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THE REDUCTION OF FLUXED AND NON-FLUXED MANGANESE ORES BY FERROMANGANESE - SILICIDE

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A Dissertation Submitted to the Faculty of Engineering, University of the Witwatersrand, Johannesburg for the Degree of Master of Science in Engineering.

Johannesburg, 1975

UNDERTAKING

I certify that this is my own work and has not been submitted for a Master of Science degree at any other University.

W. P Channon

W. P. Channon

December, 1975.

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ABSTRACT

Medium- and low- carbon ferromanganese are produced by the silicothermic reduction of slags containing MnO. Because of its importance in the production of refined ferromanganese, the reaction between a premelted Mamatwan manganese ore and various ferromanganese -silicide reducing alloys has been studied with and without additions of fluxing agents. This relatively low grade manganese ore is partially self-fluxing and it is necessary to optimize the amounts and timing of fluxing additions during the production of refined ferromanganese to ensure both efficient electric furnace operation and manganese extraction from the premelt. Therefore, throughout the laboratory investigation, emphasis has been placed on the implications for industrial practice.

Alloys containing different silicon concentrations were added to a premelted sample of Mamatwan ore before the sample was introduced into a molybdenum-wound resistance furnace. The reaction was carried out under an argon atmosphere and the parameters varied were reaction time reaction temperature, alloy-to-ore ratio, fluxing additions and the silicon contents of the reducing alloy. The effect of stirring of the reacting melt was also examined.

The highly exothermic nature of the reactions involved in this investigation constituted a major obstacle to any attempt to maintain close control of temperature in the system. This also adversely affected the possibilities of carrying out controlled equilibrium and kinetic studies in this slag-metal system.

Because of the highly exothermic reaction, temperature appeared to have little effect on the rates of manganese transfer to the metal and silicon transfer to the slag and an apparent equilibrium was rapidly approached. Limits were determined for the favourable effects of fluxing additions and manganese recoveries declined as the CaO-to-MgO ratio decreased for any percentage of basic flux additions. As the silicon content of the alloy was progressively increased, the recovery of manganese passed through a maximum and subsequently decreased. Similar results

were obtained with variations in the alloy-to-ore ratio. When aluminium was used as a reducing agent together with silicon, substantial increases in manganese recovery were achieved because the aluminothermic reaction displaced the apparent equilibrium. The silicon content of the resulting alloy was above the specifications for refined ferromanganese. Stirring of the reacting melts decreased the manganese recovery and this result conflicts with the results of a previous investigation but may be explained by theexothermic nature of the silicon reduction reaction.

The results obtained when used in conjunction with other physicochemical data related to this slag-metal system suggest optimum slag compositions for more efficient manufacture of medium- and low-carbon ferromanganese from Mamatwan ore.

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1. INTRODUCTION

The processes for the extraction of manganese from South African Mamatwan ore must be improved and further processes must be developed to utilise the substantial manganese ore reserves in the Northern Cape. Limited tonnages of this ore are now being used in the production of medium - and low - carbon ferromanganese.

This research project was initiated to optimize certain parameters associated with this process. It had been suggested that it is not necessary to use lime as a flux when Mamatwan ore is melted for subsequent reduction by silicomanganese. The high lime and magnesia contents in the Mamatwan ore make the ore at least partially self fluxing and hence a possible alternative to existing practice would be to:

(i) Melt the ore without fluxing additions

(ii) Mix the premelted ore with ferromanganese and after fusion add the required lime in stages to complex the resulting silica as $2CaO.SiO_2$.

It was considered that this procedure might save electric power and reduce the consumption of lime. Heat required for the dissolution of the lime could be provided by the exothermic reduction reaction and not by electric power as in present practice. Thus electric power could be saved and furnace output increased. Stricter control of the consumption of lime might be possible to give lower slag-to-alloy ratios and ultimately lower losses of MnO in the slag. Although flux additions decrease the MnO content of the slag, they do not necessarily decrease the total amount of manganese lost as larger slag volumes are created. Optimum slag compositions which result in the most efficient plant operation need not necessarily give the lowest operating expenses as the cost of raw materials to form the most suitable slag could be excessive. Thus dolomite was also considered as a possible replacement for part or all of the lime.

Other aspects of the production of medium - to low - carbon ferromanganese which required investigation were the effects of temperature, time, changes in alloy composition and stirring on the reaction equilibrium. Thus in order for the industry to more efficiently process Mamatwan ore, it is essential that the metallurgical variables be optimized.

Thus experimental investigations examined the effect on manganese recovery from the slag and alloy silicon content for variations in reaction time, temperature and the composition of the reducing alloy. The composition of the ore premelt was also varied to examine the effect of the basicity of the premelt on manganese and silicon partitioning between the alloy and the premelt.

2. RESERVES, PRODUCTION AND USES OF MANGANESE AND MANGANESE ALLOYS

2.1 Manganese Ore Deposits in South Africa

World manganese ore deposits are estimated to exceed two billion tons and the reserves in the U.S.S.R. account for over 50 per cent of this tonnage. South African ore reserves are estimated to be the second largest in the world after those of the U.S.S.R.. Most of South Africa's manganese ore is in the Kuruman - Postmasburg area of the North - Western Cape and the three types of ores are Hotazel, Mamatwan and Wessels.

Hotazel ore is mainly of the hausmannite type[1] which is rich in manganese and low in both lime and magnesia with a relatively low manganese - to - iron ratio in the order of 5 to 1. However this deposit has reserves of only three million tons.

The Mamatwan deposit is believed to be the largest single deposit of manganese ore in the world, as 50 million tons are proven with the possibility that the deposit is in excess of 400 million tons[2]. This ore is mainly braunite with smaller amounts of manganite, hausmannite and hematite Gangue minerals are mainly calcium and magnesium carbonates with some ankeritic dolomite. The ore has a consistently low iron content with manganese - to - iron ratios between 6 to 1 and 10 to 1. Unfortunately its manganese content is the lowest of the three deposits.

Ore from the Wessels deposit is intermediate in character between the Hotazel and Mamatwan types and its manganese - to - iron ratios are normally about 4 to 1. Table 1 compares the compositions of ores from other leading producers in the world.

The expansion of the South African ferromanganese industry based on these assured vast reserves of manganese ore has resulted in the initiation of research into some of the more fundamental aspects of ferromanganese production. The Mamatwan manganese

TABLE I[2 - 4]

COMPARATIVE ANALYSIS OF SELECTED ORES										
Ore	Country of origin	Chemical composition. Wt per cent.								
		Mn	Fe	Mn:Fe	P	SiO_2	CaO	MgO	Al_2O_3	CO_2 + H_2O
Mamatwan	R.S.A.	39,4	4,2	9,38	0,027	4,82	12,10	2,33	0,26	16,51
Wessels	R.S.A.	47,5	12,2	3,89	0,035	3,23	4,96	0,29	0,44	3,44
Hotazel	R.S.A.	51,4	10,3	4,99	0,023	4,59	2,52	0,44	0,25	3,56
Nikopol	U.S.S.R.	50,0	1,0	50,00	0,200	10,00	1,40	0,90	1,60	10,00
Chiatura	U.S.S.R.	48,2	1,1	43,82	0,096	9,22	2,26	0,50	1,61	11,67
Amapa	Brazil	49,0	5,5	8,90	0,090	2,50			5,50	5,00
Indian. crystalline	India	59,7	2,0	29,90		7,00	00,30	0,20	3,00	3,00

deposit is the largest South African deposit and has thus been of considerable interest in the development of this research program.

It has been shown that at present this low grade ore cannot be regarded as a suitable source of manganese for the production of high grade slag containing 40 per cent MnO. For slag containing 20 per cent MnO, maximum production is associated with minimal amounts of this ore in the mix. Mamatwan ore, because of its consistently high CaO and MgO contents, is certainly not suitable for the production of silicomanganese as high SiO_2 activities are essential in the furnace slag.

Smelting of Mamatwan ore in a blast furnace is carried out effectively as the addition of small quantities of SiO_2 results in workable slags. The only other process which uses solely Mamatwan ore is the process for the production of low - and medium - carbon ferromanganese. This process uses comparatively small amounts of ore and as the demand for refined ferromanganese alloys is increasing, this application of manganese ore is becoming more important. Consequently, research into more effective use of this low grade ore has been stimulated.

2.2 Industrial Production of Low - and Medium - Carbon Ferromanganese

Medium - to low - carbon ferromanganese is produced by the silicothermic reaction between a silicomanganese alloy and a lime - ore melt. The two most common processes are a single stage operation and a multi - stage operation. In both processes alumina is added to the furnace ore blend in the form of clay.

The single stage process uses an electric arc furnace in which silicomanganese, manganese ore and a suitable flux are melted together. Both slag and metal can be tapped intermittently from the furnace.

In the multi - stage process, a premelt of manganese and lime ore is smelted in an open arc furnace. The furnace premelt is then tapped into a ladle in which the reduction reaction is carried out by adding

silicomanganese alloy, usually in solid form. Re-ladling is used to achieve adequate mixing of the reactants. The initial lime - ore premelt normally contains 50 to 60 per cent MnO. This should be reduced to between 30 to 35 per cent MnO during reladling and this reduction in the MnO content of the slag represents a manganese recovery of approximately 40 per cent. The final slag would normally have the approximate compositions MnO 30 to 35 per cent, CaO 24 to 26 per cent, MgO 6 to 10 per cent, SiO_2 24 to 26 per cent and FeO less than 1 per cent.

The alloy manganese content would increase from between 65 to 70 per cent to between 80 to 85 per cent. Carbon concentrations in the alloy would fall to below 1 per cent with a final silicon content of approximately 1 to 1, 5 per cent.

A small amount of coal or coke is charged along with the other components to the lime - ore melt in an open arc electric furnace. The coal or coke partially reduces the higher oxides of both iron and manganese, contained in the ore, to their lowest oxide states[5, 6]. The burden is heated as it moves through the furnace and there is thermal decomposition of the manganese ore with the liberation of oxygen. However, this reaction does not go to completion, and hence a small amount of carbonaceous reducing agent is added to reduce as much of the iron and manganese to the divalent state as possible.

Carbon is used as the reducing agent for economic reasons. Silicomanganese is essential for the reduction of the lower metallic oxides to metal without the introduction of large amounts of carbon. This reducing alloy is more expensive than coal or coke and should be used only for reduction of the metals in the divalent state. The use of carbon to form melts containing lower manganese oxides should be controlled as too high a carbon addition could result in carbide formation and thus in higher carbon contents in the final refined ferromanganese. An additional important point is that the gases produced by reduction with carbon escape from the furnace whilst for reduction with silicon the silica produced has to be fluxed in order to

achieve suitable furnace operation.

This fluxing process is costly and increases the slag - to - metal ratio giving lower manganese recoveries and increased power costs. Lime has to be added to complex the silica produced by the reaction. Although the basicity of the slag can be kept constant maintaining a constant MnO activity coefficient[7], dilution of the concentration of MnO results in a reduction in its activity.

The carbon monoxide generated in the furnace is also important for the reduction of manganese oxides. These reactions may be expressed as follows:

$$2MnO_2 + CO = Mn_2O_3 + CO_2 \qquad 2.1$$

$$3Mn_2O_3 + CO = 2Mn_3O_4 + CO_2 \qquad 2.2$$

$$Mn_3O_4 + CO = 3MnO + CO_2 \qquad 2.3$$

It is thermodynamically unlikely that this reducing gas will produce manganese metal for the conditions prevailing within the furnace. Evidence for this statement is provided by examination of the reactions for reduction of manganese oxide:

$$MnO_{(s)} + CO = Mn_{(s)} + CO_2 \quad \Delta G^\circ = 104458 + 11,87T \text{ Joules} \quad (25 \text{ to } 1244^\circ C) \qquad 2.4$$

$$MnO_{(s)} + CO = Mn_{(l)} + CO_2 \quad \Delta G^\circ = 124815 - 17,14T \text{ Joules} \quad (1244 \text{ to } 1700^\circ C) \qquad 2.5$$

Interpolated ΔG° values from summations of standard free energies[8] show that manganese metal production by this gaseous reduction is thermodynamically very unfavourable. This is in agreement with statements indicating that gaseous reduction of MnO does not occur in practice[9-11].

As the furnace burden descends the burden components are preheated and manganese ore is reduced by carbon in the solid state. Eventually manganese metal and carbide may be formed. These reactions are expressed by the equations

$$MnO + C = Mn + CO \qquad 2.6$$

$$\text{and} \quad 6MnO + 8C = 2Mn_3C + 6CO \qquad 2.7$$

As the theoretical initial temperatures considering unit activity for these two reactions are 1420°C and 1223°C respectively, Mn_3C formation is the more likely thermodynamically. Excess carbon is not used in the preparation of the lime - ore melt and the problem of carbide formation does not arise.

The predominant reaction occurring during silicon reduction of the lime - ore melt is expressed as:

$$2(MnO) + [Si] = (SiO_2) + 2[Mn] \qquad 2.8$$

where the species in parentheses are in the slag and the square bracketed species are in the alloy.

This reaction is usually performed in a ladle in which crushed silicomanganese is added to the lime - ore melt. As the reduction reactions are extremely exothermic, a coolant is usually added to the melt. The coolant used is often medium - to low - carbon ferromanganese fines, generated by the crushing of this alloy before final dispatch to the steelworks. Within a short while the reaction has virtually reached completion. At this stage 'cocktailing' of the ladle is employed to increase mixing between reactants and boost manganese recovery to produce a more refined alloy.

These are the general procedures adopted in the industrial production of refined ferromanganese. Several workers have evolved modified procedures in attempts to improve the processes.

One such example is the refining of silicomanganese by the mixing of melts. Experiments on the production of medium - carbon ferromanganese by the mixing of molten silicide alloy with manganese ore - lime melts have been conducted in Russia but poor recoveries of between 29, 8 to 33, 5 per cent of the manganese

contained in the slag were achieved[12].

Bauer et al[13] mixed two melts consisting of a silicon - manganese - iron alloy and a manganese oxide melt. Gas injection was used to force the molten alloy phase upwards through the oxide melt and the alloy phase then fell back downward through the oxide phase. This procedure was continued until the composition of the alloy phase reached the desired manganese and silicon contents. Agitation of the reactants has been practised by other workers[14, 15] to increase recoveries.

The production of refined ferromanganese from liquid manganese silicide in a fuel - fired rotary furnace has been developed by Urane[16]. These methods of agitation all promote contact between the silicide reducing agent and the slag containing manganese.

2.3 Uses of Manganese Alloys

Manganese is used extensively in the iron and steel industry as a deoxidizer, desulphurizer and alloying element. This threefold role has made manganese one of the main constituents of steel and over 95 per cent of the output of manganese is consumed in steelmaking. Manganese is used by the steel industry as high - carbon ferromanganese, medium - and low - carbon ferromanganese, spiegeleisen and silicomanganese as well as manganese metal. The total world production of manganese alloys amounts to about six million metric tons annually.

The most widely used manganese alloy is high - carbon ferromanganese and the steel industry consumes approximately 7 kg per metric ton of crude steel or slightly below five million metric tons annually, based on the present world steel production.

The production of silicomanganese, the second largest 'tonnage' manganese alloy, is about 20 per cent of the tonnage of

high - carbon ferromanganese. A substantial increase in silicomanganese consumption is not expected within the near future as few steel producing countries make direct additions of this alloy to the crude steel on a large scale. However, silicomanganese is required as a raw material for the production of refined ferromanganese and hence the production of silicomanganese will increase with the production of refined ferromanganese.

The consumption of refined ferromanganese is expected to increase as less high - carbon ferromanganese is produced because of the expansion of the L.D. process and increases in the production of thinner finished steel sections which require manganese alloys with lower carbon and silicon contents. Silicomanganese and refined ferromanganese have favourable carbon - to - manganese ratios and are of particular interest for situations which require low carbon content steels. There are many different grades of refined ferromanganese, ranging from medium - carbon (0,5 to 2 per cent) to low - carbon (less than 0,5 per cent) with different manganese, silicon, phosphorous and sulphur contents.

Manganese metal, although it is not a manganese alloy, can be included in this survey. Its main outlet is in the production of non - ferrous metals and in the aluminium industry in which iron is an undesirable impurity. It is also used in the steel industry in competition with low - carbon ferromanganese, mostly in stainless and alloyed steels with extremely low carbon contents.

Ferromanganese alloy production figures are difficult to estimate accurately because they vary from one country to another according to the quality and type of steel produced, the steelmaking process and the production of cast iron. The steel industry consumes approximately 98 per cent of all ferromanganese alloys and manganese metal whilst the cast

iron industry only accounts for about 2 per cent of the total production.

The main producers of manganese ferroalloys and manganese metal during 1972 are listed in Table 2. In recent years there has been a tendency to use less manganese per metric ton of steel[18]. This decrease in manganese consumption per metric ton of steel is due, in part, to the introduction of the basic oxygen process which uses shorter blowing times so that less manganese is oxidised into the slag. Two further reasons for this reduction in the manganese content of steels could possibly be the use of iron ores and fuels with lower sulphur contents and lower manganese contents in the steels. However, as world steel production is expected to reach one thousand million metric tons in the next few years, the manganese alloy industry is expected to expand to produce about seven million metric tons per year of high - carbon ferromanganese.

This section is followed by a summary of the theoretical and experimental background for the present study in the form of a review of previous studies on the stability ranges for manganese oxides. Data on equilibrium and kinetic considerations of slag and metal systems related to the production of refined ferromanganese are also presented.

TABLE 2[17]

FERROMANGANESE ALLOY AND MANGANESE METAL PRODUCTION, 1972.
(Quantities are given in thousands of metric tons)

Producer	High-carbon Ferromanganese	Refined Ferromanganese	Silico-Manganese	Manganese Metal
U.S.S.R.	1000			
U.S.A.	675	86	170	21
Japan	470	131	466	12
France	450	55*		
Eastern Bloc	300			
Norway	250	30*	145	
R.S.A.	225	15*		12
Germany	210	40*		
India	140			
Belgium	120			
United Kingdom	110			
Canada	80			
Spain	80	15*		
Australia	70			

*Estimated

3. PHYSICAL CHEMISTRY OF FERROMANGANESE PRODUCTION

To understand the mechanism of reduction of manganese ores and the nature of the slag - metal reactions that occur during the production of refined ferromanganese, it is necessary to review previously published information on the physical chemistry of ferromanganese production.

This review of the physical chemistry of ferromanganese production will discuss the thermal deoxidation of manganese oxides, activities in slag and alloy systems as well as slag - metal equilibria and the kinetics of slag - metal reactions.

3.1 Thermal Deoxidation of Manganese Oxides

Mamatwan ore consists principally of braunite associated with other minor manganese minerals such as manganite (MnO(OH)) and hausmannite (Mn_3O_4). In natural occurrences of ore the braunite composition can be represented as $3Mn_2O_3.MnSiO_3$ and thus the braunite contains approximately 10 mass per cent SiO_2. Braunite has a wide range of possible compositions ranging from pure Mn_2O_3 to a manganese silicate containing approximately 40 mass per cent SiO_2.

Hooper[6] reported that thermal dissociation of MnO_2 commenced at temperatures above 400°C. Abdul Azim[19] discussed differential thermal analyses to show that Mn_2O_3 is formed from MnO_2 in the temperature range 500° to 600°C. Mn_2O_3 exists in two polymorphic forms, cubic αMn_2O_3 and the distorted spinel γMn_2O_3.

Dissociation of Mn_2O_3 to Mn_3O_4 has been studied by several authors[19-23]. Mn_3O_4 is the stable crystalline phase in air above 877 C. Tetragonal Mn_3O_4 ('low hausmannite') is stable from 877° to 1160°C and cubic Mn_3O_4 ('high hausmannite') with a spinel type structure, is stable from 1160°C to its melting point in air at 1567°C. Hahn and Muan[20] considers that the decomposition of Mn_3O_4 to MnO occurs at oxygen partial pressures of O to 10^{-3} atmospheres over the temperature range 1248° to 1562°C.

Davies and Richardson[24] studied the non - stoichiometric behaviour of MnO and brought this oxide into equilibrium with various partial pressures of oxygen by prolonged heating at 1500° to 1650°C. The ratio of the number of atoms of oxygen to manganese in the non - stoichiometric oxide was plotted against the oxygen partial pressure. The oxygen - to - manganese ratio increased from a value of 1 at $P_{O_2} = 10^{-9}$ atmospheres to 1,05 at $P_{O_2} = 10^{-2}$ atmospheres.

Figures 1 to 4 show equilibria between the different manganese oxides as a function of temperature and oxygen partial pressure. The corresponding equilibrium equations are given as:

$$4MnO_{2(s)} = 2Mn_2O_{3(s)} + O_{2(g)} \qquad \Delta G^\circ = 160512 - 213,26\,T \text{ Joules } (25 - 550^\circ C) \qquad 3.1$$

$$6Mn_2O_{3(s)} = 4Mn_3O_{4(s)} + O_{2(g)} \qquad \Delta G^\circ = 223212 - 165,27\,T \text{ Joules } (25 - 1100^\circ C) \qquad 3.2$$

$$2Mn_3O_{4(s)} = 6MnO_{(s)} + O_{2(g)} \qquad \Delta G^\circ = 445420 - 250,80\,T \text{ Joules } (25 - 1244^\circ C) \qquad 3.3$$

$$\text{or } \Delta G^\circ = 392251 - 214,60\,T \text{ Joules } (1244 - 1700^\circ C)$$

$$2MnO_{(s)} = Mn_{(s)} + O_{2(g)} \qquad \Delta G^\circ = 773216 - 149,39\,T \text{ Joules } (25 - 1244^\circ C) \qquad 3.4$$

$$\text{or } \Delta G^\circ = 813930 - 176,56\,T \text{ Joules } (1244 - 1700^\circ C)$$

Standard free energies for the above reactions are given over the temperature ranges indicated[8]. From the data of previous workers, it may be concluded that Mn_3O_4 was the most stable manganese oxide for the temperatures and oxygen partial pressures that prevail during the preparation of the premelts in this thesis.

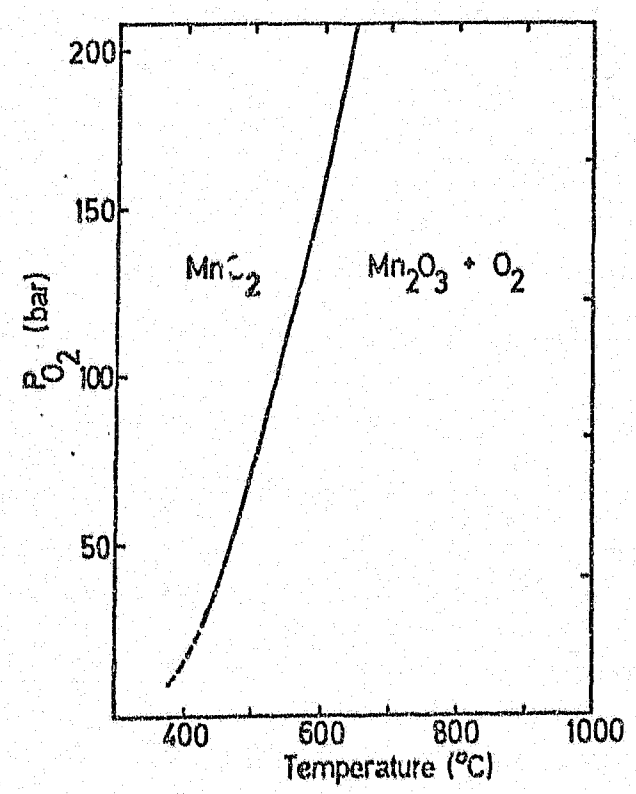


Figure 1. System Mn-O; univariant equilibrium curve between MnO_2 and Mn_2O_3 (25)

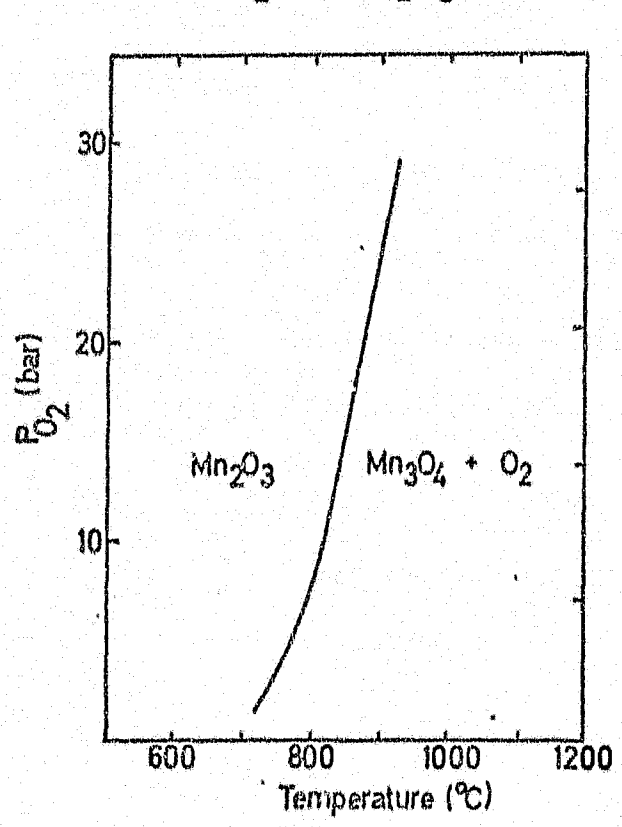


Figure 2. System Mn-O; univariant equilibrium curve between Mn_2O_3 and Mn_3O_4 (25)

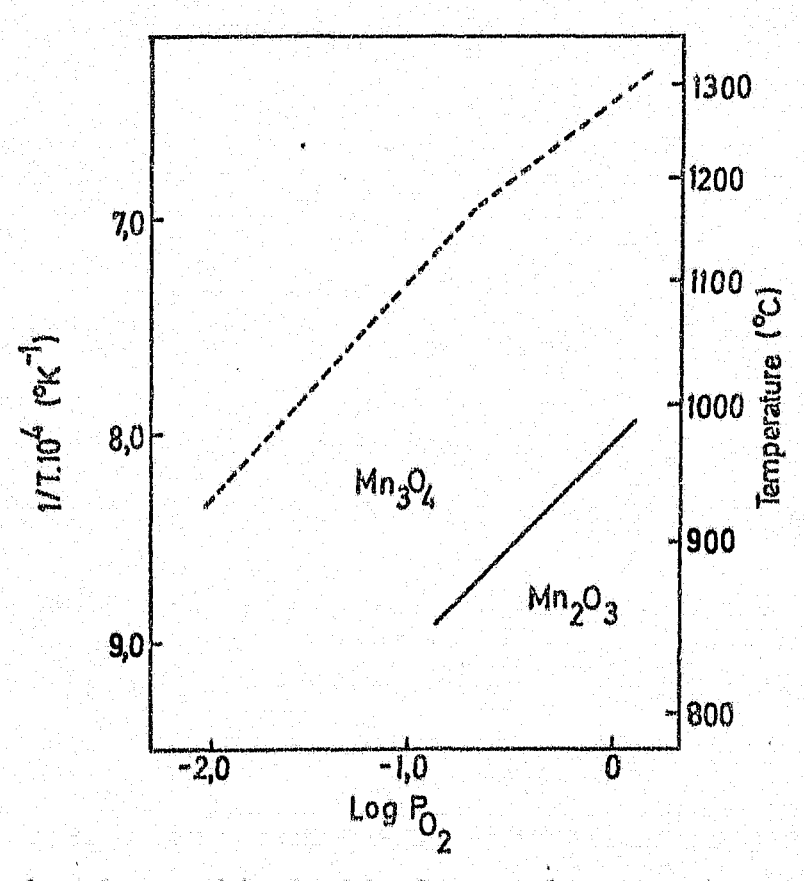


Figure 3. System Mn_2O_3-Mn_3O_4 as a function of O_2 pressure and temperature[20]. Dashed curve data of Coughlin[26].

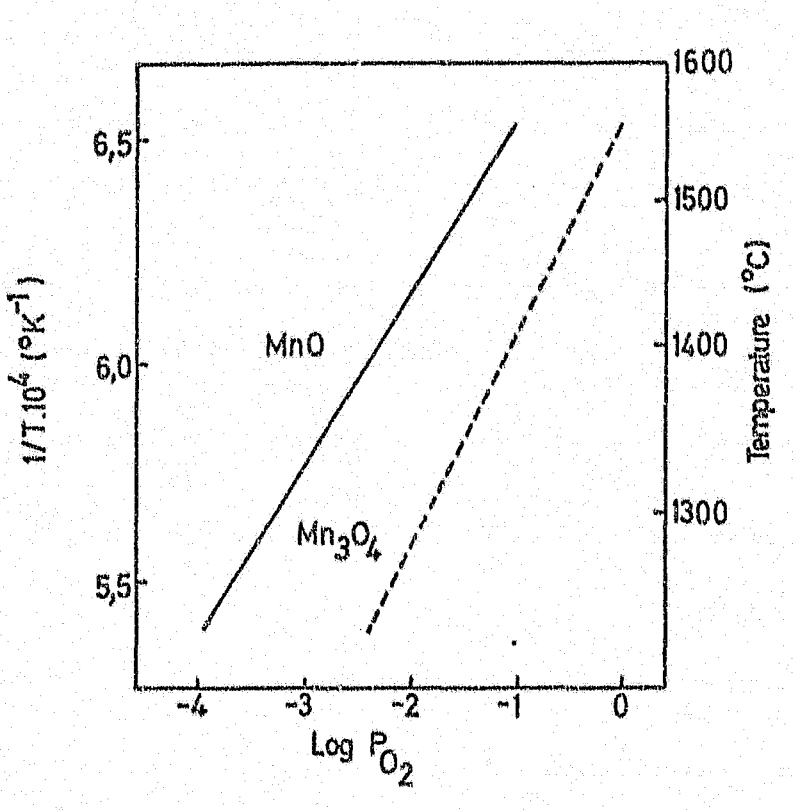


Figure 4. System MnO-Mn_3O_4 as a function of O_2 pressure and temperature[20]. Dashed curve data of Coughlin[26].

3.2 Slag systems in Ferromanganese Production

3.2.1 Properties of Ferromanganese Slags

Slag - making components are added to manganese ores for improved slag control and higher manganese recoveries in the silicothermic processes for the production of low - to medium - carbon ferromanganese. Manganese recovery from the slag is influenced by the activity of MnO in the slag and although this activity will vary during the course of the silicothermic reaction, due to silica formation, as high an activity as possible is required. Therefore, basic fluxing additions are essential to ensure both high levels of manganese extraction from the slag melt and low silica activities in the slag which result in low silicon in the alloy. The relevant reduction reaction is:

$$2(MnO) + [Si] = (SiO_2) + 2[Mn] \qquad 3.5$$

From this equation

$$a^2_{Mn} = \frac{K.a^2_{MnO}\, a_{Si}}{a_{SiO_2}} \qquad 3.6$$

For maximum manganese recovery from the slag, the activity of manganese in the alloy should be as high as possible and equation 3.6 shows that this is achieved by a high MnO activity in the slag as well as a high activity of silicon in the alloy. Higher MnO activities are obtained in basic slags which may contain some MgO, but MgO additions do not increase the activity of MnO in the slag as much as identical additions of CaO[27]. For the purposes of this discussion, basicity in ferromanganese slags in defined as:

$$\text{Basicity} = \frac{CaO\ (\%) + MgO\ (\%)}{SiO_2\ (\%)} \qquad 3.7$$

Unfortunately basic slags often have high liquidus temperatures in the temperature range 1600° to 1700°C and this means that smelting temperatures between 1650° to 1750°C are necessary.

These higher smelting temperatures result in considerable losses of manganese due to volatilization and these losses can be as much as 8 to 10 per cent of the manganese charged to the electric furnace. However under incorrect electric furnace conditions or procedure the loss may be as high as 20 per cent[28]. Thus a compromise is required between a slag possessing high slag basicity and a low liquidus temperature.

Typical variations in slag composition in the process should not involve any marked change in the liquidus temperature of the slag. The optimum slag basicity is therefore of considerable importance and its selection will depend not only on the slag properties and temperature but also on the operating characteristics of the furnace and the quality of the charge materials.

Several workers have proposed that CaO can be replaced by MgO up to a limit of 8 to 11 per cent MgO in the final slag[29-34]. This MgO addition lowers the slag viscosity at any particular temperature and slag basicity. When MgO was substituted for CaO up to concentrations between 3 to 18 per cent MgO in relatively low Al_2O_3 slags (14 to 18 per cent) the basicity was increased from the normal value of 1, 4 to 1, 6 to as high as 2, 8 without a substantial increase in the liquidus temperature and an increased manganese yield[35].

It has also been claimed that MgO and SiO_2 can be replaced by Al_2O_3 to increase manganese recovery from the slag. This has been substantiated by Jon[36] who studied the relationship between the basicity and the Al_2O_3 content of the slag. At optimum and particularly low levels of MgO, it is possible to obtain basicities greater than 3 at Al_2O_3 levels of approximately 30 weight per cent. The main advantage of Al_2O_3 slags is that the concentration of SiO_2 in the slag is reduced by dilution and the activity of SiO_2 in the melt is lowered. In addition, the activity of SiO_2 is reduced at higher basicities. Both these factors give lower silicon concentrations in the metal in equilibrium with the SiO_2 of the slag. Therefore, to obtain a high recovery of manganese, it is important to use slag compositions that

permit high ratios of Al_2O_3 to SiO_2 and bases to SiO_2 without impairing the overall fluidity[37].

The production of medium - to low - carbon ferromanganese requires a high grade of ore with a high manganese - to - iron ratio and a low SiO_2 content to prevent excessive slag formation and avoid increased flux consumption. Less slag results in lower power consumption for the electric furnace and higher manganese recovery.

Thus suitable raw materials are essential ... to achieve high production rates and to minimise the cost of production. Raw materials account for a high proportion of the cost of the product in ferromanganese production.

Dolomite may be used as a slagging component in preference to CaO[38, 39]. Dolomite is less expensive than CaO and the contained MgO tends to increase the slag fluidity, for any temperature and slag basicity.

The effect of MgO on the activity coefficient of MnO is dependent on the slag composition. For constant Al_2O_3 and SiO_2 contents and high SiO_2 values, the activity coefficient of MnO decreases[7, 40] as CaO is replaced by MgO. However in slags of high basicity, the activity coefficient of MnO increases with increasing MgO content[7].

3.2.2 Activities of Manganese(II) oxide

Several models have been advanced for the calculation of activities of components of these slags. The most important models are based on the assumption that silicon is bonded to oxygen anions and the slag structure consists of silicate anions, SiO_4^{4-}, and oxygen anions with cations such as Ca^{2+}, Mg^{2+}, Fe^{2+} and Mn^{2+}. Evidence for this model is provided by measurements of slag viscosities by Bockris et al[41, 42] and this model has been adopted by Richardson[43].

Masson[44] has extended this concept of slag structure to consider polymer formation by silicate anions in binary systems. Masson's

polymerization theory depends on the polymerization constant remaining the same for the formation of complex anions such as $Si_2O_7^{6-}$ and $Si_3O_{10}^{8-}$ from SiO_4^{4-} anions with the liberation of O^{2-} anions. Typical polymerization reactions are:

$$SiO_4^{4-} + SiO_4^{4-} = Si_2O_7^{6-} + O^{2-} \qquad 3.8$$

and $$Si_2O_7^{6-} + SiO_4^{4-} = Si_3O_{10}^{8-} + O^{2-} \qquad 3.9$$

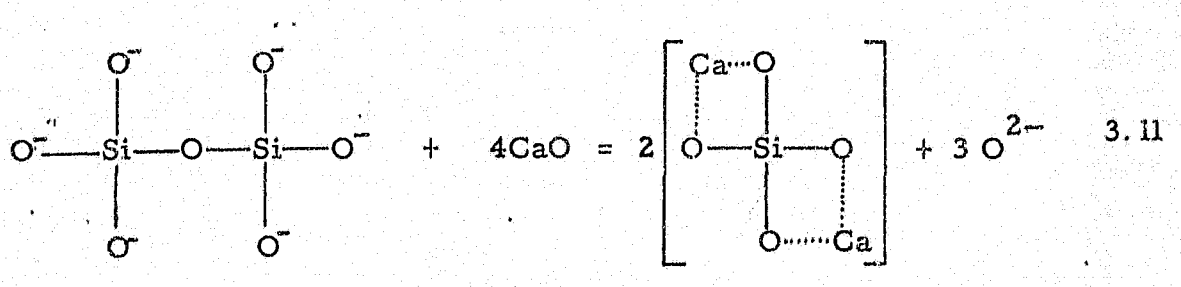
Another general concept of slag constitution has been developed by Lumsden[45] who considers oxygen anions and cations such as Si^{4+}. The existence of highly polarizing, highly charged Si^{4+} ions is considered by Johnston[46] to be most improbable. The formation of Si^{4+} ions was believed to occur by means of silica dissociation. In acid slags, excess silica over that which could be neutralised by basic oxides to give M^{2+} and SiO_4^{4-} ions may be assumed to dissociate in the form:

$$2SiO_2 = Si^{4+} + SiO_4^{4-} \qquad 3.10$$

Johnston states that dissociation of the remaining silica is most unlikely.

An explanation of the increase in the activity of MnO as slag basicity increases is possible from these models. In slags of low basicity all cations are associated with silicate anion groups and few O^{2-} ions exist. However, as the basicity increases, silicate anion groups collapse and the proportion of O^{2-} ions increases giving free O^{2-} ions. Each free O^{2-} ion liberates a divalent cation that is no longer associated with silicate anions but with free oxygen ions. By increasing the slag basicity, 'network modifying' oxide concentrations are increased. A 'network modifying' oxide is one which actively weakens or breaks up a network of other oxide groups. The mechanism proposed for achieving this break - down is the introduction of non-continuously bonded oxygen anions and cations. This mechanism

is illustrated schematically in equation 3.11:



3.11

The interaction of silicate anions with Ca^{2+} and Mg^{2+} ions is stronger than their interaction with Mn^{2+} ions These cations are preferentially associated with silicon cations to give silicate anions SiO_4^{4-}. Thus Mn^{2+} ions are free from association with silicate anions and higher activity coefficients of MnO are obtained.

The slight increase in the activity coefficient of the MnO in highly basic slags when MgO replaces CaO at constant Al_2O_3 and SiO_2 levels may be explained as a combination of two effects. The first effect is that for any particular weight addition of flux, the number of moles of flux increases as MgO replaces CaO but this basicity increase is too small to explain the rise in the activity coefficient of MnO. When MgO substitutes for some CaO the formation* of $CaMgSiO_4$ is far more likely than either the formation of Ca_2SiO_4 or Mg_2SiO_4. The standard free energy of formation of $CaMgSiO_4$ is more negative than the standard free energies of formation of the other two orthosilicates or three metasilicates as indicated in the list below where standard free energies of formation are given for solids at 1500°K.

$2CaO + SiO_2 = Ca_2SiO_4$	$\Delta G^\circ_{1500^\circ K} = -136,3$ K Joules mole^{-1}	3.12
$2MgO + SiO_2 = Mg_2SiO_4$	$\Delta G^\circ_{1500^\circ K} = -69,9$ K Joules mole^{-1}	3.13
$MgO + CaO + SiO_2 = CaMgSiO_4$	$\Delta G^\circ_{1500^\circ K} = -154,2$ K Joules mole^{-1}	3.14
$MnO + SiO_2 = MnSiO_3$	$\Delta G^\circ_{1500^\circ K} = -5,8$ K Joules mole^{-1}	3.15
$CaO + SiO_2 = CaSiO_3$	$\Delta G^\circ_{1500^\circ K} = -88,2$ K Joules mole^{-1}	3.16
$MgO + SiO_2 = MgSiO_3$	$\Delta G^\circ_{1500^\circ K} = -29,7$ K Joules mole^{-1}	3.17

* The term 'formation' is used for convenience. It must be emphasized that $CaMgSiO_4$ etc. are not present in the slag as such, but rather that Ca^{2+}, Mg^{2+} and SiO_4^{4-} ions tend to be associated together to give the overall composition $CaMgSiO_4$.

3.2.2.1 Binary Systems

The $MnO-SiO_2$ binary shows values for the activity coefficient of MnO with negative deviations from Raoults law up to approximately 70 mole per cent MnO. Positive deviations occur after 70 mole per cent manganese oxide as shown in Figure 5[47]. The $MnO-Al_2O_3$ binary system is similar to the $MnO-SiO_2$ system although at low alumina concentrations, the activity coefficient of manganese oxide is lowered further than for the same silica content as shown in Figure 6[48].

3.2.2.2 Ternary Systems

The activities of MnO in the ternary systems $MnO-CaO-SiO_2$, $MnO-MgO-SiO_2$ and $MnO-Al_2O_3-SiO_2$ are shown in Figures 7, 8, 9 and 11. These diagrams reveal that, on a mole per cent basis, the activity of MnO in the slag is raised more by CaO additions than by MgO additions and more by MgO additions than by Al_2O_3 additions. The $MnO-CaO-SiO_2$ and $MnO-CaO-Al_2O_3$ systems given in Figures 8 and 10 show that, on a molar basis, SiO_2 additions more markedly decrease the MnO activity at any fixed MnO concentration than Al_2O_3 additions. At low MnO concentrations, SiO_2 additions cause larger negative deviations from ideality for the MnO activity than do Al_2O_3 additons[40, 47, 48].

A comparison of experimental data and calculated isoactivity lines for the system $FeO-MnO-SiO_2$ at 1550°C is shown in Figure 12[49]. Isoactivity lines were calculated from the following quadratic equation developed from a regular solution model for the partial molar excess free energy of a component, i.e.,

$$\log \gamma_{MnO} = -2,2N^2_{SiO_2} - 1,0N_{FeO}N_{SiO_2} \qquad 3.18$$

In the $MnO-FeO-Al_2O_3$ system a similar quadratic expression, linking the activity coefficient of MnO to the mole fraction in the system, was put forward by these workers, i.e.,

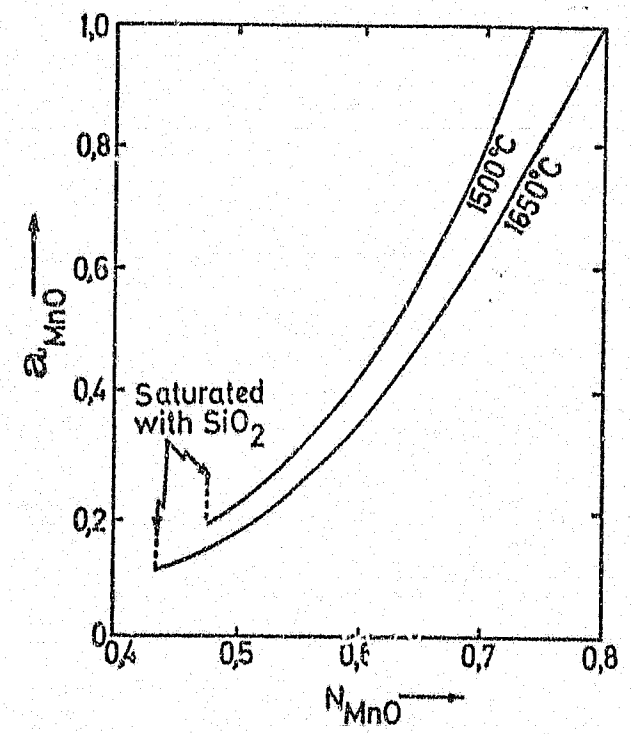


Figure 5. Activities of MnO in MnO-SiO_2 melts with reference to solid MnO as standard state. (Abraham et al[47]).

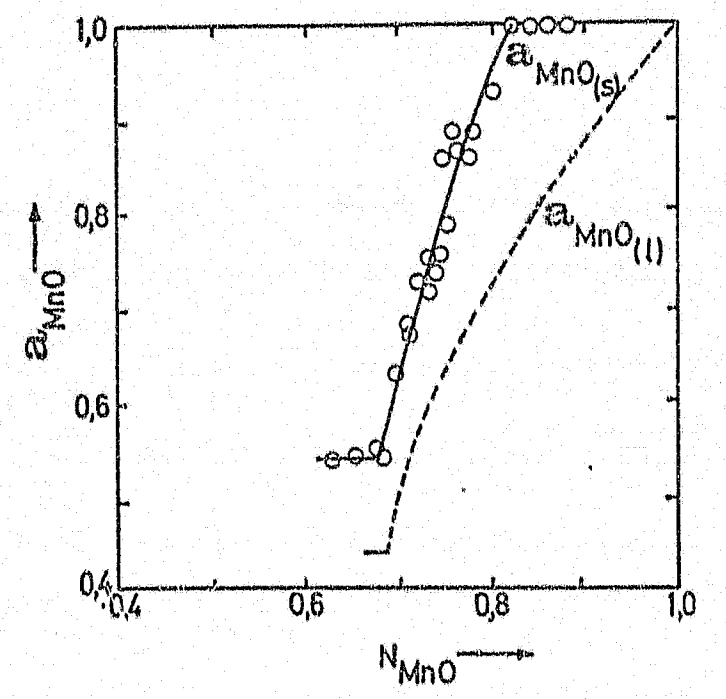


Figure 6. Activities of MnO in MnO-Al_2O_3 melts at 1650°C. Full lines and points represent results relative to solid MnO, broken lines relative to liquid MnO. (Sharma and Richardson[48]).

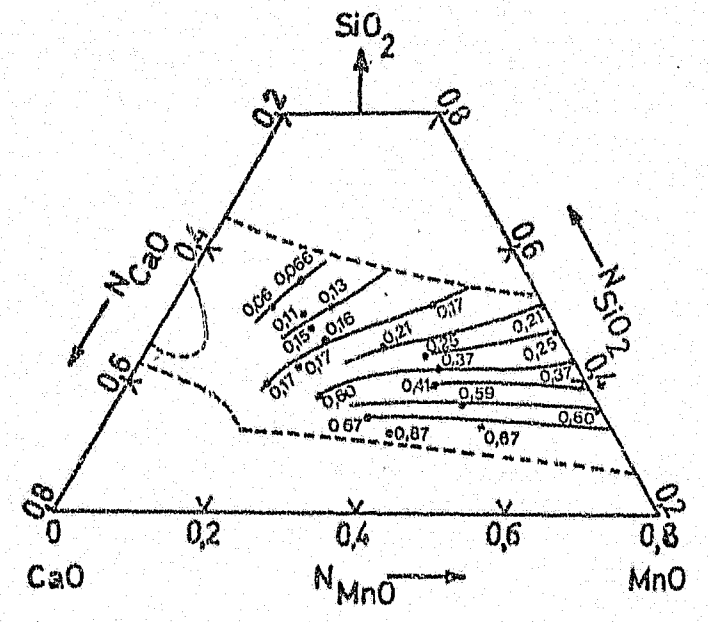


Figure 7. Activities of manganese oxide relative to pure solid MnO in MnO-CaO-SiO_2 melts at 1500°C[47]. Broken lines are probable liquidus.

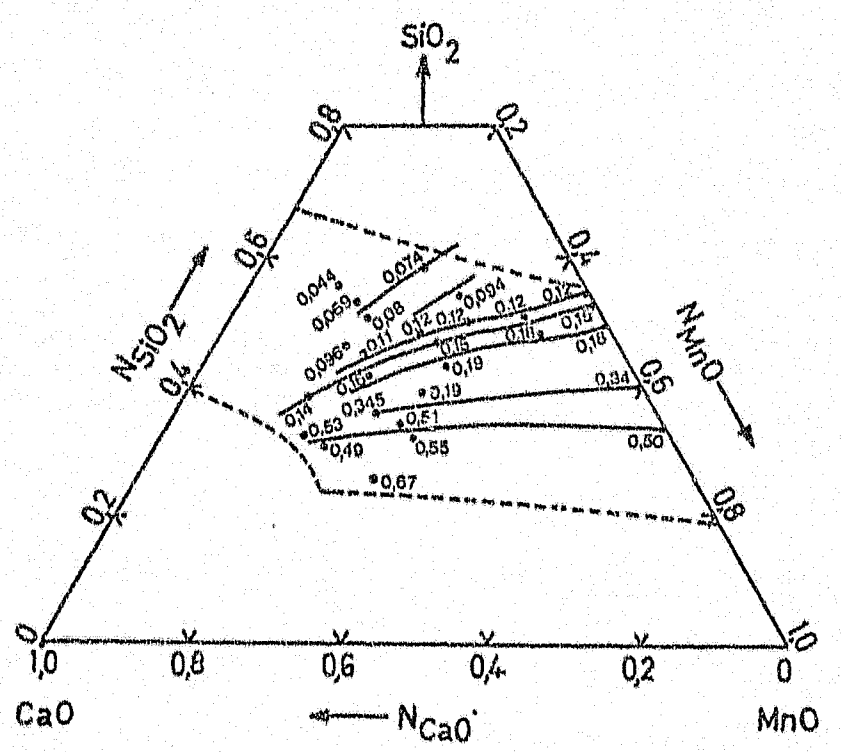


Figure 8. Activities of manganese oxide relative to pure solid MnO in MnO-CaO-SiO_2 melts at 1650°C[40, 47]. Broken lines are probable liquidus.

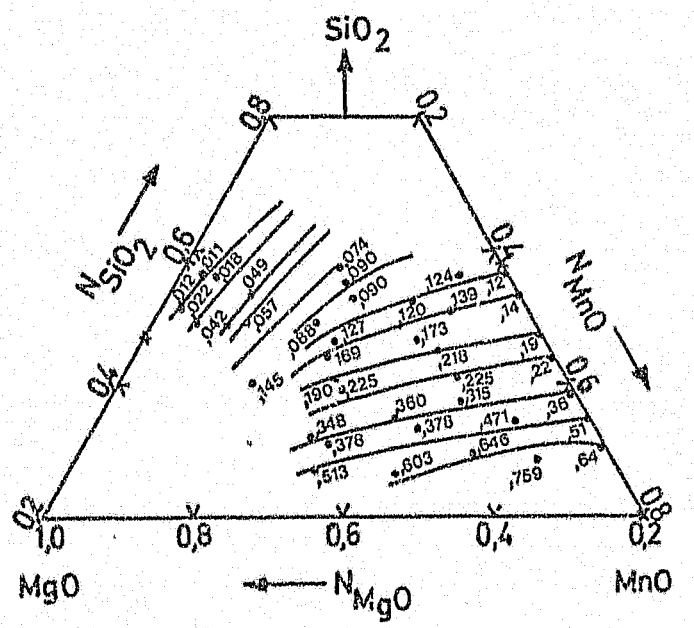


Figure 9. Activities of MnO relative to pure solid MnO in $MgO-MnO-SiO_2$ melts measured at 1650°C; crosses show liquidus limits in binary[40].

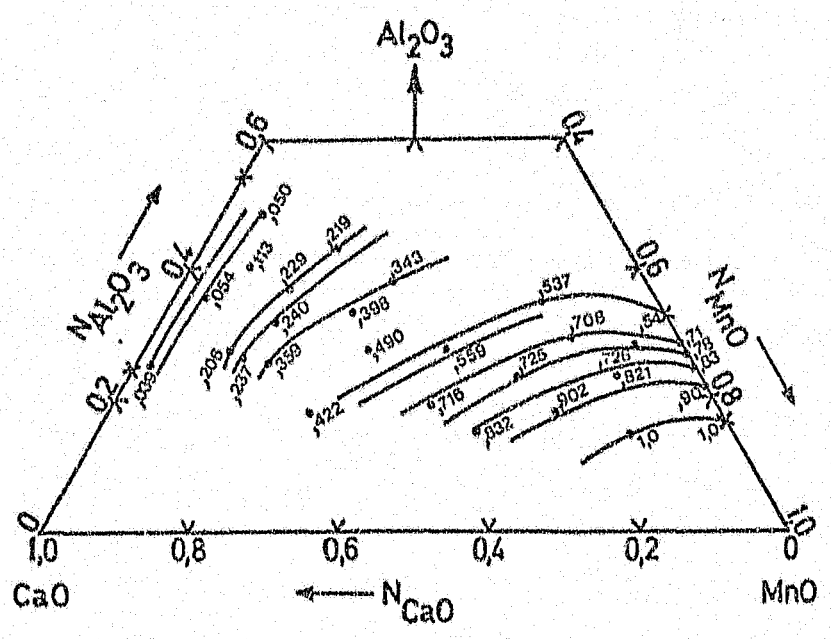


Figure 10. Activities of MnO relative to pure solid MnO in $MnO-CaO-Al_2O_3$ melts measured at 1650°C; the limiting activities in $MnO-Al_2O_3$ are taken from Sharma and Richardson[48]; crosses show liquidus[40].

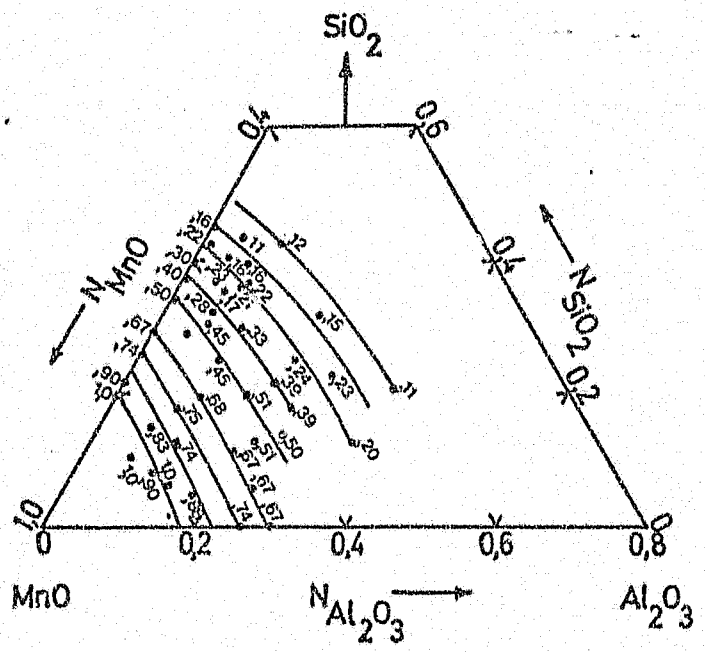


Figure 11. Activities of MnO in $MnO-SiO_2-Al_2O_3$ melts measured at 1650°C relative to pure solid[48].

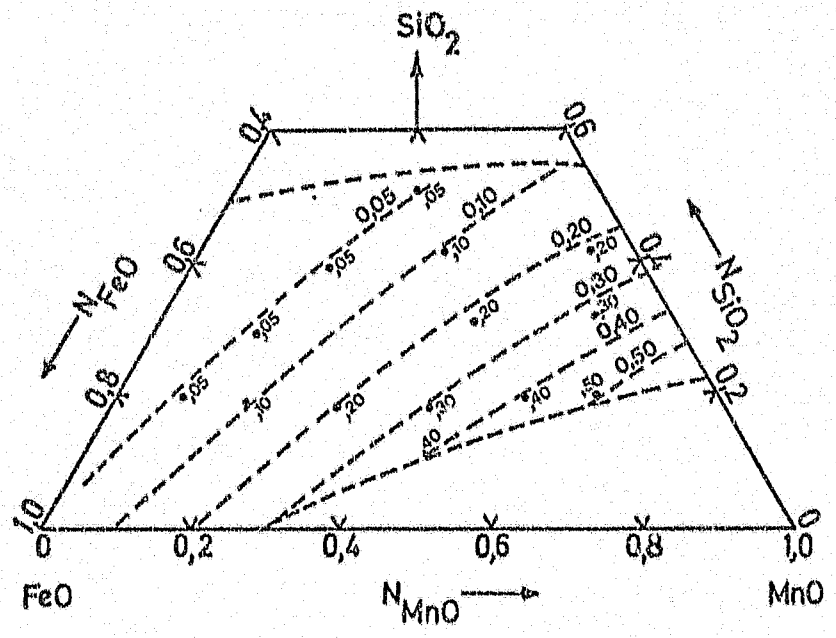


Figure 12. Comparison of calculated iso-activity curves for MnO with experimental values in the $FeO-MnO-SiO_2$ system at 1550°C; standard state pure liquid[49].

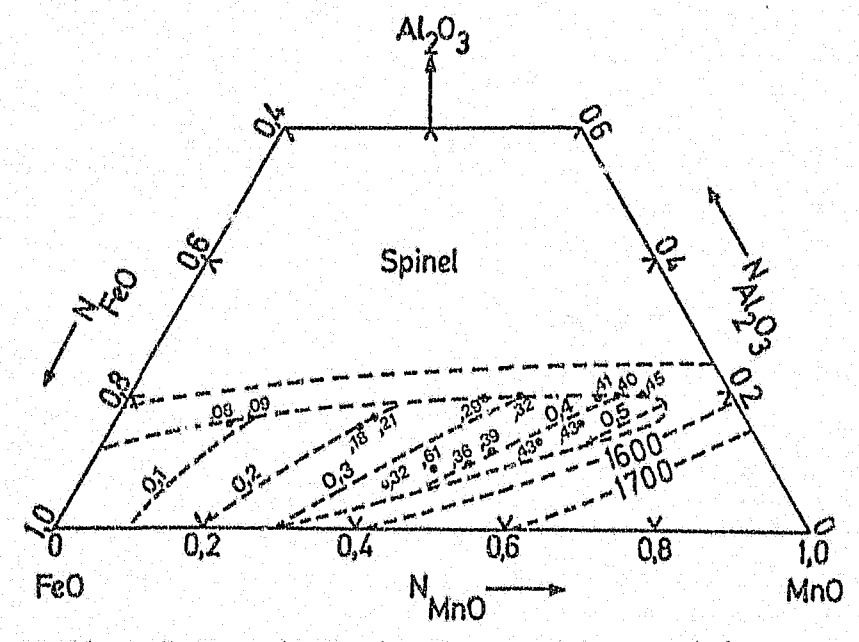


Figure 13. Comparison of calculated iso-activity curves for MnO with experimental values in the FeO-MnO-Al_2O_3 system at 1550°C: standard state pure liquid[49].

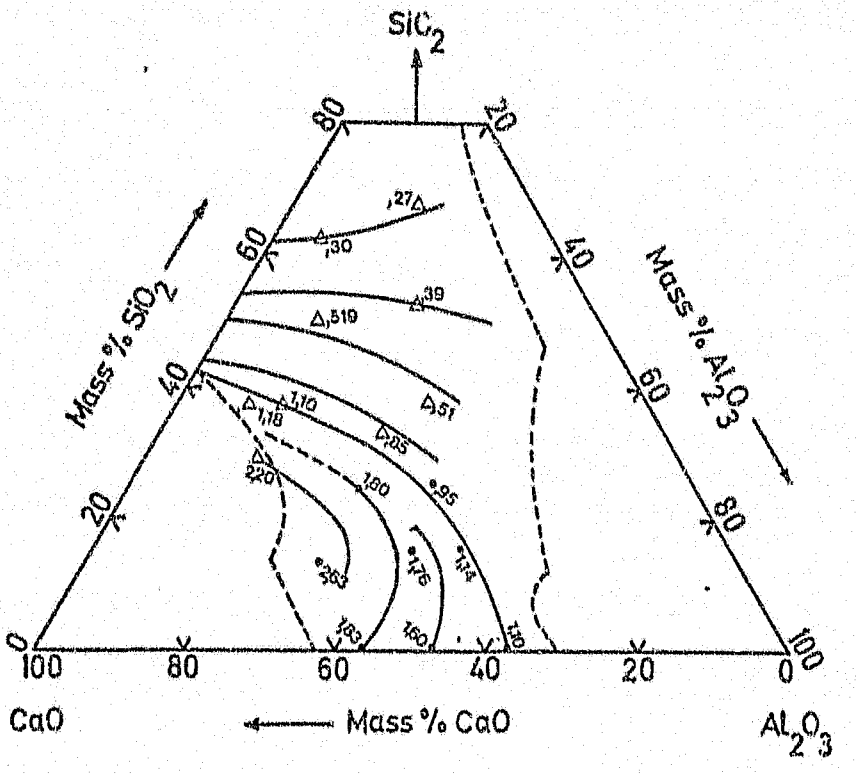


Figure 14. Activity coefficients relative to pure solid MnO at low concentrations in $CaO-Al_2O_3-SiO_2$ melts at 1650°C. measured by Mehta and Richardson[40] and Abraham et al[47]. N_{MnO} in all cases less than 0,05; broken lines show liquidus in the ternary.

$$\log \gamma_{MnO} = -0,6N^2_{AlO_{1,5}} - 0,55N_{FeO}N_{AlO_{1,5}} \qquad 3.19$$

Maruhashi[50] established that the activity of MnO in this system showed a negative deviation from ideality over all concentrations of MnO. Deviations became more marked as Al_2O_3 contents increased or as the MnO concentration increased.

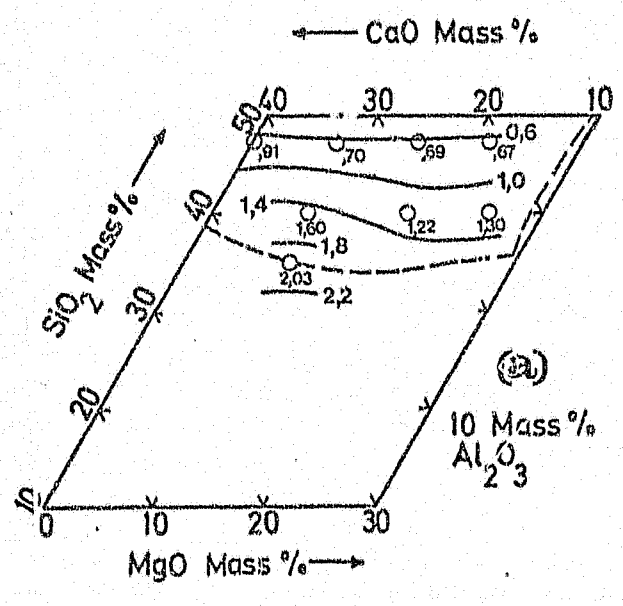
3.2.2.3 Quaternary systems

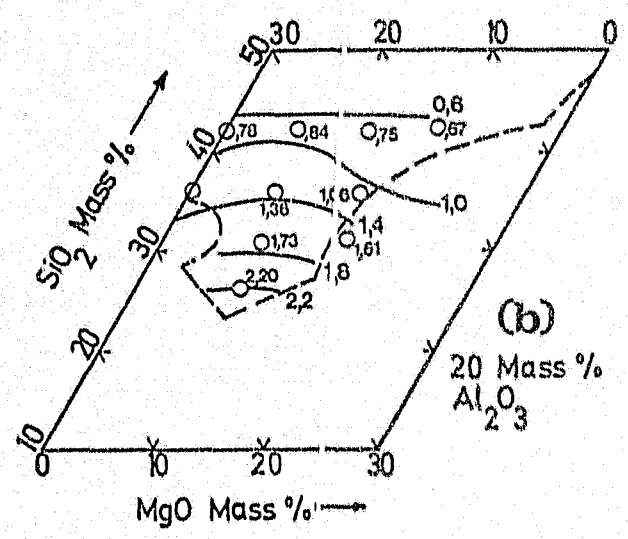
Figure 14 shows the advantages of using slags rich in CaO and Al_2O_3 to obtain high manganese recoveries in the production of ferromanganese. The amphoteric nature of the Al_2O_3 is demonstrated in this diagram. In the area of 60 mass per cent SiO_2 the activity coefficient of MnO is virtually unaltered by the substitution of Al_2O_3 for CaO[40, 47]. In this region the Al_2O_3 is acting as a base. However, for mass percentages of SiO_2 less than 30, the substitution of Al_2O_3 for CaO markedly lowers the activity coefficient of MnO and thus Al_2O_3 is acting as an acid.

Derived expressions for the activity coefficient of MnO in MnO-FeO-Al_2O_3-SiO_2 quaternary systems have been obtained at 1550 °C by Sommerville et al[49] and, for example,

$$\log \gamma_{MnO} = -2,2N^2_{SiO_2} - 0,6N^2_{AlO_{1,5}} - 1,0N_{FeO}N_{SiO_2} - 0,55N_{FeO}N_{AlO_{1,5}} - 1,3N_{SiO_2}N_{AlO_{1,5}} \quad \ldots\ldots \quad 3.20$$

Calculated and measured activities agree to within 0,03 for the compositions studied. These values were derived on the basis of regular solution theory, the standard state in all cases being pure liquid oxide at the temperature concerned.





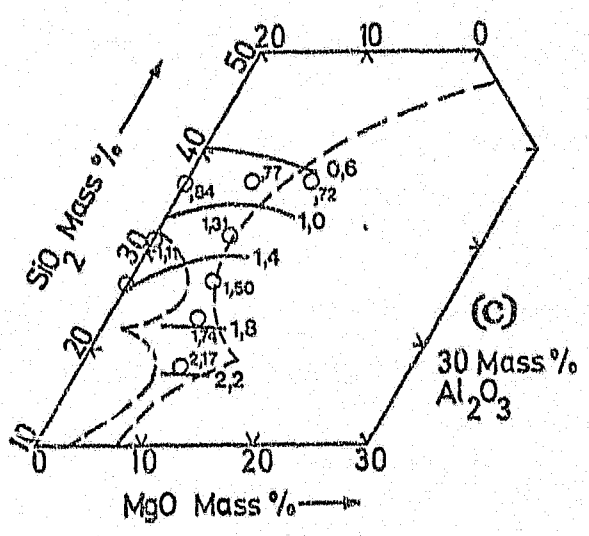
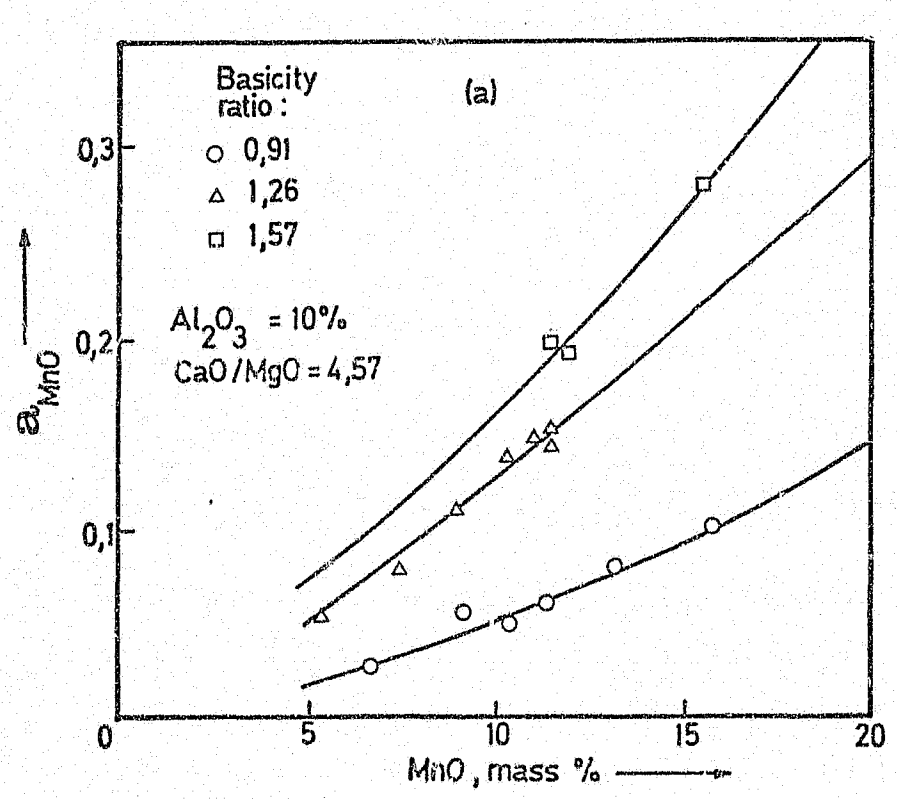


Figure 15. Activity coefficients of MnO relative to solid at concentrations of 13 mass per cent in SiO_2-Al_2O_3-MgO-CaO-MnO slags at 1500°C. Broken lines show 1500°C liquidus isotherms without MnO[7].



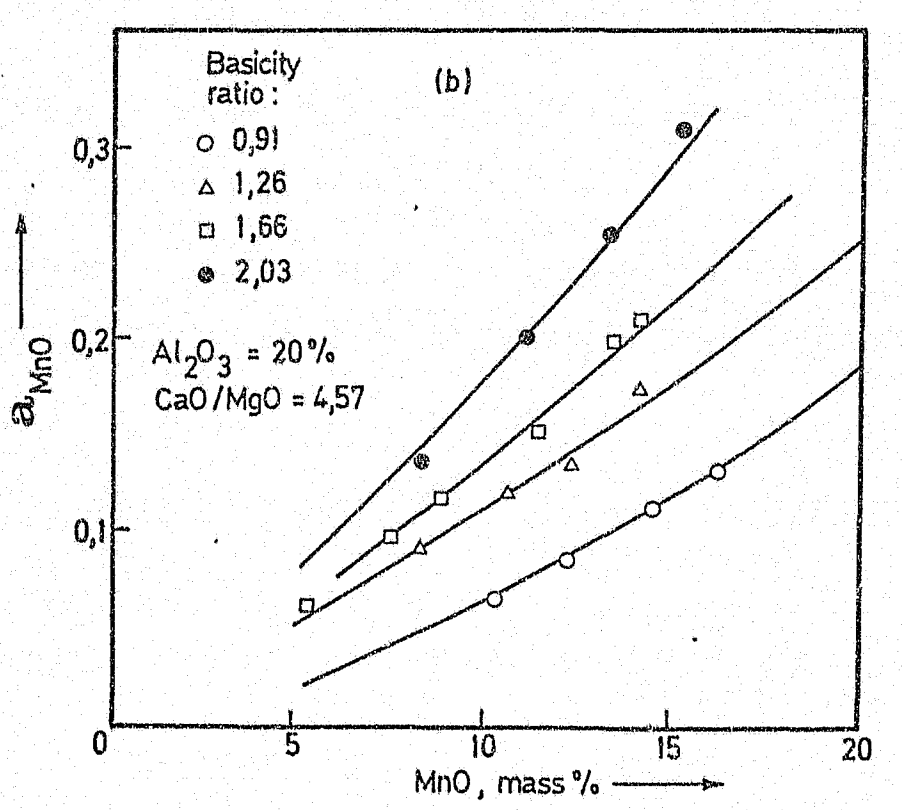


Figure 16. Activities of manganese (II) oxide, relative to solid, in SiO_2-Al_2O_3-MgO-CaO-MnO slags[7].

Warren et al [7] measured activities of MnO, relative to solid, in slags associated with the production of high-carbon ferromanganese alloys. The slags used were from the SiO_2-Al_2O_3-MgO-CaO-MnO system with selected Al_2O_3 contents and CaO-to-MgO ratios.

The activity coefficient of MnO was shown to be affected by the MnO concentration in the melt over the range 5 to 20 mass per cent MnO for various basicity ratios. Activity coefficients of MnO at a concentration of 13 mass per cent were plotted as isoactivity contours on a pseudoquaternary system SiO_2-Al_2O_3-CaO-MgO. These isoactivity contours are shown in Figures 15a to 15c at Al_2O_3 concentrations of 10, 20 and 30 mass per cent respectively. Increasing basicity ratio increases the activity coefficient of MnO. At constant Al_2O_3 and SiO_2 levels, as CaO is replaced by MgO, the activity coefficient of MnO decreases for high SiO_2 levels whereas in basic slags where SiO_2 is low the activity coefficient first increases until the CaO-to-MgO mass per cent ratio approaches four.

An increase in the Al_2O_3 content, for a given basicity ratio, decreases the activity coefficient of MnO in the more basic slags but appears to have little effect on the more acid slags. The small effect exerted on the MnO activity when the slag Al_2O_3 content is increased at a CaO-to-MgO ratio of 4,57 is shown in Figure 16. This CaO-to-MgO ratio is of particular interest as it is very near to the ratio of the basic fluxing components in the Mamatwan ore used in the present investigation.

3.3 Alloy Systems in the Production of Refined Ferromanganese

Medium - to low - carbon ferromanganese is normally produced by means of a ferromanganese - silicide reducing alloy. This alloy usually contains some carbon because it is manufactured in an open arc electric furnace from a charge of manganese ore, silica and coal or coke. The carbon content in the ferromanganese - silicide is inversely proportional to the silicon content of the metal.

During the production of refined ferromanganese, sufficient ferromanganese - silicide is added to the lime - ore melt to reduce the MnO content of the premelt to a concentration of 30 to 35 mass per cent from an initial value in excess of 50 mass per cent. At the same time the silicon content of the ferromanganese - silicide is reduced from an initial value to 16 to 24 mass per cent to approximately 1 mass per cent in the final alloy. The manganese content of the alloy increases from 60 to 70 mass per cent to approximately 80 mass per cent.

The ferromanganese - silicide used in ladle reactions has carbon contents which vary from less than 0,5 mass per cent, in the case of alloys containing 22 to 24 mass per cent silicon, to approximately 1,2 mass per cent for alloys containing 15 to 18 per cent silicon. The carbon concentration is reduced principally by dilution of the alloy during refining.

Although manganese and silicon are the most common alloying elements in steel, the binary and ternary systems with iron have not been completely studied. In addition no information has been found for the activity values of components in the ranges of composition of the alloy system Mn-Fe-Si-C used in the production of refined ferromanganese in South Africa.

3.3.1 The A[illegible] Systems Fe-Mn, Fe-Si and Mn-Si

Binary solutions of Fe-Si and Mn-Si exhibit strong negative deviations from ideal behaviour indicating strong attractive forces between unlike atoms[51, 52]. Studies on the Fe-Si system at 1600°C have been summarized by Darken[53] and are shown in Figure 17. Chipman et al[52] have studied the activity of silicon in FeSi melts in the temperature range 1420° to 1700°C. They found that for this binary, the effect of temperature on the activity coefficient, at constant composition, is given by the formula:

$$\frac{\partial \ln \gamma_{Si}}{\partial T} = \frac{-\bar{L}_{Si}}{RT^2} \qquad 3.21$$

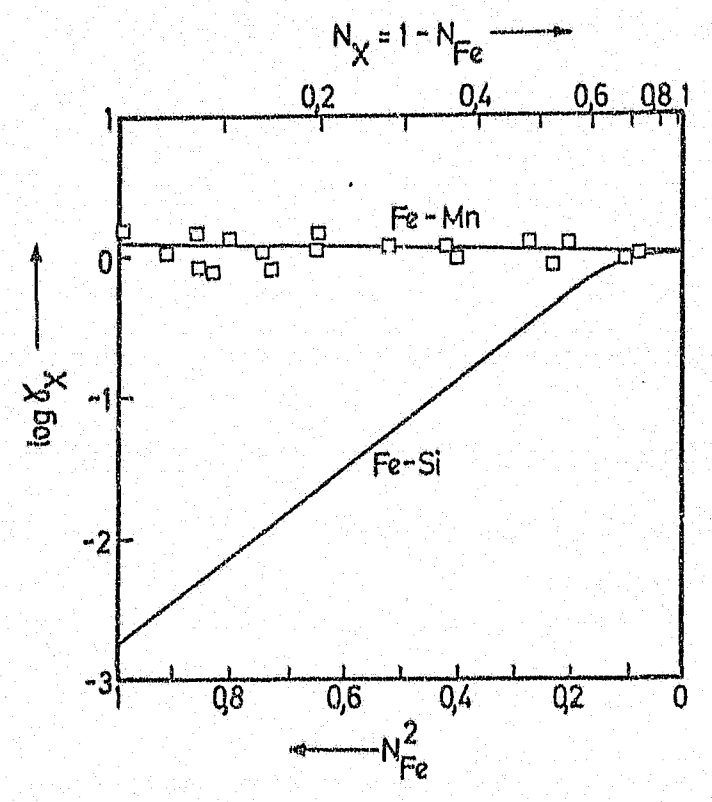


Figure 17 Activity coefficient of X for liquid Fe-X alloys at 1600°C[53].

where γ_{Si} = activity coefficient of silicon in ferrosilicon alloy.

T = absolute temperature. (^{o}K)

$\bar{L}_{Si}$ = heat of mixing of silicon in iron. (K cal.)

For any particular molar concentration of silicon they found that γ_{Si} increased with temperature. This observation has been verified by Tolstoguzov et al[54].

Solutions of the Fe-Mn system are almost ideal[53-55] and activities of both components only show slight negative deviations from Raoult's Law[56].

3.3.2 The Alloy Systems Fe-Mn-C, Fe-Si-C, Mn-Si-C and Fe-Mn-Si-C

The production of ferromanganese - silicide inevitably results in carbon solution in the metal phase and this carbon affects the activity coefficients of components in the alloy. Thus the solubility of carbon in Fe-Mn-Si alloys must be known in order to study slag - metal equilibria in ferromanganese production.

The carbon content of graphite - saturated liquid iron above 1153°C is given by Chipman et al[52] as:

$$\%C = 1,34 + 2,54 \times 10^{-3} T\ (^{o}C) \qquad 3.22$$

This is illustrated in Figure 18.

For graphite-saturated manganese above 1322°C the carbon content becomes[52]:

$$\%C = 2,68 + 3,52 \times 10^{-3} T\ (^{o}C) \qquad 3.23$$

The solubility of graphite in Fe-Mn, Mn-Si and Fe-Si alloys was interpolated from the results of previous workers by Skiredj and Elliott[57] and is shown in Figures 19 to 21 respectively. In the Fe-Mn system, carbon solubility increased as iron is replaced by manganese at any particular temperature in the range 1400 to 1650°C. However, in the Fe-Si and Mn-Si systems, as silicon replaced the other major alloy

where γ_{Si} = activity coefficient of silicon in ferrosilicon alloy.

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$$\%C = 2,68 + 3,52 \times 10^{-3} T\ (^{o}C) \qquad 3.23$$

The solubility of graphite in Fe-Mn, Mn-Si and Fe-Si alloys was interpolated from the results of previous workers by Skiredj and Elliott[57] and is shown in Figures 19 to 21 respectively. In the Fe-Mn system, carbon solubility increased as iron is replaced by manganese at any particular temperature in the range 1400 to 1650°C. However, in the Fe-Si and Mn-Si systems, as silicon replaced the other major alloy

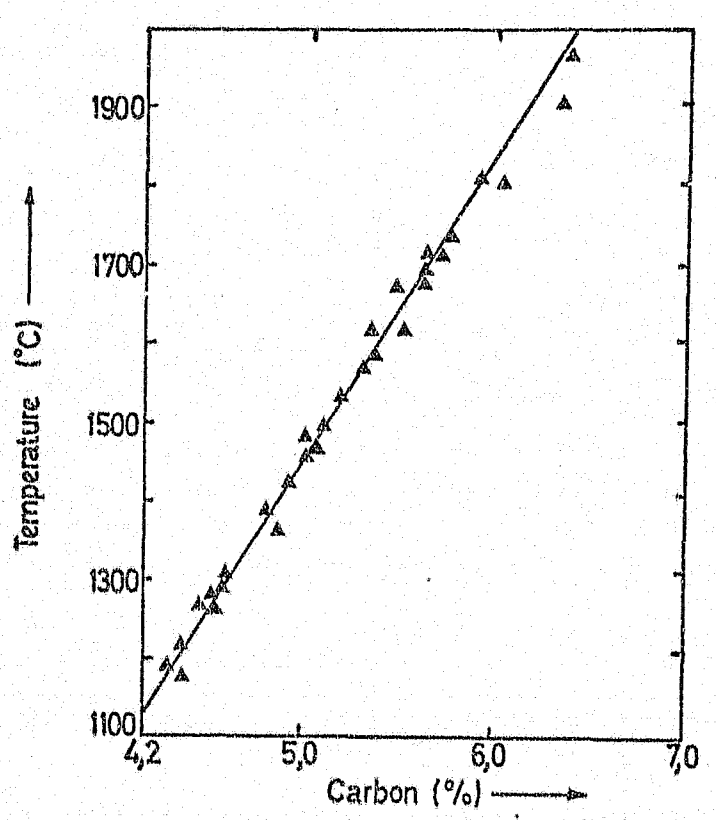

Figure 18. Solubility of carbon in iron[59].

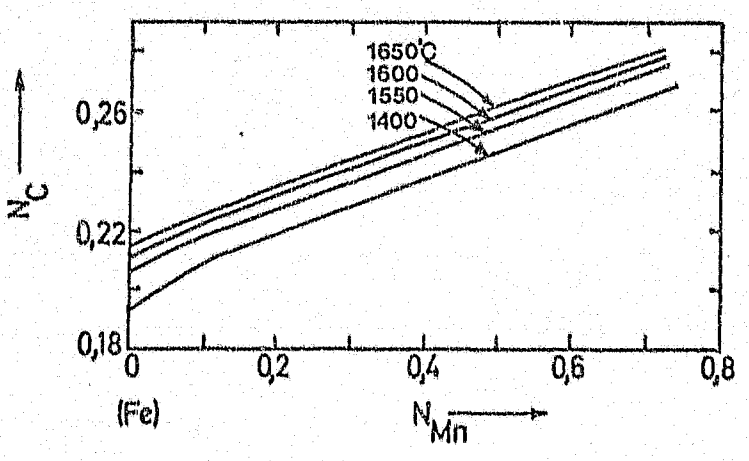

Figure 19. Solubility of graphite in Fe-Mn alloys[57].

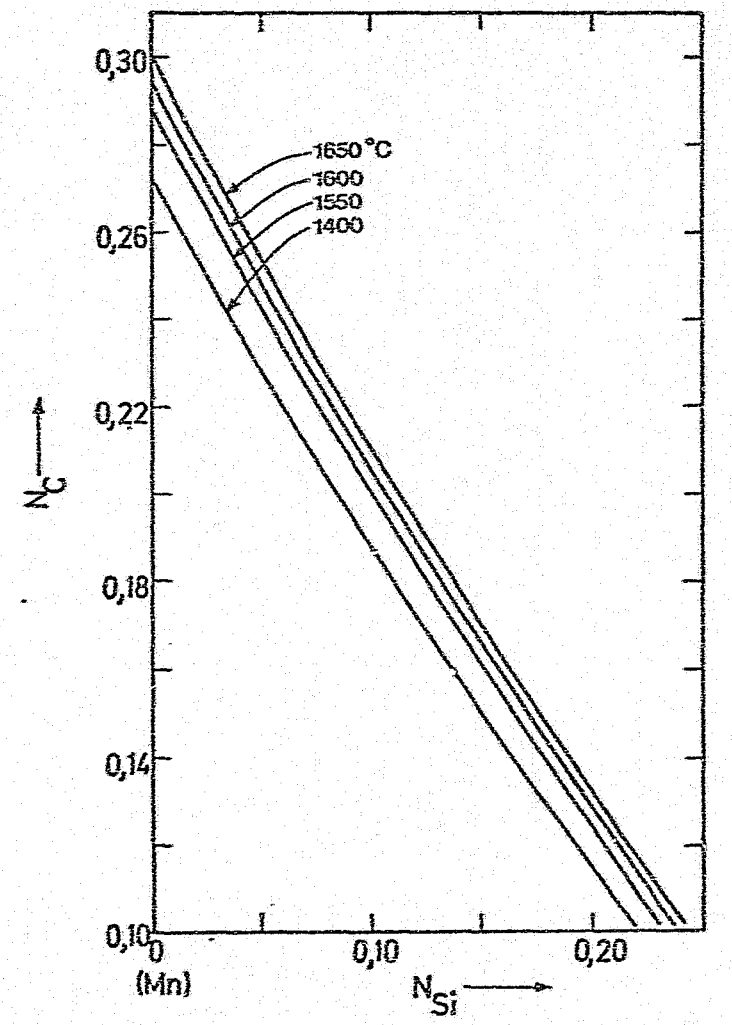

Figure 20. Solubility of graphite in Mn-Si alloys[57].

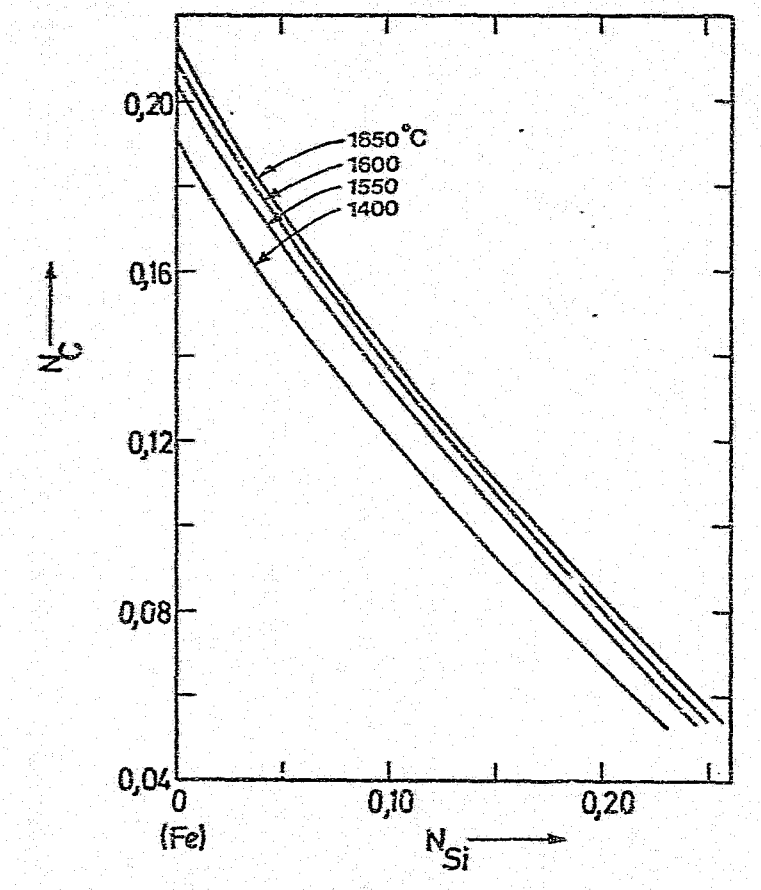

Figure 21. Solubility of graphite in Fe-Si alloys[57].

component, there is a considerable decrease in carbon solubility. For the temperature range considered, increased temperature increases the solubility of carbon in all three systems.

Turkdogan and Hancock's[58] data for the solubility of graphite in Fe-Mn-Si alloy at 1400°C and 1500°C shows that its solubility is a maximum in alloys high in manganese and low in silicon. As the iron - to - manganese ratio or the alloy silicon content increased the graphite solubility diminished[59, 60]. This observation agrees with those for its solubility in the Fe-Mn, Fe-Si and Mn-Si systems. The effect is illustrated in Figure 22.

In the Fe-Si-C alloy system, the activity coefficient of silicon increases with increasing carbon content at all temperatures in the range studied by Chipman et al. Activity coefficients of silicon in the binary system Fe-Si were compared with activity coefficients in the ternary Fe-Si-C at any silicon atom fraction between 0 and 0,35 and the values were found to be higher in the ternary system than in the system without carbon.

In the Mn-Si-C system there is a marked increase in the activity coefficient of silicon for silicon atom fractions between 0,1 to 0,2 in the temperature range 1350° to 1450°C[58].

Only a single reference was obtained for values of the silicon activity coefficient in Fe-Mn-Si-C alloys and in this case for equilibrium between an alloy and a slag. Tolstoguzov[61] considered alloy systems containing between 60 to 78 per cent manganese and 0,07 to 23,6 per cent silicon. The activity coefficient of silicon in the metal at 1570°C was found to increase marginally as the slag basicity ratio increased from 0,8 to 1,3. However, average values of $-\log_{10} \gamma_{Si}$ for three different silicon levels, namely 1, 5 and 15 mass per cent, were given as 1,55, 1,82 and 1,48 respectively.

It is evident, from the available literature, that further research work should be initiated on activity determination in the quaternary

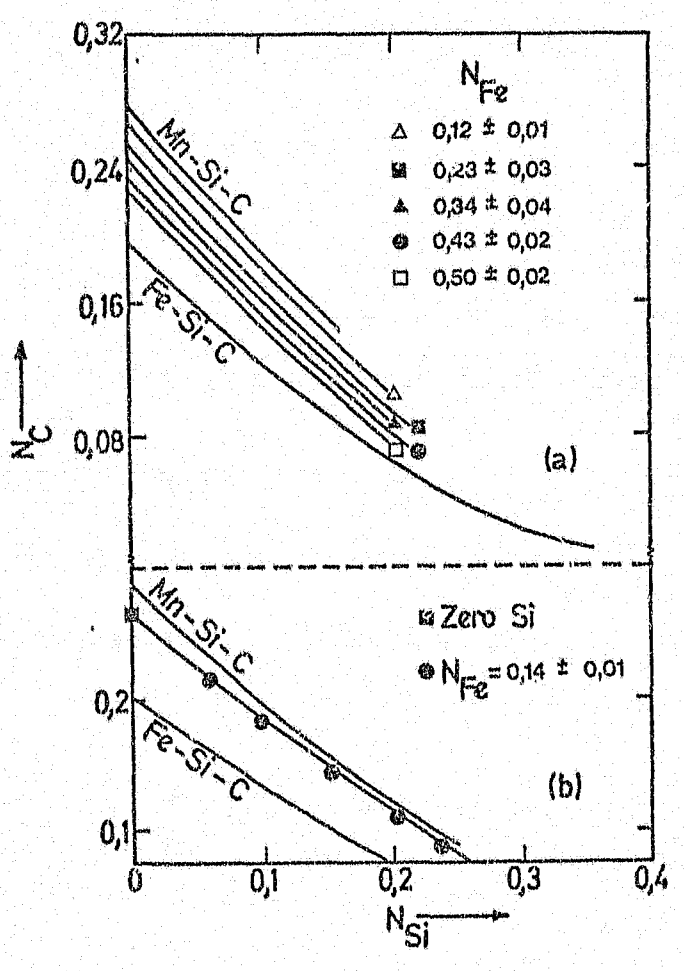

Figure 22. Solubility of graphite in Mn-Fe-Si melts at:
(a) 1400 °C
and (b) 1500 °C . (58).

Fe-Mn-Si-C alloy system, especially in the range of alloy compositions that exist in the production of refined ferromanganese in South Africa.

3.4 Reduction Reactions

3.4.1 Slag - metal Equilibria

The reduction of manganese oxide from a basic slag by silicon dissolved in a liquid ferromanganese alloy is the most important reaction occurring during the production of refined ferromanganese. Theoretically, both FeO and MnO should be present in the ore - lime melt which is subsequently reduced by silicide. However, in most South African ores, the manganese - to - iron ratio is high, leading to low iron concentrations in the ore premelt. Furthermore, FeO is reduced considerably faster than MnO[62]. Boronenkov et al[63], who have studied the kinetics of reduction of iron and manganese by carbon from $CaO-Al_2O_3-MgO-FeO-MnO$ melts state that reduction of manganese oxide from the slag will not occur until the FeO concentration has been reduced to its equilibrium value with metallic manganese (about 0,1 mass per cent FeO).

Standard free energies of reduction reactions encountered during production of refined ferromanganese are shown in Figure 23. These standard free energy values are related to one mole of metal produced and not, as is usually practised, standardised to a mole of oxygen removed from the oxide. The non - continuity of the standard free energies, results from a lack of thermodynamic data in the temperature ranges shown. Thus, at temperatures below the breaks, solid components are considered standard state whereas above this, liquids prevail. From this figure, it is apparent that at the temperatures used in ferromanganese production, the reaction most likely to proceed thermodynamically is that of the reduction of FeO by silicon to form iron and silica.

Thus it is concluded that iron reduction will occur preferentially

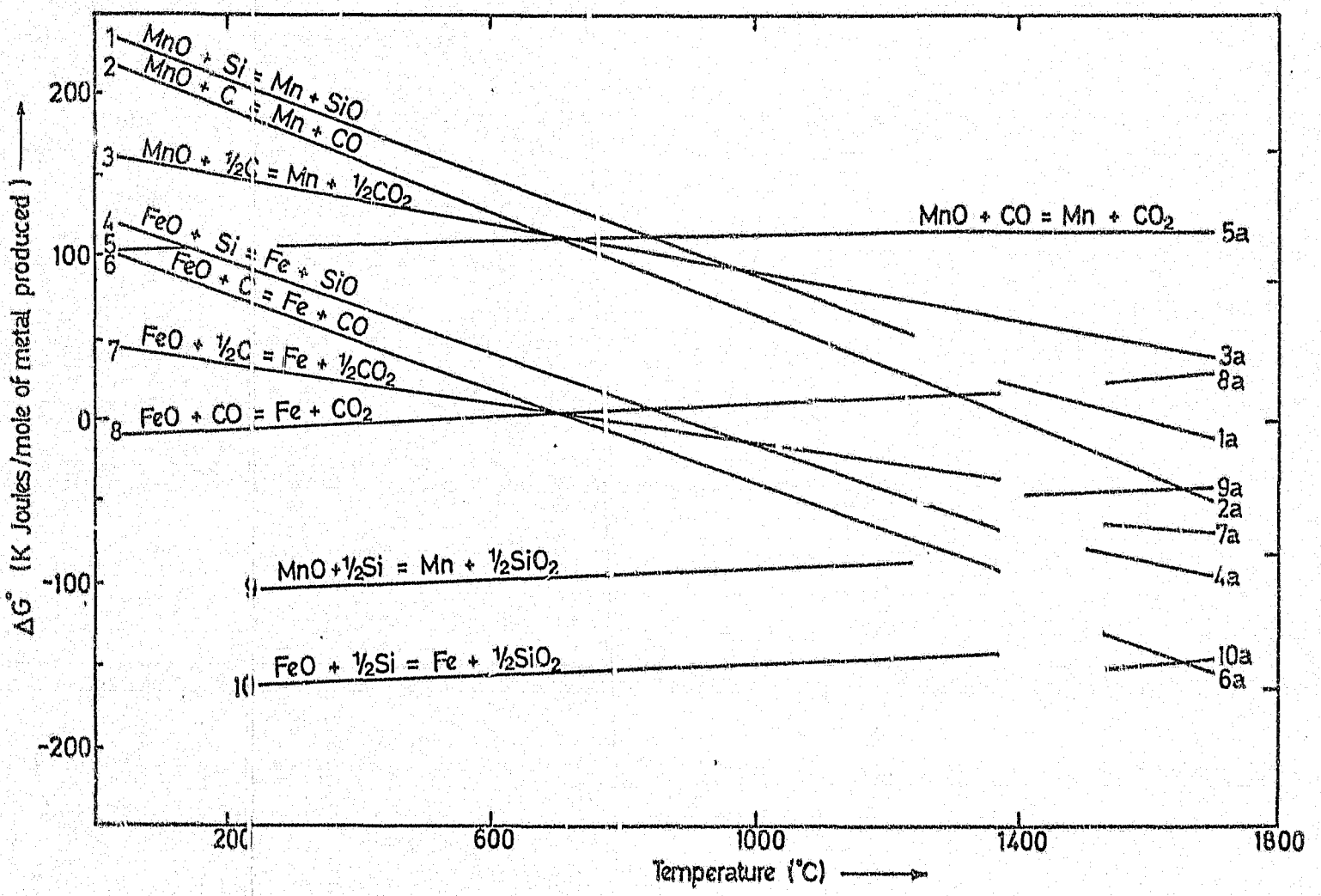

Figure 23. Standard free energies of some reduction reactions encountered in medium- to low- carbon ferromanganese production[64, 65].

resulting in the initial dilution of the reducing silicide alloy with iron. Once this reaction has been completed manganese mass transfer will occur from the slag to the alloy lowering the silicon concentration and increasing the manganese content of the final refined ferromanganese.

The final equilibrium manganese oxide content in the slag depends on the presence of lime and/or magnesia in the slag. If lime or magnesia are not present it is more difficult to reduce MnO from the manganese silicate melt.

When a reacting melt is deficient in basic fluxing components, the following reactions may occur[66]:

$$MnSi + 2Mn_3O_4 = Mn + 2MnO.SiO_2 + 4MnO \qquad 3.24$$

$$MnSi + 4MnO = 3Mn + 2MnO.SiO_2 \qquad 3.25$$

$$\Delta G^\circ = 13480 - 18,68T \text{ (at } 1638^\circ \text{ to } 1800^\circ K) \text{ Joules}$$

$$MnSi + 3MnO = 3Mn + MnO.SiO_2 \qquad 3.26$$

$$\Delta G^\circ = 6508 + 2,33T \text{ (at } 1410^\circ \text{ to } 1548^\circ K) \text{ Joules}$$

The standard free energies of formation of the compound MnSi were calculated for the following absolute temperature ranges as:

$$\Delta G^\circ = -71687 - 1,705\ T \text{ Joules } (298^\circ \text{ to } 1000^\circ K) \qquad 3.27$$

$$\Delta G^\circ = -78329 + 4,937\ T \text{ Joules } (1000^\circ \text{ to } 1410^\circ K) \qquad 3.28$$

$$\Delta G^\circ = -87930 + 11,721\ T \text{ Joules } (1410^\circ \text{ to } 1548^\circ K) \qquad 3.29$$

$$\Delta G^\circ = -40596 - 18,856\ T \text{ Joules } (1548^\circ \text{ to } 1683^\circ K) \qquad 3.30$$

$$\Delta G^\circ = -89799 + 10,379\ T \text{ Joules } (1683^\circ \text{ to } 2000^\circ K) \qquad 3.31$$

$$\Delta G^\circ = -77288 + 4,222\ T \text{ Joules } (1000^\circ \text{ to } 2000^\circ K) \qquad 3.32$$

Reactions 3.24 and 3.25 are more likely to occur and to proceed with tephroite ($2MnO.SiO_2$) formation* and are characteristic of the production of alloy from a non-fluxed premelt. Thus, if CaO or other basic fluxing materials are not present in the charge, it is more difficult to reduce manganese oxide to manganese in the alloy. The

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* See comment p. 21.

manganese is reduced to its lower oxide and remains as tephroite* in the slag.

When adequate fluxing additions are present, reactions which could occur during the refining process are similar to:

$$MnSi + 2Mn_3O_4 + 2CaO = Mn + 2CaO.SiO_2 + 6MnO \quad 3.33$$

$$MnSi + 2MnO + 2CaO = 3Mn + 2CaO.SiO_2 \quad 3.34$$
$$\Delta G^\circ = -115673 - 3,98T \text{ (at } 1683^\circ \text{ to } 1800^\circ K) \text{ Joules}$$

$$MnSi + 3MnO + CaO = 3Mn + \tfrac{1}{2}(2MnO.SiO_2) + \tfrac{1}{2}(2CaO.SiO_2) \quad 3.35$$
$$\Delta G^\circ = -43923 - 15,09T \text{ (at } 1638^\circ \text{ to } 1800^\circ K) \text{ Joules}$$

$$MnSi + 2\tfrac{1}{2}MnO + CaO = 3Mn + \tfrac{1}{2}(MnO.SiO_2) + \tfrac{1}{2}(2MnO.SiO_2) \quad 3.36$$
$$\Delta G^\circ = -130980 + 45,02T \text{ (at } 1500^\circ \text{ to } 1683^\circ K) \text{ Joules}$$

$$MnSi + 2MnO.SiO_2 + 4CaO = 3Mn + 2(2CaO.SiO_2) \quad 3.37$$
$$\Delta G^\circ = -235660 + 4,97T \text{ (at } 1683^\circ \text{ to } 1800^\circ K) \text{ Joules}$$

$$MnSi + 2(MnO.SiO_2) + 6CaO = 3Mn + 3(2CaO.SiO_2) \quad 3.38$$
$$\Delta G^\circ = -361920 - 10,37T \text{ (at } 1400^\circ \text{ to } 1700^\circ K) \text{ Joules}$$

In the absence of CaO or MgO additions, reduction of manganese from $MnO.SiO_2$ (rhodonite)* and $2MnO.SiO_2$* is almost impossible. This is confirmed by the following equations, where unit activities of the reacting components are considered.

$$MnSi + 2MnO.SiO_2 = 3Mn + 2SiO_2 \quad 3.39$$
$$\Delta G^\circ = 12966 + 16,68T \text{ Joules}$$

$$MnSi + 2(MnO\ SiO_2) = 3Mn + 3SiO_2 \quad 3.40$$
$$\Delta G^\circ = 16114 + 2,13\ T \text{ Joules}$$

Manganese reduction from tephroite* and rhodonite* in the presence of calcium orthosilicate* is thermodynamically feasible.

$$MnSi + 2MnO.SiO_2 + 2(2CaO.SiO_2) = 3Mn + 4(CaO.SiO_2) \quad 3.41$$
$$\Delta G^\circ = -67432 + 13,08\ T \text{ Joules}$$

$$MnSi + 2(MnO.SiO_2) + 3(2CaO.SiO_2) = 3Mn + 6(CaO.SiO_2) \quad 3.42$$
$$\Delta G^\circ = -94117 - 9,95\ T \text{ Joules}$$

Thus it is apparent that fluxing additions have a marked effect

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* See comment p. 21.

on the distribution of silicon and manganese between the slag and the metal and on the final equilibrium in a slag-metal reaction. Optimization of types and quantities of fluxing material is therefore essential to alter the equilibrium, increase the overall recovery of manganese and increase the manganese content of the final metal. At equilibrium, equation 3.5 can be represented by its equilibrium constant as:

$$K = \frac{[a_{Mn}]^2 \cdot (a_{SiO_2})}{(a_{MnO})^2 \cdot [a_{Si}]} \qquad 3.43$$

This slag-metal relationship, associated with the production of medium - and low - carbon ferromanganese, has been examined by Barcza[67]. Synthetic standard slags were made from the pure components MnO_2, CaO, MgO and SiO_2. A variety of compositions were chosen, representing a typical Mamatwan ore which had been subjected to a wide range of fluxing additions. The slag premelts formed were reacted with a 22 per cent silicon ferromanganese - silicide alloy at 1500°C under an atmosphere of argon. It was found that manganese recovery increased substantially from 32 to nearly 60 per cent as the CaO addition was increased from 0 to 30 per cent. With further CaO additions, manganese recoveries declined. It was further observed that, for a basicity ratio of four to three, as MgO replaced CaO there was an increase in manganese recovery from 50 to 57 per cent until a CaO-to-MgO ratio of one-to-one was achieved. The basicity ratio has a profound effect on manganese recovery which reached a maximum at a CaO-to-MgO ratio of four to three.

The equilibrium has also been studied by Turkdogan and Hancock[58] as well as by Schenck et al[68, 69] who equilibrated Fe-Mn-Si-C alloys with MnO containing slags at temperatures between 1450° and 1550°C. Turkdogan and Hancock[58] equilibrated carbon - saturated Mn-Si melts with $MnO-SiO_2$ slags up to SiO_2 saturation under a carbon monoxide pressure of 1 atmosphere and with SiO_2 - saturated slags at varying carbon monoxide pressures at 1350°, 1400° and 1450°C. The conclusions reached by Turkdogan and Hancock[58]

were:

(i) for a given iron concentration, an increase in the CaO-to-SiO_2 ratio increases the slag-metal distribution ratio of silicon but decreases the manganese ratio. These results are shown in Figures 24 and 25.

(ii) for a given CaO-to-SiO_2 ratio, the silicon distribution ratio increases with decreasing iron content of metal, whereas the reverse is true for the manganese distribution.

(iii) in CaO-MnO-SiO_2 slags containing Al_2O_3, silicon and manganese distribution ratios increase as the Al_2O_3 content is reduced from 20 to 0 mass per cent or from a mole fraction of 0,14 to 0. This phenomenon is illustrated in Figure 26.

This latter conclusion is disputed by Selmer Olsen[70], who correlated MnO and CaO-to-SiO_2 ratios in slags in equilibrium with constant silicon concentrations in metals and found that Al_2O_3 content did not appear to interfere with this correlation. Further evidence for this view has been provided by Stukel and Cocubinsky[71] who found no significant effect on manganese distribution when the slag Al_2O_3 content was varied from 8,1 to 36,4 mass per cent.

The present investigation used a Mamatwan ore and pure fluxing components and covered a wide composition range in order to incorporate all the fluxing possibilities experienced with this ore in practice. The ore premelt composition ranges are:

MnO 50 to 60 per cent, CaO 15 to 40 per cent, MgO 3 to 20 per cent, Al_2O_3 less than 15 per cent, SiO_2 less than 6 per cent and FeO less than 7 per cent.

From daily slag and metal analyses of a ferromanganese blast furnace Turkdogan[72] found that at a given CaO-to-SiO_2 ratio, the MnO-to-Mn ratio is directly proportional to the Si-to-SiO_2 ratio This proportionality factor decreased slightly as the silicon content of the metal increased. The conclusion was that equation 3.43

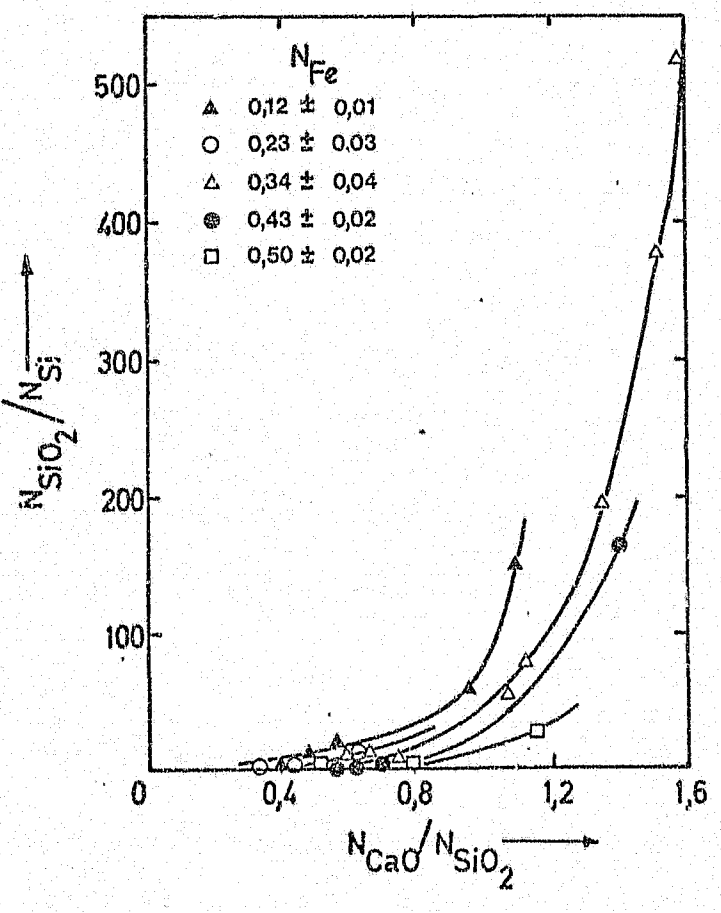

Figure 24. Effect of CaO-to-SiO_2 ratio and iron concentration in the metal on the slag-to- metal silicon distribution ratio at 1400°C[58].

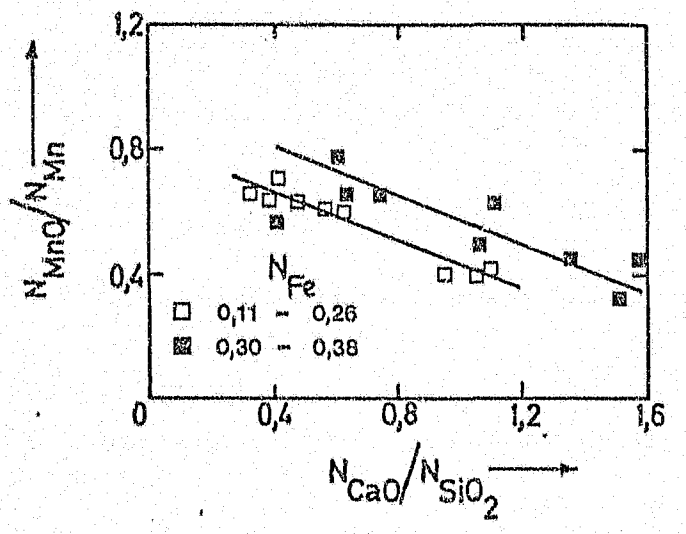

Figure 25. Variation of manganese distribution ratio with CaO-to-SiO_2 for two ranges of iron concentrations at 1400°C[58].

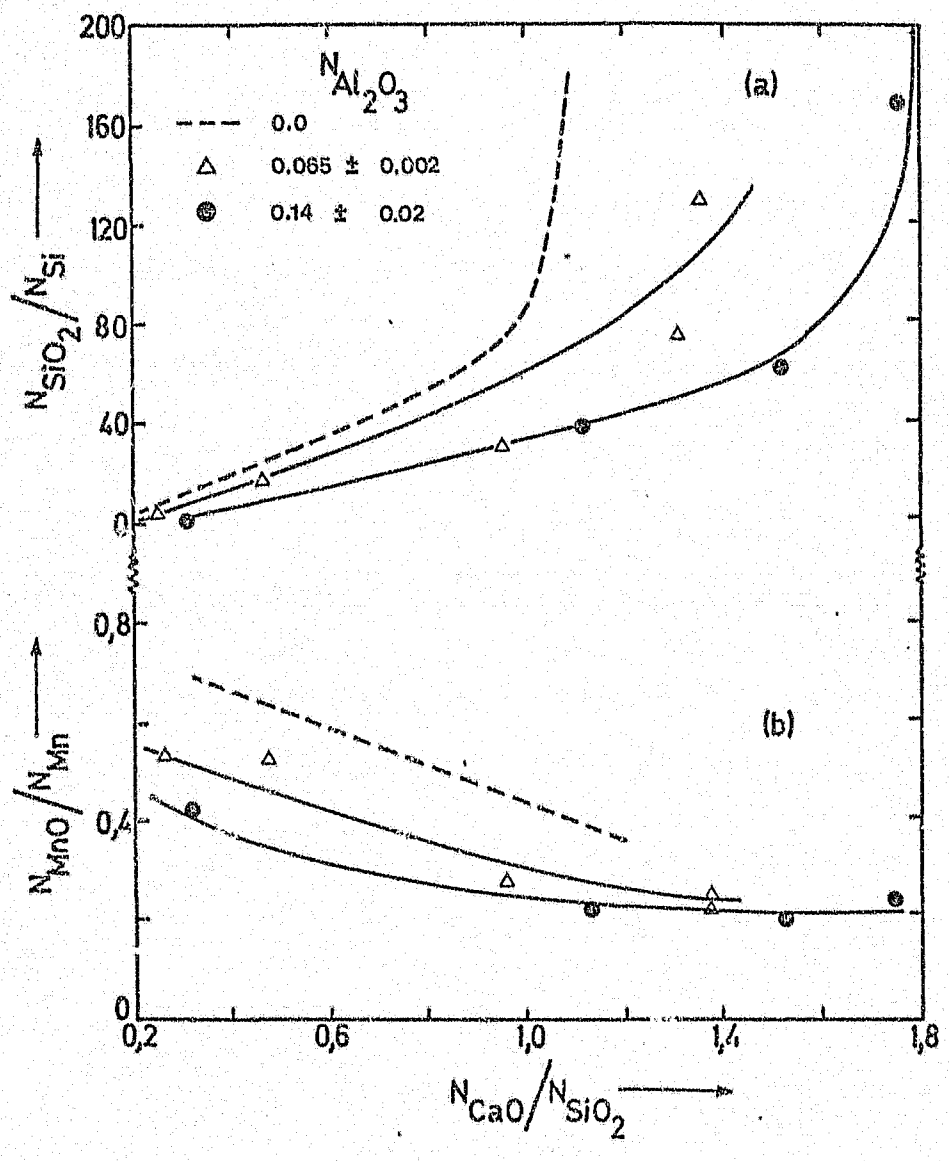

Figure 26. Variation of slag-to-metal (a) silicon and (b) manganese distribution ratios with CaO-to-SiO_2 for different alumina concentrations at 1400°C. (Reference 58)

determined the manganese that could be reduced from a given slag. This is not altogether correct, as in practice although the manganese distribution is close to the equilibrium value, the silicon distribution is not.

Unfortunately, little data is available on activities in slag and metal systems related to equilibria in the production of refined ferromanganese and thus few thermodynamic interpretations of equilibria can be attempted.

3.4.2 Slag - metal Kinetics

Equilibrium relations pertinent to the reduction of manganese oxide have been studied in order to establish the mechanisms which control the rate of the process. The equilibrium of interest, as given previously in equation 3.5 is that between silicon in the reducing alloy and MnO in the slag. For this two - phase slag - metal reaction, the kinetics can be divided into the following principal steps:

(i) transport of the reactants from the bulk phases to the slag - metal interface.

(ii) phase boundary reaction, which itself may involve several steps.

(iii) transport of the reaction products from the slag - metal interface into the bulk phases.

Under most conditions, it has been found that significant concentration differences occur only in the vicinity of the interface. According to Wagner[73] the theoretical analysis need only consider concentration gradients in the boundary layer and concentration differences in the bulk layer may be disregarded.

The possible rate - controlling steps can be either diffusion control, chemical reaction control or a combination of these. If the chemical reaction step is much faster than one or more of the

diffusion steps, equilibrium is reached at the interface, and the overall rate of the process is determined by the diffusion of one or more of the reacting species to or from the interface. If, however, the chemical reaction step is the slow step, the concentration of any component is essentially the same at the slag - metal interface as it is in the bulk of the phase, and the process rate is determined by the rate of the phase boundary reaction.

In order to determine the rate limiting step for the reaction in equation 3.5 Daines and Pehlke[74] have considered the effects of several variables on the kinetics of MnO reduction from basic slags by silicon dissolved in liquid iron. These variables included stirring rate, temperature, melt geometry and concentration. On finding the large influence of stirring (Figure 27) and the small influence of temperature (Figure 28) on reaction rate, they described the experimental system as diffusion controlled. By a process of elimination, it was concluded that the rate limiting step was attributed to the diffusion of manganese in the metal phase.

This conclusion is supported by Calderon et al[75] who studied manganese diffusivities in Fe-Mn systems for which the activation energy of manganese diffusion was small and assumed to be independent of concentration. Other authors[76-77] have emphasized the necessity for as large as possible a surface area for reaction between metal and slag. If a large surface area is obtained, reaction kinetics are improved by supplying a larger interface from which the manganese can diffuse. The kinetics of reduction of manganese oxide from slags, by silicon in an iron alloy, are therefore attributed to diffusion control, unlike reduction by carbon in liquid iron which is due to chemical reaction at the interface[78, 79].

When a process is limited by a slow diffusion step, the rate can be defined mathematically by applying Fick's first law which states that the flux of component i is proportional to the concentration gradient of component i in the direction of diffusion.

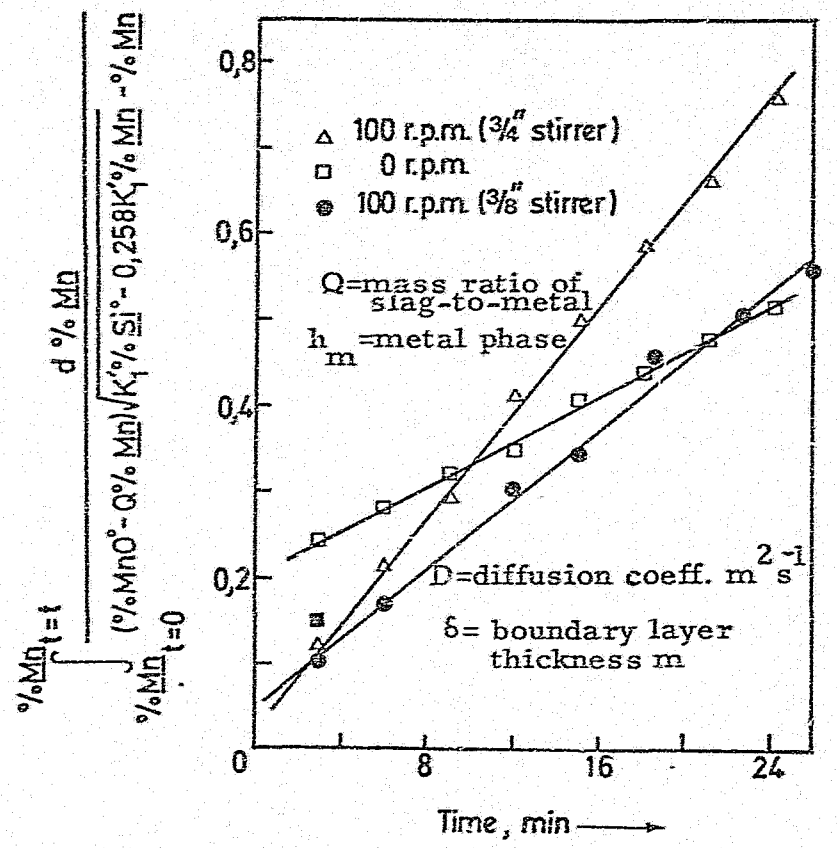

Figure 27. The effect of stirring rate on the reaction:

$2(MnO) + [Si] = (SiO_2) + 2[Mn]$ (74)

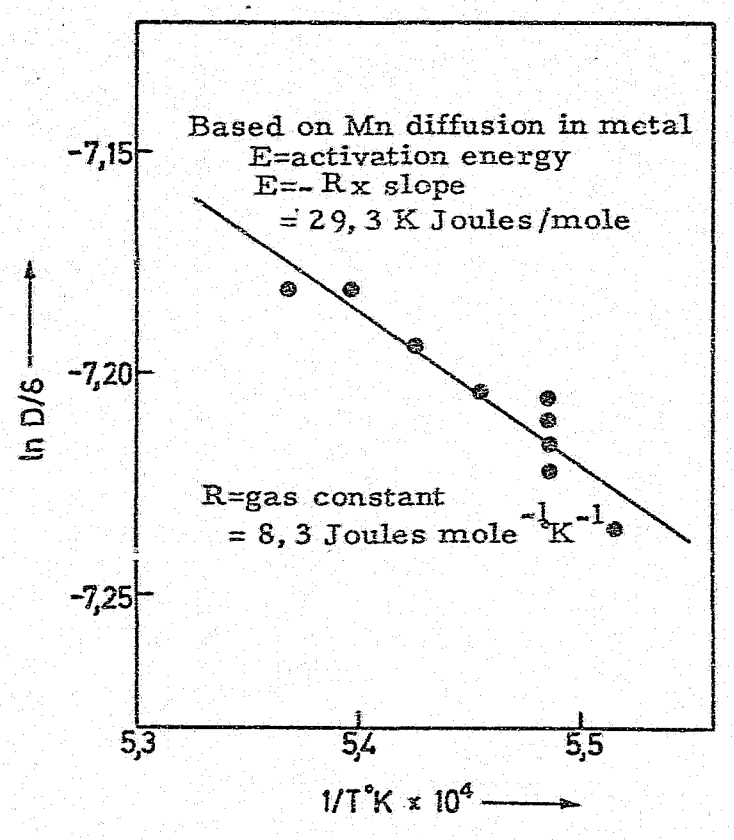

Figure 28. The effect of temperature on the reaction;

$2(MnO) + [Si] = (SiO_2) + 2[Mn]$ (74)

$$J_i = -D \frac{\partial C_i}{\partial y} \qquad 3.44$$

where J_i = Molar flux of component i, moles $m^{-2} s^{-1}$,
D = Diffusion coefficient, $m^2 s^{-1}$,
C_i = Concentration of component i, moles m^{-2},
and y = Rectangular coordinate m.

Equation 3.44 can be rewritten as:

$$\frac{dn_i}{dt} = \frac{D A}{\delta} \left[C_{i(\text{interface})} - C_{i(\text{bulk})} \right] \qquad 3.45$$

where n_i = Moles of component i,
t = Time, s,
A = Interfacial area, m^2,
and δ = Boundary layer thickness, m

The concentration of component i at the interface is that concentration which is in equilibrium with the other components at their instantaneous compositions in the bulk phase.

As the diffusion of manganese is considered the rate - limiting step in equation 3.43, Daines and Pehlke have shown that at any time during the course of this reaction the concentration of MnO in the slag can be related to that of manganese in the metal, which is always zero at t =O, by the stoichiometric relationship:

$$\%MnO = (\%MnO)^{\circ} - \left[\frac{W_M \cdot MW_{MnO}}{W_S \cdot MW_{Mn}} \right] \%[Mn] \qquad 3.46$$

where $(\%MnO)^{\circ}$ = Initial MnO weight per cent,
W_M = Weight of metal phase, Kg,
W_S = Weight of slag phase, Kg,
MW_{MnO} = Molecular weight of MnO,
and MW_{Mn} = Atomic weight of Mn.

As previously stated, Daines and Pehlke [74] showed that for manganese oxide reduction from basic slags by silicon dissolved in liquid iron the rate limiting step was diffusion of manganese in the metal phase for low silicon concentrations in the liquid iron phase.

As the initial alloy silicon concentration increased the value for D/δ decreased markedly for silicon in the metal and to a lesser extent for manganese in the metal as shown in Figures 29 and 30. D and δ refer to the diffusion coefficient and effective thickness of the concentration boundary layer respectively. The rate equations for the diffusion of silicon and manganese in the metal phase are given respectively by equations 3.48 and 3.47 as:

$$\int_{\%[Mn]_{t=0}}^{\%[Mn]_{t=t}} \frac{d(\%[Mn])}{((\%MnO)^{o} - Q\%[Mn])\sqrt{K'_1\%[Si^{o}]} - 0,258K'_1\%[Mn] - \%[Mn]} \qquad 3.47$$

and

$$\int_{\%[Mn]_{t=0}}^{\%[Mn]_{t=t}} \frac{0,258d(\%[Mn])}{\%[Si^{o}] - 0,258\%[Mn] - \frac{\%[Mn]^2}{(K'_1((\%M \quad Q\%[Mn]^2))}} = \frac{Dt}{\delta h_m} \qquad 3.48$$

where h_m = height of metal phase, m,

and Q = slag - to - metal ratio.

For a diffusion controlled reaction, an equation of the type

$$\text{Rate} = B \times \text{Driving Force} \qquad 3.49$$

will determine reaction rate where B is defined as the reaction rate constant.

From Daines and Pehlke's work, the driving force is increased by approximately three times with increased silicon concentration and the reaction rate should also increase by three times. This increase in reaction rate was not obtained and in fact the reaction rate decreased

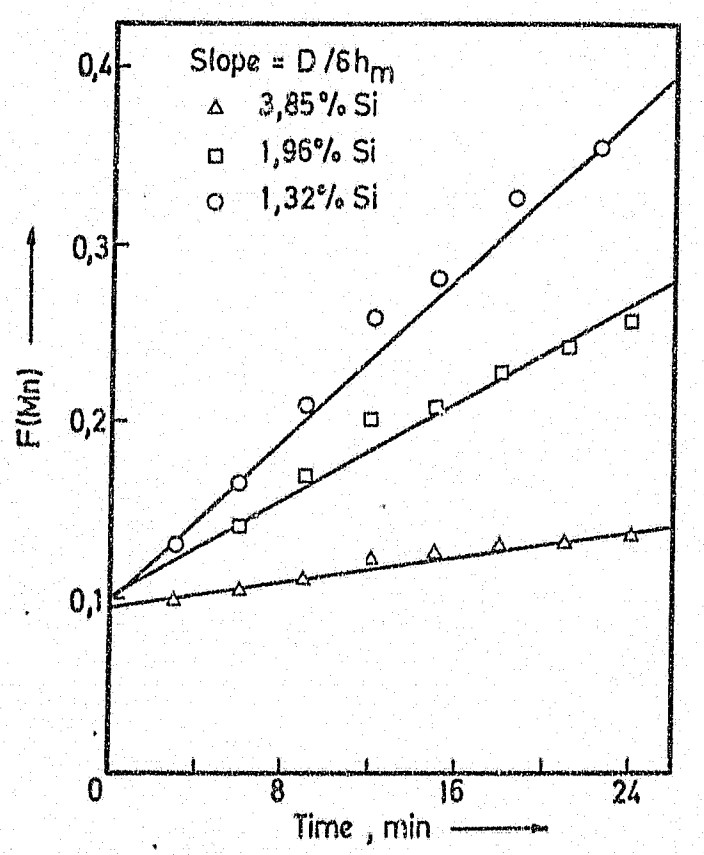

Figure 29. Effect of silicon concentration on the reaction: $2(MnO) + [Si] = (SiO_2) + 2[Mn]$; model for silicon diffusion in metal[74].

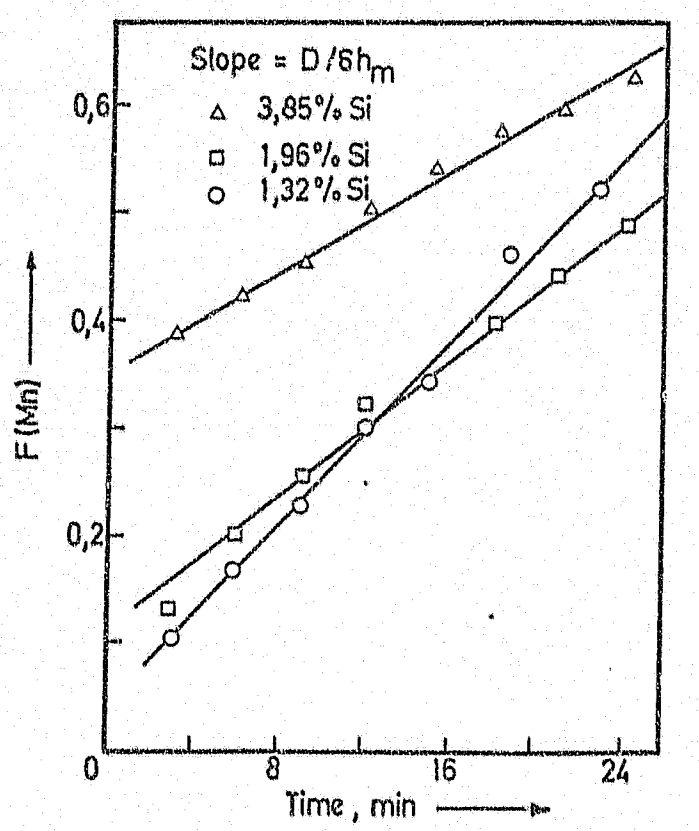

Figure 30. Effect of silicon concentration on the reaction: $2(MnO) + [Si] = (SiO_2) + 2[Mn]$; model for manganese diffusion in metal[74].

when these silicon concentrations were considered.

The work of Daines and Pehlke is only concerned with a small concentration range of silicon but Calderon et al[75] have studied manganese and silicon diffusion in liquid iron over the whole range of composition. Available literature on silicon and manganese diffusion in binary alloys is limited and data on diffusivities in the ternary Fe-Mn-Si system have not been published.

The relationships between diffusion coefficients and concentrations for the Fe-Mn and Fe-Si systems at 1600°C are given in Figures 31 and 32. For the binary Fe-Mn system the diffusion coefficient of manganese is a minimum at about 30 mass per cent manganese. For the binary Fe-Si system, the maximum value of the diffusion coefficient is at a silicon mole fraction of 0,4. Variations in the diffusion coefficients are far greater for the Fe-Si system than for the Fe-Mn system for which the diffusion coefficient of manganese does not change very much over the whole composition range.

During the silicothermic reduction of a manganese ore premelt, for each gram mole of silicon which diffuses towards the slag - metal interface, two gram moles of manganese product must diffuse away from the slag - metal interface and into the bulk metal phase to maintain equilibrium conditions at the slag - metal interface during the course of this reaction.

3 5 Summary

From this review of previous work it is apparent that further research must be conducted to improve the knowledge of the physical chemistry of slags and alloys used in the production of medium - and low - carbon ferromanganese. Particular attention should be given to the determination of the activities of components in both MnO slags and ferromanganese - silicon alloys.

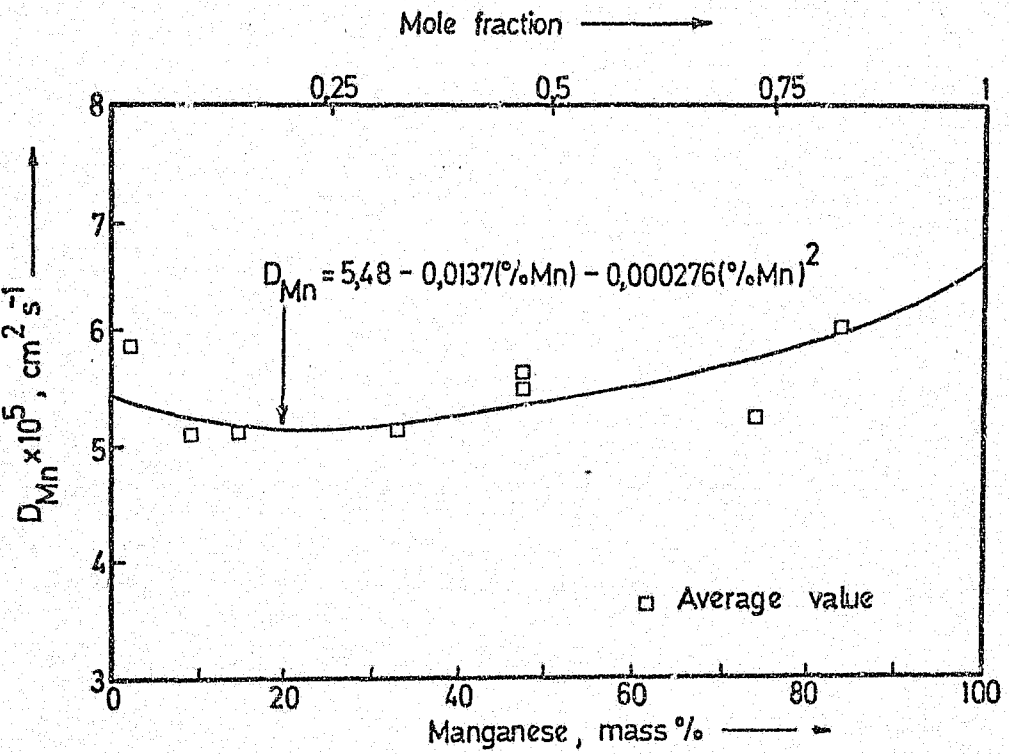

Figure 31. Relationship between diffusion coefficient of manganese and concentration for the Fe-Mn system at 1600°C[75].

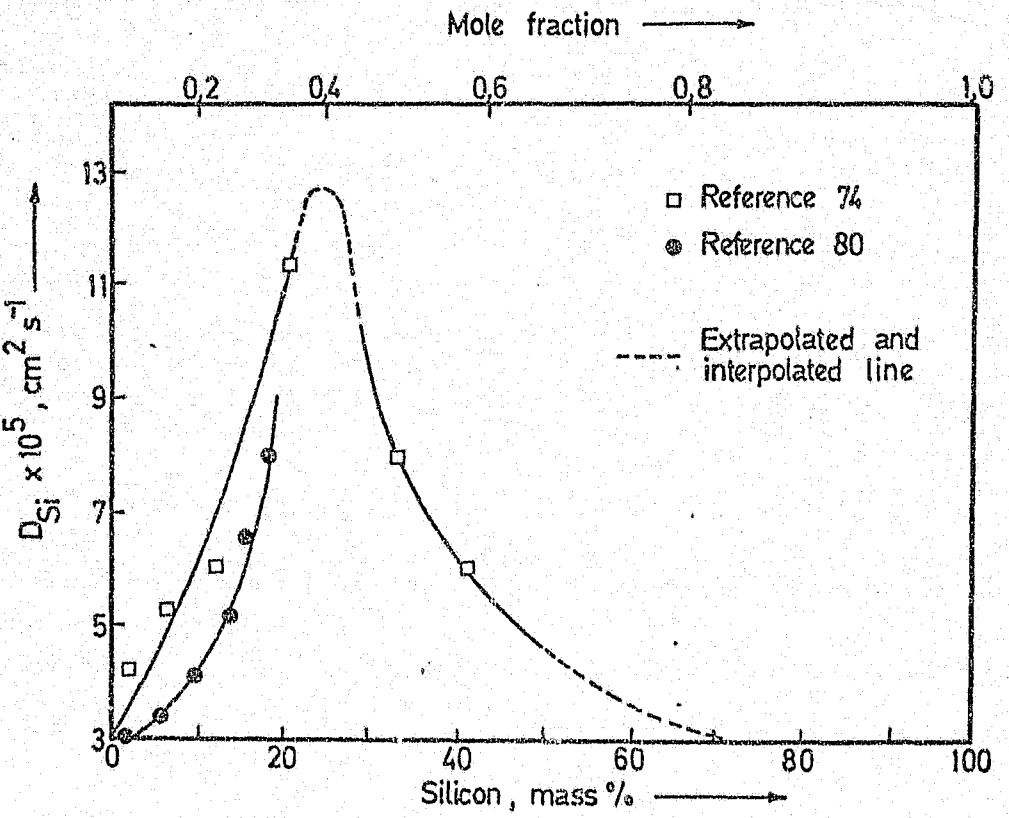

Figure 32. Relationship between diffusion coefficient of silicon and concentration for the Fe-Si system at 1600°C[75].

It should be emphasized that there is very little data on the activities of components in the Fe-Mn-Si system. Data on the activities of components in this alloy system, with particular reference to compositions used in medium - and low - carbon ferromanganese production, would be a sound foundation for future studies on the kinetics and equilibrium of the silicothermic reduction.

4. EXPERIMENTAL

4.1 Materials

The metal and slag compositions chosen were representative of those used in the production of medium - and low - carbon ferromanganese in South Africa. Hence the experimental results could be compared with data obtained in industry as well as with more fundamental data.

4.1.1 Materials in Slag Premelt

Mamatwan ore was used for the premelt in preference to Hotazel and Wessels ores because there are virtually unlimited reserves of Mamatwan ore The analyses of the run - of - mine ore and the premelt are shown in Table 3.

A bulk sample of this ore was crushed and pulverized in a Keegor rotating disc pulverizer to reduce the sample to -48 mesh (Tyler) This sample was coned and quartered so as to form batches of approximately 500 g and the final ore sample for subsequent fluxing was taken from these batches.

Three forms of fluxing additions were used during the investigation: lime (Baker analysed reagent), magnesia (chemically pure) and Transvaal dolomite. These three forms of fluxing additions were heated at 1000°C for two hours before use to drive off any contained volatiles, cooled and stored in a desiccator.

The dolomite was a Transvaal Dolomite Series type with the analysis shown in Table 3. The analysis is representative of this dolomitic deposit in which some manganese is present in the carbonates If dolomite is to be used industrially in the production of medium - to low - carbon ferromanganese it will undoubtedly be from this deposit.

4.1.2 Reducing Alloy Materials

An industrial ferromanganese - silicide alloy was used in most

TABLE 3

CHEMICAL COMPOSITIONS OF ORE AND [illegible]ITE
(mass per cent)

Constituent	Mamatwan Ore		Dolomite
	As mined	Premelt	Calcine
*MnO_2	29,14		
*MnO	25,03		0,81
Mn_3O_4		64,80	
H_2O	1,80		0,53
CO_2	15,44		45,95
Fe_2O_3	6,22	7,74	1,07
MgO	2,77	3,35	18,75
CaO	13,04	15,57	30,43
Al_2O_3	0,14	0,17	0,08
SiO_2	4,57	5,52	1,67
Other minor Components	1,85	2,85	0,71
Mn	37,79	46,92	
Fe	4,35	5,39	
Mn:Fe	8,69	8,70	

*These are manganese oxide contents normally reported in chemical analyses. However, manganese oxides are present in the Mamatwan ore mainly as braunite ($3Mn_2O_3$) and hausmannite (Mn_3O_4)[81].

experiments. This alloy was crushed to -48 mesh (Tyler) and had the typical composition given in Table 4.

TABLE 4

CHEMICAL COMPOSITION OF INDUSTRIAL ALLOYS USED
(mass per cent)

Constituent	FeMnSi	FeSi
Mn	65,20	
Si	22,46	46,25
Fe	11,05	50,10
C	0,49	
Other minor components	0,80	3,65

Synthetic reducing alloys were prepared by mixing chemically pure metal powders in the correct proportions for the required alloy composition and melting the mixture in a Degussa resistance furnace under argon.

4.2 Preparation of the Slag Premelt

Every sample contained 25g of Mamatwan ore, regardless of whether fluxed or unfluxed reactions were considered. When fluxing additions were utilised, the components were weighed on a balance and intimately mixed with the aid of a pestle and mortar. Final weighing into an A2 alumina crucible ensured that a 25g ore sample was transferred and the Mettler HIOw single pan electromechanical balance had a full scale deflection of 160g and a rated accuracy of 0,1 mg.

The crucible and sample were then introduced to a globar muffle-type furnace at 1500°C . Volatile constituents of the ore were eliminated and thermal decomposition of the higher oxides

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of manganese occurred before the sample eventually melted in air. On formation of a premelt the crucible was cooled, reweighed and the weight loss recorded. This weight loss was not consistent because the ore samples were not completely homogeneous. However, these variations in sample weight losses were less than 1,5 per cent of the original sample weight and thus well within the limits of experimental accuracy encountered during the reduction reactions.

4.3 Alloy preparation

Both synthetic and industrial reducing alloys were used. The alloy most used was a locally produced industrial ferromanganese - silicide alloy which had been pulverised to -48 mesh (Tyler) and thoroughly mixed.

Several procedures were tried for the preparation of synthetic ferrosilicon, ferromanganese - silicide and ferromanganese - silicon -aluminium alloys. Chemically pure aluminium, iron, manganese and silicon metal powders were used as well as commercial ferrosilicon and ferromanganese - silicide alloys.

Attempts to melt the mixtures of metal powders in a vertically - wound molybdenum resistance - type furnace under an argon atmosphere were not successful as the alloy analysis was considerably different from the expected composition.

A Degussa carbon resistance furnace was then used for alloy preparation. Samples were heated to 1500°C in the resistance furnace and held at this temperature under vacuum for 15 minutes. On cooling and reweighing it was found that extensive volatilization had taken place leaving less than half of the initial alloy sample.

The samples were then melted in the resistance furnace under an argon atmosphere. The heating chamber was initially evacuated and backfilled with argon two times whilst at room temperature. The two gas ports were then closed and the sample heated. During the heating period, atmospheric pressure was maintained within the

chamber by allowing argon to escape through the gas exit port. Once the sample had achieved a temperature of 1500°C it was held at this temperature for 15 minutes before being cooled. The alloys lost approximately 0,15 mass per cent and their chemical analyses were very close to the predicted analyses. These reducing alloys were then used for the recovery of manganese from ore and lime - ore melts.

4.4 Apparatus for Slag - Metal Studies

A vertical - tube molybdemum resistance furnace was used for this investigation. The molybdenum windings of the furnace were supported on an alumina tube, through which passed the reaction tube. This recrystallized alumina reaction tube was 55mm in diameter and 1000mm in length and the molybdenum windings were protected from oxidation by purging with ammonia. At the temperatures around the reaction tube this gas decomposes to give an atmosphere of nitrogen and hydrogen. The apparatus is shown schematically in Figure 33 and a photograph of the furnace and equipment is shown in Plate 1.

A 'double - ganged' variac system, capable of supplying 50A and 220V, was operated manually to achieve the required temperature. For this furnace and variac, the temperature did not fluctuate by more than $\pm 5^{\circ}C$ from the required value over extended periods prior to the silicothermic reaction (refer Section 4.6). Temperature in the 'hot zone' of the furnace could be maintained at within $9^{\circ}C$ of the required value over a vertical distance of 60mm. Furnace temperature was monitored with a Pt-6 per cent Rh/Pt-30 per cent Rh thermocouple held in a recrystallized alumina sheath and the thermocouple junction was positioned at the reaction tube wall 5mm above the top of the crucible.

An argon atmosphere was maintained within the reaction tube by passing argon at 1 litre per minute through the reaction tube from the top. The crucible support rod was attached to a sand

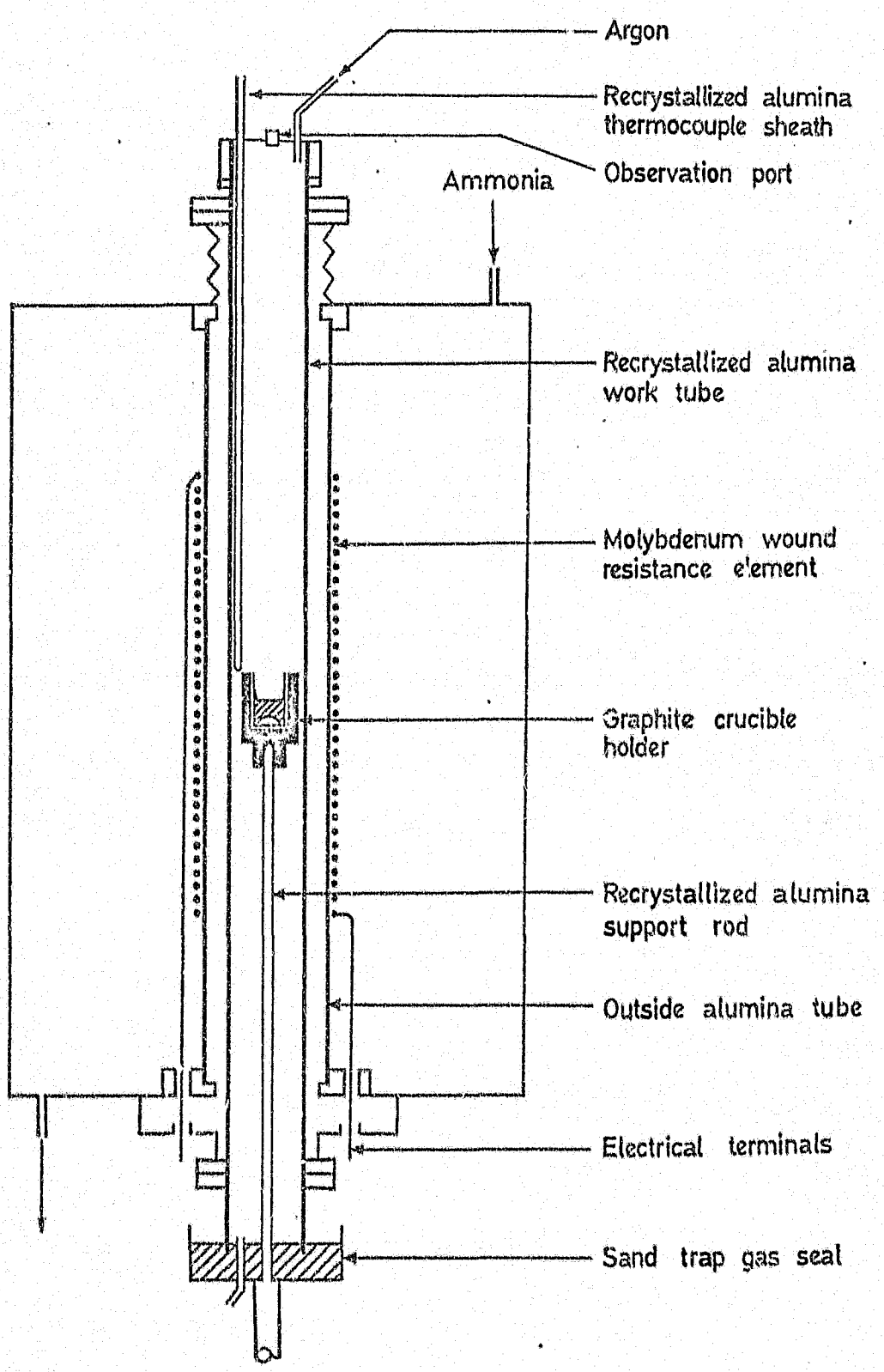

Figure 33 Apparatus for slag-metal studies

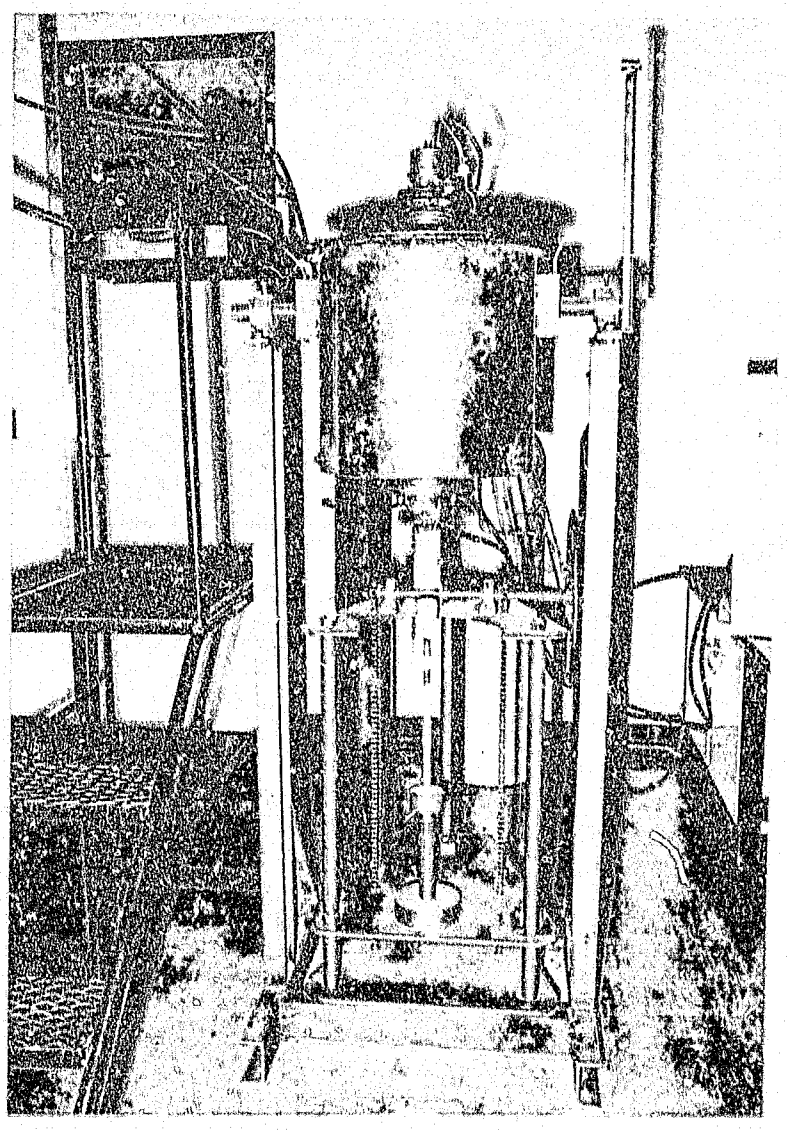

Plate 1. Apparatus for slag-metal studies.

trap which sealed the lower end of the reaction tube once a reaction was in progress and a graphite crucible holder was attached to the upper end of the support rod. This holder was used to position the crucible in the furnace 'hot zone' and ensured that the furnace reaction tube was protected against slag or alloy spillage if the crucible cracked.

During preheating the sample prior to the silicothermic reaction, the lower end of the reaction tube was exposed to the atmosphere conditions. Trial experiments were conducted over time periods of 5 to 20 minutes, in which the crucible and reaction components were held just below the 'hot zone' at a temperature of approximately 1100°C to assess the effect of oxidation of the ferromanganese-silicide and the premelt. After typical reduction experiments, conducted for 15 minutes, no variation in manganese recovery was apparent and thus it was concluded that the effect of oxidation during the crucible heating cycle was consistent over the investigation period.

A study of the reduction reactions involving both metal and slag phases leads to the problem of a suitable choice of crucible material. Fine grained, low porosity, recrystallized alumina crucibles were selected for experimental work after dissolution tests using less expensive mullite crucibles (Al_2O_3 + 5% SiO_2 maximum) proved unsuccessful. Using these recrystallized alumina crucibles, it was found that the amount of Al_2O_3 dissolved in the slag reached a maximum of 15 per cent of the total slag mass over a period of 15 minutes during typical unfluxed reactions in which slag attack was most severe.

The dissolution of Al_2O_3 will dilute the slag MnO concentration by increasing the slag mass containing a particular mass of MnO. The activity of MnO will be altered as a consequence. However, this fluctuation in the MnO activity is minimal and the phenomenon can be depicted in Figures 16a and 16b in Warren et al[7] have considered slags of varying basicity. In these plots, a constant value of CaO-to-MgO of 4,57 has been maintained and the slag Al_2O_3 content has been increased from 10 to 70 mass per cent. The CaO-to-MgO ratio of the unfluxed Mamatwan ore used in the present study is

4, 62 to 1 and this ratio is very close to the ratio used by Warren et al[7].

4.5. Procedure

The required composition and weight of alloy was added to the slag premelt in the crucible. The alumina crucible and the graphite holder were raised slowly into the vertical-tube molybdenum resistance furnace whilst flushing continuously with argon. The crucible was held just below the 'hot zone' for some time so as to reach a steady temperature and was then introduced into the middle of the 'hot zone' which was at a pre-set temperature in the range 1450°C to 1600°C.

The reduction reaction was assumed to begin when examination through the observation port revealed that the molten alloy had sunk through the underlying slag. A negligible amount of reaction occurred before the alloy sank through the slag and the reduction reaction was characterized by vigorous stirring and heat evolution due to the exothermic nature of the reaction. The procedure adopted to determine the effect on the sample temperature of this exothermic reaction is described in Section 4.6.

Once the reaction had proceeded for the required time at a specific temperature, the crucible was quenched in air. The alloy button was covered by slag and hence did not oxidize as it cooled On reweighing the alloy, a mass change could be recorded which was the sum of the masses of iron, manganese and silicon transferred between the metal and the slag. In experiments in which aluminium was used as a co-reductant with silicon, this alloy mass change also included the oxidation of aluminium and its transfer to the slag phase. The basis of these calculations is outlined in Appendix 1.

When the effect of stage-wise additions of lime was examined, the non-fluxed reaction was allowed to continue for 5 minutes before calcined pure lime was introduced to the reaction crucible through a mullite tube (10mm internal diameter) positioned through the

viewing port at the top of the furnace work tube. Once the lime charge had been added, the mullite tube was plugged in order to maintain the argon atmosphere within the furnace. The reactions then proceeded for various times, the maximum period being 15 minutes. A decrease in temperature of between 10° and 20°C was observed as lime was added to the reacting melt.

Experimental work was also carried out on the effect of stirring of the reacting melt with a 4-bore alumina insulation rod coupled to a variable speed motor. The alumina stirring rod passed through a gas seal at the top of the furnace This seal was made by fixing a cup to the alumina rod which could spin freely within an oil bath. The oil bath was rigidly attached and sealed to the top of the furnace work tube.

For stirring experiments the initial procedure was similar to that outlined previously. Once the reaction had commenced, the preheated stirring rod was introduced rapidly into the melt and its tip positioned in the slag phase. The rotation speed was set at 200 r. p.m. although it was difficult to measure this speed accurately.

On completion of the reduction reaction the alloy button was separated from its corresponding slag and weighed. From the increase in alloy mass, manganese recovery could be calculated. Periodic chemical analyses of the slag or alloy were used to check the recoveries of both manganese and iron as well as indicating the extent to which silicon or aluminium had been oxidised from the metal phase.

4.6. Variation in Melt Temperature

Heat is generated in the reacting melt by the exothermic reduction reaction and this phenomenon complicates the development of an increased understanding of slag - metal relationships in the production of medium- and low- carbon ferromanganese. The silicothermic reaction means that there is no temperature control during the initial stage of reaction and hence equilibrium and particularly kinetic studies of this process become very difficult.

This temperature increase was monitored using two Pt-6%Rh/Pt-30%Rh thermocouples contained in recrystallized alumina sheaths. One thermocouple was positioned at the top of the crucible side wall while the other was immersed in the reacting melt as the alloy sank through the underlying slag.

The thermocouple at the crucible side wall, or the control thermocouple, initially registered a temperature of 1500°C in the furnace 'hot zone'. When the crucible, containing the ore premelt and ferromanganese-silicide was moved from its preheat position into the 'hot zone' this control thermocouple registered adrop of approximately 10°C before suddenly rising as the reaction commenced after a short time lapse. At this point in time the second thermocouple was immersed in the reacting melt. Thus, by monitoring temperature using two thermocouples simultaneously a direct comparison could be made between the control thermocouple and that situated in the reacting melt. Measurement of the temperature of the reacting melt was not possible throughout every run because the platinum - rhodium thermocouples were attacked and failed and shielding of the thermocouple by a sheath would have meant increased refractory attack coupled with a decrease in the rate of temperature response.

Comparisons between the melt and control thermocouple temperatures are shown in Figure 34 for three separate reactions using different ratios of industrial ferromanganese silicide to ore premelt. The temperature recorded by the thermocouple in the reacting melt increased much more rapidly than the temperature recorded by the control thermocouple.

Temperatures in the reacting melt reach a constant value approximately three minutes after the beginning of a reaction whilst the control thermocouple is very slow in returning to 1500°C, the temperature at which the furnace was set before the introduction of the crucible into the 'hot zone' of the furnace.

The furnace 'hot zone' was adjusted to a temperature of 1500°C initially, but after reaction, the melt cooled to a temperature within 8°C of this pre-setting. Therefore, although the control

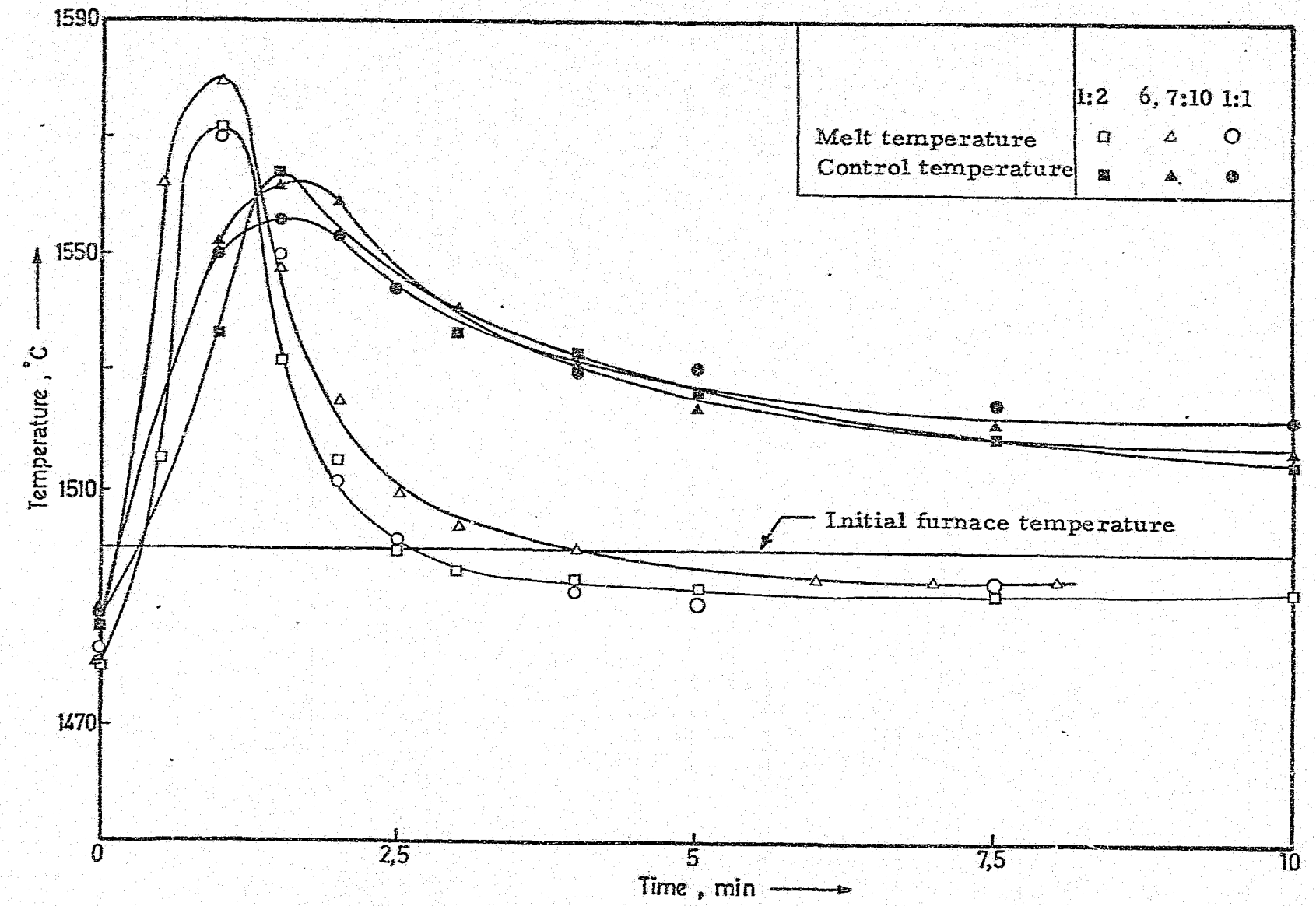

Figure 34. Temperature variations as unfluxed reactions proceed.

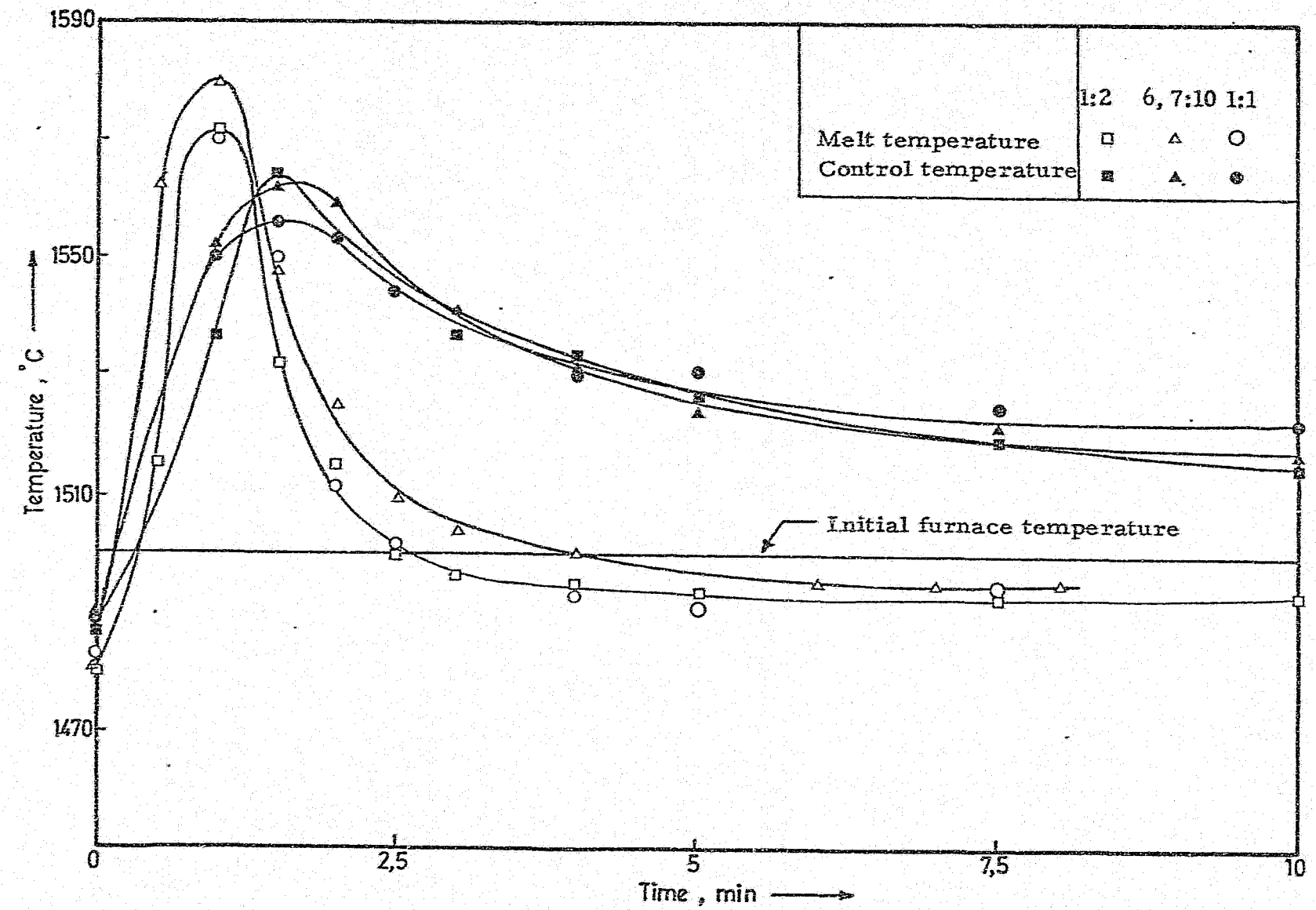

Figure 34. Temperature variations as unfluxed reactions proceed.

thermocouple temperature lagged the actual melt temperature during the course of a reaction, the final melt temperature corresponded closely to the initial furnace temperature.

The most important feature of the change in melt temperature with time is the sudden temperature increase of approximatly 90°C during the first minute of reaction. This dramatic temperature increase will profoundly affect the reaction kinetics and approach to equilibrium of the slag - alloy system. However as the experimental programme in this thesis was directed primarily towards the optimization and understanding of industrial practices it was not considered necessary to improve melt temperature control.

Temperature measurements were also conducted by positioning a thermocouple at the base of the graphite crucible holder. The temperatures at this point were consistently very much lower than those measured in the melt. It was therefore concluded that the monitoring of temperature at the crucible side wall was sufficiently accurate.

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