REDUCTION OF CHROMITE ORE AT DIFFERENT FLOW RATES OF INERT GAS

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ABSTRACT

Pre-reduction of chromite outside the submerged-arc furnace(SAF) can significantly lower the specific power consumption in the SAF process. Conventional processes for the pre-reduction of the ore operate at relatively high temperatures, at 1400-1500 °C. It is possible to enhance the rate of reduction at low temperatures by optimizing the flow rate of inert gas over the reaction site. The influence of the flow rate of inert gas on the rate of reduction of chromite ore was investigated. The rate of reduction initially decreased wit the flow rate of the gas. It increased subsequently at higher flow rates to be followed by a decrease again. There was an optimum flow rate at which maximum reduction could be obtained. It was possible to achieve high levels of reduction at 1200 °C by optimising the flow rate of the gas. The degree of reduction obtained was comparable to that obtained at 1400-1500 °C, by conventional process routes.

1. INTRODUCTION

Attempts have been made to reduce the chromite ore outside the submerged-arc furnace(SAF) using cheaper sources of energy such as fossil fuels, in order to reduce the consumption of electric power in the SAF. Processes are available for the pre-reduction of the ore outside the submerged-arc furnace[1]. The 'pre-reduced' ore is charged into the SAF. These processes of pre- reduction usually operate at about 1400°-1500°C. A process that operates at low temperatures will have several advantages such as less operational cost; less capital cost and increased life of refractory used in the 'pre-reduction' furnace. Experiments were carried out to explore the possibility of reducing the chromite ore at relatively lower temperatures using carbon as the reducing agent. Several parameters can be optimized to enhance the rate of reduction at low temperatures. Since the reduction involves gaseous products and reactants, it will be possible to alter the rate of reduction by altering the rate at which these gases are swept away from the reaction site. Experiments were conducted to understand the influence of flow rate of inert gas on the rate of reduction of chromite ore using carbon as the reductant.

2. REDUCTION OF CHROMITE ORES

The chromite ores have a spinel structure which can be represented by the general formula $(Fe,X)O.(Cr,Y)_2O_3$ .Here, X and Y are elements which dissolve in the two different cationic sub-lattices. The two lattices are the tetrahedral and octahedral sites in the structure, respectively. Divalent cations such as Mg occupy the tetrahedral site and trivalent cations such as Al, Fe etc. occupy the octahedral sites. Iron gets reduced easily compared to chromium. In the later stages of reduction, complex carbides of iron and chromium are formed. The reduction reaction can be represented to occur through direct reaction between carbon and the oxide:

$$M_xO_y + yC = xM + yCO \tag{1}$$

However, usually carbon first gets oxidized to carbon monoxide which in turn reduces the oxides. The reaction is represented by:

$$C + CO_2 = 2CO \tag{2}$$

$$M_xO_y + yCO = xM + yCO_2 \tag{3}$$

It is believed that the reduction of chromite ores follows the latter mechanism. The Boudard reaction, reaction (2), is rate controlling at low temperatures. Above 1000°C, it is rapid and is not expected to control the rate of reduction.

3. ENHANCEMENT OF REDUCTION RATE

Table 1 compiles the extent of reduction observed by various investigators at different temperatures and time intervals. It is observed that generally iron gets reduced completely at 1100°C. The reduction of chromium is initiated at 1200°C and is complete around 1500°C. Presence of silica can enhance the reaction rate. A low melting slag formed during the reduction process breaks down the grains exposing larger areas to reduction. The melting point of the slag is reduced by the dissolution of CrO in the slag. The CrO, in turn, is reduced by contact with carbon. However, the liquid slag can block the pores of the pellets of (ore+reductant) mixture and arrest the flow of the gas away from the reaction site. This can retard the reaction. The influence of catalyst on enhancing the rate of Boudard reaction has been reported by several investigators. The reduction of chromium oxide occurs at a temperature at which this reaction is not rate-determining. Hence, these catalysts have little effect on the reduction rate at these temperatures.

The reduction of the oxide is accompanied by the formation of a gaseous product. If this is removed continuously from the reaction site, the reaction can be driven in a direction facilitating the reduction of the oxide and the formation of the metal. Consideration of expression (3) above, would show that any attempt at removing the gaseous reaction product would remove one of the reacting species viz. the CO gas, from the reaction site. This will adversely affect the reaction rate. The same is true for reaction (2), also. On the other hand, if the reaction proceeds through direct reduction as given by equation (1), removal of the gaseous reaction product can help in enhancing the rate of reaction. The gaseous phase can be removed by flushing the system with a stream of an inert gas at a suitable flow rate. Therefore, studying the effect of the flow rate of the inert gas can help in elucidating the mechanism of reduction and possibly lead to a method of enhancing the reduction rate.

Table 1: Degree of reduction of chromite ores reported by various authors

| Type of ore	Temp(^{0}C)	Time(min)	%Reduction	Reference
High Plateau	1200	60	10	13
Skoumtsa	1200	60	16	14
Transvaal	1200	30	75	15
South African	1200	40	25	14
Synthetic	1210	45	30	16
Cypriot	1200	40	35	14

4. INFLUENCE OF INERT GAS FLOW RATE ON THE REDUCIBILITY OF OXIDES

No study has been reported on the influence of the flow rate of inert gas on the carbo-thermic reduction of chromite ores. However, similar studies have been carried out in the case of other oxides. Chen[2] studied the rate of reduction of zinc oxide with carbon.

$$ZnO(s) + CO(g) \rightarrow Zn(g) + CO2(g) \tag{4}$$

$$C(s) + CO2(g) \rightarrow 2CO(g) \tag{5}$$

He found that that the rate of reduction decreased with increasing flow rate of nitrogen. It was argued that as the flow rate of nitrogen increased, more of CO and CO_2 were carried away by the inert gas. The effect of

flow rate of inert gas on the segregation roasting of laterite ore has been investigated[3]. The efficiency of the segregation process depended on the flow rate of argon. Kanari and Gaballah[4] studied the kinetics of chlorination of chromite with mixtures of (Cl_2+O_2) and (Cl_2+N_2) This study showed that below a flow rate of 50 l/h, the rate of reaction increased with flow rate. The carbo-chlorination of zircon[5] represented by:

$$ZrSiO4 + 4C + 4Cl2 \rightarrow ZrCl4 + SiCl4 + 4CO \tag{6}$$
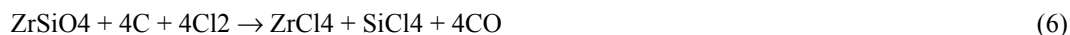
showed that, the rate of reaction increased with increase in total gas flow rate. Beyond a critical flow rate, the rate of reaction decreased. This study showed that there was an optimum flow rate at which the rate of reaction was the highest.

Y.K.Rao[6] has pointed out that the "true" direct reduction of oxides by carbon (reaction (1) above) was possible when the gaseous products of reduction were removed from the reaction system as soon as they are formed. When iron ore was reduced with carbon, an increase in the flow rate of nitrogen decreased the amount of oxygen removed from the ore due to reduction[7]. After a critical flow rate, the rate of flow of nitrogen had no effect. Literature shows that the reduction of oxides with carbon can be influenced by the flow rate of inert gas over the reaction site. If sufficient range of flow rate is employed, a peak in the degree of reduction is observed with respect to the flow rate.

5.   EXPERIMENTAL STUDIES

The apparatus used for experimental studies has been described elsewhere[8]. The experiments were carried out inside a reaction tube which had a constant-temperature zone approximately 40 mm in length. The temperature was uniform within this zone within +2 °C. Argon gas containing a maximum of 4 ppm oxygen was purified by passing it through a bed of coke maintained at 800 ×C inside a tubular furnace. Calcium chloride was used to remove moisture from the gas before it entered the furnace. The purified gas was passed through the main reaction tube which contained a quartz capsule containing a mixture of the chromite ore and coke, in the desired proportion in the constant-temperature zone of the furnace. The chemical analysis of the chromite ore used in the experiments is given in table 2. The coke used in the experiments contained 3.88% ash and 48.07% volatile matter. Time, temperature, proportion of reductant and flow rate of argon were the parameters varied during the study. When the main furnace had attained the required reaction temperature, the quartz capsule containing the reaction mixture was quickly introduced into the constant-temperature zone of the furnace. The capsule was held at this temperature for the required period of time and then quenched by pushing it rapidly to the cooler regions of the furnace at the end of the reaction period. The quartz capsule was a cylindrical bottle with two holes, measuring about 3mm diameter, one at the either end along the axial surface, parallel to the long axis. These holes served to introduce the sample and to allow the flow of argon.

Table 2: Chemistry of ore (mass%)

$Cr_2O_3(\%)$	$Fe_2O_3(\%)$	$Al_2O_3(\%)$	MgO(%)	$SiO_2(\%)$
43.0	23.0	2.38	2.47	15.30

5.1 Degree of Reduction

The following definition was used in analysing the experimental data.

Percentage reduction,

R=(oxygen removed/theoretical oxygen removed if all Cr&Fe in the ore are reduced)*100   (7)

To analyse the influence of various parameters on the reducibility of the ores, it is essential to understand the mechanism of reduction of ores. Various studies have shown that the reduction of iron in the ore is completed before the reduction of chromium occurs[9,10,11]. Therefore, it is possible to split the change in mass

into two categories: (a) that occurring due to the reduction of iron, in the initial stages and (b) that due to the reduction of chromium in the latter stages. The difference between the actual change in mass and that required for the complete reduction of iron oxide is taken to be arising out of the reduction of chromium oxide. Therefore, it is possible to estimate the extent of reduction of chromium using the following expression:

$$\%(Cr)_{Red} = [(\text{change in mass} - \text{change in mass for complete reduction of Fe}) / \text{mass loss for complete reduction of Cr})*100] \tag{8}$$

Tables 3-5 give the experimental results obtained on the reduction of the chromite ores under various conditions.

Table 3: Reduction of chromite ore at 1200^0C and flow rate 1 litre/minute, ore/coke (mass ratio)=10/2; reduction period = 60 minutes

Time(min)	%Red	(%Cr)red
60	37.61	6.34
120	39.40	9.04
180	42.96	14.38
240	44.22	16.27

Table 4: Reduction of chromite ore at 1200^0C and flow rate 1 litre/minute, ore/coke (mass ratio) = 10/4; reduction period = 60 minutes

Time(min)	%Reduction	((%Cr)red
60	37.98	6.92
120	43.35	14.96
180	47.84	21.72
240	51.33	26.95

Table 5: Reduction of chromite ore at 1200^0C for 60 minutes, ore/coke (mass ratio)= 10/12

F.L.(l/m)	%Reduction	(%Cr)red
1	52.45	28.63
2	54.19	31.24
3	51.03	26.50
0.125	57.98	36.92

Figure 1 illustrates the influence of argon flow rate on the extent of reduction measured in terms of mass loss. The extent of reduction is higher at higher flow rates and then it decreases at intermediate flow rates. Subsequently, it increases. A similar trend is observed at other temperatures and time intervals, also, as seen in figure 2.
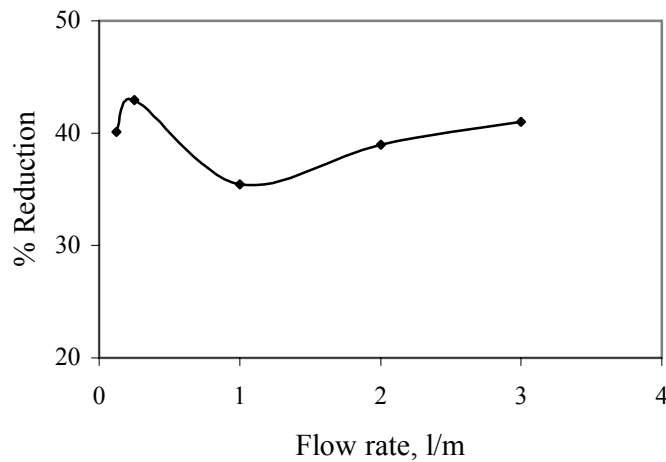
Figure 1: Influence of Argon Flow rate on Reduction at 1200 ℃ (time= 60 minutes; ore/coke (mass ratio) =10/12)
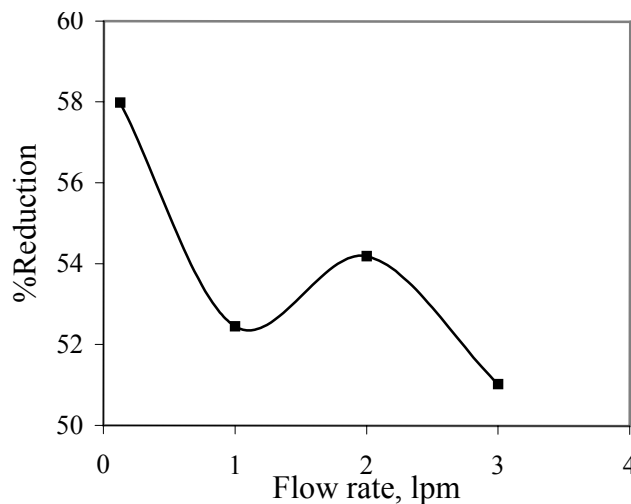

Figure 2: Influence of Argon Flow Rate on Reduction at 1250 ℃ (time=60 minutes; ore/coke (mass ratio) = 10/12

6. DISCUSSION

The rate of reduction increases initially with increase in flow rate of argon. It is possibly becausee the inert gas sweeps CO_2 gas away from the reaction site. This enhances the rate of reduction of the oxide by CO gas since the gaseous product of the reduction reaction is removed from the reaction site. However, as the flow rate increases further, the depletion of CO_2 gas from the reaction site is enhanced to such a level that the oxidation of carbon by CO_2 is reduced and the generation of CO by this oxidation reaction is retarded. Therefore, there is an optimum flow rate at which maximum reduction of iron and chromium from the ore can be obtained. More experimental investigations are required to confirm this mechanism of the influence of flow rate on the reduction. However, there is adequate experimental evidence to show that the level of reduction ob-

tained at 1200 °C can be as high as 40% reduction of chromium and 100% reduction of iron at the appropriate flow rate of argon[12]. The results are comparable to those obtained in the existing industrial processes of pre-reduction of chromite ore at 1400-1500 °C. It is obvious that the present study has demonstrated that high levels of pre-reduction of chromite ore can be obtained at relatively low temperatures. The process can overcome many of the drawbacks of pre-reduction at high temperatures, as already discussed.

7. CONCLUSION

Experimental investigations show that high degrees of reduction of chromium and iron in chromite ore can be achieved by optimising the flow rate of argon gas over the reaction site. There is an optimum flow rate at which maximum reduction can be obtained. The degree of reduction obtained at 1200 C, using this process is comparable to that obtained in conventional industrial pre-reduction processes at 1400-1500 °C.

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