Liquidus Temperatures and the Activities of Manganese (II) Oxide in Slags Associated with the Production of High-carbon Ferromanganese Alloys

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SYNOPSIS

The slags studied were those arising during the production of ferromanganese in South Africa, which belong to the system SiO_2—Al_2O_3—MgO—CaO—MnO.

It was found that the liquidus temperatures for slags having an MnO content of 13 per cent by mass are somewhat lower than those for slags belonging to the quaternary system SiO_2—Al_2O_3—MgO—CaO.

The activity coefficients of MnO are presented as contours of iso-activity coefficients on pseudoternary sections. The contours are derived from graphs in which the activity of MnO is plotted as a function of the concentration of MnO for various basicity ratios expressed as

$$\frac{\text{CaO(mass \%)} + \text{MgO(mass \%)}}{\text{SiO}_2\text{(mass \%)}}$$

The graphs are presented for selected concentrations of Al_2O_3 and selected ratios of CaO to MgO. These contours show that, within the compositional limits of the study, the MnO concentration in a slag affects the activity coefficient of MnO and that, at Al_2O_3 contents of 10, 20, and 30 per cent, the activity coefficient of MnO, when the MnO content is 13 per cent by mass, is markedly affected by the basicity of the slag.

INTRODUCTION[1-3]

High-carbon ferromanganese is commonly produced both in blast furnaces and in submerged-arc electric smelting furnaces. When electric smelting is used in their production, two processes are employed, referred to as the high-slag (or enriched) and low-slag (or discard) practices. In low-slag practice, the final slags are discarded, whereas, in high-slag practice, the manganese-rich slags are used for the production of silicomanganese alloys. They are eminently suitable for this process because the manganese-to-iron ratio is high, the silica content is high, and the phosphorus content is low. High-slag practice is often the more economical one because the total recovery of manganese is greater.

Most South African manganese ore is suited to the low-slag practice because it contains a high proportion of calcite and dolomite. The purpose of the investigation described here was to provide data that would permit the optimization of slag compositions used during this process so that the manganese losses to the slag would be reduced.

The discard slags from South African ores, whether produced in an electric smelting furnace or a blast furnace, fall within the investigated composition range: silica 18 to 47 per cent, alumina 10 to 30 per cent, magnesia 0 to 25 per cent, lime 33 to 46 per cent, and manganese(II) oxide additions from 5 to 20 per cent.

The reactions that occur in the two types of furnace are essentially similar. The higher oxides of manganese are converted into manganese(II) oxide either by thermal decomposition or by reduction with carbon monoxide at relatively low temperatures. These reactions occur relatively high up in the furnace so that, at the temperatures prevailing in the hottest zone, it is possible for the entire reduction to be expressed as follows:

$$MnO + C \rightarrow Mn + CO$$
$$6MnO + 8C \rightarrow 2Mn_3C + 6CO.$$

The theoretical initial temperatures of the above reactions are 1420°C and 1223°C respectively, indicating that reduction to Mn_3C is more likely, which explains why it is impossible for ferromanganese of low carbon content to be obtained at normal pressure when carbon is used as the reducing agent. In the actual furnace, the reactions are not quite so simple, because the manganese in the ores is present not entirely as free oxide but often as complex silicates, carbonates, and other compounds, and often closely associated with clay, bauxite, and other minerals. Before the reduction temperature is reached, the MnO combines with the silicates in the ore, gangue, and ash of the reducing agent, so that reduction down to Mn_3C takes place from the semifused charge and the liquid slag. The process differs from that of pig-iron production, in which the iron oxides can be reduced to the metallic state by carbon monoxide before they have the opportunity of entering the slag. It is believed that, in ferromanganese furnaces, the iron oxides are also reduced higher up in the furnace, and the iron carbide thus formed can reduce the MnO as it falls through the slag. Silicon that is produced by the reduction of SiO_2 by solid carbon at higher temperatures may also reduce some of the MnO in the slag, but the extent to which these processes occur is not known.

A search through the available literature revealed that, although a reasonable amount of work has been done on the determination of MnO activities in slags, especially those related to steel production, differing techniques have frequently led to conflicting results[4-11]. Furthermore, activity values are lacking for the slag compositions that are of most interest to ferromanganese producers in South Africa. Of the methods used, equilibrium techniques have been the most prominent. The following three equilibria have been exploited in these studies:

$$(FeO) + Mn \rightleftharpoons (MnO) + Fe \quad (1)$$
$$(MnO) + C \rightleftharpoons Mn + CO \quad (2)$$
$$(MnO) \rightleftharpoons Mn + \tfrac{1}{2}O_2. \quad (3)$$

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Turkdogan[7] used the results of Stukel and Cocubinsky[12] and the equilibrium expressed by equation (2) to calculate the activity of MnO, relative to pure liquid MnO, in SiO_2—Al_2O_3—CaO—MnO melts, but the results are in conflict with those of other investigators[8-9], who measured them, relative to pure solid, at 1650°C by exploiting equation (3).

Some investigations have aimed at the measurement of liquidus temperatures of some binary and ternary slags containing manganese (II) oxide[13-17], but no reference could be found to any determinations of the liquidus temperatures of slags that are of interest in this investigation.

LIQUIDUS TEMPERATURES

In the production of ferromanganese, the temperature of the process should be kept relatively low so that the manganese losses to the stack through volatilization are reduced and an undesirable amount of silica reduction from the slag is prevented. Because slags of relatively low liquidus temperature are required, the need for a knowledge of these temperatures is obvious if proper optimization of slag composition is to be achieved. Also, only slags of low liquidus temperatures (below 1500°C) can be used in determinations of the activity of MnO in slags at 1500°C.

Experimental Technique

The classical quench method described by Day *et al.*[18] was chosen for this investigation, rather than the hot-stage microscope or differential thermal analysis. The choice was influenced by the facts that manganese slags are fluorescent, volatile, and corrosive, and have low crystallization potentials.

A vertically wound molybdenum furnace was used for the quenching experiments, in which the power input was controlled by a continuously variable transformer. The temperature of the hottest zone of the furnace could be controlled to ± 2°C of the required temperature.

The slags used for these determinations had the same compositions as those used in the activity measurements, and the MnO concentrations were held at 13 per cent by mass.

Silica (reprecipitated), alumina (chromatographic grade), magnesia (chemically pure), and lime (analytical reagent) were all heated at 1100°C for two hours so that any moisture present would be driven off, and were then allowed to cool under a partial vacuum in a desiccator. Manganese (II) oxide was prepared by the method of Abraham *et al.*[8], i.e., by the reduction, in a stream of hydrogen at 1100°C, of manganese dioxide that was prepared from electrolytic manganese and concentrated nitric acid.

From the chemically pure oxide components, 3 g samples of homogeneous synthetic slags were made by the following method: the components were melted in a platinum crucible in a horizontally wound furnace and were then allowed to cool; the solidified melts were crushed and remelted twice if they formed a glass on cooling, and three times if crystalline material formed; during the melting process, a slow stream of gas (CO_2+H_2 premixed in the ratio of 5 to 1) was passed through the furnace tube. Previous investigators have shown that this atmosphere is sufficiently reducing to maintain the manganese component as MnO. An analysis of several slag samples for manganese showed that, because of the short time required for melting, the MnO concentration did not vary from the original concentration by more than 0,5 per cent.

A charge of about 100 mg of the crushed, premelted material was placed in a platinum tube that was closed at one end, had a diameter of 3 mm and a length of 8 mm, and was fabricated from 0,125 mm sheet. This tube was then sealed in a silica tube that had frequently been flushed with argon and evacuated. The silica tube was suspended by thin platinum wire in the vertical furnace next to a measuring thermocouple. It was held at the desired temperature long enough for it to attain a close approach to equilibrium and was then quenched in brine. The measuring thermocouple (Pt—6%Rh/Pt—30%Rh) was checked frequently against calibrated Pt/Pt—13%Rh and Pt/Pt—10%Rh thermocouples.

The time necessary for the attainment of equilibrium, which was determined by the method of Osborn *et al.*[19], was found to vary from 1 to 4 hours, depending on whether the slags were basic or acidic in nature.

Because all the slags examined formed glasses on being quenched, precipitated phases present in the slags could be detected by an examination of polished specimens under a microscope and by an analysis of the polarized light transmitted through fine grains of the material. Etching for 15 to 30 seconds with a 1 per cent hydrochloric acid solution frequently improved the aspect of the crystalline material in the polished specimens.

Results

The liquidus temperatures so determined are given in Table 1, which also shows the original composition and the liquidus temperatures of the slags that did not contain MnO.

The main effect of the addition of MnO to the slags generally is to lower the liquidus temperature. There are a few exceptions, especially in slags with an alumina content of 10 per cent. The concentration of the MnO left in final ferromanganese slags can therefore be expected to produce a general lowering of the liquidus surfaces of the SiO_2—Al_2O_3—MgO—CaO system in those slags.

ACTIVITIES OF MnO

Theoretical considerations indicate that the activity of the components is an important factor to be considered when slag compositions are optimized. This is especially so in the production of ferromanganese, where it has been shown that MnO in the slag is fairly close to equilibrium with respect to manganese in the alloy[12]. Therefore, the higher the activity coefficient of the MnO in the slag, the lower will be the resultant MnO concentration at equilibrium.

Experimental Method

Many methods are available for the determination of the activities of components in solution, but not all are suitable for the determination of the activity values of metal oxides in molten slags. The method used by Abraham *et al.*[8] was chosen because of its experimental simplicity and because the slag does not become contaminated by the crucible materials. In this method, strips of platinum foil are equilibrated with slag in a platinum crucible under a partial pressure of oxygen imposed by gas mixtures of hydrogen, carbon dioxide, and nitrogen. The activities of MnO can be calculated from the equation

$$a_{MnO} = \sqrt{P_{O_2}/P^1_{O_2}} \cdot a^1_{MnO}, \qquad (4)$$

Table 1

Composition and liquidus temperatures of slags having an MnO content of 13 per cent by mass

Slag no.	Slag composition in percentage mass without MnO				B.R.*	Liquidus temp. without MnO†	Liquidus temp. with 13% MnO‡
	Al_2O_3	SiO_2	CaO	MgO			
R1	30,00	36,60	33,40	0,00	0,91	1420	1370±10
R2	30,00	31,00	39,00	0,00	1,26	1505	1475±9
R3	30,00	26,30	43,70	0,00	1,66	1540	1505±5
R4	30,00	36,60	27,40	6,00	0,91	1410	1383±5
R5	30,00	31,00	31,99	7,01	1,26	1470	1340±12
R6	30,00	26,30	35,85	7,85	1,66	1500	1475±10
R7	30,00	22,75	38,78	8,47	2,08	1470	1443±7
R8	30,00	18,00	42,66	9,34	2,89	1480	1445±25
R9	30,00	36,60	22,10	11,30	0,91	1515	1486±14
R10	30,00	31,00	25,81	13,19	1,26	1560	>1520
R11	30,00	26,30	28,92	14,78	1,66	1575	>1550
S1	20,00	41,82	38,18	0,00	0,91	1290	1279±15
S2	20,00	35,43	44,57	0,00	1,26	1480	1440±13
S3	20,00	30,05	49,95	0,00	1,66	1530	1515±15
S4	20,00	41,82	31,32	6,86	0,91	1290	1275±20
S5	20,00	35,43	36,56	8,01	1,26	1410	1367±13
S6	20,00	30,05	40,98	8,97	1,66	1460	1390±10
S7	20,00	26,00	44,30	9,70	2,03	1480	1436±7
S8	20,00	41,82	25,27	12,91	0,91	1320	1354±10
S10	20,00	35,43	29,51	15,06	1,26	1480	1418±18
S11	20,00	30,05	33,05	16,90	1,66	1520	1465±11
S12	20,00	41,82	19,09	19,08	0,91	1420	1410±13
T1	10,00	47,07	42,93	0,00	0,91	1400	1282±13
T2	10,00	39,86	50,14	0,00	1,26	1450	1515±5
T3	10,00	33,81	56,19	0,00	1,66	1800	>1550
T4	10,00	47,07	35,22	7,71	0,91	1305	1270±15
T5	10,00	39,86	41,13	9,01	1,26	1370	1350±15
M4	10,00	35,00	45,12	9,88	1,57	1495	1420±20
T6	10,00	33,81	46,10	10,09	1,66	1560	>1550
T9	10,00	47,07	28,41	14,52	0,91	1350	1308±10
T10	10,00	39,86	33,18	16,96	1,26	1380	1410±10
T11	10,00	33,81	37,18	19,01	1,66	1520	1537±13
T12	10,00	47,07	21,46	21,46	0,91	1405	1432±13
T13	10,00	39,86	25,07	25,07	1,26	1460	1480±10

*B.R. = classical basicity ratio, viz, $\frac{CaO+MgO}{SiO_2}$ percentage mass.

†Taken from the results of Osborn *et al.*[19]

‡The ± value indicates the precision of the measurement.

where P_{O_2} is the partial pressure of oxygen prevailing at the time of the experiment, $P^1_{O_2}$ is the pressure of oxygen that would be in equilibrium with pure MnO and an alloy that contains the same amount of manganese as formed in the slag experiment, and a^1_{MnO} is the activity of the stoichiometric MnO in the non-stoichiometric oxide that would be in equilibrium with $P^1_{O_2}$. Values of $P^1_{O_2}$ and a^1_{MnO} have been measured by Abraham *et al.*[20] and Davies and Richardson[21] respectively.

Materials and Apparatus Used

The purity of the dry oxide components and their preparation are the same as described previously. The platinum strips were made from 0,05 mm foil (99,98 per cent pure), and the containers for holding the slag samples were cold-pressed from platinum sheet, 0,125 mm thick; they were cylindrical in shape and had a diameter of 10 mm and a depth of 3,5 mm. The containers were supported on trays of high-grade alumina cement, which had been moulded, dried at 1200°C, fashioned into the required shape, and finally fired at 1500°C. The mass of the trays was low (about 10 g) so that they could cool as rapidly as possible when removed from the hot zone of the furnace.

Mixtures of hydrogen, carbon dioxide, and nitrogen were produced either by individual metering of the purified commercial gases with capillary flowmeters containing n-dibutyl phthalate, or by the mixing of prebottled mixtures in the same manner. The nitrogen was first passed over copper turnings at 500°C so that as much oxygen as possible could be removed, and all the gases were dried by passage over anhydrous magnesium perchlorate. The oxygen potentials developed in the gas mixture at the hottest zone of the furnace were calculated by the application of available thermodynamic data on the species H_2, H_2O, CO, and CO_2.

A horizontal molybdenum-wound furnace fitted with a recrystallized-alumina reaction tube, 55 mm in diameter and 1000 mm long, was constructed for this investigation. The molybdenum windings of the furnace were supported on a separate alumina tube, within which the reaction tube was held. The whole arrangement is shown in Figure 1. During the course of the equilibrium runs, spectrographically pure argon, instead of the normal ammonia, was passed over the furnace windings so that diffusion of hydrogen from the protective atmosphere into the reaction tube would be prevented.

Power was supplied through a continuously variable transformer and was controlled with a CAPA P.I.D. controller in conjunction with a 12 kVA thyristor.

Temperatures were measured with a Pt—6%Rh/Pt—30%Rh thermocouple contained within a recrystallized alumina sheath and held 5 mm above the sample. The temperature was checked at regular intervals with a calibrated Pt/Pt—10%Rh thermocouple.

Procedure

The procedure is essentially the same as that used by Abraham *et al.*[8].

The platinum—manganese alloy was dissolved in aqua regia and diluted to a known volume. Suitable aliquot volumes were taken, and the manganese concentration was determined on a Techtron atomic-absorption spectrophotometer, model AA4 or AA5.

The slag was digested in hydrofluoric and perchloric acids in a Teflon beaker and heated just to dryness. The residue was dissolved in hydrochloric and nitric acids, and the solution was diluted to a known volume. Suitable aliquot volumes were taken, and the manganese was determined on the Techtron atomic-absorption spectrophotometer.

Results

A number of preliminary experiments were done as a check of whether possible sources of systematic error were causing significant inaccuracies.

The extent to which the MnO or other components volatilized was determined on two separate samples of a typical SiO_2—Al_2O_3—MgO—CaO slag without MnO. The samples were heated at 1500°C in a gas mixture of the same proportions as those used in the experiments, giving an oxygen partial pressure of 5×10^{-2} N/m^2 at the temperature involved. After 4, 8, and 12 hours, the samples were removed from the furnace and their mass was measured. The net average loss in mass was found to be 0,16 per cent, 0,20 per cent, and 0,26 per cent respectively. From this loss it was inferred that the losses of SiO_2 and MgO from the melt at this temperature and oxygen pressure were insignificant.

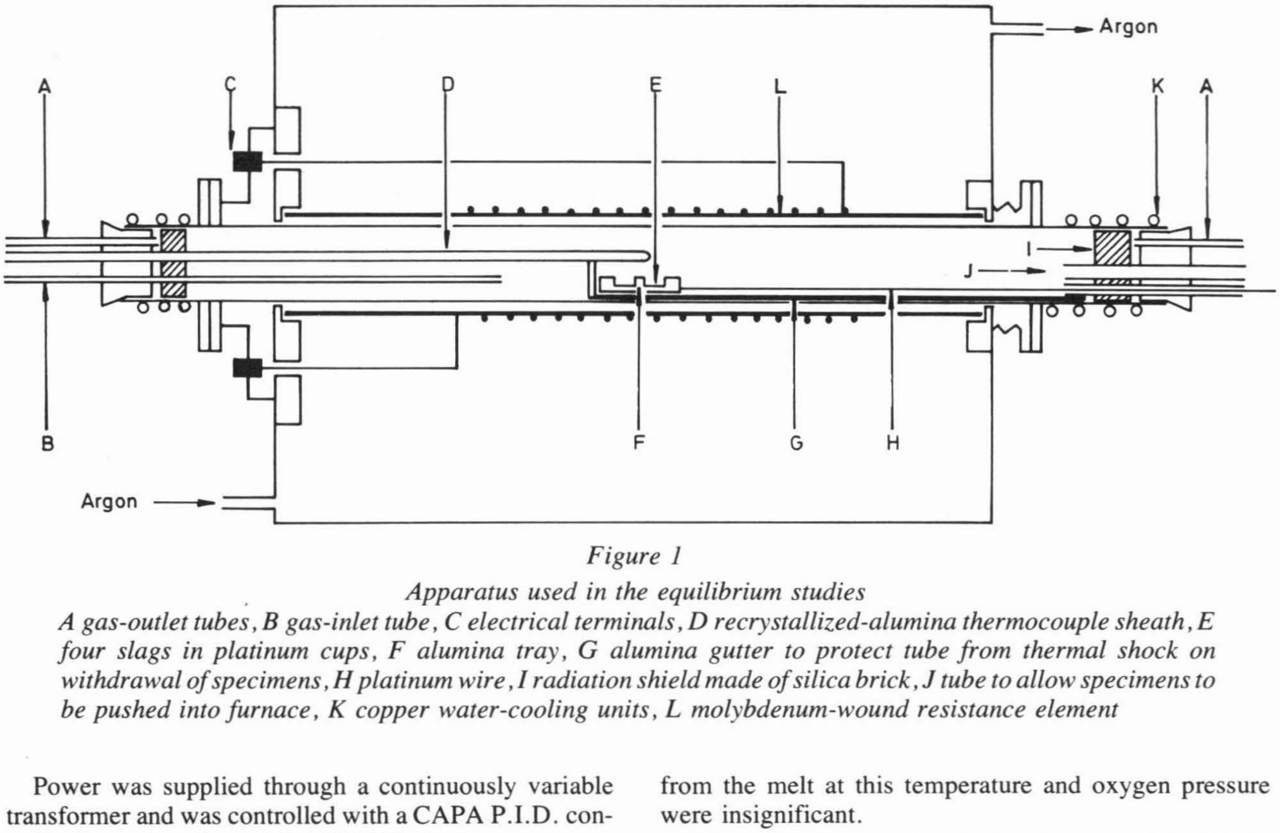

Figure 1

Apparatus used in the equilibrium studies

A gas-outlet tubes, B gas-inlet tube, C electrical terminals, D recrystallized-alumina thermocouple sheath, E four slags in platinum cups, F alumina tray, G alumina gutter to protect tube from thermal shock on withdrawal of specimens, H platinum wire, I radiation shield made of silica brick, J tube to allow specimens to be pushed into furnace, K copper water-cooling units, L molybdenum-wound resistance element

With a similar typical melt, this time containing MnO, activity equilibrium experiments were carried out for 4, 8, and 10 hours. The results showed that the equilibrium had not been reached after 4 hours, but, since the activities determined at 8 and 10 hours were the same, it was assumed that the equilibrium was reached in 8 hours. A period of 8 to 9 hours was therefore taken as a safe standard period for each experiment.

Experiments on slags of the same composition as before were done with total gas flowrates of 100, 400, and 600 ml/min. The results at flowrates of 100 ml/min gave activity values that were far too high, whereas the activity values at the other two flowrates were essentially the same. The high values that resulted from the lower flowrates were probably due to the thermal diffusion of hydrogen molecules to the hot zone of the furnace. Since gaseous reactions are extremely rapid at the high temperatures involved, gaseous equilibrium is almost certain to be attained at the flowrates used in the experiment, viz, 600 ml/min at room temperature.

The results of the activity experiments are presented in Figures 2a to 2k, where the activity of MnO is plotted against the concentration of MnO for various basicity ratios

$$\frac{\text{CaO(mass\%)}+\text{MgO(mass\%)}}{\text{SiO}_2\text{(mass \%)}}.$$

For each graph, the concentration of Al_2O_3 and the ratio of CaO to MgO were kept constant.

From these graphs, the activity coefficient of MnO at a concentration of 13 per cent by mass can be evaluated, and the values so obtained can be plotted as contours of iso-activity coefficient in the pseudoquaternary system SiO_2—Al_2O_3—CaO—MgO. Such plots are shown in Figures 3a, 3b, and 3c for Al_2O_3 contents of 10, 20, and 30 per cent respectively.

Discussion

Random errors (fluctuations of temperature, variations in gas composition, and errors in the analyses of Mn in the alloy and MnO in the slag) amount to about 10 per cent, and the scatter about the curves through the points in Figures 2a to 2k is consistent with this value. Systematic error arises mainly from errors in the results obtained from experiments in which solid MnO is equilibrated with platinum foil under atmospheres of controlled oxygen potential. In this paper the calculation of a_{MnO} in the slag is based on the values of equilibrium concentrations of manganese in platinum determined by Abraham *et al.*[20]. If the values of Smith and Davies[22] had been used, then the calculated values of a_{MnO} in the slags would have been lower by up to 30 per cent. At present, the reasons for the discrepancies between the results of these two investigations are not known. However, irrespective of whether the values of a a_{MnO} in the slags are calculated using the data of Abraham *et al.*[20] or Smith and Davies[22], the selection of slag compositions for smelting operations, based on the relative values of a_{MnO} in the slags, is not affected significantly.

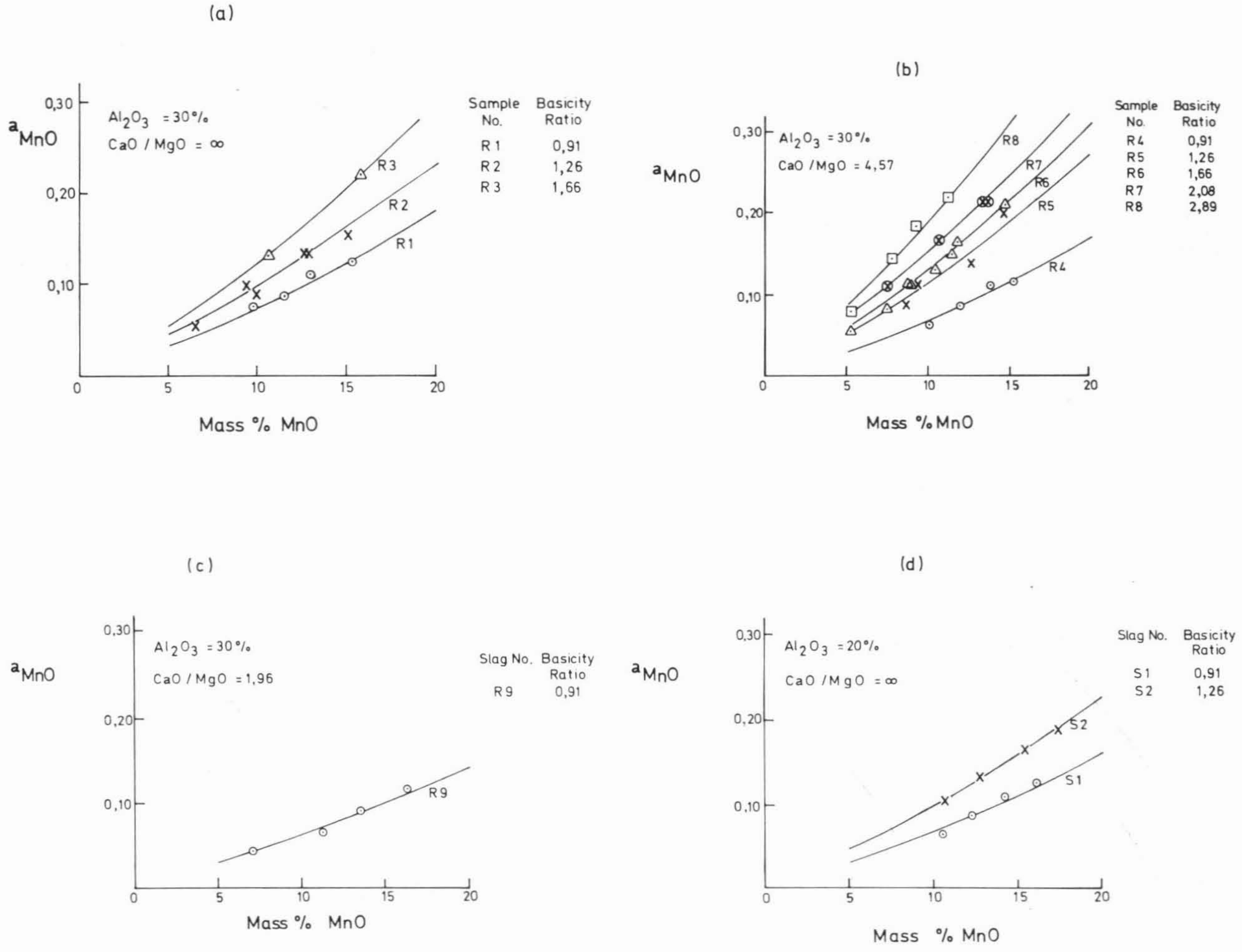

Figure 2

Activities of MnO, relative to solid, in SiO_2—Al_2O_3—MgO—CaO—MnO slags for various basicity ratios at selected Al_2O_3 contents and CaO-to-MgO ratios

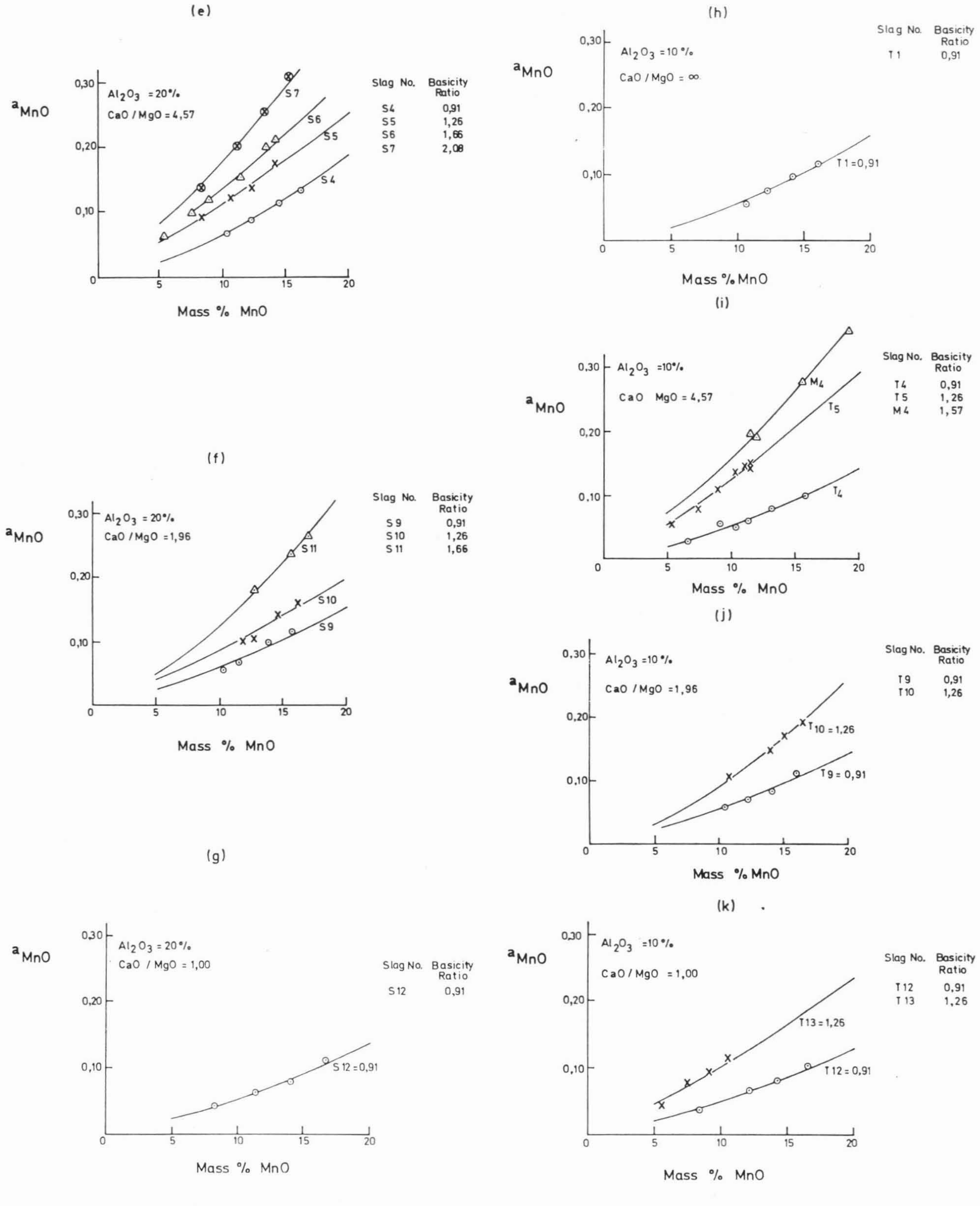

Figure 2 (cont.)

Activities of MnO, relative to solid, in SiO_2—Al_2O_3—MgO—CaO—MnO slags for various basicity ratios at selected Al_2O_3 contents and CaO-to-MgO ratios

The graphs of a_{MnO} plotted against percentage MnO, which are presented in Figures 2a to 2k, show that the concentration of MnO does affect the MnO activity coefficient. In the range of MnO concentrations used in this investigation, the activity coefficient of MnO increases as the concentration increases.

An examination of the contours of MnO iso-activity coefficients at a concentration of 13 per cent in Figures 3a, 3b, and 3c reveals the following features:

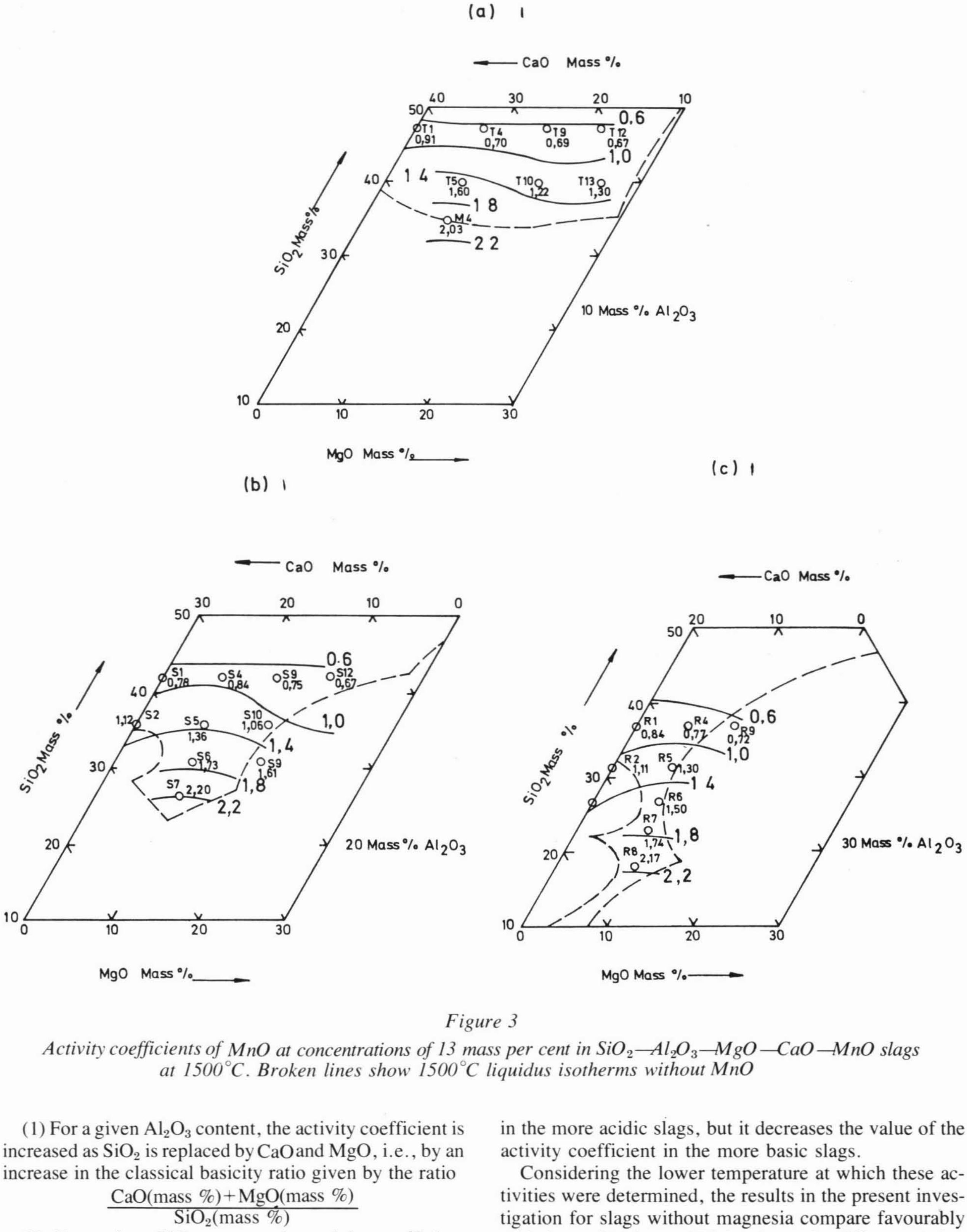

Figure 3

Activity coefficients of MnO 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

(1) For a given Al_2O_3 content, the activity coefficient is increased as SiO_2 is replaced by CaO and MgO, i.e., by an increase in the classical basicity ratio given by the ratio

$$\frac{\text{CaO(mass \%)}+\text{MgO(mass \%)}}{\text{SiO}_2\text{(mass \%)}}$$

(2) For a given SiO_2 content, the activity coefficient increases as Al_2O_3 is replaced by CaO and MgO. Here, also, the overall basicity ratio increases.

(3) For given Al_2O_3 and SiO_2 contents, the activity coefficient decreases as MgO replaces CaO on a mass-per-cent basis at high SiO_2 levels. In the more basic slags, the activity coefficient increases initially until the value of the ratio of percentage CaO to percentage MgO (both by mass) reaches about 4. This increase is evident even on a molar basis.

(4) For a given basicity, an increase in the Al_2O_3 content appears to have little effect on the activity coefficient in the more acidic slags, but it decreases the value of the activity coefficient in the more basic slags.

Considering the lower temperature at which these activities were determined, the results in the present investigation for slags without magnesia compare favourably with those of Mehta and Richardson[9], the difference being nowhere greater than 20 per cent. The chief difference lies in the finding of these authors that an MnO concentration of up to 8 per cent does not affect the activity coefficient of the MnO at 1650°C, a finding that was not substantiated by the present investigation. The results of Turkdogan[7] show greater differences, but, as has been pointed out[8], these results are not consistent with slag—metal relations in ferromanganese practice.

In the ternaries of MnO with MgO+SiO_2 and CaO+SiO_2, Mehta and Richardson[9] were able to show that CaO has a greater influence on a molar basis in degree the electrical resistivity of the slag contributes to the furnace operating resistance, although it can logically be argued that it must exert some significant influence. It is reasonable to assume, if one applies the concepts proposed by Westly, which are based on very considerable plant-operating data and experience, that it should be possible to accommodate changes in the electrical resistivity of the slag and the possible concomitant changes in the furnace operating resistance without adversely changing the heat distribution, the power input to the furnace, and the specific power consumption.

Dr D.D. Slatter :*

(a) Would Dr Jochens please comment upon whether it might not have been useful to extrapolate the activity coefficients of MnO with MnO comprising 5 and 20 per cent by mass of the slags, rather than, or in addition to, those extrapolated with MnO as 13 per cent of the slag. This would have covered the range in discard-slag composition as given by Dr Jochens in the paper.

(b) It is suggested that the change in the activity of MnO as MgO replaces CaO in the slag might be found to correlate with the relative ionic sizes of the Ca, Mg, and Mn divalent cations substituting in the silicate lattice.

Dr Jochens:

(a) The values of activity of MnO were measured for slags with MnO contents varying between 5 and 20 per cent. The values of activity coefficients of MnO were calculated from these results, arbitrarily for 13 per cent by mass in this instance, and presented as contours of iso-activity coefficients on pseudoternary sections. Obviously, the activity coefficients of MnO can be calculated for any concentration of MnO over the range of MnO concentrations investigated (5 to 20 per cent). It is not possible, however, to plot the iso-activity coefficients of MnO at more than one concentration of MnO on the same pseudoternary section. Hence, to present iso-activity-coefficient contours at other concentrations of MnO would have required the presentation of a further three pseudoternary sections for each concentration of MnO.

(b) The concept of interpreting the effects of various oxides on the thermodynamic and physicochemical properties of slags on the basis of relative ionic sizes (or cationic field strengths) is possible and useful in relatively simple systems. However, in multicomponent systems, when more than one modifying oxide is present, these concepts fail to give a satisfactory explanation of the enhanced effect of the several modifying oxides present on the activity coefficients of MnO. We have therefore attempted to rationalize the finding that the replacement of some of the CaO by MgO increases the activity coefficient of MnO, by examining the free energies of formation of the respective orthosilicates.

Mr W. A. Gericke† :

Has the activity of Cr_2O_3 in slags been determined? If not, are there any reasons for this?

Dr Jochens:

In the ferromanganese process, the motivation for measuring the activity of MnO in the slags is based on the knowledge that the final stage of the smelting process consists of reduction of MnO from the incipiently fused material or slag, which initially is very rich in MnO (above 50 per cent by mass) by solid carbon. However, when the smelting process for ferrochromium is examined, the picture is rather different. It appears that a considerable degree of reduction occurs in the solid state, and the fused non-metallic phase, which is formed with increasing temperature, contains very little FeO or Cr_2O_3. In fact, throughout the reaction, the slags contain relatively small proportions of the oxides of iron or chromium. This can be interpreted as indicating that reduction of the oxides primarily does not occur via the slag phase. Detailed examination of slags produced in South Africa indicates that the relatively high losses of chromium oxide to the slag are not associated with a high dissolved content of these oxides in the slag. The major proportion of the iron and chromium oxides in the slag are present as small, unreduced or partially reduced particles of ore that have undergone various degrees of fusion. Therefore, logically it is not the activity of the oxide in the slag that is most important. In fact, it is the entrainment of small unreacted or partially reacted particles of ore in the slag at a relatively early stage of the smelting process that inhibits their subsequent reduction with solid carbon.

Mr S. Selmer-Olsen‡:

The authors have used the rather slow method of the absorption of manganese into platinum for their activity measurements. This is a rather slow way of working. Has new equipment been developed for the rapid determination of slag activity?

Dr Jochens:

Solid-state electrolytes, especially lime-stabilized zirconium dioxide, which permit oxygen-ion conduction with negligible electronic conductivity, have been used in the laboratory for several years for measurement down to 10 p.p.m. of oxygen in unalloyed iron, which corresponds to an oxygen partial pressure of 3×10^{-13} atm. Provided that the electrolyte is capable of resisting attack from slag, this principle can be used, and is used, to determine the activities of metal oxides in slags. In fact, we attempted to use this technique in this investigation, but, owing to our very limited experience in this field at that stage, we preferred to adopt the technique described in this paper.

Recently, several industrial companies (e.g., United States Steel Corporation) conducted plant experiments to demonstrate both that oxygen sensors, based on solid-state electrolytes constructed on a principle similar to the quick-immersion thermocouple, can be used for the routine measurement of the oxygen content of steel, and that the results obtained permit the controlled deoxidation of steel.

To date, little information has been published on the use of these oxygen sensors in a slag medium on a plant scale for the evaluation of the activity of metal oxides. In principle, it should be possible, since the total time required to obtain an equilibrium reading is only a few seconds and the electrolyte should withstand the slag attack for this period of time.

However, with controlled feed to the furnace and the selection of an optimum slag composition, it should be possible to operate with a slag of consistently low MnO content. Measurement of the activity of MnO in the slag, after tapping, is too late for corrective action for that particular alloy and slag, and sufficient time is available to analyse the slag chemically and to change the feed ratios,

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if required, because of the slow response of the system.

Mr W.H. Magruder :*

To verify Dr Jochens's observations, I should like to cite our experience at our Portland (Oregon) Works (later verified by similar operations at our Ashtabula (Ohio) Works). In these cases, energy requirements for the production of ferromanganese from 100 per cent Amapa ore blends (which give self-fluxing slags at about 37 per cent Mn and are relatively high in Al_2O_3) have regularly given furnace power efficiencies approximately 5 per cent superior to other similar performance from mixed ore blends with higher SiO_2 and lower Al_2O_3 contents.

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