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Effect of Reducing Agents on Degree of Reduction of Double Layered Iron Ore Pellets

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Abstract-In the present investigation an attempt has been made to study the effect of reducing agents (Coke, Non-coking Coal, charcoal, char) on the reduction behavior of iron ore-reducing agents core double layered iron ore pellets under isothermal condition. The reduction tests were conducted in the temperature range of 1273 to 1473K for C : Fe_2O_3 ratio of core 5:1. The variables (parameters) studied were the reduction temperature and reduction time. The effect of each variable and interactional effect of each variable can be quantitatively assessed and compared. The results show highest degree of reduction with non-coking coal followed by charcoal, char and cokes fines. Among these two parameters reduction time has the strongest effect when charcoal and non-coking coal are used as reducing agents.Whereas, in case of coke and char reduction temperature has the strongest effect.

Keywords: Ore, reduction, pellet, composite, isothermal condition, double layered.

I. INTRODUCTION

Double layered pellets consist of a core of iron ore and carbonaceous material (Coke, Non-coking coal, Charcoal, Char, etc.) mixture encased in a shell of iron ore. After firing, the double layered pellet becomes double layered pre-reduced pellet (DLPR) consisting of a metallized core encased in a partially reduced and sintered iron oxide shell as shown in Fig-1 This type of pellet is obtained by single stage firing where sintering of fine particles, as well as pre-reduction takes place. The technique consists of preparing a small pellet (8 - 10 mm) from a mixture of iron oxide and reducing agents and then, coating of 1.5 - 2 mm iron ore to the surface. After induration in air, such a double layered pellets yields a double layered/composite pre-reduced pellets (DLPR/CPR)[1-7].

The shell of a double layered pre-reduced pellet acts as a weather protective shield and hence, the weather resistance of the pellet is higher than that of a conventional pre-reduced pellet. The production cost of these pellets is lower due to the single stage firing, whereas, in normal practice, pellet firing and reduction are carried out in two stages. Other advantages are the use of iron ore fines, coke/non-coking coal/charcoal/char fines, elimination of re-oxidation problem of sponge iron, good crushing strength, high bulk density, and lower swelling index[2,5].

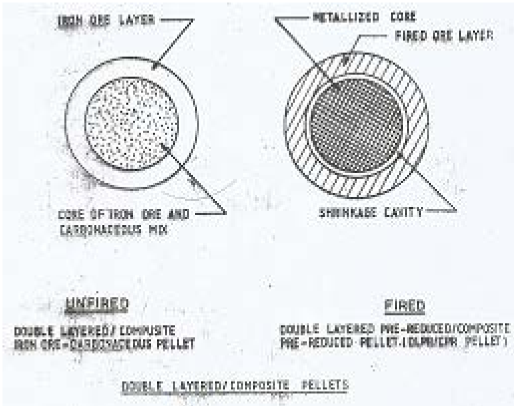

Fig1

II. EXPERIMENTAL

2.1 Raw Material

The reject of sponge iron feed - 6mm iron ore was collected from Tensa iron ore mines and heated to eliminate free and combined moisture. Iron ore assayed 61.3% Fe, 3% Al_2O_3, and 2.4% SiO_2.

Coke fines were collected from Lodna coke oven plant and non-coking coal sample was collected from Raniganj of the Eastern coalfield area. Char was produced from non-coking coal obtained from the Raniganj area of Eastern coalfield and charcoal was produced in the laboratory from wood. The proximate analysis of reducing agents are given in Table 1. Iron ore and reducing agents were crushed and ground to -0.15 mm size and stored separately.

Table 1

Sl..No.	Reducing agents	Moisture (%)	Ash (%)	Volatile matter (%)	Fixed carbon (%)
1	Coke	1.88	33.20	1.20	63.72
2	Non-coking coal	2.80	16.20	39.00	42.00
3	Char	1.45	18.00	---	80.55
4	Charcoal	---	4.60	---	95.40

Proximate analysis of reducing agents

2.2 Double layered pellet preparation

First, iron ore fines were mixed thoroughly with different carbonaceous material separately in C:Fe_2O_3 ratio of core 5:1. Moisture of 8-10% was added to these mixtures for the preparation of pellets. The pellets were made by hand rolling and the size of the pellet maintained at about 8-10 mm. These pellets were dried in the oven for 5-6 h at 378 K and weight of dry pellets was taken. Then, a 2-3 mm thick layer of iron ore was coated onto each pellet by rolling the moistened fines on the surface of the pellet. For this purpose, no external binder was used. The size of the pellet after coating was kept within a very close range (approx 12 mm). The double-layered pellet thus produced was dried in the oven for 5-6 h at 378 K, which ensured complete removal of moisture. Then the weight of each pellet was recorded and pellets were stored in a desiccator for reduction tests.

2.3 Experimental procedure

To study the reduction behavior of double layered pellets with different carbonaceous material core pellets, a series of experiment have been conducted under isothermal condition. For these tests, five pellets of each type of reducing agent core of known weight were placed in a platinum crucible. The crucibles were kept inside the furnace at a desired temperature (1273 K, 1323 K, 1373 K, 1423 K and 1473 K) for a desired time (10, 20, 30, 40 and 50 min for coke, non-coking coal, charcoal and char types reducing agents core pellets and then taken out from the furnace. The pellets were cooled and their weight losses were recorded. The weight loss in the pellet was due to loss of carbon, removal of oxygen from iron ore, and expulsion of volatile matter. The double layered pellet produced under isothermal condition was subjected to carbon analysis for estimation of unused carbon in the pellet. From these value, the degree of reduction, R, of pellets was calculated by using the equation.

$$R = \frac{\text{Weight of } O_2 \text{ removed from iron oxide}}{\text{Total weight of removable } O_2 \text{ in iron oxide}} \times 100$$

The weight of oxygen removed at different time intervals was calculated by the weight loss method. Oxygen removed = Total weight loss in the pellet - (Weight of carbon + weight of volatile matter removed). The analysis of residual carbon was carried out by a Stroheim apparatus.

III. RESULT

The effect of reducing agents (Coke, Non-coking coal, char coal, char) on degree of reduction of double layered iron ore pellets withC: Fe_2O_3 ratio 5:1 at 1473K under isothermal condition was studied. The results obtained are plotted in Fig. 1 (in 4.69). It can be seen from the figure that highest degree of reduction is obtained in core of non-coking coal and lowest in case of coke. The maximum degree of reductions obtained is highest for non-coking coal in 90% and for charcoal it is 89%. But the time required to achieve this value are 40 minutes for non-coking coal and 30 minutes for charcoal. This value is 86% and 84% for char and coke respectively. Decreasing order in degree of reduction from non-coking coal to coke may be due to decreasing order of reactivity value and percentage of volatile matter, different in ash content of non-coking coal, charcoal, char and coke. It is also observed that maximum degree of reduction in case of charcoal iron ore double layered pellets can achieve in lesser time (30 minutes) than other carbonaceous / iron ore core double layered pellets (40 minute).

The decrease in reduction time to achieve maximum degree of reduction in case of charcoal / iron ore core double layered pellet may be due to higher fixed carbon content in charcoal than other carbonaceous materials viz. non coking coal, char and coke.

Pellet disintegration was observed in case of non-coking coal / iron ore core double layered pellets only. Other double layered pellets did not show any sign of disintegration after reduction. The decrease in degree of reduction after achieving a maximum value can be seen in each type of double layered pellets as shown in Fig. 2

The reason for increase in degree of reduction on increasing temperature may be due faster rate of heat transfer as well as faster rate of reduction at higher temperature the rate of formation of carbon monoxide (CO) at higher temperature is faster because of its endothermic nature. This also may be a reason for faster rate of reduction at higher temperature. At lower temperature the heat flux is not sufficient to grant an appreciable rate of carbon gasification reaction. Hence, rate of reduction at lower temperature is low.Decrease in degree of reduction after achieving maximum reduction may be due to re-oxidation of reduced iron by inward diffusion of oxygen from the surrounding atmosphere.

The similar trends has been obtained for other temperature (i.e. 1423, 1373, 1273 and 1223K) for C : Fe_2O_3 ratio 5:1 core as shown in Fig. 3, Fig. 4, Fig.5 and Fig.6 respectively.

Among these two parameters the reduction time has strongest effect on the percentage degree of reduction when charcoal and non-coking coal are used as reducing agents whereas, reduction temperature has strongest effect in case of coke and char are used as reducing agents . Among these four types of carbonaceous / iron ore core double layered pellets charcoal / iron ore core has highest effect of reduction time and coke / iron ore core has lowest effects of reduction time on the percentage degree of reduction. On the other hand, reduction temperature has highest effect on the percentage degree of reduction for char / iron ore core double layered pellets and lowest for charcoal / iron ore core double layered pellets.

The reduction of iron oxide with non- coking coal / charcoal, char / coke in double layered pellet follows the first order reaction kinetics as shown in Fig7, Fig.8, and Fig.9and Fig.10 respectively. The maximum value of activation energy is highest (117.94 KJ/mole) for coke / iron ore core double layered pellets with C : Fe_2O_3 ratio 5:1 of core and lowest (66.88 KJ/mole) for non-coking coal / iron ore core double layered pellets with C : Fe_2O_3 ratio 5:1 of core as shown in Fig.11 and Fig.12 respectively .

The value of activation energy for charcoal / iron ore core and char / iron ore core double layered pellets with C : Fe_2O_3 ratio 5:1 are 80.15KJ/mole and 111.66 KJ/mole which is shown in Fig.13 and Fig.14 respectively.

The variation in the value of activation energy may be because of difference in gasification behavior of different reducing agents because solid state reduction depends on the gasification of reducing agents[4].

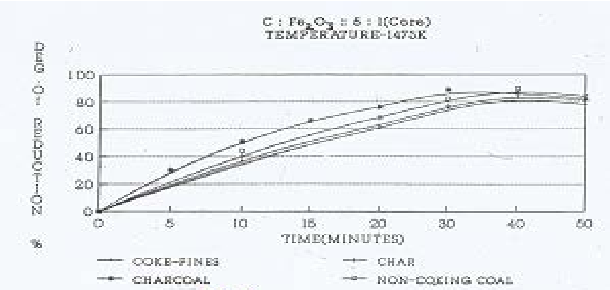

Fig 2

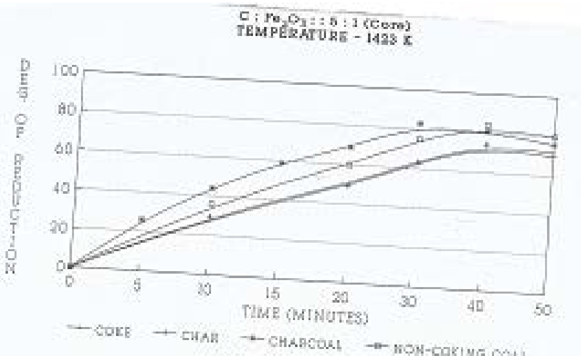

Fig 3

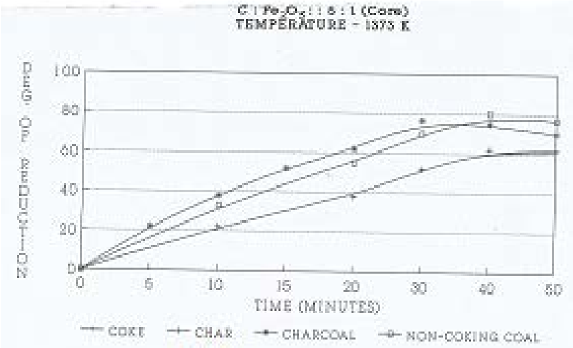

Fig 5

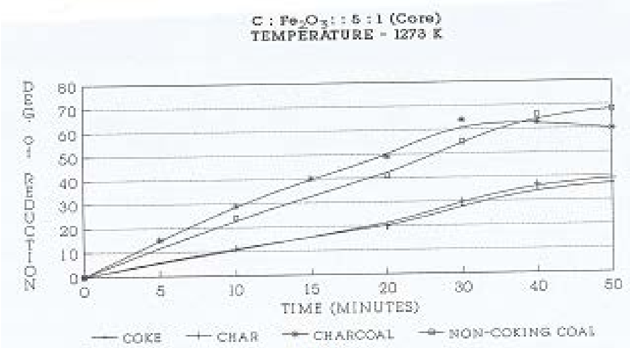

Fig 6

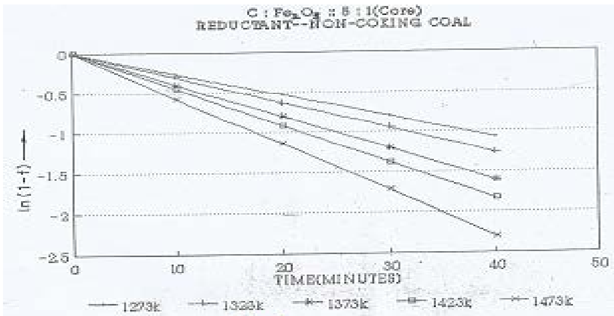

Fig 7

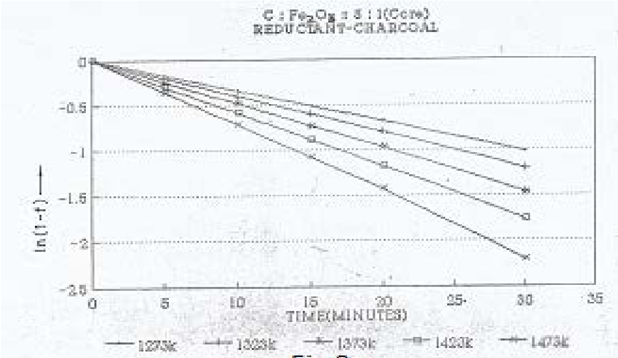

Fig 8

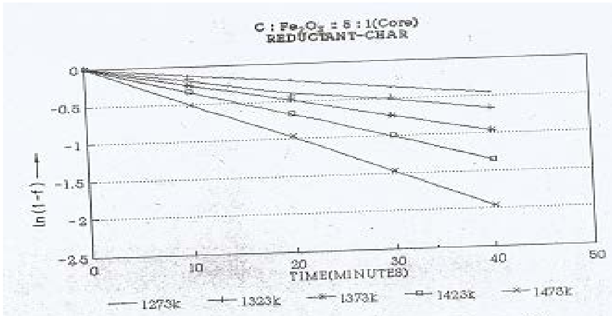

Fig 9 Plot of ln(1-f) Vs Time (t)

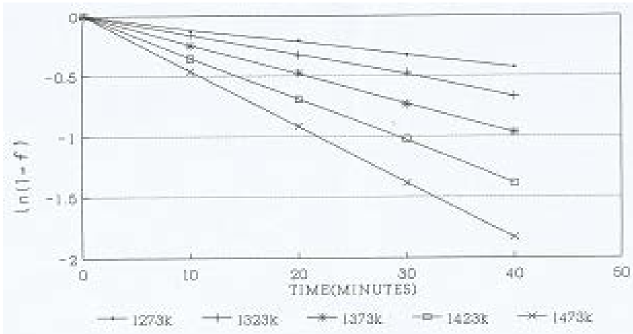

Fig 10 Plot of ln(1-f) Vs Time (t)

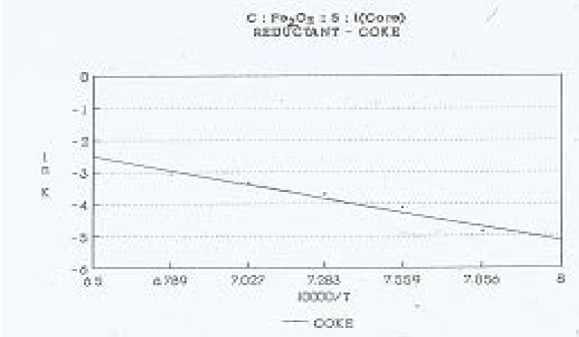

FIG. 11 Plot of ln K Vs 1/T (Arrenius Plot)

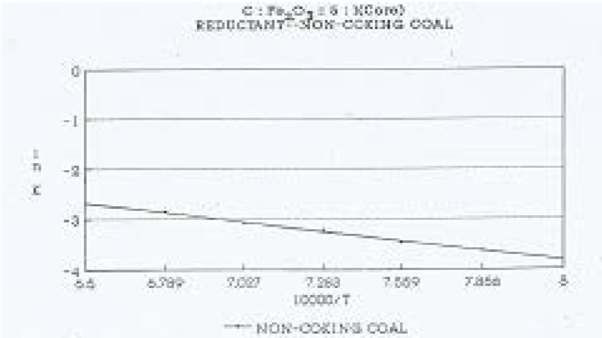

FIG.12 Plot of ln K Vs 1/T (Arrenius Plot)

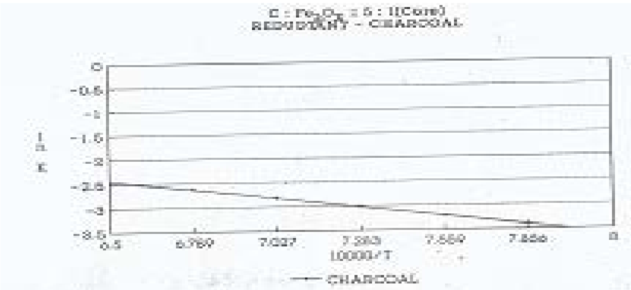

FIG. 13 Plot of ln K Vs 1/T (Arrenius Plot)

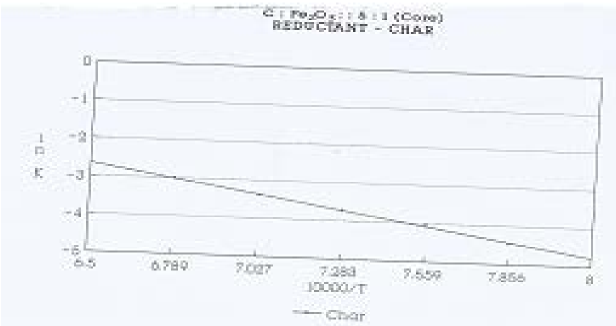

FIG. 14 Plot of ln K Vs 1/T (Arrenius Plot)

IV. DISCUSSION

When a double layered pellet containing coke, non-coking coal, char or charcoal and iron ore mixtures encased in a shell of iron ore is heated, the shell hinders gas passing from pellet out. The reduction starts taking place at the surface of the core or on the core-shell interface. The shell of a double layered pellet behaves as a porous container inside which reducing atmosphere mostly prevails. Reaction between iron oxide and solid carbon takes place inside the shell and the product CO and CO_2 diffuses outward from the core of the pellet and hence, the shell of the pellet gets partially reduced. The reduction continues until all the carbon is either consumed or escapes in the form of CO and CO_2. Further heating of the pellet results in re-oxidation of the reduced iron by inward diffusion of oxygen from the surrounding atmosphere. A decrease in the degree of reduction after achieving a maximum value has also been reported in the literature[2-5].

A higher degree of reduction is obtained at higher temperature for all the four reducing agents because of a faster rate of heat transfer as well as a faster rate of reduction. At higher temperatures, the rate of formation of carbon monoxide gas is higher because of its endothermic nature. This also is a reason for the faster rate of reduction at higher temperature. At lower temperature, the heat flux is not sufficient to grant an appreciable rate of carbon gasification reaction. Hence, the rate of reduction at lower temperature is low for all the four cases[8-13].

4.1 Physical Tests

The double layered pre-reduced pellets obtained during present study by using Coke/Char/Charcoal as reducing agents did not show any sign of disintegration but non-coking coal / iron ore core double layered pellets disintegrated during firing because of higher volatile matter content. The coke / iron ore, Char / iron ore and charcoal / iron ore core double layered pellets obtained after firing exhibited good physical properties.

Table 2

Properties of double layered pre-reduced pellets

Sl. No.	Properties	Types of double-layered pellets			
		Coke	Non-coking coal	Char	Charcoal
1.	Shatter index (+10 mm)	75%	83%	78%	78%
2.	Abrasion index (+6.3 mm surviving)	89%	90%	89%	89%
3.	Dust index (-0.6 mm)	4.4%	4.2%	4.4%	4.4%
4.	Apparent porosity	35-36%	30-32%	33-35%	34-35%
5.	Crushing strength (kg) (per pellet of 12 mm diameter)	175-180	185-195	175-185	200-210
6.	Maximal degree of reduction	84%	90%	86%	89%

For the use of these double layered pre-reduced pellets in blast furnace / steel making processes some mechanical and physical tests were performed.These includes compressive strength, shatter index, abrasion index, dust index and apparent porosity. For these mechanical and physical testing pellets (C:Fe_2O_3 ratio of core is 5:1) were produced in bulk in drum pelletizer. The bulk of the pellet (5Kg) was taken in a stainless steel container. The container was put inside the furnace maintained at 1473K. A thermocouple was fitted at the middle of the container to measure the temperature in the pellet bed. It took 35 minutes to bring the temperature at 1473K throughout the container. Then after achieving this temp, the container was kept inside the furnace for 40 minutes. Then similar experiments were repeated to produce bulk double layered pre-reduced pellets. These pellet were subjected to shatter index, abrasion index, dust index, crushing strength apparent porosity etc. The standard test methods were used for these tests[14]. The results of the physical tests for all four types of pellets are presented in Table 2.

V. CONCLUSIONS

From the present investigation, the following conclusions can be drawn

As reduction time increases, the degree of reduction of iron oxide increases to a certain level and with further increase in reduction time, either it become constants or it starts decreasing.This trend is followed for all temperature for all the four reducing agents.

As temperature increases from 1273 to 1473K the degree of reduction of iron ore increases.

Non-coking coal and charcoal yield a higher degree of reduction than char and coke. In case of charcoal, reduction rate is the highest.

The reduction time has the strongest effect when charcoal and Non-coking coal are used as reducing agents. Whereas, in the case of coke and char, the reduction temperature has the strongest effect.

Coke, char and charcoal can be used as effective reducing agents for production of double layered pre-reduced(DLPR) pellet under isothermal conditions without pellet dis integration. But in the case of non-coking coal, disintegration take place due to higher contents of volatile matter.

The reduction of iron oxide with non-coking coal / charcoal/char/coke in double layered pellet follows the first order reaction kinetics. The maximum value of activation energy is highest (117.94 KJ/mole) for coke/iron ore core double layered pellets with C : Fe_2O_3 ratio 5:1 of core and lowest (66.88 KJ/mole) for non-coking coal / iron ore core double layered pellets with C:Fe_2O_3 ratio 5:1 of core.

The value of activation energy for charcoal / iron ore core and char / iron ore core double layered pellet with C : Fe_2O_3 ratio 5:1 are 80.15 KJ/mole and 111.68 KJ/mole respectively.

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