

DIRECT PRODUCTION OF FERROMANGANESE FROM GEMCO SAND CONCENTRATE AND COAL

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ABSTRACT

BHP has investigated a two-stage process for the direct production of ferromanganese from high grade sand concentrates (48-53% Mn) produced from tailings at BHP's GEMCo mine. The process consists of a fluidised bed pre-reduction first stage followed by a DC arc smelting furnace second stage. Reducing off-gas from the smelting stage is used to pre-reduce the MnO₂ concentrate to MnO in the fluid bed. The two stages have been demonstrated separately at bench scale and coupling of the two stages is seen as the next phase in the process development. A 200mm diameter bubbling fluidised bed has been used for producing 500kg of MnO from GEMCo sand concentrate. The MnO sand has then been smelted in a 100kW DC arc furnace using char and coal as reductant. Manganese recoveries of approximately 64% to alloy have been achieved with a alloy grades of 70-77% Mn (mean 75.3% Mn). Higher manganese recoveries are believed possible with process optimisation and scale-up.

1. INTRODUCTION

The Groote Eylandt Mining Company (GEMCo, a BHP subsidiary) produces a range of lump and fines ores from the large pisolitic manganese ore deposit on Groote Eylandt in the Gulf of Carpentaria in northern Australia. As part of the processing to obtain this ore, sand-sized tailings containing significant manganese units are produced. BHP has undertaken a programme of research to recover and utilise these manganese units. Beneficiation using gravity separation methods has been carried out at pilot scale to produce over 3000 tonnes of sand concentrate with a grade over 48% Mn and a nominal sizing of -0.5+1.0mm ($d_{43}=0.276\text{mm}$, $d_{32}=0.201\text{mm}$).

Approximately 2000 tonnes of the sand concentrate has been successfully introduced at levels up to 30% into the feed of the sinter plant at the BHP Manganese TEMCO works in Tasmania. Some higher grade material has also been evaluated as a potential alternative feedstock for electrolytic manganese dioxide (EMD) production at the BHP AMCL plant in Newcastle.

Declining traditional lump iron ore reserves during the last quarter of this century, coupled with the cost and environmental penalties associated with agglomeration processes (eg

sintering, pelletising, and coking), has resulted in interest being focussed on direct smelting technologies to replace traditional ironmaking process routes. Similar pressures exist in the ferromanganese industry and BHP Manganese Development has been examining the feasibility of direct smelting technologies in manganese ferroalloy production. The GEMCO sand concentrates have been targetted as a potential feedstock for any new direct smelting technology and this paper describes work undertaken at the BHP Research Laboratories (BHPR-NL) in Newcastle to develop such a process.

2. PROCESS OVERVIEW

The relative ease of reduction of Mn ores to MnO, and the highly reducing conditions required for reduction of MnO to Mn alloy, would suggest a two-stage process for the efficient direct production of ferromanganese. Carbothermic reduction is most efficiently carried out in an electric smelting unit. The hot reducing offgas (CO, H₂) can then be used to preheat, calcine and prereduce manganese ore and fluxes in a first stage reactor. A fluidised bed was identified as the most suitable technology for the first stage and a DC arc furnace as the most appropriate for accepting a fine feed in the second smelting stage. The proposed process is shown schematically in Figure 1 with the experimental results summarised in Figure 2.

3. PREREDUCTION THERMOCHEMISTRY

3.1 Reactions

The reduction of MnO₂ ores to MnO is characterised by favourable kinetics in a complex system with intermediate sub-oxides. Oxygen removal can result simply from thermal decomposition in air: MnO₂ → Mn₂O₃ (bixbyite) at temperatures above 450°C and Mn₂O₃ → Mn₃O₄ (hausmannite) over 900°C. The presence of quartz in the ore restricts fluidisation temperatures to around 900°C. This is due to the formation of molten silicates above 1000°C by fluxing of this free silica with alkaline earth and alkali oxides from the ore.

The thermodynamic equilibrium condition for the fluidised bed reduction process has been modelled using the CSIRO-SGTE Thermodata System CHEMIX Gibbs energy minimisation program[1]. Under all conditions in the presence of CO and H₂ the equilibrium reduction product is MnO. The reaction to MnO can proceed to completion by gaseous reduction, but much lower oxygen potentials are required to yield manganese metal.

Iron oxides contained in the ore can be reduced from hydrated oxides or Fe₂O₃ (hematite) to Fe₃O₄ (magnetite), "FeO" (wüstite, Fe_{0.947}O) or metallic iron, depending on the prevailing (CO+H₂)/(CO₂+H₂O) within the bed. The oxidation state of iron can impact on the reductant stoichiometry of downstream processing and is critical in processes such as EMD production, where ferrous oxide is required for efficient acid digestion of MnO.

Overall the reaction is exothermic and can be sustained by correctly matching the ore feed rate, fluidising gas flow rate and the reactor heat losses. In practice, a balance must be maintained between avoiding distributor blockages in the fluidised bed due to premature soot generation (especially below 700°C) and liquid silicate formation, with subsequent defluidisation, at high temperatures. Metallisation of iron oxides is only exothermic for CO reduction, so any iron oxide reduction by H₂ absorbs heat.

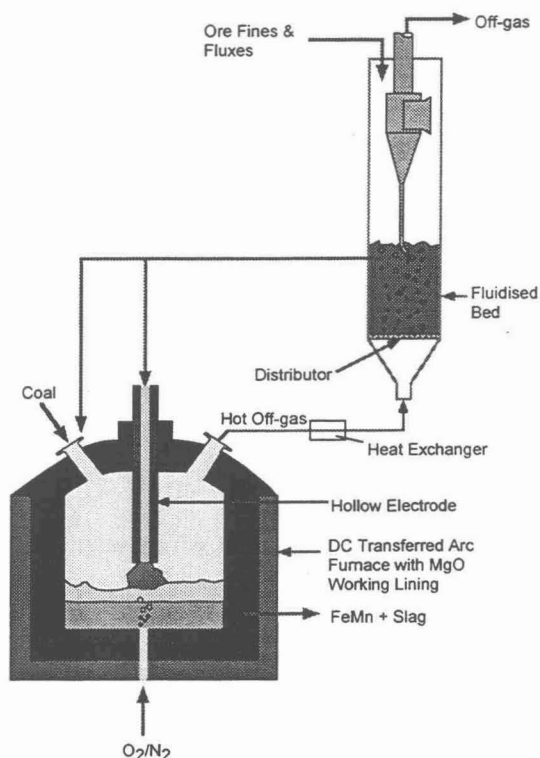
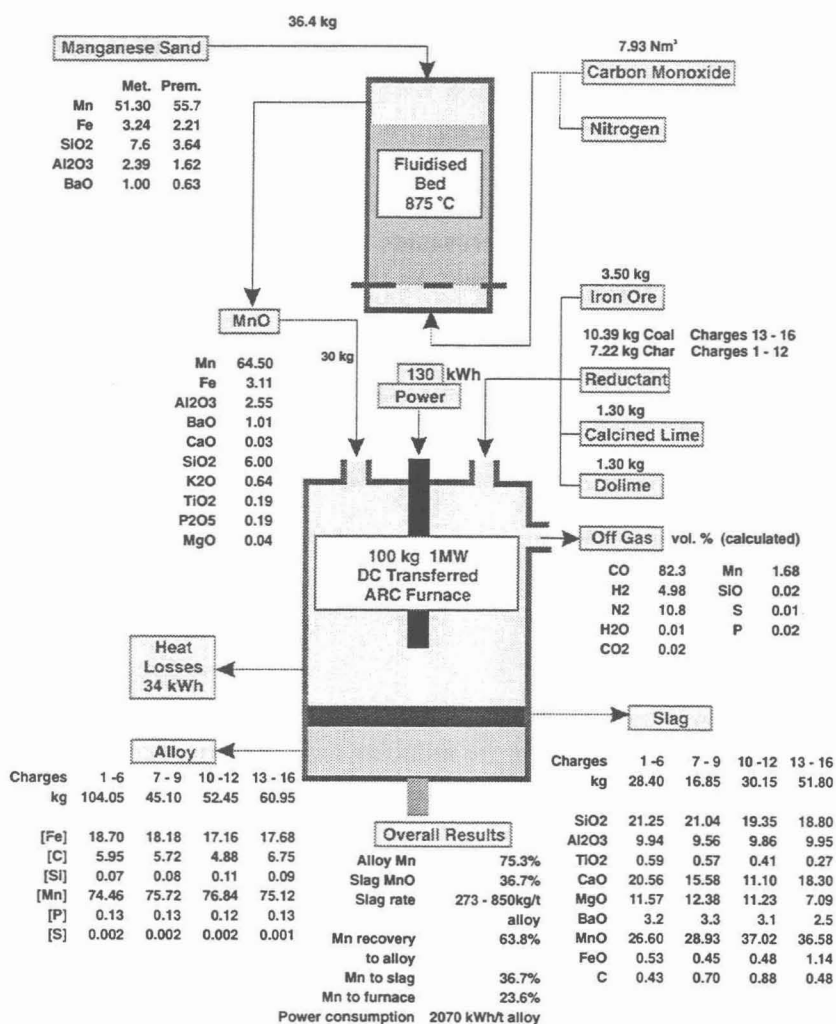


FIG. 1 BHPR-NL Process for Direct Reduction of FeMn from Ore Fines and Coal

FIG. 2 Results of Pilot Smelting Trial Using MnO Made from GEMCO Sand Concentrate Basis is 30kg Charge of MnO Sand, Analyses in wt. %



Large localised adiabatic temperature rises can occur where MnO_2 enters the bed, so it is important to limit the feed rate, maintain sufficient bed inventory and promote good backmixing to ensure rapid dissipation of this heat and avoid exceeding silicate liquidus temperatures.

3.2 Kinetics

Analysis of MnO_2 reduction kinetics is difficult due to the competing decomposition and reduction reactions. Determining rate constants for each reaction step is complicated by the need to reach reaction temperature without significant decomposition occurring. Hence the current approach has been to determine empirical rate constants for the overall reaction rather than the more mechanistic intrinsic rate constants.

In previous differential experiments conducted at BHPR-NL, GEMCo ore was found to undergo topochemical reduction under CO to manganosite:



Gaseous mass transfer in the product layer appeared to be rate-controlling for $-6.3 + 4.0$ mm ore at 900°C , although the large amount of scatter in the data due rapid rate, size degradation and reoxidation during sampling only permitted apparent rate constants to be determined using an empirical continuous model. With smaller particles under differential conditions, a single particle shrinking core model can be replaced with a continuous-reaction type reduction model. Typical apparent rate constants for the coarser ore range from approximately 0.1 min^{-1} ($p\text{CO} = 0.1 \text{ atm}$, 600°C) through 0.2 min^{-1} ($p\text{CO} = 0.55 \text{ atm}$, 750°C) to 0.6 min^{-1} ($p\text{CO} = 1 \text{ atm}$, 900°C). Gravimetric kinetic studies carried out at the University of Queensland for BHP[2] show that the specific first order kinetics rate constants for coarse GEMCo sand (0.925 mm diameter) are considerably higher, with a dependency on temperature given by the following correlations:

CO Reduction	$\log_{10}k = 0.8315 - 727.4/T \text{ min}^{-1}$	$k = 1.63 \text{ min}^{-1} \text{ at } 900^\circ\text{C}$
H ₂ Reduction	$\log_{10}k = 1.0237 - 581.0/T \text{ min}^{-1}$	$k = 3.37 \text{ min}^{-1} \text{ at } 900^\circ\text{C}$

For the size range 0.85 to 5.6 mm, the rate constants vary linearly with particle diameter d (mm):

CO Reduction at 900°C	$k = 1.7904 - 0.1812d \text{ min}^{-1}$
H ₂ Reduction at 900°C	$k = 3.7289 - 0.384d \text{ min}^{-1}$

Therefore the sand-sized ore can be expected to react very rapidly, especially if hydrogen is also present with carbon monoxide in the reducing gas. Figure 3 summarises the experimental rate data.

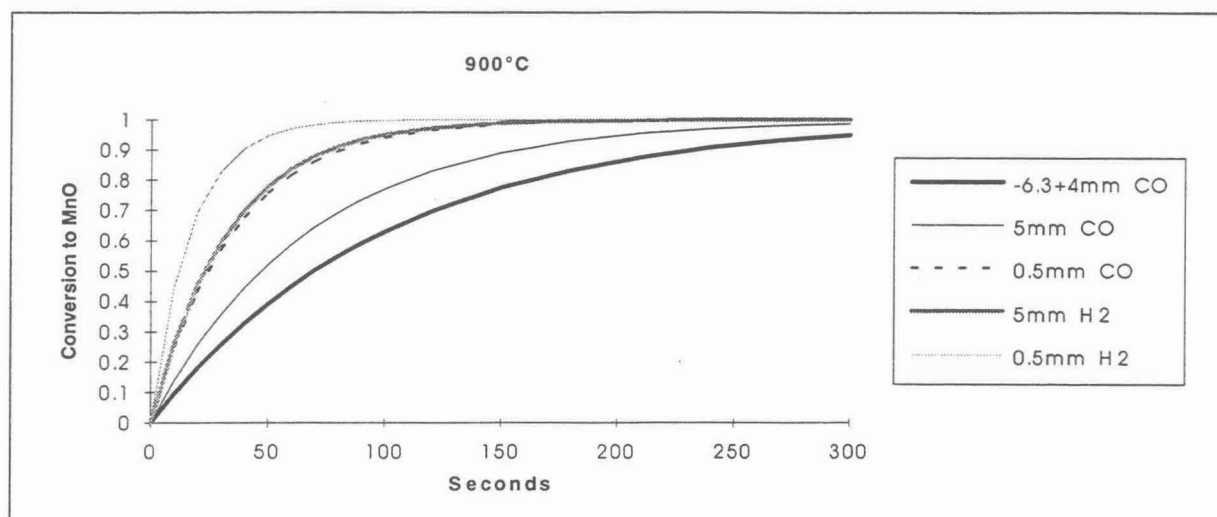
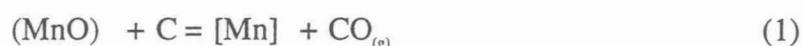


FIG 3: Predicted Conversion to MnO in a Continuous Fluidised Bed - Based on an Empirical First Order, Single Particle Continuous Reaction Model.

4 SMELTING THERMOCHEMISTRY

4.1 Equilibrium Considerations

The smelting reaction is carbothermic reduction of MnO. The carbon source may be solid reductant (coke, char, or coal) or dissolved carbon in iron;



The CSIRO-SGTE Thermodata System[1] has also been used for modelling the smelting stage of the process. However, the CHEMIX free energy minimisation routine has been customised to incorporate the activity coefficient data of Lee and Downing (1980)[3] for slags and the data of Dresler (1989)[4] for ferromanganese alloy. The calculated results for typical experimental conditions gives the equilibrium gas compositions used in Figure 2. The predicted alloy compositions range from typical high carbon grades to lower carbon alloy as the slag oxidation state increases (slag MnO rises with decreasing carbon charged relative to stoichiometric requirements). Slag make ranges from 232kg/t alloy to 606kg/t alloy, depending on the amount of unreduced MnO and the gangue content of the reductant (with a high basicity slag practice, each increment in reductant ash silica requires extra fluxing). Manganese vapour can be expected to constitute between 1.2% and 1.9% by volume of the exhaust gas under the conditions prevailing at 1550°C according to the model.

4.2 Slag Chemistry

The first criterion for selection and optimisation of slag chemistry is compatibility with the process and furnace refractory lining. Previous work with steelmaking slags[5] has shown that magnesia-carbon refractory lining life can be prolonged using slags which are slightly oversaturated with an MgO-bearing phase such as magnesio-wustite, $(\text{Mg,Fe})\text{O}$. The same

philosophy was applied to the ferromanganese smelting process, although the phase in question is $(\text{Mn,Mg})\text{O}$ - or magnesian manganosite. It is known that higher basicities tend to decrease magnesia solubility, as well as improve the manganese partition ratio between slag and metal towards the alloy. However, fume losses may be greater[5,6].

As a result, the approach to the formulation of slag chemistry has been to aim for slags more basic $(\text{CaO}+\text{MgO}+\text{BaO})/\text{SiO}_2 = 1.6$) than used in submerged arc ferromanganese production $(\text{CaO}+\text{MgO})/\text{SiO}_2 = 0.6$)[7], which are chemically neutral to a magnesia lining.

5 EXPERIMENTAL

5.1 Fluidised Bed Prereduction

A bubbling fluidised bed of diameter 200mm and height 1000mm with a nominal capacity of 30kg of GEMCO sand concentrate (600mm bed height) was designed and constructed at BHPR-NL. The bed, made from 316 stainless steel, was externally heated by radiation from an inductively heated graphite sleeve.

The MnO feedstock for the smelting runs was produced by semi-batch fluidised bed reduction of MnO_2 sand concentrate according to the following procedure:

1. Feeding 35kg of dried MnO_2 sand concentrate to the bed via the feed port.
2. Calcining MnO_2 to Mn_2O_3 by heating to 800°C using N_2 fluidising gas.
3. Introducing CO into the fluidising gas to reduce the calcined bed contents to MnO .
4. On completion of reaction (determined by presence of CO in the exit gas), flushing with N_2 fluidising gas before pneumatically transferring the bed contents into a water-cooled product bin.
5. Cooling the MnO product to $<80^\circ\text{C}$ under N_2 in the product bin before removing for storage.
6. On completion of the transfer, the next batch of MnO_2 sand was immediately fed to the reactor along with elutriated fines from the previous run, and the process repeated.

A total of 503kg of material was produced with a typical grade of 83.3% MnO . CO utilisation was essentially complete, being typically greater than 99%. The bed has been found to be well mixed and isothermal. Due to the exothermic nature of the reaction, the heating requirement, once the bed is at temperature is small, compensating only for heat losses. For the current laboratory scale equipment, the production rate is limited by the flow rate of reducing gas into the bed and the batch nature of the operation. Gas velocity is restricted by entrainment constraints and could be increased by the inclusion of a suitably designed disengagement freeboard above the bed and a dust recycle cyclone.

5.2 Smelting MnO to FeMn

The BHPR-NL 100 kg arc furnace uses a 50mm graphite cathode and a steel ring anode located in the refractory. The furnace shares a 1 MVA power supply with a 1 tonne unit and is operated typically up to 100kW. For the FeMn smelting programme an alumina backing lining and magnesia working lining were used. Charging of materials was by rotating pipe feeders through two individual feed ports located diametrically opposite to each other.

A total of 16 charges, each of 30kg MnO, were prepared using the 200mm bubbling fluidised bed as described above. The smelting campaign ran for a total duration of approximately 58 hours, including the furnace preheat phase (using a HC FeMn heel). The operating conditions, product analyses and mass balance data are summarised in Figure 2.

Of particular note was the fact that no significant change to operations was observed when the reductant was switched from char to coal. The char used was made from Victorian lignite, and has 92% C and 4.2% volatile matter. The coal is 77.8% C, 13% ash and 19.5% volatile matter and originates from the Metropolitan Colliery on the south coast of NSW. The gas make appeared to be similar for both reductants with fume loss around 20%. A noticeable increase in slag volume did result from the use of coal, however, this was no greater than that expected from the charge calculation which included the contribution of the increased ash content in the coal.

6. RESULTS OF 100 kW DC SMELTING OF FeMn FROM MnO SAND

6.1 Alloy Grade, Manganese Recovery

The results of the pilot smelting trial are presented in Figure 2. Unlike the Mintek[6] trials, iron ore had to be added to the BHPR-NL charges to raise the alloy Fe to existing market specification levels. With lower iron ore additions, alloy grades in excess of 80% Mn would be achievable, although market research would be required to determine demand.

Alloy Component	Range wt.%	Average wt.%	Mn Recovery %
Mn	70.4-77.1	Alloy 75.3 Mn	63.8
Fe	16.2-24.5	Slag 36.7 MnO	12.6
C	3.9-7.0	Offgas Losses	23.6 (by difference)
Si	0.03-0.18	Power Consumption	2070kWh/t alloy at 33-35kW heat losses
P	0.11-0.20	Electrode Consumption	5.2-6.3kg/t alloy
S	0.001-0.008		

The alloy grades are similar to those achieved at Mintek[6], where a maximum of 63% recovery to alloy was obtained at a basicity of 1.6 at the 100kVA scale. For a typical submerged arc process (TEMCO), a recovery of 79.5% Mn to the alloy is achieved at the 18-25 MW scale[7]. Manganese losses are a combination of those due to entrainment of feed, as well as manganese fume, contained in the exhaust gas. It is also important to note that the larger the scale of operation, the smaller is the contribution to fume loss by volatilisation in the arc impingement area, whose ratio to the total surface area of the bath decreases.

6.2 Slag Chemistry

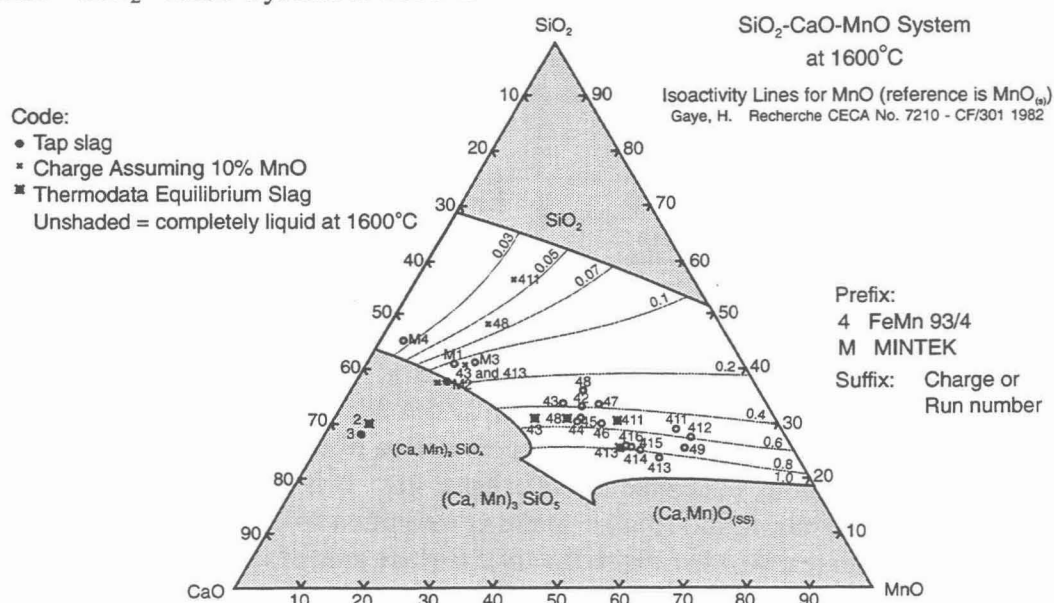
The slag chemistries are best summarised on the CaO - SiO₂ - MnO ternary phase diagram, shown in Figure 4. This diagram was originally compiled by Glasser[8] and later modified by Gaye[9] to show activity data for MnO. The phase boundaries and activities shown are for a temperature of 1600°C. By normalising slag compositions in terms of these three components, run data has been plotted (FeMn93) with that for the Mintek trials and equilibrium slags as calculated by the Thermodata model. Slags appearing on the left side of

the diagram are grouped around the 10% MnO aim compositions in addition to those obtained in the Mintek work. Such slags have liquidus temperatures in the range 1350-1500°C[8] and MnO activities less than 0.2. The FeMn93 slags are grouped in the higher MnO part of the diagram which has liquidus temperatures in the range 1200-1500°C.

In general, slags were quite fluid when tapped, but tended to froth until solidified. This indicates that reaction was continuing and CO gas evolving. With an objective of optimising the process to minimise manganese losses to the slag, ultimate slag MnO levels of ca.10% are envisaged. While this level of MnO has been allowed for in the run charges, levels closer to 20-40% (see Figure 4) have been more common due to insufficient time for complete processing. As the work at Mintek has shown[6], low MnO levels can be achieved by a simple extension of the heating time at the conclusion of feeding. The CHEMIX data also suggest that the level of reductant in the charge should be increased if the Mintek results[9] are to be reproduced. However, as a means of producing low [Si], low [C] alloy, it appears from the results that this can be achieved with acceptable recoveries to the alloy. A lower critical carbon level in the alloy would be an advantage in the production of medium carbon ferromanganese.

Apart from the MgO and MnO levels, which are refractory and process dependent, respectively, the remainder of the slag components, with the exception of SiO₂, are present in amounts proportional to those in the charged feed stocks. The high basicity slag practice has resulted in favourable silicon partition to the slag, giving very low alloy Si levels (< 0.2%). The presence of SiO gas may also contribute to minor amounts of silica fume generation.

FIG. 4 CaO - SiO₂ - MnO System at 1600°C



As the data of Figure 4 is limited to the normalised ternary coordinates, a check of the applicability of the MnO activity data for more complex systems containing minor oxides was made. This was done using recently available data in the form of the Kapoor and Froberg Slag Model (KFS)[10]. A close agreement was obtained using the KFS model, confirming the suitability of using the ternary data for this system.

6.3 Slag Mineralogy

In general, slags from the FeMn93 runs have the following features;

- dendritic and finely globular oxides, in the manganosite (MnO) - periclase (MgO) solid solution series, spinel (MgMn)Al₂O₄, FeMn globules, graphitised char or coal, and minor spinel.
- fine to coarse groundmass of crystalline silicate, in the dicalcium silicate (Ca₂SiO₄) - glaucocroite (CaMn)₂SiO₄ - tephroite (Mn₂SiO₄) solid solution series, minor gehlenite and high or low BaO glass.

Accessory phases periclase, spinel, gehlenite occur both in the slag groundmass and as coarser grains similar in size to the dendritic manganosite. There is no evidence of coarse precipitated phases apart from mangoan periclase globules, some of which have rims rich in MnO (Charges 15 and 16). This indicates that the slags have been almost fully liquid, with MgO-bearing oxide phases being the only likely solid phases to have existed at operating temperatures. The observed effective saturation of slags in MgO, as indicated by the degree of lining protection achieved with slag MgO levels below 15%, is, however, consistent with the presence of early formed dendritic and globular magnesian manganosite.

FeMn alloy occurs in all tapped slags as discrete prills, fine spheroids within or adjacent to oxide globules, and globular masses adhering to graphitised reductant. While some of the spot SEM analyses of these alloy inclusions give analyses similar to that of the bulk tapped alloy, many are iron-rich and may be mixtures of metallic iron reduced from the iron ore with manganese from the reduced MnO sand. Where alloy analyses do not sum to 100%, carbon up to saturation level can be assumed, as carbon was not determined in the SEM analysis.

Little evidence of reaction mechanisms is apparent in the SEM analysis apart from the obvious alloy formation adjacent to graphitic reductant as well as within magnesian manganosite globules. The presence of high iron content alloy within globules of magnesian manganosite does suggest that reduction of MnO by carburised iron has occurred, via the following reaction:



Given that iron oxide is more readily reduced than MnO, it is likely that iron ore will react rapidly to form a metallic phase with some dissolved carbon, which can then become an additional reducing agent for MnO in the slag.

6.4 Slag Volume

A characteristic of the process is its potential low slag volume. From Figure 2 the slag rate can be seen to vary from 273kg/t using char reductant at high basicity to 850kg/t using Metropolitan coal at a lower basicity. The flexibility in using fine feed stocks means that high fixed carbon, low ash reductants can be used without having to satisfy coking criteria. While the Metropolitan coal (13% ash) has been used for demonstration of the effectiveness of coal as a reductant, more suitable low ash reductants would be chosen in industrial practice. A low volume slag practice enables higher MnO levels to be tolerated without significantly affecting manganese recovery to the alloy.

7. CONCLUSIONS

A two-stage process for the production of ferromanganese directly from ore fines and char/coal has been developed at BHPR-NL using a 200mm diameter bubbling fluidised bed to prereduce GEMCO sand concentrate to MnO, which is then smelted in a 100 kW DC arc furnace, using char or coal as a reductant. Each stage has been demonstrated separately, with process integration seen as the goal of the next phase of development.

Manganese recoveries of approximately 64% to alloy (24% offgas losses) have been achieved with a mean alloy grade of 75.3% Mn at a power consumption of 2070kWh/t alloy. Higher manganese recoveries are believed possible with process optimisation and scale-up. To produce traditional high carbon ferromanganese alloy grades, GEMCO sand concentrates require dilution with iron ore. Alloys with Mn grades in excess of 80% should be attained with high grade GEMCO sand concentrate, without iron ore additions. The DC furnace smelting of the prereduced MnO sand offers independent slag chemistry control as the process is not constrained by slag resistivity considerations.

8. ACKNOWLEDGEMENTS

The authors gratefully acknowledge the technical assistance of T.Hetherington, S.Forrester, A.McCabe, P.Grazier, R.Gee, R.Mead, W.Hilkman, M Mason and B.England (SEM analysis), and also wish to thank the BHP Co.Ltd. for permission to publish this paper.

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