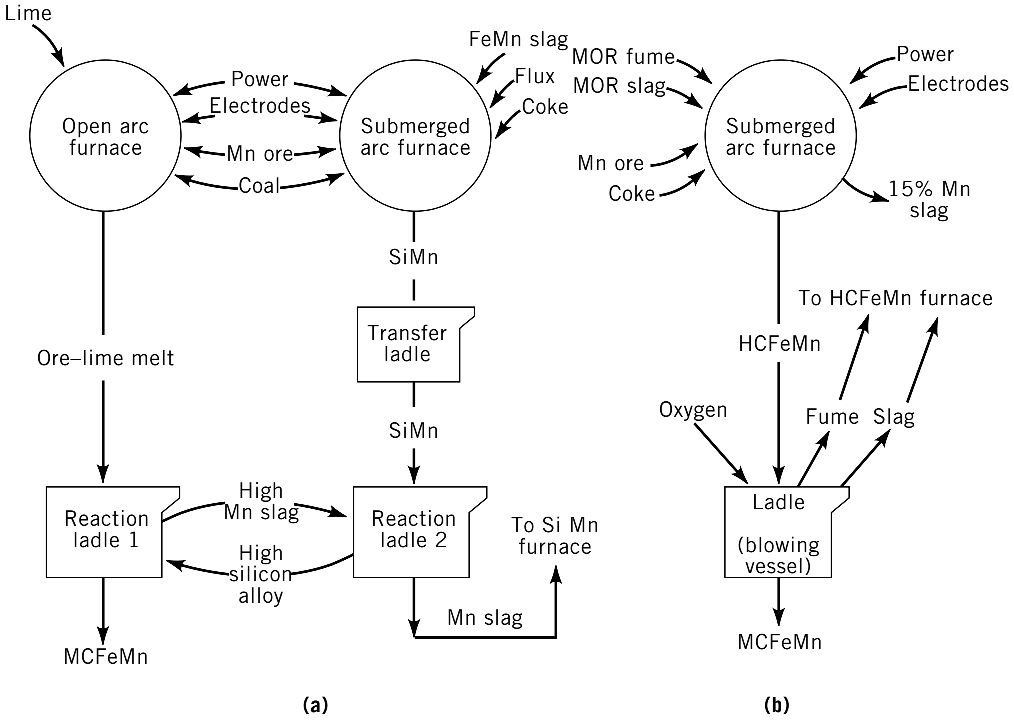

Fig. 4. Process flow sheets for (**a**) the silicothermic reduction and (**b**) the MOR process. See text.