

The reduction of fluxed and non-fluxed manganese ores by ferromanganese silicide

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SYNOPSIS

In South Africa, medium-carbon ferromanganese is produced by the silicothermic reduction of slags containing MnO. Because of its importance in the production of refined ferromanganese, a study was made of the reaction between a premelted South African Mamatwan manganese ore and various ferromanganese silicide reducing alloys, with and without fluxing agents.

Because the reaction is highly exothermic, 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 were found to decline as the ratio of CaO to MgO decreased as a result of the addition of basic flux. The recovery of manganese passed through a maximum, and subsequently decreased for variations in the ratio of alloy to ore.

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

SAMEVATTING

Mediumkoolferromangaan word in Suid-Afrika geproduseer deur die silikotermiese reduksie van slakke wat MnO bevat. Vanweë die belangrikheid daarvan in die produksie van geraffineerde ferromangaan is daar 'n studie gemaak van die reaksie tussen 'n voorafgesmelte Suid-Afrikaanse Mamatwan-mangaanerts en verskillende ferromangaansiliciedreuserlegerings met en sonder smeltmiddels.

Omdat die reaksie uiters eksotermies is, het temperatuur blykbaar baie min uitwerking op die tempo van die mangaanoordrag na die metaal en die silikonoordrag na die slak en is 'n skynbare ewewig vinnig genader. Daar is perke vasgestel vir die gunstige uitwerking van die byvoeging van smeltmiddels en daar is gevind dat die mangaanherwinning afneem namate die verhouding van CaO tot MgO verminder as gevolg van die byvoeging van basiese smeltmiddel. Die herwinning van mangaan het 'n maksimum bereik en daarna afgeneem vir variasies in die verhouding van die legering tot die erts.

Wanneer die resultate wat verkry is, saam met ander fisies-chemiese data in verband met hierdie slak-metaalstelsel gebruik word, dui hulle op die optimale slaksamestellings vir die doeltreffende vervaardiging van mediumkoolferromangaan van Mamatwan-erts.

Introduction

In South Africa, medium-carbon ferromanganese is produced by the silicothermic reduction of slags containing MnO. Because of its importance in the production of refined ferromanganese, a study was made of the reaction between premelted South African Mamatwan manganese ore and various ferromanganese silicide reducing alloys, with and without the addition of fluxing agents. This fairly low-grade manganese ore is partially self-fluxing, and it was thought necessary to determine the optimum amounts of fluxing agent and the best time for its addition to ensure efficient operation of the electric furnace and maximum extraction of manganese from the premelt. Throughout the laboratory investigation described here, the emphasis was placed on the implications of the process for industrial practice.

The highly exothermic nature of the silicothermic reduction made it impossible to maintain close control of temperature and to carry out controlled equilibrium and kinetic studies in the slag-metal system. Manganese recovery from premelted Mamatwan ore was determined as a function of reaction temperature, reaction time, alloy-to-ore ratio, and fluxing additions. *Manganese recovery* is defined as the manganese transferred from the premelted ore to the alloy expressed as a fraction

of the total manganese originally present in the premelted ore.

This investigation is part of a programme within the Pyrometallurgy Research Group of the National Institute for Metallurgy on the role played by Mamatwan manganese ore in the reactions involved in the production of manganese alloys. The processes for the extraction of manganese from Mamatwan ore must be improved, and further processes must be developed so that the substantial reserves of manganese ore in the northern Cape can be utilized. Limited tonnages of this ore are now being used in the production of medium- and high-carbon ferromanganese.

Experimental Method

Preparation of Slags and Alloys

As the metal and slag compositions chosen were representative of those used in the production of medium-carbon ferromanganese in South Africa, the experimental results can be compared with data obtained from industry.

The analyses of Mamatwan ore and the premelt from that ore are shown in Table I. In the preparation of each premelt, 25 g of Mamatwan ore, minus 48 mesh in size, was heated to 1500°C in an alumina crucible with or without the addition of flux. The volatile constituents of the ore were eliminated, and thermal decomposition

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of the higher oxides of manganese occurred before the sample eventually melted in air.

Three forms of fluxing agents were used during the investigation: lime (Baker analysed reagent), magnesia (chemically pure), and Transvaal dolomite having the analysis shown in Table I. Each of these additives was heated at 1000°C for two hours so that any contained volatiles would be driven off, and was then cooled and stored in a desiccator.

TABLE I
CHEMICAL COMPOSITION OF ORE AND DOLOMITE

Constituent	Mamatwan ore, % by mass		Calced dolomite % by mass
	As mined	Premelt	
*MnO ₂	29,14		0,81
*MnO	25,03		
Mn ₂ O ₄		64,80	
H ₂ O	1,80		0,53
CO ₂	15,44		45,95
Fe ₂ O ₃	6,22	7,74	1,07
MgO	2,77	3,35	18,75
CaO	13,04	15,57	30,43
Al ₂ O 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 the manganese oxides normally reported in chemical analyses. However, the manganese oxides in Mamatwan ore are mainly in the form of braunite (3Mn₂O₃·MnSiO₃) and hausmannite (Mn₃O₄).

The industrial ferromanganese silicide alloy used was crushed to material smaller than 48 mesh (Tyler) and had the following composition in per cent by mass: Mn 65,2; Si 22,46; Fe 11,05; C 0,49; and minor components 0,80.

Apparatus and Procedure

Fine-grained, low-porosity, recrystallized-alumina crucibles were selected for the slag-metal reaction. It was found that the amount of Al₂O₃ 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 Al₂O₃ dilutes the MnO in the slag and lowers its activity. However, Warren *et al.*¹ showed that, for a constant ratio of CaO to MgO of 4,57 and an increase in the Al₂O₃ content of the slag from 10 to 20 per cent by mass, the fluctuation in the MnO activity was very small. The CaO-to-MgO ratio of unfluxed Mamatwan ore was 4,62.

The alloy was added to the slag premelt in the alumina crucible, and the crucible and graphite holder were then raised slowly into a molybdenum-wound resistance furnace that was flushed continuously with argon. The crucible was held just below the 'hot zone' long enough for it 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 to 1600°C. The temperature in the 'hot zone' of the furnace could be maintained within 9°C of the required value over a vertical distance of 60 mm, a Pt-6%Rh/Pt-30%Rh

thermocouple being used, with its junction positioned at the wall of the reaction tube 5 mm above the top of the crucible.

It was assumed that the reduction reaction had begun when examination through the observation port revealed that the molten alloy had sunk through the underlying slag. There was very little reaction before the alloy sank through the slag, and the reduction reaction was characterized by vigorous movement and heat evolution due to exothermic reaction. The procedure adopted in determining the effect of this exothermic reaction on the temperature of the sample has been described in detail elsewhere².

Temperatures in the reacting melt reached a constant value within 10°C of the initial furnace temperature (usually 1500°C) approximately three minutes after the beginning of a reaction. The most important feature of the change in melt temperature with time was the sudden increase in temperature during the first minute of reaction. This dramatic temperature increase profoundly affected the kinetics of reaction and the approach to equilibrium of the slag-alloy system. However, since the experimental programme was directed primarily towards optimization and understanding of industrial practice, it was not considered necessary (nor was it practicable) to improve temperature control of the melt.

When 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. The alloy was reweighed, the change in mass representing the total mass of iron, manganese, and silicon transferred between the metal and the slag. The basis of these calculations has been outlined by Channon². Periodic chemical analyses of the slag or alloy were used as a check on the recoveries of manganese and iron, and indicated the extent to which silicon had been oxidized from the metal phase.

When the effect of stage-by-stage additions of lime was examined, the non-fluxed reaction was allowed to continue for 5 minutes before calcined pure lime was introduced into the reaction crucible through a mullite tube (of 10 mm internal diameter) positioned through the viewing port at the top of the furnace work-tube. After the calcined lime had been added, the mullite tube was plugged so that the argon atmosphere was maintained within the furnace. The reactions then proceeded for various lengths of time, 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.

Results

Non-fluxed Reactions

Experiments were carried out to show the effect of initial temperature on manganese recovery with time for temperatures of 1450, 1500, 1550, and 1600°C. The ratio of plant alloy to non-fluxed ore chosen was 2, which approximates the ratio used in industry. A ratio of 0,67 is necessary for the stoichiometric amount of silicon that is required to reduce all the manganese and iron oxides to the metallic state; the silicon is

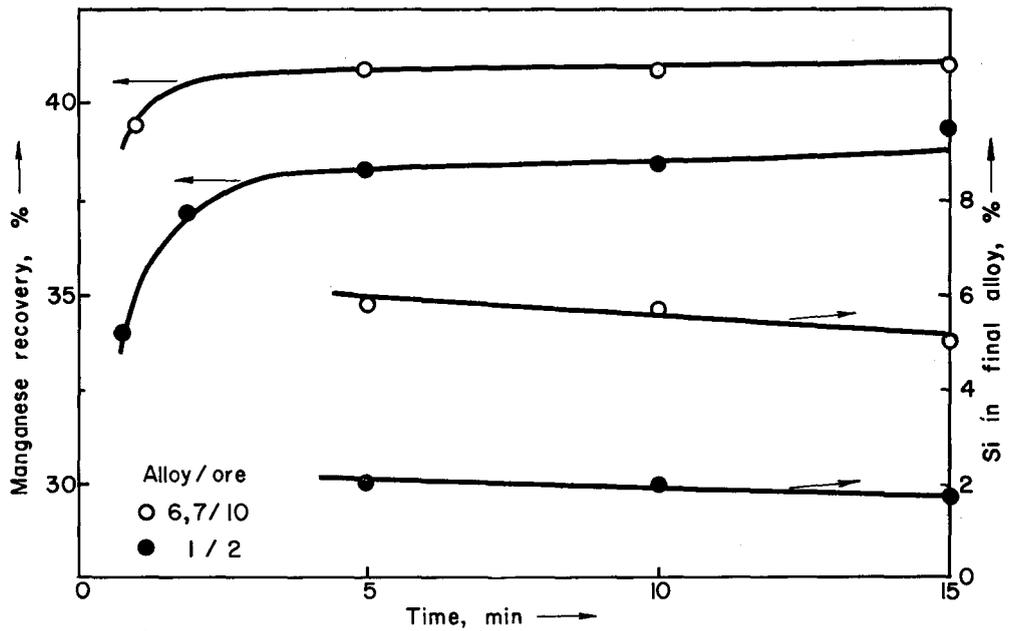


Fig. 1—Effect of variation in the plant alloy-to-ore ratio on the change in manganese recovery with time at 1500°C

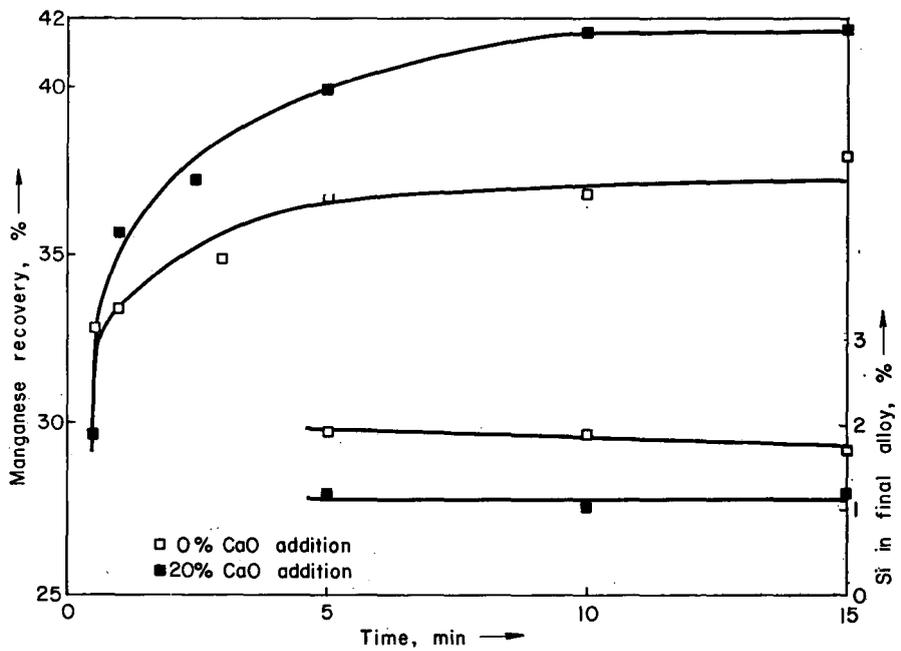


Fig. 2—Effect of CaO additions on reactions at 1500°C for a plant alloy-to-ore ratio of 0,5

supplied by ferromanganese silicide having a silicon content of 22,46 per cent by mass.

The initial temperature had little effect on manganese recoveries, and the reduction reaction appeared to be virtually complete within a few minutes of the start of the reaction. The exothermic reduction reaction made it difficult to determine the effect of variations in the initial furnace temperature. Thus, the initial temperature of the control thermocouple was held constant at 1500°C, and all subsequent experiments were carried out at that temperature.

Fig. 1 shows the manganese recovery and the silicon contents of the final alloy for the standard reaction time of 15 minutes when the stoichiometric and standard additions of silicon are in the form of plant alloy.

Fluxed Reactions

In plant operations, lime (about 20 per cent by mass) is added to the manganese ore. Fig. 2 shows that, for a particular alloy-to-ore ratio, the use of fluxes results in greater manganese recoveries from the slag and lower silicon levels in the final alloy.

A comparison of the manganese recovery when stoichiometric amounts of plant silicide were added and no flux was used with that when stage-by-stage additions of lime were made showed that there was an increase in manganese recovery of about 5 per cent by mass 5 minutes after 20 per cent CaO (by mass) had been introduced into the system. No further significant increase in recovery occurred after that time. During these small-scale experiments with stage-by-stage additions of lime, temperature control of the reacting melt was difficult because the introduction of a relatively large mass of cold lime led to lower melt temperatures and lower manganese recoveries than those during the premelting of lime and ore.

The CaO additions were varied at different alloy-to-ore ratios during experiments to show the manganese recovery from slags contacted with different alloys and containing different amounts of flux. These results are shown in Fig. 3. With increasing additions of lime, high alloy-to-ore ratios of 0,67 and 0,7 gave an increase in manganese recovery, but, with the low alloy-to-ore ratio of 0,5, manganese recovery passed through a maximum. The final silicon content of the alloy always decreased with increasing CaO content of the slag.

CaO was replaced by MgO to show the influence of MgO additions, and of the partial or total replacement of CaO by calcined dolomite, on manganese recovery. Fig. 4 shows two recovery values for MgO additions of up to 20 per cent by mass. When the MgO additions were larger, it was not possible to melt the mix of Mamatwan ore and MgO, even at a temperature of 1550°C. These two recovery values indicate that, up to a point, an increase in MgO additions results in an increase in manganese recovery, although, as shown in Fig. 4, as MgO replaces CaO at any level of flux addition and alloy-to-ore ratio, manganese recovery decreases. In addition, for both alloy-to-ore ratios and all CaO-to-MgO ratios (except 7 for an alloy-to-ore ratio of 0,67), the manganese

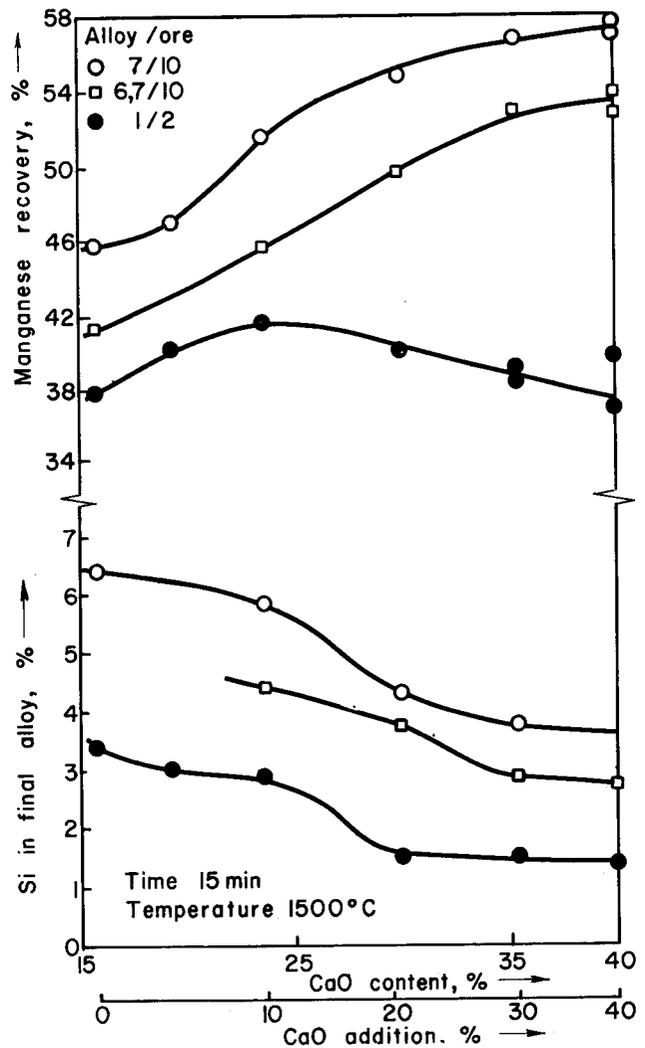


Fig. 3—Effect of CaO additions on manganese recovery and silicon content of the final alloy

recovery passes through a maximum at additions of basic flux between 20 and 30 per cent by mass.

The final fluxing agent was a calcined dolomite of the Transvaal Dolomite Series having the analysis given in Table I. At alloy-to-ore ratios of 0,5 and 0,67, calcined dolomite gave a slightly lower manganese recovery than that obtained with the corresponding amount of CaO. When an alloy-to-ore ratio of 0,5 was used, as in industrial practice, the difference in recoveries was less than 2 per cent (by mass) for fluxing additions of 20 per cent by mass.

Variations in the Mass of Plant Alloy

Manganese recovery rose progressively as the mass of industrial ferromanganese silicide alloy was increased (Fig. 5). Manganese recovery increases with higher alloy-to-ore ratios because a higher activity of silicon is maintained throughout the reduction reaction. As the mass of alloy is increased, there is less dilution of the silicon content of the alloy at any particular manganese recovery.

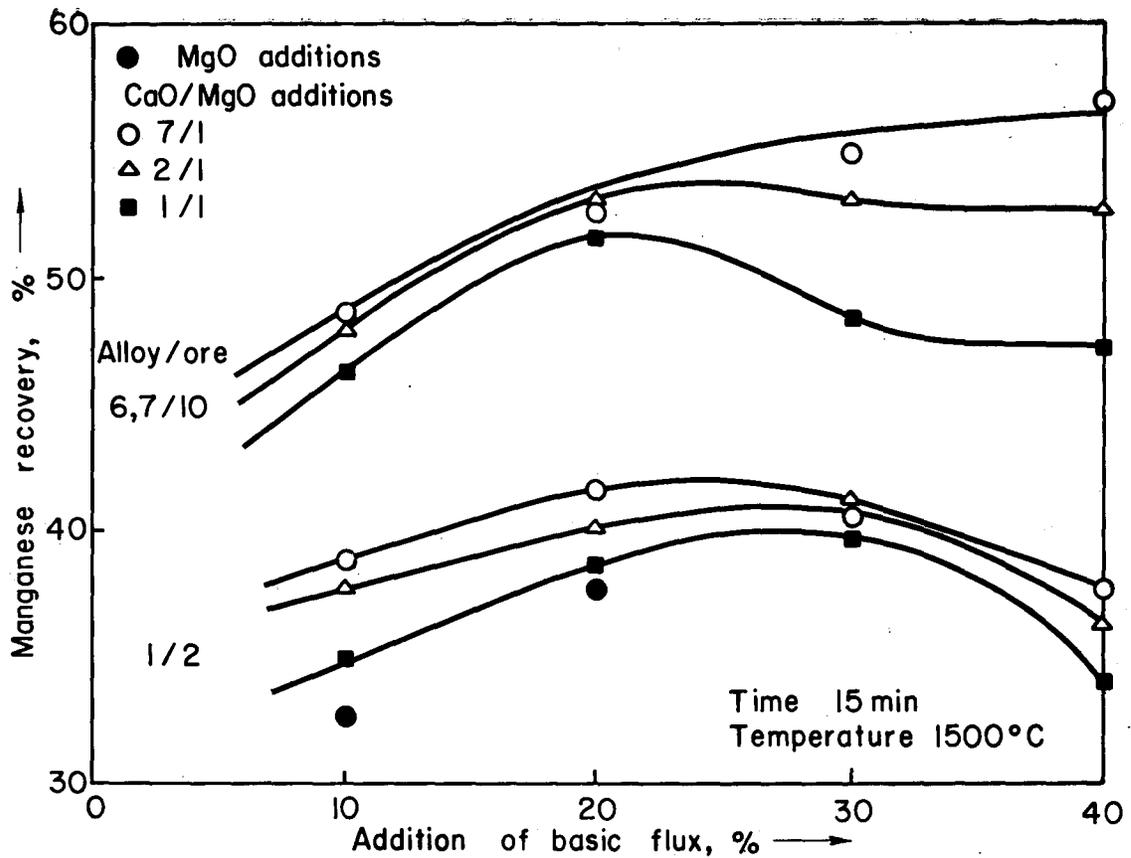


Fig. 4—Effect of CaO-to-MgO ratio on manganese recovery

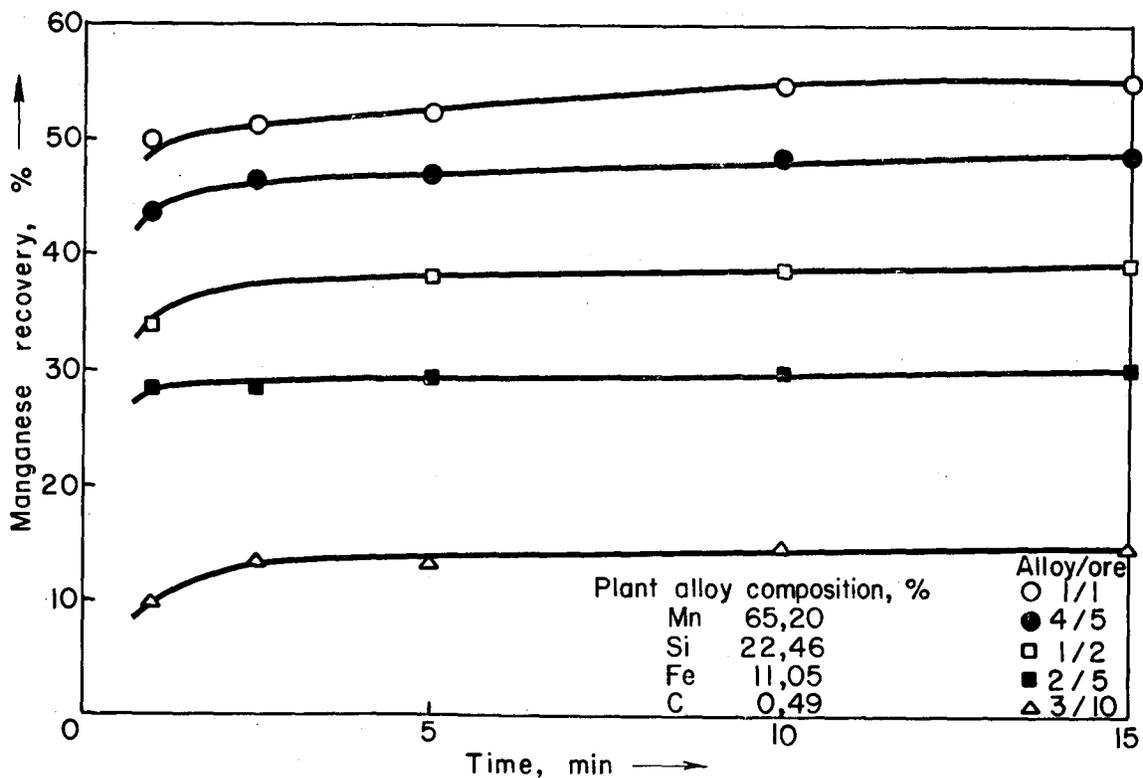


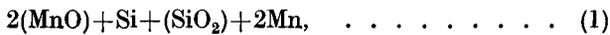
Fig. 5—Increase in manganese recovery with time for increases in plant alloy-to-ore ratio without fluxing additions at 1500°C

Discussion

Basicity and Fluxing Additions

Distribution Ratios of Silicon and Manganese

The reaction for the recovery of manganese from an MnO-rich slag is



where (MnO) and (SiO₂) are in the slag phase, and Mn and Si are in the alloy phase. It is not possible to predict the equilibrium distribution of manganese and silicon between the slag and the alloy because of the lack of fundamental data on the activities of the components in both the slag and the alloy phases².

The problems caused by this lack of fundamental data can be overcome by use of an apparent equilibrium constant $K^1_{\text{Mn-Si}}$ defined from equation (1) as

$$K^1_{\text{Mn-Si}} = \sqrt{\frac{(\text{SiO}_2)}{K_1}} = \frac{(\text{MnO}) \sqrt{[\text{Si}]}}{[\text{Mn}]}, \dots \dots \dots (2)$$

where (MnO) and (SiO₂) are mass fractions in the slag phase, and [Mn] and [Si] are mass fractions in the alloy phase. The apparent equilibrium constant depends mainly on the ratio of the manganese in the slag to that in the metal (manganese distribution ratio), which is close to its equilibrium value in practice, whereas the silicon distribution ratio is far removed from equilibrium^{3, 4}. The manganese distribution ratio is defined as (MnO)/[Mn], where (MnO) represents the MnO content of the final slag and [Mn] represents the manganese concentration of the final alloy. This ratio should be as low as possible for the maximum recovery of manganese from a manganese ore. The silicon distribution ratio is defined as (SiO₂)/[Si], where (SiO₂) represents the silica content of the final slag and [Si] the silicon concentration of the final alloy.

Table II shows the effects of types and quantities of fluxing agents on the apparent equilibrium constant. Similar tables have been prepared for plant alloy-to-ore ratios of 0,5 and 0,67 when magnesia replaces lime as a flux². As the amount of basic fluxing component, and hence slag basicity, is increased at any particular ratio of alloy to ore, there is a decrease in the value of the apparent equilibrium constant. Similar results were obtained by Schenck *et al.*^{5, 6}, who found that at 1500°C $K^1_{\text{Mn-Si}}$ varied from 0,087 to 0,042 as the slag basicity ratio $[(\text{CaO}) + (\text{MgO})]/(\text{SiO}_2)$ increased from 0,6 to 1,6. These values are in good agreement with the values in Table II for alloy-to-ore ratios of 0,5.

If market specifications are to be met, industrial processes for the production of medium-carbon ferromanganese must yield an alloy having a silicon content of less than 1,5 per cent by mass and a manganese content of approximately 80 per cent by mass. In addition, these processes must extract the manganese from the ore as efficiently as possible.

In practice, the silicon and manganese distribution ratios are such that these two conditions cannot be satisfied simultaneously. The ferromanganese producer usually decides to produce a highly refined alloy and to accept a higher loss of manganese to the slag. Hence, in industrial processes, it is more important to maintain high values for the silicon distribution ratio than to

maintain low values for the manganese distribution ratio, provided that the manganese content of the alloy is maintained at approximately 80 per cent by mass.

Figs. 6 to 8 (from Table II and similar calculations)² show that a high manganese distribution ratio is associated with a low silicon distribution ratio, whereas a low manganese distribution ratio is associated with a high silicon distribution ratio. High ratios for basicity give low manganese distribution ratios, although it is possible that this effect is caused by the decrease of the final MnO content of the slag owing to fluxing additions. Fig. 6 shows that, with increasing alloy-to-ore ratios, both the manganese and silicon distribution ratios decreased as the CaO additions were increased.

The calculations for Figs. 7 and 8 indicate that, for a decrease in the CaO-to-MgO ratio, there is an increase in the apparent equilibrium constant at any given flux addition. This increase suggests that a higher manganese distribution ratio is obtained, although dilution of the MnO in the final slag lowers the manganese distribution ratio if large amounts of flux are used. Fig. 7 shows that the manganese distribution ratio decreases for increasing CaO-to-MgO ratios with a stoichiometric amount of silicon in the reducing alloy. The values for MgO additions alone have not been plotted in Fig. 7. As CaO is replaced by MgO, there is a decrease in the silicon distribution ratio for all the levels of flux additions investigated. As the basicity ratio is increased, the silicon distribution passes through a maximum for a CaO-to-MgO ratio of 7 at an alloy-to-ore ratio of 0,67 (Fig. 7), and, for an alloy-to-ore ratio of 0,5, there are maxima in all three silicon distributions at CaO-to-MgO ratios of 7, 2, and 1.

Thus, as shown in Figs. 7 and 8, there is a particular range of basicities for the efficient refining of silicide, i.e., the achievement of a high silicon distribution ratio for particular values of CaO-to-MgO ratio and alloy-to-ore ratio. No maxima were observed in the silicon distribution ratio when pure CaO was used as a flux, and it can therefore be concluded that the MgO addition has a substantial effect on the silicon distribution ratio when large quantities of flux are used.

For large flux additions that reduced the CaO-to-MgO ratio, there was a marked decrease in the silicon distribution ratio, which can be attributed to an increasingly less favourable reaction. It is considered that this decrease is caused by an increase in the liquidus temperature of the slag, and hence in slag viscosity, as the MgO content of the slag is increased to more than 10 per cent by mass. No data were available for liquidus temperatures in the system MnO-MgO-Al₂O₃-SiO₂, except those of Warren *et al.*¹, whose liquidus temperatures were based on data for the system CaO-MgO-Al₂O₃-SiO₂⁷. Warren *et al.*¹ showed that MnO in the quaternary system usually lowers the liquidus temperatures by 30 to 40°C over the composition range investigated. Thus, the MnO in ferromanganese slags is expected to lower the temperatures of the liquidus surfaces in the CaO-MgO-Al₂O₃ system without affecting the overall configuration or the relation between the curvatures of these surfaces. The phase diagram from Osborn *et al.*⁷ may therefore be taken as a reasonably good guide to

TABLE II

DISTRIBUTION OF MANGANESE AND SILICON BETWEEN THE ALLOY AND THE SLAG FOR THE LIME-FLUXED REACTION WITH PLANT FERROMANGANESE SILICIDE AS REDUCING AGENT

Ratio of alloy to ore	CaO addition %	Final compositions				Distribution ratio		Basicity ratio (CaO) + (MgO) (SiO ₂)	Apparent equilibrium constant	
		Mass fraction in alloy		Mass fraction in slag		(MnO) [Mn]	(SiO ₂) [Si]		$K = \frac{[\text{Mn}]^2 (\text{SiO}_2)}{(\text{MnO})^2 [\text{Si}]}$	$K^1 = \frac{(\text{MnO})}{[\text{Mn}]}$
		Mn	Si	MnO	SiO ₂	CaO	MgO			
0,5	0	0,790	0,030	0,373	0,300	0,168	0,034	10,00	44,9	0,082
	10	0,798	0,028	0,314	0,272	0,245	0,031	9,71	62,7	0,066
	20	0,811	0,019	0,281	0,242	0,324	0,028	12,74	106,1	0,048
	30	0,817	0,015	0,263	0,218	0,385	0,025	14,53	140,5	0,039
	40	0,827	0,013	0,245	0,198	0,432	0,023	15,23	173,6	0,034
0,67	0	0,780	0,054	0,360	0,303	0,154	0,034	5,61	26,3	0,107
	10	0,795	0,045	0,300	0,282	0,252	0,031	6,27	44,0	0,080
	20	0,801	0,037	0,253	0,266	0,333	0,028	7,19	72,1	0,061
	30	0,814	0,028	0,218	0,248	0,369	0,025	8,86	123,3	0,045
	40	0,819	0,026	0,196	0,229	0,448	0,023	8,81	153,0	0,039
0,7	0	0,789	0,065	0,334	0,321	0,158	0,035	4,94	27,6	0,107
	10	0,799	0,059	0,269	0,304	0,258	0,032	5,15	45,4	0,082
	20	0,814	0,043	0,228	0,283	0,337	0,029	6,58	83,9	0,058
	30	0,819	0,038	0,198	0,261	0,401	0,026	6,87	117,5	0,047
	40	0,821	0,036	0,177	0,241	0,454	0,024	6,70	144,1	0,041

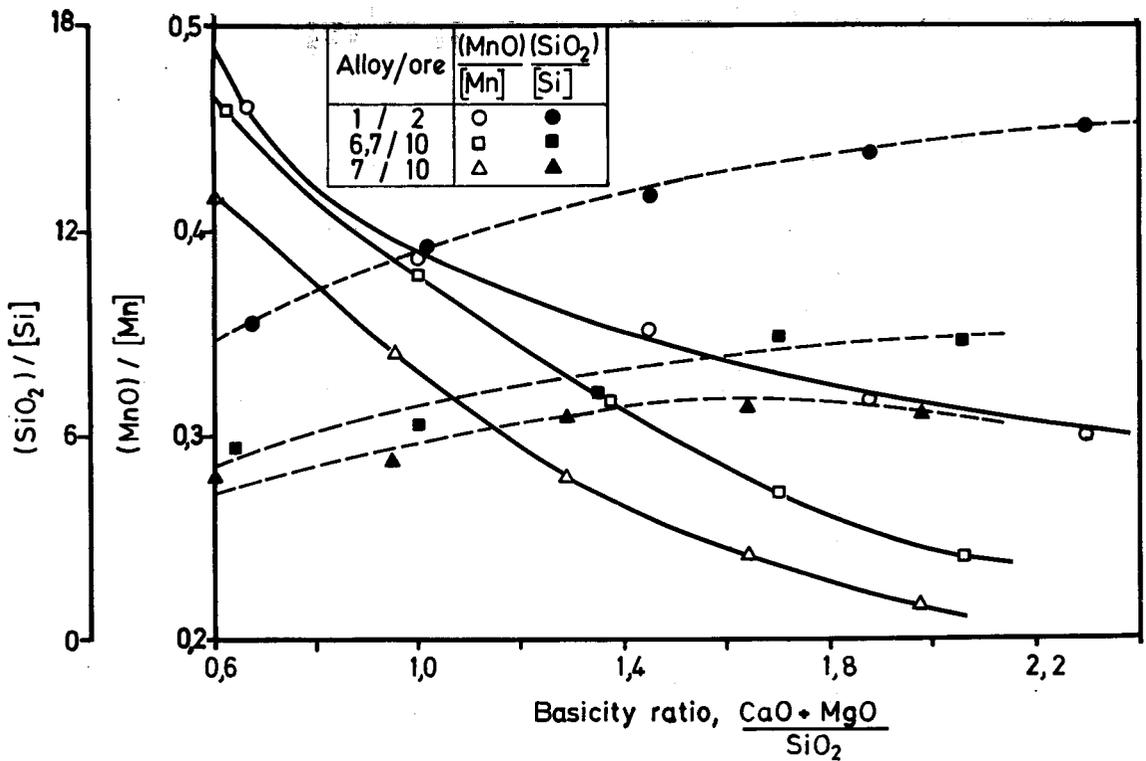


Fig. 6—Effect of CaO additions and variations in the alloy-to-ore ratio on the manganese and silicon distribution ratios

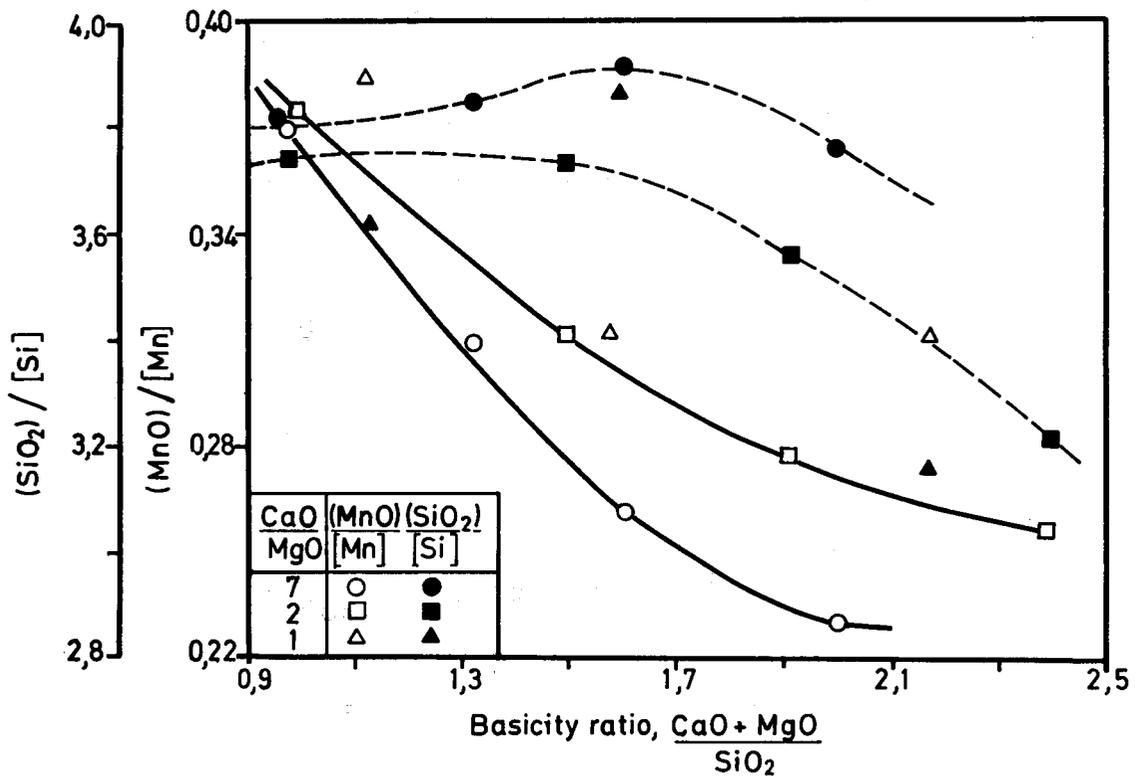


Fig. 7—Effect of the replacement of CaO by MgO on the manganese and silicon distribution ratios for an alloy-to-ore ratio of 0.67

the liquidus temperatures of slags that were recalculated by omission of the MnO content of the slag and adjustment of the concentrations of the other four components so that $\text{CaO} + \text{MgO} + \text{SiO}_2 + \text{Al}_2\text{O}_3 = 100$ per cent.

Fig. 8 shows the relation of manganese and silicon distribution ratios to the basicity ratio for a ferromanganese slag produced from manganese ore and industrial ferromanganese silicide in the ratio of 2. This ratio is used in industrial practice when the ferromanganese silicide has a silicon content of approximately 22 per cent by mass, which is reduced to less than 1,5 per cent by mass during refining. The manganese distribution ratio decreases with increasing CaO-to-MgO ratio — a similar result to that shown in Fig. 7 for an alloy-to-ore ratio of 0,67. The silicon distribution ratio also passes through a maximum that depends on the CaO-to-MgO ratio of the flux. Fig. 8 shows that the optimum for the basicity ratio of the slag lies between 1,4 and 1,8. Below a basicity ratio of 1,4, refining is poor when a high-magnesia flux is used, and, above a basicity ratio of 1,8, there is a marked decrease in the silicon distribution ratio because of the formation of slag premelts having higher liquidus temperatures (more than 1600°C) for MgO contents of more than 12 per cent by mass; hence the slag premelts have higher viscosities (approximately 0,26 N. s/m² at 1500°C⁸) than usual (approximately 0,15 N. s/m²).

A comparison of Figs. 7 and 8 reveals that high alloy-

to-ore ratios result in lower manganese and silicon distribution ratios.

Lime and Magnesia Additions

This discussion has so far centred on an examination of variations in manganese and silicon distribution ratios with slag basicity ratio, which is defined as $[(\text{CaO}) + (\text{MgO})]/(\text{SiO}_2)$. A detailed discussion of the effects of the individual fluxing agents of alumina, lime, and magnesia has been given by Channon² to highlight the importance of slag structure and properties in the production of refined ferromanganese by silicothermic reduction. The most important fluxing additions are lime and magnesia, and the principal points made by Channon for these two fluxing agents are summarized here.

Lime is used extensively in the production of medium- and low-carbon ferromanganese to increase the activity coefficient of MnO and to reduce the slag viscosity by breaking up the silicate network. However, excessive CaO markedly increases the liquidus temperatures of the slag, and the viscosity of the slag is increased at any constant temperature with a consequent decrease in the rate of reduction. The effect of increasing CaO concentration on liquidus temperature is illustrated by the quaternary system⁷ $\text{CaO}-\text{MgO}-\text{Al}_2\text{O}_3-\text{SiO}_2$, which shows that, when the slag has an MgO content of less than 15 per cent by mass, an increase in the CaO content of the slag from 40 to 50 per cent by mass raises its liquidus tem-

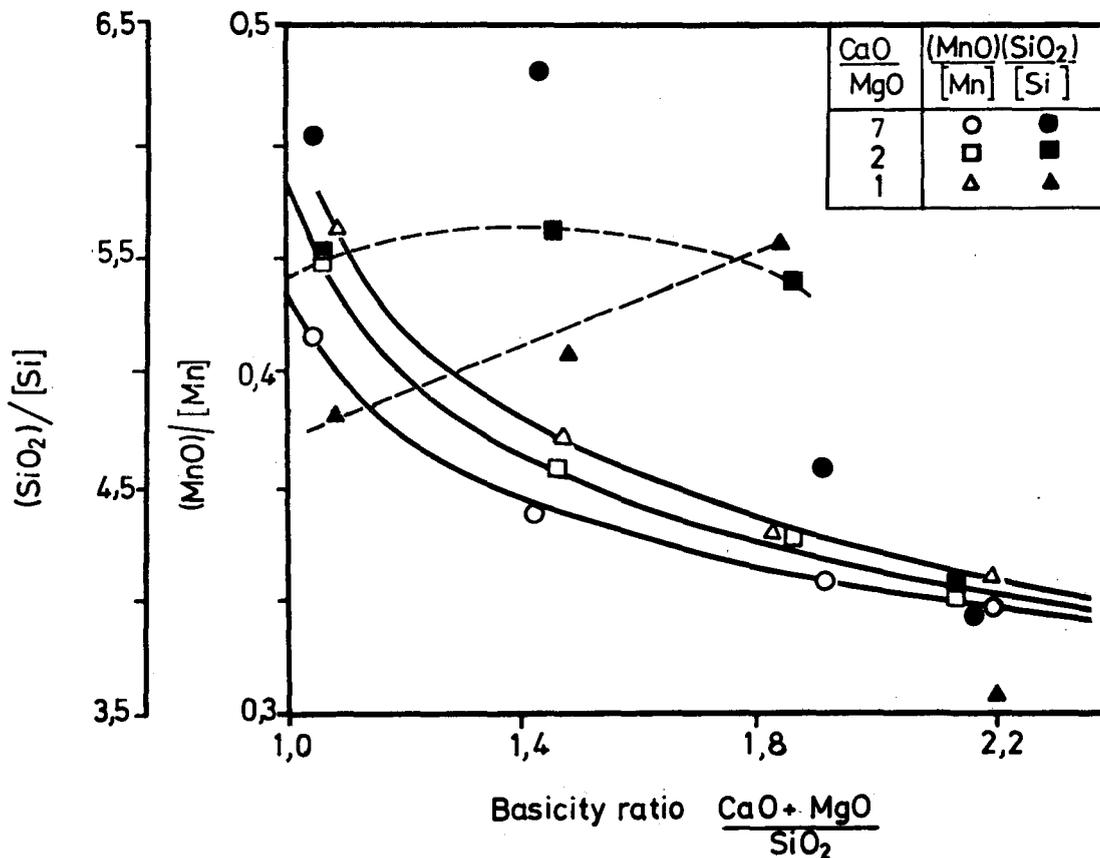


Fig. 8—Effect of the replacement of CaO by MgO on the manganese and silicon distribution ratios for an alloy-to-ore ratio of 0,5

perature from approximately 1300 to 1450°C. Further increases in the CaO content of the slag, particularly when the slag has an MgO content of less than 10 per cent by mass, result in sudden increases in the liquidus temperature; for example, at a CaO content of 55 per cent by mass, the liquidus temperature was higher than 1600°C.

For efficient extraction of manganese from a manganese ore premelt, the activity of MnO should be maintained as high as possible throughout the reduction reaction. During this reaction, the MnO activity in the slag is continually decreased because of the presence in the slag of SiO_4^{4-} ions and silicate polyanions, which are then associated with the Mn^{2+} and O^{2-} ions from the MnO. CaO is a more basic oxide than MnO, and, when it is introduced into a slag system, it liberates⁹ more O^{2-} ions than does MnO. The SiO_4^{4-} ions and other polyanions associate preferentially with Ca^{2+} ions, and the activity of the MnO in the slag is increased. Increases in the concentration of CaO in the slag increase the activity coefficient of MnO in the slag melt at any particular concentration of MnO. On the other hand, increases in CaO additions to a slag containing MnO decrease the mole fraction of MnO. Thus, although CaO additions increase the activity coefficient of MnO, excessive CaO additions may lower the MnO activity.

Fig. 2 compares the reactions for an unfluxed charge containing the stoichiometric amount of silicon with that for a charge fluxed with CaO. For a reaction time of 15 minutes, the basicity ratio of a melt of unfluxed Mamatwan ore decreased from 3,5 to less than 0,7. A slag basicity ratio of 0,7 favours the association of Mn^{2+} ions with SiO_4^{4-} ions and other silicate polyanions, and leads to an eventual decrease in the rate of manganese recovery, which therefore tends towards a constant value.

A CaO addition of 20 per cent by mass permits the establishment of more favourable distributions of manganese and silicon because of the increase in the MnO activity of the slag. For fluxing additions of 20 per cent by mass, the slag basicity ratio of $(\text{CaO} + \text{MgO})$ to (SiO_2) changes from 7,4 to 1,45 as the reaction progresses. The final value of 1,45 is in good agreement with the values of 1,3 to 1,5 in industrial practice¹⁰. The manganese recoveries of 40 per cent and the alloy silicon contents of 1,0 per cent by mass are also in good agreement with the respective values of 45 per cent and 0,8 per cent by mass obtained industrially¹⁰.

Fig. 3 illustrates the effect of variations in CaO addition on manganese recovery from the slag. For the reaction with the lowest alloy-to-ore ratio (0,5), the concentrations of silicon in the final alloy were very low. From the data of Tolstoguzov¹¹ for the Fe-Mn-Si-C system, correspondingly low values for silicon activity can be expected. The plot of manganese recovery for a low alloy-to-ore ratio passes through a maximum in recovery. The present investigation indicates that, for increasing additions of CaO, the MnO activity in the slag must increase when the CaO addition is less than 12 per cent by mass. However, at higher additions of CaO, although the activity coefficient of MnO increases¹, the lowering of the mole fraction becomes the predominant

influence upon the activity of MnO, which is decreased. The activity of the silicon in the reducing alloy is low because of the low mole fraction of silicon, and hence manganese recovery tends towards a constant value.

For higher alloy-to-ore ratios, the MnO activity eventually decreases because of excessive CaO additions, but the silicon activity in the alloy is sufficiently high to drive reaction (1) closer to equilibrium. The following silicon activity coefficients in the Fe-Mn-Si-C system have been reported¹¹ for alloys having a silicon content of 1,5 and 15 per cent by mass: 0,0282; 0,0151; and 0,0331. Consequently, it is possible that, for alloys having a silicon content up to about 6,4 per cent by mass (the highest value given in Fig. 3), the silicon activity varies almost directly with silicon content.

That substantial increases in the liquidus temperatures of the slag do not occur at these high levels of CaO addition can be inferred from the quaternary system $\text{CaO-MgO-Al}_2\text{O}_3\text{-SiO}_2$, which was studied by Osborn *et al.*⁷. During the present investigation, the CaO content of the final slag reached a maximum of 41 per cent by mass. When the CaO content was recalculated and the MnO content was ignored, the maximum CaO content was approximately 47 per cent by mass and the MgO content was approximately 7 per cent by mass. The liquidus temperature corresponding to this slag composition in the quaternary system $\text{CaO-MgO-Al}_2\text{O}_3\text{-SiO}_2$ was 1500°C, and, if MnO were introduced to the four-component system, the liquidus temperatures would be lower.

Magnesia is similar to lime in its effect on the activity of MnO in a manganese slag premelt, and is also a network modifier since it reduces the average size of the silicate polyanions in a slag. The Mg^{2+} ions preferentially associate with SiO_4^{4-} ions, increasing the number of less strongly associated Mn^{2+} ions and, as a result, the activity coefficient of the MnO is increased. The basicities of CaO and MgO are higher⁹ than that of MnO, and there should be a tendency for Ca^{2+} and Mg^{2+} ions to be preferentially associated with SiO_4^{4-} ions and other silicate polyanions such as $\text{Si}_2\text{O}_7^{6-}$ and $\text{Si}_3\text{O}_8^{10-}$. The number of less strongly associated Mn^{2+} ions in the slag increases with a corresponding increase in the activity coefficient of the MnO in the slag.

As CaO is replaced by MgO for a particular percentage of flux in the charge, there is an increase in the mole fraction of basic fluxing components as a result of the lower molecular mass of MgO than that of CaO. Hence, the mole fraction of MnO in the slag is reduced, although no dilution has occurred according to the percentage by mass of flux present. Thus, although increased MgO additions increase the activity coefficient¹, the MnO activity does not necessarily increase. Warren *et al.*¹ found that, for any given Al_2O_3 and SiO_2 contents, the activity coefficient of MnO decreases as MgO replaces CaO (according to percentage by mass) at high SiO_2 levels. In more basic slags, such as those encountered in the production of refined ferromanganese, the activity coefficient of MnO increases initially from approximately 2,0 to 2,2 until the ratio of CaO to MgO reaches about 4. However, the effect of the increase on the activity of

MnO is small compared with that of the increase in basicity.

An increase in the amount of MgO from 5 to 10 per cent by mass in slags associated with the production of medium-carbon ferromanganese lowers the slag viscosity from 0,23 to 0,21 N.s/m² at 1500°C. However, MgO additions are limited to about 10 per cent by mass, and the slag viscosity measured at 1500°C increases to 0,26 N.s/m² for 18 per cent MgO by mass⁸.

The reduction in slag viscosity for increased MgO contents in the slag was shown by Woollacott *et al.*⁸ to be less when SiO₂ was replaced by Al₂O₃ at low concentrations of MnO in the slag. At high MnO concentrations, as the Al₂O₃ content of the slag increases from 10 to 16 per cent by mass, the increase in slag viscosity with increased MgO content is less marked.

During the present study, attention was given to the possible replacement of CaO by MgO and to the complete replacement of CaO, or to its partial replacement, by calcined dolomite. If dolomite proved to be satisfactory in practice, its use, because it is abundant in South Africa, could lead to vast savings in the cost of raw materials.

As shown in Fig. 4, the use of high alloy-to-ore ratios gives increased refining of slag at any level of flux addition. However, with increased additions of flux, a maximum recovery is achieved at alloy-to-ore ratios of 0,5 and 0,67.

When MgO replaced CaO, the manganese recovery always declined at a fixed addition of flux because the mole fraction of MnO was lowered as MgO was substituted for CaO, MgO having a lower molecular mass than CaO. As mentioned previously, Warren *et al.*¹ found a slight increase in the activity coefficient of MnO as MgO replaces CaO, but, as the mole fraction of MnO decreases with increasing MgO additions, it appears that the product of the MnO mole fraction and activity coefficient results in a decreasing activity of MnO with increasing MgO additions.

For large additions of basic flux, increased liquidus temperatures and viscosities hinder the silicothermic reduction. For low alloy-to-ore ratios, this effect was observed at all ratios of CaO to MgO and was also noted when CaO was used as the flux.

For the higher alloy-to-ore ratio (0,67), this decline in manganese recovery at particularly high additions of flux became more obvious as the CaO-to-MgO ratio was lowered. The slags produced after such additions contained MgO concentrations of between 12 and 19 per cent by mass, and, as previously stated, these slags are associated with high liquidus temperatures and viscosities^{1, 8}.

Slags associated with the production of medium-carbon ferromanganese were found to have SiO₂ concentrations of approximately 35 per cent by mass when recalculated according to percentage by mass excluding MnO. CaO can be used up to concentrations of 15 per cent by mass at SiO₂ and Al₂O₃ concentrations of 35 and 15 per cent by mass respectively. However, when the MgO concentration approaches 20 per cent by mass, the liquidus temperature increases to approximately 1500°C. Additions of CaO or MgO, or both,

at this SiO₂ concentration in the slag give sudden increases in liquidus temperatures of the slag. Viscosity increases with marked increases in liquidus temperature because the superheat of the slag is less at any particular temperature.

A small decrease in manganese recovery occurs over a wide range of fluxing additions when calcined dolomite is used instead of lime. This decrease is explained by higher liquidus temperatures of the slag for calcined dolomite, and consequent increases in viscosity, as well as decreases in the activity of MnO at a particular level of flux addition. The increase in slag viscosity and decrease in the activity of MnO in the slag arise from the introduction of the MgO in the dolomite. The decline in manganese recovery with the use of calcined dolomite is not severe, and can be tolerated if the manganese losses to the slag can be offset by favourable costs for the fluxing materials, coupled with efficient operation of the arc furnace used for the preparation of the premelt.

Comparison with Previous Work

Slag-metal relations associated with the production of medium- and low-carbon ferromanganese have been investigated by Barcza¹². His studies on the reactions of the slag phase involved examination of the behaviour of ore and fluxes on being heated, as well as their behaviour during oxidation and reduction. A synthetic standard slag consisting of 55 per cent MnO₂, 35 per cent CaO, 5 per cent MgO, and 5 per cent SiO₂ (all by mass) was used. The composition of this slag was based on the chemical analysis of Mamatwan ore and limestone. The reducing agent was a plant ferromanganese silicide containing 11,1 per cent Fe, 65,6 per cent Mn, 22,4 per cent Si, and 0,46 per cent C (all by mass). As Barcza used synthetic premelts, data are available for the comparison of reactions between an alloy and a synthetic slag with reactions between an alloy and a premelt from Mamatwan ore as mined.

Typical results for variation in manganese recovery with time agreed with those of the present study in that the reaction was rapid, appeared to reach an apparent equilibrium within a few minutes, and the initial reaction temperature did not affect the manganese recovery. However, recoveries from the synthetic premelts were consistently much higher than from premelts of Mamatwan ore. The Mamatwan ore contains a small amount of iron oxide that would require silicide for its reduction, but the differences in manganese recovery from synthetic and natural premelts are substantial and cannot be explained in this way. The difference in manganese recovery is possibly due to differences between the oxidation state of the manganese in synthetic slags and that in 'natural' slags. In natural manganese slags, the manganese, when subjected to the partial pressures from oxygen and the temperatures in the reaction system, associates with the oxygen as Mn₃O₄.

The use of CaO as a flux had a much greater influence on manganese recoveries for experiments with synthetic melts. Manganese recoveries increased from 32 to nearly 60 per cent by mass as the CaO content in the premelt

was increased from 0 to 30 per cent by mass. When the CaO additions were more than 30 per cent, the manganese recovery was less. A similar decline in recovery with increased CaO additions was also observed when Mamatwan ore was used and the alloy-to-ore ratio was 0,5. The drop in recovery occurred at a CaO addition of 15 per cent by mass, or an addition of contained CaO of approximately 27 per cent by mass.

In both studies, higher alloy-to-ore ratios allowed the reduction reaction to proceed further towards completion when plant ferromanganese silicide was used.

The two studies showed the same general trends for all variations in flux and silicide additions. The single-stage reactions revealed that, even for the optimum conditions, only moderate manganese recoveries are possible because of the establishment of certain silicon and manganese distributions. Further, for a maximum recovery of manganese, the silicon content of the alloy is too high for the usual grades of medium-carbon ferromanganese. Both multistage and countercurrent reactions between slag and alloy are possible processes by which manganese recoveries can be improved¹².

Conclusions

- (1) Because of the exothermic nature of the reactions, there appeared to be no substantial increase in manganese recovery from the slag phase for increases in the reaction temperature from 1450 to 1600 °C.
- (2) For an alloy-to-ore ratio of 0,5 and CaO additions of 20 per cent by mass, the manganese recovery was 5 per cent higher from a fluxed charge than from a non-fluxed charge.
- (3) When the fluxing additions of CaO were increased to 40 per cent by mass, there was an apparent increase in the MnO activity of the slag. This activity appeared to decrease subsequently as a result of dilution effects or increased liquidus temperatures of the slag caused by larger additions of CaO.
- (4) Manganese recovery declined with decreasing CaO-to-MgO ratio for any particular addition of basic flux.
- (5) The replacement of CaO by MgO at high flux additions resulted in a marked increase in the liquidus temperature of the slag and a corresponding decrease in the manganese recovery.
- (6) The use of calcined dolomite instead of CaO as a

flux did not appreciably lower the manganese recovery.

- (7) As the alloy-to-ore ratio was increased, the recovery of manganese increased.

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Corrigenda: 'The metallurgy of tin smelting in a submerged-arc furnace', by H. A. Uys

The following *corrigenda* should be made to the above article, which was published in the January issue of the *Journal* (vol. 77, no. 6, 1977, pp. 121-125).

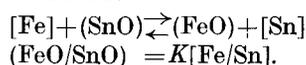
Page 121, line 2 of **The Primary Cycle**

Delete *is smelted*

Page 121, last line of left-hand column of type:

Delete 0,1 and insert 0,01

Page 125, lines 14 and 15 of left-hand column of type should read:



Page 125, the caption to Fig. 7 should read:

The relationship between the reaction constant K in the equation $(\text{FeO}/\text{SnO}) = K[\text{Fe}/\text{Sn}]$ and the ratio of CaO to SiO₂ in the secondary slag