Isothermal Reduction Kinetics of Mill Scale by Coal

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Abstract : This paper reports the kinetics of reduction of mill scale by coal. Mill scale from Chittagong Steel Mills Ltd.(CSM) and coal fines from India were used for the study. Isothermal studies were carried out at four different temperature levels from 1173 to 1323 K. Particle size, coal/mill-scale ratio and bed depth were 2.03 mm, 0.8 and 38 mm respectively. The activation energy for the reduction has been evaluated using both integral and differential approaches. The reaction kinetics follow the Ginstling-Brounsthein equation and that the activation energy value is approximately 120 kJ/mol.

Keywords : *Reduction, Mill scale, Coal, DRI.*

INTRODUCTION

Iron is produced from iron ore in blast furnace which is known as conventional method of iron making. In alternate process, metallic iron is produced by the reduction of iron ore or other iron oxide below the melting temperature of any of the material involved [1]. The product is known as direct reduced iron(DRI) or sponge iron because of its porous character, which results from the manner in which the reduction is performed.

In Bangladesh the is no reserve of iron ore but large quantities of mill scales are produced in the rolling and re-rolling mills every year. Only in Chittagong Steel Mills Ltd.(CSM), 3600 tons of mill scale are produced every year [2]. Most of these scales are wasted. Since the mill scale is a high grade iron oxide, there is a great scope to develop a process by which DRI can be produced from these mill scales. The reduced mass(ÐRI) can be used as a substitute of scrap in steel making. In the present work studies were carried out to identify the rate law and evaluate the activation energy for the reduction of mill scale by coal. Kinetics of reduction of mill scale-coal mixture is often described in terms of a pseudo-kinetic parameter, 'f', called fraction of reaction [3-6], which is defined as the ratio of weight loss in a mixture at any given time to the maximum possible weight loss at complete reduction. For true kinetic study 'f' is replaced by α which is the degree of reduction i.e. degree of oxygen removal. If there is no coal in the mixture α equals to 'f'. For a fixed iron oxide-coal system kinetic analysis using both α and f values yields similar kinetic model and activation energy values [7]. Thus, in spite of assumptions involved, 'f' can serve as a useful kinetic parameter [6].

EXPERIMENTAL

Mill scale from Chittagong Steel Mills (CSM) Ltd. and coal from India were used in this study. The analysis of mill scale and coal are given in Table 1 and 2 respectively. All reduction experiments were carried out in mild steel crucibles of diameter 50 mm and height 65 mm. Mill scale and coal of same particle sizes(2.03 mm) were mixed thoroughly and the mixture poured carefully into the crucibles. A bed depth of 38 mm and coal/mill-scale ratio of 0.8 were maintained in all experiments. The crucibles containing the reduction mixture were heated in an electrically heated muffle furnace fitted with a controller. The temperature could be controlled within $\pm 5^0$C. A reducing atmosphere was maintained by placing some crucibles full of coal in the heating chamber. A more detailed description of the experimental set-up along with figures has been given elsewhere [8]. The crucibles were heated isothermally at four temperature levels namely 1173, 1223, 1273 and 1323 K and held in the furnace for 10 to 150 minutes. After predetermined times, the samples were taken out from the furnace and the crucibles were quenched in a water tray by placing in such a way that they were half immersed. The value of fractional reaction, 'f', were obtained by weighing the mixture before and after reduction.

Table 1   Chemical Analysis of Mill scale used.

Element	Wt.%
Fe_t	72.56
Fe_3O_4	52.60
FeO	44.36
SiO_2	2.42
MnO	0.54
S and P	0.08

Mill scale and analysis supplied by Chittagong Steel Mills Ltd., Chittagong, Bangladesh and RRL, Bhubaneswar, India, respectively.

Table 2. The proximate analysis of coal used

Element	Wt.%
Moisture	3.57
Volatile Matter	34.08
Fixed Carbon	52.60
Ash	9.75

RESULTS AND DISCUSSIONS :

Kinetic study

The process parameters of the present experiments were temperature, mill scale and coal particle size, coal/mill-scale ratio and bed depth. The experimental ranges were selected after some preliminary studies. As shown in Fig. 1(a) the rate of fractional reaction decreases with an increase in average particle sizes. A similar result can be observed in the case of bed depth of the charge, which is shown in Fig. 1(b). Figure 1(c) shows that an increase in coal mill-scale ratio increases the rate of reaction. From the above studies finally an average particle size of 2.03 mm, coal/mill-scale ration of 0.8 and bed depth of 38 mm were selected for the kinetic studies because a reasonable amount of fractional reaction can be achieved after reducing the oxides under given parameters at 1273 K for 2 hours. Further decrease in particle sizes or increase in coal/mill-scale ratios will not help to increase the amount of fractional reaction significantly.
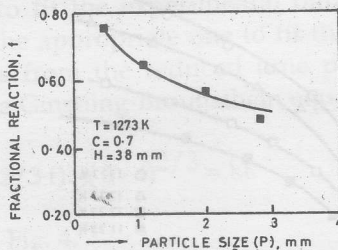
Fig. 1(a) Effect of average particle size on the fractional reaction
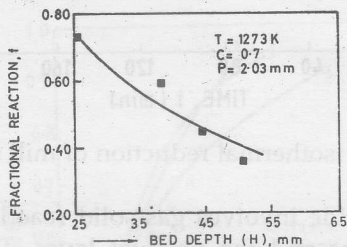
Fig.1(b) Effect of bed depth on the fractional reaction
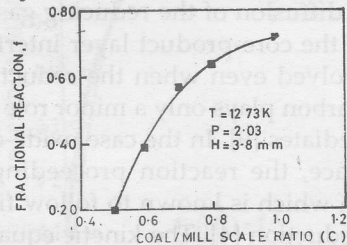
Fig. 1 (a) Effect of average particle size on the fractional reaction,
         (b) effect of bed depth on the fractional reaction,
         (c) effect of coal/mill scale ratio on the fractional reaction.

To identify the reaction mechanism, isothermal kinetic studies were carried out at four temperature levels from 1173 to 1323 K. The results are shown in Fig. 2. It shows plots of the fractional reaction (f) in the mill scale-coal mixture against time (t). The maximum possible weight loss was obtained by adding weight loss of oxygen in FeO and Fe_3O_4 and weight loss of moisture, volatile matter and fixed carbon of coal. During the initial stages the evolution of moisture and volatile matter should be rapid resulting an abrupt rise of 'f'. The volatile matter evolved in the early stages does not escape unreacted and during removal, causes reduction as well [9]. Due to this compensating effect the kinetic data seems to be quite smooth passing through origin.
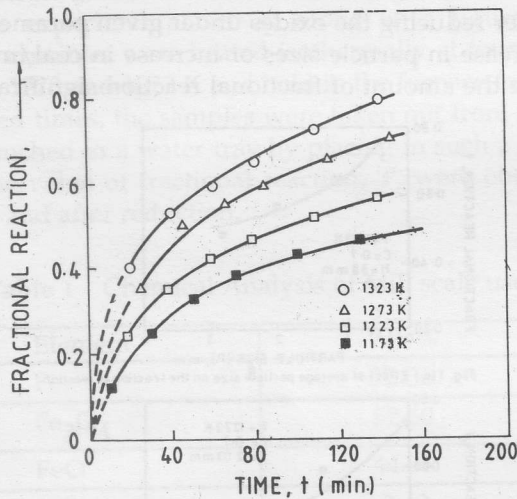

Fig. 2   Kinetics of isothermal reduction of mill scale by coal.

The reduction of a lump oxide involves 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. Solid-solid reaction between oxide and carbon plays only a minor role and reduction is mostly achieved via gaseous intermediates [9]. In the case oxide-coal mixtures, there can be no sharp reaction interface, the reaction proceeding throughout the bulk simultaneously. This reaction which is known to follow first order kinetics, may be called the total internal reduction [4]. The kinetic equation is written as

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

where k is the rate constant and t is time.

Again in oxide coal mixed system the product layer may offer resistance to the transfer of gaseous reactants at the interface, then diffusion control should be the most probable mechanism. Two types of diffusion mechanism generally are observed in iron oxide reduction. One is well known parabolic law [10].

$$f^2 = kt \tag{2}$$

the other one is Ginstling-Brounsthein diffusion model [11].

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

To get an initial idea about the kinetic law of the present study, reduced time plots were used which is shown in Fig. 3. Three commonly suggested models Parabolic, First order reaction and Ginstling-Brounsthein equation for iron oxide reduction were used to fit the experimental data. The Ginstling-Brounsthein equation seems to be the appropriate one to fit the data obtained in this study. Based on this findings from the reduced time plots, the data of Fig. 2 were plotted according to the Ginstling-Brounsthein equation.

$$(1- 2/3 \, f) - (1 - f)^{2/3} = kt$$
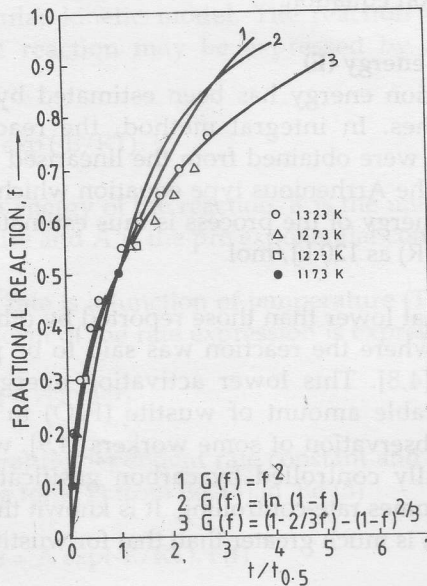
The plots are shown in Fig. 4.

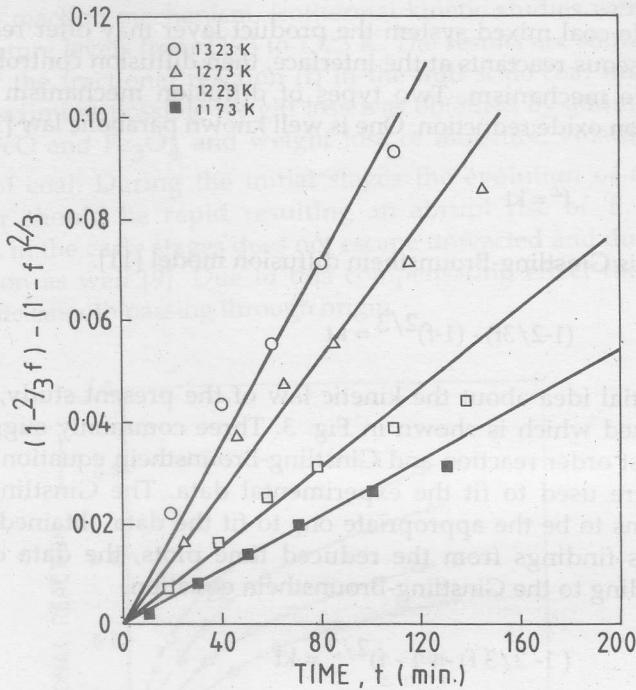**Fig. 3** Reduced time plots for isothermal kinetic data shown in Fig. 2

Fig. 4   Isothermal kinetic data according to Ginstling-Brounsthein reaction equation.

Evaluation of kinetic energy (E)

The apparent activation energy has been estimated by both the integral and differential approaches. In integral method, the reaction rate constants of various temperatures were obtained from the linearised plots of Fig. 4 and then plotted according to the Arrhenious type equation which is shown in Fig. 5. The apparent activation energy of the process is thus estimated from the Arrhenious type plot (slope = - E/R) as 120 kJ/mol.

This value is somewhat lower than those reported by other workers on iron ore-coal mixed systems where the reaction was said to be primarily controlled by carbon gasification [4,8]. This lower activation energy value is due to the presence of considerable amount of wustite (FeO) in the mill scale. This is consistent with the observation of some workers [4,9], who showed that, while the reaction is initially controlled by carbon gasification, in the late stages wustite reduction becomes rate-controlling. It is known that the activation energy for carbon gasification is much greater than that for wustite reduction [10].
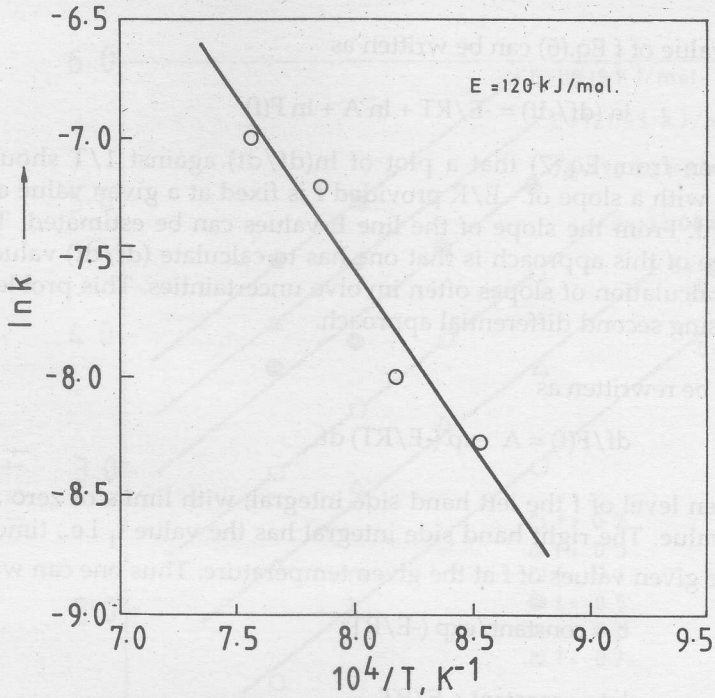
Fig. 5 Arrhenius type plots for kinetic data of fig. 4.

The E values can also be calculated using differential approaches without reference to any particular kinetic model. The reaction rate constant of any temperature dependent reaction may be expressed by an type exponential equation

$$k = A \exp(-E/RT) \qquad (4)$$

where E is the activation energy of the reaction, R is the universal gas constant, T is the reaction temperature and A is the pre exponential constant.

At any given time the rate is a function of temperature (T) and f and therefore, the general differential form of the rate expression is expressed as

$$df/dt = k(T). F(f) \qquad (5)$$

where k(T) is the temperature dependent rate constant and F(f) is an appropriate function of f. Substituting for k(T) from Eq. (4) in Eq.(5)

$$df/dt = A \exp(-E/RT). F(f) \qquad (6)$$

For a fixed value of f Eq.(6) can be written as

$$\ln (df/dt) = -E/RT + \ln A + \ln F(f) \tag{7}$$

It can be seen from Eq.(7) that a plot of $\ln(df/dt)$ against $1/T$ should give a straight line with a slope of $-E/R$ provided f is fixed at a given value and $F(f)$ is kept constant. From the slope of the line E values can be estimated. The major disadvantage of this approach is that one has to calculate (df/dt) values from f-t plots but calculation of slopes often involve uncertainties. This problem can be solved by using second differential approach.

Eq. (6) can be rewritten as

$$df/F(f) = A \; \exp (-E/RT) \, dt. \tag{8}$$

For any given level of f the left hand side integral, with limits of zero and f, has a constant value. The right hand side integral has the value t_f i.e., time required to obtain the given values of f at the given temperature. Thus one can write

$$t_f = \text{constant}/\exp (-E/RT) \tag{9}$$

or

$$\ln t_f = \text{constant} + E/RT \tag{10}$$

In other words plot of $\ln t_f$ against $1/T$ should be linear and the slope should yield the values of E.

For this purpose, values of time required to achieve a particular value of 'f', t_f, were first estimated at different 'f' values. Then $\ln t_f$ vs. $1/T$, K^{-1} were plotted as shown in Fig. 6. E value for 'f' in the range of 0.2 to 0.7 are in the range of 119 to 126 kJ/mol. It is thus found that the apparent activation energy values obtained by the different approaches are identical. This may be taken as an evidence to support the kinetic law identified.

CONCLUSIONS

From the results of this study, the following conclusions can be drawn:

1.　　The kinetic data of reduction of mill scale by coal fits the Ginstling-Brounsthein equation

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

2.　　The apparent activation energy evaluated from the experimental data is approximately 120 kJ/mol.
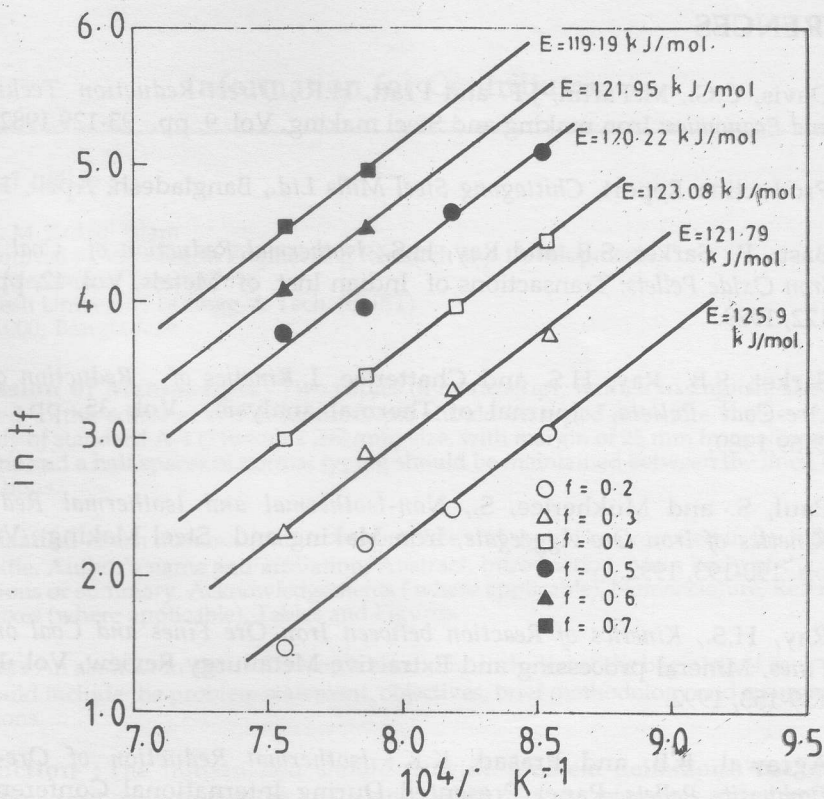
Fig. 6 Calculation of apparent activation energy using the differential approach.

NOMENCLATURE

A   :   Pre exponential factor of Arrhenius equation
C   :   Coal/Mill scale ratio
E   :   Activation energy
f   :   Fractional reaction
H   :   Bed depth
k   :   Slope of the lines, reaction rate constant
p   :   Particle size
R   :   Universal gas constant
T   :   Reaction temperature
t   :   Time
t_f :   Time required to obtain certain value of f

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