INFLUENCE OF TEMPERATURE AND PARTICLE SIZE ON REDUCTION OF CHROMITE ORE

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ABSTRACT

Experiments were conducted to study the influence of temperature, particle size and ore/coke ratio on the kinetics of reduction. The rate of reduction increased with temperature. The reduction of iron was completed at shorter time intervals at temperature above 1000ºC. Usually the reduction of chromium commenced after the reduction of iron was almost complete. Reduction was controlled by diffusion at low temperatures and by chemical reaction at higher temperatures. The nature of the reducing agent had a very significant influence on the rate of reduction. The study showed that chromium was converted into the carbide during reduction. Increasing the size of the reducing agent increased the rate of reduction initially. After a critical size, the rate of reduction decreased. However, increasing the size of the ore particle decreased the rate of reduction, initially. Beyond a critical size, it increased. An optimum particle size of the chromite ore and that of coke must be chosen, particularly in the production of agglomerates to achieve maximum degree of reduction.

1. INTRODUCTION

Different types of ores are used in the production of ferro-chromium in the submerged-arc furnace [S.A.F.). The ores may be used in the lumpy form or as agglomerates such as briquettes and pellets. A blend of ores and a blend of lumps and agglomerates are used simultaneously in the process to meet various process requirements. It is necessary to understand the kinetics of reduction of the ores and the influence of operation parameters on this in order to optimise the operation parameters. Experiments were carried out to understand the influence of temperature, particle size and ore/coke ratio on the reducibility of two types of chromite ores.

2. REDUCTION OF CHROMITE

The reduction of the chromite can be represented by :

$$FeCr_2O_4 + 4C \rightarrow Fe + 2Cr + 4CO \qquad (1)$$

Usually, the carbides are formed during reduction with carbon. They are complex containing more than one ion in the cationic sub-lattice:

$$FeCr_2O_4 + 4C \rightarrow Fe_3C + 2Cr_7C_3 + 4CO \qquad (2)$$

The actual mechanism of reduction is believed to occur in two steps as given below:

$$FeCr_2O_4 + 4CO \rightarrow Fe + 2Cr + 4CO_2 \qquad (3)$$

$$C + CO_2 \rightarrow 2CO \qquad (4)$$

Barcza et.al.[1] studied the reduction of chromite using a thermal balance. Reduction occurred above $1000^{O}C$. Higher the Cr/Fe ratio, higher was the temperature at which the maximum rate of reduction occurred. The rate of reduction decreased after reaching a maximum. The kinetics of reduction was best described by :

$$1-(2/3)x - (1-x)^{2/3} = kt \qquad (5)$$

where ‘x’ is the fraction reduced and ‘t’, the time. The authors argued that the rate decreased with increasing particle size since the specific surface area decreased and the reduction depended increasingly on the diffusion of carbon through the bulk of the particle. Rankin[2] studied the reduction of chromite ore in the temperature range 1100^{O}C-1500^{O}C. The author concluded that in the case of reduction with graphite also, the reduction proceeded through reaction between the ore and carbon monoxide. Whereas pure CO gas did not reduce the chromite ore, CO in equilibrium with graphite reduced. Vazarlis and Lekatou[3] argued that reduction was through solid carbon. The reduction kinetics was best described by expression [5], above. The rate constant increased with decreasing particle size of the ore and that of the reductant. Lekatou and Walker[4] studied the solid state reduction of chromite ore in the temperature range 1100^{0}C-1470^{0}C. Briquettes of 1cm diameter were used. It was shown that CO was the only gaseous reaction product. At any given temperature, there was an optimum time and carbon addition after which no further increase in reduction occurred. The authors described the mechanism of reduction:

a) At 1000 ^{O}C, metallisation occurred within the grain close to the surface. Nuclei of iron were formed to be immediately followed by carburisation.
b) In the second stage, metallisation proceeded by the growth of the metallic nuclei and the diffusion of iron and chromium to the surface.
c) In the third stage, CO diffused through pores created in the spinel due to the reduction reaction in the spinel.
d) Internal metallisation followed the above, through a mechanism involving the transfer of carbon.
e) Eutectic compositions formed in the gangue and at the grain boundaries. Chromium dissolved in the slag as Cr^{2+}.

Nafziger et.al.[5] studied the reduction of two types of chromite ores using different reducing agents, in the temperature range 1100^{0} C-1500^{0}C. Among the reductants used (coal char, coke breeze, metallurgical coke, petroleum coke and shell carbon), coal char provided the highest degree of reduction. At 1400^{0}C and 1500^{0}C, metallurgical coke provided the best results. In all cases, the degree of reduction was the highest in the first 15 minutes. These authors argued that the formation of a mixed (iron, chromium) carbide acted as an effective reducing agent and as a medium to transport carbon to the chromite. Nafziger et.al[6] studied the reduction of four chromite ores. They used a rotary kiln to carry out the studies. Nearly complete reduction of iron plus chromium was obtained at 1350°C. A temperature of 1150°C was required for iron reduction. Reddy et.al[7] carried out reduction studies on three chromites using TGA. It was found that the reduction rate dropped significantly when the C/FeO ratio was increased. The reduction in the rate was attributed to the lowering of the P_{CO2}/P_{CO} ratio which decreased the rate of oxidation of carbon per unit mass of carbon. If the reduction rate is controlled by the rate of oxidation of carbon, this effect is expected. Perry et. al.[8] have modeled the reduction of chromite. They have considered each chromite particle as comprised of concentric layers of spinel unit cells. One-eighth of the 64 tetrahedral sites in the spinel are occupied by divalent cations and one-half of the 32 octahedral sites are occupied by trivalent cations. The cations are interchanged between the unit cells by the presence of CO on the surface of the particle. The reduction mechanism is described as follows:

a) Reduction of trivalent iron ions at the surface of the particle.
b) The inward diffusion of Fe^{2+} interstitials formed by the reduction of trivalent ion in unit cells on the surface.
c) The reduction of Fe^{2+} in normal unit cells on the surface leading to outward diffusion of Fe^{2+} ions. This is balanced by the inward diffusion of Mg^{2+} ions.
d) Reduction of Cr^{3+} to Cr^{2+}.
e) Reduction of Fe^{2+} in the inner core. This is caused by the migration of Cr^{2+} either from the sesquioxide or from the surface of the inner spinel.
f) Reduction of the chromium ions in the sesquioxide and in the spinel.

Soykan et.al.[9] proposed a mechanism of reduction which consisted of the reduction of Fe^{3+} ions on the surface of the particle to the divalent state. This was followed by the reduction of Fe^{2+} to metallic iron and Cr^{3+} to Cr^{2+}. The Cr^{2+} ions diffused inward reducing Fe^{3+} to Fe^{2+} inside the spinel. This resulted in zoning of the particle. The inner core consisted of the original chromite. The outer zone was iron-depleted. The final product of reduction was a spinel, $MgAl_2O_4$, free from iron and chromium.

During the reduction of chromite ores, the following stages of reduction occur: (a) reduction of iron oxide to iron, (b) conversion of the iron into the carbide, (c) reduction of chromium oxide and (d) conversion of the chromium into the carbide. Steps (b) and (c) may occur parallely, depending on the conditions. The iron oxide may act as a carrier of carbon and enhance the rate of reduction. In the latter stages of reduction, an iron-chromium liquid alloy may form at high temperatures. This liquid, enriched in carbon, may enhance the rate of reduction. Higher level of carbon dissolved in iron will lower the melting point of the alloy and assist in early formation of the liquid. Therefore, the formation of this liquid depends on the kinetics of reduction of the chromium and iron oxides and the temperature of reduction. This liquid breaks down the ore dissociating the grains. This enhances the rate of reduction. Addition of flux has a similar role on the kinetics of reduction. A flux that can form a low-melting slag combining with the gangue of the ore can break down the ore. CrO dissolves in this slag and this enhances the rate of reduction. On the other hand a flux that does not form a low-melting slag can actually retard the reduction process by increasing the distance between the ore particle and the reductant.

It is observed that up to 40% reduction, the rate is controlled by the interface area between the reduced and unreduced part of the ore[10]. In most of the ores, 40% reduction would represent a case when all the iron in the ore alone is getting reduced with no reduction of chromium. It is believed that even at high temperatures, reduction of chromium starts only after the reduction of iron is completed[10,11]. The mechanism of reduction may depend on the experimental conditions. But, it is likely that in most cases, reduction progresses through the reaction between the ore and CO gas until the formation of a liquid phase, metal or slag. It has been generally observed that, lower the Cr/Fe ratio in the ore, higher is the reducibility. This is usually attributed to the higher amount of iron formed which acts as a catalyst for the reduction of chromium by forming the carbide, Fe_3C.The ores with higher and lower Cr/Fe ratios usually have different crystallographic structures and different types of gangue materials. Moreover, the oxidation state of iron also would be different in these two types of ores. No single model of the kinetics of reduction can adequately describe the process. The kinetics of reduction would depend on the temperature, the extent of reduction and other conditions.

3. EXPERIMENTS

The experimental apparatus used in this study has already been described[12]. It consisted of a train of two tubular furnaces, one of which was filled with coke to remove oxygen from a stream of argon. The purified gas was passed through the main furnace containing a mixture of the ore and the reducing agent in a quartz capsule. The capsule was introduced into the ‘constant-temperature’ zone of the furnace when the required temperature was attained. After being kept at the temperature for the desired period of time, the capsule was quenched by pushing rapidly to the cooler regions of the furnace. Mass of the capsule containing the sample was recorded at the beginning and at the end of the experimental run.

Two types of ores were used in the experimental investigation, hard lumpy ore and friable ore. The chemical analyses of the ores are given in table 1. Raw coke and devolatalised coke were used as the reducing agents. Raw coke contained about 51% volatile matter and 3.88% ash. Devolatalised coke was obtained from the raw coke by heating the raw coke in argon atmosphere at 1000 °C.

Table 1 : Chemical analysis of the ores used in experiments (wt%)

Ore Type	**Cr_2O_3**	**Fe_2O_3**	**Al_2O_3**	**CaO**	**MgO**	**SiO_2**
Hard lumpy	39.02	11.73	8.62	2.90	18.93	15.02
Friable	41.02	26.45	13.87	0.20	8.30	5.30

The present study and reports in literature show that iron gets reduced at lower temperatures and the reduction of chromium commences after almost all the iron in the ore has been reduced. Therefore, in the temperature range and time interval when iron alone is reduced, the degree of reduction has been defined as the ratio of the mass loss during the reduction run to that expected if all the iron in the ore gets reduced. Similarly, in the temperature range and time interval where chromium gets predominantly reduced, the degree of reduction is defined as the ratio of the mass loss during the reduction run to that expected when all the chromium in the ore gets reduced. There can be an overlap of the reduction of iron and chromium at longer time intervals, particularly at higher temperatures. The region of overlap is not significant. Therefore, it does not influence the kinetic analysis to a significant extent.

The degree of reduction of iron was defined by :

$$(\%R)_{Fe} = [(W_2 - W_1) / W_{Fe}] \times 100 \qquad (6)$$

where 'W_2' is the mass of the (ore+reductant) mixture before the commencement of the experimental run; 'W_1', the mass of the mixture at the end of the experimental run and 'W_{Fe}', the total mass loss to be expected if all the iron in the sample is reduced and carbon monoxide is the gas formed.

When the total mass loss exceeds that to be expected from the reduction of all the iron in the sample, the reduction of chromium is assumed to have commenced. When the reduction of iron is complete, the degree of reduction is represented by (%R)Cr which is defined by :

$$(\%R)_{Cr} = [(W_2 - W_1)/W_{Cr}] \times 100 \qquad (7)$$

where 'W_1' and 'W_2' have the same meaning as above. W_{Cr} is the loss in mass to be expected if all the chromium in the sample is reduced and carbon monoxide is the gas formed. Iron was in the form of Fe_2O_3[14]. This was taken into consideration when computing $(\%R)_{Fe}$.

4. RESULTS AND DISCUSSION

4.1 Reduction of Friable Ore with Devolatalised Coke

The percentage reduction of chromium increased with increasing temperature and time. The rate of reduction increased up to a maximum with time and then became constant. At low temperatures (900-1150°C), iron was reduced predominantly. At 1150°C, after 180 minutes of reduction period, iron oxide was reduced completely and chromium oxide started getting reduced. Chemical analysis of partly reduced ores did not show presence of any metallic chromium. Iron was reduced at shorter time intervals whereas chromium took longer intervals at any given temperature. In the higher temperature range, 1200-1300°C, after 180 minutes of reduction period, percentage metallisation of iron and chromium decreased. This may be due to the fact that more of carbides were formed in this region and the analytical technique used did not analyse the metals in the carbide. The results of the experiments are summarised[12] in table 2.

Table 2: Reduction of Friable ore With Devolatalised Coke

Temp(°C)	Time(min)	$(\%Fe)_R$	$(\%Cr)_R$
1000	20	30.97	0
	60	57.79	0
	120	75.65	0
1050	20	35.97	0
	60	61.26	0
	120	77.90	0
1100	20	46.14	0

Table 2: Reduction of Friable ore With Devolatalised Coke (Continued)

	60	75.98	0
	120	94.13	0
1150	20	48.77	0
	60	77.44	0
	120	99.65	0
1200	20	63.92	nf
	60	86.70	nf
	120	100.00	6.21
1250	20	69.24	nf
	60	96.29	nf
	120	100.00	17.45
1300	20	84.13	nf
	60	100.00	17.61
	120	100.00	41.96

Note : nf – not found

4.2 Reduction of Friable Ore with Graphite

Chromium in the ore was not reduced by graphite in the temperature range studied whereas iron was reduced. The mass loss in the sample was less than that required for 100% reduction of iron in the ore. Chemical analysis of the reduced samples also did not show the presence of metallic chromium. The results are given in table 3.

Table 3: Reduction of friable ore with graphite

Temperature, °C	Time, minutes	(%Fe)R
900	45	16.69
	60	18.00
1000	45	33.47
	60	37.01
1050	45	50.87
	60	56.21

4.3 Reduction of Friable Ore with Raw Coke

Table 4 gives the reducibility of friable ore with raw coke[12]. Whereas chromium was not reduced until the temperature reached 1200 ×C when devolatalised coke was used as the reducing agent, the reduction of chromium started at 1000 ×C, when raw coke was used as the reducing agent. More than 90% reduction of chromium was achieved at 1150 ×C. the degree of reduction of iron was also higher when raw coke was used compared to the case when devolatalised coke was employed.

Table 4: Reduction of Friable Ore With Raw Coke

Temp(°C)	Time(min)	$(\%Fe)_{Red}$	$(\%Cr)_{Red}$
900	30	28.88	Nf

Table 4: Reduction of Friable Ore With Raw Coke (Continued)

	60	32.80	Nf
	120	37.80	nf
1000	30	60.61	nf
	60	93.06	nf
	120	100.00	13.99
1050	30	92.69	nf
	60	100.00	15.15
	120	100.00	41.49
1100	30	100.00	nf
	60	100.00	32.27
	120	100.00	60.46
1150	30	100.00	34.07
	60	100.00	63.36
	120	100.00	91.44

Note : **nf- not found**

4.4 Effect of Ore Size on Reducibility

Figures 1 and 2 describe the effect of the size of the ore on its reducibility. Raw coke was used as the reducing agent. The size of the reducing agent was 250 µm. The ore/coke (mass) ratio was 2.0, for friable lumpy ore and 2.5 for hard lumpy ore.

The reduction reaction was carried out for one hour at each temperature. The rate of reduction decreased with increasing size of ore. This can be due to the decrease in specific surface area available for reduction with increasing size of the ore particle. However, on increasing the size of ore particle from 250 to 300 µM, the rate of reduction increased. It is possible that the nature of the rate-controlling mechanism changes on increasing the size. It is seen that at the lowest particle size of the ore, chromium gets reduced but not at higher particle sizes. This behavior is exhibited by both types of ores.

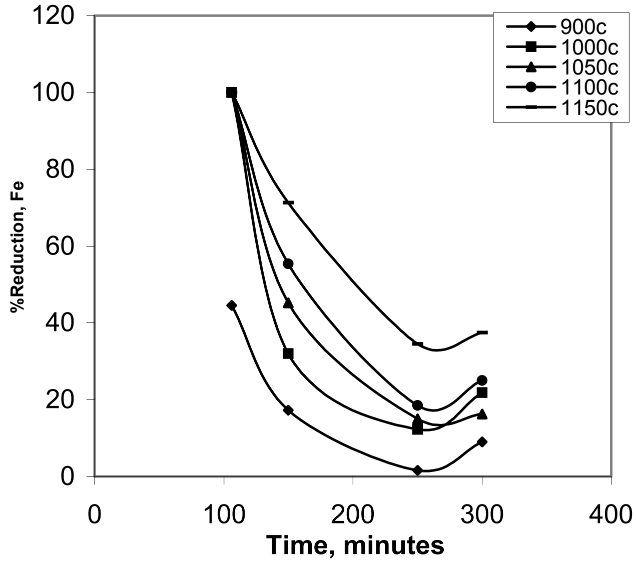

Figure 1: Influence of size of friable lumpy ore on rate of reduction

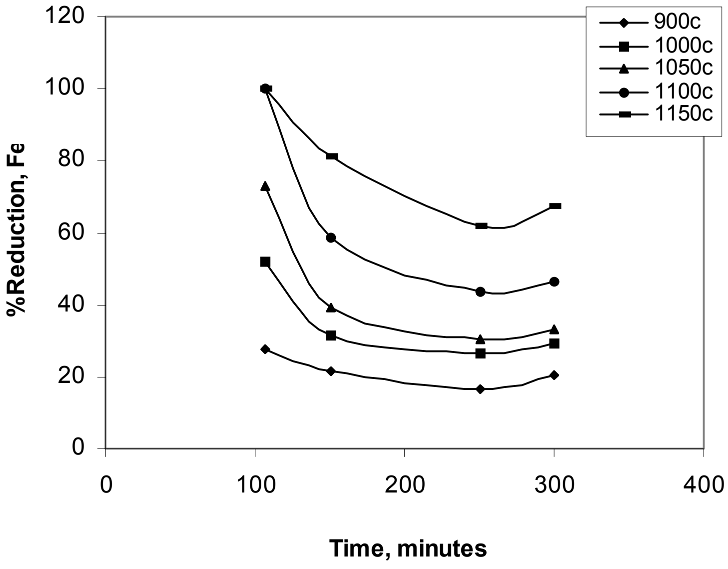

Figure 2: Influence of size of hard lumpy ore on rate of reduction

4.5 Effect of Size of Reducing Agent on Rate of Reduction

Figures 3 and 4 show the effect of the size of the reducing agent on the reducibility of the friable lumpy ore and hard lumpy ore, respectively. Raw coke was used as the reducing agent**.** The size of the ore was 106 µm**.** The ore/coke ratio was 2.0 for friable ore and 2.5 for hard lumpy ore. The reduction time was one hour**.** It is seen that the recovery of iron, $(\%Fe)_R$ increased with increase in the particle size of the reducing agent, initially The recovery decreased with further increase in the particle size of the reducing agent.

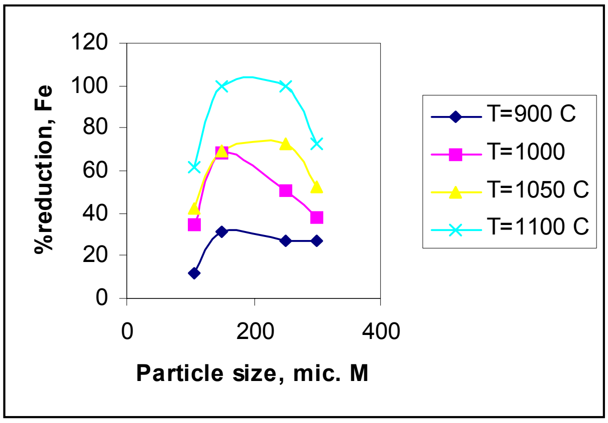

Figure 3: Influence of size of reductant on the reduction of hard lumpy ore

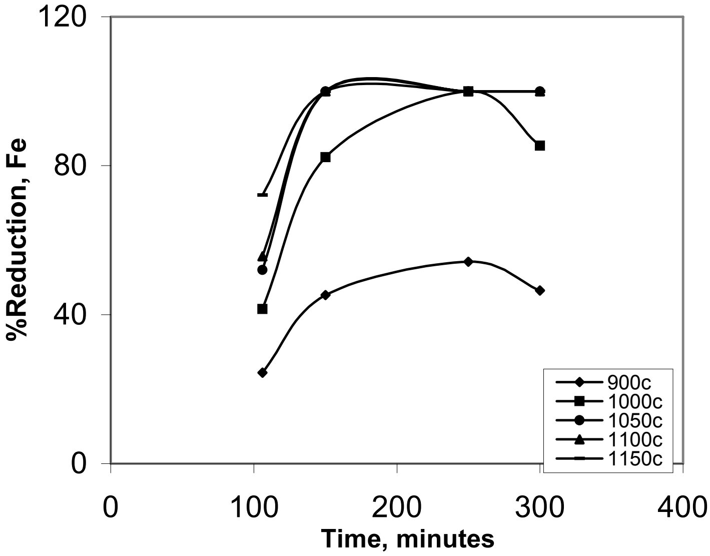

Figure 4: Influence of size of coke on rate of reduction of iron in friable lumpy ore

4.6 Discussion

The investigation showed that iron in the chromite ores was reduced at lower temperatures, ahead of chromium. The reduction of chromium started after almost all the iron in the ore was reduced. Measurement of mass loss and chemical analysis of the reduced samples confirmed this. Carbides of iron and chromium were formed as established elsewhere through XRD studies[13]. Raw coke was more effective as a reducing agent compared to the devolatalised coke. The high level of volatile matter in the raw coke, apparently, enhanced the rate of reduction. Reduction was controlled by diffusion at low temperatures and by nucleation at high temperatures[12]. The influence of particle size on the rate of reduction is complex. This phenomenon has to be investigated in greater detail to optimise the parameters in the production of suitable agglomerates.

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