

Reduction of Iron Ore with Non Coking Coal

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Abstract- During the past century, many efforts were made to develop processes for producing iron for steel making without the use of coke. This becomes vital where country like India has limited reserve of coking coal. Coke making is extremely problematic from environmental point of view. The reduction of iron ore with non coking coal or gas below the melting point of the iron produced is classified as Direct Reduction process and product referred to as Direct Reduced Iron (DRI). The iron making reactions in iron oxide plus carbon involve the disappearance of two solid phases (iron oxide and carbon) and formation of two phases (metallic iron and gases). The location of the regions where the production of DRI is concentrated is determined by two factors: the availability of cheap natural gas or non coking coal plus the availability of high quality iron bearing raw material (65% Fe content or more). In the present investigation an attempt has been made to study the direct reduction behaviour of iron ore fines with non-coking coal fines. For this purpose the effect of reduction time, temperature and Fe₂O₃ : C ratio on degree of reduction has been studied. It is observed that degree of reduction increases with increase in Fe₂O₃ : C ratio, temperature and time. The value of activation energy in the temperature range 1173-1323 K is 203.2 KJ/mole.

Key words: Degree of reduction, Fe₂O₃ : C ratio, Activation energy.

I. INTRODUCTION

Production of steel through the conventional blast furnace and basic oxygen furnace route requires good quality coking coal, which India has limited reserve. Coke making is extremely problematic [1,2] from environmental point of view, as many of the hydrocarbons driven off during the coking process are hazardous. In addition all varieties of coal are not suitable for the production of coke. India is the third largest producer of coal in the world [3]. Major reserves are of non coking coal (around 85 percent) [4], while coking coal reserves are 15 percent only. Therefore, evolution of a technology for the reduction of iron ore using abundantly available non coking coal was contemplated, giving birth to Direct Reduced Iron Technology (DRI). Sponge Iron is the main product obtained by Direct Reduction Process. Iron Ore (Hematite) and non coking coal are prime raw material for the production of Reduced Iron. These are charged into a rotary kiln/furnace in requisite proportion along with some limestone/ dolomite [5,6,7,8,9,10,11]. Coal plays a dual role in the process by acting as a reductant as well as a fuel for providing heat to maintain the required temperature inside the Kiln (1223-1323 K). India emerged as one of the main producers of DRI in the world and the largest in coal based DRI. The country like India where availability of coking coal is meager but other gaseous (natural gas) or solid fuels like non-coking coal are readily and abundantly available, an alternative method of iron production using other fuel may play a major role.

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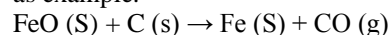
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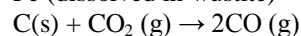
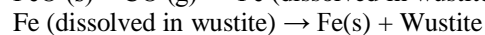
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The use of DRI process may also eliminate the costly raw material preparation, coke making and high temperature agglomeration. The capital and operating costs as well as generation of pollutants may also be reduced. It is desirable to use iron ore concentrate and coal directly. These are two ways to achieve this goal. In smelting reduction, they are charged to the vessel separately. In kiln/other furnace, ore/coal agglomerates are used.

In iron making system, carbon acts the reductant which removes the combined oxygen from iron oxides as well as the fuel and it reacts with molecular oxygen to generate heat. The reduction of iron oxide in iron ore-carbon mixture [2,5,12,13,14] in a retort is used for making high quality sponge iron for decades. Carbon reacts with O₂ and CO₂ as the intermediate reactants to form CO as the reductant. In the overall reaction of hematite reduction by carbon, there are five solid phases i.e. Hematite(H), Magnetite (M), Wustite (W), Metallic Iron (Fe) and Carbon (C), [5,15] and the gaseous phase. There are many chemical equations that are thermodynamically possible but kinetically insignificant by comparison with competing mechanisms. The case of wustite reduction by carbon and carbon monoxide is given as example.



The above equations may break down into more elementary steps as follows



The iron making reactions in iron oxide plus carbon involve the disappearance of two solid phases (iron oxide and carbon) and formation of two phases (metallic iron and gases). The fast generation of a large volume of gases within a small space leads to the build-up of gaseous pressure that result in viscous flow to blow the gas out of the mixture agglomerate of iron ore and coal.

In the present investigations, reduction of iron ore with non-coking coal fines has been carried out. The effect of Fe₂O₃:C ratio, time and temperature on degree of reduction under non-isothermal condition has been studied.

II. EXPERIMENTAL

For reduction of iron ore fines (Size -212 μ + 75 μ, having about 65% Fe content) with non coking coal fines (Size - 212μ, Ash 22.4%, VM 24.1%), Silica crucibles were used. The crucibles containing iron ore and coal of different ratio were kept inside the muffle furnace at room temperature. The furnace was switched on. After reaching the particular temperature viz. 1173 K, 1223K, 1273 K, 1323 K for different time interval i.e. 0 minute, 15 minute, 30 minute, 45 minute, 60 minute, 75 minute and 90 minute under non-isothermal condition, the crucibles were taken out and kept for cooling. Then the weight loss was recorded and carbon analysis of each sample was carried out to know the consumption of carbon for reduction of iron ore.

The degree of reduction of the iron ore fines was calculated by using the following equation.

Degree of reduction = $\frac{\text{Weight of Oxygen removed from Iron}}$

Oxide

Total weight of Removable Oxygen in the Iron Oxide

The weight of oxygen removed at different time intervals was calculated by weight loss method. The residual carbon analysis of reduced sample was carried out by CHNS analyzer.

• $Fe_2O_3 : C$ ratio was calculated on the basis of equation : $Fe_2O_3 + 3C = 2Fe + 3CO$

From the above reaction for calculation of $Fe_2O_3 : C$ (1:1),160 g of iron oxide react with 36 g of carbon to produce 112 g of Fe and 84 g of carbon monoxide. The similarly stoichiometric ratio of $Fe_2O_3:C$ 1:1.25,1:1.5,1:1.75 and 1:2 have been calculated and used to conduct the reduction experiments.

III. RESULTS AND DISCUSSION

The reduction behavior of iron ore fines with coal fines was carried out at four different temperatures 1173 K, 1223 K, 1273 K, 1323 K at the interval of 50 K for different time intervals 0,15,30,45,60,75,90 minute with different $Fe_2O_3 :C$ ratio under non-isothermal condition. The reduction results obtained are shown in Table 1,2,3,4 and they are plotted in Figure 1,2,3,4. In these graphs degree of reduction has been plotted against time. The intercept at Y-axis shows the degree of reduction achieved during heating of the sample upto the reduction temperature. From these results the following observations are made.

- At 1173 K, there is not much difference in reduction behaviour at different $Fe_2O_3 : C$ ratio but degree of reduction increases with increase in time. Similar findings have also been observed at temperatures 1223 K, 1273 K, and 1323 K. It has been observed at 1323 K that rate of reduction is faster.
- It has been also found that for all $Fe_2O_3 : C$ ratio, the rate of reduction in temperature range 1173 K to 1273 K rises slowly but at 1323 K, the rate of reduction is rapid. Highest degree of reduction (89.1 %) has been achieved at 1323 K for 1:1.75 $Fe_2O_3 : C$ ratio after 90 minutes reduction. The degree of reduction has been found to decrease (86.7 %) when $Fe_2O_3 : C$ ratio was increased from 1: 1.75 to 1:2.It may be because of reoxidation of freshly reduced iron by carbon dioxide. The results presented in Table 1,2,3,4 and plotted in Figure 1,2,3,4 have been analysed by shrinking core model for monized particle. For this purpose equation $1-(1-f)^{1/3} = K_c t$ has been used. The plot has been shown in Figure 5. The value of K_c (Rate constant) at each temperature has been calculated. Value of K_c are given in Table 5. The value of K_c at different temperature has been used to calculate activation energy for the process. For this purpose $\ln K_c$ has been plotted against $1/T$ in Figure 6. The value of activation energy is 203.2 KJ/mole.

Table 1: Effect of $Fe_2O_3 : C$ ratio on Degree of Reduction (Under Non-Isothermal condition at 1173 K)

S no.	Time (in minutes)	Degree of Reduction (%) of different $Fe_2O_3 : C$ ratio				
		1:1	1:1.25	1:1.50	1:1.75	1:2.00
1	0.0	14.4	18.1	19.1	20.1	20.0
2	15	17.1	21.5	22.0	22.5	22.4
3	30	20.5	23.8	24.8	25.4	25.2
4	45	23.1	25.5	27.2	28.0	27.5
5	60	24.8	26.1	28.0	29.1	29.0
6	75	25.4	27.1	29.2	30.2	30.0
7	90	26.1	27.5	31.1	32.4	32.2

Table 2: Effect of $Fe_2O_3 : C$ ratio on Degree of Reduction

(Under Non-Isothermal condition at 1223 K)

Serial no.	Time (in minutes)	Degree of Reduction (%) of different $Fe_2O_3 : C$ ratio				
		1:1	1:1.25	1:1.50	1:1.75	1:2.0
1	0.0	20.1	21.5	22.1	23.1	22.9
2	15	23.2	25.0	26.3	27.8	27.0
3	30	26.1	28.1	30.5	30.9	30.6
4	45	28.8	31.5	33.4	35.9	33.9
5	60	31.1	34.4	40.2	41.7	40.5
6	75	33.1	37.8	40.7	43.8	41.8
7	90	35.1	40.1	41.7	46.5	43.8

Table 3: Effect of $Fe_2O_3 : C$ ratio on Degree of Reduction (Under Non-Isothermal condition at 1273 K)

S no	Time (in minutes)	Degree of Reduction (%) of different $Fe_2O_3 : C$ ratio				
		1:1	1:1.25	1:1.50	1:1.75	1:2.00
1	0.0	27.5	28.0	29.1	30.1	29.8
2	15	35.2	42.2	46.9	50.2	49.2
3	30	38.1	48.1	52.1	64.3	57.1
4	45	44.3	53.1	55.1	71.0	64.1
5	60	48.1	55.4	58.3	72.1	69.4
6	75	52.0	57.0	64.1	74.1	71.0
7	90	58.1	62.0	70.5	80.5	72.0

Table 4: Effect of $Fe_2O_3 : C$ ratio on Degree of Reduction (Under Non-Isothermal condition at 1323 K)

S. no	Time (in minutes)	Degree of Reduction (%) of different $Fe_2O_3 : C$ ratio				
		1:1	1:1.25	1:1.50	1:1.75	1:2.00
1	0.0	38.1	39.5	41.1	42.8	42.0
2	15	42.7	47.1	49.1	53.0	52.0
3	30	50.7	54.1	58.1	65.3	62.1
4	45	56.5	59.3	62.3	72.1	71.6
5	60	60.4	63.2	68.3	76.0	75.2
6	75	65.7	68.1	72.0	80.0	78.8
7	90	70.0	73.1	79.1	89.1	86.7

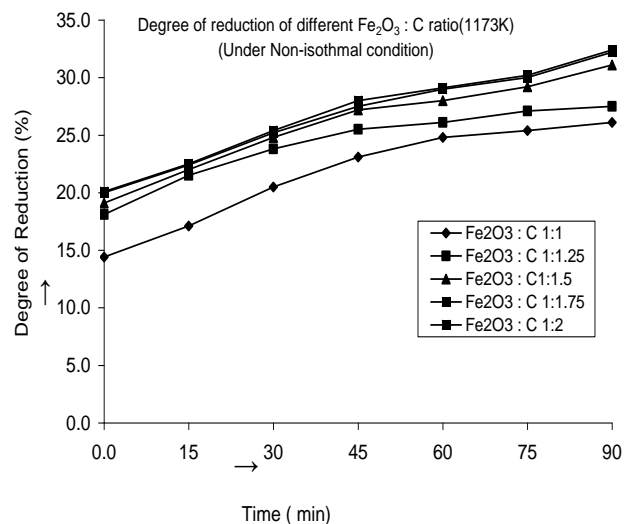


Figure 1 : Degree of reduction vs. Time plot at 1173 K temperature for different proportion of iron ore and coal

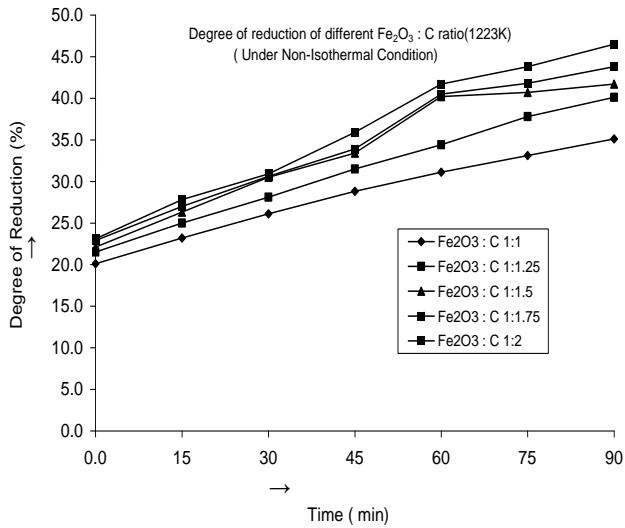


Figure 2: Degree of reduction vs. Time plot at 1223 K temperature for different proportion of iron ore and coal

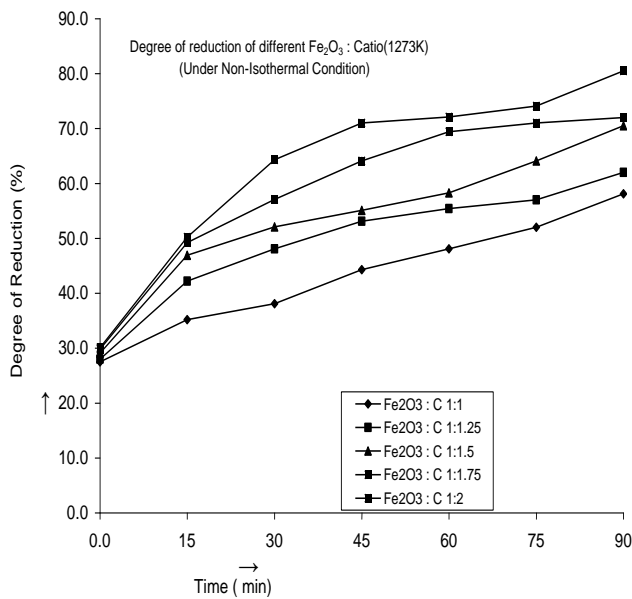


Figure 3: Degree of reduction vs. Time at 1273 K temperature and different proportion of iron ore and coal

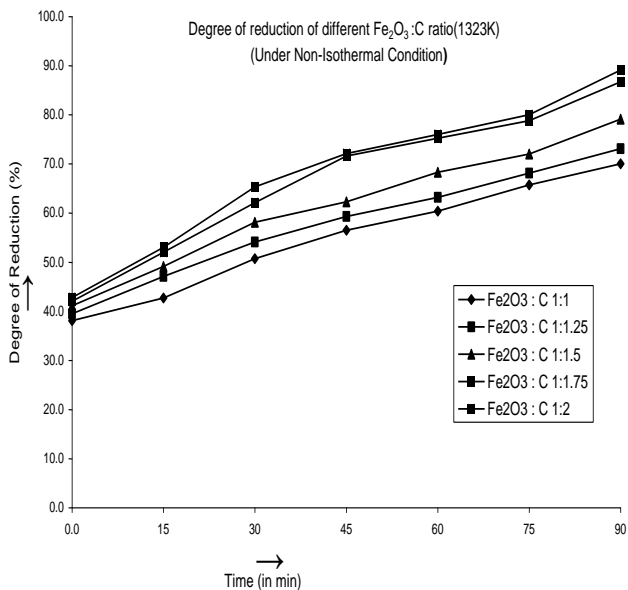


Figure 4: Degree of reduction vs. Time plot at 1323 K temperature for different proportion of iron ore and coal

Table 5 : Fractional reduction(f) and 1-(1-f)^{1/3} at different temperature(K)

Time in Min.	Fractional reduction(f) % at different temperature (K)				1-(1-f) ^{1/3} at different temperature (K)			
	1173 K	1223 K	1273 K	1323 K	1-(1-f) ^{1/3} at 1173 K	1-(1-f) ^{1/3} at 1223 K	1-(1-f) ^{1/3} at 1273 K	1-(1-f) ^{1/3} at 1323 K
0	20.10	23.10	30.10	42.80	0.072	0.084	0.113	0.170
15	22.5	27.80	50.2	53	0.081	0.103	0.207	0.223
30	25.4	30.9	64.30	65.3	0.093	0.116	0.291	0.297
45	28	35.9	71.00	72.1	0.104	0.138	0.338	0.347
60	29.1	41.7	72.1	76	0.108	0.165	0.347	0.379
75	30.2	43.8	74.1	80	0.113	0.175	0.363	0.415
90	32.4	46.5	80.50	89.10	0.122	0.188	0.420	0.522

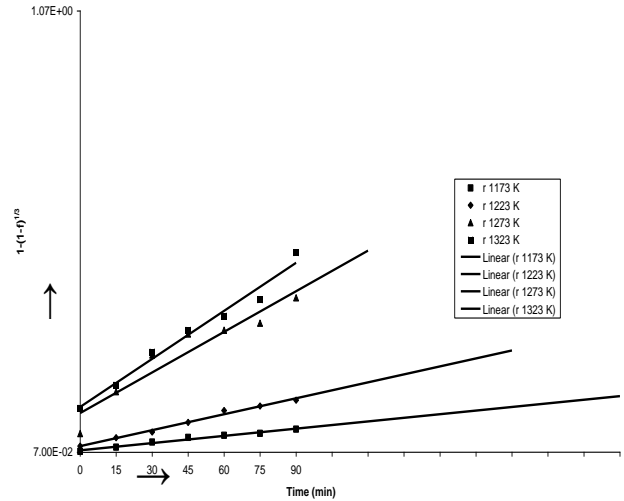


Figure 5: 1-(1-f)^{1/3} vs. Time plot at different temperatures

Table 6: Rate constant at different temperatures (in Kelvin)

Temperature (T)	Rate constant K _C	ln Kc	1/T
1173	0.0008	-7.13	8.525 X 10 ⁻⁴
1223	0.0009	-7.01	8.176 X 10 ⁻⁴
1273	0.0014	-6.57	7.855 X 10 ⁻⁴
1323	0.0035	-5.655	7.558 X 10 ⁻⁴

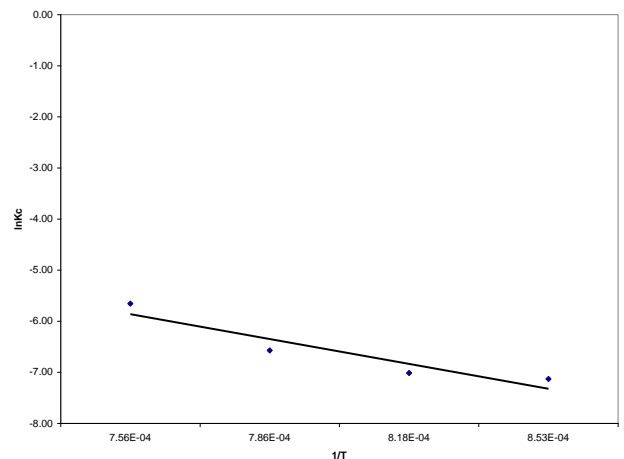


Figure 6: lnK vs. 1/T plot (Arrhenius plot)

IV. CONCLUSION

Based on the results obtained and observation made, the following conclusions have been drawn.

- (1) Degree of reduction increases with increase in Fe_2O_3 : C ratio, temperature and time.
Maximum degree of reduction was observed at Fe_2O_3 : C ratio of 1:1.75 .
- (2) The reduction reaction follows first order shrinking core model for monosized particle $1-(1-f)^{1/3} = K_c t$
- (3) The value of activation energy in the temperature range 1173-1323 K is 203.2 KJ/mole.

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