The resistivity of mixtures of Mamatwan manganese ore and reducing agents

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SYNOPSIS

An investigation is described in which the resistivities of Mamatwan manganese ore, Delmas coal, and Iscor coke, at temperatures or up to 1400°C were determined, as well as the resistivities of mixtures of ore of a constant size range with Delmas coal or Iscor coke of three different size ranges.

The resistivities of the ore and the coal were characteristic of those for semi-conducting materials, were strongly influenced by temperature, and decreased by several orders of magnitude between room temperature and 1000°C. The resistivity of the coke changed only slightly between room temperature and 1400°C, and the resistivity of the coal approached that of the coke at 1300°C. This provides support for the theory that the resistivity of carbonaceous reducing agents is primarily a function of heat treatment, and not of the rank and composition of the coal.

Above 1200°C, the resistivity of mixtures of ore and coke fell steeply owing to an increase in the volume fraction of coke in the mixture and to the formation of slag. The results were similar for the three different size ranges of coke.

The extremely high resistivities of ore–coke and ore–coal mixtures at low temperatures indicate that there is unlikely to be much conduction of current in the higher regions of a furnace. Thus, the resistance of a furnace is governed mainly by the conditions at the electrode tips and in the molten regions. To explain the very low resistances of furnaces, usually, about 1 mΩ, it would be necessary for investigations to be conducted under conditions similar to those in the active zone of a furnace.

SAMEVATTING

'n Ondersoek word beskryf waarin die spesifieke weerstand van Mamatwan-mangaanerts, Delmas-steenkool en Yskor-kooks by temperature van tot 1400°C bepaal is, asook die spesifieke weerstand van mengsels van erts met 'n konstante groottestrek en Delmas-steenkool of Yskor-kooks met drie verskillende groottestrekke.

Die spesifieke weerstand van die erts en die steenkool was kenmerkend van dié vir halfgeleidende materiaal is sterk deur temperatuur beïnvloed en het tussen kamertemperatuur en 1000°C met verskeie grootteordes afgeneem. Die spesifieke weerstand van die kooks het net effens verander tussen kamertemperatuur en 1400°C en die spesifieke weerstand van die steenkool kom by 1300°C na aan dié van die kooks. Dit staaf die teorie dat die spesifieke weerstand van koolstofhoudende reduseermiddels in die eerste plek 'n funksie van hittebehandeling is en nie van die rang en samestelling van die steenkool nie.

Bo 1200°C het die spesifieke weerstand van mengsels van erts en kooks skerp gedaal as gevolg van 'n toename in die volumefraksie kooks in die mengsel en as gevolg van slakvorming. Die resultate was min of meer dieselfde vir die drie verskillende groottestrekke kooks.

Die uiters hoë spesifieke weerstand van mengsels van erts en kooks en erts en steenkool by lae temperature dui daarop dat daar waarskynlik nie veel stroomgeleiding in die hoër dele van 'n oond sal wees nie. Die weerstand van 'n oond word dus hoofsaaklik deur die toestande by die punte van die elektrodes en in die vloeidele bepaal. Om die baie lae weerstand van oonde, gewoonlik ongeveer 1 mΩ, te verklaar sal daar ondersoeke ingestel moet word in omstandighede soortgelyk aan dié in die aktiewe sone van 'n oond.

Introduction

It has been claimed that the maximum production of a submerged-arc furnace is a function of the resistance of the burden[1-3]. This claim has led to studies of the variation with temperature of the electrical resistivity of different components of the burden[2, 4-7], of mixed burdens[2, 4-7], and of the slag layer[4, 8]. However, the resistance of the burden and the mode of conduction also depend on the layout of the electrode system and the furnace. By September 1975, when this investigation was begun, resistance measurements had been made on components of burdens for the production of ferrochromium[5, 6], but none had been made on components of burdens for the production of ferromanganese. The aim of the present investigation was the measurement of resistance as a function of temperature for mixtures of Mamatwan manganese ore and Iscor metallurgical coke or Delmas coal.

The measurements were carried out simultaneously with 'stationery charge in controlled environment'

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(SCICE) experiments, the results of which have been reported elsewhere[9].

Experimental Method

Materials

The materials used were Mamatwan manganese ore, Iscor metallurgical coke, and Delmas coal. These materials were supplied by Metalloys Ltd from the Meyerton plant of Samancor. Their analyses are given in Tables I and II.

The materials were crushed and screened, and the size ranges retained for the resistance measurements were 2,83 to 12,7 mm for the ore, and 2,83 to 6,35 mm, 6,35 to 9,5 mm, and 9,5 to 12,7 mm for the reducing agents. Hence, the resistivity of mixtures of Mamatwan manganese ore of constant particle size and Delmas coal or Iscor metallurgical coke was determined for three different particle sizes of the carbonaceous reducing agents. A description of the technique for the preparation of the charge has already been given[9].

Apparatus and procedure

The charges of ore and coke contained 3400 g of ore and 600 g of coke, and the charges of ore and coal contained 3040 g of ore and 960 g of coal.

The resistance measurements were made on the apparatus shown in Fig. 1, which has been described

TABLE I

TABLE I

PROXIMATE AND ASH ANALYSES OF THE REDUCING AGENTS

Constituent		Delmas coal % by mass	Iscor coke % by mass
Fixed carbon		48,55	79,07
Volatile matter		28,33	2,75
Ash		15,65	15,98
Moisture		6,11	1,28
Sulphur		1,20	0,72
Phosphorus		0,16	0,20
Ash analysis:	MgO	2,79	1,19
	Al_2O_3	26,38	30,05
	SiO_2	43,38	50,58
	CaO	7,87	4,37
	Mn_2O_3	0,95	0,40
	Fe_2O_3	7,74	7,37
	S	2,48	0,35

TABLE II

THE CHEMICAL COMPOSITION OF MAMATWAN MANGANESE ORE

Constituent	% by mass
MgO	3,10
Al_2O_3	<0,10
SiO_2	4,27
CaO	12,96
Mn_2O_3	55,90*
Fe_2O_3	5,99
Cr_2O_3	0,36
P_2O_5	0,17
K_2O	0,21
CO_2	14,91
H_2O	0,54

*This is the total manganese content of the ore expressed as Mn_2O_3

in detail elsewhere[9]. The charge was contained in a graphite crucible, 150 mm in internal diameter and 515 mm deep, which acted as a susceptor when heated by a 40 kW 3 KHz induction furnace. Aluminous-porcelain sheaths and alumina cement were used where necessary to ensure that conduction took place over a constant surface area of electrode irrespective of the level of the solid or partially fused charge in the crucible.

The lower edge of the conducting part of the electrode stood 40 mm above the bottom of the crucible, in which a recess 10 mm deep had been drilled. The bottom section of the central electrode was located in this recess, and, by the use of a bridge during charging and a centring device after that, the correct positioning of the electrode and the control thermocouple was ensured.

A heating rate of 350 °C an hour was used for all the experiments.

Determination of resistance

The circuit shown in Fig. 2, was used to measure the resistance of ore and coke mixtures, ore and coal mixtures, or any of these materials individually.

Long coaxial leads twisted round each other were used to connect the measuring instruments, which were positioned about 2 m away from the furnace in order to minimize the effect of induced fields. The current through the charge was measured with an avometer, and the voltage across the charge was determined by a digital multimeter with an impedance of 10 MΩ. The voltmeter
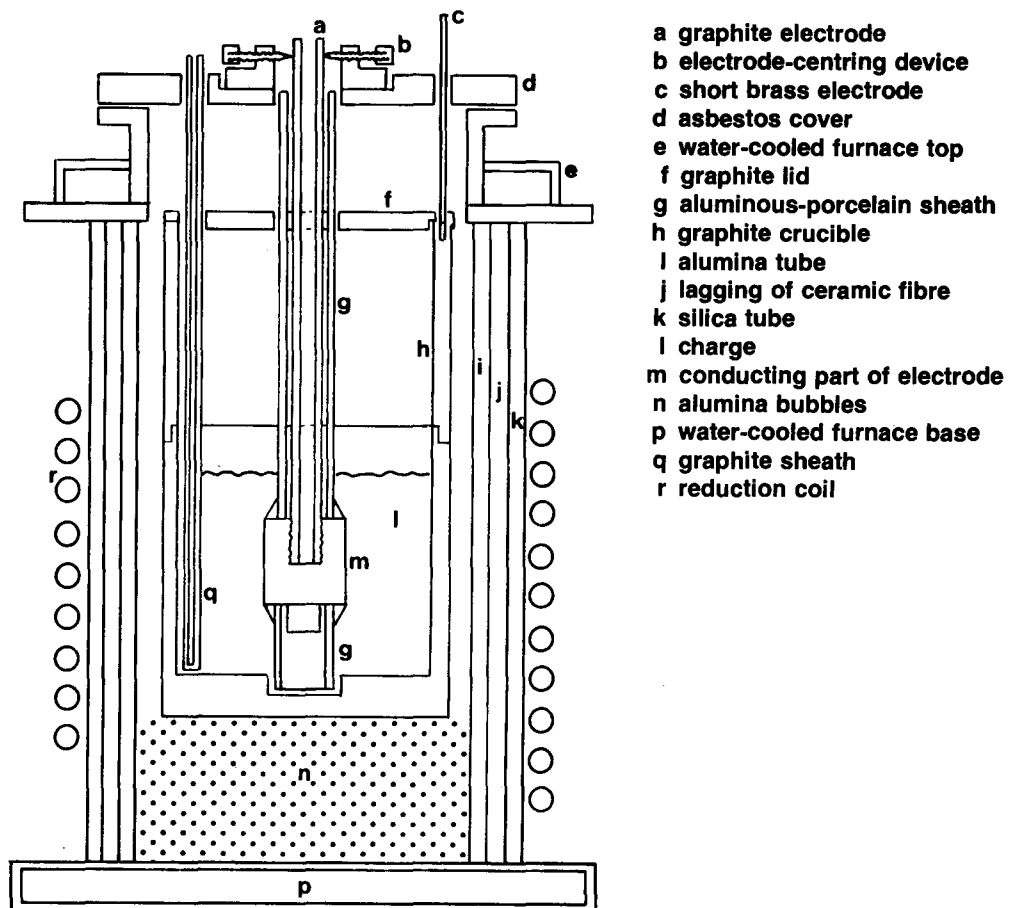

a graphite electrode
b electrode-centring device
c short brass electrode
d asbestos cover
e water-cooled furnace top
f graphite lid
g aluminous-porcelain sheath
h graphite crucible
I alumina tube
j lagging of ceramic fibre
k silica tube
l charge
m conducting part of electrode
n alumina bubbles
p water-cooled furnace base
q graphite sheath
r reduction coil

Fig. 1.—Schematic section of the apparatus used for measuring resistivity
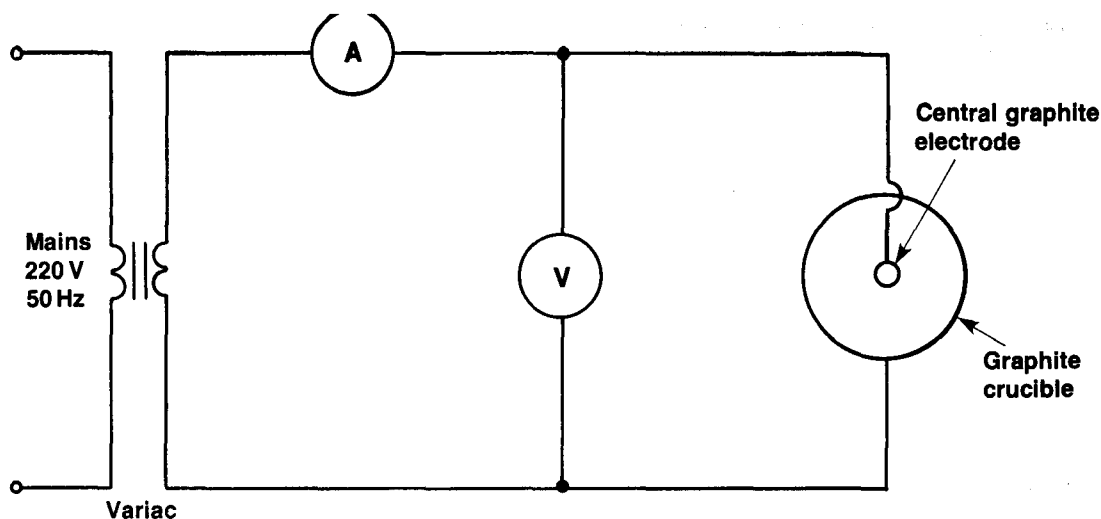
Fig. 2.—The apparatus used in determining the resistance of charges

was connected across the charge itself so that errors would be at a minimum.

The error introduced by the relatively low impedance of the multimeter is high at low temperatures for coal and for mixtures of ore and coal, but it decreases rapidly with increasing temperature. The error in the measurement of the resistance of these charges at room temperature is 17,6 per cent, decreasing to 0,2 per cent at about 600°C. The error in the measurement of the resistance of charges of ore and of mixtures of ore and coke at room temperature is negligible. By the use of this apparatus, the resistance of each of the charges with increases of temperature and at constant temperature was determined. The charges are listed in Table III.

The resistance of the different charges was converted to resistivity by the determination of the cell constant (shape factor) of the apparatus. The cell constant was determined by measurement of a system similar to that shown in Fig. 2, in which the crucible contained a salt solution of known resistivity. The value of the cell constant was found to be 2,64 m^{-1}.

Variation in volume fraction of the components

One variable that has a significant influence on the resistivity of a charge is the proportion by volume of either the ore or the reducing agent[6]. The volume fraction of each of the components in the SCICE charges was estimated by the independent measurement of the bulk volumes of the reducing agents and the ore, followed by the measurement of their combined volume when the mixture was not compacted. The compaction of

TABLE III

EXPERIMENTAL CHARGES

Charge	Size range of reducing agent mm
Ore	
Iscor coke	2,83 to 6,35
Delmas coal	2,83 to 6,35
Ore and coke	2,83 to 6,35
Ore and coke	6,35 to 9,5
Ore and coke	9,5 to 12,7
Ore and coal	2,83 to 6,35
Ore and coal	6,35 to 9,5
Ore and coal	9,5 to 12,7

the mixture during charging reduced the volume by about 1 per cent.

The proportion by volume of reducing agent was found to be 39 per cent coke in mixtures of coke and ore, and 45 per cent coal in coal–ore mixtures. These measurements were made with ore particles ranging in size between 2,83 and 12,7 mm and particles of reducing agent ranging in size between 2,83 and 6,35 mm. The volume of the charges was found to remain approximately constant irrespective of the size range of the reducing agent. The volume fractions were therefore assumed to be approximately constant at room temperature.

It has been suggested[6] that the variations in resistance at temperatures between 400 and 1200°C in a chromite–char mixture are due to the expansion and contraction of the components of the charge. This theory was tested on the charges under consideration by the measurement of the effect of increases of temperature on the volume of each of the different charges.

The measurement of changes in volume with increasing temperature could also provide information on the rate of increase in the volume fraction of the reducing agent in the mixture, because the ore and the reducing agent diminish in volume at different rates. This could significantly affect the variation of the resistivity of the charge with increases in temperature.

The changes in volume of charges of ore, ore and coke, and ore and coal were measured from determinations of the level of the charge in the crucible with increases in temperature. A graphite slab 20 mm thick was placed on top of the charge, and a mass of 2,5 kg was placed on top of the slab. The level of the charge was determined by the lowering of an alumina sheath through the cover of the furnace until it touched the top of the mass.

Results and Discussion

Effect of temperature on the resistivity of the components

Fig. 3 gives plots of resistivity against temperature for the materials used in this investigation, which show that the resistivities of both Delmas coal and Mamatwan ore change markedly with increasing temperature,

whereas the resistivity of coke changes only slightly with temperature.

Most refractory materials exhibit a resistance–temperature relationship that approaches the Arrhenius-type relationship proposed by Rasch and Hinrichsen[10], which can be expressed as follows:

$$\rho = Ae^{B/T}, \qquad \qquad \qquad \qquad (1)$$

or

$$\ln \rho = \ln A + B/T, \qquad \qquad \qquad (2)$$

where ρ is the specific resistance,
  T is the absolute temperature, and
  A and B are constants.
The values of A and B can vary with the temperature range considered.

The plot of $\ln \rho$ against reciprocal temperature for each material is shown in Fig. 4. It can be seen that the

variation of resistivity with temperature follows the Arrhenius-type equation to a good approximation. The resistivity of the ore deviates from this relationship for temperatures higher than 1000 °C because of the formation of liquid slag, and a change from electronic to ionic conduction.

The variations in the resistivity of coal between 25 and 450 °C appear to be due to the loss of volatile matter. Urquhart[5] attributed similar variations in resistivity during the heating of coal char to the initiation of the loss of volatile matter. A comparison of curves I and II between 25 and 450 °C in Fig. 5 indicates that the coal begins to contract slightly as soon as heating starts. Further loss of volatile matter between 450 and 800 °C results in a very marked decrease in resisitivity (Fig. 3). The very steep decrease in resistivity between

X   Mamatwan ore   2,83 to 12,7 mm
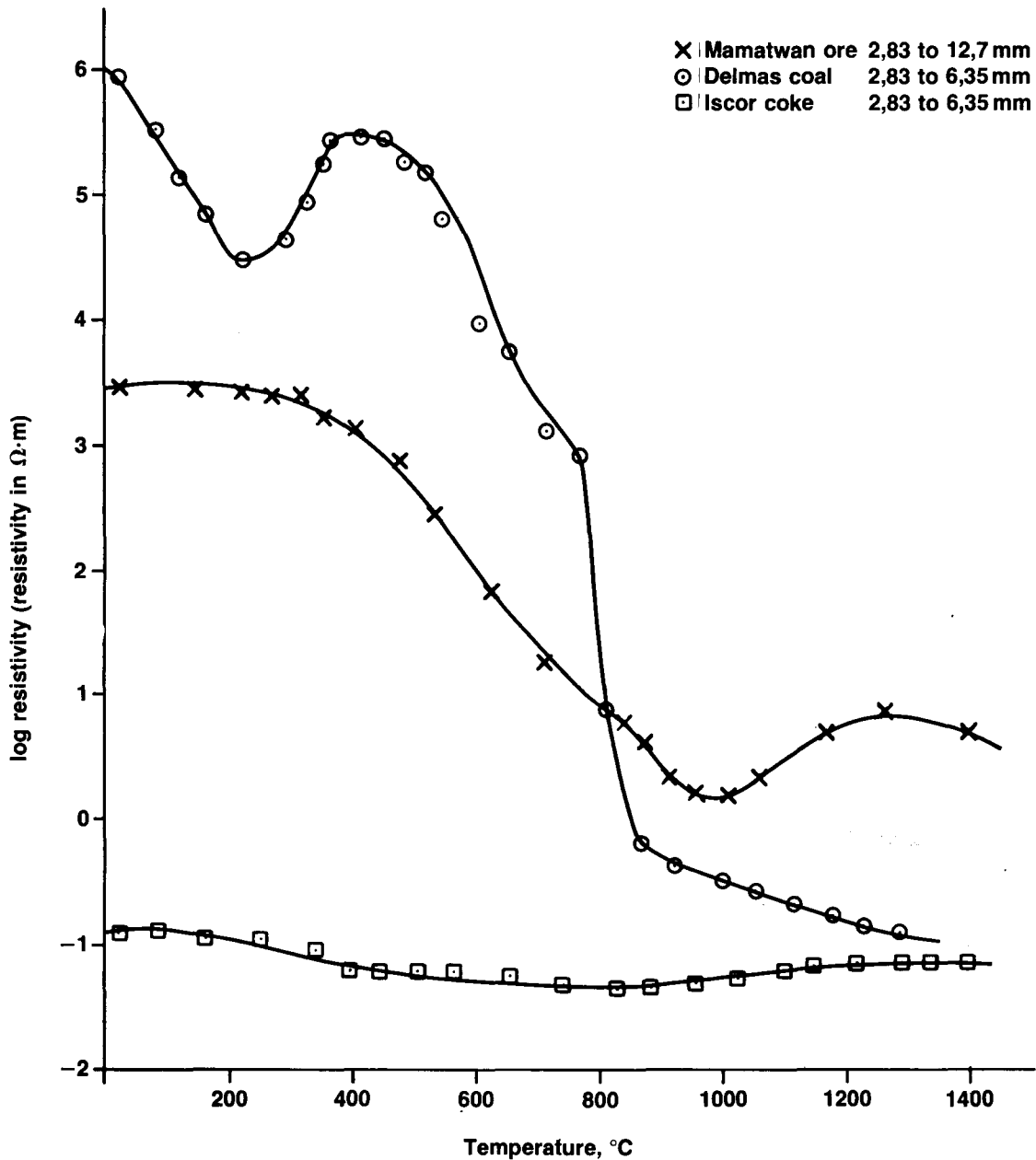⊙   Delmas coal   2,83 to 6,35 mm
▢   Iscor coke   2,83 to 6,35 mm

Fig. 3.—The variations in the resistivities of Mamatwan ore, Delmas coal, and Iscor coke with increasing temperature
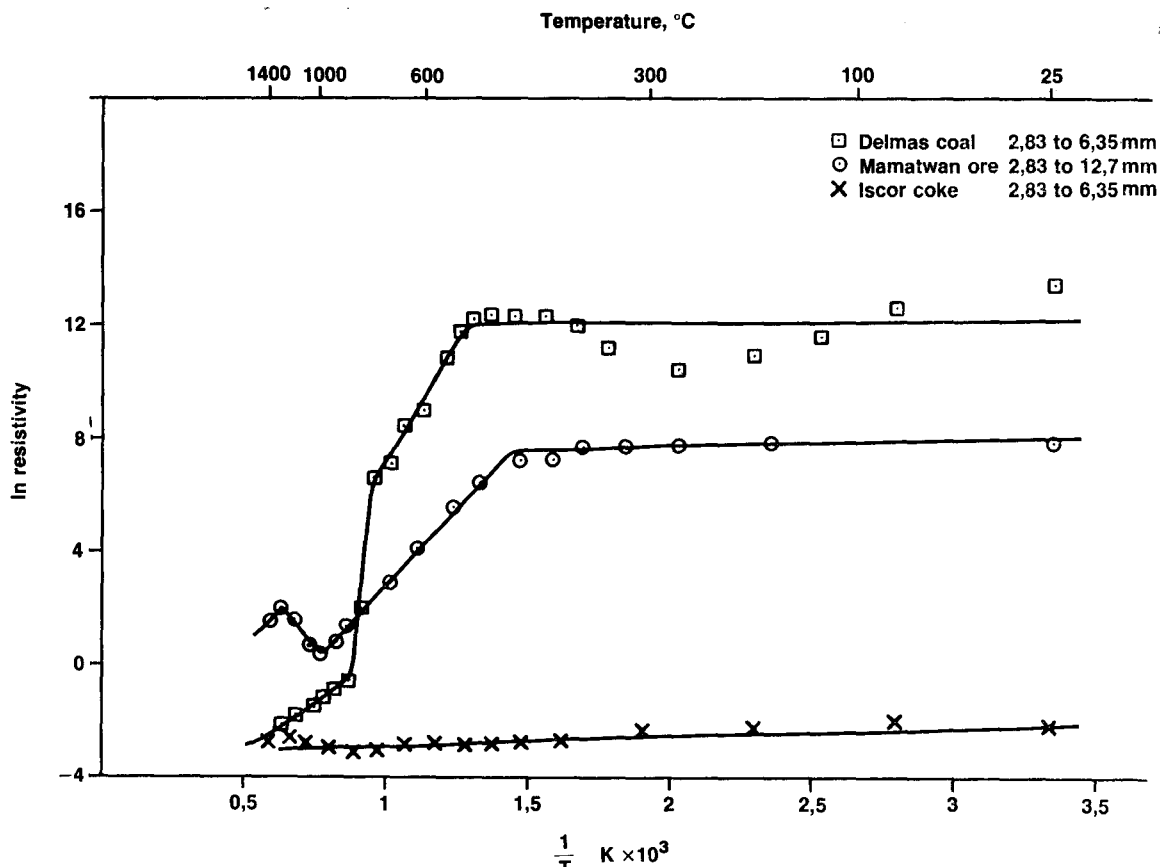
Fig. 4.—Arrhenius-type plots of the resistivity of Mamatwan ore, Iscor coke, and Delmas coal

about 800 and 900 °C coincides with an increase in the thermal conductivity of the coal. This was apparent from the marked decrease in the temperature difference between the inner and outer thermocouples in the charge during the heating of the coal.

Fig. 5 shows that the rate of change in the volume of coal–ore mixture altered between 800 and 900 °C. A comparison of curve II with curves I and III shows that this change in rate was due to a relatively rapid contraction of the coal up to 800 °C and a slower rate of contraction above 900 °C. The slow decrease in resistivity above 900 °C was probably because of the gradual loss of volatile matter. At 1200 °C or higher, the resistivity of the coal becomes virtually the same as that of the coke. Rennie[7] obtained similar results during a study of the electrical characteristics of coke, anthracite, charred coal, and charred anthracite. These results agree with the finding of other investigators[11, 12] that the resistivity of a carbonaceous reducing agent is primarily a function of heat treatment, and not of the rank and composition of the original coal.

The resistivity of the ore decreases only slightly between 25 and 350 °C because there is little change in its structure over this temperature interval. The decrease in resistivity between 400 and 1000 °C is due to the decomposition of carbonates, and the formation of lower oxides of manganese and iron. This is consistent with previous observations that the resistivity of oxides decreases as the ratio of metal to oxygen in the oxide increases[2, 7, 13].

The structural changes that occur in the ore at temperatures between 400 and 1000 °C are not well known. Pilter[14] showed that a concentration of carbon monoxide in the atmosphere of as little as 10 per cent will, between 25 and 800 °C, reduce the higher oxides of manganese to manganous oxide. Because the ore in the present study was heated in a graphite crucible, an appreciable amount of carbon monoxide must have been present, and the equilibrium concentration of carbon monoxide in the presence of carbon dioxide and solid carbon rises[15] steeply from about 2 per cent at 400 °C to about 99 per cent at 1000 °C.

The turning point at 1000 °C in the plot of resistivity against temperature (Fig. 3) corresponds to the maximum volume of the charge of ore shown in Fig. 5. The volume of the charge decreases rapidly above 1000°, whereas the resistivity increases between 1000 and 1300 The rapid decrease in the volume of the charge above 1000 °C shows that drastic changes are taking place in the structure of the ore.

The results of De Villiers[16] and Pentz[17] show that the initial stages of the reduction of the ore involve the formation of a sponge-like structure that contains most of the metallic oxides, whereas the decomposition products of carbonates can occur as loose particles in the interstices. Free silica, liberated from the braunite, is probably also present. With an increase in temperature above 1000 °C, the sponge-like structure collapses to form grains of impure manganous oxide while the gangue oxides react to form the slag[9]. Both processes result in a
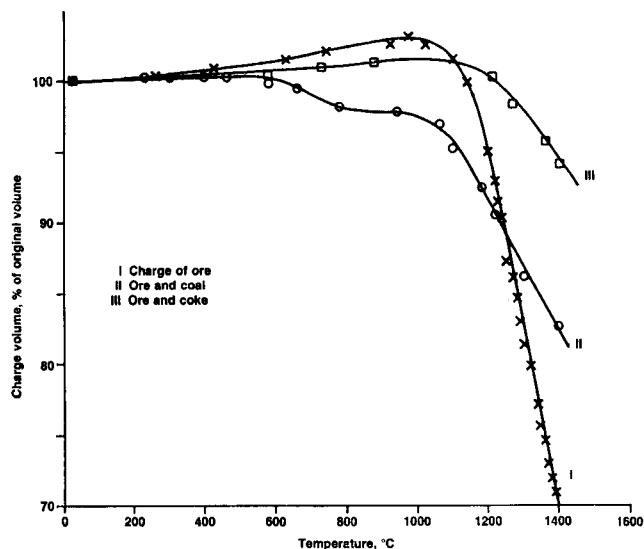
Fig. 5.—The variations, with increasing temperature, in the volumes of charges of ore, ore and coal, and ore and coke

drastic reduction in the volume of the ore. The mode of conduction then changes from electronic conduction through the spongy oxide to ionic conduction through the slag, which now forms a more or less continuous path through the charge. This is accompanied by an increase in the resistivity owing to the low mobility, concentration, and degree of dissociation of the ions. The decrease in the resistivity above 1300 °C is probably due to an improvement in the above three factors, and to improved contact between particles of ore.

The resistivity of the coke varied only slightly between 25 and 1400 °C owing to the high thermal stability of this material. Some variation in the resistivity of the coke can be expected because of the reaction and fusion of the ash constituents at high temperatures. The resistivity of the coke, measured at room temperature in this investigation, is approximately the same as that of coal char[5] at 1400 °C.

Volume changes during the heating of the charges

The ore and reducing agent diminish in volume at different rates when they are heated, and the resistance of the charge is influenced by the volume of ore and reducing agent at any time. The approximate changes in volume during the heating of the three charges are shown in Fig. 5. The ore loses about 18 per cent of its mass when calcined[17, 18] at 1000 °C owing to the decomposition of carbonates and the thermal dissociation of higher oxides. The loss of mass in the case under consideration must have been even higher than 18 per cent because the ore was heated in a graphite crucible, and the higher oxides of manganese and iron were reduced to their lowest oxidation states. Yet the volume of the ore at 1000 °C was higher than its initial volume. The increase was due to a more open structure, which resulted from the cracking of the ore and the decomposition of the carbonates. The volume began to decrease beyond 1000 °C owing to the formation of slag. The mixture of ore and coke expanded less than the charge of ore. This could be because the coke contracted

slightly or because the ore expanded less owing to the increased partial pressure of carbon monoxide that prevailed in the system. The volume of the mixture decreases between 1200 and 1400 °C at a rate much lower than that for the charge of ore, indicating that the ore diminishes in volume at a much higher rate than the coke.

The initial volumes of ore and coke in the mixture were 1800 and 1100 ml respectively, whereas the combined volume was 2800 ml. From the curve of volume against temperature (curve I, Fig. 5) the calculated volume of ore in the mixture at 1300 °C is 1470 ml if it is assumed that the presence of coke does not affect the volume of the ore. The volume of the mixutre at 1300 °C is 2720 ml, which gives a theoretical volume of coke in the mixture of 1259 ml at 1300 °C if it is assumed that the coke does not take part in any chemical reactions. Hence, the volume fraction of coke in the mixture increases with heating. The coke inhibits subsidence of the charge, probably by forming a more or less continuous network throughout the charge that decreases the resistivity.

The charge of ore and coal showed very little expansion between room temperature and 500 °C, indicating that the coal begins to contract as soon as heating starts. The charge contracted fairly rapidly between 500 and 800 °C
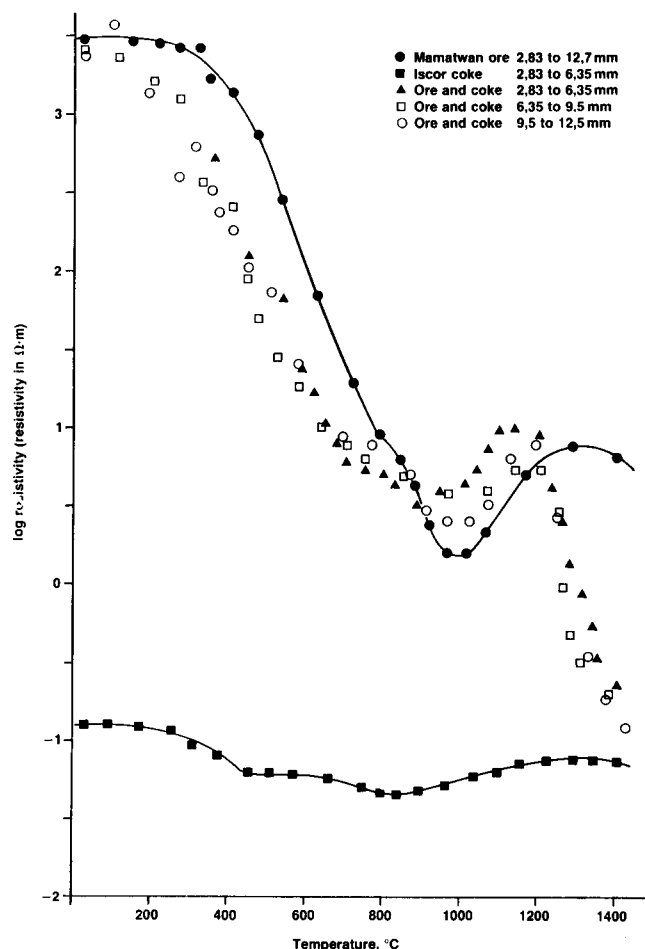

Fig. 6.—The variations, with increasing temperature, in the resistivities of mixtures of ore and coke containing coke of different size ranges

owing to the evolution of volatile matter. Contraction was very slow between 800 and 1000 °C, and very rapid above 1000 °C. It has been seen that the thermal and electrical conductivities of coal increase rapidly above 800 °C when most of the volatile matter has been eliminated.

The charges of ore and coal, and of ore and coke, showed similar rates of contraction during the stage of rapid contraction.

Resistivities of charges of ore and reducing agent

The variation in the resistivity of mixtures of ore and coke with increasing temperature is shown in Fig. 6. The curves of resisitivity against temperature for each component of the charge are superimposed for comparison.

From Fig. 6 it can be seen that the resistivity of mixtures of ore and coke is determined mainly by the resistivity of the ore, although coke lowers the resistivity of the charge at temperatures between 25 and 900 °C. This decrease in resistivity results from the low resistivity of coke, and the reduction of oxides to a lower oxidation state.

The most important factor is probably reduction to lower oxides with lower resistivities. Fig. 6 shows that the resistivities of the ore and of the mixture of ore and coke are almost identical at 25 °C. Thus, coke has virtually no influence on the resistivity of the mixtures at that temperature. Systems composed of particles of a conductor and an insulator show an abrupt increase in resistivity when the volume fraction of the insulator particles exceeds a certain critical value[6, 19, 20]. This has been shown[20] to be due to the disruption of continuous current paths formed by the conducting phase in the insulating matrix. Willand[6] found that the resistance of mixtures of chromium ore and char increased dramatically when the volume fraction of the ore was increased above 35 per cent. The resistance of the system showed only slight changes when the volume fraction of the char was increased above 70 per cent. This explains the finding that, in coke-ore mixtures up to temperatures of 1200 °C, the resistivity is determined primarily by the resistivity of the ore. The volume fraction of ore up to that temperature was about 60 per cent.

The resistivity of the mixtures begins to drop as soon as heating starts, whereas that of the ore remains constant up to 350 °C. As shown in Fig. 5, the changes in volume experienced by a charge of ore and by a mixture of ore and coke between 25 and 900 °C are not very different, indicating that the volume fraction of coke in the mixture remains reasonably constant. These results support the theory that the decrease in the resistivity of mixtures of ore and coke between 25 and 900 °C is mainly due to the reduction of the higher oxides of manganese to a lower oxidation state.

The resistivity of a mixture of ore and coke is higher than that of the ore between 900 and 1200 °C. This increased resistivity is probably related to the physical and chemical changes that take place between these temperatures. It was observed that the sintering and consolidation of the ore were much more pronounced in the absence of a reducing agent. This could be because the reduction of ferrous oxide to metallic iron does not occur, or because of the physical separation of ore particles by coke particles.

The resistivity of the mixture drops rapidly above 1200 °C owing to the rapid contraction of the ore and the formation of slag. The contraction of the ore results in an increased volume fraction of coke in the mixture, and improved contact between particles. Willand[6] showed that small increases in the proportion of conductor reduced the resistance of the system significantly in that range of compositions in which the resistance of the mixutre is determined primarily by the resistance of the insulator.

Downing *et al.*[4] found that equal volumes of coke and molten slag have comparable resistances. However, in the mixtures considered in this investigation, the proportion of slag formed by heating to 1400 °C and then cooling was very small. It can therefore be said that the reduction in resistivity between 1200 and 1400 °C was attributable mainly to the rapid contraction of ore particles, which resulted in an effective increase in the volume fraction of coke in the charge.

It can be seen from Fig. 6 that no definite changes occurred in the resistivities of ore–coke mixtures for coke in the ranges 2,83 to 6,35 mm, 6,35 to 9,5 mm, and 9,5 to 12,7 mm. Hence, for temperatures below 1200 °C, the resistivity of the charge was determined mainly by the resistivity of the ore. The differences between the curves for the three mixtures were no greater than the differences obtained in duplicate experiments. Some variations between the curves for identical charges can
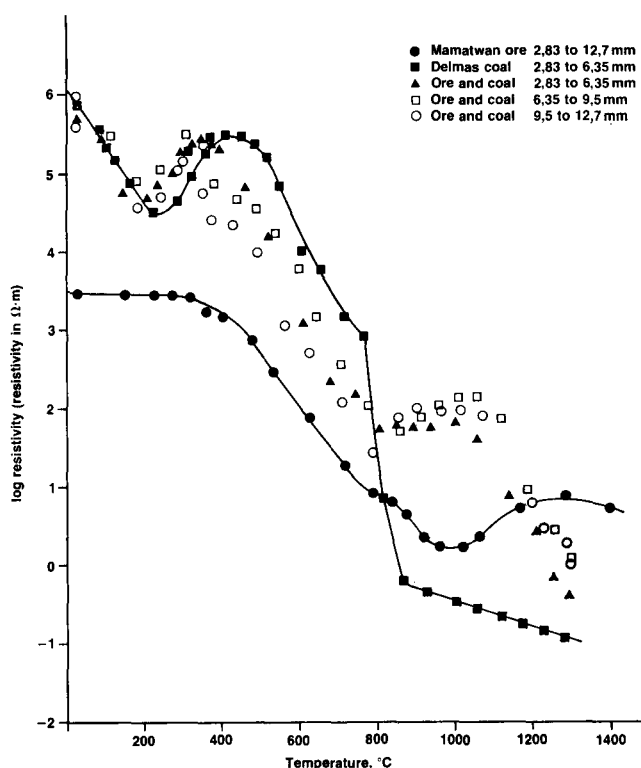

Fig. 7.—The variations, with increasing temperature, in the resistivities of mixtures of ore and coal containing coal of different size ranges

be expected owing to segregation and some re-arrangement of the bed during heating.

For temperatures below 1200 °C the coke did not form continuous current paths through the charge. Thus, the use of coke of different sizes in these size ranges cannot be expected to influence the resistivity of the charge significantly.

The resistivity of mixtures of ore and coke held at constant temperature showed an initial steep decrease, and then remained essentially constant. The period for the rapid decrease in resistivity was longer at low temperatures, and after two hours the resistivity at 1200 °C was 0,5 Ω.m, whereas at 1400 °C it was 0,1 Ω.m. The essentially constant value of the resistivity after the initial drop can probably be explained by the fact that the rate of mass loss is very low during retention of the charge at temperatures up to 1400 °C. This indicates that the proportion of slag and the volume fraction of the reducing agent in the charge remain approximately constant.

The resistivity of the coke–ore mixtures at 1400 °C was slightly lower than that of the coke at the same temperature.

The variation in the resistivity of mixtures of ore and coal with increasing temperature is shown in Fig. 7. The curves of resistivity against temperature for the ore and the coal individually are superimposed for comparison. It can be seen that, at temperatures of less than 600 °C, the resistivity of the mixtures is influenced strongly by the resistivity of the coal. Between 600 and 750 °C, the resistivity of the mixtures appears to be influenced by the resistivities of both the coal and the

ore. As shown in Fig. 5, the coal begins to contract at 600 °C and reduces the volume fraction of the coal in the mixture. It can also be seen from Fig. 7 that the resistivity of the mixtures continues to drop at temperatures beyond 600 °C, when the volume of the charge is reduced to less than the original volume. Hence, changes in resistivity cannot be related to the expansion and contraction of the charge.

The resistivity of the mixtures is higher than that of both the ore and the coal at temperatures between 800 and 1200 °C. The effect is similar to that observed for mixtures of ore and coke. For mixtures of ore and coal, the rapid decrease in resistivity starts at about 1050 °C, as compared with 1200 °C for mixtures of ore and coke. This appears to be related to the fact that mixtures of ore and coal begin to contract rapidly at 1050 °C, whereas for mixtures of ore and coke the same stage is reached at 1200 °C. This is further evidence that the rapid decrease in resistivity at high temperatures is mainly because of an increase in the volume fraction of the reducing agent.

At a constant temperature of 1300 °C, the resistivity decreased rapidly during the first 40 minutes and remained reasonably constant during the next 80 minutes. As for the lower temperatures, the size range of the coal did not have a definite influence on resistivity. The resistivities recorded at the end of a retention time of 2 hours ranged between 0,26 and 0,35 Ω.m.

The value of ln ρ in equation (2) was plotted against reciprocal temperature for mixtures of ore and coal, and of ore and coke, that contained reducing agents in the size range 6,35 to 9,5 mm. The activation energies for
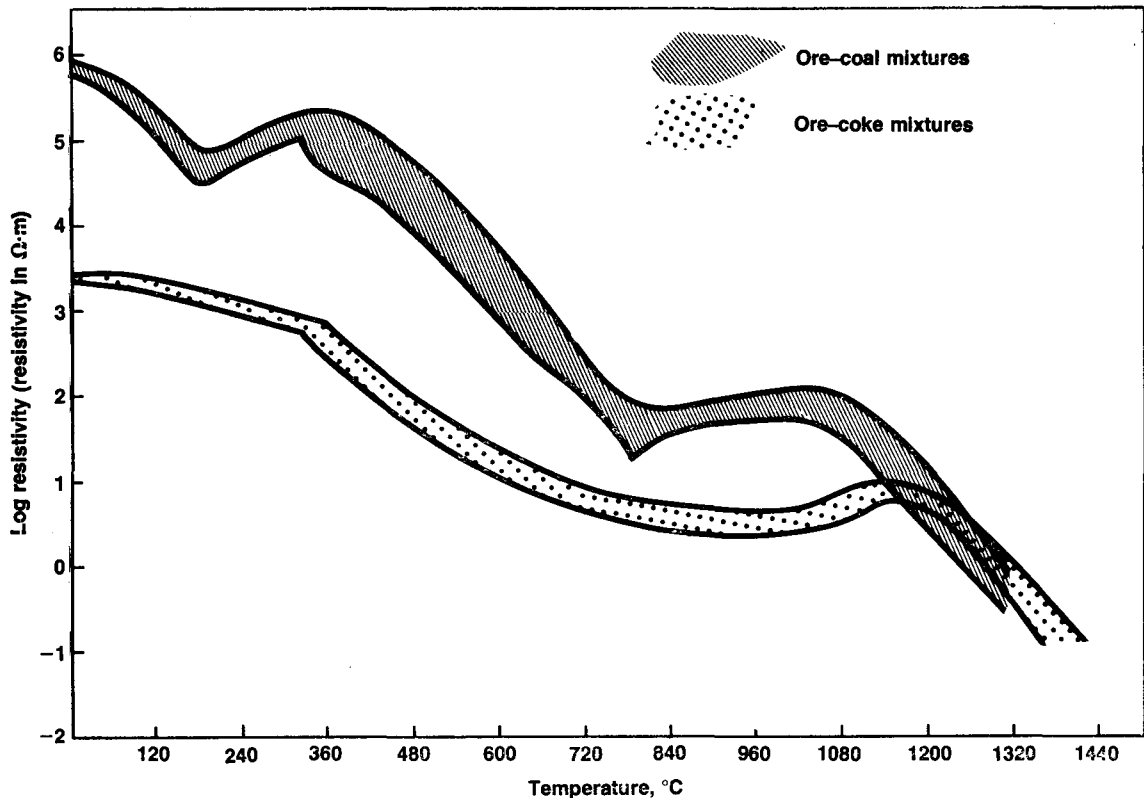

Fig. 8.—A comparison of the resistivities of mixtures of ore and coke, and of ore and coal, for different particle sizes of the reducing agents

conduction at temperatures greater than 1080°C are very similar for the two types of mixture, indicating that the mechanism for conduction is the same in the two cases.

Until now it has generally been accepted[2, 6, 7, 13, 21, 22] that the resistivity of a bed of materials decreases as the particle size of its components increases. This has been attributed to the fewer 'contact resistances' that result from an increase in the particle size of the materials.

Recent work done by Dijs[23] has shown that the resistivity of a bed of ore of fixed size, and of a reducing agent, may decrease to a minimum as the size of the reducing agent is increased, and then increase with a further increase in the size of the reducing agent. The variations in resistivity diminish rapidly as the mean size of both the reducing agent (conductor) and the ore (insulator) increases. When the mean size of the ore is 10 mm, no appreciable variations in resistivity occur when the mean size of the reducing agent is varied between 5 and 10 mm. These results were obtained at room temperature with mixtures of silica and char in the proportions 1:1 by volume, and show that, as for the SCICE charges, the resistivity can remain reasonably constant for considerable variations in the size of the reducing agent.

The resistivities with increasing temperature of mixtures of ore and coke and of ore and coal are shown as resistivity bands in Fig. 8. It will be seen that the resistivities of the two types of mixture are markedly different at low temperatures, but are similar at about 1200°C. This result could be expected in view of the fact that the resistivity of the two types of mixture is strongly influenced by the resistivity of the reducing agent for temperatures greater than 1200°C, and that the resistivity of the two reducing agents is very similar at 1200°C.

The variations in resistivity have been discussed with reference to temperature, and this assumes that, at a heating rate of 350°C an hour, the evolution of gaseous products from the ore and the coal was rapid enough to keep pace with the rising temperature. It is possible that a change in heating rate might alter the resistivity at a particular temperature. However, this would influence only the measurements taken at temperatures of 1000°C or less.

Summary and Conclusions

(1) The resistivity of good conductors is 10^{-7} Ω.m or less and that of insulators is 10^{11} Ω.m or more, whereas semi-conductors have intermediate resistivities[24]. The materials used in this investigation had resistivities in the semi-conductor range for temperatures of up to 1400°C. The ore and the coal each showed a negative temperature coefficient of resistivity, which is typical of semi-conducting materials.

(2) The resistivity of Delmas coal decreased markedly between 400 and 900°C owing to the evolution of volatile matter. The resistivities of coal and coke became similar at about 1300°C. This conforms to the theory[12] that the resistivity of carbonaceous reducing agents is primarily a function of heat treatment, and not of the rank and composition of the original coal.

(3) The resistivity of Mamatwan ore decreased rapidly when it was heated above 350°C owing to the decomposition of calcite and dolomite, the reduction of the higher oxides of manganese, and improved semi-conduction.

(4) The resistivity of mixtures of ore and coke is governed by the resistivity of the ore up to about 1200°C. At higher temperatures, the resistivity falls steeply and approaches that of coke owing to an increase in the volume fraction of coke and the formation of slag. The resistivity of mixtures was relatively insensitive to variations in the particle size of coke within the size ranges 2,83 to 6,35 mm, 6,35 to 9,5 mm, and 9,5 to 12,7 mm.

(5) The resistivity of mixtures of ore and coal was governed by the resistivity of the coal up to about 600°C. At higher temperatures, the resistivity appeared to be influenced by the resistivities of both the ore and the coal. Similarly, the resistivity of mixtures was relatively insensitive to variations in the particle size of coal within the ranges 2,83 to 6,35 mm, 6,35 to 9,5 mm, and 9,5 to 12,7 mm.

(6) It appears that the resistivity of mixtures of ore and coal and of ore and coke, was influenced more by variations in the packing of the bed than by differences in the particle size of the reducing agents. Mixtures of ore with coal or coke show similar behaviour with increasing temperature, although the resistivity of ore–coal mixtures is higher up to 1150°C. Above that temperature, the resistivity of the two types of mixture is similar. From this, it appears that the resistance of industrial furnaces should remain constant irrespective of whether coal or coke is used as the reducing agent, but in practice the resistance of a furnace increases when coal is used.

(7) The physical characteristics of Delmas coal and Iscor coke are substantially different: the coal is much weaker and has a layered structure. Under the conditions prevailing in the furnace shaft and in the active zone, the coal may break up into small particles owing to physical stresses and melting of the ash constituents. Thus, no direct comparisons can be made between the resistance of a furnace operating on coal and that of the same furnace operating on coke of the same initial size.

(8) The extremely high resistivities of ore–coke and ore–coal at low temperatures indicate that there is unlikely to be much conduction of current in the higher regions of a furnace. Thus, the resistance of a furnace is governed mainly by the conditions at the electrode tips and in the molten regions. The conditions in the lower part of the furnace are not well known, but it is generally accepted that boiling and turbulence occur, together with a local increase in the proportion of reducing agent.

(9) The resistivities measured in this investigation relate to those areas in the furnace where the charge is solid or partially fused. Under these conditions, the amount of slag that forms is small, its content of

manganous oxide is low, and segregation of the reducing agent is not expected to take place. Underneath the tips of the furnace electrodes, the charge is completely molten, the slag has a high manganous oxide content, and a buildup of reducing agent occurs. It is known that the resistivity of the slag decreases as its content of manganous oxide increases[4,8]. Thus, the resistivity of such a mixture can be expected to differ substantially from that of the experimental charges used in this investigation.

(10) To explain the very low resistances of furnaces, usually about 1 mΩ, it would be necessary for investigations to be conducted under conditions similar to those in the active zone of a furnace.

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References

1. SELMER-OLSEN, S. S. Trends in ferro-alloy production. *J. S. Afr. Inst. Min. Metall.*, vol. 71, no. 11. 1971. pp. 210-214.
2. LORENZ, M., and MARINCEK, B. The electric resistance of charge materials in electric smelting furnaces. *Schweizer Archiv.*, vol. 35. 1969 pp. 91-105.
3. CORREA DA SILVEIRA, R. Electrical and metallurgical reasons for some charges employed in electrical reduction furnaces producing ferro-alloys. *RM. Metallurgia*, BISI 8045. May 1969.
4. DOWNING, J. H., and URBAN, L. Electrical conduction in submerged-arc furnaces. *J. Metals*, N. Y., Mar. 1966 pp. 337-344.
5. URQUHART, R. C. A study of the production of high-carbon ferrochromium in the submerged-arc furnace. Ph.D. Thesis, University of the Witwatersrand, Johannesburg, 1972.
6. WILLAND, K., and JOCHENS, P. R. Measurement of the electrical resistance of ferrochromium furnace charges.

7. RENNIE, M. S., JOCHENS, P. R., and SOMMER, G. The electric resistance characteristics of the charge in electric reduction furnace. Johannesburg, National Institute for Metallurgy, *Report* 1606. Feb. 1974.
8. WOOLLACOTT, L. C., et al. The viscosities and electrical conductivities of slags associated with the production of high-carbon ferromanganese alloys. Johannesburg, National Institute for Metallurgy, *Report* 1687. Jan. 1975.
9. KOURSARIS, A., and SEE, J. B. Reactions in the production of high-carbon ferromanganese from Mamatwan ore. *J. S. Afr. Inst. Min. Metall.*, vol. 79, no. 6. 1979. pp. 149-158.
10. RASCH, E., and HINRICHSEN. Uber ein Besiehung zwischen Elektrishen Leitfähigkeit und Temperatur. *Z. Elektrochem.*, vol. 14., 1908. p. 41.
11. ANON. Electrical conduction in coals and cokes. *Coal* research in the *C.S.I.R.O.*, Australia. Aug. 1962. pp. 2-6.
12. INOUYE, K., and ROPPONGI, A. Structure of coke II — Physical properties of coke produced from various blended slacks. *Fuel*, vol. 34. 1955. pp. 471-479.
13. CORREA DA SILVEIRA, R. Electrical characteristics of some raw materials and loads for the production of cast iron in electrical reducing furnaces. *Metallurgia A.B.M.*, vol. 23, no. 119. 1967. pp. 739-744.
14. PILTER, P. The reduction, in the solid state, of manganese ores with carbon monoxide and hydrogen. *Kohaszati Lapok*, vol. 11. 1967. pp. 492-500.
15. BODSWORTH, C., and BELL, H. B. *Physical chemistry of iron and steel manufacture.* 2nd ed. Longman, 1972. p. 126.
16. DE VILLIERS, J. P. R. A mineralogical investigation of natural and heated Mamatwan manganese ore. Johannesburg, National Institute for Metallurgy. Unpublished.
17. PENTZ, R. D. An investigation of the beneficiation of low grade manganese ore with special reference to its reducibility. M.Sc. Thesis, University of Potchefstroom, 1970.
18. GRIMSLEY, W. D. A study of the reduction characteristics and mechanisms of reduction of manganese ore by solid carbon. M.Sc. Thesis, University of the Witwatersrand, Johannesburg, 1977.
19. BUECKE, F. Electrical resistivity of conducting particles in an insulating matrix. *J. Appl. Phys.*, vol. 43, no. 11. Nov. 1972.
20. GREKILA, R. B., and TIEN, T. Y. Conductivity discontinuity in a two-phase system. *J. Am. Cer. Soc.*, vol 48, no 1. 1965. pp. 22-25.
21. SCHEIDIG, K., et al. On the electric conductivity of coke. *Koks smola, gaz*, vol. 4, no. 12. 1969. pp. 362-367.
22. CORREA DA SILVEIRA, R. The influence of sizing charcoal on the productivity of electric reduction furnaces. *Metallurgia A.B.M.*, vol. 29, no. 189. Aug. 1973. pp. 543-546.
23. DIJS, H. M. A laboratory investigation of reducing agents for use in the electric-smelting industry. Johannesburg, National Institute for Metallurgy, *Report* 1997. Dec. 1978.
24. *Encyclopedia of science and technology*, vol. 12. New York, McGraw-Hill.

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