Slag–metal equilibrium in the production of low-carbon ferromanganese

by N. A. BARCZA*, Ph.D. (Wits.) (Member)

SYNOPSIS

An investigation was conducted into the reactions between the slag system $MnO-CaO-MgO-SiO_2-(Al_2O_3)$ and the alloy system Mn–Fe–Si–(C). Synthetic slags representative of plant melts and a plant alloy were reacted in alumina crucibles at temperatures of 1400°C, 1450°C, 1500°C, and 1600°C. In similar experiments, slags were used that comprised a South African manganese ore with various amounts of lime and several synthetic alloys with various silicon contents and manganese-to-iron ratios. These experiments were conducted in a vertical molybdenum-wound resistance furnace with full temperature control. Slag-to-alloy ratios were also varied during the tests.

The rate of reduction of Mn_2O_3 and the MnO from the slag by the silicon in the alloy was extremely rapid, most of the reaction being completed within five minutes. The strongly exothermic nature of the reaction resulted in considerable generation of heat at the slag–alloy interface, causing convectional stirring of the contents of the crucible and promoting the rate of reaction.

Equilibrium was usually attained after fifteen minutes. The major limitation governing the recovery of manganese is the need for the silicon content of the alloy to meet a maximum specification of 2 per cent. Higher concentrations of silicon in the final alloy of between 8 and 12 per cent favour good recoveries of manganese from the slag, but, since such an alloy is not salable, lower recoveries must apparently be tolerated. In alloys of 2 per cent silicon, low activities of the silicon are responsible for poor recoveries of manganese.

The activity of MnO in the slag can be increased by moderate additions of CaO and small amounts of MgO, i.e., by an increase in the basicity of the slag.

SAMEVATTING

Daar is ondersoek ingestel na die reaksies tussen die slakstelsel $MnO-CaO-MgO-SiO_2-(Al_2O_3)$ en die legeringstelsel Mn–Fe–Si–(C). Sintetiese slakke wat verteenwoordigend is van aanlegsmeltings en 'n aanleglegering is in alumina-kroesies by temperature van 1400°C, 1450°C, 1500°C en 1600°C met reagense behandel. Slakke bestaande uit 'n Suid-Afrikaanse mangaanerts met verskillende hoeveelhede kalk en verskeie sintetiese legerings met 'n verskillende silikoninhoud en mangaan/ysterverhouding is in dergelike eksperimente gebruik. Hierdie eksperimente is uitgevoer in 'n vertikale weerstandsoond met 'n molibdeenwikkeling met volle temperatuurbeheer. Die verhouding tussen die slak en legering is ook gedurende die toetse gewissel.

Die reduksietempo van Mn_2O_3 en die MnO uit die slak deur die silikon in die legering was uiters vinnig en die grootste deel van die reaksie is binne vyf minute voltooi. Die sterk eksotermiese aard van die reaksie het 'n aansien-like ontwikkeling van hitte by die slak–legeringtussenvlak tot gevolg gehad wat konvensionele roering van die inhoud van die kroesie veroorsaak het en die reaksietempo verhoog het.

Ewewig is gewoonlik na vyftien minute bereik. Die belangrikste beperking op die herwinning van mangaan is die vereiste dat die silikoninhoud van die legering aan 'n maksimum spesifikasie van 2 persent moet voldoen. Hoër silikonkonsentrasies van tussen 8 en 12 persent in die finale legering bevorder goeie mangaanherwinnings uit die slak, maar aangesien so 'n legering nie verkoop kan word, moet laer herwinnings blykbaar aanvaar word. In legerings met 2 persent silikon is die lae aktiwiteit van die silikon verantwoordelik vir die swak herwinning van mangaan.

Die aktiwiteit van MnO in die slak kan verhoog word deur matige byvoegings van CaO en klein hoeveelhede MgO d.w.s. deur die basisiteit van die slak te verhoog.

Introduction

In 1974, Mikolajczak[1] predicted an increased demand for refined ferromanganese alloys due to increased use of the Linz–Donawitz (L.D.) process, as well as increased production of thinner finished steel products necessitating the use of manganese alloys with low-carbon contents. At that time, South Africa was rated as the sixth largest producer of medium-carbon ferromanganese by the Perrin[2] process. At the beginning of 1974, the two 1,2 MV.A furnaces that had been used to produce low-carbon ferromanganese in South Africa were closed down because the operation was not economically feasible. At that time it was realized that there was a lack of fundamental knowledge in this field, and the Pyrometallurgy Research Group of the National Institute for Metallurgy (NIM) was asked by the Technical Subcommittee of the South African Ferro Alloy Producers' Association to undertake an investigation into the relations between slags and alloys associated with the production of low-carbon ferromanganese.

The objects of this research were to determine the rate of reaction between the slags and alloys associated

with low-carbon ferromanganese, and to measure the state of equilibrium attained. A further important problem requiring investigation was the oxidation of the slag, and to some extent of the metal. A range of synthetic manganese oxide slags and slags based on manganese ore were used in conjunction with several synthetic ferromanganese alloys and a typical alloy from a ferromanganese plant. The ferro-alloy industry was particularly interested in the recovery of manganese and the utilization of silicon.

As the slag and the alloy phases are complex, a mass-transfer model was devised for the reaction between the slag and the alloy relating to the transfer of manganese from the slag to the alloy and the transfer of silicon from the alloy to the slag. This model permits the final chemical composition of both the slag and the alloy to be determined if the initial compositions of both phases and the change in mass of the alloy as a result of the mass transfer during reaction are known. The model was extended to cover the various stages of reaction between the phases and to include the simultaneous reduction or oxidation of the slag phase by a gaseous phase. The initial oxidation state of the manganese before any reaction occurred between the slag and the metal was

*National Institute for Metallurgy, Randburg, Transvaal.

studied in the preliminary investigation of the slag-forming components.

Choice and Preparation of Materials

The compositions of most of the slags were chosen to represent industrial slags associated with the production of medium-carbon ferromanganese by the Perrin[2] process as well as the single-stage low-carbon ferromanganese process that has been abandoned in South Africa. In this process, manganese ore, burnt limestone, and ferromanganese silicide are reacted simultaneously in a small electric-arc tilting furnace by a batch process.

A typical South African manganese ore, i.e., Mamatwan ore, was used in the preparation of several slags. Ferromanganese silicide from an actual plant was used for many of the reactions, but several synthetic alloys were used in this investigation to demonstrate the effect of variations in the silicon content and of the manganese-to-iron ratio on the recovery of manganese.

The non-stoichiometric behaviour of MnO was studied by Davies and Richardson[3] but, for the conditions related to this field of investigation, there was some uncertainty about the oxidation state of the manganese in the slag phase. In the present investigation, preliminary tests were carried out on the deoxidation behaviour of MnO_2, since this oxide was selected as the source of manganese oxides for the slag phase. MnO_2 was chosen because the exact quantity of manganese in the slag could be determined easily by calculation of the amount of manganese in the MnO_2. Furthermore, the amount of oxygen removed (or deoxidation) during the making of a slag premelt could be determined and, hence, the oxidation state of the manganese could be calculated. The synthetic slags were prepared by the weighing of pure chemical compounds to make up a total mass of

TABLE I

CHEMICAL COMPOSITIONS (%) OF MAMATWAN ORE AND SYNTHETIC SLAGS

Constituent	Mamatwan ore		Lime-ore melt (standard slag)	High-grade slag
	Uncalcined	Calcined at 1200 °C* (mass loss from ore = 17,4)		
MnO_2	32,7	—	55	30
MnO	25,0	—	—	—
Mn_3O_4	—	66,2	—	—
H_2O	2,9	—	—	—
CO_2	13,6	—	—	—
Fe_2O_3	6,0	7,3	—	—
CaO	12,1	14,6	35	35
MgO	2,3	2,8	5	5
Al_2O_3	0,2	0,2	—	—
SiO_2	4,8	5,8	5	30
Mn	39,4	47,7	34,8	18,9
Fe	4,2	5,08	—	—
†CaO/MgO	Standard	5,2	7,0	7,0
‡(CaO + MgO)/ SiO_2	ratios used	3,0	8,0	1,3

*Mass loss from ore = 17,4%.
†The CaO/MgO ratio in the synthetic slags representing the lime-ore melt was varied from 7:1, 3:1, 1,5:1, and 1:1, and in the high-grade slag from 10:1, 8:1, 3:1, 1:1, and 0,33:1.
‡The (CaO + MgO)/SiO_2 ratio in the synthetic slags representing the lime-ore melt was not varied, but in the high-grade slag the following ratios were used: 6:1, 3,67:1, 2,5:1, 1,8:1, 1,33:1, 0,75:1, and 0,4:1.

TABLE II

CHEMICAL COMPOSITIONS (% BY MASS) OF THE PLANT ALLOY AND VARIOUS SYNTHETIC ALLOYS OF FERROMANGANESE SILICIDE

Alloy no.	Si	Fe	Mn	Si/Mn
Plant*	22,5	11,1	65,2	0,35
1*	5	10	85	0,06
2*	10	10	80	0,13
3*	20	10	70	0,29
4*	30	10	60	0,50
5*	50	10	40	1,25
6*	70	10	20	3,5
7*	100	0	0	—
8†	10	18	72	0,14
9†	20	16	64	0,31
10†	30	14	56	0,54
4†	50	10	40	1,25

*Fe content constant at 10%, Mn/Fe ratio variable.
†Fe content variable, Mn/Fe ratio constant at 4.

25,0000 g. These slags can be divided into four groups, as follows:

(1) lime–ore melts (approximately 50 per cent MnO),
(2) high-grade slags (approximately 30 per cent MnO), which are slags used for reaction purposes,
(3) low-grade slags (15 to 20 per cent MnO), and
(4) discard slags (less than 15 per cent MnO), which are slag products.

Lime–ore melts are associated with the Perrin[2] process, high- and low-grade slags are produced in electric-smelting furnaces for the production of high-carbon ferromanganese, and discard slags are produced by furnaces for the production of ferromanganese silicide in which the MnO content can be as low as 5 per cent. The low-grade slag can be regarded as being representative of the final slag composition from the process for the production of low- to medium-carbon ferromanganese. The complete analyses for the range of slags used in the experiments and those for the Mamatwan ore are shown in Table I, only those for the discard and low-grade slags being omitted. The predried pure chemical components comprising the three slags used were weighed in the proportions shown in Table I and then mixed thoroughly in a pestle and mortar. The ore-based slags were prepared by weighing of the components on a chemical balance and mixing in a pestle and mortar. The Mamatwan ore was crushed to material smaller than 100 mesh (Tyler). The only component added to these ore-based slags was pure CaO in the following proportions: 10, 20, 30, and 40 per cent by mass. An ore melt consisting solely of Mamatwan ore was also prepared to demonstrate the reaction of an unfluxed ore with ferromanganese silicide.

All the premixed slag-forming components were stored in a desiccator until required for premelting. The slag-forming powders were added to an alumina crucible and were weighed on a chemical balance. To form the premolten slag, the crucibles and their contents were subsequently heated to 1500 °C in a small chamber furnace. Prior to the fusion process, all the volatile constituents (i.e., carbon dioxide and water) were removed from the ore and the MnO_2 and other higher oxides of manganese in the ore were thermally deoxidized. It has been shown[4] that Mamatwan ore consists essentially of braunite, hausmannite, and some calcite.

The industrial ferromanganese silicide was crushed to material smaller than 100 mesh; its chemical composition (in per cent by mass) was as follows: manganese 65,2, silicon 22,5, iron 11,1, and carbon 0,47. The synthetic alloys were made from pure metallic powders that were weighed on a chemical balance in the proportions shown in Table II. The total mass of the metal was 12,50000 g. The metal powders to comprise the alloys were premelted in alumina crucibles in a vertical molybdenum-wound resistance furnace at a temperature of 1500 °C in a reducing atmosphere of hydrogen and nitrogen in a ratio of 0,33. The alloy was then crushed to material smaller than 100 mesh before being reacted with the slag.

Experimental Techniques

The thermal behaviour of the manganese oxides during the premelting of the slag phase was studied with the aid of a Stanton thermal microbalance. The balance has full atmosphere control and was operated at a controlled heating cycle from room temperature to 1500 °C at the rate of 6,7 °C per minute. Hahn and Muan[5], who studied phase equilibria in the system Mn_2O_3–Mn_3O_4–MnO, mention that the various oxides of manganese are stable crystalline phases that can be converted from one oxidation state to another by variation of the temperature and of the partial pressure of oxygen. The present investigation of the high-grade and standard slags and Mamatwan ore was aimed at a determination of the degree of deoxidation of the higher oxides of manganese. Samples of 5,000 g were used for these tests, the samples being placed in small, fine-grained, low-porosity recrystallized-alumina crucibles and heated in a thermal balance. The crucibles were cylindrical, being 40 mm in height and 30 mm in inside diameter.

The tests involving the reaction between the slags and the alloys were carried out in a vertical molybdenum-wound resistance furnace. The chosen mass of alloy was placed on top of the premolten slag in the alumina crucible, which had been reweighed after the premelting stage. The total mass of the crucible, the slag, and the alloy was recorded, and the crucible was placed in a graphite holder. The holder was then raised slowly into the furnace, which was flushed continually with spectrographically pure argon. After the crucible and its contents had reached a temperature between 1200 °C and 1250 °C (i.e., below the liquidus temperatures of both the slag and the alloy) while being held in the furnace tube immediately below the hot zone, the crucible was rapidly introduced into the hot zone. The preset temperature of this zone was 1500 °C for most of the tests, although temperatures of 1400 °C, 1450 °C, and 1600 °C were also used.

The furnace temperature was controlled by a Eurotherm phase-angle thyristor unit on which adjustments can be made for temperature overshoot, temperature undershoot, and current limit, as well as temperature control by way of a Pt–6% Rh/Pt–30% Rh thermocouple positioned above the sample in the centre of the reaction tube in the central region of the hot zone. A second thermocouple of the same type, which was used to monitor the temperature of the sample from beneath

the crucible, was introduced by way of the support rod for the graphite-crucible holder. The apparatus is illustrated in Fig. 1.

It was assumed that the reaction between the slag and the alloy had commenced when the surface of the molten alloy had disappeared beneath the slag. Very little reaction took place during this incubation period preceding the sinking of the alloy through the slag layer. The reaction was studied through the observation port at the top of the furnace work tube, and it was seen that considerable stirring of the contents of the crucible took place due to the strongly exothermic nature of the reaction.

During the raising of the sample-holder and the crucible plus contents into the hot zone of the furnace, a drop in temperature of approximately 25 °C occurred within the hot zone. However, the preset temperature was rapidly restored because of the relatively large heat capacity of the furnace and the quick response of the thyristor unit, which increased the power input to the furnace to meet the sudden demand created by the shock introduction of the sample-holder and crucible plus contents. Some overheating of the sample environment also took place during the exothermic stage of the reaction, although temperatures much higher than 20 °C above the preset value seldom occurred. However, this overheating within the slag and the alloy phases appeared to generate temperatures far above the 20 °C measured externally from the crucible, and this sharp increase in temperature had a marked influence on the
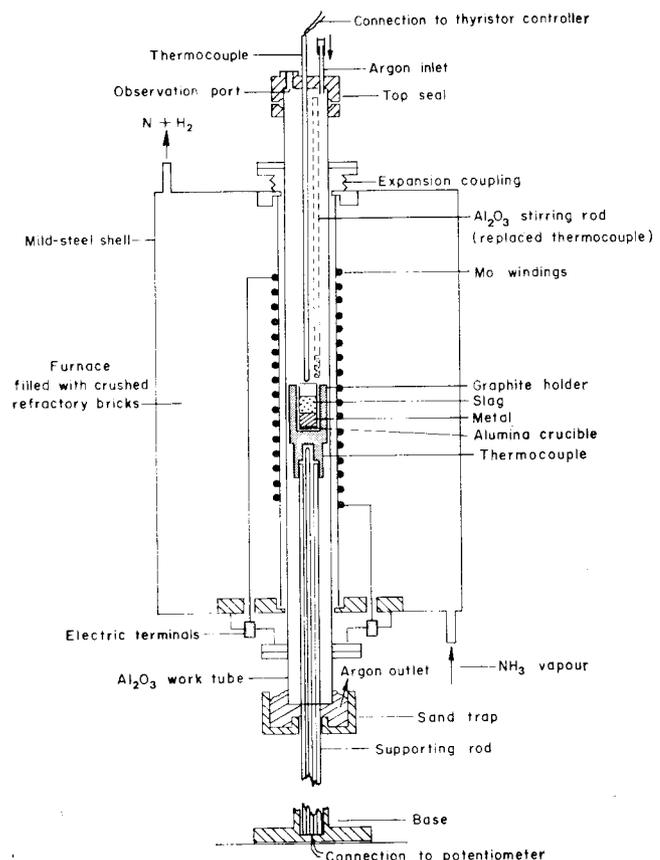

Fig. 1—The molybdenum-wound resistance furnace

rate of the reaction and hence on the approach to equilibrium between the slag and the alloy phases.

Studies on the rate of reaction were hampered by the uncontrollable nature of the reaction between the slag and the alloy, but samples were nevertheless withdrawn from the furnace at selected times from the start of the reaction and quenched in air. The sample within the crucible was protected from oxidation during this period by a special refractory lid. After the crucible had cooled, it was removed from the graphite holder and the contents of the crucible were broken out for weighing of the alloy bead. From the change in mass of this alloy bead, the transfer of silicon and manganese could be calculated by use of the mathematical expression derived from the mass-transfer model proposed by Barcza[6]. Confirmation of the predicted analyses of the resulting slag and alloy was obtained by chemical analysis of a cross-section of samples of the slag and the alloy. These experiments were extended to include reactions in oxidizing and reducing environments. The argon used to flush the work tube was replaced with air or, alternatively, with hydrogen and nitrogen in a ratio of 3 to 1. During these experiments, the change in the total mass of the crucible was noted so that the degree of oxidation or reduction of the manganese oxides could be determined.

Dissociation of MnO_2 and Ore

The thermogravimetric tests carried out in air or argon on the slag representing the lime–ore melt and the high-

and low-grade slags established that MnO_2 deoxidizes to Mn_3O_4, which is a 1-to-1 ratio of the Mn_2O_3 and MnO oxide states (i.e., half Mn^{3+} and half Mn^{2+}) irrespective of the type of slag being melted. The dissociation of this stable oxide form was completed by the time the temperature of the furnace linked to the Stanton thermal balance had reached 1200 °C. The application of the mass-transfer model to the system under consideration became feasible once the resulting oxidation state in the premelted slag had been determined.

The premelting in the chamber furnace in air of the many slags used in the study of reactions between the slag and the alloy confirmed that the oxidation state resulting from dissociation was Mn_3O_4. The mass of oxygen lost from a given mass of MnO_2 was used as the determining factor.

Reaction between Slag and Alloy

Various factors affect the rate of reaction and the equilibrium between the slag and the alloy.

Temperature

The results for the reactions conducted at the four selected temperatures (1400 °C, 1450 °C, 1500 °C, and 1600 °C), are shown in Fig. 2. The calculated values for the mass of manganese transferred from the standard slag to the plant alloy, based on the mass-transfer relation shown in equation (1), agreed closely with the results based on analysis of the alloy after reaction. Table III gives a comparison of the results for various reaction times at 1500 °C. The changes in composition
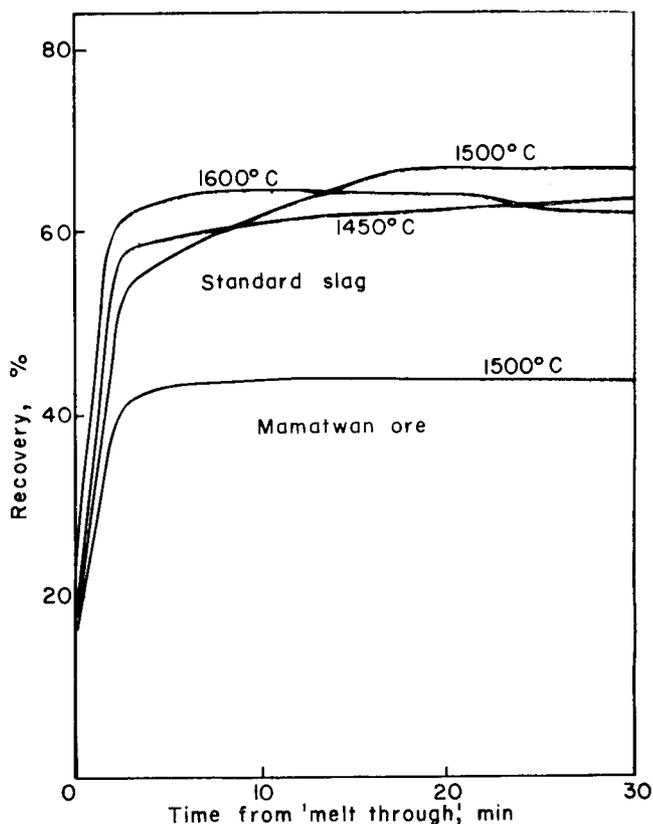

Fig. 2—The rate of recovery of manganese from the standard slag and from a Mamatwan-ore melt at several selected furnace temperatures
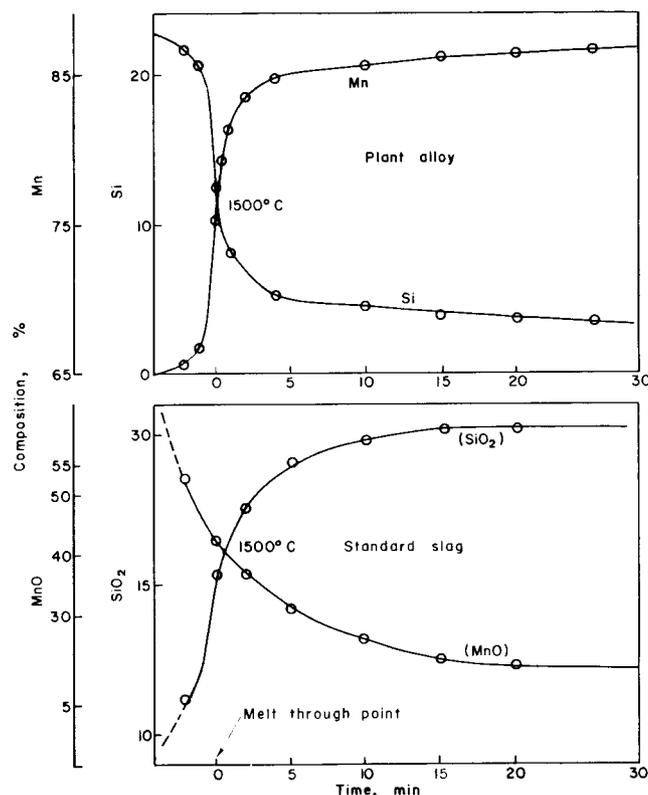

Fig. 3—The change in composition of the phases during the reaction between the slag and the alloy

for manganese and silicon in the slag and the alloy are shown in Fig. 3. The equation used for calculation of the mass transfer of manganese was

$$\triangle M_{Mn}^{a} = 1,343 \ \triangle M_{OBS}^{a} + 0,3431 \cdot M_{Mn}^{s}(1-X), \quad \cdot \quad (1)$$

where $\triangle M_{Mn}^{a}$ is the mass of manganese transferred from the slag to the alloy,

$\triangle M_{OBS}^{a}$ is the net change in the mass of the alloy,

M_{Mn}^{s} is the number of grams of manganese initially in the slag, and

X is the fraction of oxygen lost from a given mass of MnO_2 in the primary slag during preheating.

The derivation of this equation is shown in the Addendum.

Fig. 4 shows the variation in the distribution ratio $(MnO)/\underline{Mn}$ with changes in temperature from 1400°C to 1600°C, the minimum value occurring at 1500°C.

Ratio of Slag to Alloy

Fig. 5 shows the variation in the recovery of manganese

TABLE III

COMPARISON BETWEEN ANALYTICAL AND THEORETICAL RESULTS (MASS FRACTION) BASED ON THE PROPOSED MODEL FOR MASS TRANSFER

Reaction time	Temperature	Analytical results				Theoretical results based on derived mass transfer equation (1)*			
		Plant alloy		Standard slag		Plant alloy		Standard slag	
min	°C	$\underline{Mn}$	$\underline{Si}$	(MnO)	(SiO₂)	$\underline{Mn}$	$\underline{Si}$	(MnO)	(SiO₂)
5	1500	0,854	0,047	0,229	0,266	0,848	0,052	0,236	0,272
10	1500	0,878	0,031	0,195	0,329	0,855	0,047	0,221	0,283
15	1500	0,864	0,037	0,185	0,293	0,864	0,039	0,189	0,298
20	1500	0,858	0,048	0,174	0,290	0,866	0,038	0,194	0,301
25	1500	0,862	0,037	0,185	0,280	0,867	0,037	0,191	0,303
30	1500	0,861	0,032	0,193	0,295	0,867	0,037	0,191	0,303
5	1600	0,851	0,047	0,163	0,272	0,859	0,043	0,163	0,290

Note: Underlining denotes that the constituent is in the metal phase, and parentheses that the constituent is in the slag phase.

*The composition of the Mn and Si and (MnO) and (SiO₂) in the products was calculated from the initial composition of the alloy and slag and from the Mn and Si mass transfer, which in turn was determined by weighing the alloy bead after reaction for the given time and substituting the value in the mass-transfer equation (1).
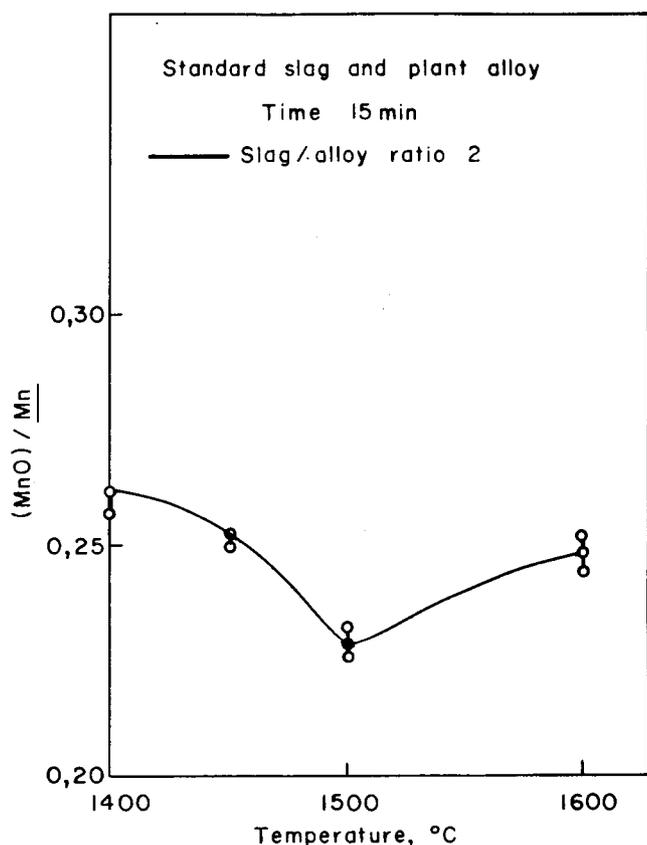

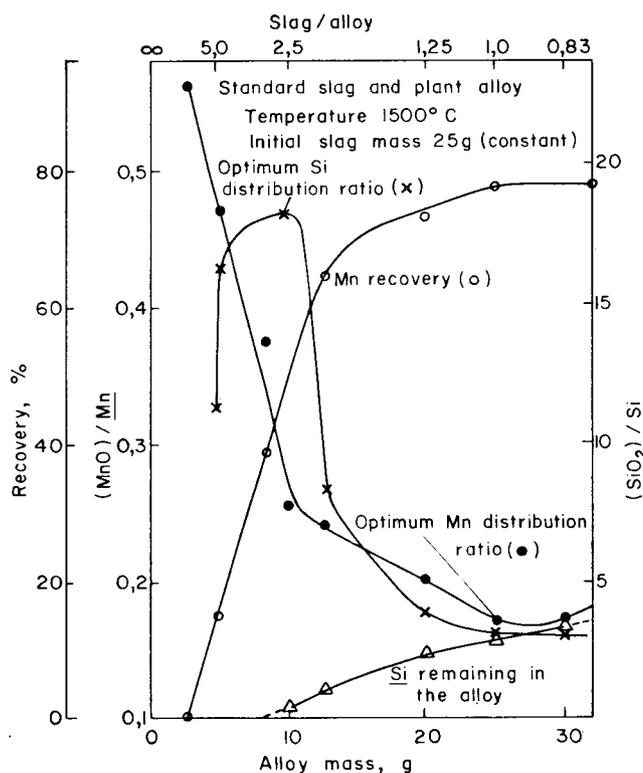Fig. 4—The effect of temperature on the manganese distribution ratio at equilibrium

Fig. 5—The effect of the slag-to-alloy ratio on the recovery of manganese and on the distribution ratios of manganese and silicon at equilibrium
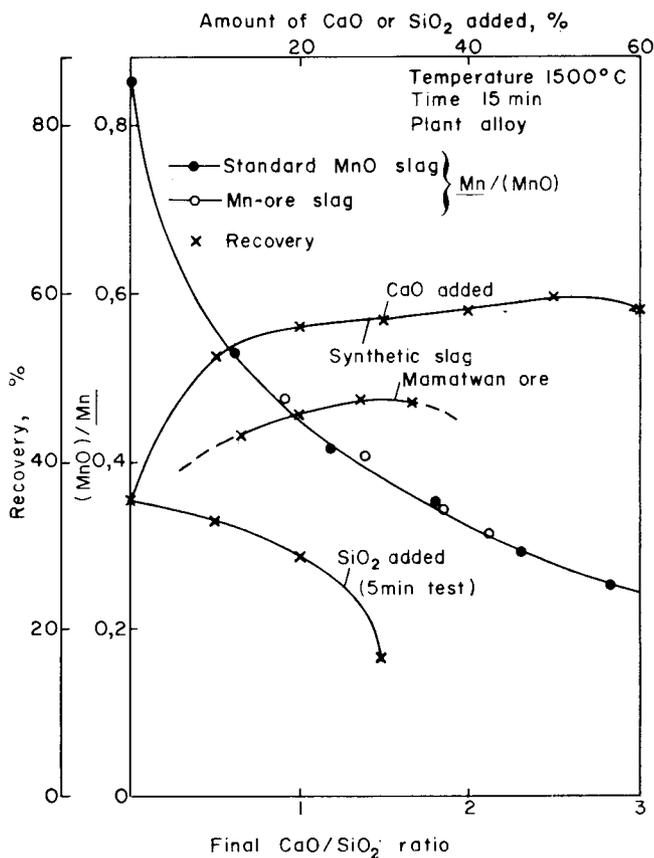
Fig. 6—The effect of the amount of CaO or SiO$_2$ added and the final CaO/SiO$_2$ basicity ratio on manganese recovery and distribution ratio
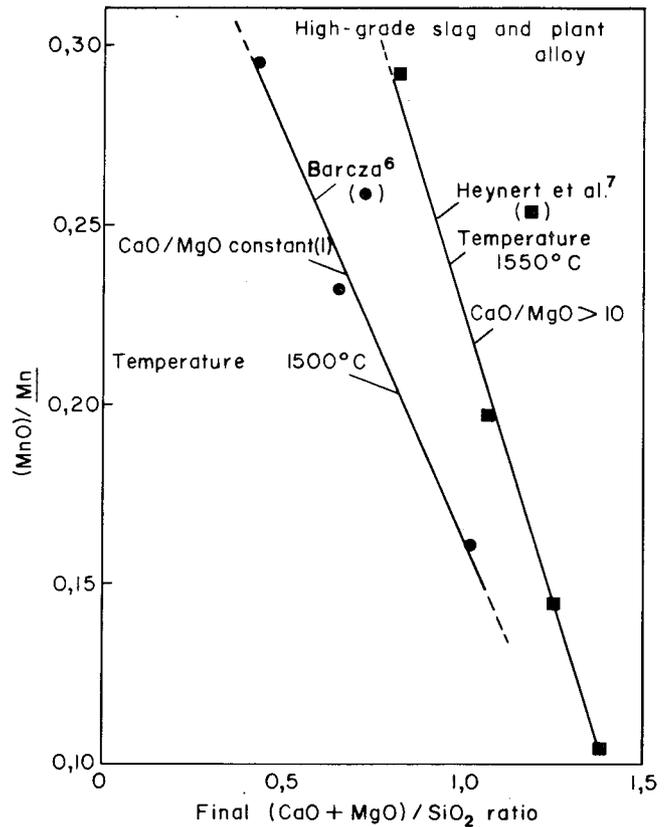

Fig. 8—The relation between the final basicity ratio and the manganese distribution ratio at equilibrium
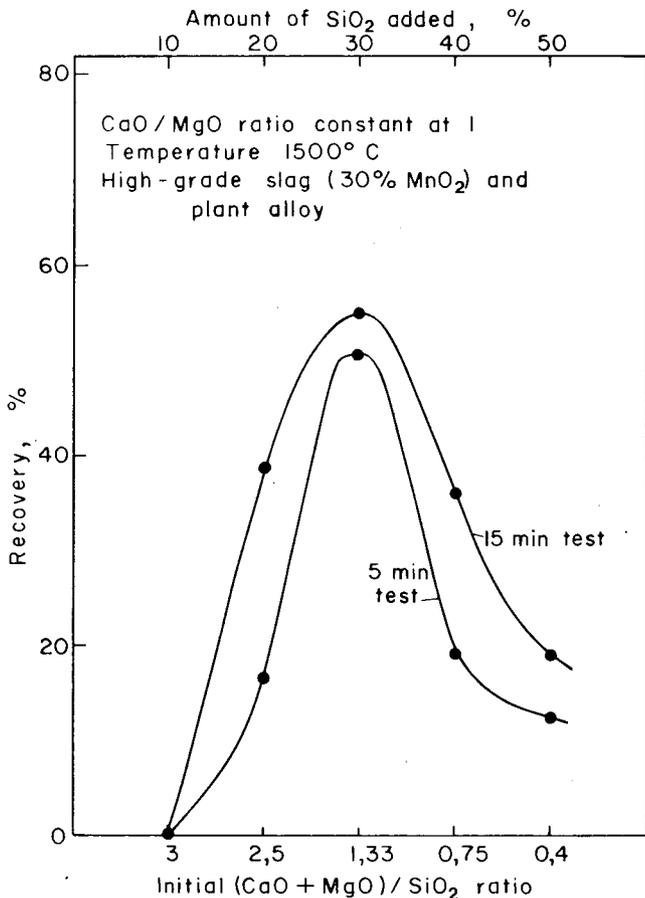

Fig. 7—The effect of the initial basicity ratio on the recovery of manganese from high-grade slag
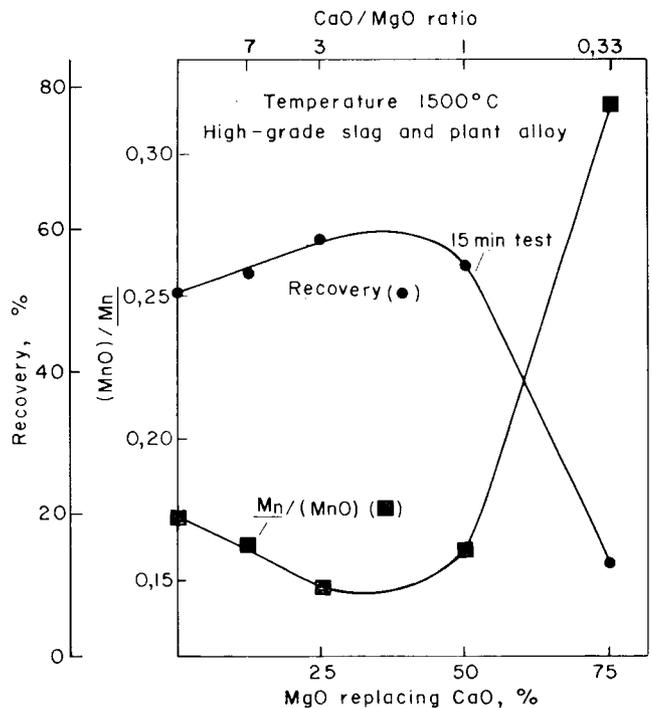

Fig. 9—The effect of the chosen CaO/MgO ratio on the manganese recovery and distribution ratio at equilibrium

and the distribution ratio (MnO)/$\underline{\text{Mn}}$ with change in the slag-to-alloy ratio from 5 to 0,83, the minimum value occurring at a ratio of 1.

Composition of Slag and Alloy

The variation in manganese recovery and distribution ratio (MnO)/$\underline{\text{Mn}}$ with additions of CaO, MgO, and SiO$_2$ and with changes in the final CaO/SiO$_2$ ratio, the initial and final (CaO+MgO)/SiO$_2$ ratio, and the CaO/MgO ratio are shown in Figs. 6, 7, 8, and 9 respectively.

The variation in manganese recovery and distribution ratio with increasing initial silicon in the alloy is shown in Fig. 10. Initial silicon contents (per cent by mass) of 10, 22,5, 30, 50, 70, and 100 were used. The minimum distribution ratios for (MnO)/$\underline{\text{Mn}}$ were obtained for the following instances:

an initial basicity ratio (CaO+MgO)/SiO$_2$ of 1,33
a basic oxide ratio of CaO/MgO of slightly more than 3, and
an initial silicon content of 30 per cent.

No minimum value for (MnO)/$\underline{\text{Mn}}$ was obtained for increases in the CaO/SiO$_2$ ratio, since dilution of the (MnO) results in a levelling off in the recovery of manganese up to a ratio of 3. The optimum amount of CaO added for maximum recovery of manganese was 20 per cent by mass, as shown in Fig. 6.

Discussion

Phase Systems

According to Muan[8, 9], MnO$_2$ is stable only up to 425 °C, dissociating to Mn$_2$O$_3$ and then to Mn$_3$O$_4$ with increasing temperature. The Mn$_3$O$_4$ oxidation state was found to be very stable under neutral or oxidizing conditions up to temperatures of 1600 °C, and lower oxidation states in the form of increasing ratios of Mn^{2+} to Mn^{3+} were achieved only in reducing atmospheres of either carbon monoxide or hydrogen. The monitoring of the change in mass of a given initial quantity of MnO$_2$ provided a convenient reference for determination of the resulting oxidation state. The mechanism of dissociation of MnO$_2$ was not studied since the only aim of these tests was to establish the resulting oxidation state of manganese after premelting of the initial slags prior to testing of the reaction between the slag and the alloy. The slag-forming components had no noticeable effect on the degree of dissociation of the MnO$_2$ since Mn$_3$O$_4$ was formed in all the unreduced premelted slags. The melting characteristics and liquidus temperatures of manganese oxide slag systems have been studied extensively. The following systems have been investigated:

the MnO-SiO$_2$ system[10] and the CaO-MnO-SiO$_2$ ternary system[11] by Glasser, the MgO-MnO-SiO$_2$ system by Glasser and Osborn[12], the CaO-MnO system by Ribound and Muan[13], and the MgO-CaO-MnO-Al$_2$O$_3$ system by Warren[14]. In this project, the liquidus temperatures for most of the slags considered were expected to be below 1500 °C in accordance with those findings[10-14], and this prediction was confirmed during the premelting tests. The only slags with higher liquidus temperatures were those with MgO/CaO ratios greater than 0,66 for a basicity ratio (CaO+MgO)/SiO$_2$ of 1,33.

Rate of Reaction

Very rapid reaction between the slag and the alloy was observed at temperatures of 1400 °C, 1450 °C, 1500 °C, and 1600 °C, and equilibrium was usually reached within 5 to 10 minutes from the start of reaction. Two reactions were observed, the first taking place mainly during the incubation period before final melting of the alloy bead through the slag. Table IV shows the decrease in value with time for the analyses of the Mn$_2$O$_3$ or Mn^{3+} concentration during this stage as given by the following deoxidation reaction:

$$2(\text{Mn}_2\text{O}_3) + \underline{\text{Si}} = 4(\text{MnO}) + (\text{SiO}_2), \qquad \ldots \ldots (2)$$

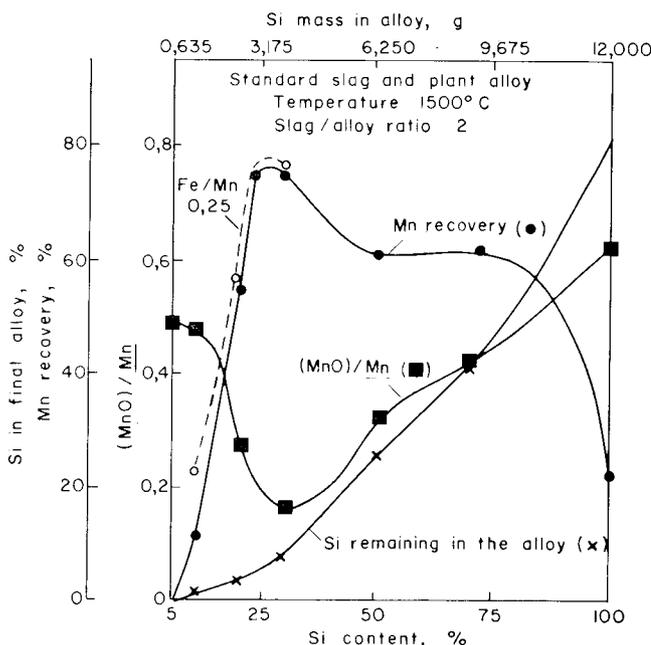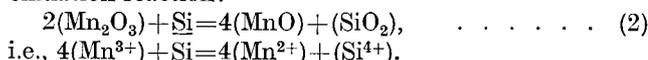i.e., $4(\text{Mn}^{3+}) + \underline{\text{Si}} = 4(\text{Mn}^{2+}) + (\text{Si}^{4+})$.

Fig. 10—The effect of the initial silicon content of the alloy on the manganese recovery and distribution ratio at equilibrium

TABLE IV

THE AMOUNT OF REDUCTION OF Mn^{3+} AND Mn^{2+} WITH TIME IN THE STANDARD SLAG

Time, min	Analytical value % by mass			Theoretical value % by mass		
	Mn$_3$O$_4$	Mn^{3+}	Mn^{2+}	Mn$_3$O$_4$	Mn^{3+}	Mn^{2+}
Premelt (std slag) 55% MnO$_2$	51,51	18,11	11,57	51,81	18,63	18,63
< 1 (before melting)	49,58	6,38	29,29	42,96	*0,0	30,91
0	38,58	3,25	24,50	42,59	*0,0	30,63
0,5	32,41	0,27	23,03	36,67	*0,0	26,38
1	30,80	0,25	22,15	33,40	*0,0	24,02

*Values of 0,0 are assumed since all the Mn^{3+} is reduced to Mn^{2+} prior to the commencement of reduction of Mn^{2+} to metal.

The Mn^{2+} and Mn$_3$O$_4$ concentrations are also shown in Table IV.

The second reaction took place between the MnO or Mn^{2+} and the remaining silicon in the alloy and is shown by the reaction for the recovery of manganese:

$$2(\text{MnO}) + \underline{\text{Si}} = 2\underline{\text{Mn}} + (\text{SiO}_2), \qquad \dots \dots \dots \quad (3)$$

i.e., $2(\text{Mn}^{2+}) = \underline{\text{Si}} = 2\underline{\text{Mn}} + (\text{Si}^{4+})$.
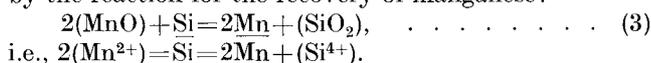
The influence of the chosen system temperature on the reaction was masked by the exothermic heat liberated from the reaction at the interface between the slag and the alloy. The effect of temperature on the rate of reaction between the slag and the alloy could therefore not be studied satisfactorily. After the rapid part of the reaction had been completed during the initial 5 minutes, a much slower rate of reaction was observed during the final 10 minutes before the attainment of equilibrium. Stirring of the alloy and the slag failed to increase the rate of reaction and merely increased the Al$_2$O$_3$ content of the slag.

The results of these tests indicate that the conventional stirring caused by thermal gradients between the reaction interface and the bulk phases was sufficient to assist in the transport of the reactants and products to and from the slag–alloy interface. The diffusion of the individual species could therefore not be regarded as being responsible for the rate-controlling stage of the reaction as it was for the system studied by Daines and Pehlke[15]. That system contained very low concentrations of MnO and silicon, and the evolution of heat was negligible.

The fact that no marked changes can be detected in reaction rates with temperature or stirring complicates the modelling of this system, and conventional techniques for solving the rate of reaction cannot be readily applied. The chemical reaction at the interface between the slag and the alloy is apparently the rate-determining stage, even though the influence of furnace temperature could not be detected with the chosen experimental approach. The rate of heat generated from the slag–alloy interface by means of differential thermal analysis could possibly provide some reliable data for the reaction rate versus temperature under the non-isothermal conditions prevailing. On this laboratory scale, the reaction rate was rapid and the dimensions of the reaction vessel small; therefore, it was not considered to be a fully representative system that could be used for an adequate study of plant conditions, and the subject was not pursued any further. Larger-scale plant operations could be regarded differently, and the reaction rates for various types of mixing are being investigated further.

Factors Affecting Equilibrium

The state of equilibrium attained between the slag and the alloy was judged to have been reached once the net transfer of manganese from the slag to the alloy and of silicon from the alloy to the slag had ceased. The influence of temperature, the ratio of the slag to the alloy, and the compositions of the slag and the alloy on the equilibrium conditions were examined by plotting of the manganese distribution ratio against the chosen variable. Distribution ratios for silicon, i.e., (SiO$_2$)/$\underline{\text{Si}}$, were also plotted in some instances.

The values for the concentrations of manganese and silicon in the alloy and their respective oxides in the slag were expressed as mass fractions rather than as activity values since, in most instances, such values were not available in the literature. The distribution ratios for (MnO)/$\underline{\text{Mn}}$ and (SiO$_2$)/$\underline{\text{Si}}$ were derived from these values from the mass fractions. The apparent equilibrium constant was expressed as

$$K^1{}_{\text{Mn},\text{Si}} = \frac{(\text{MnO}).\text{Si}^{\frac{1}{2}}}{\underline{\text{Mn}}}, \qquad \dots \dots \dots \dots \quad (4)$$

which is the same expression as that used by Heynert et al.[7], and was determined by use of mass fractions.

Temperature

The results for the determination of the influence of temperature on the distribution ratio of (MnO)/$\underline{\text{Mn}}$ suggests that a minimum value occurs at 1500 °C. The higher values for the (MnO)/$\underline{\text{Mn}}$ ratio at 1400 °C and 1450 °C possibly occurred because these temperatures are close to the liquidus temperature of the slag and the reaction might have been incomplete or subjected to a somewhat different reaction mechanism. The higher distribution values at 1600 °C can possibly be explained by the less-favourable thermodynamic relations, i.e., the $\triangle G^0_T$ value is less negative at 1600 °C than at 1500 °C. The overheating of the two phases as a result of the exothermic reaction could possibly also be responsible for this minimum point, as shown in Fig. 4. The higher (MnO)/$\underline{\text{Mn}}$ distribution ratio at 1600 °C could have been the result of a small vapour loss of MnO from the slag, causing less manganese to be reduced to the metal. A small overall loss in mass from the crucible was observed during these high-temperature tests that would partly explain the higher (MnO)/$\underline{\text{Mn}}$ distribution value at 1600 °C.

Slag-to-alloy ratio

From the results of the experiments in which the mass of the alloy was increased in relation to the constant initial mass of the slag (25 g), four stages of change in mass can be observed. For small additions of alloy (less than 3,28 g), there was a net mass loss from the alloy. Insufficient silicon was available from the small quantity of alloy to reduce all the Mn^{3+} to Mn^{2+}. Hence, either no reduction of manganese occurred or, alternatively, even if some manganese was formed, insufficient manganese was gained to cause a net mass gain because of the relatively greater mass loss of silicon. The first stage covers the region from zero mass loss up to the stage where no further increase in mass loss with increase in alloy mass occurs, i.e., the minimum mass point. The second stage lies between this minimum point and the so-called break-even point, where the alloy mass has returned to its original value. In this stage, the mass gain due to transfer of manganese is sufficiently great to more than compensate for the mass loss of silicon, and this results in a net gain up to the break-even point. The third stage of mass change occurred when further additions of alloy were made and an overall net increase in mass took place. The fourth stage of mass change is characterized by a negligible increase in manganese recovery for increasing addition of the alloy.

The activity of the MnO in the slag therefore appears

to be the limiting factor, which, in this instance, results in no further recovery of manganese. The optimum ratio of the slag to the alloy for the standard slag and plant alloy appears to be close to 1, as shown in Fig. 5, where the minimum (MnO)/$\underline{Mn}$ value was 0,170. The (SiO$_2$)/$\underline{Si}$ value of 3,16 is not favourable at this stage since the alloy contains far too much silicon to meet the required silicon specification for a low-carbon ferromanganese, i.e., less than 2 per cent. The silicon content was, in fact, still 10,82 for this particular slag-to-alloy ratio. The optimum (SiO$_2$)/$\underline{Si}$ ratio was achieved for a slag-to-alloy ratio of 2,5.

Composition of alloy and slag

Increase of the silicon content of the alloy up to a value of 30 per cent decreased the (MnO)/$\underline{Mn}$ distribution ratio, as can be seen in Fig. 10. The mimimum distribution ratio was 0,169. When the silicon content of the initial alloy was increased to more than 30 per cent, a decrease in the manganese distribution ratio occurred. Very little reaction took place when pure silicon was reacted with the slag. The only possible reason that can be postulated is that surface tension at the interface inhibits diffusion across the reaction interface. Even when the contact area at the interface was increased by stirring, virtually no reaction occurred. The silicon alloy formed a spherical bead, unlike the flat beads formed from alloys containing smaller quantities of silicon, which suggests that greater surface-tension effects are present in the alloy having a high silicon content.

The slag composition had considerable influence on the final state of equilibrium attained. When CaO, MgO, and SiO$_2$ were added singly or in combination, marked changes occurred in the recovery of manganese and in the distribution ratios between the slag and the alloy. SiO$_2$ is one of the reaction products; therefore, as the reaction proceeds, the basicity ratio expressed as (CaO+MgO)/SiO$_2$ decreases. The addition of SiO$_2$ to MnO$_2$ to form a premelted slag that was reacted with the alloy in a ratio of 2 resulted in a dramatic decrease in the manganese recovered from the slag, as shown in Fig. 6.

When the basicity ratio of the standard slag (expressed as CaO/SiO$_2$) is increased, there is a marked decrease in the (MnO)/$\underline{Mn}$ distribution ratio, with a corresponding increase in the recovery of manganese (see Fig. 6). The CaO/MgO ratio was altered when MgO was added to the high-grade slag to replace some of the CaO. The optimum MgO content corresponds to a CaO/MgO ratio of about 3, which is an approximate 1-to-1 mixture of the fluxes lime and dolomite (see Fig. 9).

The ratio (CaO+MgO)/SiO$_2$ was varied, and the optimum recovery of manganese was observed for an initial ratio of 1,33 in the high-grade slag (see Fig. 7).

Theory of Slag–Alloy Equilibrium

The activity of the MnO in the slag and of the silicon in the alloy are of major interest in attempts to understand the state of equilibrium attained.

Activities in the slag phase

Very few fundamental thermodynamic data are available for the slag compositions associated with the production of low- to medium-carbon ferromanganese. The

trends observed by Warren[14] for similar slags associated with the production of high-carbon ferromanganese could be applicable to the behaviour of the slags studied in this project. The addition of limited amounts of CaO to the slag increases the activity coefficient of MnO and reduces the viscosity of the slag. Larger additions of CaO cause an increase in the liquidus temperature and overall dilution of the MnO. Partial replacement of the additions of CaO by the additon of MgO can result in a corresponding improvement in the manganese distribution ratios as shown in Fig. 9. MgO has a lower molecular mass than has CaO, and there is an overall increase in the mole fraction of the basic fluxes. However, MgO tends to increase the liquidus temprature of the slag at far lower concentrations than does CaO, and hence the CaO/MgO ratio should not be less than about 3 for a slag with (CaO+MgO)/SiO$_2$ of 1,33 if optimum recoveries are to be obtained (see Fig. 9).

When the concentration of the basic oxides of Ca^{2+}, Mg^{2+}, and Mn^{2+} are low, these cations become associated with the larger ionic groups of SiO$_2$ and, as a result, very few free O^{2-} anions exist. MnO therefore has a very low activity coefficient. As the content of the basic oxides is increased, the SiO$_2$ network is broken down into smaller anionic groups and more free O^{2-} ions are present. The role of these two basic oxides in breaking up the silicate network is even more important when secondary SiO$_2$ is formed as a product of the reaction. Warren[14], Channon and See[16], and Woollacott *et al.*[17] discuss the physicochemical properties of MnO slags in detail.

Activities in the alloy phase

Very little can be done to improve the activity of silicon in the alloy. Channon and See[16] showed that ferrosilicon is a better silicon-containing alloy than is ferromanganese silicide because it has higher silicon activity. However, the manganese content of the resulting alloy is too low since 80 per cent is the minimum value specified. If silicon is added to iron, the activity of the silicon is far lower than would be the case for ideal liquids, and a similar deviation was found in the Mn–Fe–Si alloys used by Turkdogan and Hancock[18, 19]. The activity of silicon in the system Fe–Mn–Si–C is also low according to Tolsotoguzov[20]. The concentration of silicon drops as equilibrium is approached; therefore, extremely low silicon activities can be expected. High ratios of alloy to slag, or initial silicon contents in the alloy of up to 30 per cent, favour low (MnO)/$\underline{Mn}$ distribution ratios because of the relatively high silicon content of the alloy at equilibrium.

Equilibrium constants

If activity values are available for the MnO and SiO$_2$ in the slag and for the manganese and silicon in the alloy, the equilibrium constant is expressed as

$$K_{Si,Mn} = \frac{a_{\underline{Mn}}^2 \cdot a_{(SiO_2)}}{a_{MnO}^2 \cdot a_{\underline{Si}}}, \qquad \ldots \ldots \ldots \ldots (5)$$

where a is the activity of the component indicated by the subscript.

The compositions of the slag and alloy shown in Table V were similar to those of the slags investigated by

Warren[14] and Sharma and Richardson[21], and those of the alloys studied by Ohtani[22] and Rawling and Elliot[23]. The approximate activity values were used in the calculation of the equilibrium constant. The compositions of the slag and the alloy shown in Table V resulted from the reaction between the standard slag and a synthetic alloy having an initial silicon content of 30 per cent. The slag-to-alloy ratio was 2, and the furnace temperature was 1500 °C.

$$K_{\text{Si,Mn}} = \frac{(0,85)^2 \cdot (0,10)}{(0,14)^2 \cdot (0,05)} = 73,7. \quad \ldots \ldots \ldots \quad (6)$$

The value in equation (6) is in close agreement with McGannon's value[24] of 76,2, which was obtained at 1600 °C. Many of the apparent equilibrium values differ from this value as a result of the deviation of the SiO_2 and silicon activities from the ideal (see Table VI).

The other expression for the apparent equilibrium constant was $K^1_{\text{Mn,Si}}$, and the values shown in Table VI range from 0,035 to 0,104. These values correspond fairly closely to those given by Heynert et al.[7] and Channon and See[16] for similar basicity ratios in the final slag. As the alloy in equilibrium with the slag investigated by Heynert et al.[7] was high-carbon ferromanganese, some difference in the distribution between the slag and the alloy can be expected.

Conclusions

(1) At a temperature of 1200 °C, MnO_2, the initial oxide form of manganese used in these tests, dissociates thermally to Mn_3O_4 in air. The higher oxides in the Mamatwan manganese ore were also expected to dissociate to Mn_3O_4. The composition of the slag did not alter the degree of deoxidation of MnO_2 to Mn_3O_4.

(2) Investigation of the rate of reaction between the slag and the alloy is complicated by the fact that constant temperature cannot be maintained because of the strongly exothermic nature of the reaction. The rate of reaction is extremely rapid as a result of the geometry of the apparatus used for these tests, and stirring and furnace temperature in the range 1400 °C to 1600 °C had little effect on the rate. The mechanism that appears to result in rapid reaction is thermal convectional stirring.

(3) The activity of MnO in the slag can be increased by additions of CaO until dilution of the MnO causes a decrease in the recovery of manganese. The optimum addition was 20 per cent by mass for pure

TABLE V

ACTIVITY VALUES FOR COMPONENTS IN THE SLAG AND THE ALLOY AT EQUILIBRIUM

Constituent		Content, %	Approx. activity	Reference
Slag	MnO	14,3	0,14	13
	CaO	32	—	—
	MgO	4,0	—	—
	SiO_2	33,5	0,10	21
	Al_2O_3	Approx. 5,0	—	—
Alloy	Mn	84,5	0,85	22
	Fe	7,5	—	—
	Si	8,0	0,05	23

TABLE VI

THE EFFECT OF CHANGES IN THE SLAG COMPOSITION ON THE APPARENT EQUILIBRIUM CONDITIONS

Basicity ratio		Mass fraction				Final basicity ratio	Distribution ratios			Apparent equilibrium constants*		
$\dfrac{CaO}{MgO}$	$\dfrac{(CaO + MgO)/SiO_2}{(\text{initial})}$	ΔM^a_{Mn} g	Alloy		Slag		$\dfrac{(CaO + MgO)/SiO_2}{}$	$MnO/\underline{Mn}$	$SiO_2/\underline{Si}$	$K_{\text{Si,Mn}}$	$K^1_{\text{Mn,Si}}$	$\log K_{\text{Mn,Si}}$
			$\underline{Mn}$	$\underline{Si}$	(MnO)	(SiO_2)						
7,00	6,00	3,4650	0,864	0,039	0,198	0,298	1,69	0,229	7,64	145,5	0,035	−1,46
1,00	0,40	0,8895	0,708	0,170	0,208	0,559	0,42	0,294	3,29	38,1	0,094	−1,03
1,00	0,75	1,6645	0,736	0,149	0,171	0,507	0,64	0,232	3,40	63,0	0,070	−1,16
1,00	1,33	2,5925	0,766	0,124	0,123	0,434	1,02	0,161	3,50	135,7	0,044	−1,36
1,00	2,50	1,8260	0,741	0,144	0,169	0,308	1,70	0,228	2,14	41,1	0,067	−1,17
—	1,33	2,4300	0,761	0,128	0,131	0,427	1,04	0,172	3,34	112,6	0,048	−1,32
7,00	1,33	2,5525	0,765	0,125	0,125	0,432	1,03	0,163	3,46	129,4	0,045	−1,35
3,00	1,33	2,7640	0,771	0,120	0,114	0,440	1,01	0,147	3,67	167,7	0,040	−1,40
1,00	1,33	2,5930	0,766	0,124	0,123	0,434	1,01	0,161	3,50	135,7	0,044	−1,36
0,33	1,33	0,6170	0,698	0,179	0,221	0,362	1,15	0,317	2,02	20,1	0,104	−0,98
3,00	8,00	5,6370	0,864	0,039	0,199	0,298	1,69	0,230	7,64	144,0	0,035	−1,46
1,50	8,00	4,8210	0,845	0,055	0,244	0,267	1,83	0,289	4,85	58,2	0,052	−1,28

$K_{\text{Si,Mn}} = \dfrac{(MnO)^2 \cdot (SiO_2)}{(Mn)^2 \cdot Si}$ and $K^1_{\text{Mn,Si}} = \dfrac{(MnO) \cdot Si^{\frac{1}{2}}}{Mn}$, where the concentrations are expressed as mass fractions instead of as activity values to give the so-called apparent equilibrium constants

*$K_{\text{Si,Mn}}$ constants

MnO_2 and about 30 per cent by mass for the Mamatwan ore. The addition of MgO instead of CaO according to mass percentage results in a moderate increase in the recovery of manganese down to a CaO/MgO ratio of 3 and a subsequent decrease in the recovery. The liquidus temperature of the slag melt was increased considerably by CaO additions of over 40 per cent or by ratios of CaO/MgO less than 3. The higher liquidus temperatures resulted in greatly impaired reaction conditions.

(4) The recovery of manganese increased considerably with decreases in the ratio of the slag to the alloy, the optimum slag-to-alloy ratio for manganese recovery being 0,8. However, this low ratio had two adverse effects: the low manganese and the high silicon contents of the alloy after reaction. A ratio of 2 is necessary to meet the required silicon and manganese specifications, i.e. 80 per cent and less than 2 per cent respectively for the alloy. In practice, under these conditions, lower manganese recoveries must therefore be expected.

(5) As the silicon content of the alloy increased up to 30 per cent, the recovery of manganese became higher. A decrease was observed in the recovery of manganese for silicon values of 50, 70, and especially 100 per cent. This unexpected decrease may be due to a change in the interfacial tension between the slag and the alloy that manifested itself as a tendency for the alloy to become increasingly spherical as the silicon content increased. High contents of the residual silicon were obtained in alloys with initial silicon contents of 30 per cent and more. The optimum silicon content for a slag-to-alloy ratio of 2 was 22,5 per cent, which is that of the plant alloy. A higher ratio of slag to alloy would be required for an alloy with a silicon content of 30 per cent if the alloy product were to meet the required specifications. However, ferromanganese silicides having silicon contents of 30 per cent are considerably more difficult to produce than those with contents of 16 to 23 per cent.

(6) In summary, the implications of these laboratory tests on synthetic and plant starting materials is that, although the rates of reaction are rapid, the equilibria are unfavourable for plant operation. This means that relatively high MnO contents in the slag must be accepted in the conventional single-step slag–alloy reaction if 2 per cent silicon in the alloy (which is the specification) is to be achieved. The MnO in the slag can be decreased to some extent by an increase in the CaO or MgO, or both, up to a maximum basicity ratio of 1,33 for the high-grade slag. However, the results indicate that the single-step process as commonly practised is not suitable, and the reaction equilibria and rate of reaction indicate that multiple-contact techniques would favour the reaction. This aspect is to be the subject of further study.
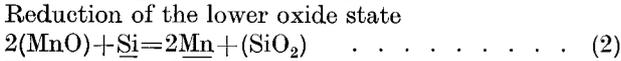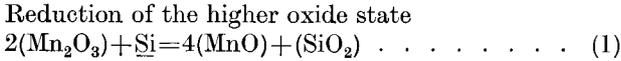
Acknowledgements

References

1. MIKOLAJCZAK, L. Ferro-manganese review. Metall. Bull. Mont., no. 40. Apr. 1974. pp. 21-23.
2. PERRIN, M. R. Rev. Metall., vol. 43. 1945. pp. 185-191. S.A. BRD. Patent 924568 (1955).
3. DAVIES, M. W., and RICHARDSON, F. D. The non-stoichiometry of manganous oxide. Trans. Faraday Soc., vol. 55. 1959. pp. 604-610.
4. DE VILLIERS, J. P. R. A mineralogical investigation of natural and heated Mamatwan manganese ore. Johannesburg, National Institute for Metallurgy, Technical Memorandum, Project 07772, no. 1. 9th May, 1973. (Confidential).
5. HAHN Jr, W. C., and MUAN, A. Studies in the system Mn–O: The Mn_2O_3–Mn_3O_4 and Mn_3O_4–MnO equilibria. Am. J. Sci., vol. 258. Jan. 1960. pp. 66-78.
6. BARCZA, N. A. Slag and metal equilibrium studies associated with the production of low-carbon ferromanganese. Ph.D. Thesis, University of the Witwatersrand, Johannesburg, 1976.
7. HEYNERT, G., WILLEMS, J., OELSEN, W., and SCHURMANN, E. Metallurgy of ferromanganese. Stahl u. Eisen, vol. 77. Nov. 1957. pp. 1717-1728. (In German).
8. MUAN, A. Phase equilibria at high temperatures in oxide systems involving changes in oxidation state. Am. J. Sci., vol. 256. Mar. 1958. pp. 171-207.
9. MUAN, A. Equilibrium measurements involving oxide and alloy phases at high temperatures. College of Mineral Industries, Pennsylvania State University, Contribution No. 64-53. pp. 126-139.
10. GLASSER, F. P. The system MnO–SiO_2. Am. J. Sci., vol. 256. Jun. 1958. pp. 398-412.
11. GLASSER, F. P. The ternary system CaO–MnO–SiO_2. J. Am. Ceram. Soc., vol. 45, no. 5. 1962. pp. 242-249.
12. OSBORN, E. G., DE VRIES, R. C., GEE, K. H., and KRANER, H. M. Optimum compositions of blast furnace slag as deduced from liquidus data for the quaternary system CaO–MgO–Al_2O_3. Trans. AIME, vol. 200. 1954. p. 42.
13. RIBOUND, P. V., and MUAN, A. Melting relations of CaO–manganese oxide and MgO–manganese oxide mixtures in air. J. Am. Ceram. Soc., vol. 46, nol 1. Jan. 1963. pp. 33-36.
14. WARREN, G. F. Measurement of the activity of manganese(II) oxide in slags associated with the production of ferromanganese. M.Sc. Thesis, University of the Witwatersrand, Johannesburg, 1972.
15. DAINES, W. L., and PEHLKE, R. D. Kinetics of manganese oxide reduction from basic slags by silicon dissolved in liquid iron. Trans. Metall. Soc. AIME, vol. 242. Apr. 1968. pp. 565-575.
16. CHANNON, W. P., and SEE, J. B. The reduction of fluxed and nonfluxed manganese ores by ferromanganese silicide. J. S. Afr. Inst. Min. Metall., vol. 77, no. 8. Mar. 1977. pp. 151-162.
17. WOOLLACOTT, L. C., JOCHENS, P. R., and HOWAT, D. D. The viscosities and electrical conductivities of slags associated with the production of high-carbon ferromanganese alloys. INFACON 74. Glen, H. (ed.). Johannesburg, South African Institute of Mining and Metallurgy, 1975. pp. 227-232.
18. TURKDOGAN, E. T., and HANCOCK, R. A. Equilibrium measurements between carbon-saturated Mn–Fe–Si melts and CaO–Al_2O_3–MnO–SiO_2 slags. Trans. Instn. Min. Metall., vol. 67. 1957-58. pp. 575-601.
19. TURKDOGAN, E. T., and HANCOCK, R. A. Equilibrium measurements between carbon saturated FeMnSi melts and CaO–Al_2O_3–MnO–SiO_2 slags. Trans. Instn Min. Metall., vol. 68. Jan. 1959. pp. 273-274.
20. TOLSOTOGUZOV, N. V. Distribution of silicon and manganese between metal and slag in the production of manganese alloys. Izv. Vuz Chern. Metall., vol. 9, no. 2. 1966. pp. 56-62. (In Russian).
21. SHARMA, R. A., and RICHARDSON, F. D. Activities of manganese oxide, sulfide capacities, and activity coefficients in aluminate and silicate melts. Trans. Metall. Soc. AIME, vol. 233. Aug. 1955. pp. 1586-1592.
22. OHTANI, M. Activities of manganese and carbon in Fe–C–Mn melts. Tokyo, Tohoku Daigaku Research Institute, Science Report, vol. 9. 1959. pp. 426-433.
23. RAWLING, J. R., and ELLIOT, J. F. The reduction of silica

in blast-furnace slag–metal systems. *Trans. Metall. Soc. AIME*, vol. 233. Aug. 1965. pp. 1539-1545.
24. McGANNON, H. E. The making, shaping and treating of steel. 8th edition. Pittsburgh, U.S. Steel. 1964. pp. 341-362.

Addendum

The following two chemical reactions are used as the basis for the derivation of the mass-transfer model:

Reduction of the higher oxide state

$$2(Mn_2O_3) + \underline{Si} = 4(MnO) + (SiO_2) \quad \ldots \ldots \quad (1)$$

Reduction of the lower oxide state

$$2(MnO) + \underline{Si} = 2\underline{Mn} + (SiO_2) \quad \ldots \ldots \ldots \quad (2)$$

The alloy undergoes a change in mass during the reaction as it gains Mn in exchange for the Si it loses. This is according to reaction (2). The alloy can also undergo a loss in mass when Si is lost but no Mn is gained, as shown by reaction (1).

If the mass of the alloy at any specific stage during the reaction between the two phases is M_{OBS}^A and the resultant change from its original mass is $\triangle M_{OBS}^A$, the following equation can be used to describe this change:

$$\triangle M_{OBS}^A = M_{OBS}^A - M_I^A, \quad \ldots \ldots \ldots \ldots \quad (3)$$

where M_I^A = the initial mass of alloy.

The following are the most important parameters that concern reaction and subsequent mass transfer:

$\triangle M_{Mn}^A$ = the mass transfer of Mn from the slag to the alloy

$\triangle M_{Si}^A (_{Mn}{}^{3+})$ = the mass transfer of Si from the alloy to the slag for the reaction $(Mn^{3+2} \to (Mn^{2+})$

$\triangle M_{Si}^A (_{Mn}{}^{2+})$ = the mass transfer of Si from the alloy to the slag for the reaction $(Mn^{2+}) \to \underline{Mn}$.

The actual nature of the two transfer species is such that the use of the observed change in mass as an experimentally measurable quantity is feasible. The reason for this fact is twofold. Firstly, there is a factor of almost 2 in the ratio of the atomic mass of Mn to that of Si (Mn=54,94 and Si=28,06). Secondly, an exchange of 1 mole for 2 takes place according to reaction (2).

The ratio of $Mn/Si = \dfrac{2(54,94)}{28,06} = 3,915$.

The only parameter measured experimentally for each stage of the slag–alloy reaction is $\triangle M_{OBS}^A$. This observed value for the mass transfer comprises two distinct phenomena: a gain in mass, and a loss in mass. The net mass transfer can therefore be expressed as

$$\triangle M_{OBS}^A = \triangle M_{Mn}^A - \triangle M_{Si}^A. \quad \ldots \ldots \ldots \ldots \quad (4)$$

In other words, the observed change in the mass of the alloy is equal to the mass gained by the alloy because of the Mn recovered in accordance with reaction (2) minus the mass of Si lost from the alloy as Mn^{3+} is reduced to Mn^{2+} and Mn^{2+} is reduced to Mn.

Thus, $\triangle M_{Si}^A = \triangle M_{Si}^A (_{Mn}{}^{3+}) + \triangle M_{Si}^A (_{Mn}{}^{2+}). \quad . \quad . \quad (5)$

Equation (2) therefore becomes

$$\triangle M_{OBS}^A = \triangle M_{Mn}^A - \left(\triangle M_{Si}^A (_{Mn}{}^{3+}) + \triangle M_{Si}^A (_{Mn}{}^{2+}) \right).$$

$$\ldots \ldots \ldots \quad (6)$$

The proportion of Si transfer from the alloy to Mn transfer to the alloy will depend entirely on the ratio of Mn^{3+}/Mn^{2+} in the slag phase at the commencement of reaction. $\triangle M_{Si}^A (_{Mn}{}^{3+})$ is the change in mass associated with the reduction of Mn^{3+} to Mn^{2+}. This amount of Si is directly related to the initial Mn^{3+} content of the slag.

Under most atmospheric conditions, both Mn^{3+} and Mn^{2+} are contained in the slag phase, and therefore the theoretical stoichiometric quantity of Si required for complete reaction will depend on both the amount of MnO in the slag phase and the ratio of Mn^{3+}/Mn^{2+}.

From reaction (1), it can be noted that the Si is effectively combining with O_2 in the following manner:

$$\begin{array}{ccc} Si & +O_2 & = SiO_2. \quad \ldots \ldots \ldots \quad (7) \\ 28,06 & 32 & \end{array}$$
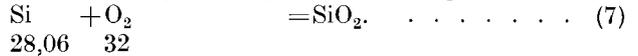
The value of $\triangle M_{Si}^A (_{Mn}{}^{3+}) = O_2 (_{Mn}{}^{3+}) \cdot \dfrac{28,06}{32}$

$$= 0,8769 \cdot O_2 (_{Mn}{}^{3+}), \quad . \quad (8)$$

where $O_2 (_{Mn}{}^{3+})$ is the oxygen associated with the Mn^{3+}.

According to reaction (2), the ratio of Mn mass transfer to that of Si transfer can be written as

$$\frac{\triangle M_{Mn}^A}{\triangle M_{Si}^A (_{Mn}{}^{2+})} = 3,915. \quad \ldots \ldots \ldots \ldots \quad (9)$$

If equations (8) and (9) are substituted into equation (6), the following expression is obtained:

$$\triangle M_{OBS}^A = \triangle M_{Mn}^A - \left(0,8769 \cdot O_2 {}_{(Mn^{3+})} + \frac{\triangle M_{Mn}^A}{3,915} \right)$$

$$= \triangle M_{Mn}^A \left(1 - \frac{1}{3,915} \right) - 0,8769 \cdot O_2 {}_{(Mn^{3+})}.$$

When the equation is solved in terms of $\triangle M_{Mn}^A$, an equation for the mass transfer of Mn, based on the observed change of mass of the alloy and the initial Mn^{3+} content of the slag phase, can be derived:

$$\triangle M_{Mn}^A = 1,343 \cdot \triangle M_{OBS}^A + 1,1777 \cdot O_2 {}_{(Mn^{3+})} \cdot (10)$$

Now $O_2 {}_{(Mn^{3+})} = \dfrac{16(1-X)}{54,94} \times M_{Mn}^S$

$$= 0,2913 (1-X) \cdot M_{Mn}^S, \quad \ldots \ldots \quad (11)$$

where M_{Mn}^S = the quantity of Mn in the slag in grams
X = the fraction of O_2 lost from a given mass of MnO_2.

Equation (11) can be substituted into equation (10) to give the following general equation for the mass transfer of Mn:

$$\triangle M_{Mn}^A = 1,343 \cdot \triangle M_{OBS}^A + 0,3431 \cdot M_{Mn}^S(1-X),$$

$$\ldots \ldots \ldots \ldots \quad (12)$$

where $\triangle M_{Mn}^A$ = mass transfer of Mn

$\triangle M_{OBS}^A$ = observed change in mass of the alloy

M_{Mn}^S = the mass of Mn in the slag

X = the O_2 fraction dissociated from MnO_2.