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THERMOGRAVIMETRIC STUDIES ON THE REDUCTION OF HEMATITE ORE FINES BY A SURROUNDING LAYER OF COAL OR CHAR FINES. PART 2. NON-ISOTHERMAL KINETIC STUDIES

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ABSTRACT

A kinetic study on the non-isothermal reduction of a column of iron ore fines by a surrounding layer of char fines is the main theme of this paper. A study on isothermal reduction by coal/char fines was described in Part 1 of this communication.

In the present work the degree of reaction at a given instant has been described as in Part 1, i.e., as the ratio of weight loss at that instant to the maximum possible weight loss. Reduction experiments have been carried out on three different sample sizes. Samples of ~1 g were used in a thermogravimetric set-up and continuous measurements of weight loss analysed in terms of the degree of reaction. Some fixed time reduction experiments have been carried out on large (~15 g) samples where the reduced sample was chemically analysed for the degree of reduction. In addition, a thermal analyser was used to study reduction in a thoroughly mixed ore–char system (sample size, ~30 mg).

It is shown that while the reaction in a mixed system is characterized by uniform internal reduction, reduction in an unmixed system is characterized by diffusion of gases through a porous product layer, the reaction being controlled by gasification of carbon.

INTRODUCTION

Iron oxide reduction has been widely studied in the last three decades. The bulk of these studies were, however, carried out using gaseous reductants and studies on reduction by solid carbonaceous materials have received attention only in recent years. Various workers have studied the kinetics of reduction of iron oxides by solid reductants [1–7] employing the traditional isothermal approach. Although this is a very useful and commonly used technique, isothermal kinetic studies have certain limitations which can be overcome by using the non-isothermal approach. In industry, actual reactions involve non-isothermal conditions and, therefore, the results

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of the traditional kinetic studies are often unrealistic. Part 1 of this communication dealt with isothermal thermogravimetry. In the present work we describe some non-isothermal studies.

In recent years several thermal analysis studies have been reported in the literature on the reduction of iron oxides by solid reductants. Szendrei and van Berge [8] used thermogravimetry and evolved gas analysis to study the kinetics of reaction of mixtures of iron oxide and carbon powders with and without the addition of catalysts, such as sodium carbonate. They found distinct peaks in the rate of change of weight and that of generation of CO and CO_2. These steps clearly showed the multistage nature of the reaction. They also studied the effect of small additions of Na_2CO_3. Their major findings were that the catalytic effect of sodium carbonate resulted in an enhancement of the carbon gasification rate. The gasification of carbon was the rate-controlling step for uncatalyzed reactions, whereas, for catalyzed reactions, mixed control mechanisms were said to prevail. They also reported that if catalysis was suitably enhanced then the reaction could be controlled by the reduction of wustite.

Dobovisek [9] studied the effect of catalysts on the reduction of iron oxide by petrol coke in a thermal analyser. He also found the reaction to be distinctly multi-staged and used the position of the characteristic DTA peak of the reduction of Fe to metallic iron to interpret his results. He concluded that the addition of alkali carbonates significantly increased the reduction rate of iron oxide in the temperature range 700–800°C.

In the present work, the kinetics of reduction of iron oxide fines by char fines have been studied by using mixtures of the two in a thermal analyser and mixtures of ore and char in non-mixed layers in a TG set-up. In these studies the progress of the reaction was described in terms of a "degree of reaction" as recommended by Rao [5]. Further work using larger sample sizes was carried out in a muffle furnace using the reduce-and-freeze technique where the progress of reaction was estimated by means of wet chemical analysis. Thus, reduction studies were carried out at three different scales, namely, 30 mg in thermal analysis, 1 g in a TG set-up, and 15 g of ore in muffle furnace experiments.

EXPERIMENTAL PROCEDURES

Reduction of iron ore by coal char in a thermal analyser

This was studied in a Stanton-Redcroft thermal analyser (Model STA-780). The ore used was from Noamundi mines, Bihar, India (Fe, 65.28%; Fe^{2+}, 2.0%; SiO_2, 1.8%; Al_2O_3, 4.8%) and the reductant was char obtained from non-coking coal from Hutar mines, Bihar, India (moisture, 7.1%; ash, 7.0%; volatiles, 33.0%; fixed carbon, 52.9%). Charring was done at 1100°C for 30 min in an argon atmosphere. Dried ore and char ($-90+63$ μm) were mixed thoroughly, at a weight ratio of 1 : 1, in a mixer for several hours. Approximately 30 mg of the mixture was used in each experiment and the samples were heated to a maximum temperature of 1100°C under heating programmes of 10 and 20°C min^{-1}. The argon used was purified by passing it through a column of packed anhydrous calcium chloride and through alkaline pyrogallol solution. The gas flow rate was kept at 40 cm^3 min^{-1}. Reduction experiments were also carried out without using argon; in one such run, the ore–char mixture was used, while in another run, the ore and reductant were used in an unmixed manner. For this, 15 mg of ore fines were poured into the crucible and then 15 mg of char fines were poured over this layer of ore fines.

Reduction of iron by char in a TG set-up

Thermogravimetric experiments on the reduction of iron ore surrounded by char were carried out by heating a quartz crucible, containing the reaction mass, suspended from a single-pan digital balance (Mettler PC 180; sensitivity, 0.001 g). Heating was carried out in a Kanthal wound vertical-tube furnace, the temperature increased linearly by manipulating the variac manually. Prior trial and error had established the appropriate procedure for obtaining a heating rate of 10°C min^{-1} over the full range of heating.

Dried ore fines ($-500+250$ μm) and char fines ($-500+250$ μm) were heated in quartz crucibles (350 × 15 mm) in non-mixed layers. Ore fines (1 g) were poured into a paper tube (diameter, 8.2 mm) placed centrally inside the quartz crucible and 1 g of char was poured into the annular space. 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. After pouring in the contents, the crucible was tapped lightly five times and then the paper tube was withdrawn carefully. The crucible mouth was then covered with a loose refractory plug, the crucible suspended from the balance by a platinum wire, and then heated at rate of 10°C min^{-1} up to 1100°C. The loss in weight was recorded from the digital display of the balance.

Reduction of iron ore by coal in large crucibles

Dried Noamundi ore ($-500+250$ μm) and non-coking coal from Samla mines, Bihar, India (moisture, 7.3%; ash, 14.5%; volatiles, 31.8%; fixed carbon, 46.4%; size, 1000 μm) were charged into mild steel crucibles (33 mm internal diameter, 50 mm height). Ore fines (15 g) were poured into a glass tube (14 mm ID, 1 mm wall thickness) placed centrally in the mild steel crucible and 30 g of coal fines were poured into the annular space between the crucible and the glass tube. The crucible was tapped a few times and the glass tube was slowly withdrawn to allow the ore and coal columns to come into contact with each other. Six crucibles prepared in this way were placed in an electrically heated muffle furnace and heated to 1100°C. At different temperatures, a crucible was removed from the furnace and quenched with a jet of water. The partially reduced sponge iron was separated from the coal by magnetic methods, crushed to -150 μm and chemically analysed for total iron. The degree of reduction was calculated using the equation given by Chernyshev et al. [10]. Complete details of the work are available elsewhere [11].

RESULTS AND DISCUSSION

Reduction of iron ore by coal char in a thermal analyser

As mentioned previously, for quantitative analysis of the TG data, the progress of reaction has been indicated by a "degree of reaction", f, expressed as the ratio of weight loss for the mixture. From the ore and coal analysis, it is seen that the maximum possible weight loss of the char is 88.3% and the maximum weight loss of the ore is given by the amount of oxygen combined with the iron in the ore, calculated as follows

$$\frac{63.28}{111.7} \times 48 + \frac{2}{55.85} \times 16$$
$$= 27.77\%$$

Hence, the maximum possible weight loss of a mixture of 1 g of ore and 1 g of char is

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

Figure 1 shows plots of degree of reaction against temperature (K) for the reduction of ore by char under an argon atmosphere (10 and 20°C min^{-1}), in air (20°C min^{-1}) and for a non-mixed layer of ore and char in air (20°C min^{-1}). It can be clearly seen from the figure that for reduction experiments carried out in air, there is substantial oxidation of char. For the case of non-mixed layers, the layer of ore helps to reduce the extent of char oxidation but fails to eliminate it completely. Thus, for kinetic analysis only the data for reduction in inert atmosphere should be considered.

The kinetic data for a mixed system of ore and char cannot be interpreted in terms of phase boundary control or product layer diffusion control mechanisms because neither the phase boundary nor the product layer can be clearly visualized. One may, however, justifiably consider the model based on complete internal reduction [12]. Rao [5] and Seaton et al. [6], working on iron oxide–carbon mixtures, have proposed the following models which are

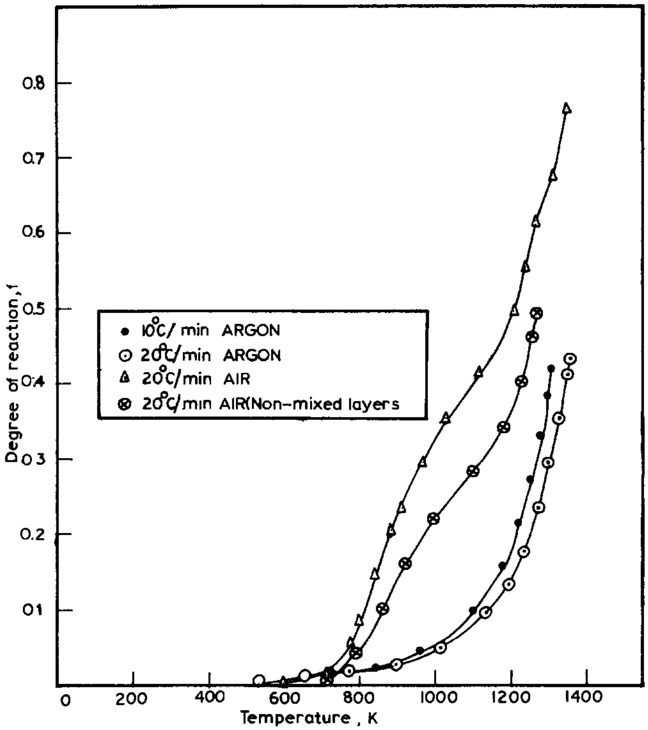

Fig. 1. Degree of reaction in ore–char mixture in the presence of air and in an argon atmosphere.

similar to that for total internal reduction. For a hematite–graphite mixture, Rao [5] proposed the equation

$$\log(1.743 - f) = -(R/2.303)t + \log(1.743) \tag{1}$$

And for hematite–coal char pellets, Seaton et al. [6] proposed

$$\ln(1 - 0.98f) = -kt \tag{2}$$

For magnetite–coal char pellets, Seaton et al. [6] proposed

$$\ln(1 - 1.037f) = -kt \tag{3}$$

where f = degree of reaction.

The present data have been analysed using the simple model

$$\ln(1 - f) = -kt \tag{4}$$

and incorporating it in the kinetic equation for non-isothermal systems.

Figure 2 shows the non-isothermal treatment of the data according to Coats and Redfern's method while Fig. 3 shows the data plotted according to Dixit and Ray's method [13]. For both treatments the equation used was $\ln(1 - f) = -kt$. The plots indicate three linear segments in the temperature ranges 539–1359 and 483–1313 K for the heating rates 20 and 10°C min^{-1},

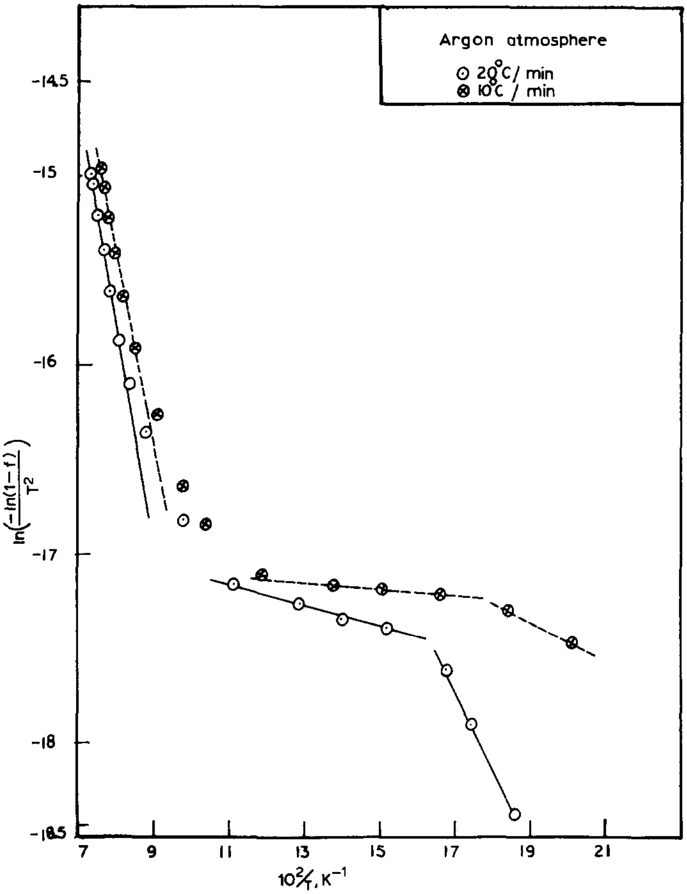

Fig. 2. Coats–Redfern plot of data for non-isothermal reaction in an ore–char mixture under an argon atmosphere.

respectively. It can be seen that the three linear segments are more prominent for the higher heating rate as compared to the lower heating rate. The apparent activation energy values for the final stage are 99 and 114 kJ mol^{-1} for Coats and Redfern's and Dixit and Ray's methods, respectively. While the apparent activation energy is rather low in the intermediate range, it is relatively high at lower and higher ranges of reaction. This finding is similar to that of Abraham and Ghosh [3], amongst others.

It is seen that linear plots are obtained using the internal reduction model in the non-isothermal kinetic equation. Thus, the basic form of the kinetic equation may be considered valid.

It is, however, not possible to say anything definite about the rate-controlling mechanism based on the value of the apparent activation energy. Various workers [2–4] studying the reduction of iron oxides by carbon have concluded, based on the activation energy values, that the gasification of carbon is the rate-controlling step. Seaton et al. [6], however, stated that such

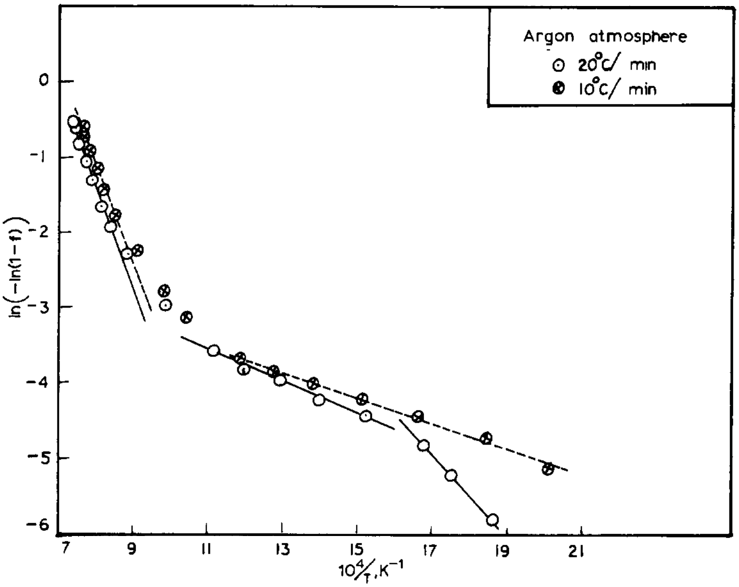

Fig. 3. Dixit–Ray plot of data for non-isothermal reaction in an ore–char mixture under an argon atmosphere.

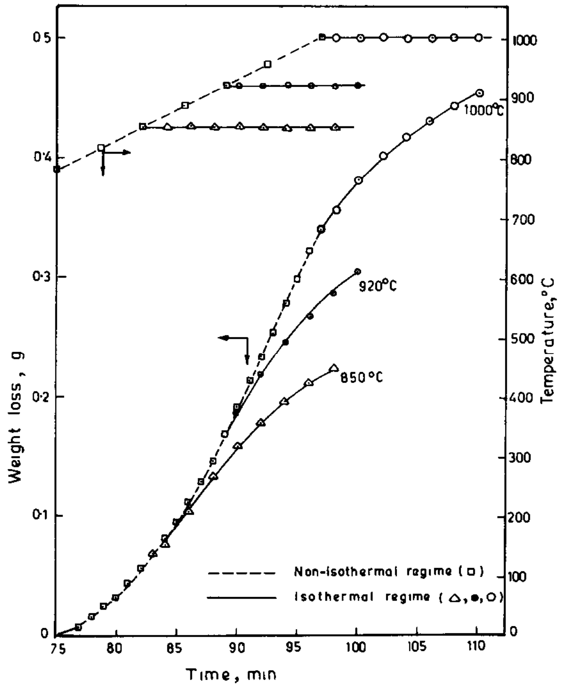

Fig. 4. Weight loss of an ore–char system during non-isothermal heating followed by isothermal heating.

conclusions, based on the magnitude of the activation energy alone, are not justified. According to them, the presence of a temperature gradient, the large effect of temperature on the reaction rate, and the strong endothermic nature of the process, indicate that the overall process could be controlled by the amount of energy available for the gasification of the carbon reaction.

Reduction of iron ore by char in a TG set-up

Figure 4 shows the weight-loss data for the reduction of ore by char under non-isothermal conditions followed by isothermal holding at predetermined temperatures. Thus, in three different runs, the samples were heated from room temperature to 350, 920 and 1000°C, respectively, at 10°C min^{-1}. At the end of the non-isothermal heating, the samples were heated isothermally at these temperatures. These runs provide reducibility data for the heating programmes indicated.

The degree of reaction was estimated by the method given in the previous section. The non-isothermal portion of the plot was kinetically analysed using the method of Ingraham as cited in the literature [13]. The special feature of this method is that knowledge of the appropriate integral form of the rate equation is not required. The plot is shown in Fig. 5 and the apparent activation energy is found to be 119 kJ mol^{-1}.

Reduction of iron ore by coal in large crucibles

The kinetic plots, expressed in terms of the degree of reduction defined as the ratio of oxygen removed to the total oxygen combined with iron in the ore, are shown in Fig. 6. It can be seen that the α–t plots shift to the left with increasing heating rate, as expected. The Coats and Redfern method of

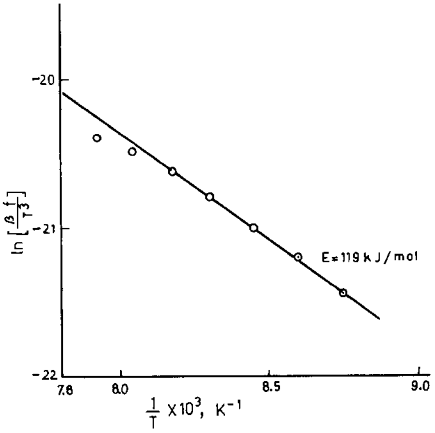

Fig. 5. Ingraham's plot of the non-isothermal data shown in Fig. 4.

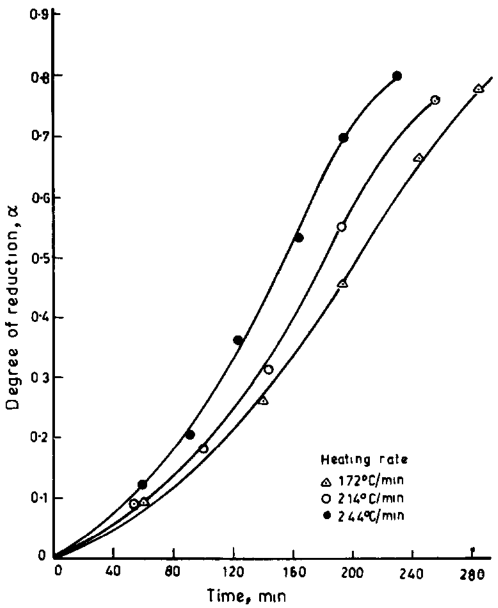

Fig. 6. Variation of degree of reduction under increasing temperature conditions for an ore–coal system.

treatment of non-isothermal kinetic data was used, and it was found that the best fit was obtained for the Ginstling–Brounshtein equation

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

This corroborates the conclusion of the isothermal studies discussed in Part 1 of this communication. The results are shown in Fig. 7. As the three different

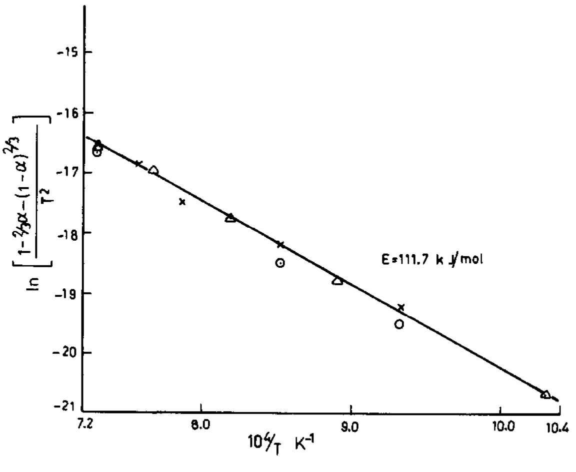

Fig. 7. Coats–Redfern plot of the non-isothermal reduction of ore by coal.

heating rates used varied over a small range, namely 1.72–2.44°C $\min^{-1}$, it can be seen that they yield a single apparent activation energy value of 111.7 kJ mol^{-1}. This study seems to indicate that the reduction of a column of iron ore fines surrounded by an annular column of char fines involves gaseous diffusion through a porous solid. Carbon monoxide generated in the char bed diffuses inwards into the ore bed and the gaseous product of the reaction, namely CO_2, diffuses outwards to the char bed to react with the carbonaceous matter to produce CO. Between the ore and char layers, a porous product of increasing thickness forms. The Ginstling–Brounshtein equation accordingly gives the best fit for the kinetic data. The rate-controlling step seems to be the gasification reaction as is more conclusively substantiated by the isothermal experiments discussed in Part 1.

CONCLUSIONS

It is shown that non-isothermal data on the reduction of iron ore by char is meaningfully analysed by various equations of non-isothermal kinetics available in the literature. While a reaction in a thoroughly mixed ore fines–char fines system appears to follow the kinetic equation for complete internal reduction, that in a system comprised of unmixed layers appears to conform to the Ginstling–Brounshtein equation for a diffusion-controlled process. These findings thus corroborate the conclusions of isothermal studies reported in Part 1 of this communication.

The apparent activation energy for non-isothermal reduction is determined to be in the range 100–120 kJ mol^{-1} which is much lower than the value determined for isothermal reduction.

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