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KINETICS OF REDUCTION OF IRON ORE–COAL PELLETS

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Kinetic data on the reduction of iron ore–coal pellets are compared with similar data for lump ore. It is shown that, when ore and coal are mixed intimately, the reduction reactions are accelerated considerably. Ore–coal pellets offer some additional advantages, as discussed in the text.

It is shown that the kinetics of ore–coal reduction can be studied by using a pseudo kinetic parameter, f (fraction of reaction), defined as the instantaneous weight loss divided by the maximum possible weight loss. Plots of f versus t have been analysed to establish the kinetic equations and evaluate the kinetic parameters.

Introduction

With the commercialisation of the different direct reduction processes (DR) and the advent of the ultrahigh-power electric arc furnace (UHP), the DR–EAF route has emerged as a promising alternate route in steelmaking. Accordingly, DR processes, both gas and solid reductant-based, are being investigated extensively. In the solid reductant-based DR processes, lump ores are reduced with lumpy non-coking coal, generally in a kiln. The reduction of iron ore pellets has also been tried sporadically.

The reduction of both ore particles and ore pellets requires a considerable time, say 3–4 hours at around 1100°. It is reported [1] that, for a given range of diameter, pellets will be in the top third of the measured reducibility range. The high reaction time required necessarily limits the throughput of the process. The reduction of simple ore pellets often poses the additional problem of swelling during reduction and consequent breakage. It is shown in this paper that the reduction reaction is significantly accelerated if the solid reductant is incorporated inside the pellet. Further, such pellets do not show significant swelling.

Reduction mechanism

The reduction of a lump ore or dense pellet involves a gas-solid reaction at a sharp interface between the unreduced core and the product layer. The reaction kinetics is generally determined by the diffusion of the reducing gases through the product layer or chemical reaction at the core–product layer interface. It should be noted that gaseous diffusion is involved even when the reductant is solid. It has now been shown [2] conclusively that the solid–solid reaction between ore and carbon plays only a relatively minor role and reduction is mostly achieved via gaseous intermediates. The overall reaction involves a cyclic mechanism in which CO_2, produced as a result of reduction of iron oxide, gasifies carbon to generate CO, which in turn produces CO_2 through oxide reduction. In the case of ore–coal mixtures, there can be no sharp reaction interface, the reaction proceeding throughout the bulk simultaneously. The permeation of reducing gases is aided by the fact that the reaction

$$C + CO_2 = 2\,CO \tag{1}$$

implies an increase in the volume of gas. This reaction, which is known to follow first-order kinetics, may be called the total internal reduction. The kinetic equation is written as

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

where k, the rate constant, is independent of the diameter of the ore–coal composite pellets, and α is the degree of reduction.

Kinetic parameter

In the case of a composite pellet, the weight loss is due to the loss of oxygen from the oxide, and of carbon and volatile matter from the solid reductant. Since these losses cannot be delineated, it is difficult to determine the degree of reduction (degree of oxygen removal) at any given time. To obviate the problem, several workers [3–5] have employed a pseudo kinetic parameter, f (fraction of reaction), defined as the ratio of weight loss at a given time to the maximum possible weight loss of the mixture. The same parameter has been employed in the present investigation and a kinetic equation established. The activation energy has been calculated by using the integral and differential approaches previously reported [6].

Experimental

The present work was carried out with iron ore from Kiriburu, Bihar, India, and non-coking coal from Raniganj. The chemical composition of the ore and the approximate analysis of the coal are listed in Table 1. Pellets were made by mixing ore fines (−180+300 mesh) and coal fines (−180+300 mesh) in two different ratios (10% and 15%), with dextrene as binder. Pellets were dried in air and then inserted into a muffle furnace maintained at a predetermined temperature. To maintain a reducing atmosphere, excess coal was kept in several crucibles surrounding the pellets. Reacted pellets were withdrawn at various time intervals and cooled under vacuum. The *f* values were obtained by weighing the pellets before and after reaction.

Table 1 Analysis of iron ore and coal used in this investigation (wt.%)

Kiriburu iron ore (Orissa, India)		Raniganj coal (West Bengal, India)	
Fe_T	63.84	Moisture	7.0
Fe_2O_3	88.05	Ash	17.5
FeO	3.64	Volatile matter	31.0
SiO_2	1.78	Fixed carbon	44.7
Al_2O_3	2.14		
CaO	0.24		
MgO	0.11		
LOI	4.01		
S	traces		
P	0.03		

Results and discussion

Swelling

Pellet diameter measurements indicated that in most cases there was a slight swelling and the formation of hairline cracks, these effects being more prominent as the temperature was elevated and the time of reduction was increased. The pellets, retained their spherical shape in all cases, however, and were hard and strong on reduction. Some preliminary trials indicated that, if the coal percentage was increased (30% or 40%), then not only was there no swelling, but there was even a slight contraction in some cases.

The reduction kinetics in the Fe_2O_3–C system depends on the way the oxide and the reductant are mixed. In a previous publication from this laboratory it was

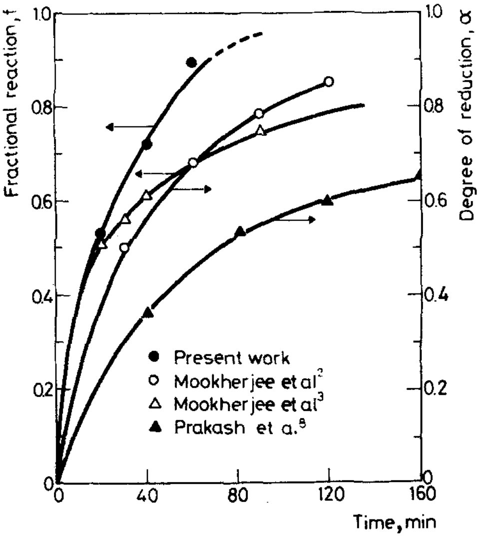

Fig. 1 Reduction of iron ore–coal pellets, iron ore particles and fines under different conditions at 1000 °C

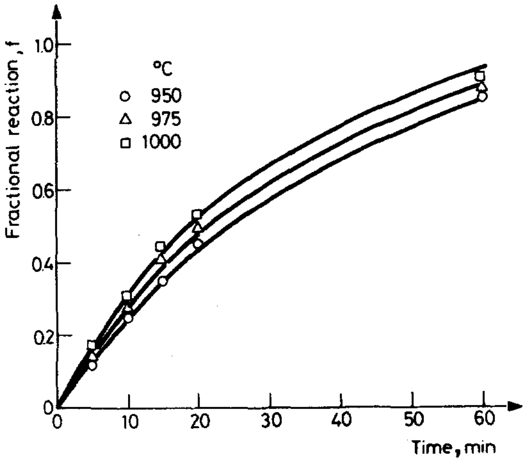

Fig. 2 Reduction of Kiriburu (India) iron ore–coal (10%) pellets

shown [7] that the reduction of lump ores in static beds by both gaseous and solid reductant follow the Ginstling–Brounshtein equation. In another publication, it was reported that the same equation also applied when a column of ore fines was reduced by a surrounding layer of coal fines [2]. In both of these cases, the reduction rate did change with the source of the ore, but the change was minor.

Figure 1 compares the reduction kinetics of ore–coal pellets at a given temperature (1000°) with that of ore under different conditions at the same temperature. It is seen that the reduction is significantly more rapid in the case of ore–coal pellets involving an intimate mixture.

Figures 2 and 3 show plots of the fraction reacted against time under isothermal conditions for two ore–coal pellet compositions. The plots in Figs 4 and 5 reveal that they both follow first-order kinetics. The Arrhenius plots in Fig. 6 are linear and yield activation energies of approximately 114 kJ/mol and 98 kJ/mol for pellets containing 15% and 10% coal, respectively. These values are somewhat lower than those reported by other workers on ore–coal systems were the reaction was said to be primarily controlled by carbon gasification.

In the differential approach, the activation energy is calculated by plotting either $\ln\left(\frac{df}{dt}\right)_f$ or $\ln(f)_f$ against reciprocal temperature. The use of $\left(\frac{df}{dt}\right)_f$ involves some uncertainties because of slope calculations. Thus, the $\ln(f)_f$ *vs.* $\frac{1}{T}$ plots may be considered more reliable. Figure 7 shows such plots for two pellet compositions at three levels of f, all data being derived from Figs 1 and 2. It is seen that the reaction rate is only marginally accelerated by an increase of the carbon content from 10% to 15%. The activation energy values indicated in the plots show that, in contrast with what was obtained via integral approach, the data relating to the two different mixtures are practically identical. The plots also indicate that the activation energy for the reduction decreases with the progress of the reaction. This is consistent with the observation of Srinivasan and Lahiri [9], who showed that, while the reaction is

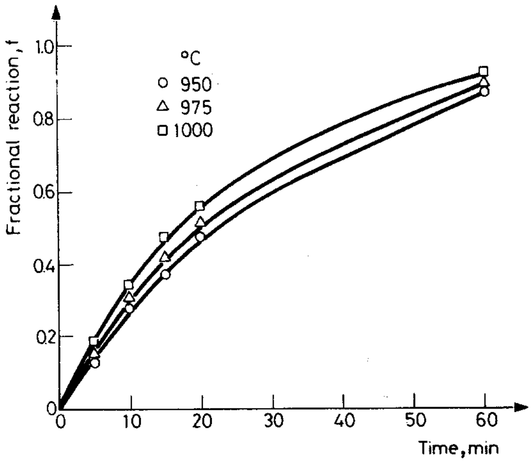

Fig. 3 Reduction of Kiriburu (India) iron ore–coal (15%) pellets

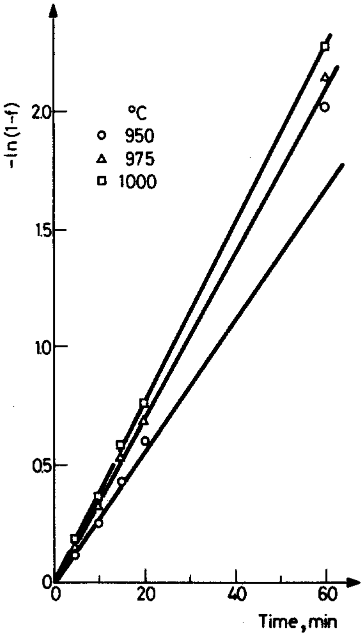

Fig. 4 Plot of $-\ln(1-f)$ *vs.* time for reduction of Kiriburu (India) iron ore–coal (10%) pellets

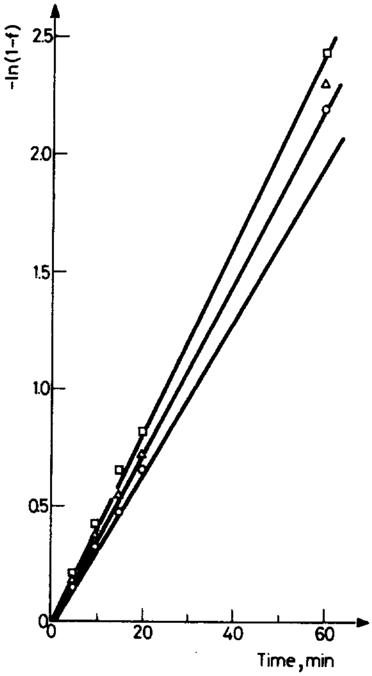

Fig. 5 Plot of $\ln(1-f)$ *vs.* time for reduction of Kiriburu (India) iron ore–coal (15%) pellets

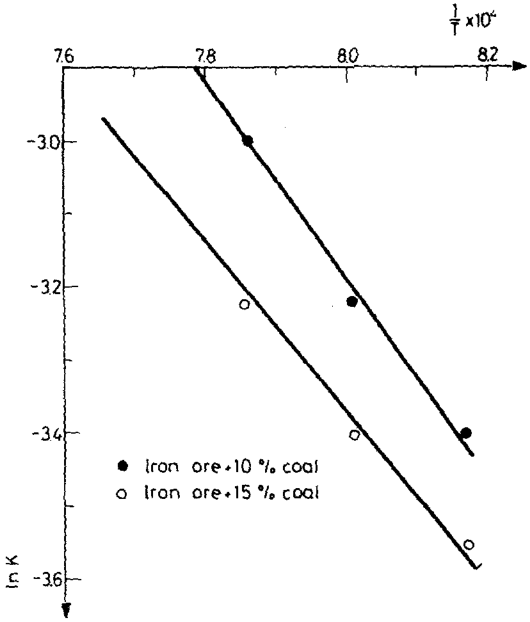

Fig. 6 Plot of ln K *vs.* $\frac{1}{T}$ for ore–coal pellet reduction

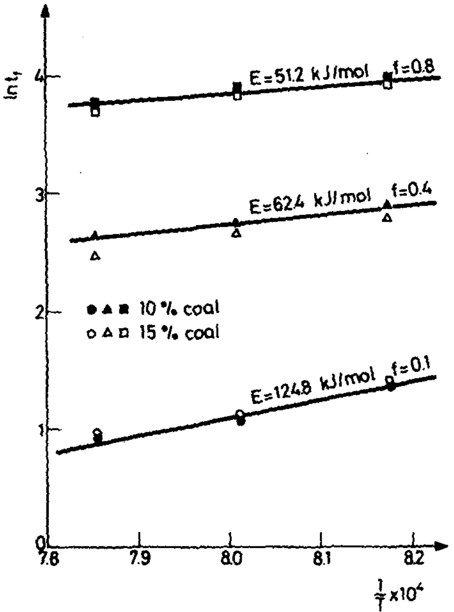

Fig. 7 Plots of ln t_f *vs.* $\frac{1}{T}$ for iron ore–coal pellets

initially controlled by carbon gasification, in the late stages wustite reduction becomes rate-controlling. It is known that the activation energy for the former is much greater than that for the latter. It may be noted that the differential approach does not assume any kinetic model, but allows for variation of the activation energy with the progress of reaction. The similarity of the E values obtained with the integral and differential approaches indicates that the kinetic equation used in the integral approach is basically correct. However, the E value obtained therefrom must be treated as only an average value. The E-value obtained from the differential approach should be regarded as more reliable.

It may be concluded that the reaction in ore–coal pellets involves the interplay of carbon gasification and the oxide reduction reaction, as in the case of any ore–coal system. However, the overall reaction is considerably accelerated because of the total internal reaction, for which simple first-order kinetics is followed. The main features of such a reaction path are the simultaneous reaction at numerous sites within a pellet and, consequently, the absence of differential resistance and a sharp reaction interface.

Conclusions

It is shown that ore–coal pellets undergo reduction without breakage or cracking due to swelling. Iron ore fines are reduced rapidly when present in ore–coal pellets. The rate of reduction in such case is several times higher than that of the reduction of lump ore or ordinary pellets, or when coal fines and ore fines form separate layers.

It is also shown that the reaction kinetics can be usefully studied by employing a pseudo kinetic parameter f (fraction of reaction), defined as the ratio of the instantaneous weight loss to the maximum possible weight loss. The apparent activation energy, calculated by using a differential approach, is found to decrease gradually with the progress of the reaction. This may be interpreted as a gradual changeover from carbon gasification control to oxide reduction control.

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Zusammenfassung — Die kinetischen Daten der Reduktion von Eisenerz-Kohle-Pellets wurde mit ähnlichen Daten von Stückerz verglichen. Es wurde gezeigt, daß die Reduktionsreaktionen im Falle einer intensiven Vermischung von Erz und Kohle erheblich beschleunigt werden. Erz-Kohle-Pellets besitzen einige zusätzliche Vorteile, auf die im Text näher eingegangen wird. Es wurde gezeigt, daß die Kinetik der Erz-Kohle-Reduktion mit Hilfe eines pseudokinetischen Parameters f (Reaktionsbruch) untersucht werden kann, der als Quotient aus aktuellem Gewichtsverlust und maximal möglichem Gewichtsverlust definiert wird. Zur Bestimmung der kinetischen Gleichungen und der Berechnung der kinetischen Parameter wurde ein $f-t$ Diagramm ausgewertet.

Резюме — Сопоставлены кинетические данные реакции восстановления брикетов железная руда–уголь с таковыми для кусковой руды. Показано, что при тщательном перемешивании руды и угля, реакции восстановления значительно ускоряются. Брикетирование руды с углем дает некоторые дополнительные преимущества. Показано, что кинетика реакции восстановления руда–уголь может быть изучена, используя псевдокинетический параметр g (доля реакции), определяемый как отношение мгновенной потери веса к максимально возможной потери веса. Графические зависимости f от t были использованы для установления кинетических уравнений и определения кинетических параметров.