KINETICS OF IRON ORE REDUCTION BY COAL AND CHARCOAL

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF
THE REQUIREMENTS FOR THE DEGREE OF

Bachelor of Technology
In
METALLURGICAL AND MATERIALS ENGINEERING

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CERTIFICATE

This is to certify that the thesis entitled, **“Kinetics of iron ore reduction by coal and charcoal”** submitted by **Sri Sandeep Kumar Baliarsingh** and **Sri Barun Mishra** in partial fulfillment of requirements for the award of Bachelor Of Technology degree in Metallurgical and Materials Engineering at National Institute Of Technology, Rourkela (Deemed University) is an authentic work carried out by him under my supervision and guidance.

To the best of my knowledge, the matter embodied in the thesis has not been submitted to any other university or institute for the award of any degree on diploma.

Date:

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ABSTRACT

In the present investigation, an attempt has been done to study the simultaneous effects of the major processing variables on the extent of reduction of iron ore pellets surrounded by coal or charcoal fines in an externally heated cylindrical steel container (diameter 5cm and height 10cm) placed in muffle furnace. The project goal is to compare the reduction potential of coal and charcoal in reduction of iron ore pellets. Wood charcoal contains very low levels of gangue, sulphur and volatile matter therefore, presenting itself as a very desirable reductant for the reduction of iron ore. The variables studied are time and temperature. The reduction was done at temperatures 850^0C, 900^0C, 950^0C and 1000^0c. The percentage (degree) of reduction of pellets was calculated at 15, 30, 45, 60 and 90 minutes, after the furnace reached the predetermined reduction temperature. The experiments were statistically designed such that the effect of each variable can be quantitatively assessed and compared. The results showed that, there is an increase in degree of reduction with increase in time and temperature and use of charcoal instead of coal also increased the degree of reduction due to higher fixed carbon content of charcoal. The percentage of swelling showed a random variation with time and temperature. The activation energy for the reduction of iron ore pellet was found to be higher in case of coal as compared to that of in case of charcoal; this indicates that reduction of iron ore by charcoal will be more favorable in case of charcoal.

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CHAPTER-1

INTRODUCTION

1.1) Introduction:

Iron is believed to be the tenth most abundant element in the universe, and the fourth most abundant in the earth's crust. Iron is the most used of all the metals, comprising 95% of all the metal tonnage produced worldwide. Iron is extracted from its ore, and is almost never found in the free elemental state. In order to obtain elemental iron, the impurities must be removed by chemical reduction.

The possible ways of iron ore reduction:

Industrially iron is produced from iron ores, principally hematite (Fe_2O_3), magnetite (Fe_3O_4) by a carbothermic reaction that is reduction with carbon, in a blast furnace at temperature about 800-1600^{O}C. In blast furnace, iron ore, carbon in the form of coke, and a flux such as limestone are fed into the top of the furnace, while blast of heated air is forced into the furnace at the bottom.

In the *blast furnace,* the coke reacts with oxygen in the air blast to produce CO.

$$2\ C+O_2 \rightarrow 2\ CO$$

The CO reduces the iron ore to molten iron becoming CO_2 in the process.

$$3\ CO + Fe_2O_3 \rightarrow 2Fe + 3CO_2$$

$$4\ CO + Fe_3O_4 \rightarrow 3Fe + 4CO_2$$

Other than this classical route that is blast furnace technology of iron production, the iron also can be produced from its ore by the *direct reduction of iron* ore by a reducing agent which is coal based or may be a gaseous reducing agent, which is called direct reduced iron (DRI) or SPONGE IRON.

Direct reduced iron (DRI) or sponge iron is a good substitute of scrap for making steel in electric arc furnace, basic oxygen furnace etc. which resulted in rapid worldwide growth in DRI production. DRI is a solid state product of direct reduction processes which is produced either in the form of lump or pellet. Availability of huge amount of non-coking coal, scarcity of coking coal deposits and industrial significance of DRI led to many efforts for the development of many direct reduction processes.

The growth of DRI industry took place in India in its nascent form in the latter half of 20th century. Until then, steel scrap formed a major part of our import next only to petroleum products. Then, Indian Government imposed curtailment measures and search for alternative measures began. In a direct reduction process, variety of reductant like lower grade coals, natural gas, charcoal etc can be used. The fast depletion of high grade coking coal reserves restricts the use of coke in the conventional blast furnace – oxygen steel making route. India being enriched with good quality iron ore and coupled with its vast reserves of non-coking coal likely to last for another 200 years or so, it is an advantageous position for coal/charcoal based sponge iron plants. The total gross reserves of coking coal and non-coking coal in India are approximately 11,602 and 71,400 million tones. India is one of the unfortunate countries, which does not have good quality of coking coals. From this consideration, the rotary kiln DR process have developed well and vigorously in the country instead of natural gas based shaft furnace or retort process. In order to accept the potential of the fact, it is rather imperative to understand the basic mechanism involved in DR process using non-coking coal/charcoal as reductant.

1.2) <u>various processes which produce DRI</u> are:

a) *Coal based processes*:

1) Rotary kiln processes (SL/RN, Krupp-CODIR, DRC, and ACCAR/OSIL)
2) Retort processes (Kinglor Metor)
3) Rotary hearth processes (Inmetco, FASTMET)

b) *Gas based processes*:

1) Shaft processes (MIDREX, HYL process, Purofer)
2) Fluidized processes (FIOR/FINMET, Iron carbide, Circored)

Iron and steel making are two of the largest energy intensive industries with the highest growth rate in energy consumption of all energy utilization sectors. In order to meet the scarcity of coking coal and growing greenhouse challenges, incorporation of renewable energy sources to the existing and emerging metallurgical operations is desirable. In this respect, charcoal can potentially be applied as fuel for minerals processing. The work presented here investigates the fundamental mechanisms of iron ore reduction with charcoal. According to US patent 4212452 a mixture of iron ore, solid carbonaceous material (cellulosic material or charcoal) as fuel, dolomite or limestone (if sulfur is present) are used for direct reduction of iron ore pellets. The American Iron and Steel Institute (AISI) Technology Roadmap Program (TRP) is conducting a project, whose goal is to use wood charcoal, a renewable energy source to reduce iron ore and waste oxides. Wood charcoal contains very low levels of gangue, sulfur, and volatile matter, therefore providing a very desirable reductant to perform the reduction of iron ore. The use of charcoal may reduce green house effect by over 90%, significantly decrease capital and operating costs, and increase productivity. Emmerich and Luengo summarized the benefits of metal smelting operations with charcoal produced from wood, which is the oldest reduction technology known dating back to the iron age.

1.3) Aims:

1) Comparison of reduction behavior of iron ore pellets by coal and charcoal.
2) Determination of activation energy for reduction of iron ore pellet by both coal and charcoal.

CHAPTER-2

Pellets

Pellets are approximately spherical lumps formed by the agglomeration of the crushed iron ore fines in presence of moisture and binders and then hardening at a temperature of 1200^0C.Binders play an important role in pellet formation. They give strong, wet and dry balls in green state and increase fire strength. The different types of binders used can be classified into following categories:

Organic binders (Dextrin, Starch, Alginate)

Inorganic binders (Bentonite, Cement, Lime, Calcium hydroxide)

Bonding mechanism involves two stages as:

(a) Nucleation (Seed formation)

(b) Growth (occurs in two ways: growth by layering and growth by assimilation)

Advantages of pellets:

1. Good reducibility
2. Good permeability
3. High bulk density
4. High iron content
5. Uniform chemical composition
6. High strength
7. Less heat consumption
8. Ease in handling

Disadvantages of pellets:

1. High cost of production due to grinding and firing.
2. Swelling and loss of strength inside furnace.
3. Sticking during firing.
4. Resistance to flow of gas more than that in sinter for the same size range due to lower void age.
5. Difficulty of producing fluxed pellets.

CHAPTER-3

Mechanism and kinetics of reduction of iron ore lump and pellet

Reaction kinetics in iron ore reduction deal with the rate at which iron oxides are converted to metallic iron by the removal of oxygen. The rate of a chemical reaction increase with increase in temperature. For this reason the reaction kinetics are not generally a matter of great importance in the blast furnace because of the high temperatures at which the furnace is operated. On the other hand, in DR processes where the iron is reduced in the solid state, the maximum temperature is below the melting temperature and the reaction rates are slower. For direct reduction of iron ore, the mechanisms are complex because the oxide must go through a series of step wise changes before the conversion is complete. The slowest step in the process determines the overall reaction rate and is referred to as the rate controlling step.

3.1) Reactions involved in iron ore reduction:

Reduction by **CO (indirect reduction)**:

Above 570^0C, iron oxide is reduced by CO in three stages:

$3Fe_2O_3 + CO \rightarrow 2Fe_3O_4 + CO_2$

$Fe_3O_4 + CO \rightarrow 3FeO + CO_2$

$FeO + CO \rightarrow Fe + CO_2$

Below 570^0C, Fe_3O_4 is directly reduced to Fe bypassing the wustite (FeO) stage.

Reduction by **Hydrogen (indirect reduction)**:

Reduction by Hydrogen occurs in three stages as follows:

$3Fe_2O_3 + H_2 \rightarrow 2Fe_3O_4 + H_2O$

$Fe_3O_4 + H_2 \rightarrow 3 FeO + H_2O$

$FeO + H_2 \rightarrow Fe + H_2O$

Reduction by **Carbon (direct reduction):**

For solid carbon in a DR process, the following three reduction reactions can be written:

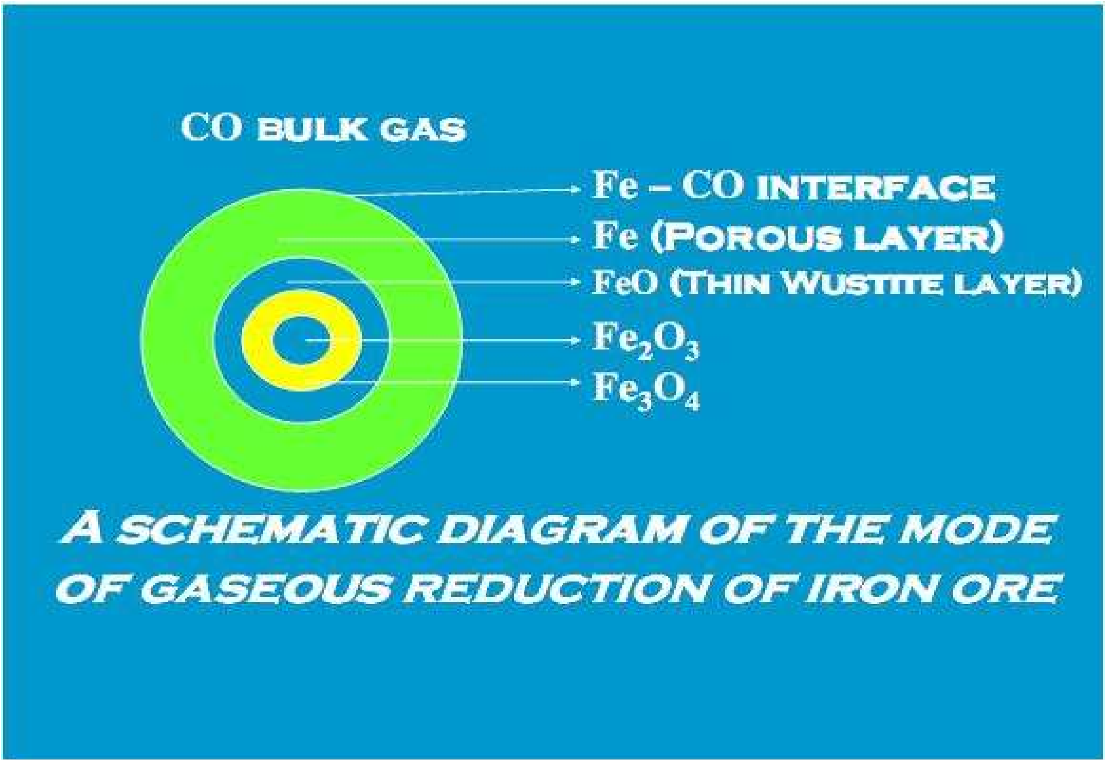
$3Fe_2O_3 + C \rightarrow 2Fe_3O_4 + CO$

$Fe_3O_4 + C \rightarrow 3FeO + CO$

$$FeO + C \rightarrow Fe + CO$$

Only a negligible amount of reduction will occur by direct contact of carbon particles with iron oxide particles since such solid-solid reactions are very slow. The actual reduction process occurs through the intermediary of CO.

3.2) Photograph of spherical model of reduction:



3.3) Rate laws in reduction:

The reduction of the iron oxides takes place in a series of sequential steps. The overall rate will be determined by the slowest process in the series. The possible consecutive steps are:

1) Transport of gaseous reductant from the bulk gas phase to the particle surface through a boundary gas film.
2) Molecular diffusion of the gaseous reductant through the product layer to the reaction interface.
3) Adsorption of the gaseous reductant at the interface.
4) Reaction at the interface (reaction between adsorbed reductant and oxygen of the lattice).
5) Desorption of the gaseous products from the interface.
6) Mass transport of iron and oxygen ions and transformations in the solid phase, formation and growth of reaction products e.g magnetite, wustite, iron.
7) Molecular diffusion of gaseous products through the product layer to the particle surface.
8) Transport of the gaseous products from the particle surface through the boundary gas film to the bulk gas phase.

The rate limiting cases are chemical controlled (steps 3 to 6) and diffusion controlled (steps 1, 6, 7, 8)

3.4) KINETICS OF DIRECT REDUCTION PROCESS

Reaction kinetics of iron ore reduction deals with the rate at which iron oxide is converted to metallic iron by removal of oxygen. The rate at which the ore is reduced influences the production rate, which ultimately determines the economic feasibility and competitiveness of the process technology involved .Thus the reaction rate in DR process is of prime importance. The reduction of iron oxide to metallic iron proceed though various kinetic steps and one of them is the slowest step, which control the overall reaction rate .The different rate controlling factors which control the overall rate of reduction are given below:

3.4.1) Boundary Layer Control

In boundary layer control the overall reduction rate is controlled by the diffusion of gas and heat through the boundary layer of the gas which builds up around each particle. The rate of diffusion of the gas through the boundary layer is proportional to the gas concentration gradient across the layer. Secondly, the rate of heat flow to the particles is proportional to the temperature gradient across the boundary layer. In most direct reduction process contact between gas and solids is achieved by counter current flow of preheated gas to the movement of the bed of solids.

3.4.2) Phase Boundary Reaction Control

The chemical reaction at the wustite -iron interface is the rate controlling factor. In this case the rate of reduction per unit area of the remaining iron oxide is found to be constant with time. This mechanism is called “Phase Boundary Reaction Control”.

When counter diffusion of reducing gas and product gas on the reduced outer layer is sufficiently fast, the concentration of reducing gas at the reacting surface is effectively the same as it’s concentration at the particle surface. In such case the rate of reaction at the wustite-iron interface would control the overall reduction rate. This mechanism is unlikely at the very start of the reduction, when the iron layer is very thin, or for very small porous grains of iron oxide**.**

3.4.3) Gaseous Diffusion Control

The rate of reducing gas inward and product gas outward through the reduced iron layer can control the rate of reduction of iron oxides. This phenomenon is generally associated with large ore particle and is known as “Gaseous Diffusion Control”.

When gaseous diffusion is the rate controlling step, the rate of diffusion of reducing gas inward and product gas outward through the porous layer of metallic iron surrounding the unreduced inner core particle, is slower than the rate of reaction. During such occurrence the concentration of the reducing gas will decrease that of product gas will increase at the interface. The change in the gas composition will slow down the reduction rate until a pseudo steady state is established. This is the pre dominant rate controlling mechanism for high temperature reduction of large (greater than 7 mm) particle beyond 50% reduction, when iron layer thickness exceeds about 1mm.

3.4.4) Mixed Control

When both Gaseous Diffusion Control and Phase Boundary Reaction Control combine influence the rate of reduction, the mechanism is referred to as "Mixed Control".

Mixed control has been proposed by several experiments to reconcile the complexities and conflicting results obtained from direct reduction of iron oxides with simpler mechanism. In mixed control, the gas boundary layer, the phase boundary reaction and gaseous diffusion act together under pseudo steady state condition to determine the overall reaction rate.

Different mathematical models equations are proposed to represent different rate controlling steps, which are given below

EQUATION	**CONTROLLNG STEP**
$1- (1-f)^{1/3} = kt$	Chemically Controlled
$- \ln (1-f) = kt$	Chemically Controlled
$[1 – (1-f)^{1/3}]^2 = kt$	Diffusion Controlled
$1- 2/3f – (1 - f)^{2/3} = kt$	Diffusion Controlled
$k' [1-2/3f – (1-f)^{2/3}] +D/r_0[1-(1-f)^{1/3}] = kt$	Mixed Controlled

CHAPTER-4

EXPERIMENTAL

4.1) Collection of raw materials:

Iron ore from Gandha Mardan (OMC Limited Ore) was collected and crushed to -100# by ball mill. Charcoal and Coal (Basundhara west grade D) were collected and crushed into size -8+16#.

Composition of GM iron ore: 90.60% Fe_2O_3 (wet), 94.58% Fe_2O_3 (dry).

Composition of Basundhara coal (grade D): Moisture Content= 5%, Volatile Matter content= 32%, Ash content= 15%, and Fixed Carbon content= 48%.

Composition of wood charcoal: Moisture content= 4%, Volatile matter content= 15%, Ash content= 26%, and Fixed Carbon content= 55%.

The iron ore fines were converted into small pellets in presence of moisture by hand rolling method. Drying of green pellets at 110^0C for 3 hours, followed by firing at 1200^0C for 1hr in a muffle furnace to obtain proper strength of pellets. The pellets were furnace cooled to room temperature.

4.2) Procedure for reduction:

Before each reduction, the pellets were dried for 1 hr at 110^0C.The pellets surrounded by coal/charcoal were reduced in a metallic container (size 5cm diameter, 10cm length) kept inside a muffle furnace until temperatures 850^0C, 900^0C, 950^0C, and 1000^0C. Out of five, four containers were taken out of the furnace in 15 minutes interval, after the furnace reached the predetermined reduction temperature and the last one was taken out at 30 minute interval. The containers were allowed to cool to room temperature in air. The initial and final weights of pellets were noted, from which weight loss (equal to oxygen removed) was calculated.

7) The degree (%) of reduction was calculated using the given formula:

$$\textbf{\% of reduction} = \frac{\textbf{weight loss of the pellet x 100}}{\textbf{Total oxygen present in pellet}}$$

.

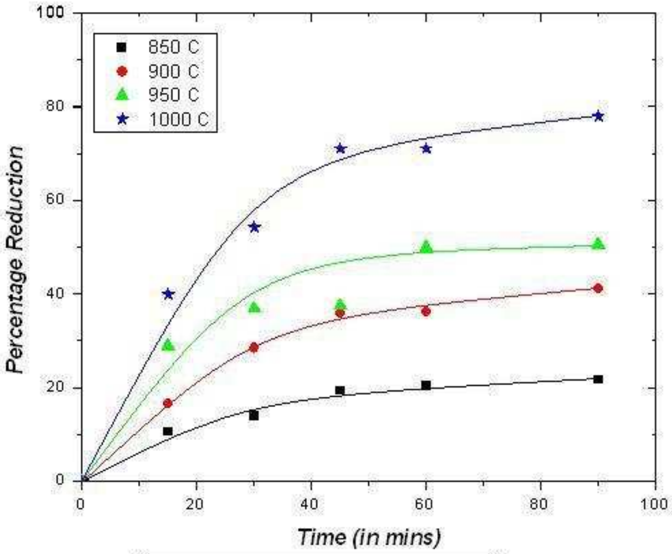
CHAPTER-5

RESULTS & DISCUSSION

Table-I

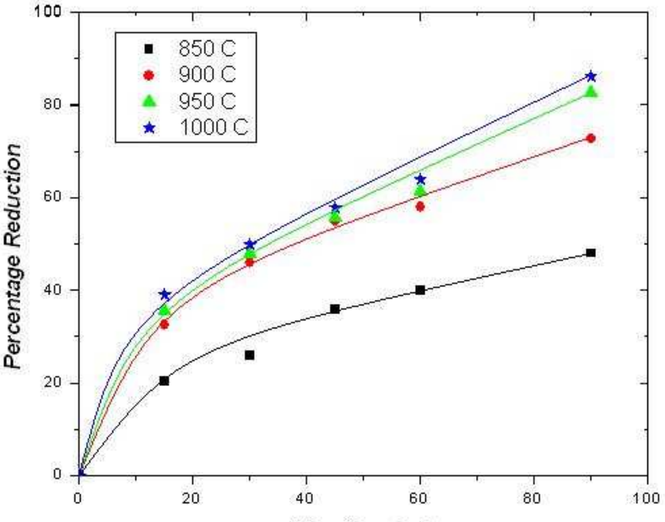
Temperature(°C)	Time (minutes)	Percentage Reduction	
		Coal	Charcoal
850	15	10.54	20.44
	30	13.93	25.93
	45	19.32	35.81
	60	20.40	39.87
	90	21.65	48.03
900	15	16.54	32.43
	30	28.44	46.02
	45	35.81	54.89
	60	36.11	57.98
	90	41.08	72.69
950	15	28.82	35.59
	30	36.93	47.81
	45	37.52	55.82
	60	49.99	61.29
	90	50.47	82.64
1000	15	39.86	39.11
	30	54.22	49.72
	45	71.10	57.92
	60	71.11	63.97
	90	78.05	86.10

Figure-I



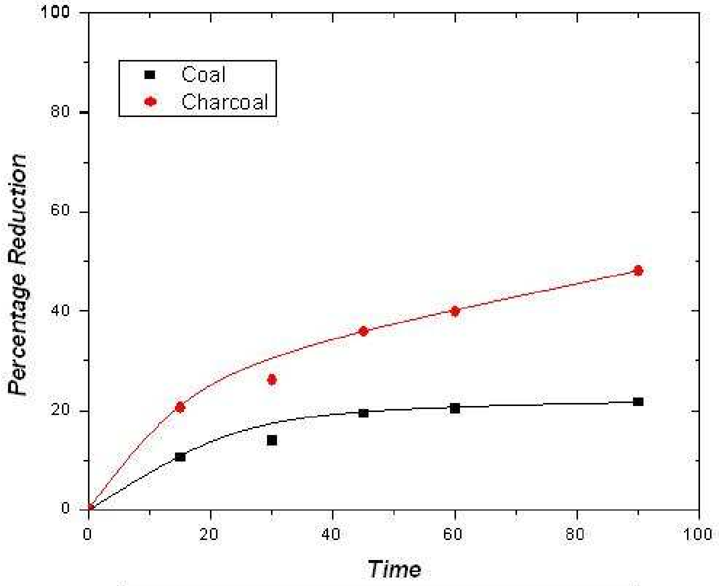
Percentage reduction vs Time curve for G M Iron ore (-100#) reduced by Basundhara mines D grade coal (-8+16#)

Figure-II



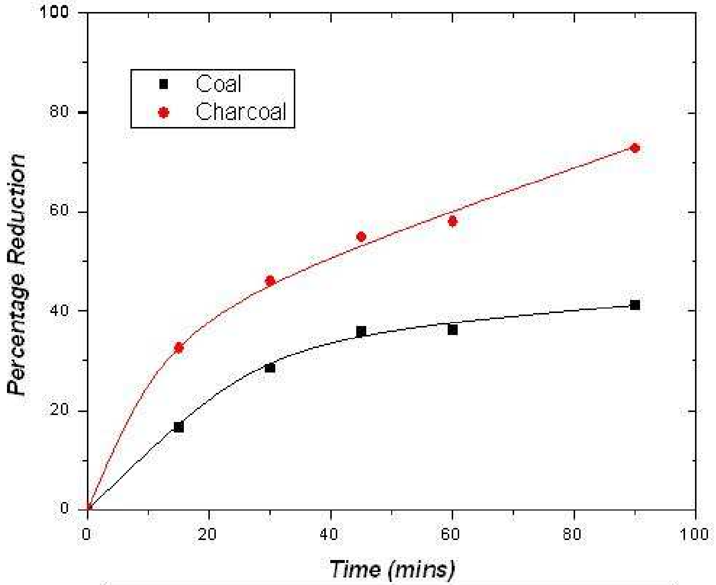
Percentage Reduction vs time for G.M iron ore pellet(-100#) reduced by Charcoal(-8+16#)

Figure-III



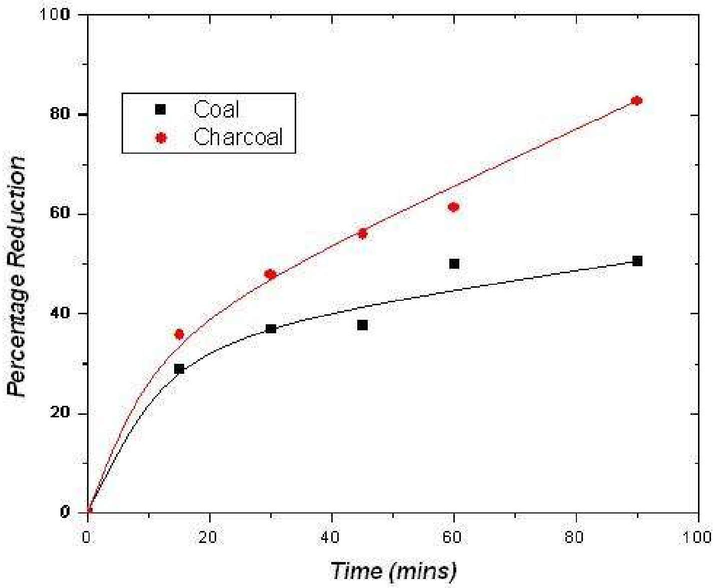
Comparision of Percentage of Reduction by Coal & Charcoal at 850 C.

Figure-IV



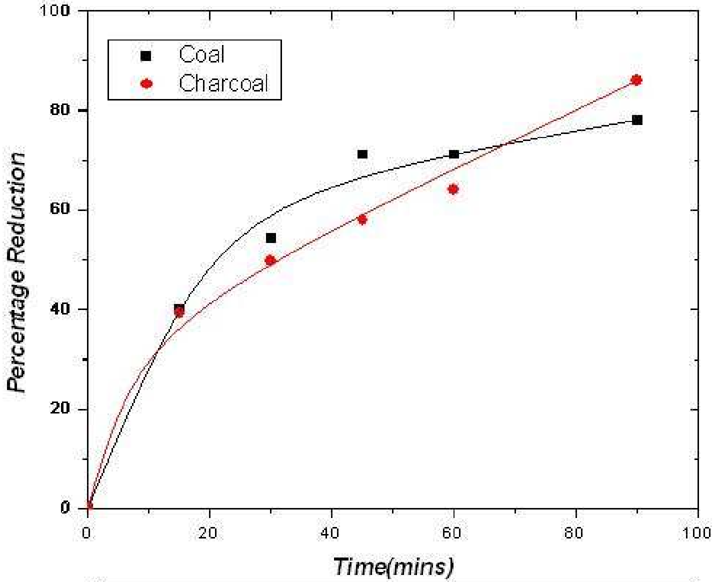
Comparision of percentage of reduction by coal & charcoal at 900 C

Figure-V



Comparision of percentage of reduction by coal & charcoal at 950 C

Figure-VI

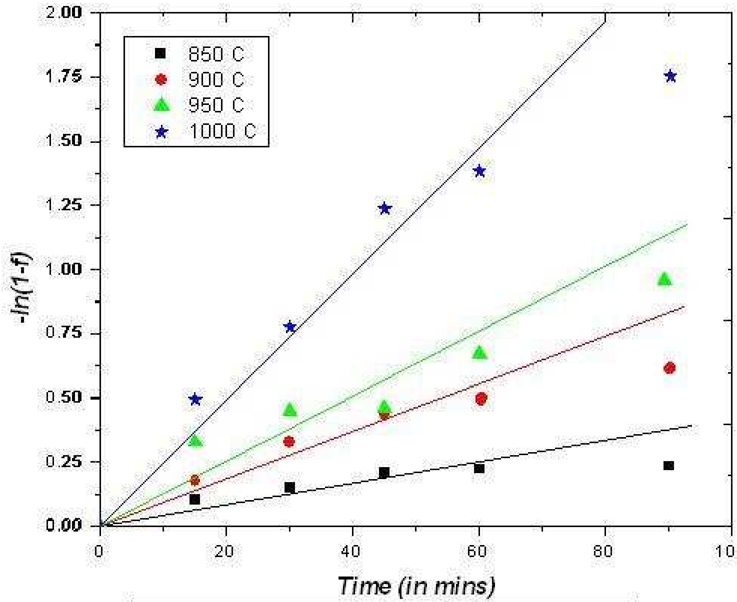


Comparision of percentage of reduction by coal & charcoal at 1000 C

Kinetic model:

The plots of –ln (1-f) vs time gave straight lines which determined the most appropriate kinetic model for iron ore reduction would be **-ln (1-f) = Kt**, where **t** is time, **f** is the fraction of reduction, **K** is the rate constant

Figure VII:

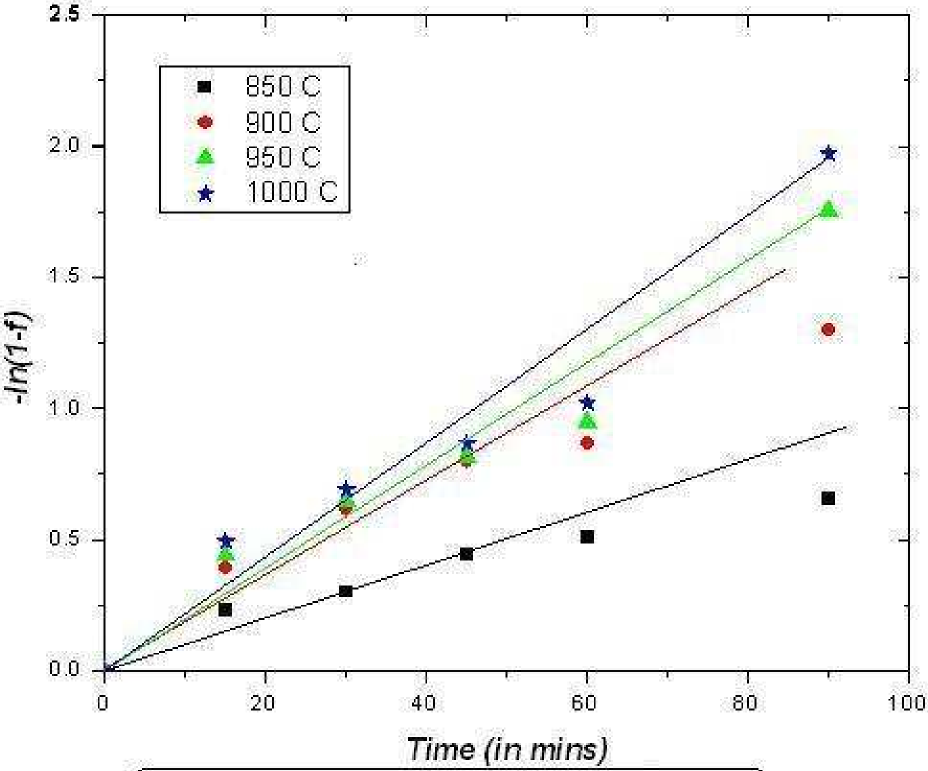


-ln(1-f) vs time plot for reduction of GM iron ore pellet(-100#) by coal(-8+16#)

Table-II

Temperature (°C)	**K** (from the above graph)
850	4.67×10^{-3}
900	9.56×10^{-3}
950	11.6×10^{-3}
1000	26.00×10^{-3}

Figure VIII:



-ln(1-f) vs time plot for reduction of GM iron ore pellet(-100#) by charcoal(-8+16#)

Table-III

Temperature (°C)	**K** (from the above graph)
850	$9.85\text{x}10^{-3}$
900	$17.6\text{x}10^{-3}$
950	$18.15\text{x}10^{-3}$
1000	$22.95\text{x}10^{-3}$

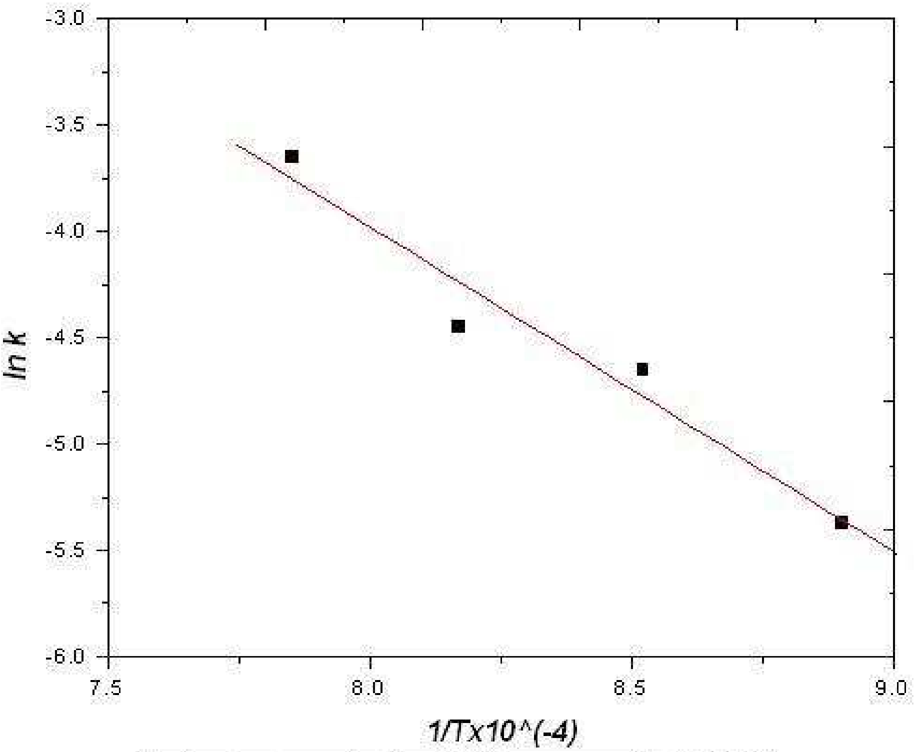
ACTIVATION ENERGY

$$\mathbf{K = A\, e^{-E/RT}}$$ (Arehenious equation)

Where **E** is the activation energy, **A** is Arehenious constant or Frequency Factor, **K** is the rate constant, **R** is the universal gas constant (8.314472 $J \cdot K^{-1} \cdot mol^{-1}$).**T** is the absolute temperature.

Slope of ln K vs 1/T plot is (-E/R).

Figure-IX:

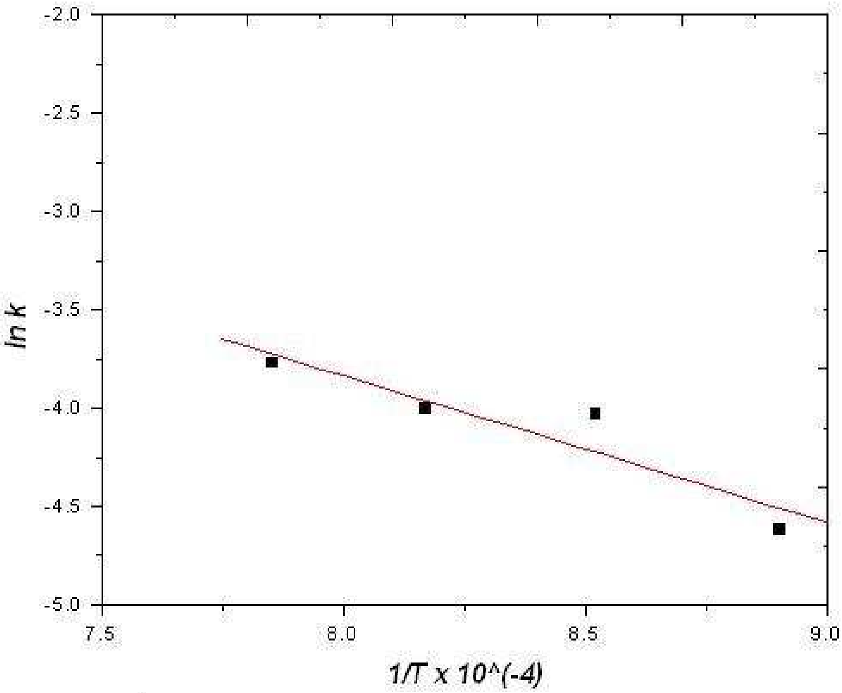


Arhenius type plot for G.M iron ore pellet(-100#) reduced by Basundhara Grade D coal(-8+16#)

Slope = -1.5 x 10^ (-4).

Activation energy = 124.71 KJ.

Figure X:



Arhenius type plot for G.M iron ore pellet(-100#) reduced by Charcoal

Slope = -0.7187 x 10^ (-4)

Activation energy = 59.75 KJ.

Table-IV

Comparison of activation energy for reduction of iron ore pellet by coal and charcoal:

Reductant	**Activation energy (K J)**
Coal	124.71
Charcoal	59.75

DISCUSSION:

For the heterogeneous (solid-gas) reduction of solid wustite by H_2 (g) or CO (g)

$FeO (s) + H_2 (g) \rightarrow Fe (s) + H_2O (g)$ (indirect reduction)

$FeO (s) + CO (g) \rightarrow Fe (s) + CO_2 (g)$ (indirect reduction)

These heterogeneous systems include three regions: bulk wustite, bulk gaseous phase and the interfacial zone.

Reaction rate = $K_f [FeO] [H_2]$ (for hydrogen gas)

Reaction rate = $K_f [FeO] [CO]$ (for CO gas)

However, because of the heterogeneity of the system concentrations of the reactants in these three systems are not the same.

In bulk wustite: $[H_2] = 0$, $[CO] = 0$ Reaction rate = 0

In bulk gas: $[FeO] = 0$ Reaction rate = 0

In interfacial zone: $[H_2] \neq 0$, $[CO] \neq 0$, $[FeO] \neq 0$

There will be a finite reaction rate of reaction in the interfacial region.

The reaction rate at the wustite-hydrogen/CO is expressed as:

Reaction rate = $K_f [FeO]^i [H_2]^i$

Reaction rate = $K_f [FeO]^i [CO]^i$

Where $[\ ]^i$ is for the concentration in the inter facial reaction zone and the rate of reaction has a unit of moles per unit area of interface per unit time.

Percentage of reduction of iron ore increased with increase in temperature and time, because this increase in temperature and time increased the rate and quantity of diffusion and chemically controlled reactions included in the mechanism of step wise reduction of iron ore pellets. Use of charcoal increased the percentage of reduction of pellets as compared to coals, because of higher fixed carbon content of charcoal. The activation energy for the reduction of pellet by coal was found to be more than that of in case of charcoal. This indicates that the reduction of pellet starts at a lower temperature for charcoal as compared to the coal and the extent of reduction in case of charcoal will be higher.

CHAPTER -6

CONCLUSION

CONCLUSION:

1) Increase in temperature, increases the percentage of reduction.
2) Increase in time, increases the percentage of reduction.
3) Increase in fixed carbon content of reductant, increases the percentage of reduction.
4) Less is the activation energy of reaction; more will be the extent of reaction.

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