

## **THERMOGRAVIMETRIC STUDIES ON THE REDUCTION OF HEMATITE ORE FINES BY A SURROUNDING LAYER OF COAL OR CHAR FINES. PART 1. ISOTHERMAL KINETIC STUDIES**

S. MOOKHERJEE \*, H.S. RAY and A. MUKHERJEE

*Department of Metallurgical Engineering, Indian Institute of Technology,  
Kharagpur 721 302 (India)*

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### **ABSTRACT**

Although there is a good deal of literature on the reduction of iron oxide by carbonaceous materials, it mostly covers systems where the oxide and reductant are thoroughly mixed. The present work concerns a system where the oxide and the reductant are not mixed.

The kinetics of isothermal reduction of a central column of ore fines by a surrounding layer of coal fines have been studied by thermogravimetry. The course of reaction has been expressed in terms of a “degree of reaction” ( $f$ ) defined as weight loss measured at a given time ( $t$ ) with respect to the maximum possible weight loss. The kinetic data expressed in terms of  $f$  have been analysed using a kinetic law appropriate for diffusion-controlled processes and apparent activation energies have been calculated for reduction by coal and char. The results have been interpreted to identify carbon gasification as the rate-controlling step.

### **INTRODUCTION**

Development of solid-reductant based direct reduction processes has generated a keen interest in the study of reduction of iron oxides by carbonaceous materials. In recent years many people have reported kinetic studies on mixtures of iron oxide and carbon [1–7]. Such studies are of relevance to conventional processes using solid reductants, such as the rotary kiln type processes. There are, however, other processes, such as the Hogenas process [8] and the Bardin Institute process [9], which do not use a mixed system. In these processes the ore and reductant essentially remain separate, coming into contact only at an interface. A second feature of these processes is that they utilize ore and coal fines directly, thus avoiding agglomeration procedures.

In the present work, the reduction of a central column of ore fines by a

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\* Presently with Regional Research Laboratory, Bhubaneswar 751 013, India.

surrounding layer of char/coal fines has been studied under isothermal conditions using a thermogravimetric set-up.

Although most studies [1–7] on the reduction of iron oxide by carbon in mixed systems have been carried out in inert atmospheres, Krascheninikov and Timofeev [10] carried out the reduction of iron oxide by carbon in non-mixed layers without using any inert atmosphere. In this case the reaction mass was heated in a closed chamber with a small outlet for the effluent gas. In the present work, the crucible was stoppered by a refractory plug. The aim was to study the reduction under atmospheres close to the real system.

Thermogravimetric studies on the reduction of iron oxides by solid reductants are complicated because both reduction of oxide and oxidation of carbon contribute towards the weight loss. It is not possible to delineate the two unless released gases are analysed. Rao [11], in his study of the kinetics of reduction of iron oxide by graphite, defined a degree of reaction at a given instant as the ratio of the weight loss of the mixture at that instant to the maximum possible weight loss for complete reduction. He reported different values for the maximum possible weight loss corresponding to complete reduction for different C/Fe<sub>2</sub>O<sub>3</sub> ratios. However, it is not clearly explained how these values were obtained.

Seaton et al. [6] used weight-loss data in conjunction with X-ray analysis for the estimation of iron and its different oxides to obtain fractional reaction plots for the reduction of hematite and magnetite pellets containing coal char.

El-Guindy and Davenport [7], in their study of the reduction of ilmenite with graphite, expressed the degree of reaction as the ratio of weight loss of ilmenite at a given time to the maximum possible weight loss obtained from the stoichiometry of the following reaction



The weight loss for ilmenite at any given time was calculated from the total weight loss of the mixture with the assumption that the product gas was composed of equilibrium CO/CO<sub>2</sub> ratio over carbon and ilmenite at the given temperature.

## EXPERIMENTAL PROCEDURE

Thermogravimetric experiments on the reduction of iron ore surrounded by coal/char were carried out by suspending a quartz crucible containing the reaction mass from a single-pan digital balance. The balance used for this purpose (Mettler PC 180) had a sensitivity of 0.001 g. Heating was carried out in a Kanthal wound vertical-tube furnace (45 × 4 cm), the temperature being controlled within ± 2°C with a JN Marshall temperature controller.

The ore used for the experiments was from Noamundi mines, Bihar, India ( $\text{Fe}_T$ , 65.28%;  $\text{Fe}^{2+}$ , 2.0%;  $\text{Al}_2\text{O}_3$ , 4.8%;  $\text{SiO}_2$ , 1.8%) and the noncoking coal was from Hutar Colliery, Bihar, India (moisture, 7.1%; ash, 7.0%; VM, 33.0%; fixed carbon, 52.9%). The ore analysis is on a dry basis while the proximate analysis of the coal is on an air-dried basis (60% RH at 40°C). Both ore and coal used were of particle size  $-500 + 250 \mu\text{m}$ . The ore was dried at 900°C for 1 h to eliminate loose moisture and structural water. For producing char, the coal was heated at 1050°C for 1 h in an argon atmosphere. For most of the experiments, char was used as the reductant except for a few where coal was used. All the raw materials used for the experiments were carefully stored in a desiccator prior to actual use.

Quartz crucibles ( $30 \times 15 \text{ mm}$ ) with hooks and containing the reaction mass, were suspended from the balance by a platinum wire. The length of the wire was adjusted to place the crucible in the hot zone of the furnace and at about 2 mm above the tip of the thermocouple. In all experiments a central column of ore particles was surrounded by an annular column of particles of the reductant.

The bulk densities of the ore and coal column were determined (1.78 and  $0.75 \text{ g cm}^{-3}$ , respectively) to allow calculation of the diameter of the ore column to be maintained such that the heights of the ore and coal columns in the crucible were equal for 1 g of each. The charging of the ore and coal/char was carried out by pouring the ore fines into a centrally placed paper tube of diameter 8.2 mm and the coal/char in the annular space. For all the experiments, weight of ore and coal/char were 1 g each. To avoid possible reaction between iron ore and quartz the crucible bottom was covered with a piece of paper which produced a thin separating layer of carbon on charring. The weight of this piece of paper (0.003–0.004 g) was negligible. After pouring in the contents, the crucible was tapped lightly five times and then the central paper tube withdrawn carefully. The crucible was then covered with a refractory plug. The furnace was heated to the desired temperature and then the crucible containing the reaction mass was lowered into the hot zone of the furnace. The loss in weight was recorded from the digital balance readings. The temperature range for this study was 850–1000°C.

### *Degree of reaction*

The progress of the reduction reaction was described by a degree of reaction as in Rao's work [11]. It was expressed as the ratio of weight loss of the total sample at any given time to the theoretical maximum possible weight loss. From the ore and coal analyses it is seen that while the amount of oxygen combined with iron in the ore is 27.77%, the amount of carbon and volatile matter in the dry coal is 93%. Thus, the maximum possible weight loss for 1 g each of ore and coal is given by  $w_{\text{max}}$ , where

$$w_{\max} = 0.2777 + 0.93 \\ = 1.2077 \text{ g}$$

Hence, the degree of reaction,  $f$ , at any time,  $t$ , is expressed as

$$f = \frac{\text{weight loss at time } t}{1.2077} \quad (2)$$

when char is used as reductant

$$w_{\max} = 0.2777 + 0.883 \\ = 1.1607 \text{ g}$$

Hence,

$$f = \frac{\text{weight loss at time } t}{1.1607} \quad (3)$$

## RESULTS AND DISCUSSION

Figure 1 shows the experimental data for loss in weight when iron ore is reduced by coal. The plot shows a very rapid weight loss in the initial stages, shown at a magnified scale in the inset. These plots are not convenient for kinetic analysis because the initial weight losses are almost entirely due to loss of moisture and volatile matter of the coal. It is, therefore, difficult to ascertain the initiation of the reduction reaction. If it is assumed that the initial weight loss is only due to the removal of moisture and volatile matter of coal, one can thus obtain approximate kinetic plots.

In 1 g of coal, the loss in weight due to the complete removal of moisture and volatile matter is 0.401 g. As the ash content is 7%, the amount of carbon left is given by

$$1 - 0.401 - 0.07 = 0.529 \text{ g}$$

Hence, degree of reaction ( $f$ ) =  $\frac{\text{weight loss} - 0.401}{0.529 + 0.2777}$ , or

$$f = \frac{(\text{weight loss} - 0.401)}{0.8067} \quad (4)$$

The time corresponding to the removal of 0.401 g of volatiles was obtained for each temperature from the magnified portion of the plot shown in the inset of Fig. 1. All subsequent time elements were corrected and, thus, modified kinetic plots could be obtained (Fig. 2).

Figure 3 shows the reduced-time plot for the data shown in Fig. 2. It shows that up to a degree of reaction of about 0.55, a Ginstling-Brounshtein type equation [ $G(f) = 1 - (2/3)f - (1 - f)^{2/3}$ ] is followed by the reacting system even when the progress of the reaction is described in terms of  $f$ . Figure 4 shows the fit of the kinetic data with the diffusion equation. The

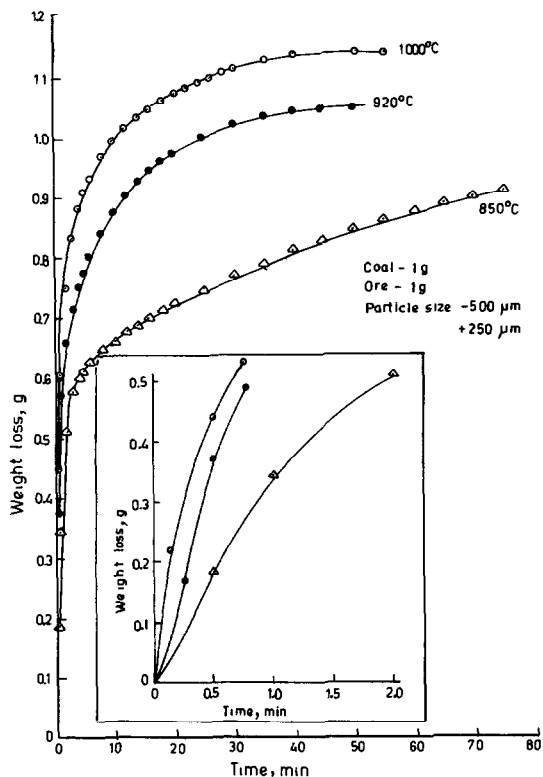


Fig. 1. Thermogravimetry of the ore-coal system.

deviation of data from the kinetic equation beyond  $f = 0.55$  may occur for several reasons, including the fact that in the final stages, when the reduction is sluggish, oxidation of char may predominate. This fit must, however, be considered somewhat empirical.

To eliminate the initial difficulty caused by the presence of moisture and volatile matter, the reduction of iron ore was also carried out using coal char. The kinetic plots of the reduction of iron ore by char and by char containing 5% sodium carbonate are shown in Fig. 5. The carbonate is known to catalyse the gasification reaction. It is seen that the presence of catalyst enhances the reaction rate at all temperatures. The reduced-time plot for these data is shown in Fig. 6, and it is seen that the diffusion equation is obeyed up to a degree of reaction of about 0.6 in this case. The kinetic data plotted directly according to the diffusion equation are shown in Fig. 7. The fit, however, is not very good. This is expected since  $f$  is not identical to  $\alpha$  and there is no theoretical basis for the use of  $f$  in the diffusion equation.

Arrhenius type plots for the reduction of iron ore by coal, char, and char with catalyst are shown in Fig. 8. The plots yield apparent activation energy values of 210, 195.8 and 168.8  $\text{kJ mol}^{-1}$ , respectively. Obviously, the presence of sodium carbonate lowers the activation energy of the process

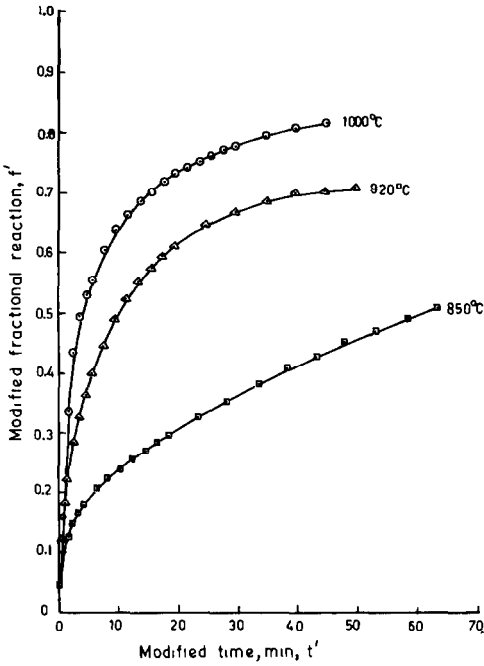


Fig. 2. Modified plot of fraction reacted against time for the ore-coal system.

quite significantly. Apparent activation energy values were also obtained using the differential method as indicated in Fig. 9. All values obtained are of comparable magnitude to those previously obtained using the integral

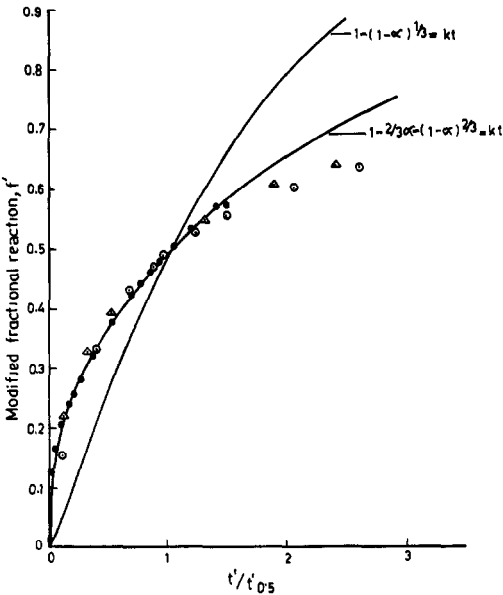


Fig. 3. Reduced time plot for the data shown in Fig. 2.

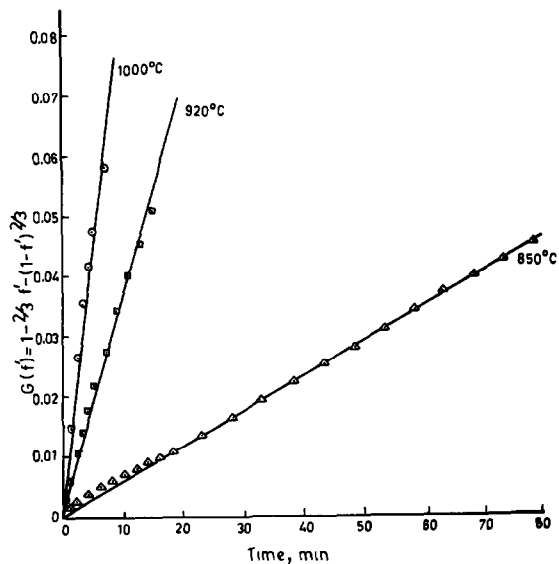


Fig. 4. Kinetic plot of the reduction of ore by coal.

approach (Fig. 8). It should be noted that, in view of the empirical nature of the kinetic law expressed in terms of  $f$ , these values should be accepted with caution. The values obtained using the differential approach show a decrease in the apparent activation energy with the progress of reaction. Otsuka and Kunii [2], Srinivasan and Lahiri [3] and Abraham and Ghosh [4] have

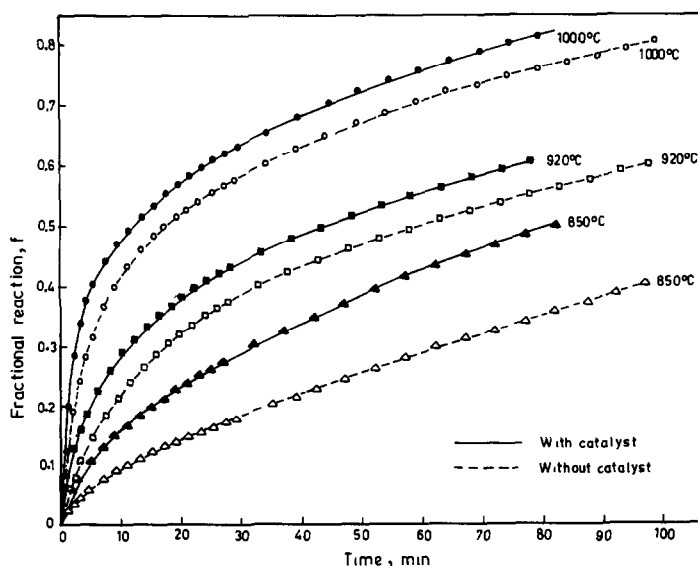


Fig. 5. Thermogravimetric measurements on the reduction of ore by char.

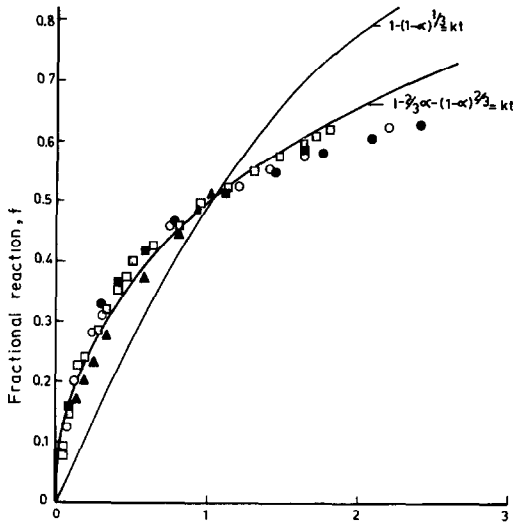


Fig. 6. Reduced time plot for the data shown in Fig. 5.

observed a similar effect in their studies on the reduction of iron oxides with carbon. They explained the phenomenon as catalysis of the rate-controlling Boudouard's reaction by metallic iron produced during the reaction. It should be noted, however, that all of their systems were intimate mixtures of fine oxide and carbon powders, whereas in the present study the ore and char are in physical contact only at the cylindrical surface of the ore column. Also, the present study had employed coarser particles of ore and char, namely,  $-500 + 250 \mu\text{m}$  for both the raw materials. In view of the fact that there is not much scope in the present system for catalysis by iron, it is difficult to say why a slight decrease in the apparent activation energy is indicated.

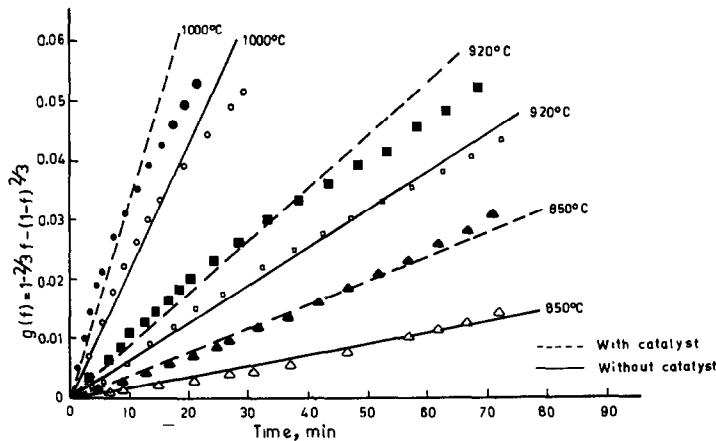


Fig. 7. Kinetic plot of the reduction of ore by char.



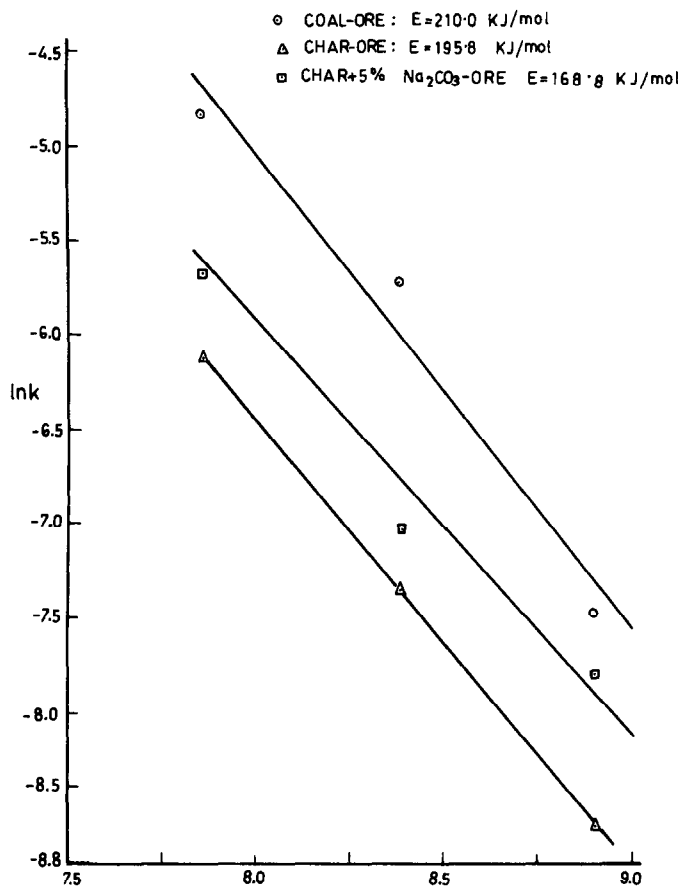


Fig. 8. Arrhenius plot for the data shown in Figs. 4 and 7.

Figure 10 shows the effect of ore and char particle sizes and of catalysis on the degree of reaction. All the runs were carried out at  $1000^\circ\text{C}$  for a period of 60 min and at the end of each run, the crucible was quickly removed from the furnace and allowed to cool. The reduced ore was then chemically analysed to obtain values of the degree of reduction ( $\alpha$ ), shown in the table with the figure. It is seen that both the degree of reaction and degree of reduction increase with decreasing char particle size and with increasing ore particle size.

The increase in the degree of reaction with decreasing char particle size indicates the importance of Boudouard's reaction in the reduction of iron ore by carbon. The enhancement of reaction in the presence of potassium carbonate in the char as catalyst further points to the importance of the gasification reaction. This is because sodium and potassium carbonates are known to be catalysts for the  $\text{C}-\text{CO}_2$  reaction [12,13]. The successful treatment of kinetic data with the diffusion equation indicated the impor-

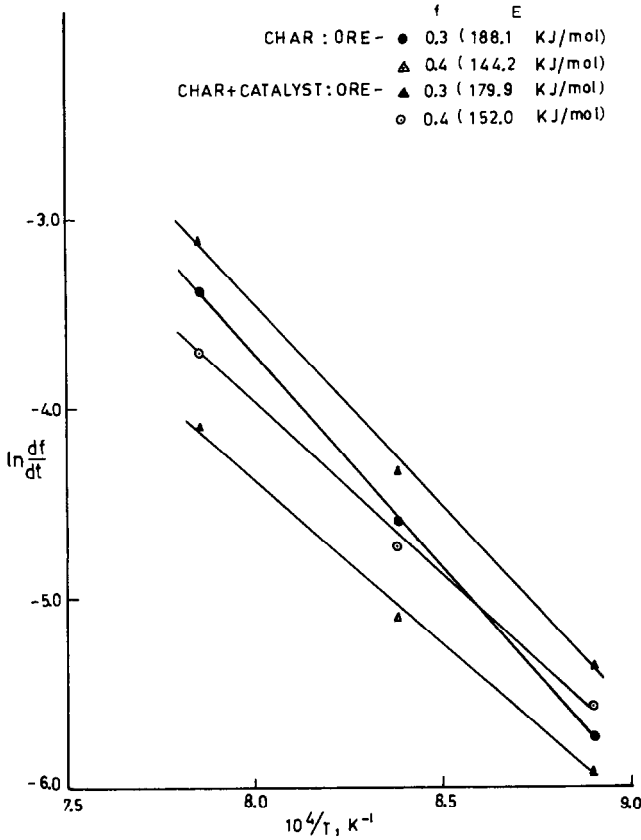


Fig. 9. Plot of logarithmic rate against reciprocal temperature.

tance of the role played by diffusion of gaseous species through a porous solid. The increase in reduction rate with increasing ore particle size further corroborates this finding. This is because, as ore particle size increases, the porosity of the iron ore column increases and, hence, the diffusivity of the gaseous species in the ore column increases. Krascheninikov and Timofeev [10] have also pointed out the importance of diffusion in such a system.

The high apparent activation energy values obtained in the present study seem to indicate that the carbon gasification reaction is the rate-controlling step. Walker et al. [14] have recommended  $360 \text{ kJ mol}^{-1}$  as the true activation energy for the reaction of carbon with carbon dioxide. It has also been said [14] that the apparent activation energy is about half the true value when it follows Zone 2 kinetics, i.e., the reaction is controlled by both pore diffusion and chemical reaction. Von Bogdandy and Engell [15] stated that the apparent activation energy is reduced to half for processes controlled by pore diffusion. For porous solids the reaction takes place in a zone which may extend to varying degrees into the reacting solid. In such a system, chemical reaction and pore diffusion interact and, according to ref. 15, this

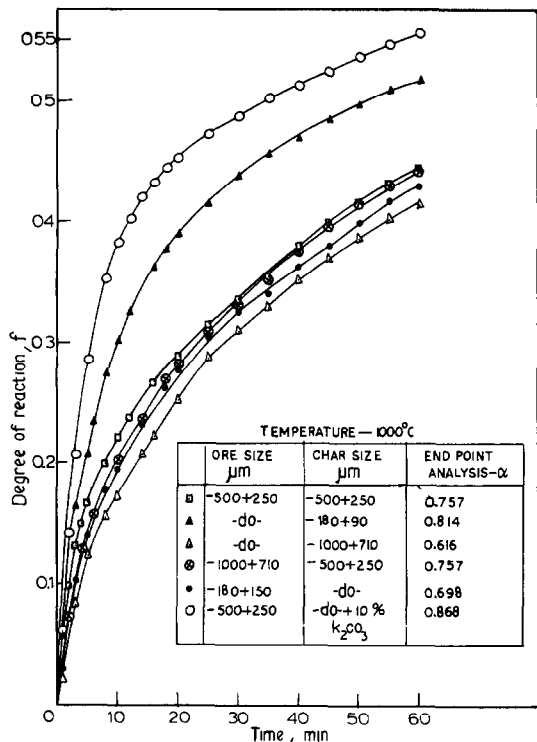


Fig. 10. Effect of ore and char particle size on the degree of reaction.

theory, developed for reactions at the surface of porous catalysts, has also been used to describe gasification of coal and coke, and the reduction of porous ores.

It can be envisaged that, during the course of reduction, a porous product layer of increasing thickness separates the layer of solid reductant from the unreduced core. While the reduction reaction involves diffusion of CO through this layer to the unreduced core, the gasification reaction would require diffusion of CO<sub>2</sub> in the opposite direction through the same porous layer. These diffusion steps must also be necessarily coupled and either one or both together may justify the diffusion-type equation.

## CONCLUSIONS

It can be concluded that diffusion of gaseous species in the porous bed plays a major role in the reduction of iron ore fines surrounded by coal/char fines.

It is shown that the initial stages of reduction are described by a Ginstling-Brounshtein type rate equation

$$1 - \frac{2f}{3} - (1 - f)^{2/3} = kt$$

where  $f$  is the degree of reaction, discussed in the text. The apparent activation energies for reduction with coal, char, and char with  $\text{Na}_2\text{CO}_3$  as catalyst are, respectively, 210, 195 and 167  $\text{kJ mol}^{-1}$ . These values, coupled with the observed effects of ore and char particle size, seem to identify the carbon gasification reaction as the rate-controlling process.

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