

# Factors affecting the resistivity and reactivity of carbonaceous reducing agents for the electric-smelting industry

by H. M. DIJS\*, B.Sc. (Chem. Eng.) and  
D. J. SMITH†, B.Sc. (Chem. Eng.), M.I. Chem. E., S.A.I. Chem. E.

## SYNOPSIS

Resistivity tests indicated that, at temperatures lower than 1450°C, reducing agents alone, as well as burdens consisting of high-carbon ferrochromium and reducing agents, exhibit wide differences in resistivity. These differences are less pronounced at elevated temperatures. The resistivity of a reducing agent and the volume fraction it occupies are important factors controlling the resistivity of burdens of high-carbon ferrochromium.

A mathematical model is formulated to describe the dependence of the resistivity of mixtures of conducting and insulating particles on the particle sizes and the volume fraction occupied by the conducting phase. The resistivity of burdens of high-carbon ferrochromium is high if the particle size of the reducing agent is larger than that of the other components of the burden.

A number of reducing agents showed small variations in their reactivity towards chromite ore in the solid state. However, with chromite ore in the liquid state, reduction proceeded more rapidly with reducing agents occupying larger volume fractions.

During the smelting of manganese ore, high initial rates of reduction were observed for reducing agents that had a high reactivity towards carbon dioxide and a high content of volatile matter, and that occupied a large volume fraction. High liquid-state reactivities were observed for reducing agents occupying a large volume fraction and having a low degree of graphitization.

## SAMEVATTING

Resistiwiteitstoetse het getoon dat reduseermiddels alleen, asook ladings bestaande uit hoëkoolstofferchroom en reduseermiddels by laer temperature as 1450°C groot verskille in resistiwiteit toon. Hierdie verskille is nie by hoë temperature so duidelik nie. Die resistiwiteit van 'n reduseermiddel en die volumefraksie wat dit beslaan is belangrike faktore wat die resistiwiteit van ladings van hoëkoolstofferchroom bepaal.

Daar word 'n wiskundige model geformuleer om die afhanklikheid van die resistiwiteit van mengsels van geleidende en isolerende partikels van die partikelgroottes en die volumefraksie wat die geleidende fase in beslag neem, te beskryf. Die resistiwiteit van ladings van hoëkoolstofferchroom is hoog as die partikelgrootte van die reduseermiddel groter as dié van die ander bestanddele van die lading is.

'n Aantal reduseermiddels het klein variasies in hul reaktiwiteit teenoor chromieterts in die vaste toestand getoon. Met chromieterts in die vloeibare toestand het die reduksie egter vinniger plaasgevind met reduseermiddels wat groter volumefraksies beslaan.

Gedurende die uitsmelt van mangaan erts is daar hoë aanvanklike reduksietempo's waargeneem vir reduseermiddels wat 'n hoë reaktiwiteit teenoor koolstofdioksied en 'n hoë inhoud aan vlugtige stowwe het en wat 'n groot volumefraksie beslaan. Daar is hoë reaktiwiteit vir die vloeibare toestand waargeneem vir reduseermiddels wat 'n groot volumefraksie beslaan en 'n lae graad van grafitiesing het.

## INTRODUCTION

The ferro-alloy industry in South Africa has expanded very rapidly over the past thirty years, and this country is now a major supplier of ferro-alloys on the world market. In 1976, a committee, known as the Char Committee<sup>1</sup>, was convened to examine the supply of carbonaceous reducing agents to the electric-smelting industry.

The Committee concluded that there was likely to be a significant shortage in the supply of some reducing agents in the future, and that the bulk of this shortage would have to be made up by char. As part of the Committee's suggested programme to identify suitable chars for the ferro-alloy industry, the National Institute for Metallurgy (NIM) undertook to determine the electrical resistivity and metallurgical reactivity of various types of reducing agents and to assess their suitability for the electric-smelting industry<sup>2</sup>.

The reducing agents considered included standard reducing agents (such as cokes and chars) and non-

commercial chars produced from a number of coals by the Fuel Research Institute (F.R.I.). These coals were charred by the F.R.I. under oxidizing and reducing conditions at temperatures ranging from 600°C to 1200°C. Table I summarizes the properties of these reducing agents.

## MEASUREMENT OF ELECTRICAL RESISTIVITY

The resistance measurements comprised the following:

- (1) determination of the resistivity of the reducing agents at room temperature and during heating to 1550°C,
- (2) determination of the resistivity during heating to 1500°C of typical burdens used in the production of standard ferrochromium containing various types of reducing agents, and
- (3) a study of the effect of the particle size of the reducing agent and other components of the burden on the resistivity of burdens of high-carbon ferrochromium.

## Resistivity at Room Temperature

The resistance of a bed of dried reducing agent was measured at room temperature with the equipment shown in Fig. 1.

\*Formerly of the National Institute for Metallurgy; now at Onderwei 43, 1273 TB, Huizen, Holland.

†National Institute for Metallurgy, Private Bag X3015, Randburg 2125, South Africa. © 1980.

The cell constant of the system was measured by the use of sodium chloride solutions of known resistivity so that the resistance values for the reducing agents could be expressed as resistivity values.

The resistivities at room temperature of two of the chars produced by the F.R.I. are shown in Table II. The other F.R.I. chars exhibited the same trends. The following conclusions can be drawn.

(1) The resistivity of a char produced under reducing conditions is usually higher than that of a char produced from the same coal and at the same temperature under oxidizing conditions.

(2) An increase in the temperature of charring results in a significant decrease in resistivity and an increase in the fixed carbon.

### Resistivity at Elevated Temperatures

Fig. 2 shows the apparatus used to obtain the resistance measurements at elevated temperatures. The particle size of the reducing agent (a mean particle size

TABLE I

ANALYSIS OF REDUCING AGENTS (IN MASS PERCENTAGE ON DRY BASIS)

Reducing agent	Fixed carbon	Volatile material	Ash
Rand Carbide char	79,8	4,5	15,7
Iscor coke	83,6	1,1	15,3
Vryheid coke	79,8	1,3	18,9
Anthracite	80,5	9,9	9,6
Electrode graphite	99,1	0,9	0,0
Springbok no. 5 char	79,0	4,3	16,8
Delmas no. 2 char	76,1	5,0	19,0
Delmas no. 4 char	73,1	5,3	21,6
Matla no. 5 char	80,9	4,0	15,5
Utrecht char	82,4	3,9	13,7
Umgala char	82,1	4,4	13,6
Blesbok no. 5 char	81,2	4,1	14,8

TABLE II

RESISTIVITY OF REDUCING AGENTS AT ROOM TEMPERATURE

Reducing agent	Charring temperature °C	Atmosphere	Resistivity $\Omega \cdot \text{cm}$
Umgala	600	Reducing	$20,8 \times 10^3$
Umgala	600	Oxidizing	$0,80 \times 10^3$
Umgala	800	Reducing	27,2
Umgala	800	Oxidizing	8,8
Umgala	1000	Reducing	2,3
Umgala	1000	Oxidizing	2,3
Delmas no. 4	600	Reducing	$20,8 \times 10^3$
Delmas no. 4	600	Oxidizing	$2,39 \times 10^3$
Delmas no. 4	800	Reducing	22,1
Delmas no. 4	800	Oxidizing	14,7
Delmas no. 4	1000	Reducing	3,6
Delmas no. 4	1000	Oxidizing	3,3

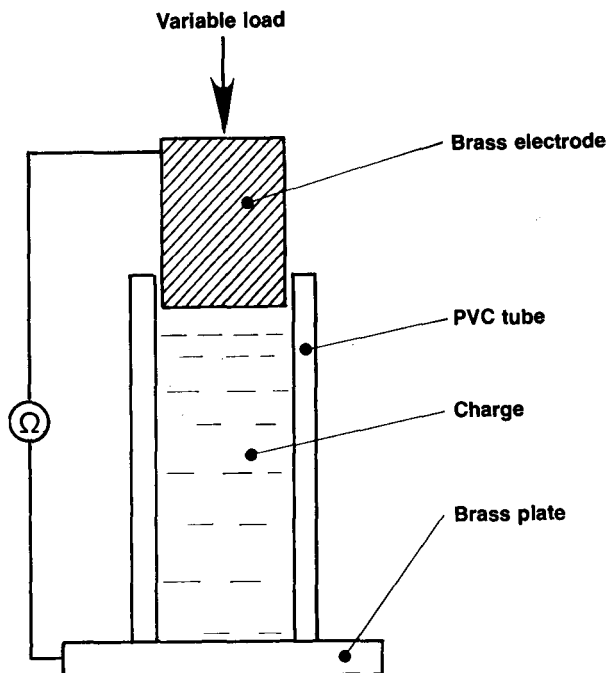


Fig. 1—Apparatus for resistance measurements at room temperature

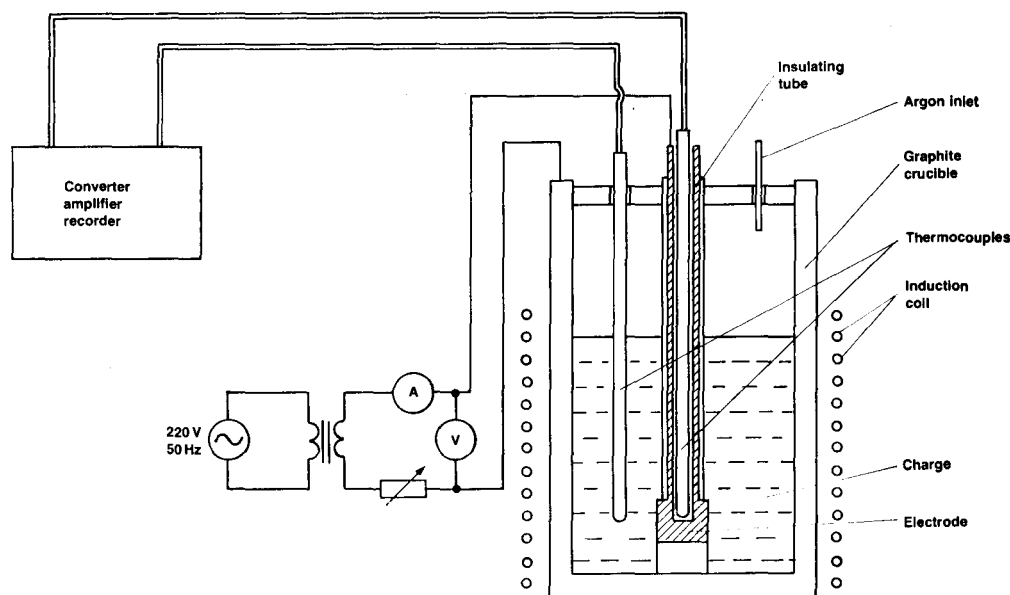


Fig. 2—Apparatus for resistance measurements at elevated temperatures

of 3,6 mm) corresponds to one-quarter of that used in industry for the production of ferrochromium. The cell constant of the system was measured with sodium chloride solution.

The results of the resistance measurements on standard reducing agents during heating to a temperature of 1550°C are shown in Fig. 3. At temperatures lower than approximately 1100°C, the ranking of the resistivities followed the ranking of the ash contents of the reducing agents. At higher temperatures, the differences in resistivity became much less pronounced, and it was observed that the ranking of the reducing agents in terms of resistivity was not the same as that at lower temperatures. For the coals charred under different oxidizing and reducing conditions, it was observed that the resistivity became independent of the charring conditions at temperatures higher than 1100°C.

### Resistivity of Burdens Containing Reducing Agents

Resistivity measurements were conducted with the apparatus shown in Fig. 2 on charges consisting of a reducing agent, Steelpoort chromite ore, dolomite, and quartzite. The amount of carbon added was 115 per cent of the stoichiometric amount, and the compositions were calculated to give the same theoretical slag composition for each test.

The results of the resistance measurements during heating to 1500°C are given in Fig. 4. At temperatures lower than 1400°C, fairly wide differences can exist in the resistivities of burdens of high-carbon ferrochromium. However, the shapes of the curves for resistivity versus temperature were similar for most of the reducing agents considered, including the various coals that were charred. The resistivity peaks observed at temperatures between 900°C and 1100°C could possibly have been caused by thermal contraction of the particles of the reducing agent<sup>3</sup>.

The resistivities of charges containing standard reducing agents other than graphite increased in the order Iscor coke < Rand Carbide char < anthracite, which is the same order as that established for these reducing

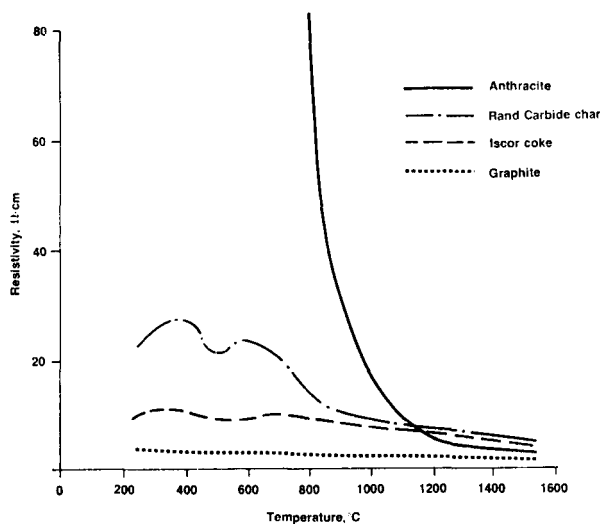


Fig. 3—Resistivity of standard reducing agents during heating to 1150°C

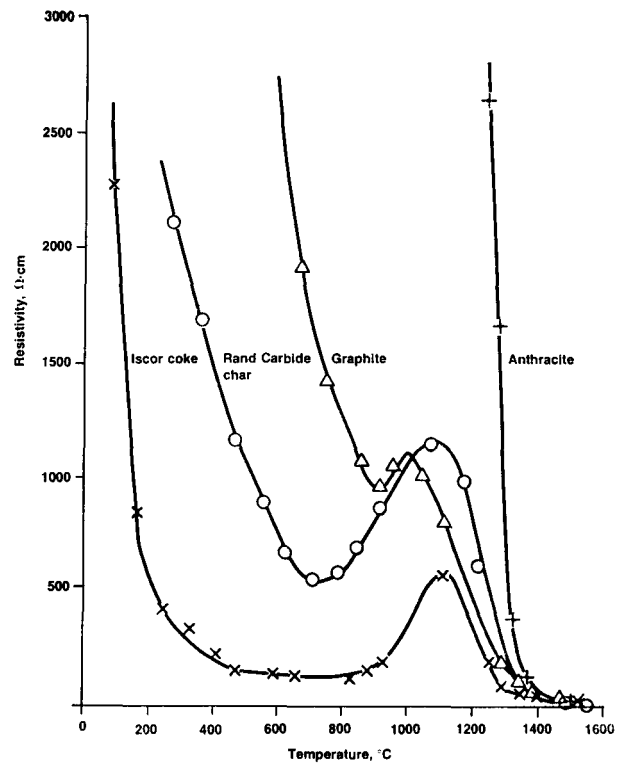


Fig. 4—Resistivity, during heating to 1500°C, of burdens of high-carbon ferrochromium containing standard reducing agents

agents in the absence of ore and fluxes. The fact that graphite occupied the lowest volume fraction of all the standard reducing agents could account for the higher resistivity of high-carbon ferrochromium containing this reducing agent as compared with the resistivity of graphite alone.

The resistance measurements on charges containing chars from the F.R.I. showed the same trends as those observed in the absence of ore fluxes: that is, chars produced in a reducing atmosphere and at low temperatures gave higher resistivities than those produced from the same coal in an oxidizing atmosphere and at higher temperatures. Burdens containing chars that occupied a low volume fraction had resistivities higher than those of burdens containing chars that occupied a higher volume fraction.

### Effect of Particle Size

The effect of the particle size of the reducing agent and of other components of the burden on the resistivity of typical burdens used in the electric-smelting industry has been the subject of a number of investigations<sup>3-7</sup>. However, some of the reported results appear to be contradictory. So that this matter could be resolved, a detailed examination was made of the effect of particle size on the resistivity of burdens of high-carbon ferrochromium.

### Theoretical Considerations

A burden of high-carbon ferrochromium can be regarded as a two-phase system of conducting particles (reducing agent) in an insulating matrix (ore and fluxes). The electrical conduction in such mixtures

occurs by means of continuous arrays of conducting particles randomly distributed throughout the insulating matrix.

The resistivity of the mixture ( $\rho_m$ ) can be expressed as follows<sup>2</sup>:

$$\rho_m = \frac{R_c L_c}{A_{pc} \{N_c (\alpha - 1)\}^{m-1}}, \text{ for } N_c < \frac{1}{\alpha - 1},$$

and

$$\rho_m = 1,0, \text{ for } N_c \geq \frac{1}{\alpha - 1}, \quad (1)$$

where  $R_c$  is the resistance of a continuous array of conducting particles per input length of the array,

$L_c$  is the length of a continuous array of conducting particles per unit length of the mixture,

$A_{pc}$  is the number of conducting particles per unit area of the mixture,

$N$  is the number fraction of conducting particles in the mixture,

$\alpha$  is the co-ordination number of a conducting particle, and

$m$  is the number of conducting particles in a continuous array.

#### Experimental Procedure

The experiments were aimed at a determination of the quantities contained in equation (1) as a function of the particle sizes of the reducing agent and other components of the burden, and as a function of the volume fraction occupied by the reducing agent. The resistance measurements were made at room temperature, Rand Carbide char being used as the reducing agent.

#### Results

The resistance of a continuous array of conducting particles per unit length of the array was determined for various particle sizes of Rand Carbide char in the absence of silica. Least squares fitting of the results gave

$$R_c = \frac{1}{d_c^2} \left( 0,89 + \frac{0,97}{d_c} \right) \Omega \cdot \text{cm}, \quad (2)$$

TABLE III

COMPARISON BETWEEN THE MEASURED AND FITTED RESISTIVITY VALUES OF MIXTURES OF CONDUCTING AND INSULATING PARTICLES  
Conducting phase: Rand Carbide char  
Insulating phase: Silica

$d_c$	$d_i$	$V_c$	Fitted	Measured
0,405	0,810	0,1	$> 2 \times 10^6$	$> 2 \times 10^6$
		0,3	$5,46 \times 10^3$	137,4
		0,5	22,5	20,0
		0,7	8,9	8,3
		0,9	5,8	5,5
		1,0	4,7	4,6
0,205	0,810	0,1	$1,24 \times 10^4$	$> 2 \times 10^6$
		0,3	152	1089
		0,5	42,4	59,8
		0,7	13,6	15,0
		0,9	9,5	10,6
		1,0	8,1	7,8

where  $d_c$  is the mean particle size of the conducting phase (char) in centimetres.

The number of conducting particles per unit of the mixture  $A_{pc}$  was determined from a count of the number of char particles on any cross-section of the char-silica mixtures after the mixtures had been set in epoxy resin.

The dependence of  $A_{pc}$  on the particle size and volume fraction of the conducting phases is given by

$$A_{pc} = \frac{0,695 V_c}{d_c^2}, \quad (3)$$

where  $V_c$  is the volume fraction occupied by the conducting phase.

The remaining parameters were derived on the assumption that the particles in the mixture were spherical:

$$N_c = \frac{1}{d_c \left( \frac{d_c}{d_i} \right)^3 \left( \frac{1 - V_c}{V_c} \right)}, \quad (4)$$

and

$$m = \frac{L_c L_s}{d_c}, \quad (5)$$

where  $d_i$  is the mean particle size of the insulating phase in centimetres, and  $L_s$  is the sample length in centimetres.

Least squares fitting of the values obtained for  $L_c$  gave the following expression:

$$L_c = \exp \{ \beta (1 - V_c) \}, \quad (6)$$

where  $\beta$  is given by

$$\beta = 4,40 - 1,18d_c - 4,18d_i. \quad (7)$$

A comparison of the measured resistivity values with the values obtained theoretically indicates that the model represents the data for measured resistivity for  $V_c$  values of 0,4 or greater (see Table III).

#### Discussion

Electrical conduction in carbonaceous materials has been the subject of several investigations<sup>8-14</sup>, which showed that the electrical resistivity of such materials is influenced by the following factors.

- (i) The resistivity of a reducing agent decreases with an increase in its carbon content.
- (ii) The volatile matter, consisting of compounds of low molecular mass and high resistivity, can be regarded as being in a mixture of macromolecular material with low resistivity. An increase of volatile matter in the reducing agent therefore increases the resistivity of the reducing agent.
- (iii) The resistivity of coal increases with an increase in its ash content. This effect is not pronounced unless the ash content is more than 20 per cent.
- (iv) Other factors affecting the electrical resistivity of carbonaceous materials are moisture content, particle size, microstructure, presence of micro-

scopic cracks, ash distribution, and geometrical arrangement and spacing of the graphitic crystallites in the material.

The effects of charring conditions on resistivity can be explained in terms of the effects of these conditions on the fixed carbon and volatile matter contained in the char. An oxidizing atmosphere and high charring temperatures result in the presence of less volatile matter (and therefore more fixed carbon), which explains the lower resistivities of the chars produced under these conditions.

In electric-smelting operations, it is considered desirable for the solid burden to have high resistivity. Such burdens require a reducing agent that has high resistivity and occupies a small volume fraction in the burden. Reducing agents with high resistivity are those that have been carbonized at low temperatures under reducing conditions. For the volume fraction occupied by the reducing agent to be small, the reducing agent should be dense and should have a high content of fixed carbon.

Figs. 5 to 7 show the effect of the particle sizes of the components of the burden, and of the volume fraction occupied by the reducing agent, on the resistivity of burdens of high-carbon ferrochromium as predicted by the mathematical model presented earlier.

Fig. 5 shows that, for a volume fraction of 0,5, the effect of the particle size of the reducing agent was most pronounced when the size of the insulating phase was small, and that, for any given particle size of the insulating phase, the resistivity of the mixture passed through a minimum as the particle size of the reducing agent increased. These minima arose because an increase in particle size of the reducing agent tends to decrease

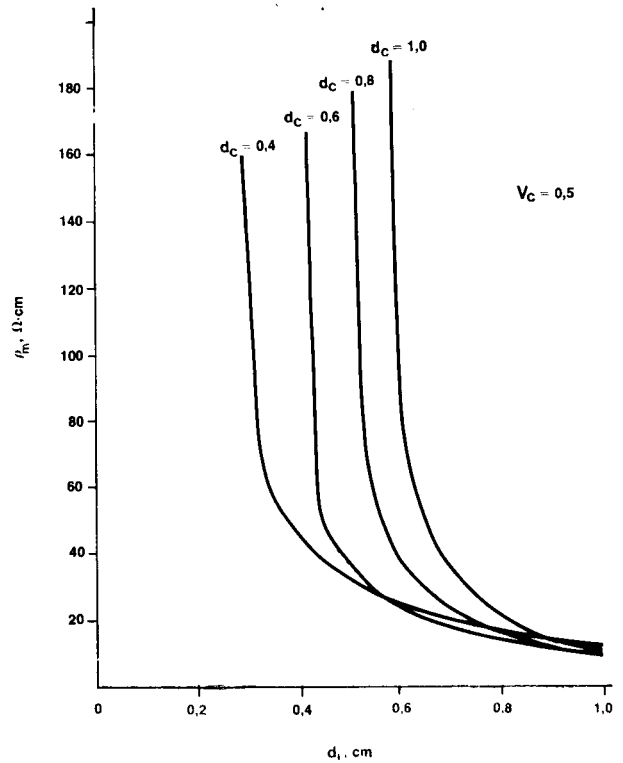


Fig. 6—Predicted effect of the particle size of ore and fluxes on the resistivity of burdens of high-carbon ferrochromium

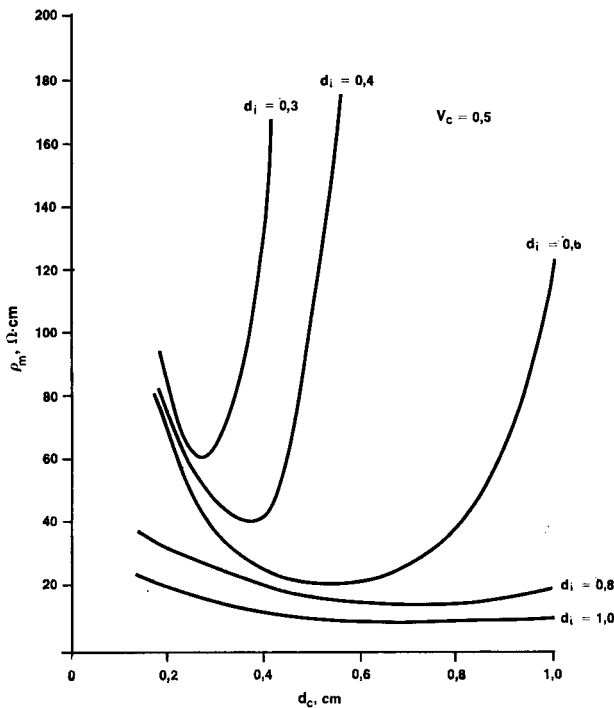


Fig. 5—Predicted effect of the particle size of the reducing agent on the resistivity of burdens of high-carbon ferrochromium

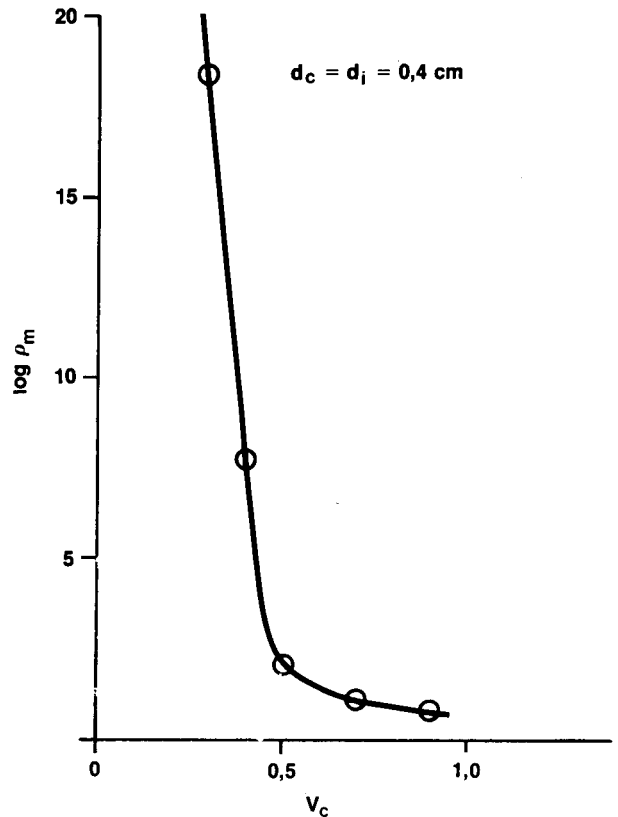


Fig. 7—Predicted effect of the volume fraction occupied by the reducing agent on the resistivity of burdens of high-carbon ferrochromium

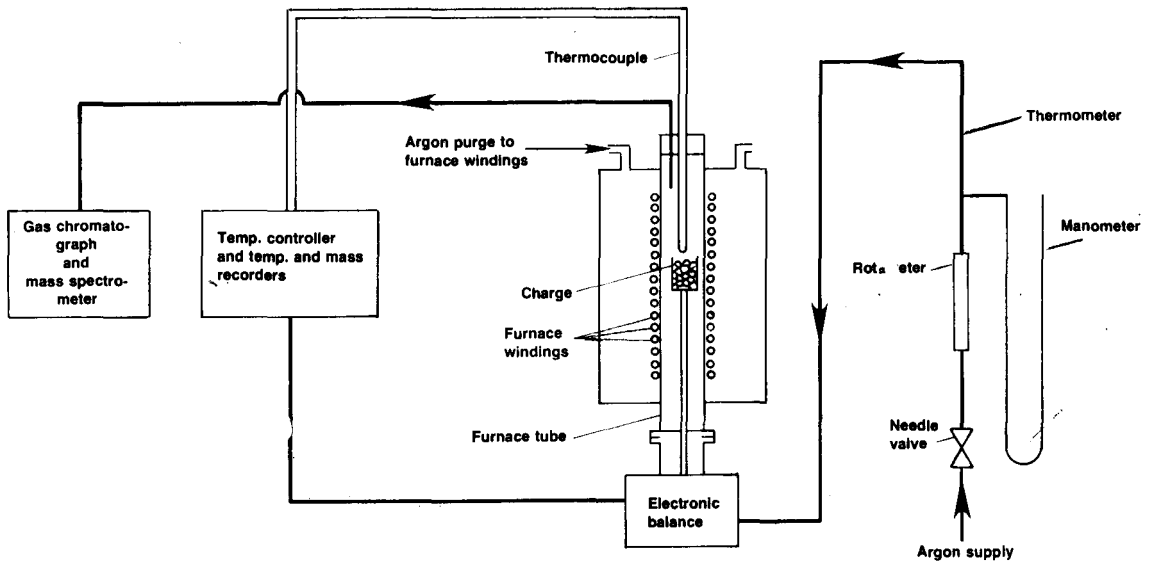


Fig. 8—Apparatus for reactivity measurements

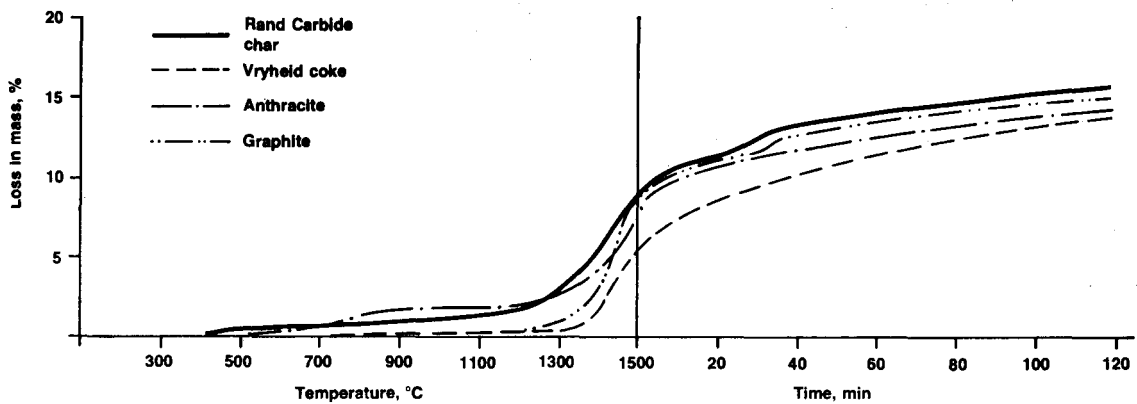


Fig. 9—Reduction of chromite ore in the solid state with standard reducing agents

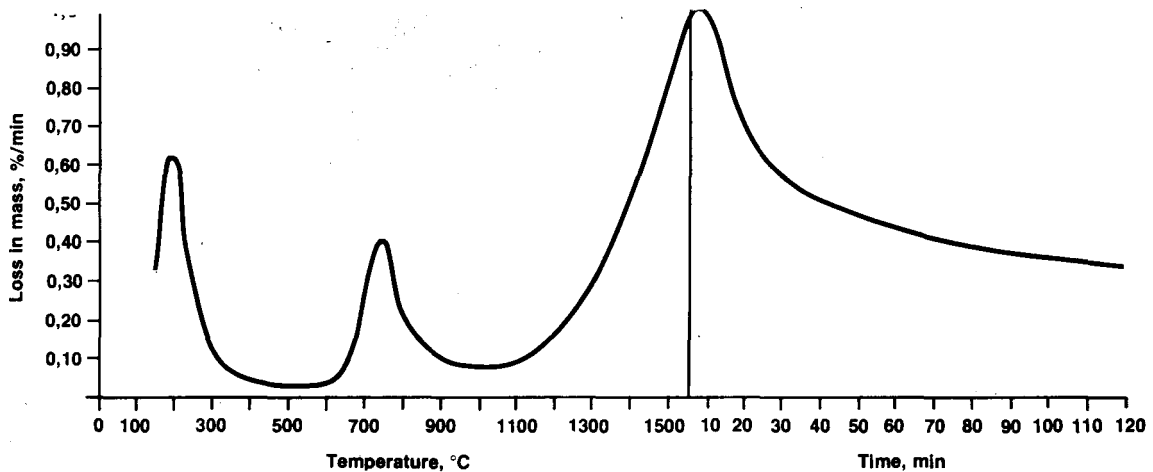


Fig. 10—Rate of loss in mass of a mixture of reducing agent and chromite ore (reducing agent: Dalmas no. 4 seam coal charred at 1000°C in a reducing atmosphere)

the resistivity of the mixture by decreasing the resistance of a continuous array of conducting particles, but also tends to increase it by decreasing the number of such arrays. For a given particle size of reducing agent, the model predicts that the resistivity of burdens of high-carbon ferrochromium will decrease with an increase in the size of the insulating components. The resistivity of these burdens can be expected to be high as long as the particle size of the reducing agent is significantly larger than that of the other components of the burden.

### Conclusions

1. The resistivity of the reducing agent, the volume fraction it occupies, and its particle size and that of the other burden components are important parameters influencing the resistivity of burdens of high-carbon ferrochromium.
2. The resistance measurements on various types of char show that the resistivity of a char depends on the type of coal from which it is produced and on the conditions under which it is produced. Chars produced in a reducing atmosphere had a higher resistivity than those produced in an oxidizing atmosphere at the same temperature and from the same type of coal. However, the effect of the charring atmosphere was small compared with that of the charring temperature.
3. A mathematical model was formulated to describe the dependence of the resistivity of burdens of high-carbon ferrochromium on the particle sizes of the reducing agent and other components of the burden, and on the volume fraction occupied by the reducing agent. High resistivity of the burden can be expected if the particle size of the reducing agent is large in relation to that of the other components of the burden.

### REACTIVITY MEASUREMENTS

The reactivity measurements involved determination of the reactivity of various reducing agents towards chromite and manganese ores in the solid and liquid states.

#### Reactivity towards Chromite Ore in the Solid State

The reactivity of reducing agents towards chromite ore in the solid state was determined with the apparatus

TABLE IV  
RESULTS OF REACTIVITY TESTS ON CHROMITE ORE IN THE SOLID STATE  
(maximum temperature 1500°C)

Reducing agent	Charring temperature °C	Atmosphere	Reduction %
Rand Carbide char	—	—	55
Vryheid coke	—	—	54,52
Anthracite	—	—	47,50
Graphite	—	—	60
Delmas no. 4	1000	Oxidizing	37
Delmas no. 4	1000	Reducing	35
Springbok no. 5	1000	Oxidizing	35
Springbok no. 5	1000	Reducing	36
Delmas no. 2	1000	Oxidizing	39
Delmas no. 2	1000	Reducing	35
Matla no. 5	1000	Oxidizing	31
Matla no. 5	1000	Reducing	35

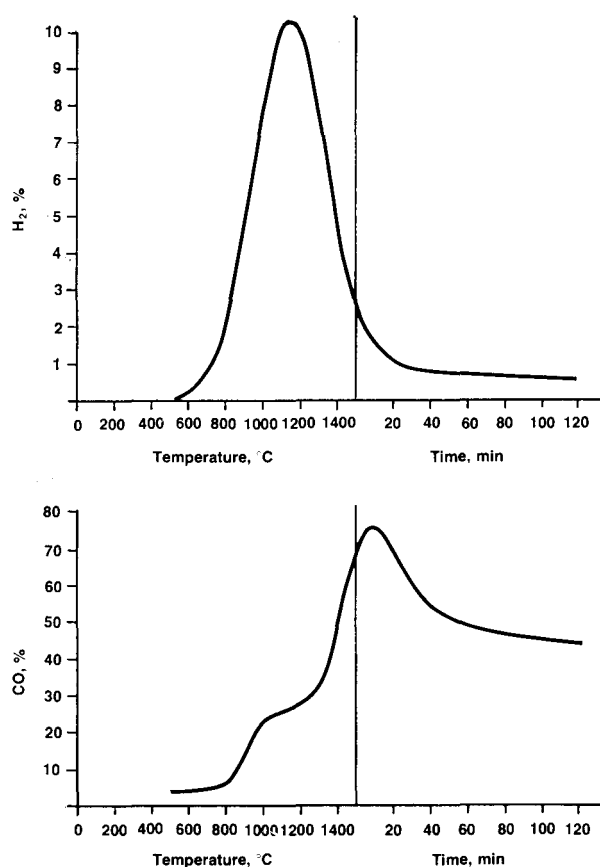


Fig. 11—Analyses of gases emitted during the reduction of chromite ore in the solid state (reducing agent: Springbok no. 5 seam coal charred at 1000°C in a reducing atmosphere)

illustrated in Fig. 8. The losses in mass for the mixture of chromite ore and reducing agent in the alumina crucible were measured on an electronic balance. The gases emitted from the furnace were analysed with a mass spectrometer and a gas chromatograph for carbon monoxide, carbon dioxide, methane, hydrogen, and argon. The sample was heated from room temperature to 1500°C at the rate of 400°C per hour, and was then held at 1500°C for 2 hours.

For the tests with standard reducing agents, the amount of carbon added was the stoichiometric amount required to reduce the iron and chromium oxides to their respective metals, but, for the tests with chars produced by the F.R.I., the amount of carbon added was 120 per cent of the stoichiometrically required amount.

The results of the experiments are summarized in Table IV, which shows the final percentage reduction. This is the amount of oxygen removed expressed as a percentage of the total oxygen contained by the iron and chromium oxides in the ore and of the percentage metallization of iron and chromium as determined from chemical analyses of the reaction products.

The reactivities of the standard reducing agents towards chromite ore in the solid state were not significantly different, except for graphite, which showed significantly better reactivity than the rest. This can be explained by the fact that graphite has the highest

content of fixed carbon and the lowest content of ash and volatile matter, occupies the smallest volume fraction (i.e., it has the highest value for fixed carbon content  $\times$  apparent density), and has a low reactivity towards carbon dioxide. This agrees with the findings of Dewar *et al.*<sup>15</sup> and Frémont-Lamouranne *et al.*<sup>16</sup>. The atmosphere under which a char from the F.R.I. was produced had little effect on the percentage reduction.

Fig. 9 shows plots of the percentage loss in mass versus temperature and time for the standard reducing agents. Curves of similar shape were obtained for the other reducing agents tested.

Plots of the rate of loss in mass versus temperature and time showed three distinct maxima at the following temperatures:

- (i) 200°C, owing to the evolution of water,
- (ii) 750°C, owing to the evolution of volatile matter (hydrocarbons), and
- (iii) 1500°C, owing to the reduction of chromite ore with the evolution of carbon monoxide.

These maxima are shown in Fig. 10, which is typical for the reducing agents used in the tests.

Fig. 11 shows a typical analysis of the gases emitted from the furnace. The evolution of hydrogen usually started at about 500°C, reaching a maximum between 850°C and 1200°C, after which its concentration decreased continuously, although its presence could be detected during the entire reaction period. Carbon monoxide evolved from the volatile matter and as a result of the reduction of the chromite ore.

Variations in the particle size of the reducing agent (see Fig. 12) resulted in an insignificant difference in the reactivity of the reducing agent. However, the rate of reduction of chromite ore increased with a decrease in the particle size of the reducing agent, as could be expected on the basis of the larger surface area available for reaction and the improved inter-particle contact, as shown by Barcza *et al.*<sup>17</sup>.

As could be expected, the rate of reduction increased with an increase in the percentage of stoichiometric carbon added, the effect being most marked for the lower percentages. The results also indicated that the differences in the reactivity of these reducing agents tend to decrease with an increase in the percentage of stoichiometric carbon added.

Silica flux added at 1500°C had no effect on the metallization of iron, but slowed down the metallization of chromium. At temperatures higher than the fusion point of the ore, silica enhanced the reduction, which is in agreement with the findings of Urquhart<sup>18</sup>.

### Reactivity towards Chromite Ore in the Liquid State

A variation of the SCICE (stationary charge in controlled environment) techniques<sup>19</sup> was used in an assessment of the reactivity of reducing agents towards chromite ore in the liquid state. Charges consisting of reducing agent, chromite ore, and fluxes were heated from room temperature to 1500°C at a rate of 350°C per hour, and were then maintained at 1500°C for a period of 2 hours. A final temperature of 1500°C was selected because the preliminary experiments had shown that this temperature was sufficiently high to cause fusion of the ore and fluxes in the charge, whereas, at higher temperatures, the thermocouples failed rapidly. The reactions taking place during heating were studied from a continuous analysis (by use of a mass spectrometer) of the gases emitted from the furnace.

Fig. 13 shows the results as a plot of percentage reduction of the ore versus temperature and time of holding at 1500°C. The percentage reduction was calculated from the gas analyses, an example of which is shown in Fig. 14. Carbon dioxide was first detected at about 400°C, and probably originated mainly from decomposition of the dolomite added to the charge as a fluxing agent. The concentration of carbon dioxide reached a maximum at about 800°C, which was the

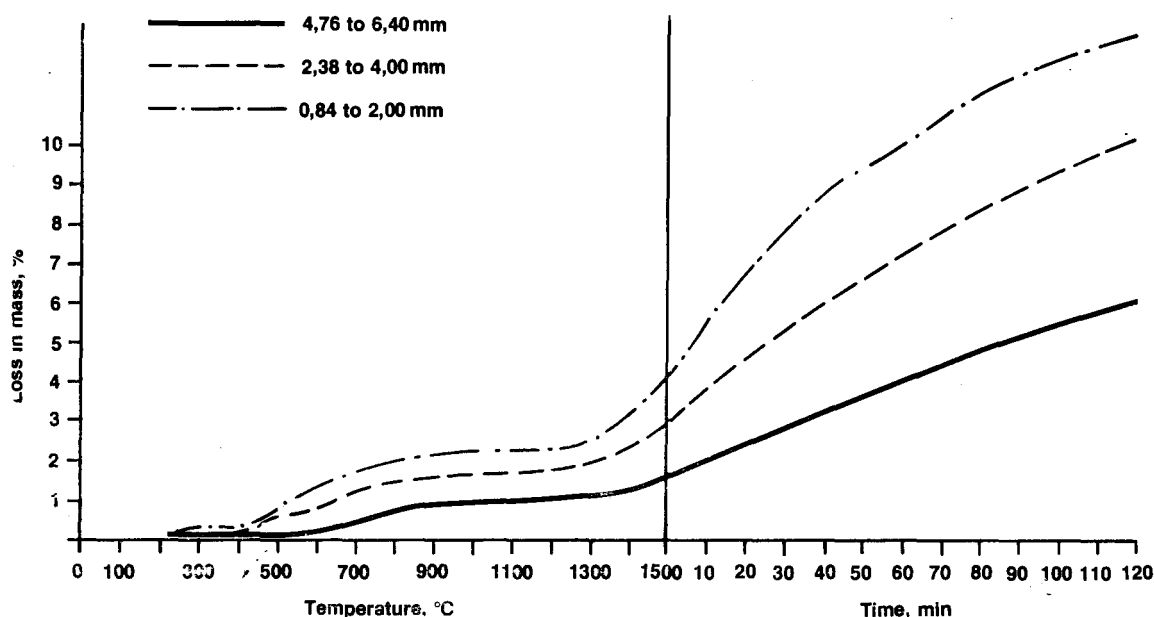


Fig. 12—Effect of particle size of reducing agent (Rand Carbide char) on the reduction of chromite ore



same temperature as that at which carbon monoxide first appeared in the effluent gas. As the reduction of chromite ore by solid carbon does not take place at temperatures as low as 800°C, it is believed that carbon monoxide was formed by the reaction of carbon dioxide with the carbon of the reducing agent according to the Boudouard reaction  $\text{CO}_2 + \text{C} = 2\text{CO}$ . The concentration of carbon monoxide reached a peak at about 1000°C, probably because the decomposition of the dolomite was nearing completion, and started to increase again at about 1100°C to 1200°C, indicating the onset of the reduction of the chromite ore. A second maximum was reached at about 1500°C, after which, during holding at 1500°C, the concentration of carbon monoxide decreased continuously.

Table V lists the reducing agents tested in order of increasing reactivity.

### Reactivity towards Manganese Ore

Charges consisting of an intimate mixture of reducing agent and manganese ore were heated in the apparatus (see Fig. 8) in an argon atmosphere at a rate of 400°C/h until a temperature of 1450°C was reached, after which this temperature was maintained for 2 hours. A final temperature of 1450°C was selected because preliminary experiments had shown that this temperature was sufficiently high for liquid metal and slag to be formed. In all the experiments, the carbon added was 100 per cent of the stoichiometric requirement.

Fig. 15 shows the curves for loss in mass when stan-

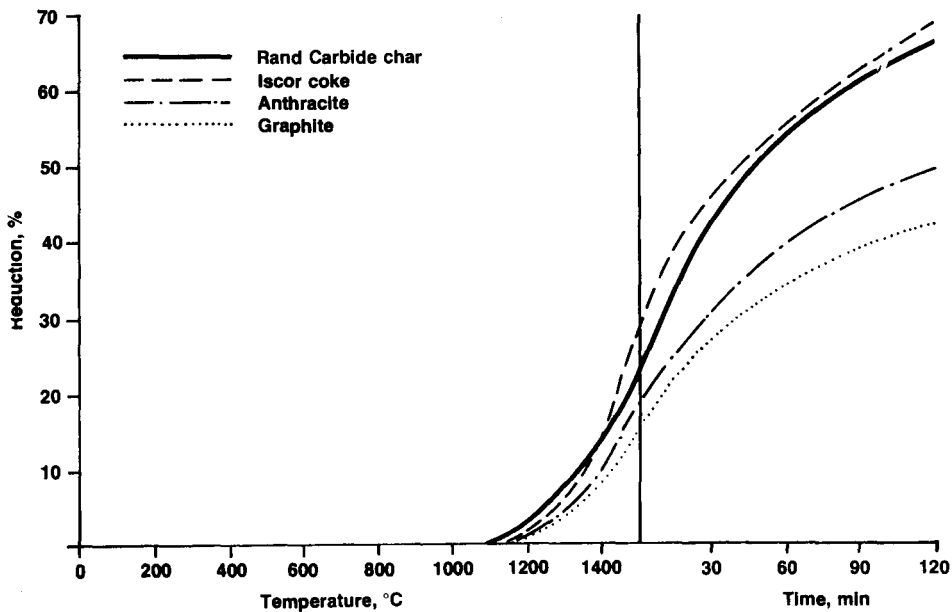


Fig. 13—Reduction of chromite ore, in the liquid state with standard reducing agents

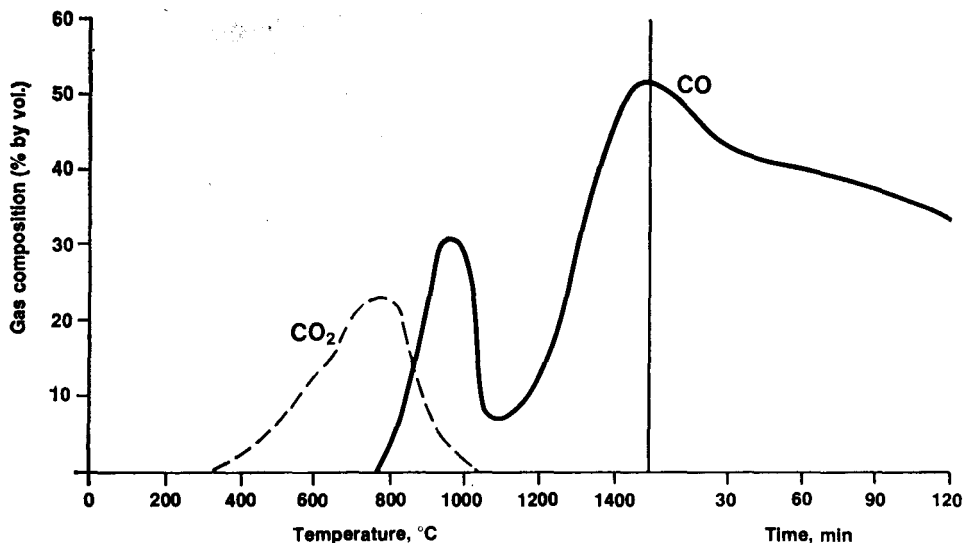


Fig. 14—Analyses of gases emitted during the reduction of chromite ore in the liquid state (reducing agent: Rand Carbide char)

standard reducing agents were reacted with natural Mamatwan ore. These curves were corrected for the evolution of water and volatile matter from the reducing agents. The curves obtained for the other reducing agents were very similar in shape.

Reduction was rapid at temperatures between 500°C and 1100°C, much slower at temperatures between 1100°C and 1400°C, and again rapid during holding at 1450°C. In accordance with the work reported by Grimsley<sup>20</sup>, it can be expected that the first stage of reduction corresponds to the reduction of iron oxide to metallic iron and the reduction of the higher manganese oxides to MnO and CaMn<sub>2</sub>O<sub>4</sub>, in addition to thermal decomposition of the ore. The second stage of reduction corresponds to the reduction, in the solid state, of MnO and CaMn<sub>2</sub>O<sub>4</sub> by carbon dissolved in the ferro-

manganese phase. The third stage of reduction therefore probably corresponds largely to the reduction of MnO dissolved in the liquid slag.

Any effect of the type of reducing agent on the reduction of manganese ore was usually apparent only during the first and final stages of reduction, was usually small, and was very similar for the natural and the preheated ore. However, the reduction behaviour of mixtures of manganese ore and graphite differed from that of mixtures containing the other reducing agents in that fusion of the ore did not take place upon heating to 1450°C. Even when the ash of Rand Carbide char was added to the mixture of graphite and ore, fusion did not occur, indicating that the distribution of ash in a reducing agent determines its fluxing behaviour.

Table VI summarizes the results obtained with various reducing agents and preheated Mamatwan ore, the values for reactivity being scaled with respect to the values obtained for Rand Carbide char. The results showed that the atmosphere under which a char is produced has little effect on its reactivity. An increase in the temperature of charring caused a decrease in the chars produced from Springbok no. 5 seam coal. However, this effect was not observed with chars produced from Utrecht coal.

TABLE V

REDUCING AGENTS IN ORDER OF INCREASING REACTIVITY TOWARDS CHROMITE ORE IN THE LIQUID STATE

(temperature 1500°C)			
Reducing agent	Charring temperature °C	Atmosphere	Reduction from metal analyses %
Utrecht	1000	Reducing	41,9
Utrecht	1000	Oxidizing	42,0
Graphite	—	—	42,6
Delmas no. 2	1000	Reducing	43,5
Springbok no. 5	600	Oxidizing	44,0
Umgala	1000	Reducing	44,2
Utrecht	600	Reducing	44,8
Utrecht	600	Oxidizing	46,7
Springbok no. 5	600	Reducing	47,3
Anthracite	—	—	50,3
Utrecht	800	Reducing	51,8
Utrecht	800	Oxidizing	53,6
Springbok no. 5	800	Reducing	54,9
Springbok no. 5	800	Oxidizing	56,4
Delmas no. 4	1000	Reducing	58,7
Matla no. 5	1000	Reducing	58,7
Rand Carbide char	—	—	65,9
Iscor coke	—	—	68,7

TABLE VI

RESULTS OF REACTIVITY TESTS ON PREHEATED MAMATWAN ORE

Reducing agent	Solid-state reactivity	Liquid-state reactivity
Rand Carbide char	1,0	1,0
Iscor coke	0,7	0,9
Anthracite	1,0	1,0
Graphite	0,8	—
Springbok	1,25	1,1
Utrecht	1,0	0,75
Delmas no. 2	1,1	1,0
Delmas no. 4	1,2	0,7
Matla no. 5	1,2	0,8
Blesbok no. 5	1,2	1,15

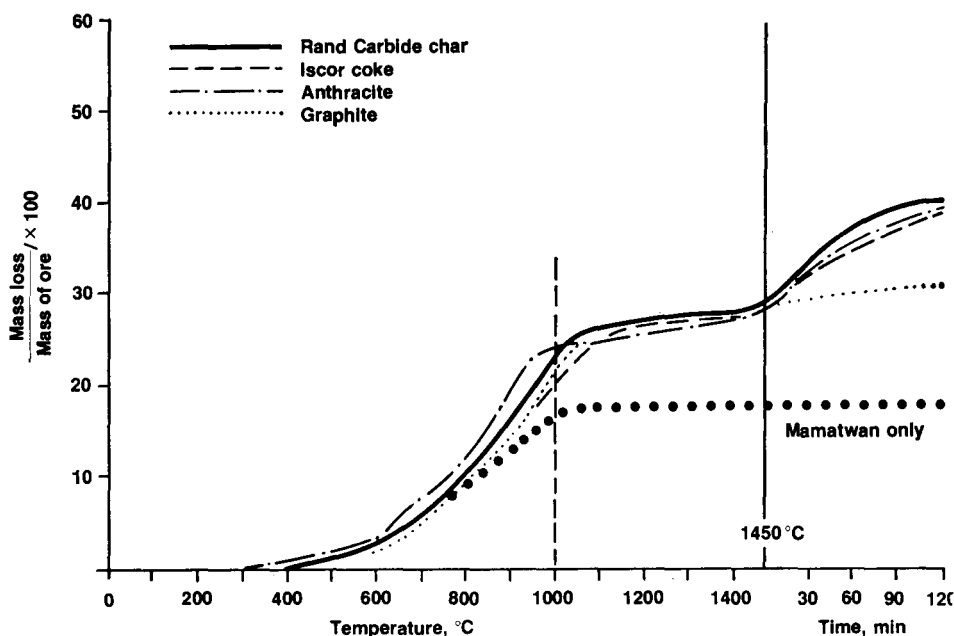


Fig. 15— Reduction of natural Mamatwan ore with standard reducing agents

In general, it was found that reducing agents that have a high content of volatile matter, that occupy a large volume fraction, and that have a high reactivity towards carbon dioxide tend to have high solid-state reactivities. Reducing agents that occupy a large volume fraction and have a low degree of graphitization tend to have high liquid-state reactivities.

As could be expected, the solid-state and liquid-state reactivity decreased with an increase in the particle size of the reducing agent, although the effect on the liquid-state reactivity was more pronounced than that on the solid-state reactivity.

Silica added as a flux to a mixture of chromite ore and reducing agent had little effect on the solid-state reactivity, except where the amount added was large (20 per cent). However, the liquid-state reactivity tended to decrease with an increase in the amount of silica added. The formation of silicates in the slag is known to hamper the reduction processes<sup>18</sup>.

### Conclusions

1. Different types of reducing agents have very similar reactivities towards chromite ore in the solid state.
2. Reducing agents occupying a large volume fraction in the burden tend to have high reactivities towards chromite ore in the liquid state.
3. Reducing agents that have a high reactivity towards carbon dioxide and a high content of volatile matter, and that occupy a large volume fraction, tend to have a high reactivity towards manganese ore in the solid state.
4. Reducing agents that occupy a large volume fraction and have a low degree of graphitization tend to have a high reactivity towards manganese ore in the liquid state.

### ACKNOWLEDGEMENT

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## Tunnelling

The Fourth Australian Tunnelling Conference, organized by the Australasian Institute of Mining and Metallurgy, is to be held in Melbourne from 16th to 18th March, 1981.

It is hoped that part of the Conference will be devoted to engineering aspects of the Melbourne Underground Rail Loop, including items such as architectural, electrical, and mechanical works. The remainder of the Conference will cover the following themes:

- (i) Future projects in mining or civil engineering involving underground excavation.

- (ii) Investigation, design, and monitoring of underground excavations.
- (iii) Case histories, new equipment, recent developments and modern management of underground construction.
- (iv) Possible innovations in underground construction by the year 2000.

All correspondence relating to the Conference should be addressed to The Chief Executive Officer, The Australasian Institute of Mining and Metallurgy, P.O. Box 310, Carlton South, Victoria, Australia 3053.