Plenary Address: The Optimum Utilization of Raw Materials in Manganese Smelting

by R.T. HOOPER* (presented by Mr Hooper)

SYNOPSIS

The correct selection and preparation of raw materials improve furnace operating conditions and result in higher thermal and metallurgical efficiencies and lower product costs in the production of manganese alloys.

The removal of fines from coke and ores is recommended for its beneficial effects of increased charge porosity and distribution of reducing gas. Coke fines can be utilized for the sintering of the fines screened from lumpy ores, and additional ore fines can be purchased to keep the sintering equipment operating to capacity. The inclusion of sinter in the burden further improves the furnace conditions and the products of smelting.

Ferromanganese slags should be utilized fully for the manufacture of silicomanganese, and the manganese contents of slags will depend on the relative demands and economics involved in the achievement of the greatest financial returns from the sale of both alloys.

INTRODUCTION

Good-quality and suitable raw materials are necessary for the efficient production of ferromanganese and silicomanganese of the compositions required by steelmakers.

The chemical composition of the manganese ore or the blend of ores will, to a large extent, determine the grade of ferromanganese, the slag volume, the slag composition, and the subsequent utilization of the slag.

The physical nature of the charge materials in regard to sizing and fines content has a very significant effect on the electric-furnace operating conditions and efficiency, especially in the manufacture of standard ferromanganese. This aspect is becoming more important with the trend towards larger furnaces, which are much more sensitive to fines in the charge than the smaller units.

Fines greatly lower the porosity or permeability of the charge, causing poor distribution of the reducing gas, high fume and dust losses, and bridging of the charge, which may result in serious eruptions or explosions during the production of standard ferromanganese.

Although the raw materials may have been screened at the source of supply, the formation of fines in handling and shipping is unavoidable. It is therefore desirable to remove such fines by screening at the smelting plant as close as possible to the furnace, prior to charge proportioning.

If sintering facilities are not available, some ore fines can be utilized in silicomanganese manufacture, where the porosity of the charge is of less importance owing to the lower rate of gas generation and greater furnace stability. However, sintering is to be recommended for optimum furnace conditions and results of operation and for complete utilization of all fines.

The smaller the particle size in the fines, the more harmful is the effect in the smelting furnace. Minus 1 mm fines are worse than minus 2 mm, and an appreciable improvement in furnace operation would result from the removal of such small sizes, if this could be done without blinding of the screens. For this reason, it is not practicable to screen stockpiled materials to less than 6mm, and furnace tests have shown that there is little further benefit, if any, from the removal of minus 12 mm material. It is therefore generally agreed that minus 6 mm material can be regarded as true fines, and, since the size passing through a screen in normal screening practice is somewhat smaller than the aperture, a 7 mm screen is necessary for the screening out of minus 6 mm fines.

THE SELECTION AND BLENDING OF RAW MATERIALS

For satisfactory furnace operation and the efficient production of manganese alloys, the raw materials should be of high quality in both their chemical and physical properties.

The suitable selection and use of raw materials are essential, not only for a high rate of alloy productivity, but also for minimizing the cost of production; the raw materials in manganese smelting account for a high proportion of the product cost.

Since manganese ore is the major constituent of the furnace charge, the selection of the ore or blend of ores is of greatest importance. Manganese ores are available from many sources and with various contents of manganese, iron, silica, alumina, lime, magnesia, phosphorus, and other impurities. The prices of ores vary according to their grades and qualities.

The blending of ores is desirable and necessary if the required ratios of manganese to iron are to be obtained for the production of the specified grades of alloy, and if slags of suitable compositions and volumes are to be formed. In this way, higher-priced, top-grade ores can be blended with cheaper, lower-grade ores to economic advantage.

For high-carbon ferromanganese, the ore or blend should contain, in addition to the required manganese-to-iron ratio, sufficient silica to form slag with manganous oxide and other bases, and sufficient alumina to ensure efficient production of silicomanganese from the slag. Phosphorus, arsenic, and other impurities that enter the metal must be low enough for the specified limits of the alloy not to be exceeded.

The form in which the manganese occurs in the ore is of some importance. It is desirable that the manganese should be present mainly as dioxide so that advantage can be taken of the exothermic reduction through the various lower states of oxidation to monoxide. Such reduction is exothermic with both carbon and carbon monoxide, particularly the latter, and the heat formed by the reactions is retained in the furnace and is transferred to the charge to

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assist in further smelting, thus reducing the amount of electric power required for smelting.

Manganese ores for the production of silicomanganese by the normal practice of smelting a slag/ore charge can be relatively high in iron because the slags from ferromanganese production have very high manganese-to-iron ratios. Siliceous manganese ores can be used because a high silica content lowers the consumption of quartzite for reduction to silicon in the silicide. However, the silica should be present in the form of free silica and not combined with manganese, because the silicates in ore, as in slag, are difficult to reduce.

Manganese ore in smaller sizings such as intermediates in the range of 9 mm to 3 mm are available from some manganese ore suppliers and can be used satisfactorily for silicomanganese manufacture. Such intermediates result from the treatment and beneficiation of lump ores at the mine. Intermediates can be used successfully for silicomanganese because the rate of gas formation in smelting is substantially less than that for a high-carbon alloy, and the charge porosity is therefore less important. However, the inclusion of ferromanganese slag in the charge increases both the porosity and the electrical resistivity of the charge.

Low- and medium-carbon ferromanganese production, which is by silicothermic smelting, requires a high-grade ore with a high manganese-to-iron ratio and low silica content if excessive slag formation is to be prevented and a high consumption of flux is to be avoided. The formation of less slag results in lower power consumption and higher recovery of manganese to the alloy. However, a high alumina content in the ore is beneficial in the utilization of the slag for silicomanganese because low-carbon ferromanganese slag has a relatively low alumina content. This is especially so if the silicomanganese charge includes a large proportion of low-carbon alloy slag, or a high-carbon alloy slag containing insufficient alumina. Alumina increases the melting temperature of the slag and the smelting temperature of the furnace, which is necessary for the production of the higher-silicon silicomanganese of lower carbon content that is required for the production of low-carbon ferromanganese.

In addition to the ore, the coke that is used as the reducing agent has a very significant effect on the results of smelting. The coke should be high in fixed-carbon content and low in ash, and should preferably display high reactivity. Gas cokes are therefore preferable when available, but metallurgical cokes in the smaller sizings, produced as screenings from iron blast-furnace coke, are quite satisfactory. A low ash content is desirable to prevent unnecessary slag formation, which is power-consuming.

For the desired slag composition in ferromanganese and silicomanganese production, some limestone or dolomite may be necessary in the charge. These materials should be high in lime and magnesia, and low in impurities. Dolomite, if available at a satisfactory price, is generally preferable to limestone, because magnesia is a more effective base than lime and tends to increase the slag fluidity.

For smooth furnace operation, the physical properties of the raw materials are as important as, or probably more important than, the chemical properties. For example, the use of high-grade raw materials with high contents of fines will result in poor furnace-operating conditions. Raw materials should therefore be purchased with low fines contents and in sizings as near as possible to the charge requirements so that crushing and the fines generated by crushing are minimized.

Ores should have sufficient strength to prevent the formation of excessive fines during shipping and handling. Fines have an adverse effect on furnace operation, and, if they are to be screened from the ore before charge preparation, as is to be recommended, the amount of fines must be minimized because they have to be utilized subsequently by some means such as agglomeration.

Another source of fines is the decrepitation of some ores by heating and thermal shock after they have entered the smelting furnace. Ores should therefore possess the property of thermal stability, which can be tested if a sample is placed in a steel box and inserted into a laboratory muffle furnace at 1000°C. Decrepitation generally results from a high content of combined water in the ore.

For standard ferromanganese production, it is common practice to use a number of ores from different sources, the ores being blended to the correct manganese-to-iron ratio for the desired grade of alloy, with a satisfactory level of impurities to enter the alloy and a suitable content of slag-forming materials to produce the desired slag composition and volume. If two ores are to be blended, they should be complementary: that is, high manganese-to-iron ratio with low manganese-to-iron ratio, higher silica with lower silica, and so on, to give the most suitable composition of the blend. However, a single ore can be used if it has a suitable composition and a high enough manganese-to-iron ratio, in which case a small proportion of iron ore or manganiferous iron ore is included in the charge to control the grade of the alloy.

STOCKPILING

The suitable stockpiling of raw materials results in improved furnace operating conditions and lower product cost. Since raw materials account for a high proportion of the product cost, they should be stored on a solid pavement to ensure recovery without wastage and to avoid contamination. Materials must also be stored separately to avoid mixing, and preferably in individual shipments. Excessive segregation, resulting from stockpiling in large conical heaps, should be avoided, and storage by a ramping system can be recommended.

Covered storage, especially for coke, is desirable but costly in capital outlay and often not practicable.

THE PREPARATION OF RAW MATERIALS

Raw materials as charged to the furnace are required to have a certain sizing and to be relatively free from fines so as to permit the free escape of reducing gas through the charge.

The largest size of manganese ore depends, to some extent, on the size of furnace, but mainly on the time of descent of the charge in the furnace to ensure that the ore is preheated before reaching the smelting zone, which is in the vicinity of the end of an electrode. For modern large manganese furnaces, the maximum size of ore is approximately 75 mm.

The upper limit of coke size in the charge is approximately 18 mm, because large coke results in low resistivity, causing shallow electrode penetration, which leads to poor furnace operating conditions with high smelting zones, poor heat transfer from gas to charge, high top-gas temperature, and high fume loss. Large coke is not completely consumed as it passes through the smelting zone, and this causes the accumulation of excessive coke beds, which result in shallow electrode penetration and its associated adverse effects.

While the removal of coke fines is necessary for better charge porosity and coke efficiency, the screening should be at approximately 6 mm and not greater. Screening at 12 mm does not increase the porosity further, but has an adverse effect on electrode penetration by removing the small coke in the range 6 mm to 12 mm, which is necessary for increased electrical resistivity of the charge.

The correct sizing of charge materials is essential for a burden that has high porosity or gas permeability, which promotes the most desirable gas conditions in the charge. Reducing gas formed in the smelting zones and in the lower reaches of the charge must escape freely and uniformly, with distribution through the maximum volume and over the largest area at the surface of the charge.

Uniform distribution of gas through the charge is necessary for the maximum transfer of heat from the hot reducing gases to the charge. As the flow of the gas and the movement of the charge are countercurrent, this heat is used for preheating and prereduction. High heat transfer or exchange results in high thermal efficiency of the furnace and a low power consumption. Uniform gas distribution promotes gaseous reduction by carbon monoxide of the higher oxides to the lower, which are the most exothermic and are indicated by a high CO_2-to-CO content of the furnace gas. It also ensures drying of the charge and removal of combined water to minimize water-gas formation, which consumes both heat and fixed carbon.

For maximum porosity of the charge and optimum gas flow through the charge, the raw materials must be screened for the removal of fines. Such screening should be as close as possible to the furnace, which is before the charge preparation or proportioning, and immediately before the raw-material bins.

The smaller the particle size of the fines, the greater its effect on charge porosity. Permeability tests prove that particle size from 1 mm to dust have the most adverse effect, and such fines are generated by shipping and handling. Fines from 3 to 1mm also affect porosity but to a less extent, whereas particles from 6 to 3 mm have little effect. However, it is not practicable to remove fines smaller than minus 6 mm from stockpiled ores and coke because of the blinding of the screens, and true fines are therefore generally regarded as minus 6 mm.

For the highest furnace and smelting efficiency, complete charge preparation involving the screening of fines from the raw materials is essential. Such fines must be utilized in some form of agglomeration such as sintering, and must be returned to the furnace as a charge material.

SINTERING

Manganese-ore fines can be sintered readily in pans or on a stand type of machine to produce a hard sinter that has good physical properties as a constituent of the smelting charge. The sintering techniques are the same as for iron ore, but the machine is much smaller on account of the small tonnages involved.

Sintering at the smelting plant is preferable to sintering at the mine, because the friability of the sinter results in the formation of a high proportion of smalls and fines during shipping and handling. Sintering at the plant, in addition to permitting the complete preparation of raw materials, does not necessitate the manufacture of a hard sinter of maximum strength, as would be required for sinter that is to be shipped. A softer sinter can be produced at a faster rate and with less fuel because it needs to be only hard enough to withstand the handling from the machine to the furnace via the raw-material bins and charge proportioning.

In recent years, almost every manganese-smelting plant in Japan has installed a small sinter machine of from 8 to 18 m^2 grate area, or a capacity of some 200 to 500 tonnes per day, for sintering the fines screened from lumpy ores.

Sintering at the smelting plant enables complete raw-material preparation to be practised by the screening of ores and coke before charge preparation. The coke fines are utilized for the sintering of manganese-ore fines, and additional fines can be purchased from ore suppliers so that the sintering machine can be operated at full capacity.

In the sintering process, the manganese content of the sinter is increased by the loss on ignition. At the sintering temperature, MnO_2 dissociates to Mn_3O_4, and combined water is removed. In view of the lower state of oxidation of manganese in the sinter, the power consumption should theoretically be higher than when lumpy oxide ore is smelted because the prereduction of the higher oxides in the sintering process results in the loss, to the furnace, of heat from the exothermic reactions involved in the reduction of MnO_2 to Mn_2O_3 and of Mn_2O_3 to Mn_3O_4. This heat is fairly appreciable for reduction by solid carbon and much more so for reduction by carbon monoxide.

In practice, however, a proportion of good-quality sinter free from fines, especially in conjunction with other screened raw materials in the charge, results in a lower power requirement for smelting. This can be attributed to the increased porosity of the charge and its beneficial effects on gas distribution, which, owing to higher thermal efficiency, more than counteract the heat lost to the furnace in the sintering process.

Good results with power savings are being achieved with some 25 to 50 per cent sinter in the ore blend for ferromanganese production. Sintered low-grade ores are also very satisfactory for silicomanganese production.

OTHER METHODS OF AGGLOMERATION

Other methods, such as pelletizing and briquetting, for the agglomeration of manganese ores are possible.

The pelletizing of manganese ores is more difficult and costly than the pelletizing of iron ores. A high firing temperature is necessary, and pellets may tend to spall during the heating and subsequent cooling. Pelletizing at the manganese-ore mine seems more feasible than sintering, because good-quality, hard pellets would produce less fines during handling and shipping. However, if any appreciable degradation did occur, screening would be necessary before charge preparation.

Little is known about the behaviour of pellets in a large smelting furnace. However, pilot-plant tests have indicated an increase in the power requirement for the smelting of pellets compared with the smelting of lumpy ore.

Hydrothermal bonding in briquette form is another possibility. A small proportion of hydrated lime is mixed with the ore, and the briquette is heated at low temperature in an autoclave. Because of the low temperature, the manganese dioxide does not dissociate but is retained in the same form as in lumpy ore. In this respect, such briquettes could have an advantage over sinter or pellets in smelting because the heat of the exothermic reactions of reduction would not be lost to the furnace.

THE UTILIZATION OF FERROMANGANESE SLAGS FOR SILICOMANGANESE

The production of standard ferromanganese by the low-manganese or discard-slag process is practised only in special circumstances. Generally, it is most economical and satisfactory to produce a slag with a manganese content between 25 and 35 per cent and to utilize this slag as a principal charge material in silicomanganese manufacture.

With the increased demand for silicomanganese by steelmakers in recent years, there is generally no difficulty in utilizing the entire production of ferromanganese slag for silicomanganese.

The manganese content of the ferromanganese slag depends on local conditions of cost and alloy demand, and can be calculated on the basis of the minimum cost of combined ferromanganese and silicomanganese production or the greatest financial return on the sale of the products.

Ferromanganese slag for subsequent utilization in silicomanganese should be solid-cast, or preferably layer-cast from the furnace in layers approximately 75 mm thick. This results in a minimum of crushing and fines generation when the slag is being prepared for the charge. The slag is normally crushed to approximately minus 75 mm, and it is generally quite unnecessary to remove any fines because it is used in silicomanganese smelting, where the porosity of the charge is less important owing to the formation of less gas than in ferromanganese production.

THE UTILIZATION OF REMELT MATERIALS

Remelts are materials containing manganese or charge materials that can be recovered by recycling or inclusion in a furnace charge.

Examples of remelts are alloy fines generated in the crushing, screening, and handling of the products, mixtures of metal and slag from skimmers and tapping launders, mixtures of spilt raw materials and plant cleanings, and materials obtained from the digging out of a furnace for replacement or repair of the lining.

Alloy fines should be recycled or returned in the charge to a furnace or furnaces used for the same product, and should be included as a constant, weighed portion of the charge. Thus, it is most desirable that the alloy fines from one week's production should be returned for remelting during the next week. Such a relatively small portion of alloy fines does not affect furnace operation adversely, especially if the other charge materials are free from fines.

Other remelt materials of heterogeneous composition and fine sizing may tend to affect the operation of a standard ferromanganese furnace adversely. Because of the versatile nature of silicomanganese smelting, such materials can be returned with economic advantage to a silicomanganese furnace, preferably as a constant, weighed portion of a charge, without any effect on furnace operating conditions.

PREHEATING AND PREREDUCTION

Preheating is applied to nickel ores for ferronickel smelting on account of the high content of free and combined water, and, as for iron ore for the electric smelting of pig iron, preheating and prereduction can be applied to certain manganese ores to improve the smelting efficiency and heat balance and thereby increase the production rate of the installed furnace capacity.

Preheating can be done in shafts or rotary kilns. The mixed charge can be heated by the hot furnace gases passing through a number of shafts installed above the electric smelting furnace. Such shafts can be incorporated in the furnace-charging system, and have the advantage of preheating and drying the charge as well as collecting and recycling much of the furnace fume.

If a rotary kiln is used, the charge mixture of ore, flux, and coke is heated to approximately 1000°C, at which temperature free and combined water is driven off, limestone is calcined, and a certain amount of reaction between oxides and carbon takes place without fusion of the charge or formation of rings in the kiln. The preheated and prereduced charge discharges into an insulated surge bin, and is transferred in insulated containers to the furnace feed bins so that the charge enters the furnace with the maximum amount of sensible heat. A proportion of bituminous coal is fed to the kiln to maintain a reducing atmosphere, and larger quantities of coal can be included as a charge material. The coal forms a char, which, being a low-temperature carbonization product, has the advantage of high reactivity for prereduction and reduction.

Prereduction and preheating processes lower the power requirement for smelting in the furnace and correspondingly increase the rate of alloy production. Preheating can be applied to many manganese ores, but the ores most suitable for prereduction in the rotary-kiln process are the harder, lumpy ores having a relatively high loss on ignition from higher oxides and remaining stable without decrepitation on being heated.

THE DRYING OF RAW MATERIALS

All modern manganese-smelting furnaces are of the closed type, and the furnace gas is scrubbed for pollution control. Large quantities of gas are produced in electric manganese smelting, amounting to some 700 m^3 per tonne of standard ferromanganese, and most smelting plants have little or no use for the gas unless they are part of an integrated steelworks or are in an industrial area in which there is an opportunity for sale of the gas.

If the gas is a waste product, the furnace operating efficiency can be improved by the installation of dryers for coke and ores. The use of dried coke, especially in areas of high rainfall, is a distinct advantage because it results in a reduction in the power consumption and ensures more constant reducing conditions with easier control of the fixed carbon.

METALLURGICAL CONTROL

Maximum efficiency in smelting is possible with suitable selection and preparation of raw materials, but only in conjunction with close metallurgical control of the entire furnace operation, which ensures not only that the quality of the product is constant, but also that the highest metallurgical efficiency is maintained.

Metallurgical control is simplified by the minimization of the metallurgical variables that result from variations in the composition of the raw materials and the mix burden.

The most important control is that of fixed carbon, which not only is reflected in the constancy of the manganese content of the slag but also is dependent on many factors such as the moisture and fixed-carbon contents of the coke, the coke efficiency, the electrode penetration, the gas temperature, and the CO_2-to-CO ratio of the furnace gas.

Another essential control, as important as alloy analysis, is the composition of the slag, particularly its basicity, which is best expressed as the molecular ratio of base to acid. Once the most suitable slag composition and the molecular ratio of base to acid have been selected for the particular smelting operation, it is necessary to maintain the latter within narrow limits.

Close metallurgical control must be maintained at all times and is possible by constant attention to the charge mix, the furnace operating conditions, and the compositions of alloy and slag.

CONCLUSION

In a modern ferro-alloy plant, the success of manganese smelting is dependent on the selection of suitable raw materials, the stockpiling and preparation of such materials, accurate charge proportioning, and the metallurgical control of the furnace operation.

The preparation of raw materials, particularly the removal of fines, cannot be too highly stressed and is most important in large modern furnaces.

The removal of fines results in increased porosity of the charge and improved distribution of the furnace gas, which increases the thermal and metallurgical efficiencies of the furnace. It also avoids bridging and promotes uniform subsidence of the charge into the smelting zones.

Maximum thermal and metallurgical efficiencies result in the greatest output of alloy from the installed furnace capacity and in the minimum cost of the product.

For economic considerations, the complete utilization of all the raw materials is essential. This is made possible by the use of coke fines for the agglomeration of ore fines that are to be included in furnace charges, and all high-manganese slags from ferromanganese production must be completely utilized in the manufacture of silicomanganese.

DISCUSSION

Mr M. Sciarone[*]*:*

What is the specific power consumption of the high-carbon ferromanganese operation?

Mr Hooper:

For current cold-charge smelting with limited raw-material preparation, the power consumption is approximately 2500 units per tonne of 76 to 78 per cent manganese alloy.

Dr R. Urquhart[†]*:*

What is your opinion of the use of separate slag and alloy tapholes in ferromanganese production?

Mr Hooper:

I do not favour separate slag and alloy tapholes in manganese alloy production, because, in my opinion, this system does not have the advantages that are claimed for it. In fact, under certain conditions it is likely to have the disadvantage of some slag being tapped with the metal and some metal with the slag. My company prefers the single taphole system with a skimmer for efficient separation of metal and slag, followed by direct-layer casting of both alloy and slag without the use of a ladle.

Professor D.B. le Roux[‡]*:*

Please expand the statement, given in your paper, that magnesia is generally a more effective base than lime. The paper implies that material smaller than 1 mm cannot be removed from the raw material because of excessive blinding of the screens. I contend that screening at 1mm, even in the dry state, is possible by use of multiple-deck shaking and vibrating screens incorporating anti-blinding devices and suitable screen-cloth design. To what extent has this problem been investigated and what types of screen have been used?

Mr Hooper:

When the molecular basicity of the slag is calculated, MgO is divided by 40, which gives a higher number than lime does. In practice, correspondingly less dolomite than limestone is required for the same silicon control and, in addition, MgO has the effect of increasing the fluidity of the slag. I have not had experience with anti-blinding devices and special screen-cloth design. Conventional vibrating screens are used at Bell Bay to remove fines below 6 mm from manganese ore, and I feel that a smaller sizing would be unsuitable since those fines are used for the manufacture of silicomanganese. When the manganese-ore sinter machine is commissioned and complete raw-material preparation is practised, fines smaller than 6 mm will be suitable for sinter-plant feed.

Professor Howat[▽]*:*

Please comment on the relative proportion of production costs in ferromanganese production that is accounted for by (a) ores, (b) coke, (c) sintering and other preparation of charge, (d) power, and (e) labour.

Mr Hooper:

The relative proportions depend on local conditions, but raw materials account for by far the largest. Here are some approximate figures: ores 50 per cent, coke 10 per cent, sintering and other charge preparation 5 per cent, power 5 per cent, and labour 5 per cent, the remainder being for electrodes, stores, maintenance, and other services.

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