Studies on Kinetics and Mechanism of Iron Oxide Reduction

Submitted in partial fulfillment of
the requirements for the Degree
of

BACHELOR OF TECHNOLOGY(B.TECH.)
in
METALLURGICAL ENGINEERING
of
KOLHAN UNIVERSITY
by

ASHISH KUMAR (MTE/570/13)
SACHIN JAGANNATH (MTE/574/13)
PRIYA KUMARI (MTE/568/13)
NARENDRA NATH MAHATO (MTE/569/13)

Under the esteemed guidance of

Prof. B.N. CHOUDHARY

DEPARTMENT OF METALLURGICAL ENGINEERING
R.V.S COLLEGE OF ENGINEERING AND TECHNOLOGY
JAMSHEDPUR – 831012

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CERTIFICATE

This is to certify that the thesis entitled "Studies on kinetics and mechanism of iron oxide reduction being submitted by student for the award of the Degree of Bachelor of Technology (B.Tech) in Metallurgical Engineering during academic session 2013-17 to the R.V.S College of Engineering & Technology affiliated to the Kolhan University is a bonafide project work carried out by him along with group members under my supervision and guidance. This thesis fulfills the requirements of regulation of the university relating to the nature and standard of work for the award of B.Tech degree and in my opinion is worthy for consideration for the award of the degree.

The results embodied in this thesis have not been submitted to any University or Institute for the award of any degree or diploma.

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Signature of External

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ABSTRACT

In the present investigation, an attempt has done to study the kinetic and mechanism of reduction of iron ore lumps surrounded by coal lumps heated in crucible placed in muffle furnace in partially open atmosphere. The process variables are temperature, time. The reduction was carried out at temperature 800, 900 and 1000^0 C with reduction time of 20,40,60,80 and 100 minutes. Proximate analysis of coal was done to determine the percentages of fixed carbon, ash, volatile matter, moisture. The reduction of iron ores were carried out in muffle furnace and were carefully monitored to avoid oxidation after being taken out of the furnace after completion of assigned time interval. The degree of reduction of iron ores were plotted against temperature and time. The results have indicated that with increase in temperature the overall percentage of reduction for the same time interval also increases. But for increased time interval the rate of reduction shows a slow decrease for holding at the same temperature.

contents

CHAPTER 1

1.1 INTRODUCTION

DRI (directly reduced iron) or sponge iron is a porous solid-state production of direct reduction process. This is produced in lump or pellet form. DRI is being used in steel making through various routes such as EAF (electric arc furnace) BOF (basic oxygen furnace), as it is very economical and readily available material to substitute steel scrap, it has been used in extensive amount. In view of this increased demand for sponge iron, Studies are being carried out to observe the reduction behaviour of iron ores by direct reduction method.

The reduction of iron ore by carbon is the most important reactions in iron making by blast furnace or any other routes of iron making. Various studies have been carried out on the reduction behaviour of iron ore mixed with coal/char/graphite /coke etc. which showed that the reduction takes place via gaseous intermediates like carbon monoxide and carbon dioxide. The actual reduction reaction does not need any gaseous medium to be carried out. Now it is a well-accepted fact that the direct reduction is mostly result of indirect reduction.

Some the various advantages of DR process over blast furnace iron making are elimination of dependence on coking coal, small module size, and optimal size DR units require lower capital investment, superior environmental friendliness and it provides improved process control and manoeuvrability. It is one of the preferred raw materials for the production of low carbon steels. It has limitations owing to its low productivity per unit volume of the reactor. Hence this process also poses some problems where economical productivity is the main concern.

This calls for some method of innovation to make this process economically viable. These studies are thus aimed at getting a better understanding of reactionkinetics at various temperatures with varying time. So that the data can be used for finding better process making method.

Chapter:- 2

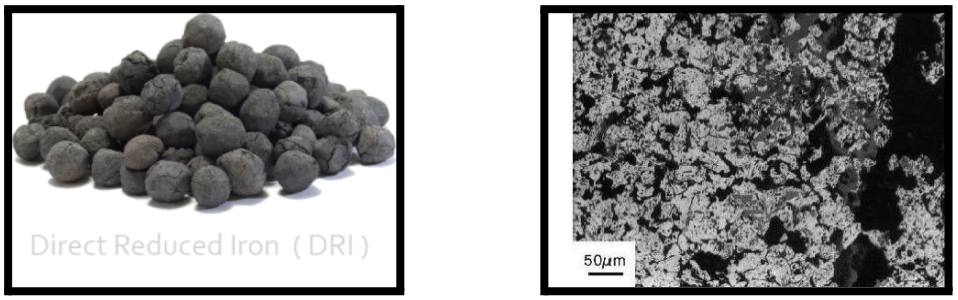
Literature Review

2.1. Alternative Iron Source

Alternative iron source produced by heating an iron ore (generally having 65 to 70 percent iron) at a temperature high enough to burn off its carbon and oxygen content (a process called reduction) but below iron's melting point(1535°C). The output is sold as pellets or hot briquetted iron (HBI) and contains from 90 to 97 percent pure iron, the rest being mainly carbon with trace amounts of other impurities. DRI is consumed primarily by mini steel mills (Figure 1a & b).

to improve the quality of their steel. Since the reduction process consumes prodigious amounts of natural gas, it is economically viable only where natural gas is abundant and relatively cheap, also called sponge iron due to its porous nature. The conventional route for making steel consists of sintering or pelletization plants, coke ovens, blast furnaces, and basic oxygen furnaces. Such plants require high capital expenses and raw materials of stringent

specifications. Coking coal is needed to make a coke strong enough to support the burden in the blast furnace. Integrated steel plants of less than one million tons annual capacity are generally not economically viable. The coke ovens and sintering plants in an integrated steel plant are polluting and expensive units.



(a)Pellates (b) Microstructure of pellet.

Figure :-a & b: Direct reduced iron

Direct reduction processes can be divided roughly into two categories, gas-based, and coal-based. In both cases, the objective of the process is to drive off the oxygen contained in various forms of iron ore (sized ore, concentrates, pellets, mill scale, furnace dust etc.), in order to convert the ore, without melting it (below 1200 °C), to metallic iron.

The direct reduction process is comparatively energy efficient. Steel made using DRI requires significantly less fuel, in that a traditional blast furnace is not needed. DRI is most commonly made into steel using electric arc furnaces to take advantage of the heat produced by the DRI product.

In modern times, direct reduction processes have been developed to specifically overcome the difficulties of conventional blast furnaces. DRI is successfully manufactured in various parts of the world. The initial investment and operating costs of direct reduction plants are low compared to integrated steel plants and

are more suitable for developing countries where supplies of coking coal are limited.

Factors that help make DRI economical:

(1) Direct-reduced iron has about the same iron content as pig iron, typically 90–94% total iron (depending on the quality of the raw ore) as opposed to about 93% for molten pig iron, so it is an excellent feedstock for the electric furnaces used by mini mills, allowing them to use lower grades of scrap for the rest of the charge or to produce higher grades of steel.

(2) Hot-briquetted iron (HBI) is a compacted form of DRI designed for ease of shipping, handling, and storage.

(3) Hot direct reduced iron (HDRI) is iron not cooled before discharge from the reduction furnace that is immediately transported to a waiting electric arc furnace and charged, thereby saving energy.

(4) The direct reduction process uses pelletized iron ore or natural "lump" ore. One exception is the fluidized bed process which requires sized iron ore particles.

(5) The direct reduction process can use natural gas contaminated with inert gases, avoiding the need to remove these gases for other use. However, any inert gas contamination of the reducing gas lowers the effect (quality) of that gas stream and the thermal efficiency of the process.

(6) Supplies of powdered ore and raw natural gas are both available in areas such as Northern Australia, avoiding transport costs for the gas. In most cases the DRI plant is located near natural gas source as it is more cost effective to ship the ore rather than the gas.

(7) This method produces 97% pure iron.

India is the world's largest producer of direct-reduced iron, a vital constituent of the steel industry. Many other countries use variants of the process, so providing iron for local engineering industries.

Sponge iron is not useful by itself, but can be processed to create wrought iron. The sponge is removed from the furnace, called a bloomery, and repeatedly beaten with heavy hammers and folded over to remove the slag, oxidize any carbon or carbide and weld the iron together. This treatment usually creates wrought iron with about three percent slag and a fraction of a percent of other impurities. Further treatment may add controlled amounts of carbon, allowing various kinds of heat treatment (e.g. "steeling").

Today, sponge iron is created by reducing iron ore without melting it. This makes for an energy-efficient feedstock for specialty steel manufacturers which used to rely upon scrap metal (Figure 2).

2.2. Redox reaction

Redox (short for reduction–oxidation reaction) is a chemical reaction in which the oxidation states of atoms are changed. Any such reaction involves both a reduction process and a complementary oxidation process, two key concepts involved with electron transfer processes. Redox reactions include all chemical reactions in which atoms have their oxidation state changed; in general, redox reactions involve the transfer of electrons between chemical species. The chemical species from which the electron is stripped is said to have been oxidized, while the chemical species to which the electron is added is said to have been reduced. It can be explained in simple terms:

- Oxidation is the loss of electrons or an increase in oxidation state by a molecule, atom, or ion.

- Reduction is the gain of electrons or a decrease in oxidation state by a molecule, atom, or ion.

As an example, during the combustion of wood, oxygen from the air is reduced, gaining electrons from the carbon.[2]Although oxidation reactions are commonly associated with the formation of oxides from oxygen molecules, oxygen is not necessarily included in such reactions, as other chemical species can serve the same function.[2, 3]

The reaction can occur relatively slowly, as in the case of rust, or more quickly, as in the case of fire. There are simple redox processes, such as the oxidation of carbon to yield carbon dioxide (CO_2) or the reduction of carbon byhydrogen to yield methane (CH_4), and more complex processes such as the oxidation of glucose ($C_6H_{12}O_6$) in thehuman body.

Reduction

$$\text{Oxidant} + e^- \longrightarrow \text{Product}$$

(Gain of Electrons) (Oxidation Number Decreases)

Oxidation

$$\text{Reductant} \longrightarrow \text{Product} + e^-$$

(Loss of Electrons) (Oxidation Number Increases) (2.1)

2.3. Natural gas reaction

Natural gas is a naturally occurring hydrocarbon gas mixture consisting primarily of methane, but commonly including varying amounts of other higher alkanes, and sometimes a small percentage of carbon dioxide, nitrogen, hydrogen sulfide, or helium. It is formed when layers of decomposing plant and animal matter are exposed to intense heat and pressure under the surface of the Earth over millions of years. The energy that the plants originally obtained from the sun is stored in the form of chemical bonds in the gas.

Natural gas is a fossil fuel used as a source of energy for heating, cooking, and electricity generation. It is also used as fuel for vehicles and as a chemical feedstock in the manufacture of plastics and other commercially important organic chemicals. It is a non-renewable resource[4].

Natural gas is found in deep underground rock formations or associated with other hydrocarbon reservoirs in coal beds and as methane clathrates. Petroleum is another resource and fossil fuel found in close proximity to and with natural gas. Most natural gas was created over time by two mechanisms: biogenic and thermogenic. Biogenic gas is created by methanogenic organisms in marshes, bogs, landfills, and shallow sediments. Deeper in the earth, at greater temperature and pressure, thermogenic gas is created from buried organic material [5, 6].

When gas is associated with petroleum production it may be considered a byproduct and be burnt as flare gas. The World Bank estimates that over 150 cubic kilometers of natural gas are flared or vented annually. Before natural gas can be used as a fuel, most, but not all, must be processed to remove impurities, including water, to meet the specifications of marketable natural gas. The by-products of this processing include: ethane, propane, butanes, pentanes, and higher molecular weight hydrocarbons, hydrogen sulfide (which may be converted into pure sulfur), carbon dioxide, water vapor, and sometimes helium and nitrogen [7].

Natural gas is often informally referred to simply as "gas", especially when compared to other energy sources such as oil or coal. However, it is not to be confused with gasoline, especially in North America, where the term gasoline is often shortened in colloquial usage to gas.

Natural gas was used by the Chinese in about 500 BCE. They discovered a way to transport gas seeping from the ground in crude pipelines of bamboo to where

it was used to boil salt water to extract the salt. The world's first industrial extraction of natural gas started at Fredonia, New York, United States in 1825. By 2009, 66 000 km³ (or 8%) had been used out of the total 850 000 km³ of estimated remaining recoverable reserves of natural gas. Based on an estimated 2015 world consumption rate of about 3400 km³ of gas per year, the total estimated remaining economically recoverable reserves of natural gas would last 250 years at current consumption rates. An annual increase in usage of 2–3% could result in currently recoverable reserves lasting significantly less, perhaps as few as 80 to 100 years [8-10].

Reduced iron derives its name from the chemical change that iron ore undergoes when it is heated in a furnace at high temperatures in the presence of hydrocarbon-rich gases, carbon monoxide or elementary carbon. Direct reduction refers to processes which reduce iron oxides to metallic iron at temperatures below the melting point of iron. The product of such solid state processes are called direct reduced iron. The reducing gas is a mixture of gases, primarily hydrogen (H_2) and carbon monoxide (CO). The process temperature is typically 800 to 1200 °C [11].

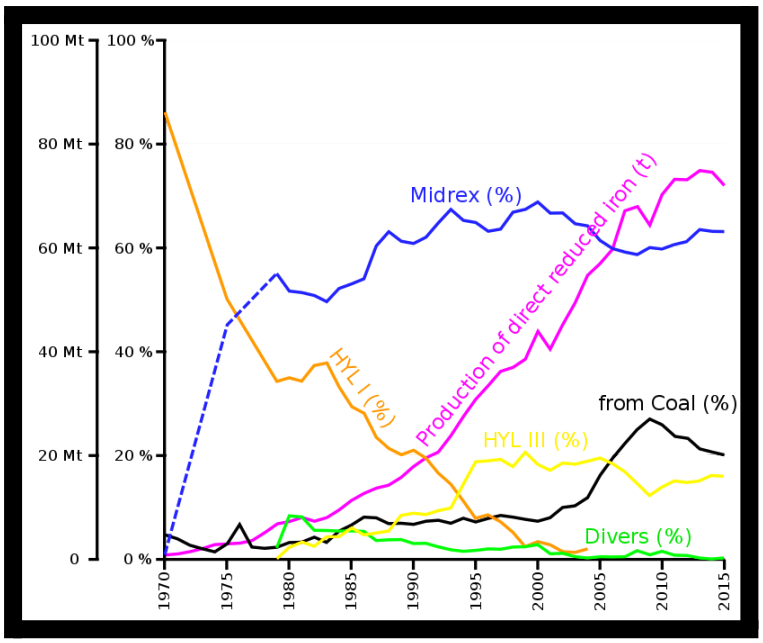


Figure 2.2: DRI production (mt) in different years.

2.4. Iron ores

Iron ores (Figure 3) are rocks and minerals from which metallic iron can be economically extracted. The ores are usually rich in iron oxidesand vary in color from dark grey, bright yellow, or deep purple to rusty red. The iron itself is usually found in the form of

Magnetite (Fe_3O_4,72.4%Fe), hematite (Fe_2O_3,69.9%Fe), goethite (FeO(OH),62.9% Fe), limonite ($FeO(OH)\cdot n(H_2O)$) or siderite ($FeCO_3$, 48.2% Fe).

Ores containing very high quantities of hematite or magnetite (greater than about 60% iron) are known as "natural ore" or "direct shipping ore", meaning they can be fed directly into iron-making blast furnaces. Iron ore is the raw material used to make pig iron, which is one of the main raw materials to make steel—98% of the mined iron ore is used to make steel. Indeed, it has been argued that iron ore is "more integral to the global economy than any other commodity, except perhaps oil" [24, 25].

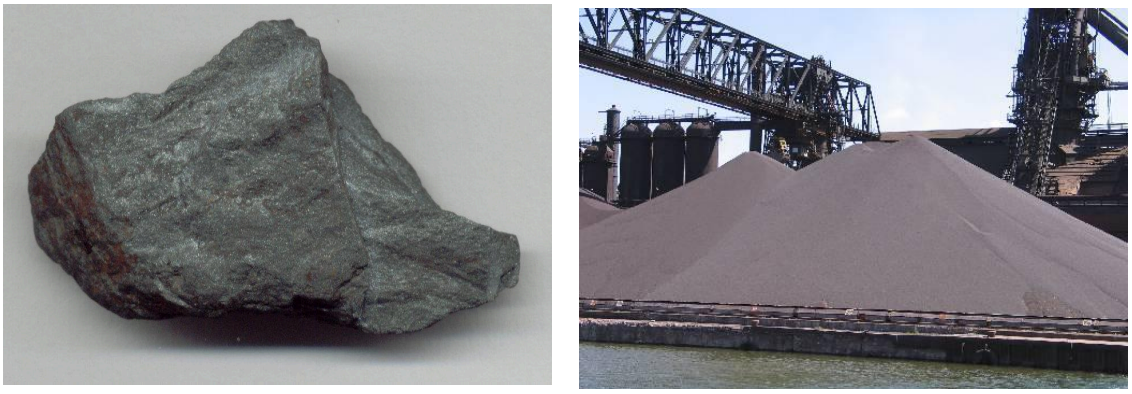


Figure 2.3: (a) Iron ore and (b) processing.

2.4.1. Magnetite (Fe_3O_4, 72.4%Fe)

Magnetite (Figure 4) is a mineral and one of the main iron ores. With the chemical formula Fe_3O_4, it is one of the oxides of iron. Magnetite is ferrimagnetic; it is attracted to a magnet and can be magnetized to become a permanent magnet itself. It is the most magnetic of all the naturally-occurring minerals on Earth. Naturally-magnetized pieces of magnetite, called lodestone, will attract small pieces of iron, which is how ancient peoples first discovered the property of magnetism. Today it is mined as iron ore.

Small grains of magnetite occur in almost all igneous and metamorphic rocks. Magnetite is black or brownish-black with a metallic luster, has a Mohs hardness of 5–6 and leaves a black streak [26-28].

Figure 2.4: Magnetite Iron ore.

2.4.2. Hematite (Fe_2O_3, 69.9%Fe)

Hematite, also spelled as hematite, is the mineral form of iron(III) oxide (Fe_2O_3), one of several iron oxides. Hematite crystallizes in the rhombohedra lattice system, and it has the same crystal structure as limonite and corundum. Hematite and limonite form a complete solid solution at temperatures above 950 °C (1,740 °F).

Hematite is colored black to steel or silver-gray, brown to reddish brown, or red. It is mined as the main ore of iron. Varieties include *kidney ore*, *martite* (pseudo morphs after magnetite), *iron rose* and *specula rite* (secular hematite). While the forms of hematite vary, they all have a rust-red streak. Hematite is harder than pure iron, but much more brittle. Magnetite is a hematite- and magnetite-related oxide mineral.

Huge deposits of hematite are found in banded iron formations. Gray hematite is typically found in places that can have still standing water or mineral hot springs, such as those in Yellowstone National Park in North America. The mineral can precipitate out of water and collect in layers at the bottom of a lake, spring, or other standing water. Hematite can also occur without water, however, usually as the result of volcanic activity.

Clay-sized hematite crystals can also occur as a secondary mineral formed by weathering processes in soil, and along with other iron oxides or oxyhydroxides such as goethite, is responsible for the red color of many tropical, ancient, or otherwise highly weathered soils.

2.4.3. Goethite (FeO (OH), 62.9% Fe)

Goethite (FeO(OH)) (Figure 5) is an iron bearing hydroxide mineral of the diaspore group, is found in soil and other low-temperature environments.

Goethite has been well known since ancient times for its use as a pigment (brown ochre). Evidence has been found of its use in paint pigment samples taken from the caves of Lascaux in France. It was first described in 1806 based on samples found in the Hollertszug Mine in Herdorf, Germany. The mineral was named after the German polymath and poet Johann Wolfgang von Goethe (1749–1832).

In 2003, nanoparticulate authigenic goethite was shown to be the most common diagenetic iron oxyhydroxide in both marine and lake sediments.[29, 30]

Figure 2.5: Goethite iron ore.

2.4.4. Limonite ($FeO(OH)\cdot n(H_2O)$)

Limonite (Figure 6) is an iron ore consisting of a mixture of hydrated iron(III) oxide-hydroxides in varying composition. The generic formula is frequently written as $FeO(OH)\cdot nH_2O$, although this is not entirely accurate as the ratio of oxide to hydroxide can vary quite widely. Limonite is one of the two principal iron ores, the other being hematite, and has been mined for the production of iron since at least 2500 BCE.[31, 32]

Figure 2.6: Limonite iron ore

2.4.5.Siderite ($FeCO_3$, 48.2% Fe).

Siderite is a mineral composed of iron (II) carbonate ($FeCO_3$). It takes its name from the Greek word sideros, "iron". It is a valuable iron mineral, since it is 48% iron and contains no sulfur or phosphorus. Zinc, magnesium and manganese commonly substitute for the iron resulting in the siderite-smithsonite, siderite-magnesite and siderite-rhodochrosite solid solution series.

Siderite has Mohs hardness of 3.75-4.25, a specific gravity of 3.96, a white streak and a vitreous lustre or pearly luster.

It crystallizes in the trigonal crystal system, and are rhombohedral in shape, typically with curved and striated faces. It also occurs in masses. Color ranges from yellow to dark brown or black, the latter being due to the presence of manganese.

Siderite is commonly found in hydrothermal veins, and is associated with barite, fluorite, galena, and others. It is also a commondiagenetic mineral in shales and sandstones, where it sometimes forms concretions, which can encase three-dimensionally preservedfossils.[33] In sedimentary rocks, siderite

commonly forms at shallow burial depths and its elemental composition is often related to thedepositional environment of the enclosing sediments.[34] In addition, a number of recent studies have used the oxygen isotopic composition of sphaerosiderite (a type associated with soils) as a proxy for the isotopic composition of meteoric water shortly after deposition.[35]

Figure 2.7: Siderite iron

2.5 IRON ORE AND COAL RESERVES IN INDIA

Coal deposits in India are mainly confined to eastern and south central parts . The states of Jharkhand, Odisha, Chhattisgarh, West Bengal, Andhra Pradesh, Maharashtra and Madhya Pradesh account for more than 99% of the total coal reserves in India. As on 31.03.12 the estimated reserves of coal was around 293.5 billion tonnes, an addition of 7.64 billion over the last year (Table 1.1). The total estimated reserve of coal in India as on 31.03.11 was around 285.86 billion tonnes.

Table 1.1 : State wise Estimated Reserves of Coal in India as on 31.03.2011 and 31.03.2012

#

States/ UTs	Proved		Indicated		Inferred		Total		Distribution (%)	
	31.03.2011	31.03.2012	31.03.2011	31.03.2012	31.03.2011	31.03.2012	31.03.2011	31.03.2012	31.03.2011	31.03.2012
Andhra Pradesh	9.30	9.57	9.73	9.55	3.03	3.03	22.05	22.16	**7.71**	**7.55**
Arunachal Pradesh	0.03	0.03	0.04	0.04	0.02	0.02	0.09	0.09	**0.03**	**0.03**
Assam	0.47	0.47	0.05	0.05	0.00	0.00	0.51	0.51	**0.18**	**0.17**
Bihar	0.00	0.00	0.00	0.00	0.16	0.16	0.16	0.16	**0.06**	**0.05**
Chhattisgarh	12.88	13.99	32.39	33.45	4.01	3.41	49.28	50.85	**17.24**	**17.32**
Jharkhand	39.76	40.16	32.59	33.61	6.58	6.58	78.94	80.36	**27.61**	**27.38**
Madhya Pradesh	8.87	9.31	12.19	12.29	2.06	2.78	23.13	24.38	**8.09**	**8.31**
Maharashtra	5.49	5.67	3.09	3.11	1.95	2.11	10.53	10.88	**3.68**	**3.71**
Meghalaya	0.09	0.09	0.02	0.02	0.47	0.47	0.58	0.58	**0.20**	**0.20**
Nagaland	0.01	0.01	0.00	0.00	0.31	0.31	0.32	0.32	**0.11**	**0.11**
Odisha	24.49	25.55	33.99	36.47	10.68	9.43	69.16	71.45	**24.19**	**24.34**
Sikkim	0.00	0.00	0.06	0.06	0.04	0.04	0.10	0.10	**0.04**	**0.03**
Uttar Pradesh	0.87	0.88	0.20	0.18	0.00	0.00	1.06	1.06	**0.37**	**0.36**
West Bengal	11.75	12.43	13.13	13.36	5.07	4.83	29.96	30.62	**10.48**	**10.43**
All India Total	**114.00**	**118.15**	**137.47**	**142.17**	**34.39**	**33.18**	**285.86**	**293.50**	**100.00**	**100.00**
Distribution (%)	**39.88**	**40.25**	**48.09**	**48.44**	**12.03**	**11.31**	**100.00**	**100.00**		

#source- Energy statistics, by central statistics office, India

The majority of iron ore production also comes from southern and eastern parts of India .The contributing states are Andhra Pradesh, Chhattisgarh, Goa, Jharkhand, Karnataka, Madhya Pradesh, Maharashtra, Orissa, and Rajasthan. The total production of iron ore from all parts of India stand at 127719 thousand tones. It puts India in a unique position to give emphasis on the development of sponge iron industries. As the production rate of iron ores is high the ores can be subsequently used both for blast furnace and production of DRI.

STATE-WISE PRODUCTION OF IRON ORE DURING THE LAST THREE YEARS

(in Thousand Tonnes)

State	2008-09	2009-10	2010-11(P)	2011-12(P) (Apr-Dec)
India	**212960**	**218553**	**207998**	**127719**
Andhra Pradesh	10112	6246	1435	1297
Chhattisgarh	29997	26211	29146	23583
Goa	31195	38136	36723	23090
Jharkhand	21329	22547	23174	15639
Karnataka	46971	43163	37878	11247
Madhya Pradesh	412	1058	1745	941
Maharashtra	294	283	1520	1056
Orissa	72627	80896	76350	50842
Rajasthan	23	13	27	24

P: Provisional, Source : MCDR Returns

2.5.1 SPONGE IRON PRODUCTION SCENARIO IN INDIA

In the last decade the production of sponge iron has increased dramatically in India. Today India is the major producer of sponge iron in the world. Due to low availability of natural gas resources in India, large emphasis is given to production by the use of coal. The coal reserves in India are estimated to last for another 190 years hence it calls for modern innovations to shift the trend of production towards sponge iron. However the production is seriously constrained by the low availability of good grade ores which results in poor metallization, high volume of ash and fines that are generated. Rise of the sponge iron industry has helped the Indian steel industry – especially through the DR-EAF routes – to overcome a crippling shortage and rising price of scrap feed for steel making. The primary push for the growth of this sector has come from the rapid expansion of secondary steel making in India in the last decade and a

	2000-01	2001-02	2002-03	2003-04	2004-05	2005-06	2006-07
Total Sponge Iron	5.481	5.443	7.858	9.877	12.54	14.825	18.345
CAGR (%)							***22.3%***
Gas-based Sponge Iron	3.453	3.180	3.624	3.976	4.643	4.545	5.265
% Share in total	63%	58.4%	46.1%	40.3%	37.0%	30.7%	28.7%
CAGR (%)							***7.3%***
Electric Arc Furnace	5.418	4.377	5.297	6.324	7.994	8.569	10.033
CAGR (%)							***10.8%***
Coal-based Sponge Iron	2.028	2.263	4.234	5.901	7.897	10.280	13.080
% Share in total	37%	41.6%	53.9%	59.7%	63%	69.3%	71.3%
CAGR (%)							***36.4%***
Induction Furnace	8.043	8.253	9.014	10.477	13.193	13.493	15.390
CAGR (%)							***11.4%***

Source: Joint Plant Committee

2.5.2DIFFERENT ROUTES OF SPONGE IRON PRODUCTION

The process of DRI or sponge Iron making can be classified into different categories, which are as follows.

a>Rotary Kiln Process.

Rotary Kiln Processes are highly useful for Sponge Iron Production using non-coking coal as reductant . The Iron Ore in the form of lump is charged from one end blended with non-coking coal and heated from the other end, thus keeping counter movement of air current and raw materials . The DRI comes out as product from opposite end .The Rotary movement of the Kiln requires good strength of raw materials during reduction such as tumbler index ,abrasion index and thermal degradation strength etc.. Generation of fines from poor raw materials promote ring formation leading to poor performance and decreased productivity.

b>Retort Process.

In Retort process the reactor vessel is a retort where the charge is fed from top end remains stationary till reduction, thus it works in batches .a mixture of hot gases contains about 89% of reducing gases (75% H2 +14%CO) moves between ore bed held in three retort. The three retort works in cycle covering three stages, each approximately 3hrs duration. The first stage consist of heating and preliminary reduction of pellet charged. Once preliminary reduction is completed the reactor is switched onto second stage of reduction by means of automatic valve manipulation during which bulk of reduction takes place. The total process needs along time of about 23/24 hrs.

c> Rotary hearth process. This process iron oxide fines, coal fines and binder are mixed together and palletized . As the hearth rotates around the circular furnace, the pellets are heated to 1250oC- 1350oC and the iron oxide is reduced to metallic iron. Residence time in hearth is around 15-25 mins. during which 90-95% of iron oxide is converted in to metallic iron. Burner fuel for RHF can be in the form of pulverized coal , natural gas, and coke oven gas , coal oil mixture. Volatiles and CO gas evolved from the pellets are combusted within the RHF thus providing a significant portion of total heat requirement.

2.5.3 SELECTION OF IRON ORES FOR SPONGE IRON MAKING

During sponge iron manufacturing, iron ore is reduced in solid state. Unlike the conventional steel melting processes, the gangue in iron ore cannot be separated as slag. Hence, it becomes essential to select an ore with high iron content and a low gangue content, to optimize yield during steel making. The parameters that are kept in view while selecting iron ore for sponge iron making are

a> Chemical composition

(i) Iron content:- This should be high (at least above 65%) . the more the iron content the better is the productivity and better is the economic output of the process.

(ii) Gangue content:- The gangue content should be low , as this process poses problem of slag removal and disposal. The higher gangue content results in extra investment in the enrichment of ore and lower productivity. Hence the ores having a maximum gangue content of 10-20 percent are considered best for DR process

(iii) Sulphur, Phosphorous, Alkali contents:- while Sulphur and Phosphorous cause removal problems , cause hot shortness and cold shortness respectively , alkaline elements attack on the refractory lining of blast furnace/reduction unit and decrease its service life.

b> Reducibility

It is desired that the ores should have a very high extent of reducibility for higher rate of reduction and higher productivity. It can be affected by various factors such as porosity and presence of catalytic impurities. The reducibility is inversely proportional to the time required to reach some arbitrarily chosen degree of reduction .

For best process control it is should be taken care that the reducibility i.e. dR/dT=0.5% per minute. Hematite ore is the most popular ore for use in DR process because of its better reducibility than magnetite.

c> Physical properties

Size: - particle size is a very important parameter to consider while selecting iron ores particles size should range from +6 to +18 mm with particle diameter ranging from 10.5 mm to 11.5 mm. Higher the size the lesser is the rate of reduction, lower productivity. The process is carried out by optimizing in the sampling of the raw materials

Tumbler index :- it is known as the resistance to degradation by impact. It is a very important factor since in the rotary kiln process the ores are constantly in impact with wall linings and other ores, hence it is imperative that they have high tumbler index to stop generating fines.

Abrasion index: - it is a measurement of the breakage or degradation due to abrasion. It is a standard test which is determined along with measurement of tumbler index.

Shatter index:- It is the resistance to breakdown upon fee fall from a height . it is a indication of strength of the ore . Lower the shatter strength higher is the strength of coal.

Thermal degradation index:- The exposure of iron ores to hot gases during stages of charging can cause them to expand and contract causing thermal decrepitating . This results in generation of fines. It is undesirable hence thermal degradation index should be measured to ensure better process control.

2.5.4 SELECTION OF COAL FOR SPONGE IRON MAKING.

The properties to be considered for selection of coal for direct reduced iron production are as follows.

* Proximate Analysis

Fixed Carbon

#Volatile matter

#Ash

Moisture

* Sulphur

* Ash fusion temperature

* Ash chemistry

* Particle size

* Caking Index

* Bulk density

SULPHUR CONTENT

Sulphur is present in the coal in two forms; Organic sulphur and pyretic sulphur. The pyretic sulphur can be present as sulphide or sulphate .The amount of sulphur present as sulphate is usually very low. However this should be determined, because it drops the ash fusion temperature .Sulphurs poise show that around 80-84% of sulphur leaves the kiln in the off gas and in the char, under Indian condition.

ASH FUSION TEMPERATURE

Ash Fusion temperature is a vital parameter for smooth operation of the kiln. In this temperature the coal ash starts to fuse. But for selection of coal, the initial distortion temperature should also take into account. The coal ash comes in intimate contact with other chemical compounds in the kiln forming low melting eutectic, promoting accretion formation in the kiln, and hampers the

furnace operation. Consequently, the Initial Deformation Temperature (IDT) of coal ash should 2000C more than the operating temperature.

ASH CHEMISTRY

The coal ash chemistry is studied to evaluate coal for direct reduction process. The silica ratio of the ash should be above 80% . It is found that , the ash fusion temperature has linear relationship with constituent of the ash.

Silica Ratio= % SiO2/(%CaO+%MgO)

Ash Fusion Temperature in Centigrade = 2344 2SiO2/ Al2O3

FeO+CaO+MgO+K2O+Na2O

Alkali Ratio = (% Ash in coal) . (K2O +Na2O) in ash.100

The alkali ratio in coal should be minus than 0.3. High alkali ratio, shows low ash fusion temperature.

PARTICLE SIZE:-The span of the coal ought to be such that it blends well with charges as the charge move along the oven. Size of the coal should not be fine, else it causes carbon misfortune. The span of the coal ought not be expansive as it will coast on the highest point of the charge cot. The more level size is dead set from the fluidizing speed of coal, the coal fines are not alluring . However a little sum may stay in the charge. The extent of the -5 mm measure in the coal food ought not surpass 5-10%.

The coal from the release end is blown to meet the diminishment response and high temperature prerequisite .The measure of the molecule relies on upon the toss needed to achieve a specific separation in the furnace. By and large the blown coal size extends between 3mm to 25 mm.

CAKING INDEX:-High caking index coal causes accumulation and reduces the char reactivity of the coal, it also causes accretion creation in the kiln and hinder operation of the kiln. Therefore caking index of the coal should be less than three, preferably less than one.

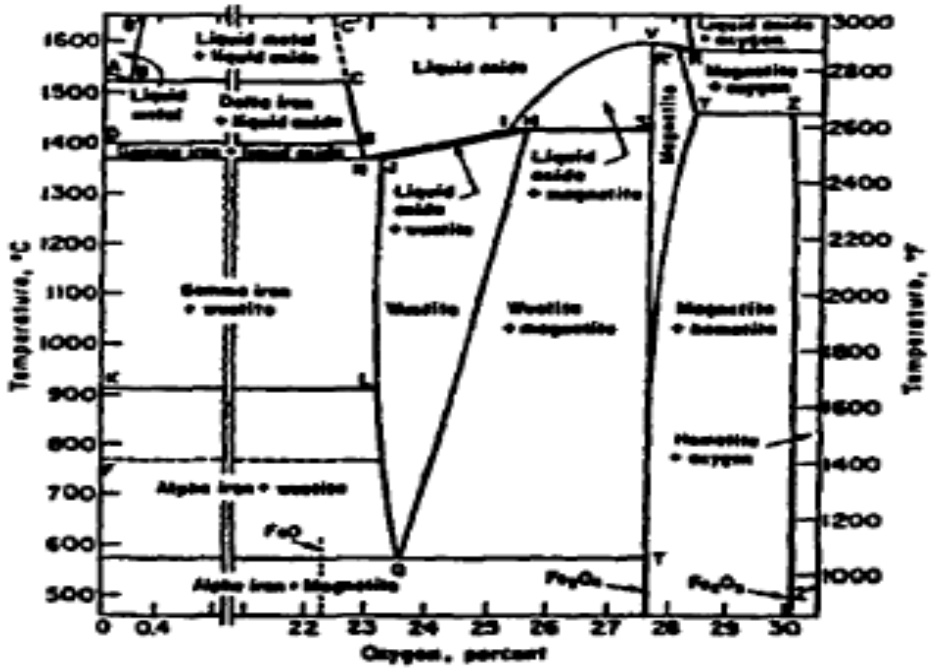
BULK DENSITY :-The bulk density of coal plays an important role in the productivity performance of the kiln. In common the coal with higher volatile matter have smaller bulk density, and occupy larger space in the kiln., thereby decreasing available kiln volume for production. Experience in DRI production indicates that the bulk density of the coal (sized) should be 800kg/m.

2.6 **The thermodynamics of iron oxide reduction**

The thermodynamics of iron oxide reduction have been the subject of many books (Bodsworth, 1963; Bogdandy and Engell 1971; Strassburger, 1969; Ross,

1980). This review includes the iron-oxygen system and equilibrium relations between iron oxides, carbon monoxide and hydrogen. [37]

Iron-oxygen system



Point	Temperature		Oxygen, percent	Point	Temperature		Oxygen, percent
	deg F	deg C			deg F	deg C	
A	2796	1535	0	N	2500	1371	22.92
B	2775	1524	0.16	Q	1058	570	23.57
C	2775	1524	22.63	R	2881	1583	28.30
D	2552	1400	0*	R'	2881	1583	28.06
F	1418	770	0*	S	2593	1423	27.64
H	2593	1423	25.60	V	2907	1597	27.64
I	2593	1423	25.26	Y	2651	1455	28.36
J	2500	1371	23.15	Z	2651	1455	30.04
K	1670	910	0*.	Z'			30.06
L	1670	910	23.15				

*The effect of dissolved oxygen on these temperatures is not known but is presumably very small.

Figure The binary system of iron-oxygen

(Darken and Gurry, 1946)

The system may be best described in the phase diagram by Darken and Gurry (1946) as shown in Figure 2.8.

Iron oxides may exist in three forms, i.e. hematite (Fe_2O_3), magnetite (Fe_3O_4) and wustite (FeO) depending on temperature and oxygen potential of the system. Although the non-stoichiometric wustite is usually written as FeO or Fe_xO, the actual oxygen content in wustite has a wide range from 23.1 to 25.6 wt%. The value of x in Fe_xO is less than unity and close to 0.95 when it coexists with metallic iron.

2.6.1 The sequence of the reduction of iron oxides by gases

The reduction of hematite to produce iron takes place step-wise, with porous magnetite and wustite (at a temperature above 570°C) as intermediates as shown in Figure 2.9. At temperatures below 570°C wustite will not form.

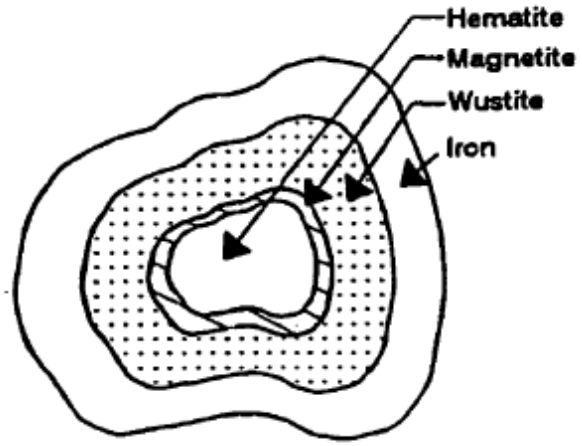


Figure Cross-section of a partially reduced dense iron ore particle showing Topochemical type of reduction.

2.6.2 Equilibrium compositions between iron oxides and reducing gases

Carbon monoxide and hydrogen are the most common reducing agents used in commercial processes. Some thermodynamic data (Bogdandy and Engell, 1971; Ross, 1980) are given below as examples. Heats of reactions for the stoichiometric equations (per gram moles at 250^{0}C) are included.

$3Fe_2O_3 + CO = 2Fe_3O_4, + CO_2$ $\quad \Delta H^o = -52{,}869$ J/g-mole

$Fe_3O_4 + CO = 3Fe0 + CO_2$ $\quad \Delta H^o = 36{,}250$ J/g-mole

$FeO + CO = Fe + CO_2$ $\quad \Delta H^o = -17{,}305$ J/g-mole

At a temperature below 570°C, magnetite is reduced directly to metallic iron

$$\frac{1}{4}$$

$$-Fe_3O_4 + CO = \frac{3}{4}$$

$Fe + CO_2$ $\quad AH^0 = -3{,}916$ J/g-mole

The equilibrium constant, X, of reactions listed above can be calculated from the standard free energy change of these reactions as a function of temperature (Elliott and Gleiser, 1960; Bogdandy and Engell, 1971). As an example, for reaction (2.4), the equilibrium constant can be calculated as follows

$$1n\, k = \frac{-\Delta G^0}{RT} \tag{2.6}$$

$$K = \frac{a_{Fe} \times P_{CO_2}}{a_{Fe}o \times P_{CO}}$$

The iron and wustite are assumed to be essentially pure solids, hence, their activities may be considered to be unity, then the equilibrium ratio of partial pressure in the wustite reduction may be calculated from Equation 2.7.

$$K \frac{Pco_2}{P_{co}}$$

(2.7)

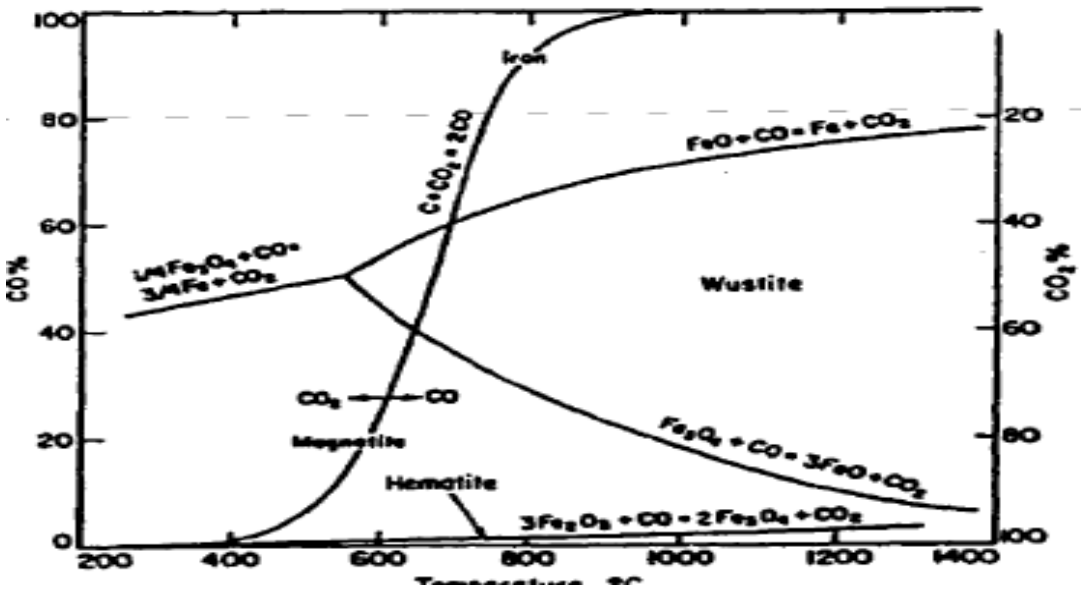


Figure:- Equilibrium gas compositions versus temperature diagran for the iron-carbon-oxygen system (Ross, 1980)

Similar calculations could be made for the other three reactions. The equilibrium phase diagram (super-imposed with that for carbon-carbon oxides system) is shown in Figure 2.10.

The reduction of iron oxides by hydrogen is endothermic for reactions (2.9) and (2.10) . The heat of reactions at 25OC are listed below

$3Fe_2O_3 + H_2 = 2Fe_3O_4, + H_2O$ ΔH^o = -11,715 J/g-mole (2 .8)

$Fe_3O_4 + H_2 = 3FeO + H_2O$ ($T \geq 570^0C$) ΔH^o = -77,405 J/g-mole (2 .9)

$FeO + H_2 = Fe + H_2O$ ΔH^o = 23,849 J/g-mole (2 .10)

$$\frac{1}{4}Fe_3O_4 + H_2 = \frac{3}{4}Fe + H_2O \quad (T < 570°C)$$

ΔH^o = 37,238 J/g-mole (2 .11)

The phase diagram of the H-O-Fe system is shown in Figure 2.11.

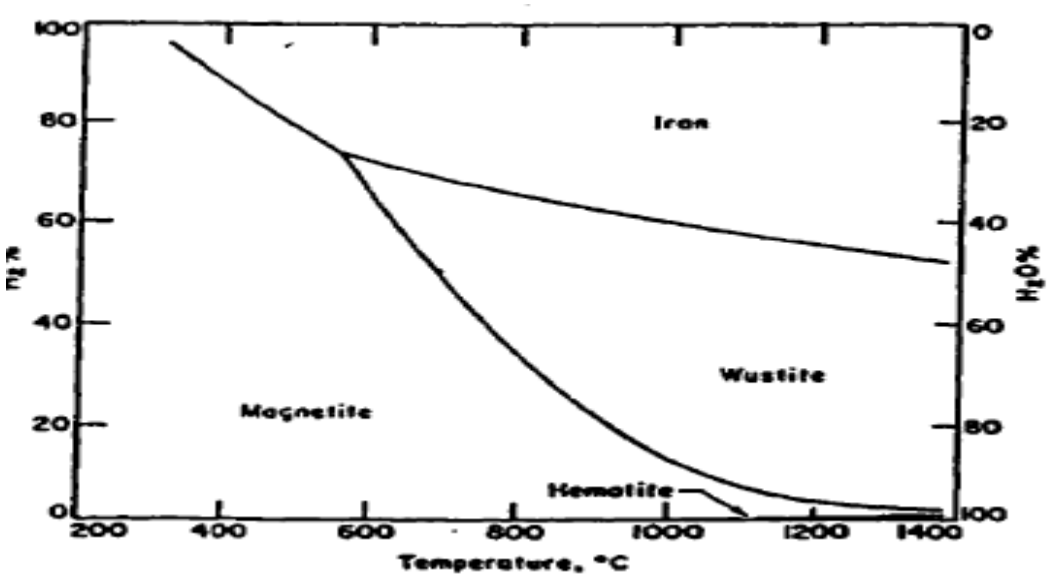


Figure 2.11 Equilibrium gas compositions versus temperature diagram for the iron-hydrogen-oxygen system (Ross, 1980)

2.6.3 Reactions between gases and solid carbon

The equilibrium curve for solid carbon and CO-CO, mixture (as shown in Figure 2.10) is highly endothermic

$CO_2+C=2CO$ $\Delta H^o = 172{,}464$ J/g-mole (2 .12)

This reaction is commonly known as Boudouard reaction, or carbon gasification. This reaction is highly endothermic and has very large activation energy for chemical kinetics; therefore, it proceeds at an appreciable rate only at sufficiently high temperatures for a given reactivity of carbon.
The similar reaction in carbon and Hz-H_2O mixture is given below

$H_2O+C=CO+H_2$ $\Delta H^o = 131{,}294$ J/g-mole (2 .13)

In the presence of solid carbon, Reactions (2.12) and (2.13) may restore the reducing power of local gas to sustain the reduction of iron oxides at the expense of heat.

2.6.4 Kinetics of reduction of iron oxides by CO and H_2

In the kinetic study of the reduction of iron oxides by CO and Hz, a spherical pellet is usually used for mathematical modeling because of its simple geometry and its similarity to commercial products. In this section, the shrinking core mode1 22 which was developed in the study of pellet reduction are briefly reviewed. Rate controlling steps and values of rate constants reported in the literature are discussed.

2.6.5 The reduction of a single oxide particle

The monitoring of reduction kinetics of a single oxide particle is usually carried out by suspending a spherical sample from a balance in a flowing-gas stream of known composition and temperature for continuous measurement of weight

loss. The pioneer work was done by McKewan (1958) who studied magnetite reduction by hydrogen at temperatures less than 570°C. In order to analysis the weight-loss data, the experiment is usually designed for:

(1) isothermal conditions;

(2) single solid/ solid interface where gas/solid reaction takes place; and

(3) dense specimens.

A sketch showing the reduction of a dense wustite sphere by CO is given in Figure 2.12.

The system is made of three phases: the gaseous phase, the porous layer of solid product, and the un-reacted pore-free solid reactant. The removal of oxygen from wustite takes place at a sharp iron/wustite interface, which shrinks parallel to the initial outer surface of the pellet, and results in weight-loss. The removal of oxygen proceeds through the following steps occurring successively during the reaction:

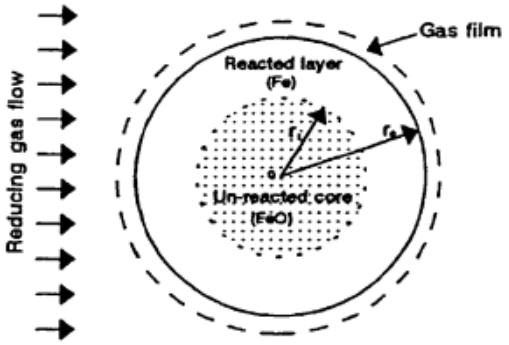


Figure 2.12 Schematic illustrations of a partially reduced dense wustite pellet and a shrinking core mode1

(a) Transport of gaseous reactant (CO) from bulk gas to exterior surface of the particle through a gaseous boundary - layer ;

(b) Diffusion of gaseous reactant (CO) through the porous iron layer to the iron/wustite interface;
(c) Reduction of wustite by gaseous reactant to form metallic iron and gaseous product (CO,) at the iron/wustite interface;

(d) Diffusion of gaseous product (CO*) outward through the porous iron layer; and,

(e) Transport of the gaseous product (CO,) from the 24 exterior surface of the particle to the bulk gas through the gaseous boundary layer.

Mathematically, the rate equations of these sequential steps may be expressed in three general classifications as follows (Spitzer et al, 1966):

(i) Mass transfer through a gas film (steps (a) and (e)), the molar flux of CO from the bulk gas phase to the exterior surface of the sphere is given by:

$$= - h_{co} 4\pi \qquad (2.14)$$

Similarly the molar flux of C4 from the exterior surface of the sphere to the bulk gas phase is given by:

$$= - 4\pi$$
(2.15)

where $\dot{n}_{co}^{m}$, is molar flow of CO from bulk gas to exterior surface of the pellet, $\dot{n}_{co_2}^{m}$ is molar flow of CO_2 from exterior - surface of the pellet to bulk gas, mole/s; h_{co} and h_{co_2} are mass-transfer coefficients for CO and CO_2, m/s; and C_{co}^{b} , C_{co}^{o} , $C_{co_2}^{b}$ and $C_{co_2}^{o}$ are concentrations of CO and CO_2 at bulk gas phase and the exterior surface of the particle, mole/m^3, respectively.

(ii) Diffusion through porous product layer (steps (b) and (d)).

The molar flows of CO and CO_2 ($\dot{n}_{co}^{p}$ and $\dot{n}_{co_2}^{p}$) by diffusion through the porous iron layer are given by:

$$= - 4\pi$$
(2.16)

And

$$= - 4\pi$$
(2.17)

respectively. Where D_{effco} and D_{effco_2} are effective diffusivities for CO and CO_2, m^2/s, respectively.

(iii) Interfacial chemical reaction (step (c))

Oxygen removal from FeO/Fe interface by reaction (3) is usually considered as a first order, reversible reaction with respect rate of to the concentration of a gaseous composition. Its interfacial reaction is expressed as

$$= - \qquad (2.18)$$

Where $\dot{r}_o$ is the rate of oxygen removal, mole/s; k is the rate constant, m/s; and K_C is the equilibrium constant.

Each step may contribute resistance to the completion of the overall chemical reaction. The slowest step among these five which are connected in series will provide the largest resistance to the overall reaction. If a step is much slower than al1 others so that resistances attributed to the other steps become relatively insignificant, this step is called rate-limiting or rate-controlling.

2.6.6 Mathematical modelling of isothermal systems

McKewan (1960) observed the rate of weight loss due to the removal of oxygen at magnetite/iron interface in spherical pellets (0.009 m in diameter) at a temperature lower than 570°C is proportional to the area of the iron/iron oxide interface. He proposed an 'area-controlled modelf Le. the rate of reduction was controlled by gas-solid interfacial reaction (Equation 2.18). He assumed that the un-reacted core of magnetite retains the shape of a sphere but shrinks with increased reaction time. The rate of reduction, in terms of rate of removal of oxygen per unit time, may be expressed as:

$$-\frac{dw_0}{dt} = -\rho_0 \; 4\pi r^2 \frac{dr}{dt}$$

where $\frac{dw_0}{dt}$ is the rate of removal of oxygen in the solid specimen, mole/s; r is radius of the un-reacted core, m; and ρ_0 . is the oxygen density of the solid reactant, mole/m^3 .

Let us assume the particle which is participating in reduction reaction are spherical in nature for which the reaction is phase boundary type, then the presence or absence of product layer the rate of reaction depends on the interface area.

$$-\frac{dw}{dt} \propto A.C \Rightarrow -\frac{dw}{dt} = KAC \tag{8.1}$$

Negative sign indicates that with increase in time the wt. decreases

[Where,

K → Reaction constant

A → Interface area for chemical reaction

C → Concentration of the reagent fluid.]

If "r" be the radius of the spherical molecules, participating in the equation (8.1) can be re-written as

$$-\frac{d}{dt}\left[\frac{4}{3}\pi r^3.\rho\right] = K.4\pi r^2.1 \tag{8.2}$$

[Where, $A = 4\pi r^2$, C=1]

Reaction not started so, C = 1, for unreacted core sphere.

$$\Rightarrow -\frac{dr}{dt} = \frac{3K}{\rho} \tag{8.3}$$

$$\Rightarrow -\frac{dr}{dt} = \frac{K'}{\rho} \tag{8.4}$$

$$\Rightarrow -\int_{r_0}^{r} dr = \frac{K'}{\rho}\int_0^t dt \tag{8.5}$$

$$\Rightarrow -(r - r_0) = \frac{K'}{\rho}\, t \tag{8.6}$$

$$\Rightarrow (r_0 - r) = \frac{K'}{\rho}\, t \tag{8.7}$$

Again,

$$\alpha = [\text{degree of reaction at } (t = t_0)] = \frac{W_0 - W}{W_0} = \frac{\text{Change in wt.}}{\text{Initial wt.}} \tag{8.8}$$

Since, the weight decreases with time. So, degree of reduction (α) expressed as

$$Degree\ of reduction\ (\alpha) = \frac{\text{Initial wt.} - \text{Final wt.}}{\text{Initial wt.}} \tag{8.9}$$

$$\Rightarrow \alpha = \frac{W_0 - W}{W_0} = 1 - \frac{W}{W_0} = 1 - \left(\frac{{}^4/_3\pi r^3\rho}{{}^4/_3\pi r^3\rho}\right) = 1 - \left({}^r/_{r_0}\right)^3 \tag{8.10}$$

$$\Rightarrow \left(\frac{r}{r_0}\right)^3 = 1 - \alpha \tag{8.11}$$

$$\Rightarrow {}^{r}/_{r_0} = (1-\alpha)^{1/3} \tag{8.12}$$

$$\Rightarrow r = r_0 (1-\alpha)^{1/3} \tag{8.13}$$

Replacing the in equation (8.13) in equation (8.7), we will get,

$$\Rightarrow \left[r_0 - r_0(1-\alpha)^{1/3}\right] = \frac{K't}{\rho} \tag{8.14}$$

$$\Rightarrow r_0\left[1-(1-\alpha)^{1/3}\right] = \frac{K't}{\rho} \tag{8.15}$$

$$\Rightarrow r_0\left[1-(1-\alpha)^{1/3}\right] = \frac{K't}{\rho} \tag{8.16}$$

The above equation (8.16) is known as **Mckewan relation or model**

If we will take the experimental data and plot $\left[1-(1-\alpha)^{1/3}\right]$ vs t and getting a straight line, then we can say reduction reaction obeys Mckewan relation.

By integrating Equations 2.18 and 2.19, McKewan (1960) obtained following equation for the calculation of the degree of reduction or the size of the core as a function of the time of reaction.

$$r_o \rho_o \left(1-(1-\varphi)^{1/3} = kT\right) \tag{2.20}$$

Where φ is the fraction of the magnetite reduced and expressed as

$$\varphi = 1 - \left(\frac{r_i}{r_o}\right)^3 \tag{2.21}$$

This model fits his data very well as shown in Figure 2.13 except at very long reaction times.

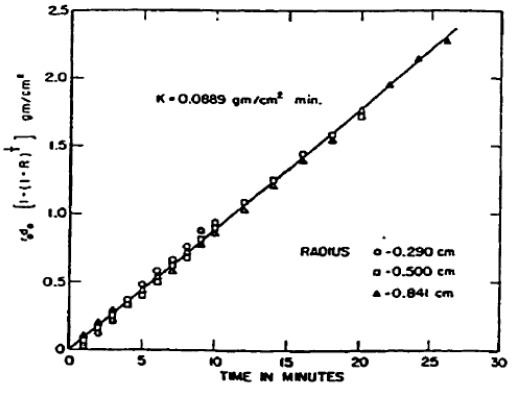


Figure 2.13 interfacial reaction mechanisms, linear relationship between the thickness of reacted layer and time (McKewan, 1960)

Kawasaki et al (1962) used larger artificial pellets with a diameter of 0.015 to 0.044 m and conducted the experiments at temperatures of 870 to 1200°C. They reported that their data can be explained very well by a model which assumed the rate of overall reaction is controlled by gaseous diffusion through the porous product layer except at the early period of reduction. Their resulting diffusion mechanism equation is the integrated form of equation 2.14, 2.16 and 2.19,

$$\frac{W_o r_o}{A_o(C_o - C_o)}\left[\frac{3}{2}1-(1-\varphi)^{1/3}-\frac{r_o\varphi}{(r_o+y)}\right]=D_{eff}t \qquad (2.22)$$

where W_O is oxygen molar weight loss of the oxide when fully reduced, mole; A_o is outside area of the specimen, m^2; and y is gas film thickness surrounding specimen, m. Their experimental and theoretical results are found in Figure .

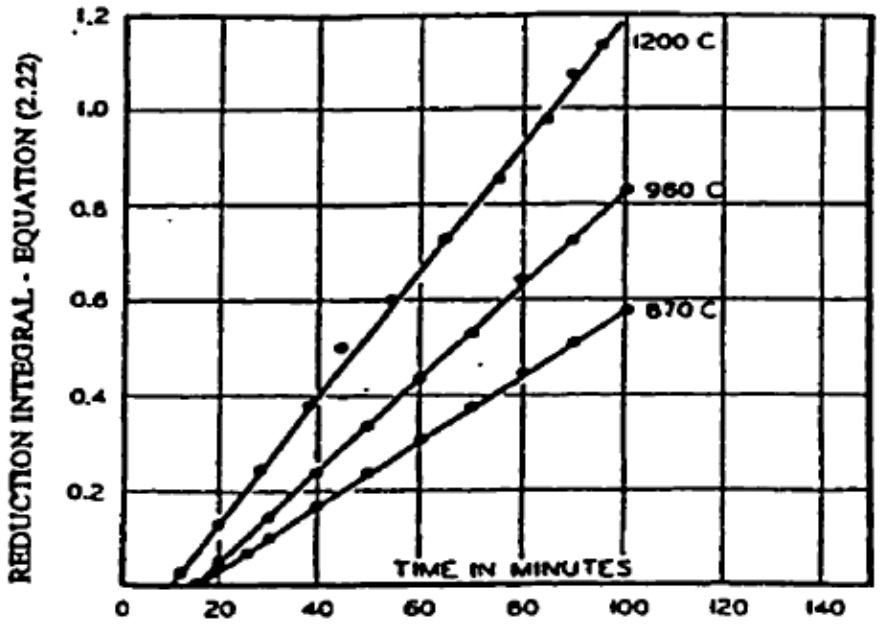


figure:-Diffusion mechanisms for reduction of 0.028 m hematite sphere from wustite to iron by carbon monoxide (Kawasaki et al, 1962)

Lu (1963) recognized that interfacial reaction control and gas diffusion control are two extreme situations in the reduction of a iron oxide. During a reduction reaction, it is 29 possible that rate control may shift gradually from one mechanism to another. Lu (1963) proposed a mixed control model to include interfacial reaction and diffusion steps. In order to eliminate the unknown concentration of gaseous reductant in the interface, Lu proposed a quasi-steady state model to connect steps (b) and (c) in Section 2.8.1 and derived a general rate equation in the integrated form as follows

$$\frac{r_o D_{eff} k C_o t}{\rho_o} = D_{eff} r_o (r_o - r) + \left(k/6\right)(r_o^3 + 2r^3 - 3r_o r^2) \quad (2.23)$$

Experimental data reported by McKewan (1960) and by Kawasaki et al (1962) is explained very well for the whole range of degree of reduction based on Equation 2.23.

Spitzer et al (1966) and Nabi and Lu (1968) extended Lu's model to include al1 five steps to a system with up to 3 reacting solid/solid interfaces, i. e. Fe_2O_3/Fe_3O_4, Fe_3O_4, /FeO and FeO/Fe interfaces. The model is limited for the case that kinetics of al1 heterogeneous reactions are assumed to be first order with respect to the concentration of gaseous reactants and products, and that diffusion coefficients are independent of gas concentration.

2.6.7 Determination of the value of the rate constant of an interfacial reaction

The rate constant k is a temperature-dependent parameter usually to be determined from kinetic data obtained isothermally according to a mathematical model. The meaning of a rate constant is determined by the rate expression adapted for a heterogeneous reaction. For low temperature reduction of magnetite to metallic iron k is defined as the rate constant, the single kinetic parameter, for forward reaction (McKewan, 1960).

The common approach in determining a value of a rate constant of an interfacial reaction is by careful experimental design to minimize the effect of transport steps, so that a simple mathematical model, such as Equation 2.18, could be used to analyze the data. It should be borne in mind that Equation 2.18 is for a special case, Le. Solid reactant is pore-free and spherical, and gas-solid reaction takes place at a sharp solid-solid interface (Topochemical) as depicted in Figure 2.12. However, most specimens used in kinetic studies are multi-grain samples (green pellet) or porous agglomerates; therefore, the gas-solid reaction usually takes place in a reacting zone with a certain thickness as shown in Figure 2.15. Then the rate of reaction should be expressed as

$$r_o = A_z K\left(C_{co} - C_{co_2} / K_e\right) \tag{2.24}$$

Where 4 is the area of reaction surface at time t.

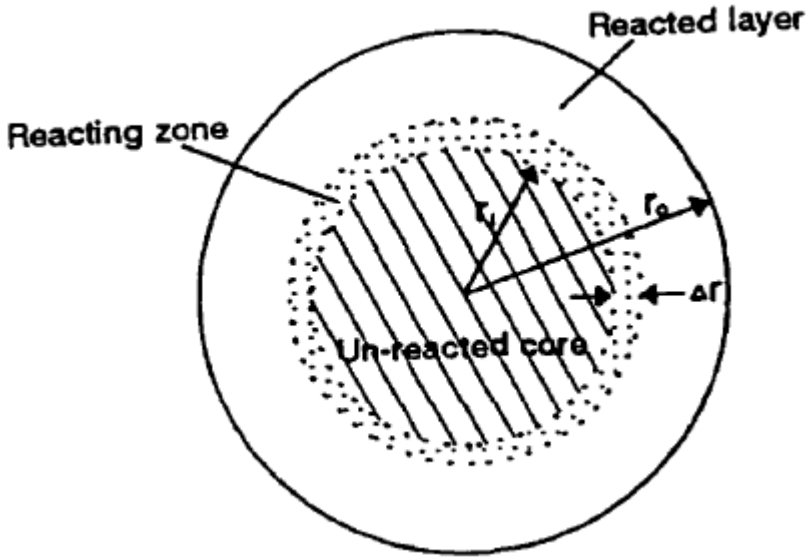


Figure 2.15 Schematic illustration of a partial reduced wustite pellet of high porosity

As the rate of reduction is usually measured by specimen weight loss, the value of gas-solid interfacial area must be provided before the value of rate constant could be determined using equation 2.24.

Another special case is that the solid reactant is small in size and highly porous, so that pores are open and well connected with the external surface. Due to the ease of mass transfer through void space by gaseous diffusion, the whole specimen takes part in the chemical reaction with slightly varying intensity in different regions at the sane the. The initial interfacial area for the gas-solid reaction of the specimen at the start of the reaction is the total solid surface of the specimen, decreases with time

$$A_Z = \frac{4}{3}\pi r_0^3 \rho\, a_s$$

at t=0 (2.25)

Where ρ is the density of the solid reactant, and a, is specific surface area of the solid reactant. The a, is usually determined by B. E. T. Method.

However, most of the solid reactants used in the experiments represent neither of these two special cases. In general, in the analysis of experimental data, the product A& in Equation 2.24 can not be separated without additional information.

Although numerous works have been conducted for the purpose of evaluation of kinetic parameters, there are only a few with the proper experimental design and mathematical modelling so that rate constants could be extracted from data with a defined meaning. Only those papers with some details on experimental conditions and mathematical modelling are selected for review here.

Figure 2.16 shows the plot of rate constant for wustite reduced by CO against the reciprocal temperature, reported by different investigators. The difference in the reported values is substantial. The reported experimental condition is listed in Table 2.5. It is clear that the use of Equation 2.18 would result in an

under-estimation in the value of reaction surface area, and thus an over-estimation in the value of the rate constant, from the value hand, the use of Equation of their 2.25 has 33 product A$. On the other the opposite effect. [37]

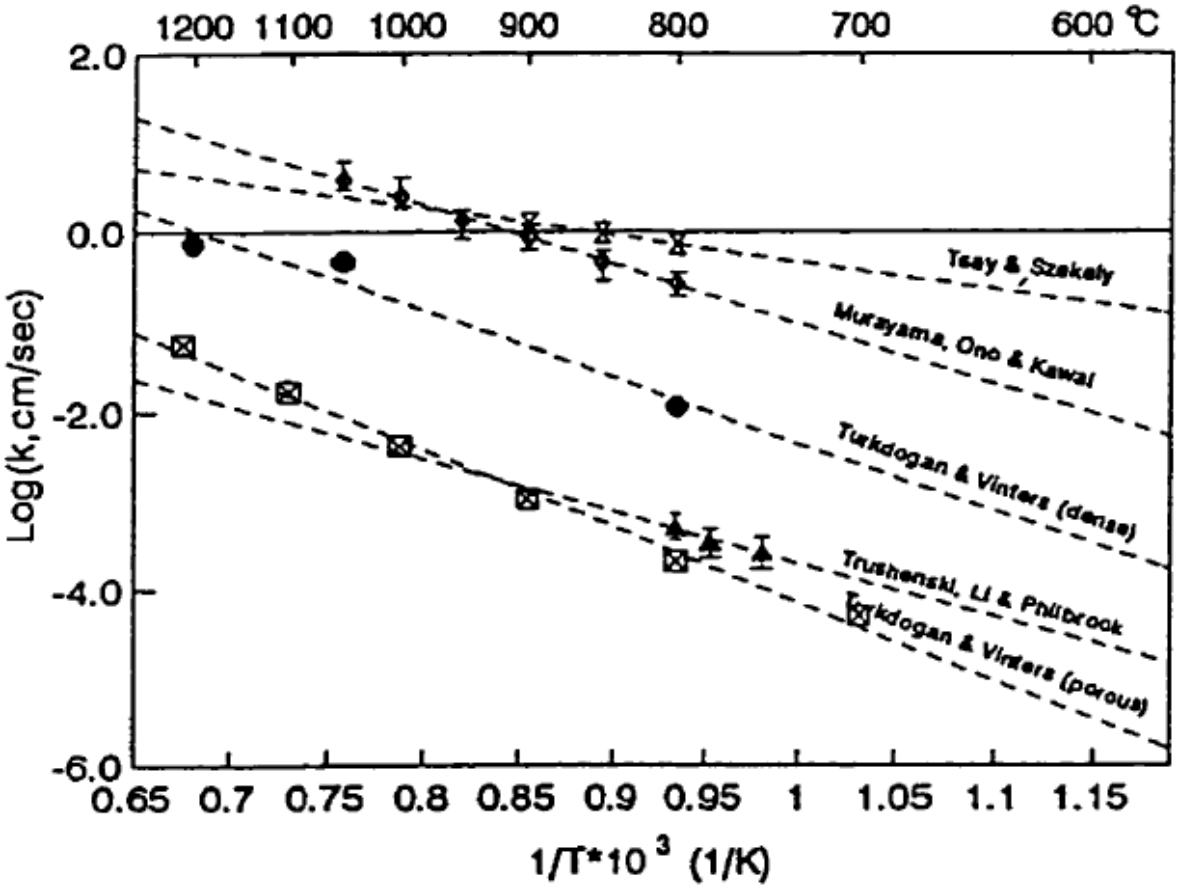


Figure 2.16 Plot of rate constants temperature for reduction against the reciprocal of Fe0 by CO

2.7 Mechanism and kinetics of reduction of iron ore lump by coal lump

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.

2.7.1 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.

2.7.2 Photograph of spherical model of reduction:

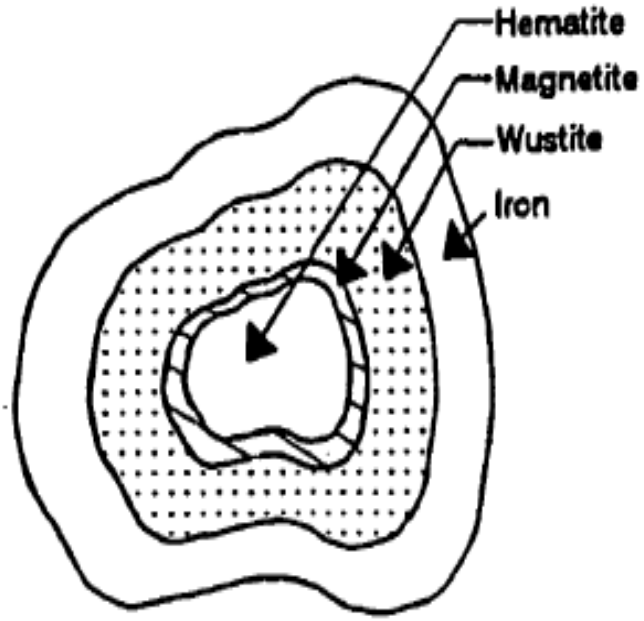


Fig.: Cross-section of a partially reduced dense iron ore particle showing Topochemical type of reduction.

2.7.3 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)

2.8 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:

2.8.1 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.

2.8.2 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**.**

2.8.3 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.

2.8.4Mixed 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:

2.8.5 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

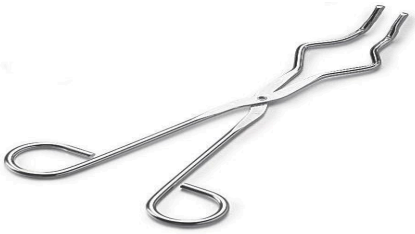
[1-2/3f – (1-f)2/3] +D/r0[1-(1-f)1/3] = kt Mixed Controlled.

Chapter-3

EXPERIMENTAL MATERIAL AND EXPERIMENTAL SET-UP

1.coal lumps **2. Hematite ore**

3. muffle furnace **4. oven**



5. Tongs

6. Crucible **7. Hand gloves**

8. Digital weighing balance

Figure :- Experimental materials and equipments.

Figure:- Experimental set up

chapter-4

DETAIL OF EXPERIMENTS PERFORMED

4.1 Proximate Analysis

Determination of moisture, volatile-matter, ash and fixed carbon in coal comprises its proximate analysis.

a) Determination of moisture content: Loss in weight of coal caused by heating of coal sample for one hour at 105˚C is the moisture content of coal. A known amount of finely powdered coal sample is kept in a silica crucible and heated in a muffle furnace at 105-110˚C for one hour. There after the crucible is taken out weighed. The percentage of moisture is given by

Weight of sample = 1gm

Weight of crucible = 10.94 gm

Weight of crucible + sample = 11.94 gm

Weight of crucible + sample after heating at 110˚C for 1 hour = 11.910 gm

% moisture in coal = {loss in wt. of coal X 100}/ wt. of coal initially taken

$$= \frac{11.940-11.910}{1} \times 100 = 3.00\ \%$$

b) Determination of Volatile Matter: It is the loss in weight of moisture free powdered coal when heated in a crucible fitted with cover in a muffle furnace at 900˚C for 7 minutes.

Weight of sample = 1 gm

Weight of crucible = 10.89 gm

Weight of crucible + sample = 11.87 gm

Weight of crucible + sample after heating at 900˚C for 10 minutes = 11.590 gm

% volatile matter ={ loss in wt. of moisture free coal X 100}/ wt. of moisture free coal taken - % moisture content

$$= \frac{11.870-11.590}{0.980} \times 100 - 3 = 28.57 - 3 = 25.57\%$$

c) Determination of Ash content: It is the weight of residue obtained after burning a weighed quantity of coal in an open crucible (i.e. in presence of air) at 800˚C in a muffle furnace till a constant weighed is achieved.

Weight of sample = 1 gm

Weight of crucible = 10.89 gm

Weight of crucible + sample = 11.69 gm

Constant weight of crucible + sample obtained after heated at 800 ˚C = 11.370 gm

% ash in coal = {wt. of residue ash formed X 100} / wt. of coal initially taken

$$= \frac{11.370-10.89}{0.99} \times 100 = 48.48\ \%$$

d) Determination of Fixed Carbon: It is determined indirectly by deducting the sum total of moisture, Volatile matter, and ash percentage from 100. % fixed carbon in coal = 100-(% moisture+% ash+% volatile matter)

= 100-(3+48.48+25.57)

= 19.95 %

4.2 Experimental procedure for iron ore reduction

1. Three haematite iron ore lumps were taken.
2. These ores were grinded by stone grinder to shape in to spheres.
3. The three spherical ores are weighed by electronic balance.

4. The ore spheres were dehumidified by heating in muffle furnace for 1 hour at 950^0C.

5. The spherical ores were further weighed to determine weight of moisture free ore.

6. All three spherical ores were kept in three separate crucibles and covered by coal lumps.

7. crucible containing ore spheres covered by coal lumps were heated in muffle furnace at temperatures 800, 900 and 1000^0C separately in different steps.

8. Each crucible at different temperatures were taken out from the furnace at time interval 20, 40, 60, 80 and 100 minutes and weight were recorded.

9. Then initial weight of the iron oxide pellet and the final weight of the iron oxide pellet is measured and the percentage reduction is calculated.

FORMULA USED TO CALCULATE DEGREE OF REDUCTION

$$\text{\% of reduction} = \frac{\text{Loss in weight due to removal of oxygen in iron ore lump} \times 100}{\text{Total weight of oxygen initially present in iron ore lump}}$$

10. The graph is plotted between reduction ٪ vs time for three samples.

11. Then a straight line plot between $1-(1-R)^{1/3}$ vs time was drawn. The slope of the graph gives K (rate constant). Then graphs were drawn for ln (K) vs $1/T\times104$. Slope of the graph gives the value of activation energy which was been calculated from Arrhenius Equation:

$$K=Ae-E/RT.$$

Where K= Rate constant

P= Pre-exponential factor

E= Activation energy

R= Gas constant

T= Temperature in Kelvin

Chapter-5

Experimental result

Table 5.1: Illustration of degree of reduction, % of reduction and $fr_0[1-(1-\alpha)^{1/3}$ at different temperatures

Temperature °C	Time	Degree of Reduction (α)	% of Reduction	$fr_0[1-(1-\alpha)^{1/3}$
800	20	0.002	0.2	0.04284
	40	0.004	0.4	0.08568
	60	0.006	0.6	0.08996
	80	0.008	0.8	0.11566
	100	0.009	0.9	0.1328
900	20	0.07	7.0	1.1368
	40	0.111	11.1	1.6211
	60	0.140	14.0	2.0674
	80	0.154	15.4	2.2834
	100	0.162	16.2	2.4093
1000	20	0.107	10.7	1.5067
	40	0.156	15.6	2.2367
	60	0.213	21.3	3.1225
	80	0.274	27.4	4.1194
	100	0.293	29.3	4.4413

Table 5.2: Proximate analysis of coal

CONTENT	PERCENTAGE
ASH CONTENT	48.48%
FIXED CARBON	19.95%
MOISTURE	3%
VOLATILE MATTER	25.57%

Graphical Analysis

This plot shows the reduction behavior of three samples which were held at temperatures of 800, 900 and 1000°C for 20, 40, 60, 80 and 100 minutes

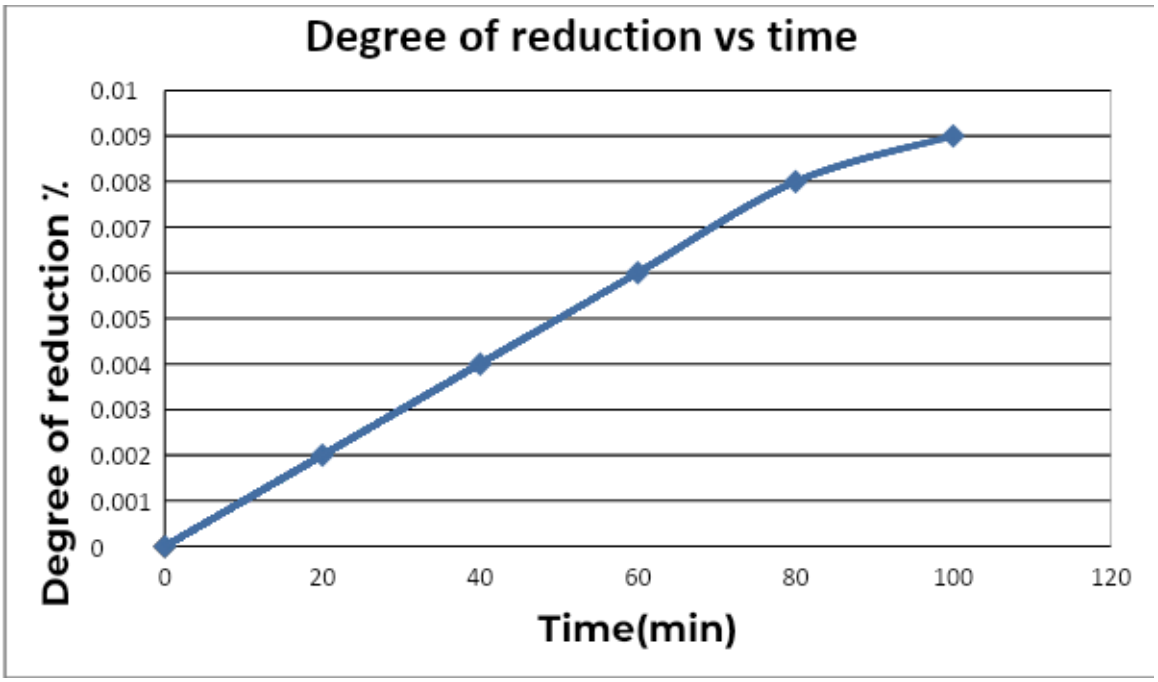


Fig.5.1 :- Effect of time on degree of reduction at 800^0C.

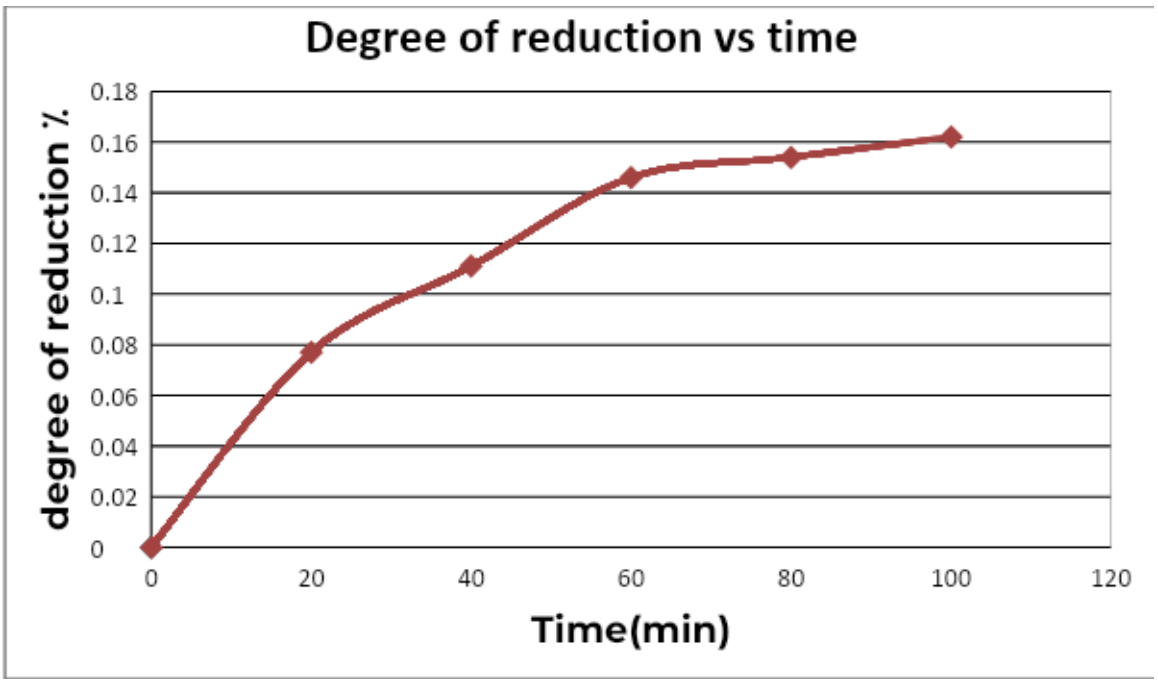


Fig.5.2 :- Effect of time on degree of reduction at 900^0C.

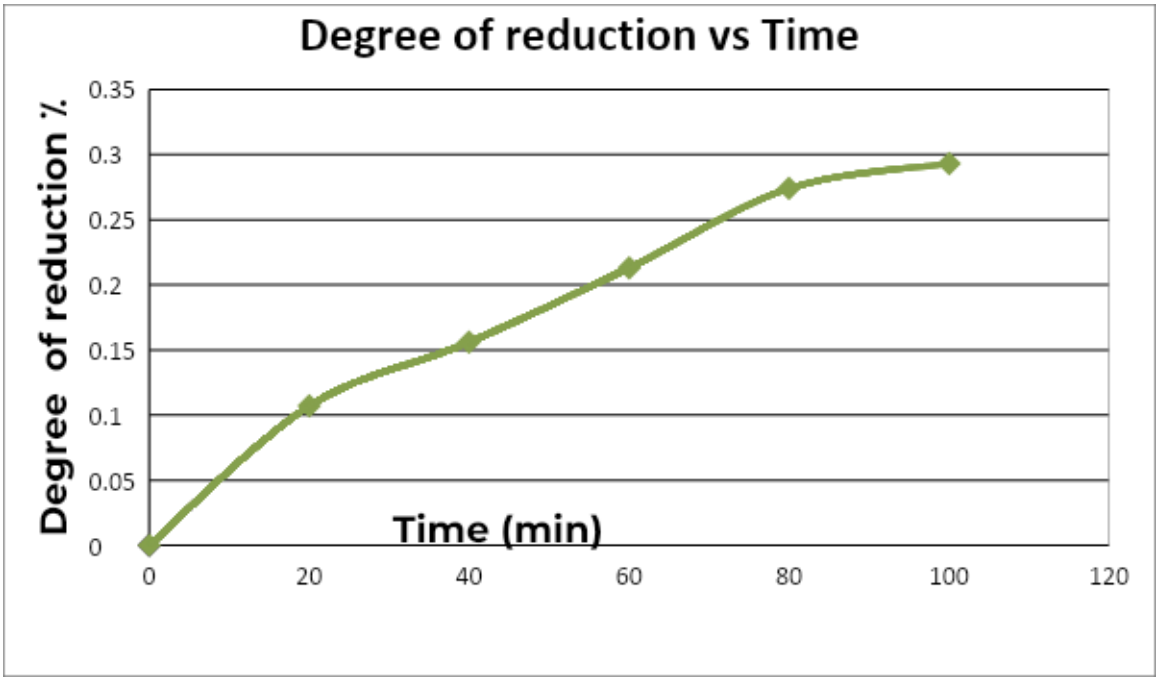


Fig.5.3 :- Effect of time on degree of reduction at 1000^0C.

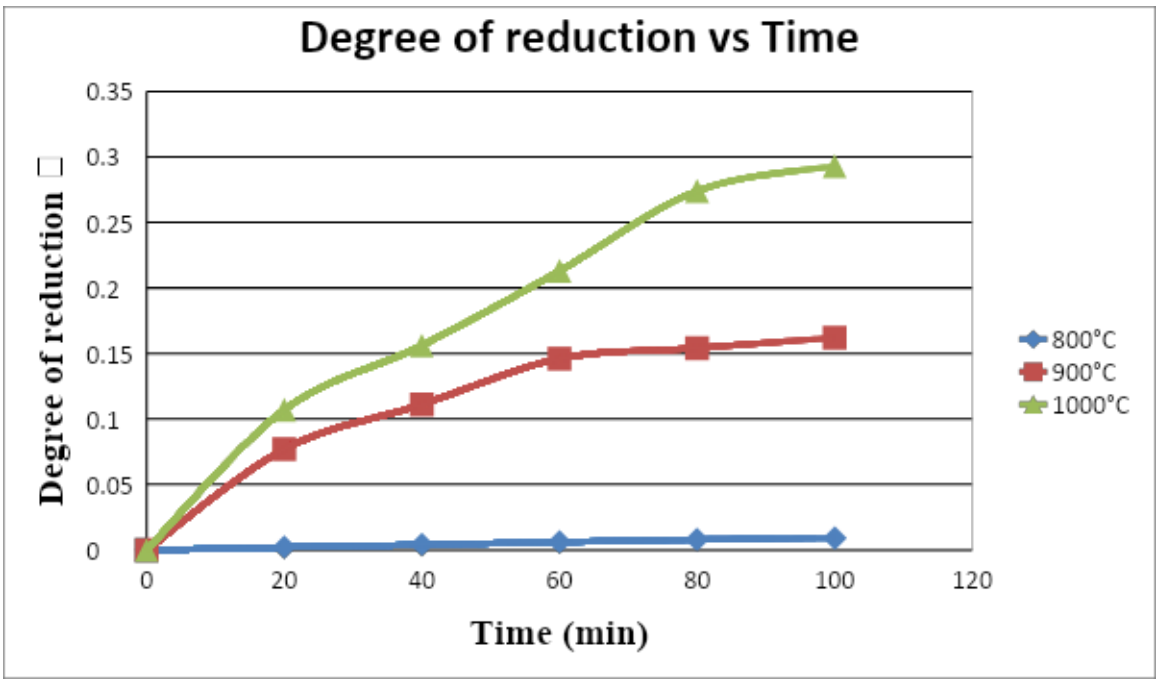


Fig.5.4 :- Effect of time on degree of reduction at 800, 900 and 1000^{0}C.

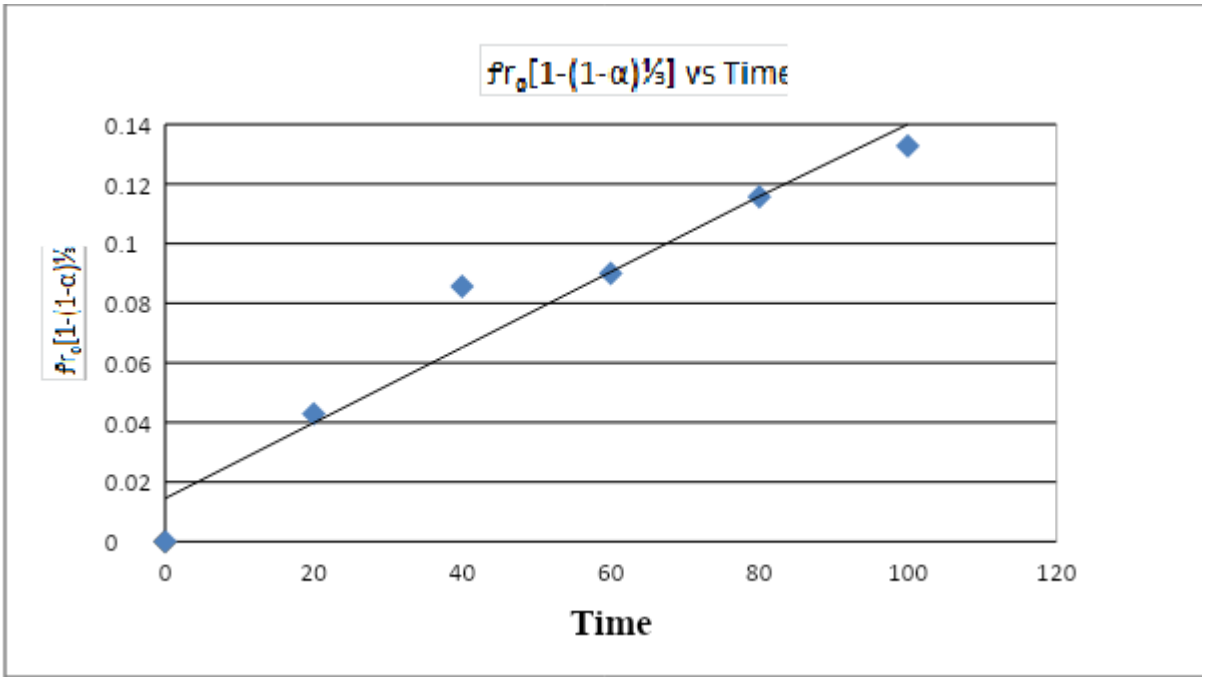


Fig. 5.5: $fr_0[1-(1-\alpha)^{1/3}]$ vs Time **at 800^{0}C**

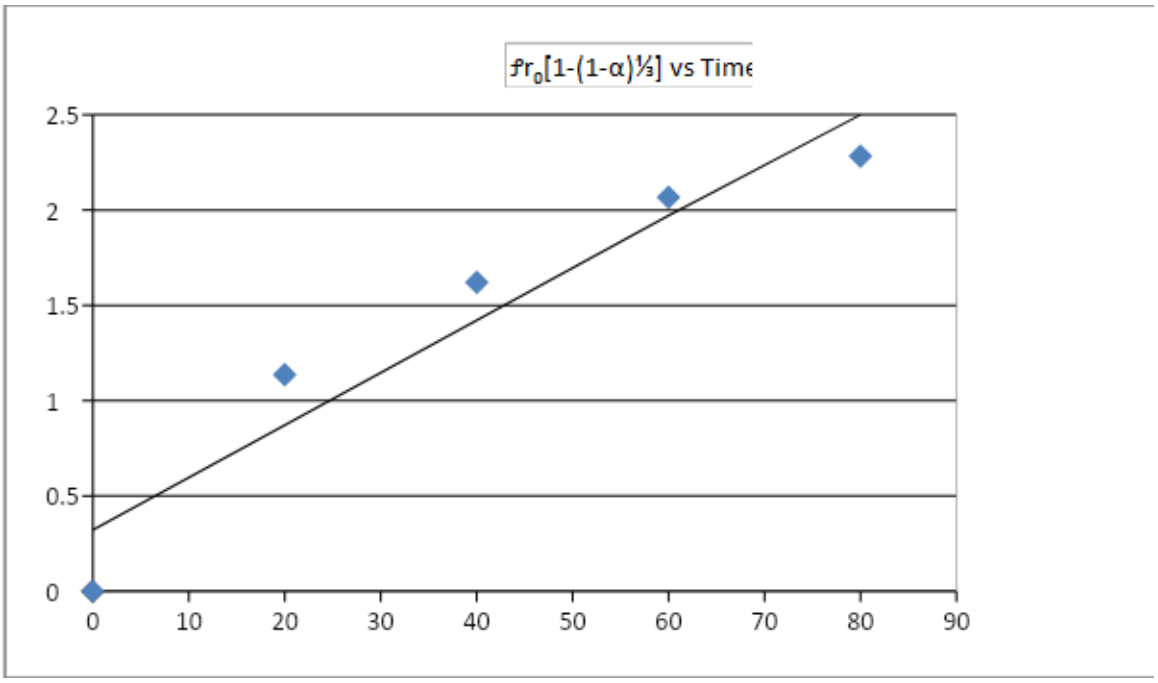


Fig. 5.6: $\mathcal{F}r_0[1-(1-\alpha)^{1/3}]$ vs Time **at 900°C**

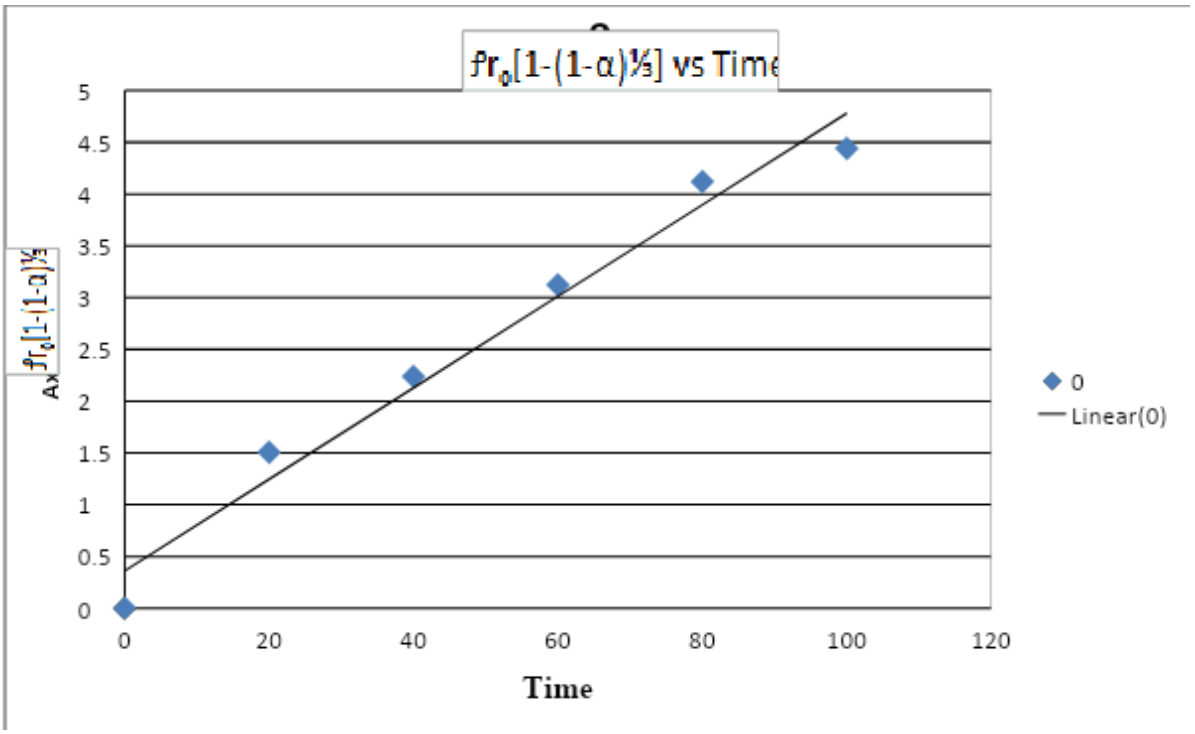


Fig. 5.7: $fr_0[1-(1-\alpha)^{1/3}]$ vs Time **at 1000°C**

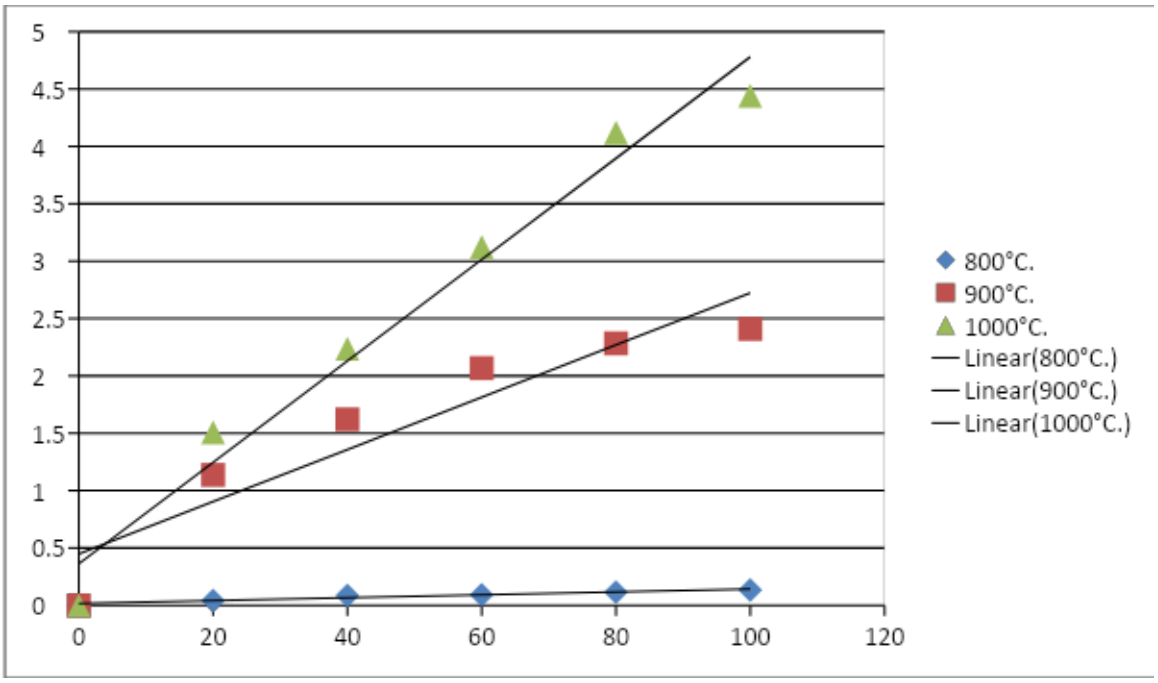


Fig.5.8: $fr_0[1-(1-\alpha)^{1/3}]$ vs Time **at 800,900,1000°C**.

With the help of the Arrhenius equation we can calculate the activation energy

$$K=Ae^{-E/RT}$$

Where, K = Rate Constant,

A= Arrhenius Constant,

E= Activation Energy,

R= Gas Constant,

T= Temperature.

When a graph is plotted between lnK and 1/T we get a straight line where, x= (1/T),

y=lnK

ln(K) vs. (1/Tx104)

We plotted the graph of ln (K) vs. (1/Tx10^4) for spherical iron ore. Then calculated the value of Activation Energy from,

K = A e-E/RT

Table 5.3 : Rate constant at different temperatures

Temp.(^{0}C)	Temp.(K)	1/T × 10^4	K	lnK
800	1073	9.319	0.001	-6.90775
900	1173	8.525	0.028	-3.57555
1000	1273	7.855	0.049	-3.01593

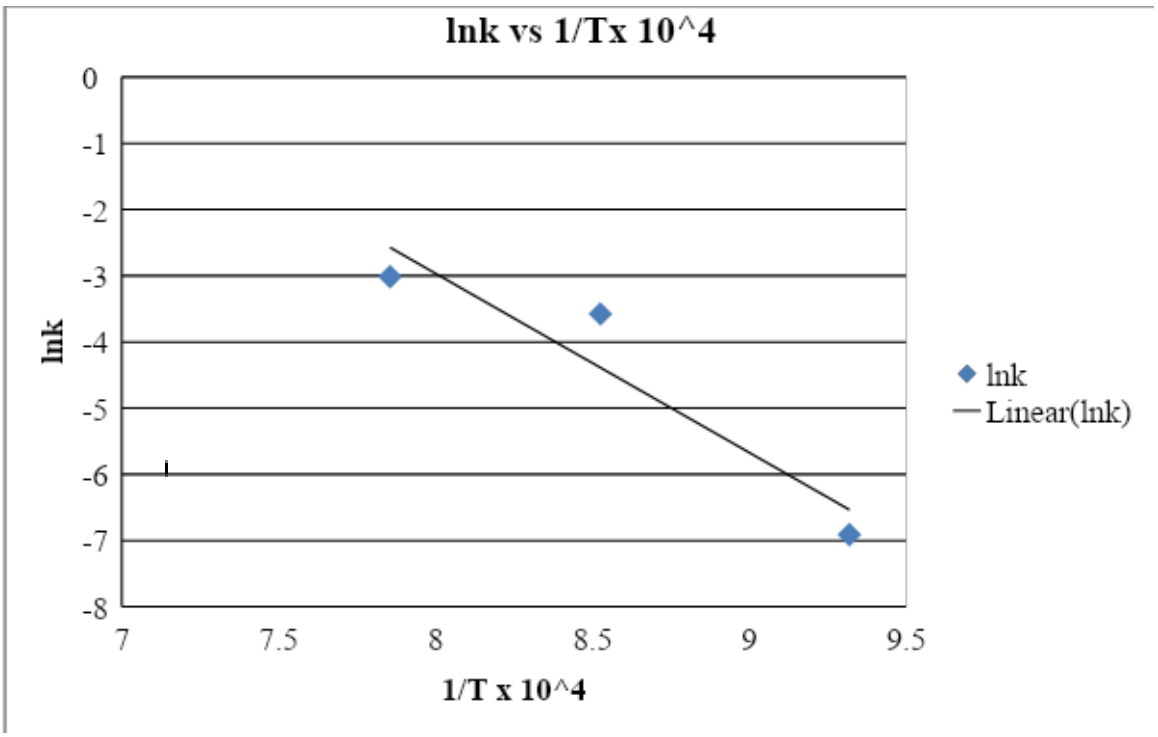


Fig.5.9: lnk vs 1/T

From Arrhenius equation,
K = A e-E/RT

lnK= A- E/RT
Slope = -E/R= -2.705 x 10^4
-E/R= 27050
E=27050×8.314=224893.7
Activation energy=224.8937KJ/mole

Percentage of reduction of iron ore increased with increase in temperature and time. These were illustrated in Figs. 5.1, 5.2, 5.3 and 5.4. Because this increase in temperature and time increased the rate of diffusion i.e., flux and chemically controlled reactions included in the mechanism of step wise reduction of iron ore lumps.

From the equation we have,

$$\mathbf{K = A\ e^{-E/RT} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)}$$

$$\mathbf{\rho r_o\ [1- (1-\alpha)^{1/3}] = Kt \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots (2)}$$

$\rho r_o\ [1- (1-\alpha)^{1/3}]$ had been plotted against time respectively at 800,900 and 1000^0C which were shown in Figs. 5.5, 5.6 and 5.7. From these plots, rate constants were calculated from respective slopes. As degree of reduction, i.e. α increased with increasing temperature, accordingly rate constant dependent on degree of reduction also increased with increase in temperature as per Arrhenius equation (1) and from above kinetic equation (2) . These were shown in Fig. 5.8. lnK vs 1/T had been plotted from which activation energy was calculated and was equal to 224.8937KJ/mole It was illustrated in Fig. 5.9.

Chapter-5

Discussion

1) Increase in temperature, increases the percentage of reduction.
2) Increase in time, increases the percentage of reduction.
3) Activation Energy E was found to be 224.8937KJ/mole.

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