Study of Reduction Kinetics of Mill Scale by Low Grade Coal

Ph.D. THESIS

by

Rahul Sen
(ID: 2013RMT9038)

DEPARTMENT OF METALLURGICAL & MATERIALS ENGINEERING
MALAVIYA NATIONAL INSTITUTE OF TECHNOLOGY JAIPUR,
JAIPUR-302017, RAJASTHAN (INDIA)

JULY 2018

Study of Reduction Kinetics of Mill Scale by Low Grade Coal

A THESIS

Submitted in partial fulfillment of the
requirements for the award of degree

of

DOCTOR OF PHILOSOPHY

in

METALLURGICAL AND MATERIALS ENGINEERING

by

Rahul Sen
(ID: 2013RMT9038)

DEPARTMENT OF METALLURGICAL AND MATERIALS ENGINEERING

MALAVIYA NATIONAL INSTITUTE OF TECHNOLOGY JAIPUR,

JAIPUR-302017, RAJASTHAN (INDIA)

JULY 2018

This thesis is dedicated to

***My Parents**: Sh. Ram Gopal Sen & Smt. Pushpa Sen*

***My Wife**: Antima & **Son:** Honey*

***And specially my Bua:** Srimati Gita Devi Sen*

For their unconditional love, support and especially never ending patience

DECLARATION

I, **Rahul Sen,** declare that this thesis titled, **“Study of Reduction Kinetics of Mill Scale by Low Grade Coal”** and the work presented in it, are my own. I confirm that:

- This work was done wholly or mainly while in candidature for a research degree at this university.
- Where any part of this thesis has previously been submitted for a degree or any other qualification at this university or any other institution, this has been clearly stated.
- Where I have consulted the published work of others, this is always clearly attributed.
- Where I have quoted from the work of others, the source is always given. With the exception of such quotations, this thesis is entirely my own work.
- I have acknowledged all main sources of help.
- Where the thesis is based on work done by myself, jointly with others, I have made clear exactly what was done by others and what I have contributed myself.

Date:

Rahul Sen
(ID: 2013RMT9038)

CERTIFICATE

This is to certify that the thesis entitled **“Study of Reduction Kinetics of Mill Scale by Low Grade Coal”** being submitted by **Rahul Sen (ID 2013RMT9038)** is a bonafide research work carried out under my supervision and guidance in fulfillment of the requirement for the award of the degree of **Doctor of Philosophy** in the Department of Metallurgical & Materials Engineering Malaviya National Institute of Technology, Jaipur, India. The matter embodied in this thesis is original and has not been submitted to any other University or Institute for the award of any other degree.

.

Prof. Dr. Upender Pandel
(Supervisor)
Dept. of Met. & Mat. Engg.
Malaviya National Institute of Technology
Jaipur

Date:

Place:

ACKNOWLEDGEMENT

I avail this opportunity to extend my hearty indebtedness to my guide **Prof. Dr. Upender Pandel**, Department of Metallurgical and Materials Engineering, Malaviya National Institute of Technology Jaipur, for his invaluable guidance, untiring efforts and meticulous attention at all stages during my Ph.D. Research work. I would also like to convey my deep regards to **Prof. Dr. M.K. Banerjee,** Steel Chair Professor**,** Department of Metallurgical and Materials Engineering, MNIT Jaipur for his guidance for technical issues for which this research work has come to fruition.

I sincerely extend thanks to **Prof. Dr. A.K. Bhargava** Head of the Department, Metallurgical and Materials Engineering, MNIT Jaipur and **Dr. R.K. Duchaniya**, P.G. Coordinator, Metallurgical and Materials Engineering Department, MNIT Jaipur for his encouragement and necessary permission to carry out the work.

I am thankful to **Shri Lalchand Kumawat Ji,** Technical Assistants, Department Metallurgical & Materials Engineering, MNIT, Jaipur for their co-operation in experimental work.

Special thanks to **all the staff members of my department** for being so supportive and helpful in every possible way.

Last but not the least I am grateful to all known and unknown persons who helped me directly or indirectly during my project work.

Date: 30/07/2018 **(Rahul Sen)**

ABSTRACT

The research work is on reduction kinetics of mill scale reduction by low grade coal. The study work comprises the effect of various process parameters on reduction of mill scale by low grade coal and finding the kinetics behind the process. The optimization of certain process parameters were carried out in part of preliminary study work and isothermal kinetic study was done in final study work. The parameters studied in research work were: time (15, 30, 60, 90, 120, 150 minutes), temperature (850, 900, 950°C), particle size of mill scale and coal (30-90, 90-150, 150-210, 210-270 microns), ratio of mill scale-coal in crucible {(1:0.9), (1:1), (1:1.1), (1:1.2), (1:1.3), (1:1.4), (1:1.5)}, addition of limestone (0, 5, 10, 15, 20% - w.r.t. weight of mill scale taken) and arrangement of mill scale and coal in crucible (Mixed, central, alternate concentric and layered). The results were characterized by using XRD (X-Ray Diffractometer), SEM (Scanning Electron Microscope) and EDS (Energy-dispersive X-ray spectroscopy) techniques.

The study of parameters reveled that maximum reduction of 93.5% was found in sample reduced in mixed arrangement, of particle size 90-150, ratio 1:1.3, having 10% limestone at temperature 950 °C and time 150 minutes. The characterization study unveils the disappearance of the oxide phases and increase of metallic iron content after reduction of mill scale by low grade coal. The results of kinetic study shows that the minimum activation energy found in samples reduced in mixed arrangement, then equal in layered arrangement and alternate concentric and last in central arrangement. The samples reduced in mixed arrangement were found to be chemically controlled, the kinetic data fits on first order equation model: $F1 = -\ln(1-\alpha)$ and the samples reduced in central, alternate concentric and layered arrangement found to be diffusion controlled, the kinetic data fits on the Ginstling-Brounshtein reaction model : $D4 = (1 - \frac{2}{3}\alpha) - (1-\alpha)^{2/3}$.

The study work will helpful in utilizing the low grade coal for the mill scale reduction. Giving idea on various parameter values, in which the reduction could be found maximum. The kinetic study useful in understanding the rate at which the iron oxide present in mill scale get converted into metallic iron. The rate of process influences the productivity of the work. This research work helpful in minimizing the steel industry waste (mill scale), utilization of low grade coal for such process and saving energy of steel industries.

Contents

List of Tables

List of Figures

List of Appendix

List of Abbreviations

MS = Mill scale
BF = Blast furnace
BOF = Basic oxygen furnace
EAF = Electric arc furnace
DR = Direct reduction
DRI = Direct reduced iron
$G(\alpha)$ = Integral expression of kinetic equation
k = Reaction rate constant
Ea. = Activation energy
R = Gas constant
T = Temperature
t = Time
P = Pellet
L = Lump
B = Briquettes
P.S = Preliminary Study
$C_{fix.}$ = Fixed carbon
Fe_T = Total iron
Fe_M = Metallic iron
DOM = Degree of metallization
DOR = Degree of reduction

CHAPTER - 1

INTRODUCTION

1.1 Background

Conventionally steel produced from Blast Furnace (BF) via basic oxygen process and still it is the highest for steel making process. The integrated steel production method requires large capital, land, machines, labor, cheap and easy availability of raw materials, electricity etc. In addition these production produces so much pollution in environment in all solid, liquid and gaseous form like mill scale, slag, oil sludge etc. With the due course of development and time, there arises a great need for production of steel from other methods. Of course the electric arc furnace is nice clean process of making steel from the scrap as compared to BF. But it completely depends upon the availability of scrap. Due to the inflexibility of the process, some different raw material required which can be utilized as charge in electric arc furnace. The development of the direct reduction process is the remarkable discovery in that work. [1, 2]

The term direct reduction can be defined as a reduction of oxides of iron ore to metallic iron in the solid state at high temperature in the presence of suitable reductants without undergoing the melting process. The oxygen present in iron oxides is removed during the reduction process to give porous spongy structure called as Direct Reduced Iron (DRI) or sponge iron which can be used as a feed material for electric arc furnace [3, 6].

In the process of making steel from both the routes (BF via BOF and EAF), various wastes generated during the steel production. Mill scale is one of the waste generated during the continuous casting and hot rolling of steels. It is an oxide layer formed on the surface of steel during hot rolling process. Mill scale constitutes iron (60 to 70 %) in form of oxides such as Wusite (FeO), Hematite (Fe_2O_3), Magnetite (Fe_3O_4) and traces of non-ferrous elements. Mill scale can be reduced by the process of direct reduction. The reduced matter thus obtained can be utilized as feed material for the production of steel [3-6]. There are many hot rolling industries in Jaipur city and in nearby areas, producing tons of mill scale every day. In addition there are huge reserves of low grade coal production at Matasukh coal mines, Nagur district, Rajasthan- India. This low grade coal constitutes high moisture content and volatile matter as compared to fixed carbon. Therefore the given low grade coal is not fully utilized for industrial purpose and if it is transported to long distances, it remains not much economical.

In this research, study of reduction kinetics of mill scale (obtained from nearby hot rolling industries) by low grade coal (of Matasukh coal mines, Nagaur) was done. Effect of various possible parameters on mill scale reduction has been studied. The reduction study was carried out in fixed size alumina crucible. The optimization of certain parameters were carried out in part of preliminary study work. In the final study the effect of different arrangements of raw materials in crucible on reduction of mill scale was estimated. The isothermal kinetic study for different arrangement study was also carried out. Kinetic study includes the identification of reaction mechanism equation and calculation of activation energies. Characterization study includes: XRD, SEM and EDS of reduced and unreduced mill scale sample.

1.2 Thesis Outline

This thesis has been divided in five chapters:

- **Chapter 1** deals with the background of research related subjects. Some basics of direct reduction also discussed in short. The motivation and overview of the research work also been presented along with the thesis outline.
- **Chapter 2** deals with the basics of all the research related topics. The topics include- steel and its production methods, waste from steel industry, mill scale, direct reduction process. Details of direct reduction process include its types, mechanism, kinetics, effect of process parameters, previous research work and gap in field of coal based direct reduction. The chapter ends with objective and scope of research work
- **Chapter 3** deals with the materials and methods used in the thesis. The chapter discuss about the raw materials used, their analysis and procedure of analysis. Stoichiometric calculation, formulae used, experimental procedure

and experimental flow chart of the research work. It also provides the information on characterization techniques used in research work.

- **Chapter 4** In this chapter the result of reduction of mill scale by low grade coal for certain parameters have been discussed. The aim of this chapter was to optimize the reduction parameters for the final study. The parameters studied in part of preliminary study work were: (i) effect of particle size (30-90, 90-150, 150-210, 210-270µ), (ii) effect of ratio {(1:0.9), (1:1), (1:1.1), (1:1.2), (1:1.3), (1:1.4), (1:1.5)} of mill scale and coal in crucible, (iii) effect of addition of catalyst (0, 5, 10, 15, 20 %) at fixed time (150 minutes) and temperature (950°C). The effect of parameters were calculated in terms of degree of reduction and influence of parameters on reduction also discussed.
- **Chapter 5** deals with main (final) study of the research work on – Effect of mill scale reduction by low grade coal for different arrangements (mixed, central, alternate concentric and layered) in crucible. The value of kinetic parameters were calculated for the given study. For calculating the kinetic parameters, the final study was carried out at different time and temperatures. The kinetic parameters include the rate constant, activation energy and identification of rate control equation for the samples reduced in different arrangement. The characterization study by XRD, EDS, SEM for samples studied in research work were shown.
- **Chapter 6** deals with the conclusions derived from research work and suggestions for future work.

CHAPTER - 2

LITERATURE REVIEW

In this chapter all the important topics beginning from the basics to the subject of final research work were discussed in detail. The topics include- steel and its production methods, waste from steel industry, mill scale, direct reduction process. Details of direct reduction process include its types, mechanism, kinetics, effect of process parameters, previous research work and gap in field of coal based direct reduction. The chapter ends with objective and scope of research work.

2. Steel and its production methods

Steel is the most extensively used material in the world. It is widely used in area of construction, automobiles, defense, telecommunication, electronic parts and equipment's, devices, machineries, utensils etc. In fact development of nation depends upon steel production and its utilization. Majorly there are two different routes for steel making, as shown in figure 2.1 [1, 2]. First is conventional process of steelmaking in integrated steel plant of blast furnace (BF) and basic oxygen furnace (BOF). Second is includes the use of scrap and DRI (direct reduced iron) as charge in Electric arc furnace (EAF) [2,22,23,25,30,31] The DRI produced separately by reduction of iron ore in direct reduction furnaces.

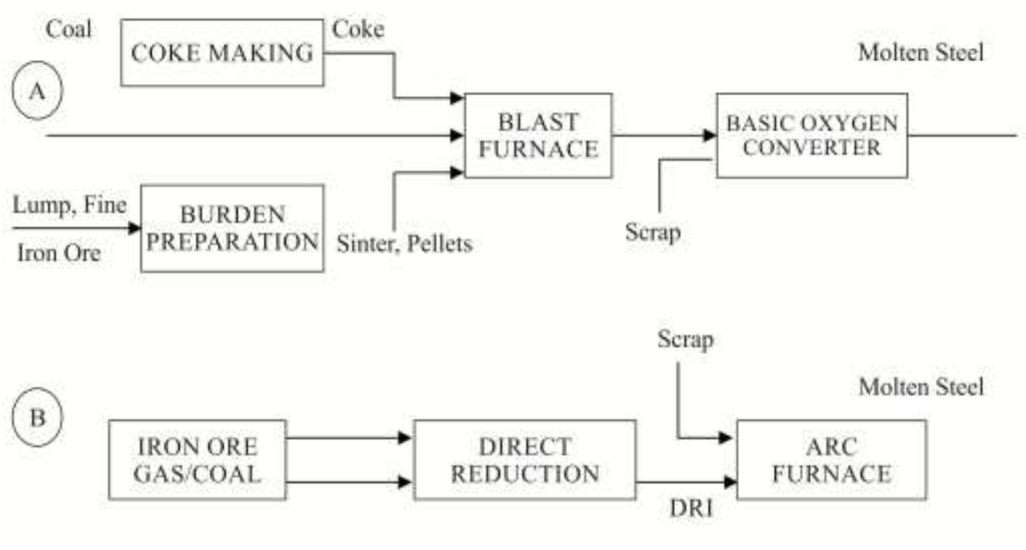


Figure-2.1: Routes of steel making process [3]

The molten steel produced from both the routes is cast into different solid shapes like billets, blooms, sheets etc., during continuous casting process. Further these different solid shapes subjected to various forming process like rolling, forging, wire drawing etc. in steel equipment's making industries, as shown in figure 2.2, [18, 19, 25].

2.1 Steel making in integrated steel plant

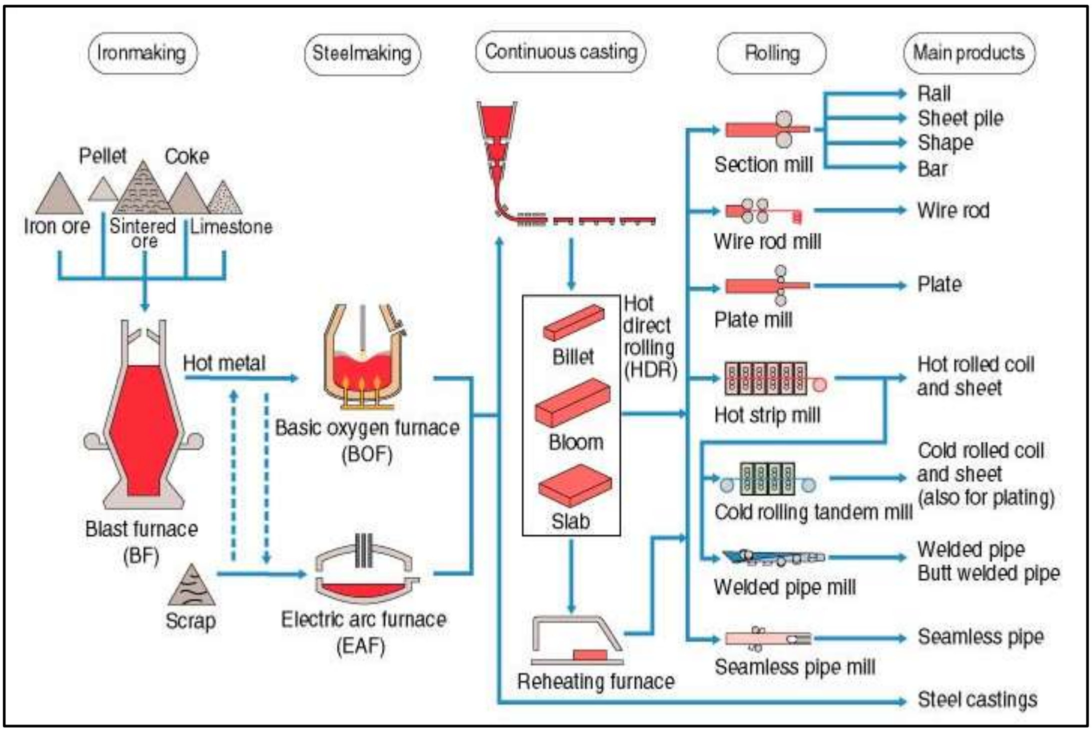


Figure-2.2: Production of steel and its primary solid products in integrated steel plant [4]

2.1.1 Blast furnace

BF is a tall shaft reactor. The charge is introduced to the furnace at the top which consists of iron ore, scrap, flux (limestone) and coke. Coke has different roles in BF. First, it is a heating source for the furnace due to its reaction with air and second, it acts as a reductant to reduce the iron ore. Since there are different regions inside the furnace in terms of temperature and gas composition, various reactions occur in blast furnace depending on the position within the furnace, as shown in blast furnace figure 2.3 [5, 22, 30, 31].

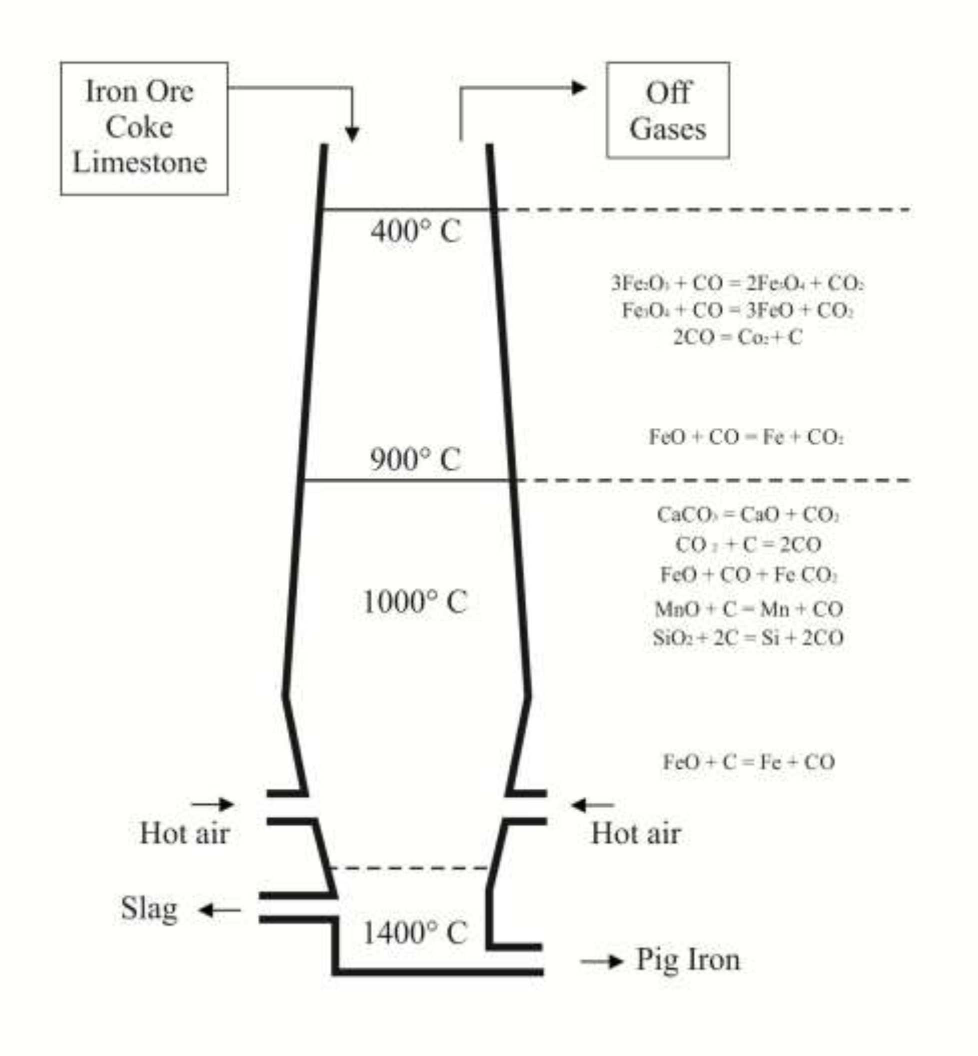


Figure 2.3: Schematic diagram of blast furnace

As the iron melts, it descends and accumulates at the bottom of furnace. At different tapping times, slag and carbon saturated iron, known as hot metal or pig iron are drained through tapping holes. Hot gases produced from the coke burning exit through top of the furnace after they participated in the reactions. The average composition of pig iron is shown in Table 2.1 [2, 22, 30, 31]

Table-2.1: Average composition of hot metal produced in blast furnace.[2]

Element	Iron	Carbon	Sulphur	Phosphorus	Silicon
Composition (in weight %)	94	4.5 - 4.7	0.02- 0.06	0.08	0.3-0.8

Although blast furnace is still the dominant process for making iron, it is accompanied with some disadvantages. Blast furnace utilizes metallurgical grade coke to heat up and reduce iron oxide. However, coke is expensive and causes significant CO_2 emissions. Moreover, blast furnace projects carry a high capital cost; hence minimum capacity constraint is inherent to the process. Consequently, other processes may be employed including mini blast furnace, smelting reduction and direct reduction [6, 22, 30, 31, and 44].

2.1.2 Basic oxygen furnace

This steelmaking method involves selective oxidation of C and Si in the hot metal by blowing oxygen to the convertor. The process was first developed in 1947 at Linz and Donawitz (two 7 towns in Austria) [7, 8]. In different geographical areas it may be known as basic oxygen furnace, BOS (in UK) or LD in other European countries. The schematic diagram of BOF is shown in Fig 2.4. The charge materials of BOF contain mainly hot metal while the remaining is scrap. The portion of scrap depends on the price and availability of scrap as well as Si and C content of hot metal, thus it varies from one steel plant to another. However, it may constitute up to 30% of charge material

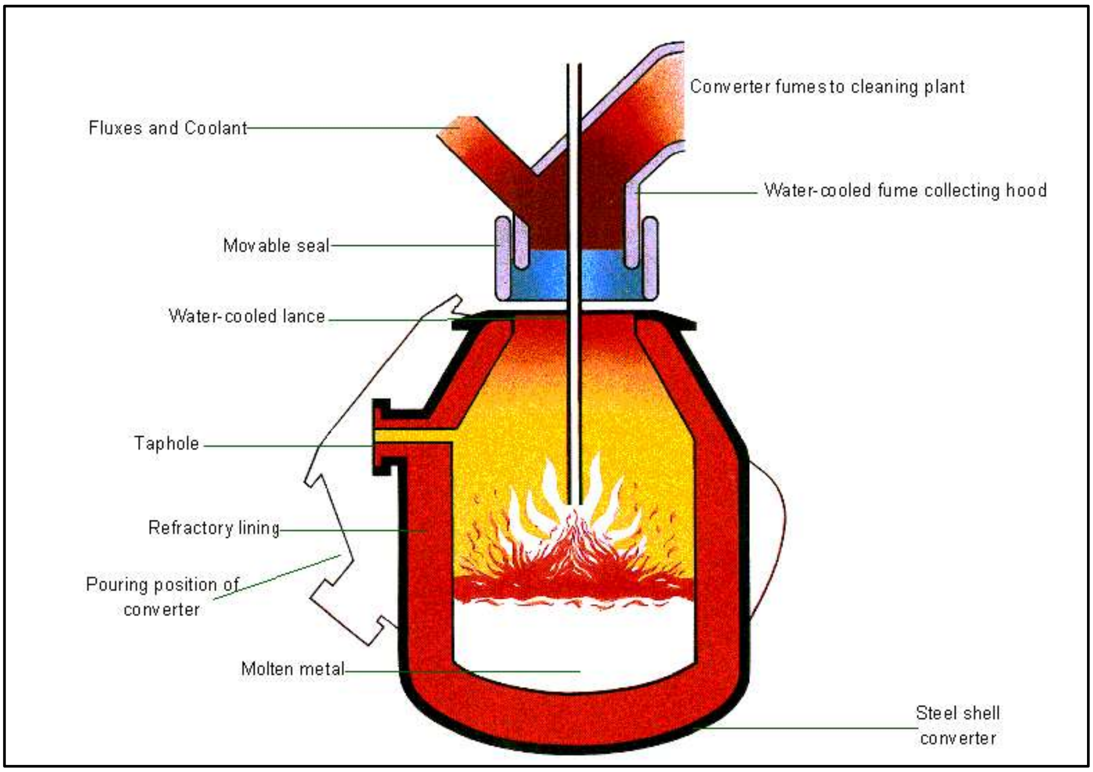


Figure 2.4 Basic oxygen furnace or converter

By blowing oxygen into the molten metal, some impurities including Si, P, Mn and S areremoved from steel bath by oxidation according to the following reactions (2.1-2.4).

$Si + O_2 = SiO_2$ (2.1)

$P + 5/4\ O_2 = 1/2(P_2O_5)$ (2.2)

$Mn + 1/2\ O_2 = MnO$ (2.3)

Meanwhile, steel is decarburized through reaction 2.4

$C + 1/2O_2 = CO\ (gas)$ (2.4)

Before each run depending on the carbon target, calculations should be carried out to estimate the charge and oxygen ratio in order to meet the final quality of steel. These calculations are based on the mass and heat transfer inside the furnace [8].

2.1.3 Electric Arc Furnace

In electric arc furnace (EAF) utilizes several graphite electrodes to heat up the charge (scrap and other materials) through the generation of electric arc between them and converts them into fine molten steel, as shown in figure 2.5.

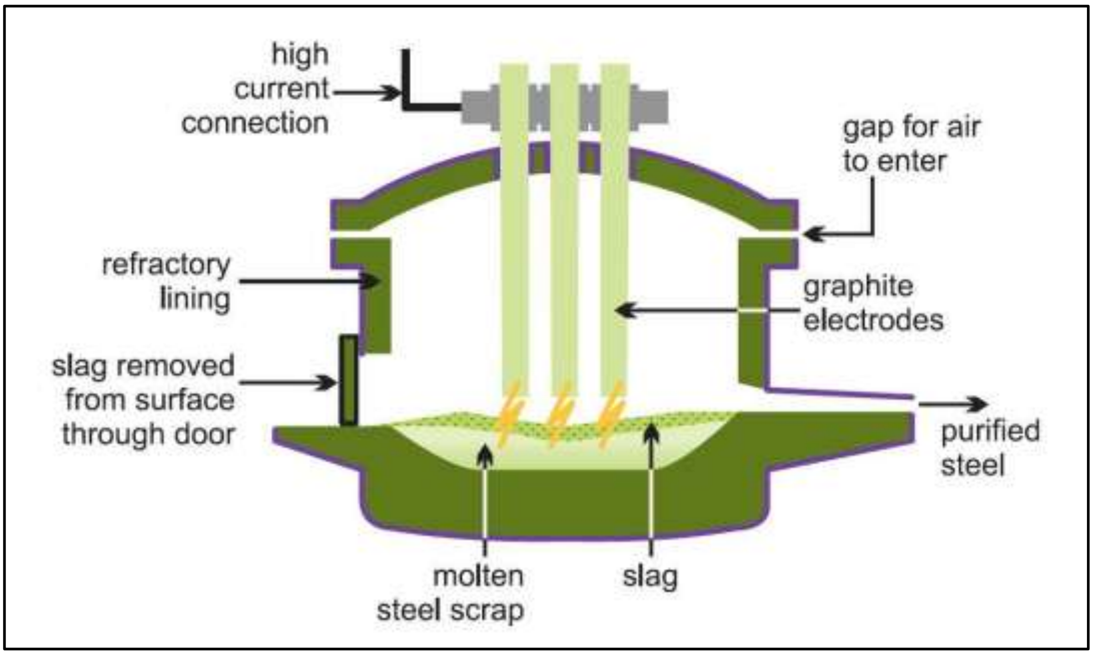


Figure-2.5: Electric arc furnace

Depending on the grade of steel and melting conditions in the furnace, the charge composition is estimated, and then fed to the furnace (furnace charging). In the next step the furnace roof is put on and as mentioned before by passing high voltage current in the electrodes the charge begins to melt (melting). Refining involves removing undesired impurities such as phosphorus, sulfur, silicon and also carbon. Once the bath is completely molten, the oxygen lance is inserted into the bath and by blowing oxygen most of impurities are oxidized. This process continues until the target carbon content in the bath is achieved. After refining, the slag that contains removed impurities from the previous step is tapped out (de-slagging). Finally, the steel produced is tapped and transferred to other furnace (usually ladle furnace) for further processing [9, 10, 31, 44].

The steel making through EAF plant is less expensive, clean, easy installable as compared to former processes. However the production depends upon the availability of scrap [11, 12, 31, 44]. This problem was greatly solved in past decades by melting of direct reduced iron (DRI) with the scrap in EAF. The charges used for melting in electric furnace are:

i) **Scrap** – Scraps are generated within the steelmaking and forming processes, e.g. metallic losses in slag, chop-out from continuous casting or rolling operation, defected and rejected a portion of casting etc.

ii) **Direct reduced iron (DRI)** – The product forms when the reduction iron ore reduced by suitable reductants in different reduction furnace is called DRI. It can be directly added as charge in EAF. DRI is produced in many forms. These are lump, pellets, hot briquetted iron (HBI), fines, and cold briquettediron (CBI). [13-15,30,31,44]

2.1.4 Continuous casting process

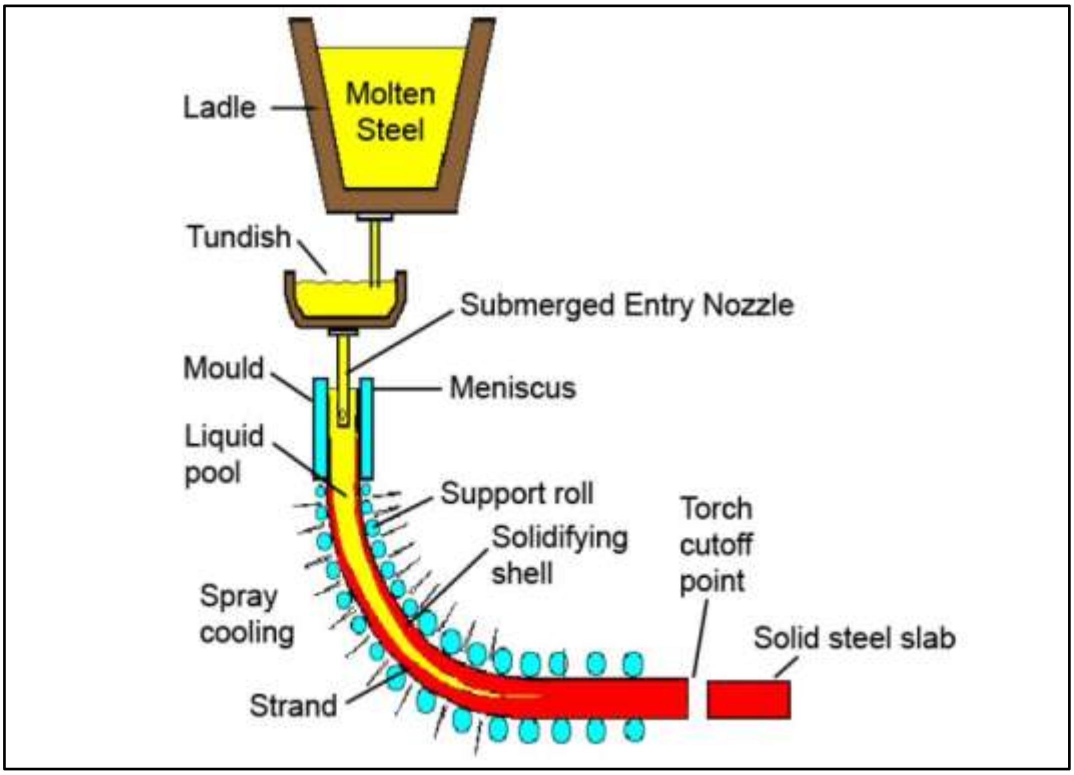


Figure 2.6 Continuous casting process

The molten steel brought from basic oxygen furnace or from electric arc furnace in ladle is sent for solidification and casting in continuous casting plant. The schematic diagram of continues casting process shown in figure 2.6. A two way stopper at the bottom of the ladle is removed, and the metal flows into a reservoir called a tundish. This is filled with the entire load from the ladle. As it is being filled, it releases the molten steel in a continuous stream through a hole in its base. The steel flows out at a steady rate and is distributed into a series of moving molds. The metal solidifies as it moves through a roller pron. Next, the metal enters the straightener. The straightener contains rollers that reshape the slightly curved metal in form of flat slab, bloom and billets. The dimension and figure of these products showed in figure 2.7.

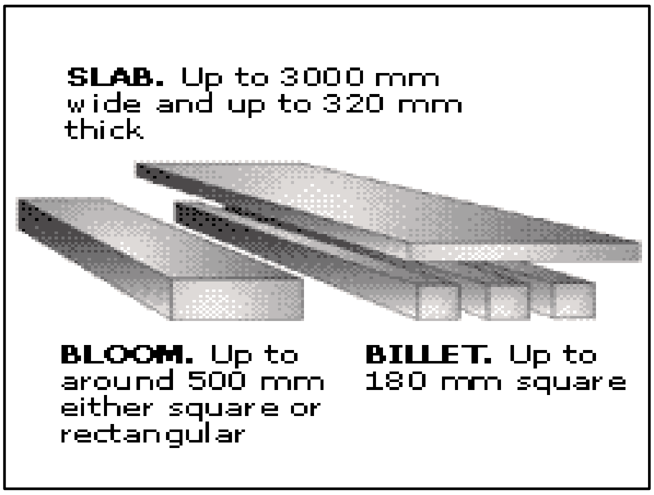


Figure-2.7: Products of continuous casting process

The cast products from the continuous casting units in form billets, slabs, blooms sent to those industries which produce the steel made machineries, items. In that companies further operations like forging, casting, extrusion, rolling etc carried out to produce the forms like plates, tubes, wires, rods etc. (as shown in figure2.8) [16-18, 31].

2.1.5 Hot rolling

Hot rolling is process in which the solid metal or alloy is passed between the small gaps of two parallel rolls in presence of strong compressive forces which decrease the thickness or diameter of the passed section and increases its length. It is very important forming process to change the shape of the products obtained from continuous casting units. Mostly this operation carried out at high temperature, above the recrystallization temperature to remove the residual stresses and easy deformation of the object. This type rolling carried out at high temperature (400-700°C) called hot rolling process. Generally during such operations scales of metal oxides forms on the surface of hot rolled product. Rolling operation carried out below the recrystallization temperature called as cold rolling [19, 20, 32, and 44].

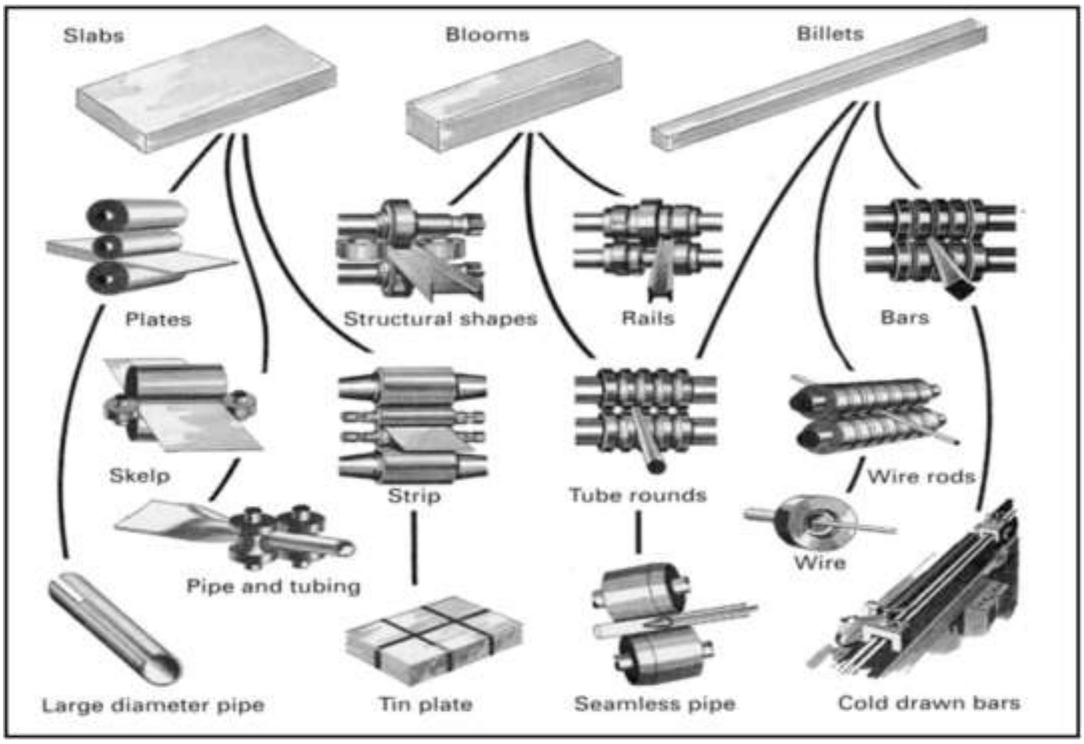


Figure 2.8: **Flow diagram showing different rolling products and their uses**

2.2 Waste production in integrated steel plant [21-30]

During the making of iron and steel, many type of wastes generated in large amount at various stages of production. The different types of waste are shown in table 2.2.

Table 2.2: Types of waste materials produced in integrated steel plants.

Unit	Solid wastes (process unit)	Solid waste (pollution control unit)
Coke oven and by-product plant	• Coke breeze • Tar sludge • Acid sludge	• Coke fines
Sinter, raw material handling and refractory plant	• Undersize sinter • Fines	• Dust
Blast furnace Steel making shop	• Slag • Slag • Broken refractory	• BF flue dust • SMS dust
Rolling mills	• End cutting • Broken refractory	• **Mill scale** • Oily sludge

At present time, environmental related issues are increasing day by day which has risen a task for the steel manufacturers to use the waste by-products generated in the industry.Mill scale is one of the waste produced during the steel making process is utilized in the steel production. [32-38]

2.3 Mill scale: Steel industry waste

Mill scale is an oxide layer formed on the surface of steel during hot rolling process (as shown in figure 2.9 and 2.10). The oxides of iron are formed on the surface of metal like arising out of continuous casting, soaking, reheating and rolling operations. Normally, mill scale thickness is less than 2.00 mm. It constitutes iron (60 to 70 %) in form of oxides such as Wusite (FeO), Hematite (Fe_2O_3), Magnetite (Fe_3O_4) and traces of non-ferrous elements. About 20% mill scale produced during the process can be recycled at the steel plants without any pre-treatments and the rest of the mill scale is used for land filling due to oil contamination. Mill scale is contaminated of lubricants, oils and greases from the machines and equipment's linked with rolling operations. It is generally produced in the range of 2 to 3% of the steel produced.

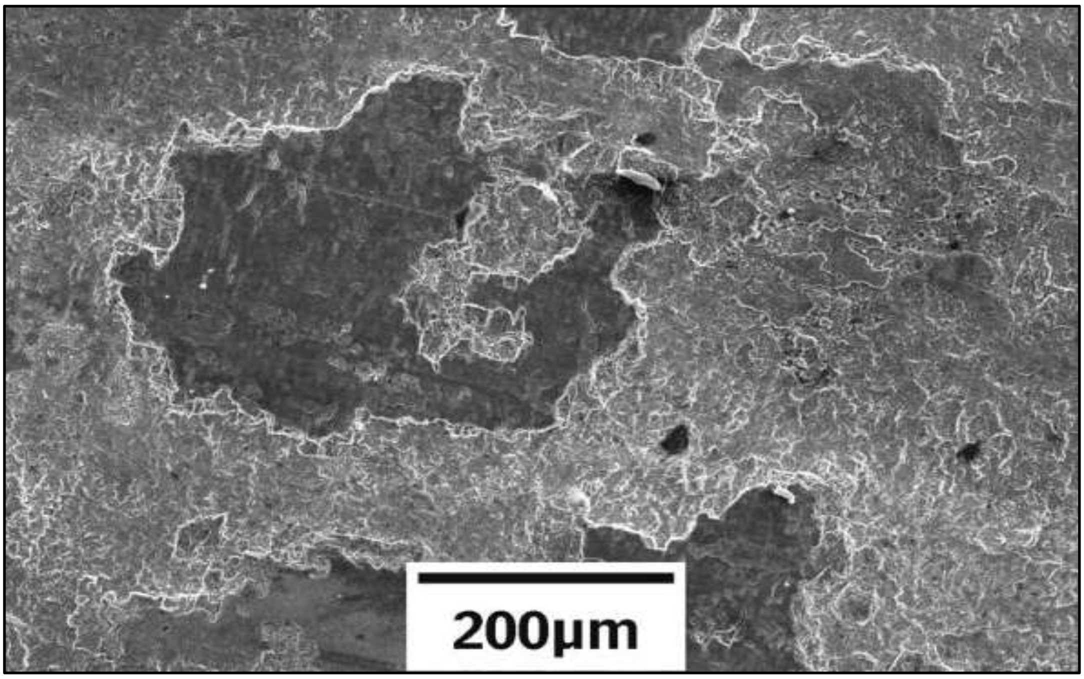


Figure-2.9: SEM micrograph shows the surface of hot rolled steel and mill scale formed on the surface. [4]

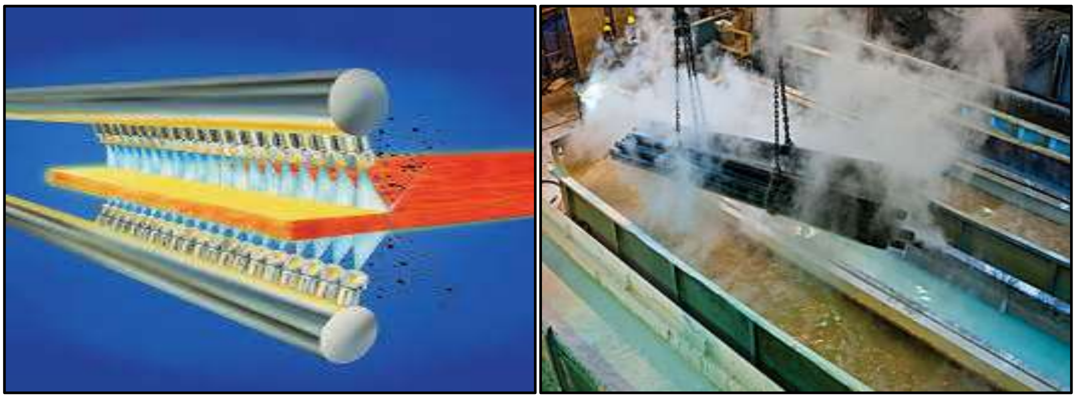
Figure-2.10: Mill scale wastage produced during hot rolling

2.3.1 Removal of Mill Scale

Mill scale can be removed by two process; they are following:

(a) **Water Treatment:** The high-pressure water jet is commonly used to remove the mill scale from hot strip surface of the steel, shown in figure 2.11 A [39]

(b) **Pickling Process:** Steel strips pulled through various dilute acid baths kept at temperatures around 180-200°C at speeds approx. 540 feet's per minute, then rinsed with water sprays and air drier (figure 2.11B). Chemical inhibitors are further added to discourage the acid from attacking the steel base [40].



(A) **(B)**

Figure-2.11: (A) Water Treatment for removal of mill scale [39] and (B) Pickling Process for removal of mill scale [40]

2.3.2 Mill Scale production

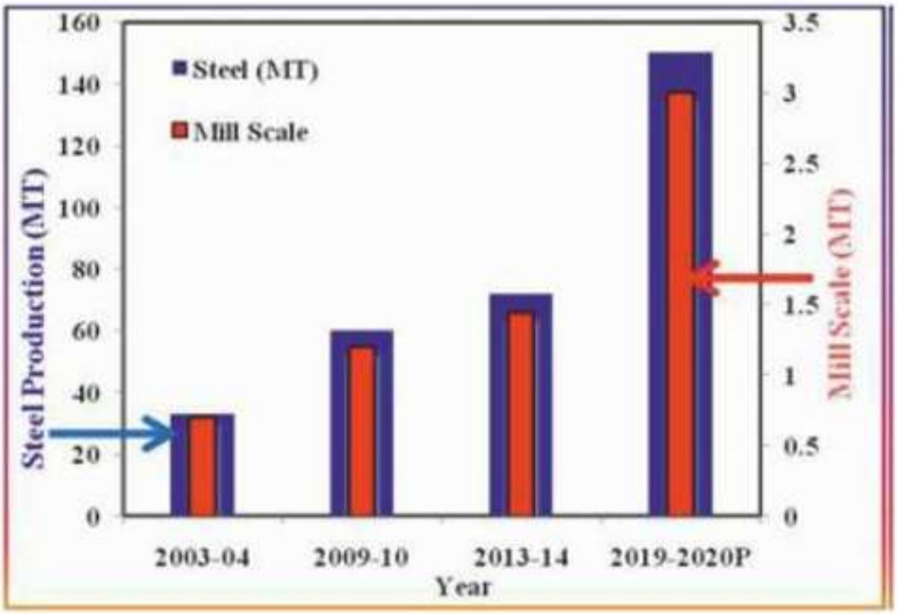


Figure-2.12: The generation of steel and corresponding mill scale in India

With increase in production of steel, the mill scale generated from continuous cast and hot rolling plants also got increased year by year. The figure 2.12 shows the production of steel and mill scale (in million tonnes) in India from last decades and expected production in future years. In 2003-04, the production of mill scale was only 0.7MT in India while the production of steel was almost some greater than 25MT. After some year in 2009-10, the production of steel was increases and it achieved 60MT. In 2003-04, the production of mill scale was only 0.7MT in India while the production of steel was almost some greater than 25MT. After some year in 2009-10, the production of steel was increases and it achieved 60MT. That's mean the production of mill scale was obviously increased and reached to the 1.20MT. But in 2013-14, the rapid growth in the production of steel and it achieved 70 MT while the production of mill scale also increased by 1.45MT. In 2019-20, as per expectation, the production of steel will be 150MT and the production of mill scale will be 3MT. Demand of today is to optimize the available resources and reutilize the waste materials. The mill scale (steel waste) enriched in iron. It can be reduced via direct reduction process to suitable product, which could be utilized in steel production. The literature work on mill scale reduction is discussed in last section of the chapter named -previous work done on mill scale reduction [41, 42, and 43].

2.4 Direct Reduction process

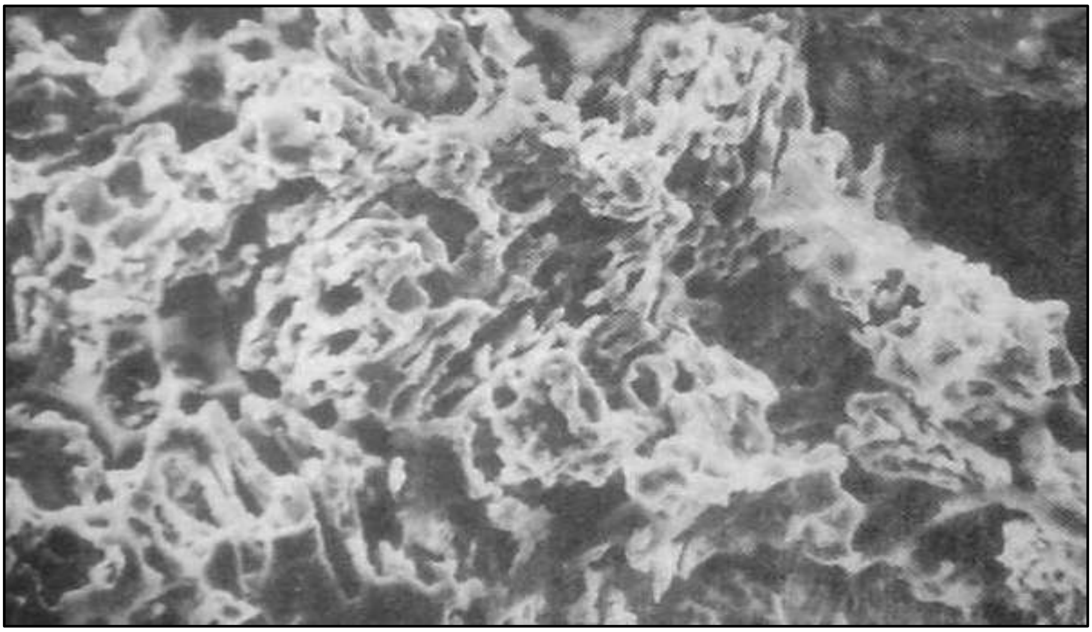
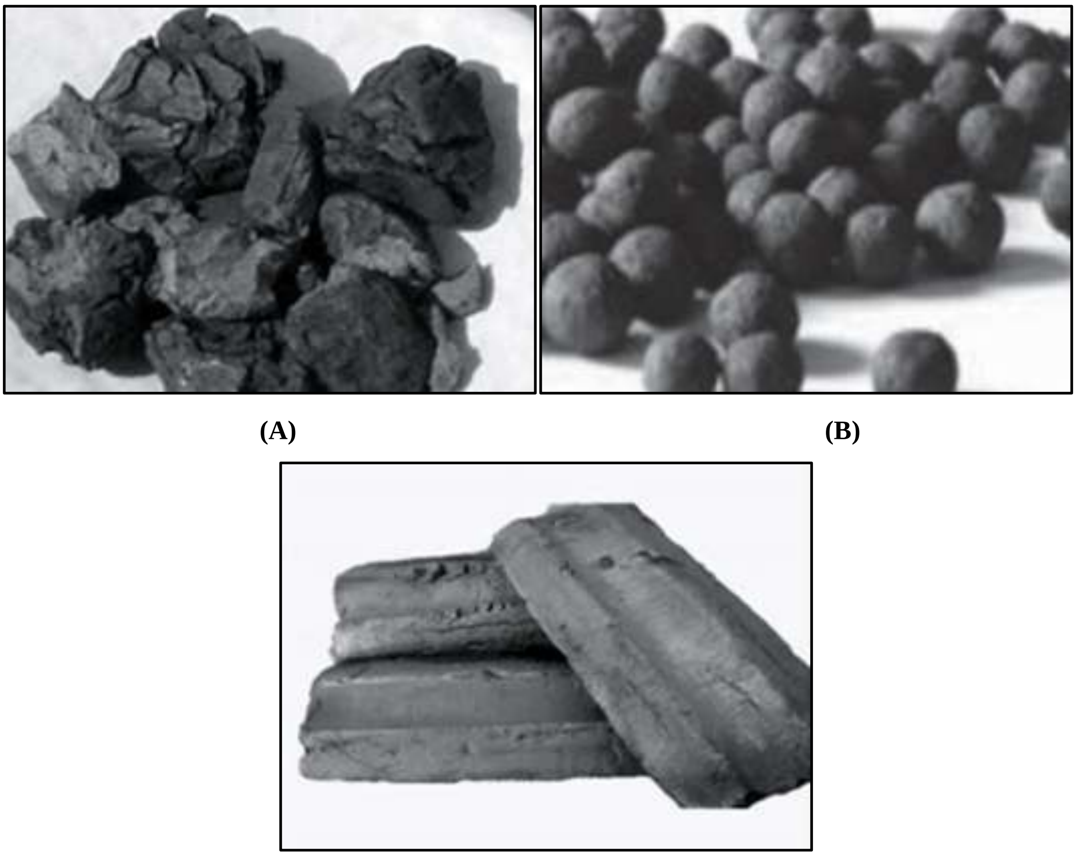


Figure-2.13: Micrograph of Direct Reduced Iron (sponge iron), magnification x300

From last 40 years onwards, direct reduction (DR) process has rapid development in the making of iron. The term direct reduction can be defined as a reduction of oxides of iron ore to metallic iron in the solid state at temperature below the melting point (T< 1150°C) in the presence of suitable reductants without undergoing the melting process. The oxygen present in iron oxides is removed during the reduction process to give porous spongy structure called as Direct Reduced Iron (DRI) or sponge iron, as shown in figure 2.13 [3, 6, 45-49].

2.4.1 Scenario of DRI

Electric steel making uses steel scrap as a primary feed material for steel production, and it occupies 28-30% of steel production in the world. Secondary steel zones search for some other steel scrap because of non-reasonable price in the inconsistent quality of the available material. DRI is a suitable solution for these problems and also used in making a good quality steel. The world recognizes the DRI production is cheaper, good-quality, high- indictment material. DRI extends thickness in content, size and also consists of low residual components. In the electric steelmaking, DRI plays an alternative role of scrap. DRI is a pure material which deduces from iron components. DRI production reduces impurities in the scrap and also upgrades the steel quality. DR requires lesser energy compared to BF process because of DR works at lower temperature. DRI makes high-class steel with the help of electric furnaces. The DRI produces in different forms, as per requirement, as shown in figure 2.14 [50-52, 54].



(A) **(B)**

(C)

Figure-2.14: Different forms of DRI (A) Lump, (B) Pellet, and (C) HBI

2.4.2 Types of DR processes: On the basis of reductant, the DR processes are classified into two groups and their classification shown in table 2.3:

- Gas based DR production (gaseous reductant)
- Coal based DR production (solid reductant)

Table-2.3: Type of direct reduction process.
(Rank based on production-popularity in the world.)[46]

Process	Type of reactor	Type of ore use	Type of reductant	Rank
MIDREX	Shaft	Lump/pellet	Gaseous	1
HyL	Retort	Lump/pellet	Gaseous	2
SL/RN,KRUPP,ACCAR, CODIR,TDR	Rotary kiln	Lump/pellet	Solid	3
HIB	Fluidized bed	Fines	Gaseous	4

2.4.2.1 Gas-based processes:

Natural gas acts as reductant agent where the natural gas should be reformed. In solid state, lump iron ores are diminished and oxygen is removed from the iron oxide with a reductant agent like gas.The reduction gases like CO and H_2 are producedby using Ni or Al_2O_3 (catalysts) at 950 ^{0}C (1223K). The reactor contains the reduction gases inflated upto 1000^{0}C (1273K) temperature and pressure (up to 5bars).If CH4 is present in the reducing gas, it results in carburization of the reduced product.The gas based reduction processes is restricted in outside areas because of low prices where the natural gas is available. According to flow of reducing gas nad rector design, the gas based direct reduction process further divided in categories shown in table 2.14. Midrex (1969) and HyL (II–1957, III–1980) uses natural gas as reductant agent for commercial processes. From the literature data, it was found out that Midrex process covers 78.8% of DRI production in the world.[3, 46,50,52]. The process flow chart of Mydrex process is shown in figure 2.15.

Table-2.4: Gas-based processes

Retort processes	Shaft furnace processes	Fluidized bed processes
HyL I, Hoganas	Midrex, HyL III, Plasmared, Armco, Purofer, NSC,HyL IV	FIOR, Finmet, Circored

Advantages of gas-based processes:

i) Gas-based plants have a less capital cost per tonne compared to coal-based plants(1.8–2 times higher).

ii) Gas-based DRI plants have higher productivity against coal-based plants.

iii) Gas based plants contain higher carbon and metallization in the DRI production.

iv) Gas based processes are extremely energy efficient.

v) Gas based processes are highly standardized, and plants do not create any maintenance issues.

vi) In environmental point of view, gas-based plants are pollution free source

Midrex process

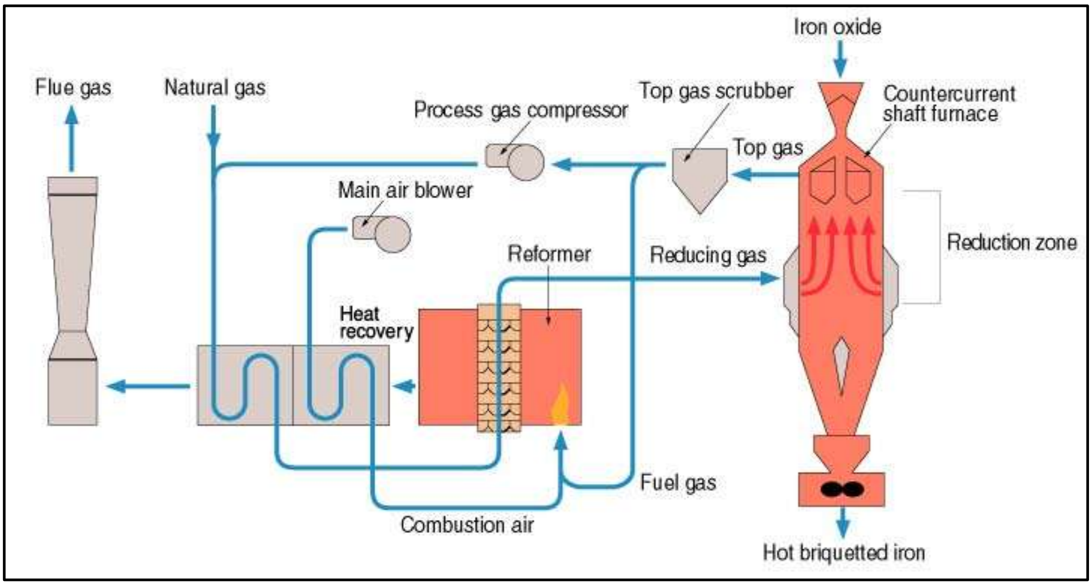


Figure-2.15: Process flow sheet of Midrex process of direct reduction

The principle of counter flow followed for the reducing gases which get develops in the shaft furnace in order to reduce iron ore present in it.The important components of this furnace are counter current shaft furnace, combustion chamber, air reformer, cooling system.

The principle of this process is the reduction of iron ore in a shaft furnace by reducing gases in accordance with the counter flow principle. The main components of the process are the shaftfurnace, the gas reformer, and the cooling system. The flow of reducing gas and solid materials controlled time to time to operate at correct conditions. The main bed temperature for the reduction is maintained by is maintained to obtain appropriate reduction, metallization and carbon content in the product. The vessel of the furnace made up of steel and inside there is reformatory lining for high temperature working operations. The charge fed from top of the shft furnace where it settle down automatically under force of gravityThe charge flows step wise from preheated zone to the bottom cooled zone where the prepared DRI taken out from sealing windows present in bottom of the furnace. The process gases are checked by insert gases which are passed through seal legs. At last the fines present in DRI are screened. The fines may be finally briquetted to make them a usable DRI product.

2.4.2.2 Coal-based processes:

In coal based direct reduction processes, the non-coking coal acts as reductant agent. The carbon monoxide (CO) gas produced during the reduction, indirectly reduces the iron ore. Limestone or dolomite often added in reactors with the charging material, which act as catalyst - to increase the gasification reaction. After the reduction and cooling, magnetic separation method used to separate metal from reduced charge material containing ash, lime materials, etc. Hot briquetting & feeding process are not feasible for coal-based production. DRI is not applicable at high temperatures in separation process by the magnetic separators. The various type of coal based DR process according to the reactor design is mentioned in table 2.5. The advantages and disadvantages of coal based DR processes are given below:

Table-2.5: Coal-based processes

Rotary kiln–based processes	Shaft furnace–based processes	Rotary hearth furnace (RHF)-based processes
SL/RN, DRC, CODIR, SIIL ACCAR, TDR,OSIL and Jindal	Kinglor, Metor, NML, Vertical Retort	INMETCO, FASTMET, Comet

Advantages of coal-based processes:

i) Non-coking coal is used

ii) Easily installable, small-scale units can be planted.

iii) Less complicated in operation technique

Disadvantages of coal-based processes:

i) Energy consumption is high (16.0–21.0 GJ/t).

ii) Lower productivity (0.5–0.9 t/m^3/day).

iii) Hot feeding & briquetting not applicable because of ash, char present in DRI.

Those countries which are rich in natural gases or hydrogen - utilizes these gases for reduction of iron ore. While countries possess coal reserves, utilizes coal for reduction of iron ores. Mostly bituminous coal or grade lower than bituminous coal found in India. So mostly coal based reduction are popular in India. Among the coal based reduction processes SL/RN process is most extensively used in the world and in India also. The process flowchart of SL/RN process is shown in figure 2.16 [3, 46, 53-62].

SL/RN Process

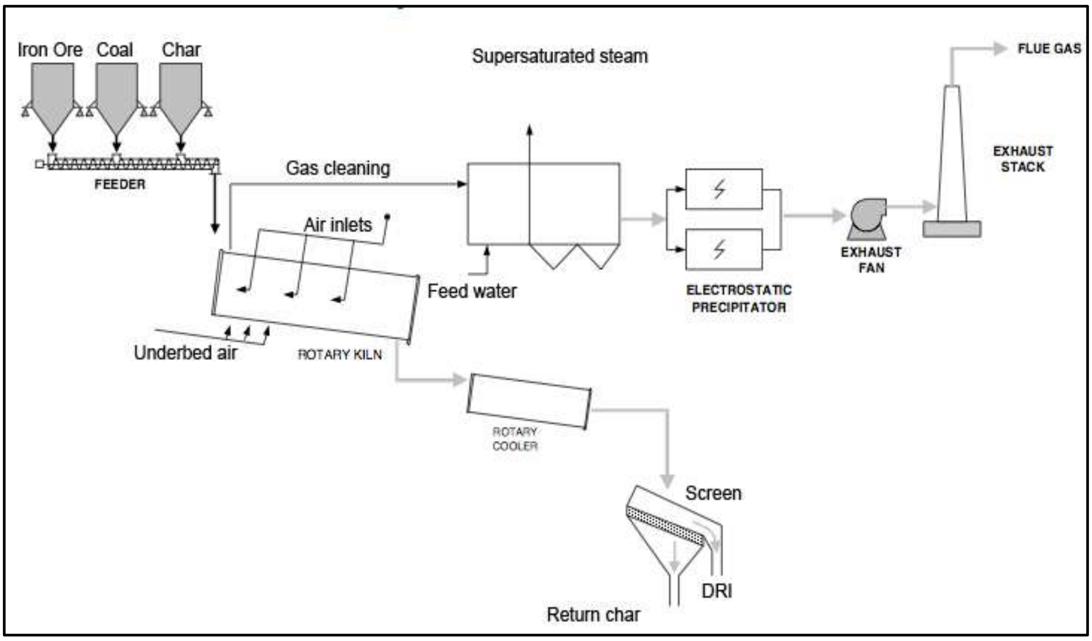


Figure-2.16: Process flow sheet of SL/RN process of direct reduction

The SL/RN name refers to Stelco-Lurgi and Republic Steel-National Lead which was develpoed by their joint efforts. It is the most widely running process in coal based type of direct reduction processes. The charge in form of iron ore crused to suitable size, coal and flux forming agents like limestone and dolomie also added. In the rotary kin the iron ore passed down and hold at the diffferent heating seaction by the movement of rotary kiln. The heat maintained at different zones (preheated of temperature around 900 to 1100°C and reduction zone of about 1050 to 1100°C. The redcued product, that is DRI colleted from the last section of the rotary kiln where it is transferrred to rotary drum colled by water sprayers at 100°C. After some hours of holding the DRI descharged and transferred to subsequent units where the cooled product is screened and magnetically separated to remove char and ash.[3, 53-62].

2.4.3 Coal based mill scale reduction.

As the mill scale constitutes same iron oxides as present in iron ores, so the reduction mechanism and the kinetics behind the process is similar as in iron ore reduction.The solid state reduction process generally operate at temperature below

1100°C, in order to prevent the formation of any semi solid phases. Lime stone or dolomite often added as catalyst, to increase the gasification reaction.

2.4.3.1 Reduction mechanism of mill scale or iron ore reduction

As the reduction of mill scale in this research work was carried out in crucible or fixed bed, so the reduction mechanism was stated in terms of fixed bed conditions (i.e. in crucible reduction). During the reduction process, the iron oxides present in mill scale or iron ore get reduced to metallic iron in solid state. The reactions involved in this reduction process are:

i) Reduction by carbon (direct reduction):

$$3Fe_2O_3 + C \rightarrow 2Fe_3O_4 + CO \tag{2.5}$$

$$Fe_3O_4 + C \rightarrow 3FeO + CO \tag{2.6}$$

$$FeO + C \rightarrow Fe + CO \tag{2.7}$$

In the process of reduction, very less and initial amount of reduction take place by direct contact of carbon particles with iron ore particles. Most of the reduction happens due to indirect reduction, by carbon monoxide (CO) gas, which get produces in intermediate of the reduction process [64-66].

ii) Reduction by CO (indirect reduction):

$$3Fe_2O_3 + CO \rightarrow 2Fe_3O_4 + CO_2 \tag{2.8}$$

$$Fe_3O_4 + CO \rightarrow 3FeO + CO \tag{2.9}$$

$$FeO + CO \rightarrow Fe + CO \tag{2.10}$$

The necessary carbon monoxide (CO) for reduction process produces by Boudouard reaction (eq. 2.11 and 2.12)

iii) Boudouard reaction:

$$C + O_2 \rightarrow CO_2 \tag{2.11}$$

$$CO_2 + C \rightarrow 2CO \tag{2.12}$$

iv) Decomposition of limestone ($CaCO_3$):

$$CaCO_3 \rightarrow CaO + CO_2 \tag{2.13}$$

$$CO_2 + C \rightarrow 2CO \tag{2.14}$$

The limestone added as catalyst consists calcium carbonate which decomposes to CaO and CO_2. Thereby, the gasification reaction gets accelerated.

Explanation of reduction mechanism: With increase in temperature during the reduction the carbon monoxide and carbon dioxide (CO_2) starts forming inside the crucible by the Boudouard reaction (equation 2.11 and 2.12). The reduction mechanism could be understandable from the figure 2.17 of partially reduced single mill scale or iron ore particle during the direct reduction process.

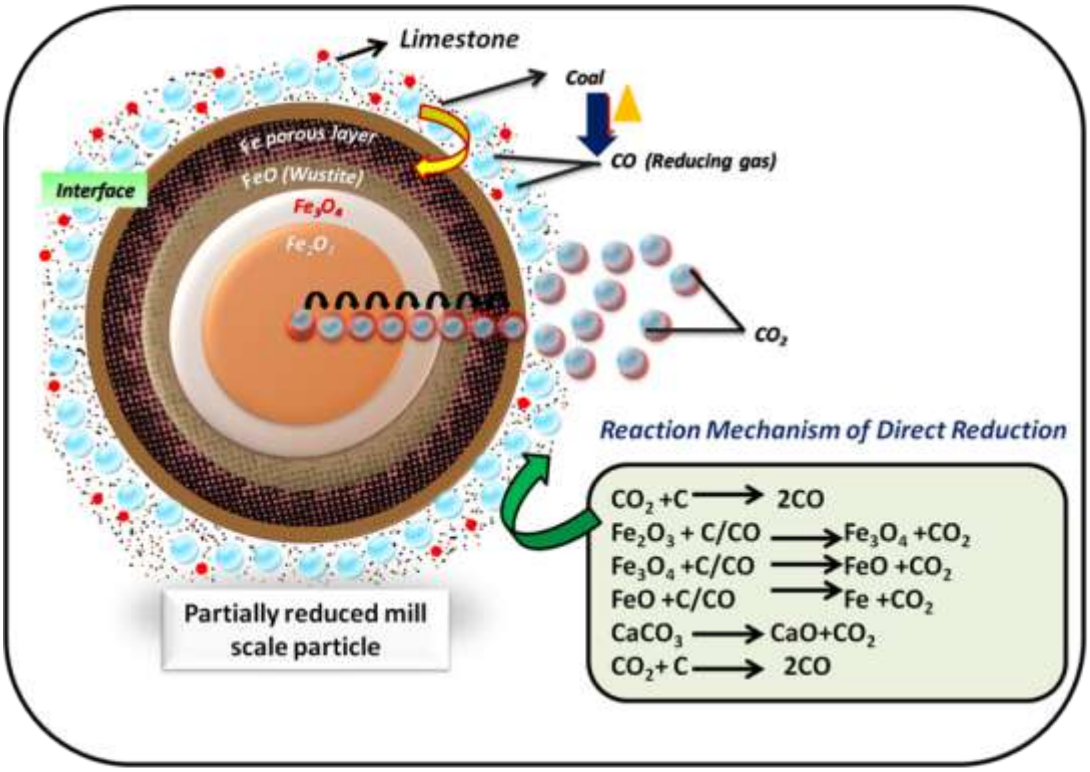


Figure-2.17: Model of partially reduced mill scale or iron ore particle.

The carbon (C) and carbon monoxide (CO) both works as reducing agent. However the maximum reduction happens due to CO gas due to its higher flow ability and diffusive nature than solid carbon. The carbon and CO gas gets adsorb on the interface of mill scale particle and later get diffuse into different layers. During the operation the iron oxides gets reduced to simpler forms and last to the metallic iron by various chemical reactions, as stated before. The iron oxides present in it are reduced in three stages at temperatures above 570°C.

$$Fe_2O_3 \rightarrow Fe_3O_4 \rightarrow FeO \rightarrow Fe \qquad (2.15)$$

The oxygen combined with different iron oxides in particle, starts getting removed from surface to the core of mill scale particle in form of carbon dioxide. Due to presence of solid carbon and bulk reducing gas outside the surface particle the attack of reducing agents on iron oxides to convert them into metallic iron is more rigorous from surface to core. So automatically the layers of Fe_2O_3, Fe_3O_4, FeO and Fe gets develops from core to the surface of particle. The removal of oxygen from iron oxides leads to increase in formation of porous structure and subsequently the metallic content increases w.r.t to total iron in the reduced mill scale. The kinetcs which undertook during the reduction of any coal based iron ore reduction process is detialed next.

2.4.3.2 Kinetics of reduction process

Kinetics of iron ore or mill scale reduction concerned with the rate at which the oxides in iron ore got converted into metallic iron or the rate of oxygen removal from iron oxides. The rate of reaction during the reduction affects the production of rate of the DRI (or product of DR) thus obtained by direct reduction. The production rate determines the feasibility and competitiveness of the product in market. So the rate of reaction is very important in direct reduction process. During the reduction of iron ore by suitable reductant, the reaction proceeds with different rates during the process. In the process the iron oxides got converted into metallic iron or the oxygen is removed from oxides, giving rise to increase in metallic iron content into product. This rate of conversion at some steps become higher and at some steps in reduction becomes slower. So the overall completing of reduction depends upon the step having the slowest rate during the process. It is like a single relay race, in which the completeness of the race does not depends upon the person who runs fast, but depends upon the person who run slow, because the speed or rate of the slowest person will determine at what minimum time the last man reaches the final line. Similarly in reduction process, the slowest step will decides the overall rate of reduction. So first there is need to understand the different rate controlling factors which controls the overall rate of reduction. [63,64]

2.4.3.3 Rate controlling factors

When the various sequential steps of reduction and reactions going on during the process, certain factors which control the overall rate of reduction, also referred as rate controlling factors. These factors are shown below:

i) **Boundary Layer Control**: In this factor the overall rate of reduction is due to gas diffusion and the boundary layer heat which developed around each particle. The diffusion rate of gas between the boundary layer is proportional to the direction and rate of temperature change over the layer (also called as gas concentration gradient). In most cases of direct reduction process the flow of preheated gases toward the beds of particles makes the solid and gas contact.

ii) **Phase Boundary Reaction Control:** Rate controlled by the chemical reaction at the wustite iron interface. The rate of reduction per unit area is found to be constant for the rest iron oxide. The concentration at the surface of reacting is same at the surface of particle. It is due to diffusion of reducing gas and product gas at the reduced outer surface is fast. In this situation, overall rate control due to the reaction at wustite iron interface. 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**.**

iii) **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 ratecontrolling mechanism for high temperature reduction of large (greater than 7 mm) particle beyond 50% reduction, when iron layer thickness exceeds about 1mm.

iv) **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.[64-68]

2.4.3.4 Equations for rate controlling steps: Different mathematical models equations are proposed to represent different rate controlling steps [64-66], which are given in table 2.6:

Table-2.6: Selected reaction mechanism equation for different rate controlling steps:

Equation	Rate control
$\mathrm{kt} = -\ln(1-\alpha)$	Chemically controlled
$\mathrm{kt} = 1-(1-\alpha)^{1/3}$	Chemically controlled
$\mathrm{kt} = [1-(1-\alpha)^{\frac{1}{3}}]^2$	Diffusion controlled
$\mathrm{kt} = (1-\frac{2}{3}\alpha)-(1-\alpha)^{2/3}$	Diffusion controlled
$\mathrm{kt} = \mathrm{k}'(1-\frac{2}{3}\alpha)-(1-\alpha)^{\frac{2}{3}}+\mathrm{D}/\mathrm{r}_0[1-(1-\alpha)^{\frac{1}{3}}]$	Mixed controlled

2.4.3.5 Analysis of kinetic data

Kinetic studies are proposed to find out the discrete parameters involved in the reaction process. The analysis of these discrete parameters means identification rate at which iron oxides getting converted into metallic iron or the activation energy required to complete the reduction reactions. It is determined by identification of rate control mechanism. Based on kinetic law the below section consists of some mathematical procedures which are required for identification of reaction mechanism.

***Arrhenius equation*:** Commonly reaction rate depends on the factor called temperature when the temperature change there is a rapid change in the reaction rate.

Each event has weighted mean which is a constant reaction rate value k that cause the transformation in the process. If there is a variation in the transformation of the individual events, then the k value changes with the change in temperature. The range of temperature should be not too broad. Most reaction rates accept the Arrhenius equation based on the temperature dependence (eq.2.15) [69-72]. Both homogeneous and heterogeneous reactions are suitable for Arrhenius equation mentioned below:

$$k = Aexp^{-\frac{E_a}{RT}} \text{------} \quad (2.15)$$

Where

k= Constant reaction rate
T= Temperature (in Kelvin)
A= Pre-exponential factor or frequency factor
E_a=Activation energy depends on the reaction mechanism
R=Gas constant

Determination of kinetic parameters

i) **Integral approach:** The reaction progress is evaluated regarding the degree of transformation and expressed as α in the studies of isothermal kinetics. The value of α alters from 0 (zero) to unity. The ratio of detached oxygen from feed to the combination of iron and oxygen in the feed is known as the degree of reduction which also expressed with α. Based on the given temperatures, the plot drawn on α versus time (t). The plotted data corresponded into a useful form of the incorporated kinetic equation. Some reaction mechanisms have an integral expression on kinetic equations were widely known [73]. G(α), α is propo^{r}tional to t. The constant reaction rate expressed with k which acquires from the slope G(α) against time(t). The constant reaction rates estimated from various temperatures in the isothermal analysis. The equation 2.15 is temperature dependence of the rate constant

$$lnk = -\frac{E_a}{RT} + lnA \text{------} \quad (2.16)$$

From the plot, a slop of straight line (E/R) obtained from ln k versus 1/T. The activation energy value contributes to the slope of this linear plot. The frequency factor (A) attains from the intercept.

ii) **Differential approach:** The earlier recognition of the relevant function G(α) constructed by an integral approach which is the determined through the trial and error approaches. When the necessary kinetic data is linearized, then the rate of reaction can estimate. The α and temperature (T) function are considered to carry the reaction rate at any given time. So the rate of expression can be demonstrated through the common differential form is

$$\frac{d\alpha}{dt} = \text{k (T)} \,.\, \text{f(} \alpha \text{)} \tag{2.17}$$

Where,

k (T)=temperature dependent rate constant

f (α)=appropriate function of α.

Substituting k (T) from Eq. 2.15 in 2.17 we get:

$$\frac{d\alpha}{dt} = A.exp^{-\frac{E_a}{RT}}.\text{f}(\alpha) \tag{2.18}$$

Equation 2.18 can be written as

$$\int \frac{d\alpha}{dt} = k \int dt = A \int exp^{-\frac{E_a}{RT}} dt \text{ ------} \tag{2.19}$$

The value of t at R.H.S. integral, zero limits at L.H.S. integral and α value is constant at any level of α, i.e., at any given temperature, the αvalues are obtained in the required amount of time. Thus it can be written as,

$$t_0 = \frac{constant}{exp^{-\frac{E_a}{RT}}} \tag{2.20}$$

or

$$ln\ t_0 = constant + \frac{E_a}{RT} \tag{2.21}$$

The plot between ln t_0 and 1/T is linear. The activation energy can calculate at different reaction stages with the help of plots of different levels of α. However, f(α) describes the kinetics reaction itself.

iii) **Reduced time plots:** The reaction mechanism identification is an essential step in many reaction systems is to analyze the kinetic data. The initial identification is possible using in many cases known as reduced time plots [74, 75]. There is a broad analysis of reaction in the solid state based on such plots, but there is a limit in chemical metallurgy application [76]. The reaction mec^{h}anism checks through this method and hence G(α) can treat as an appropriate function. In reduced time plots, dimensionless time can handle as the kinetic relationships [75].

We have:

$$G(\alpha) = kT \tag{2.22}$$

If α = 0.5 then g(0.5) = $kt_{0.5}$where 0.5 fractions are obtained in the required amount of time $t_{0.5}$.

Dividing Eq. 2.22 by this and obtained Eq. 2.22 in modified form will be:

$$G(\alpha) = G(\alpha)_{\alpha=0.5} \,.\, \mathrm{t}/t_{0.5} \text{------} \tag{2.23}$$

$$G(\alpha) = B(\mathrm{t}/t_{0.5} \text{-----}\,) \tag{2.24}$$

Where B = constant dependent on *G(α).*

Eq. 2.24 is dimensionless and depends on the constant kinetic rate. Without regarding the nature of the system, any given temperature or various others factors, the reaction alters on kinetic data. So reduced time plot applies to each mechanism. Keattach and Dollimorell [75] use reduced time slots to define an approach for some of the reaction mechanism (shown in table 2.7), and they passed the values of $t/t_{0.5}$ for various α values (shown in table 2.8). Initially, the described procedure involved in the tabular values of function G(α) for different reaction mechanisms for various α values. The $t/t_{0.5}$ values calculated by using these G(α) values. Plotting between the α values and $t/t_{0.5}$ computed values used to draw plots of the different reaction mechanisms [77]. Experimental data laid over on these master plots and empirical data could fit in any one of the theoretical expression which identified by the reaction mechanism in the reduced time slots.

Table-2.7: Reaction mechanism equations for which the $t/t_{0.5}$values computed by Keattach and Dollimorell [76, 77]

S.No	Reaction mechanism equation, G (α)
1	$D1(\alpha) = (\alpha)^2$
2	$D2(\alpha) = (1-\alpha)\ln(1-\alpha) + \alpha$
3	$D3(\alpha) = [1-(1-\alpha)^{\frac{1}{3}}]^2$
4	$D4\ (\alpha) = (1-\frac{2}{3}\ \alpha) - (1-\alpha)^{2/3}$
5	$R2(\alpha) = 1-(1-\alpha)^{1/2}$
6	$R3(\alpha) = 1-(1-\alpha)^{1/3}$
7	$F1(\alpha) = -\ln(1-\alpha)$
8.	$A2(\alpha) = -\ln(1-\alpha)^{1/2}$
9.	$A3(\alpha) = -\ln(1-\alpha)^{1/3}$

Table-2.8: Variation of α and $t/t_{0.5}$ for given reaction mechanism equations.

α	D1(α)	D2(α)	D3(α)	D4(α)	F1(α)	R2(α)	R3(α)	A2(α)	A3(α)
0.1	0.040	0.033	0.028	0.032	0.152	0.174	0.165	0.390	0.533
0.2	0.160	0.14	0.121	0.135	0.322	0.362	0.349	0.567	0.685
0.3	0.360	0.328	0.295	0.324	0.515	0.556	0.544	0.717	0.801
0.4	0.640	0.609	0.576	0.595	0.737	0.768	0.762	0.858	0.903
0.5	1	1	1	1	1	1	1	1	1
0.6	1.44	1.521	1.628	1.541	1.322	1.253	1.277	1.15	1.097
0.7	1.96	2.207	2.568	2.297	1.737	1.543	1.607	1.318	1.198
0.8	2.56	3.115	4.051	3.378	2.322	1.887	2.014	1.524	1.322
0.9	3.24	4.363	6.747	5.028	3.322	2.334	2.602	1.822	1.492

2.4.4 Effect of process parameters on reduction.

In the field of direct reduction various investigators always tried to improve the quality of product obtained on reduction of iron ore (or mill scale or other iron oxides bearing raw materials). It was done by altering the various process parameters which affect the percentage or degree of reduction. The general parameters which affect the reduction are:

i) Temperature of reduction.

ii) Time of reduction.

iii) Particle size of raw materials or pellet size.
iv) Presence of catalyst.
v) Nature and reactivity of reductant and reducible material (iron ore)
vi) Ratio of reductant to reducible material orFe_2O_3/C ratio
vii) Mixing of reductant and reducible material

Certainly the various process parameters effect the reduction, however they are interconnected to each other also. It is not mandatory that the same particle size, ratio, addition of catalyst addition, heating will give the same result for some other materials. That is, every time when some investigates on direct reduction of same material (iron ore, or mill scale or any other iron oxide bearing material), some different percentage of reduction was found. The result of direct reduction was specific according to study of process parameters. However the effect was almost same in all reductions like with increase in time, temperature, ratio, quality of reductant the reduction increases up to a limit then becomes constant. With increase in catalyst addition also increases the reduction for certain interval of time and temperature. With decrease in particle size reduction increase, but not always. In fact the, some particle size range of particles show higher reduction for one reductant and lower for some other reductant. It also depend upon packing of raw materials and permeability present in given set of conditions for of the reductant to reduce iron ore or mill scale.

2.5 Previous investigations done on mill scale reduction.

Many investigators had been done studies on direct reduction of iron ore [78-91]. But few investigations were done on mill scale reduction [92-105]. Among that studies of mill scale reduction, very few found out the kinetics of reduction process [92-97]. Some investigators used solid reductants and some gaseous reductants. The overall previous literature work studied on mill scale reduction can be divided in two categories:

i) Kinetic study of mill scale reduction by solid or gaseous reductants (e.g. Solid = Coal, coke, graphite etc. and Gaseous = H_2 gas, CO gas etc.)[92-97]
ii) Non- kinetic studies on mill scale reduction [98-105].

i) **Previous investigations on kinetic study of mill scale reduction by solid or gaseous reductants:** The information in tabular form (table 2.9) given before the explanation of previous works on mill scale reduction kinetics:

Table-2.9: Previous investigations on kinetic study of mill scale reduction by solid or gaseous reductants.[92-97]

Forms: (P = Pellet, L= Lump, B=Briquettes), T = Temperature, P.S = Particle size, $C_{fix.}$ = Fixed carbon, R = Reducing agent, $E_{a.}$ = Activation energy, Fe_T =Total iron, Bed = Crucible or tray or other, Furnace = Reduction furnace

Author, Year	Form, Bed, Furnace	Reducing agent (R)	Kinetic, Non kinetics values, Activation Energy (Ea. in KJ/Mole)	Particle size (P.S)	T (°C)
A.K.M.M Rahman, 2009	L, Mill Scale in centre, coal around in crucible, in muffle furnace	Coal (C_{fix} =52.60) , Limestone	$G(\alpha) = (1 - \frac{2}{3}\alpha) - (1 - \alpha)^{2/3}$, $E_{a.}$ = 147 KJ/Mole	P.S = 2.30 mm	800,850 900,950, 1000,1050
Çamci, L, 2001	P (Fe_t =57.2%) inrotary tube furnace	Coke (C_{fix} =81.22), Graphite C_{fix} =98.58)	$G(\alpha) = (1 - \frac{2}{3}\alpha) - (1 - \alpha)^{2/3}$, $E_{a.}$ = 48.5 KJ/Mole	Pellets ofP.S = 325 Mesh	900, 950, 1000,1050, 1100
Onuralp Yucel, 2013	P(Fe_t = 70.95%) in rotary kiln	Coke(Ck.) and Anthracite (An.) (Stoichiometric 150 and200%)	$G(\alpha) = 1 - (1 - \alpha)^{1/3}$ Ea. = 170 (For 200% An.), 316 (150% An.), 55.22 (200% Ck.), 127 (150% Ck.)	Pellets of P.S = 45-90µm	1050, 1100, 1050
M.C. Bagatini, 2011	P (Fe_T = 69.7%), in crucible in Electro thermo balance furnace	CO gas	$G(\alpha) = 1 - (1 - \alpha)^{1/3}$ Ea =79-81	Pellets of P.S = 0.3 -0.6 mm	900, 1000, 1100, 1200
N.M. Gaballah,2014	B (Fe_t = 69.33%), in crucible in Electro thermo balance furnace	H_2 gas with N_2 gas initially	$G(\alpha) = (1 - \frac{2}{3}\alpha) - (1 - \alpha)^{2/3}$ Ea =72.25 and $G(\alpha) = 1 - (1 - \alpha)^{1/3}$ Ea =61.5	Compressed briquettes of P.S = 75 µm.	650, 750, 850, 900, 950
C. Joshi, 2015	L(Fe_t58.6%),, in tray in horizontal tube furnace	H_2 gas with N_2 in ratio of 1:9	$G(\alpha) = (1 - \frac{2}{3}\alpha) - (1 - \alpha)^{2/3}$ Ea = 47.3	Pellets of P.S = 6 µm	600, 700, 800, 900, 1000, 1100

Mill scale reduction kinetics using solid reductants: Among those who had done investigations on isothermal reduction of mill scale by coal or carbon bearing materials, only three research work were on the kinetics of mill scale reduction. In first research work **A.K.M.M. Rahman *et al*.** [92] had done the isothermal kinetics study of mill scale reduction using coal in crucible (fixed bed) with powdered mill scale column surrounded by coal in crucible. He studied the effect of particle size, bed depth, ratio of mill scale/coal and reaction temperature. In it, the kinetic data fits on the Ginstling-Brounshtein reaction model. The activation energy for the overall process was found to be 147 KJ/Mol. This was the only research work done on kinetic study of mill scale reduction by coal, in powdered form on fixed bed. The second investigator **Ladin Camchi *et al.***[93] who had done the kinetic study on mill scale reduction, reduced the mill scale in rotary kiln furnace (moving bed) under argon gas atmosphere in form of cold bonded pellets prepared by mixing graphite and coke. The pellets having coke as reducing agent shown better reduction. The plot of experimental data found to be according with the Ginstling-Brounshtein equation and activation energy of process found to be 48.5 KJ/Mole. The third investigator **Onuralp Yucel *et al.*** [94] prepared pellets of mill scale with 5% molasses and reduced it by stoichiometric calculated 150% and 200% metallurgical coke and anthracite in rotary kiln for different time and temperatures. The experimental data fits on the chemically controlled equation. The activation energies were 170.78 KJ/Mole (in 200% anthracite), 316.06KJ/Mole (in 150% anthracite), 55.22 KJ/ Mole (200% metallurgical coke) and 127.03 KJ/Mole (150% metallurgical coke). [92-94]

Mill scale reduction kinetics using gaseous reductants* [95-97]:** The use of gaseous reductant give higher value of reduction as compared to coal based reduction, but is economical for those countries where gas reductants are conveniently available. **Maurício Covcevich Bagatini** ***et al*.**[95] done the isothermal kinetics study of mill scale reduction in from self-reducing banquettes by carbon monoxide in alumina crucible and his experimental data results fits with the chemically controlled unreacted shrinkage core model equation and the activation energy found to be 80 KJ/Mol. On the other hand, **N. M. Gaballah *et al*.** [96] used different flow rate of hydrogen gas for reduction of mill scale − molasses (2%) made briquettes in nickel chrome crucible suspended in termobalance apparatus. The experimental data fits on the diffusion controlled equation and activation energy found in between 61.5 to 72 KJ/Mole. In the similar attempt **C.Joshi *et al. [97] had done the kinetic study of mill scale reduction in form of lump placed in tray in horizontal tube furnace by hydrogen gas to obtain sponge iron for powder metallurgy applications. The experimental data fits with the Ginstling-Brounshtein reaction model and Ea was found to be 47.3 KJ/Mole.

ii) Previous research work on non-kinetic studies of mill scale reduction.

The non- kinetic studies of mill scale reduction can be conveniently understand in sentence form as written below:

- **Raaft Farahat *et al.*** [98] reduced the composite pellet made up of mill scale and anthracite coal at different time temperature and reducing agent. He obtained the 82% metallic iron in the product which was comparable to the commercially available DRI which possess 85% metallic iron. **N.A. El-Hussiny *et al.*** [99] investigated the effect of replacing some amount of iron ore concentrate by mill scale in sintering process by keeping different concentration of coke breeze and he concluded that the replacement of iron ore concentrate by 5% mill scale increases the amount of readymade sinter, sinter strength and productivity of the sinter machine and the blast furnace yard. **M.I. Martini *et al.*** [100] obtained the sponge iron by reducing the mill scale, by reducing it with coke in initial stage and by treating it further in hydrogen gas atmosphere at final stage. Similar to that work **H. Ibrahim Unal *et al.*** [101] reduced the iron oxides present in mill scale by using coal and combo of coal and hydrogen in two different steps and concluded that reduction using both carbon and hydrogen in different steps show higher reduction than using single coal reductant. In a different way of investigation **Mamdouh Eisaa *et al.*** [102] used graphite and coke for carbothermic reduction of mill scale in submerged arc furnace with addition of different flux materials. He concluded high purity iron can recovered using suitable flux material and controlling reducing agent. However, in other work **O.**

Benchiheub *et al.*[103] obtained the iron powder having total iron of 98.4% and metallic iron about 97% by reducing the mill scale powder with carbon monoxide gas in vertical shaft furnace. **Dayanand Paswan *et al.*** [104] used non-coking coal for the reduction of mill scale pellets in clay crucible. The diameter of the pellets was found to decrease on reduction and shrinkage was found to increase with time and temperature. In the similar conditions **Rounak Sneh Anand *et al.***[105] prepared the green pellets using (90%) mill scale and (10%) slime fines and reduced it with coal fines and developed high grade DRI which was cost-effective and energy efficient. Other than the reduction studies, some other behavior also noticed by investigators like **T. Umadevi *et al***.[106] who studied the behavior of pellets prepared by addition 10 to 40% mill scale with iron ore in order to use pellets in Corex and BF iron making units. She concluded that the sample pellets having 10% mill scale, possess optimum chemical, metallurgical and physical properties. Similar attempt made by **Bruno Deves Flores *et al.*** [107] who prepared the self-reducing blends using 85% mill scale and 15% petroleum coke by weight and studied the structural behavior occurs on the samples at different time and temperatures till the melting occurs. The work concluded that the melting behavior of blends linked with the carburization process of iron.

2.6 Research gap

Assessment of knowledge or research gap :It has been found by studying the previous research works that the effect of various process parameters like time, temperature, particle size, percentage of reductant were studied in many studies, but effect of different possible arrangements of raw materials (mill scale, carbonaceous material) in crucible was not studied in any single study. Kinetic study on mill scale reduction worked out on very limited researches. Among them, some were gas based reduction and some were solid based reduction. But the kinetic studies scares in use of low grade coal for reduction of mill scale.

Proposed solution to research gap: On account of these scarcities in previous research work, the proposed solution to research gap was to study the reduction of mill scale by utilizing low grade coal for different parameters (including reduction in different arrangements in crucible). Thereby finding out the optimized results and calculating the kinetics behind the reduction process. So the objectives of the given research work were:

1. Study of mill scale reduction by low grade coal in crucible.
2. Optimization of various process parameters, including the different possible arrangements of raw materials in crucible.
3. Study the kinetics of the mill scale reduction on optimized parameters.

To achieve the possible objectives, the overall study was carried out in two steps - (A) Preliminary study and (B) Final study. In preliminary study, effect of certain process parameters were checked -to find the optimum conditions for mill scale reduction when reduced by low grade coal. The variables which shown the best or optimum result in preliminary study, were taken as constant parameter for the final study. The final study work was on kinetics of mill scale reduction by low grade coal for various possible arrangements in crucible.

A. **Preliminary Study**: The parameter studies which were carried out in part of preliminary study work includes:

- (i) Effect of particle size of mill scale and coal (Particle size = 30-90, 90-150, 150-210, 210-270µm)
- (ii) Effect of ratio of ratio of mill scale and coal (Ratio = 1:0.9, 1:1, 1:1.1, 1:1.2, 1:1.3, 1:1.4, 1:1.5)
- (iii) Effect of addition of limestone (Percentage of limestone w.r.t weight of mill scale = 0, 5, 10, 15, 20 %).

B. **Final study work:** In the final study effect of possible arrangements of raw materials in crucible was studied. Isothermal kinetics of mill scale reduction were carried out for the same. Characterization of samples were done. For calculating the kinetic parameters, the final study was carried out at different time and temperatures. The different arrangement, time and temperature which were taken in the final study shown below:

- (i) Arrangements = Mixed, central, alternate concentric and layered.
- (ii) Temperatures = 850, 900 and 950°C
- (iii) Timings = 15, 30, 60, 90, 120 and 150 minutes**.**

CHAPTER - 3

MATERIALS AND METHODS

This chapter deals with materials and methods used in this research work. The chapter discuss about the raw materials, some configurations used in the research work. Procedure for analysis of raw materials and results of analysis. The formulae used and stoichiometric calculations done in the research work. Information of characterization techniques used in the research work. Detailed experimental procedure employed in reduction of mill scale by low grade coal, with the flow chart of the research work was also given.

3.1 Raw Materials.

a) **Mill Scale:** Iron bearing material, of which reduction was done

b) **Low grade coal:** Reductant, which possess fixed carbon for reduction of mill scale

c) **Limestone:** Works as catalyst and also helps in scavenging sulphur

The source of obtainment and the price index of raw materials shown in table 3.1:

Table-3.1: The source and cost of raw materials used in the research work

Raw material	Price (₹ /Kg)	Source of obtainment
a) Mill scale	2 to 5	Hot rolling industry, Jaipur, India
b) Low grade coal	0.5 to 3	Matasukh coalmines, Nagaur , Rajasthan, India
c) Limestone	5 to 10	Local market, Jaipur

3.2 Configurations used in the research work

The configurations used for reduction of mill scale by low grade coal in the given research work is shown in table 3.2:

Table-3.2: Configurations used in research work

i) Type of Crucible:	Alumina
ii) Size of crucible:	a) Internal diameter = 35 mm b) Outer diameter = 39 mm c) Internal height = 55 mm d) Outer height = 56 mm
iii) Lid (cover) of crucible:	4 mm thick (internal diameter) lids, made up of soft refractory brick and 1 mm thick glass wool.
iv) Weight of mill scale taken in crucible for each study :	15 gram

3.3 Analysis of raw materials

The result of total research work depend upon the analysis of the raw materials. Certain tests or examinations have been carried out to understand the detailed or basic knowledge of raw materials used. These tests were explained systematically- step by step, because they were the building block of the research work. These tests include:

1. Proximate analysis of coal
2. Chemical analysis of limestone
3. Chemical analysis of mill scale (before and after the reduction)
4. Calculation of oxygen present in iron oxides of mill scale

3.3.1 Proximate analysis of coal

There are two methods for analysis of coal, which are- Analytical and Proximate analysis. In the two methods, the proximate analysis method is most widely used method in finding the contents of coal.

Percentage of moisture:

i) A known weight (wt.) of finely powdered coal sample was kept in silica crucible and heated in a muffle furnace at (105-110) °C for 1hr.

ii) Crucible was taken out and cooled in a desiccator and weighed.

iii) The process of heating, cooling and weighing was repeated a number of times until a constant weight was obtained.

Percentage of volatile matter:

i) It is the loss in wt. of moisture free powdered coal when heated in a crucible fitted with a cover in a muffle furnace at 750°C for 7min.

$$\frac{\boldsymbol{loss\ in\ wt\ of\ moisture\ free\ coal\ \times 100}}{\boldsymbol{original\ wt\ of\ coal\ sample}}$$

$$\boldsymbol{= percentage\ of\ volatile\ matter}$$

Percentage of ash in coal:

i) It is the wt. of residue obtained after burning a weighed quantity of coal in an open crucible i.e in presence of air at 750°C in a muffle furnace.

$$\frac{\boldsymbol{wt\ of\ residue\ \times 100}}{\boldsymbol{wt\ of\ coal\ sample}} \boldsymbol{= percentage\ of\ ash}$$

Fixed carbon (C %) in coal:

i) Fixed carbon % was calculated by reducing above findings in coal by 100%

$$\boldsymbol{Fixed\ carbon\ =\ 100 - (\%moisture + \%volatile\ matter + \%ash)}.$$

Result of proximate analysis of coal:

The low grade coal used in the research work contain **25.6%** fixed carbon. The value of fixed carbon percentage of low grade coal was utilized in stoichiometric calculation of coal, required for reduction of mill scale. The result of proximate analysis is shown in table 3.3:

Table-3.3: Result of proximate analysis of low grade coal used in the research:

Proximate analysis of coal (in weight %)			
Fixed carbon	**Ash**	**Volatile matter**	**Other components**
25.64	10.02	25.28	39.06

3.3.2 Chemical analysis procedure for limestone: The analysis of limestone was carried out in the chemical analysis lab of Jindal Saw Industry, Bhilwara (Rajasthan). The following standard procedure for analysis of lime stone was carried out.

i) Accurately weighted 2.5 g of sample was taken in a beaker. 40-50 ml dilute HCl was added and the beaker was immediately covered by glass cover. On disappearance of effervescence, the lower surface of the cover glass was washed into the beaker and the contents of the beaker were allowed for drying and baking at 110 to 115°C. On baking for about 20 to 25 minutes, the beaker containing sample was cooled to room temperature. About 25 to 30 ml dilute hydrochloric acid (40 percent) was added into it. The material boiled in presence of acid and then filtered out. The residue left at filter paper was transferred to the beaker and the adhering material remaining at the sides of beaker was washed by the hot water. The filtrate was collected, in the same beaker as (A).

ii) The filter paper containing residue and char was heated in platinum crucible at low temperature. Finally it was ignited at 900 to 950°C and cooled.

iii) The residue in the platinum crucible was fused with about 3 g of fusion mixture (mix carbonates of sodium and potassium in equal proportion.). The melt was cooled and extracted in about 50 ml of dilute hydrochloric acid (40 percent). The filtrate from (a) was mixed and the process of drying and baking was repeated. The baked mass was extracted with about 30 to 40 ml of dilute hydrochloric acid and filtered out. All the silica in the beaker was transferred to the filter thoroughly by means of hot water. Silica on the filter free from chlorides was washed by means of hot water. The filtrate and its washing were collected in the same beaker, named as (B).

iv) The filter with its residue was transferred into a previously weighed platinum crucible and the filter paper was heated at a low heat without burning the paper. Later it was ignited at 900” to 950°C to a constant mass. The residue was moistened by with few milliliters of dilute sulphuric acid (1: 1) and also 10 ml of hydrofluoric acid was added. The matter was evaporated to dryness, ignited and cooled.

v) The residue was fused thoroughly left over in the platinum crucible (d). Fuse thoroughly the residue (d) left over in the platinum crucible. After vitalization of silica with 1 to 2 g of fusion mixture and the extract was added in dilute hydrochloric acid to the filtrate reserved under (c). The combined filtrates were mixed with that reserved under (a). The final filtrate was transferred to 250 ml volumetric flask and made up to the main solution volume. Suitable aliquots (small amounts from the whole) were taken for determination of calcium oxide and magnesia.

vi) Determination of CaO by EDTA Method - 4 suitable aliquot of main solution was titrated against standard EDTA using Patton & Reeder's indicator at pH 12.The change in color from wine red to clear blue indicated the end point.

vii) Preparation done for (a) Sodium Hydroxide Solution (4N) - 80 g of sodium hydroxide in a 500 ml volumetric flask was dissolved and solution was made up to the mark with water. (b) Patton and Reeder's Indicator- 100 mg of the indicator was grinded with 10 g of sodium or potassium sulphate until a homogeneous mixture was obtained. Later it was stored in an air-tight bottle. (c). 18.613 g of disodium-dihydrogen-ethylenediammetetra-acetate was dissolved in one litre of water.

viii) 10 ml sample from main solution was taken in a 250 ml conical flask. 5 ml of glycerol was added in flask with constant stirring. 2 ml triethenolamine/diethyl amine was added with 10 ml of NaOH(4N) and shaked well to adjust the pH 12. Approx 50 ml of water was further added with 50 mg of solid Patton and Reader's indicator. The solution was titrated against 0.01M EDTA, the end point is change in color from wine red to greenish blue.

ix) Alternate procedure was followed when manganese present in high amounts.-10 ml of main solution (e) has been taken into a 250 ml conical flask. 2 to 3 drops of nitric acid was added, followed by 50 mg of potassium periodate. The flask was kept on water-bath till it was changed into pink colour. The solution was shaked well and allowed to cool to room temperature. 5 ml of glycerol was added with constant stirring and2 ml of diethyl amine/Triethanolamine followed by it. Few drops of sodium hydroxide solution were added and solution was shaked well to adjust the pH 12. Approximately 50 ml of water was further added with 100 mg of solid Patton and Reeder's indicator and titrated against 0.01 M EDTA solution. The end point of the titration was identified when one to two drops of EDTA produced the sharp change in colour from violet to blue.

Calculations done for result of limestone analysis

1 ml of 0.01 M EDTA = 0.560 8 mg CaO

$$\boldsymbol{CaO\ \%\ by\ mass} = \frac{\mathbf{0.5608} \times \mathrm{V}}{\boldsymbol{m}}$$

Where V = volume in ml, of EDTA used; and m = mass in g, of sample taken.

The result of chemical analysis of limestone shown in table 3.4.

Table-3.4: Result of chemical analysis of limestone (in weight %) used in the research work

Calcium Oxide (CaO)	Magnesium Oxide (MgO)	Loss on ignition (LOI)	Other components
53.28	4.5	3.4	8.22

x) A theoretical value of $CaCO_3$ was calculated from the chemical analysis of limestone or raw meal by assuming that all of the CaO analyzed was present as $CaCO_3$. It is then a simple matter of converting the % CaO firstly into moles of CaO, then into moles of $CaCO_3$ and then into % $CaCO_3$ by the following calculations;-

$\% CaCO_3 = \% CaO / 56.1 \times 100.1$ or $\% CaCO_3 = \% CaO \times 1.784$

Available lime stone = 53.28 % CaO, So, $CaCO_3 = 1.78 \text{ x } 53.28 = 95.05 \%$

Result of Chemical Analysis procedure of Limestone:

The limestone used in the research consist **95%** Calcium carbonate ($CaCO_3$). For research work the limestone supposed to contain **100% $CaCO_3$** (ignoring 5 %).

3.3.3 Chemical analysis of Mill Scale (before and after the reduction)

In chemical analysis of unreduced and reduced mill scale, many reagents have been prepared before performing the chemical analysis. After that metallic iron, ferrous iron (Fe^{+2}), total iron & ferric iron (Fe^{+3}) were calculated. For convenient and easy understanding of the work done in chemical analysis of mill scale before & after the reduction, the procedure followed was picked up individually as given below:

1. Chemical used in analysis
2. Preparation of Reagents
3. Metallic iron chemical analysis procedure
4. Ferrous iron (Fe^{+2}) chemical analysis procedure in Mill scale and DRI
5. Total iron chemical analysis procedure
6. Ferric iron (Fe^{+3}) calculation

3.3.3.1 Chemicals used in analysis

- Concentrated Hydrochloride Acid
- Barium Diphenylamine Sulphonate
- Tin Chloride
- Orthophosphoric Acid
- Sulphuric Acid
- Mercury Chloride
- Iron Chloride
- Potassium Dichromate
- Ammonium Ferrous Sulphate

3.3.3.2 Preparations of reagents

Barium Diphenylamine Sulphonate (BDS) Solution

i) 0.5 gram of BDS was weighted on watch glass using 3 decimal electronic weighing machine, and then transferred into a beaker with the help of a brush.

ii) 100 ml of distilled water was poured into the beaker and stirred manually.

iii) 10-12 drops of concentrated sulphuric acid was added in the beaker till the solution became milky in colour. The solution was store in a black bottle.

Tin chloride solution

i) 7 gram of tin chloride was weighted and transferred into an empty beaker.

ii) 75 ml distilled water was poured into that beaker. After that the solution became milky in colour.

iii) 25 ml concentrated hydrochloride acid (HCL) was poured into the solution, after which it turned colorless. The solution was later stored in black bottle.

Mix Acid

i) Initially, 300 ml distilled water was poured into an empty 2000 ml beaker.

ii) 150 ml of sulphuric acid was poured gently into the beaker. Due to which the beaker became hot, so kept in the water bath for some time for cooling.

iii) 150 ml Orthophosphoric Acid poured slowly into the beaker and again the beaker was kept in water bath for some time for cooling.

iv) 400 ml distilled water was added into the beaker. The 1000 ml mix acid was stored into a jar.

Mercury Chloride solution

i) 6 gram mercury chloride was weighted on watch glass on electronic weighing machine and then gently transferred into a beaker using a brush.

ii) 100 ml distilled water was poured into the beaker and stirred manually by hand. The solution was stored in a dipping bottle.

Ferrous Chloride solution

i) 25 gram Ferrous Chloride was weighted and then transferred into a beaker.

ii) 100 ml distilled water was poured slowly into the beaker. The beaker became hot, so manually stirred for some time..

iii) The hot beaker was cooled in fan air for some time and then beaker was put into a water bath for better cooling.

iv) **NOTE:** Solution get expires within 24 to 48 hours; it was used within few hours of its preparation. Ferrous chloride is sticky in nature, so the moisture was avoided during formation of solution.

Potassium Dichromate solution

i) 20 to 30 gram of Potassium Dichromate was taken in a beaker.

ii) The beaker was kept into the oven and allowed to heat at 100°C for 45 min to 60 min for removal of moisture.

iii) In that hot condition, exact 4.903 gram of potassium dichromate was weighted with the help of watch glass and gently transferred into a conical flask with the help of a brush.

iv) 500 ml distilled water was poured into the conical flask using funnel and a magnetic bead for magnetic stirring was put into that conical flask.

v) The conical flask was put for magnetic stirring for 60 to 90 minutes.

vi) After that the solution was gently transferred into a beaker and further 500 ml distilled water was poured into it. The 100 ml solution was stored in a jar.

0.1N Potassium Dichromate solution

i) 1 gram Ammonium Ferrous Sulphate was weighted with the help of watch glass and gently transferred in an empty beaker with the help of a brush.

ii) 100 ml distilled water was poured into it.

iii) 5 to 7 ml concentrated Sulphuric Acid was added into it.

iv) 10 ml mix acid was also poured into the beaker.

v) 2 to 5 drops of Barium Diphenylamine Sulphonate was added as indicator.

vi) The solution was titrated against 0.1 N Potassium Dichromate. The burette reading was noted down at end point when the solution to violet colour. Normality by the formula given below:

$$\boldsymbol{Normality = \frac{Given\ weight\ (4.903) \times 1000}{Equivalent\ weight\ (392.1) \times burette\ reading}}$$

vii) **Note:** For 0.1 normality- Factor is 0.005585, so the factor was calculated according to the normality of prepared solution by formula given below.

$$\boldsymbol{Factor = \frac{Normality \times 0.005585}{0.1} \times 100}$$

3.3.3.3 Procedure of chemical analysis and calculation of -Metallic Iron (Fe_m)

i) 0.2-0.25gm of sample was weighted on 3 digit electronic weighing machine.

ii) The sample from watch glass was transferred to conical flask using a brush.

iii) 35ml of freshly prepared ferric chloride ($FeCl_3$) was added in the beaker.

iv) Afterwards 100ml of distilled water was also added in the beaker.

v) The beaker was allowed for the magnetic stirring for 60 to 90 minutes.

vi) 40-45ml of mix acid was added to it, followed by 50ml of distilled water. (Note: Distilled water was added to lighten the color of solution).

vii) 4-5 drops of Barium disulphonate (BDS) as indicator was added in solution.

viii) The solution was titrated against 0.1N $K_2Cr_2O_7$. The end point was obtained when the solution turned into violet.

ix) In the given chemical analysis, the metallic iron reacted with 3 molecules of $FeCl_3$. Due to which the burette reading came 3 times, so the formula was divided by 3, in order to obtain right value of metallic iron percentage, as given below:

$$\boldsymbol{Fe\ (Metallic) = \frac{Burettee\ reading \times Normality\ factor (K2Cr2O7\ solution)}{Sample\ Weight\ \times\ 3} \times 100}$$

3.3.3.4 Chemical analysis test procedure for calculating -Total Iron (Fe_T)

i) 0.2-0.25gm of sample weighted using 4 digit electronic weighing machine.

ii) The sample was transferred from watch glass to the beaker using a brush.

iii) 40ml of cons. HCl was poured into the beaker containing the sample. The solution was turned into yellowish colour appeared.

iv) The solution was heated for 25-30 min. During heating the HCl was added time to time till the sample got dissolved fully. (Note: if sample did not get completely dissolve even after an hour; we assume it that the particles observed were impurities.

v) Tin chloride ($SnCl_2$) was added drop wise in hot condition till the solution turned to colorless.

vi) 30-40 ml of distilled water was added later. The solution was allowed to cool in a water bath for some time.

vii) 20-25 drops of $HgCl_2$ was added to the beaker. Due to which a white precipitate was formed on it.

viii) Then 10ml of mix acid was added to make the solution acidic.

ix) Distilled water was also added as per requirement to make the solution light.

x) 4-5 drops of Barium disulphonate (BDS) was added into it as indicator.

xi) The solution was titrated against the 0.1N Potassium dichromate ($K_2Cr_2O_7$). The end point was when the solution turned into violet.

$$\boldsymbol{Fe\ (Total)} = \frac{\boldsymbol{Burettee\ reading \times Normality\ factor(K2Cr2O7\ solution)}}{\boldsymbol{Sample\ Weight}}$$

3.3.3.5 Chemical analysis test procedure for calculating - Ferrous iron (Fe^{+2})

i) Sample of weight around 0.2 to 0.25 gram was taken in the conical flask

ii) 1 gram $NaHCO_3$ (sodium bicarbonate) was added in the conical flask.

iii) 2 to 3 drops of distilled water were added, just to make lighter in color.

iv) 40 to 50 ml conc HCl was added and the flask was covered with watch glass.

v) Little gas bubbles got started evolving in the beaker and coming out from small gap between watch glass and flask.

vi) The conical flask was put on hot plate at temperature about 100 to 150°C for 15 to 20 minutes until all the bubbles disappeared and sample got dissolved.

vii) More 30 ml HCl was added to makeup the solution in beaker.

viii) 10 -15 ml distilled water (DW) was added to cool it.

ix) When the solution got cooled down, 15 to 20 ml mix acid was added into it.

x) The solution was stirred manually and cooled. It became light in colour.

xi) 2 to 5 drops of BDS was added as indicator.

xii) The solution was titrated against 0.1N $K_2Cr_2O_7$ solution.

$$\boldsymbol{Ferrous\ iron\ (Fe+2)} = \frac{\boldsymbol{Burettee\ reading \times Factor(K2Cr2O7\ solution)}}{\boldsymbol{Sample\ Weight}}$$

xiii) Note: The above formula holds good for iron ore or mill scale and when it is required to calculate for DRI, just subtract the metallic iron to total iron percentage to get Fe^{+2} in DRI.

xiv) When the above formula value multiplied by 1.29 (multiplication factor i.e. amount of FeO in terms of Fe^{+2}), the wustite (FeO) percentage was obtained.

3.3.3.6 Calculations for- Ferric iron (Fe^{+3})

i) In mill scale or iron ore the ferric iron percentage calculated by subtracting ferrous iron and metallic iron from total iron:

$$\mathbf{Fe(T) = Fe(M) + Fe^{+2} + Fe^{+3}}$$

Or $$\mathbf{Fe^{+3} = Fe(T) - \{Fe(M) + Fe^{+2}}$$

Result of chemical analysis of mill scale; shown in table 3.5

Table-3.5: Result for result of chemical analysis of mill scale

Total iron (%)	Metallic iron (%)	Fe^{+2} (%)	Fe^{+3} (%)
67.3	**1.3**	**41.31**	**24.69**

Calculation of oxygen present in iron oxides of mill scale

i) O_2 present in iron oxides in mill scale = O_2 with Fe $^{+2}$(i.e. FeO) + O_2 with Fe $^{+3}$ (i.e. Fe_2O_3)

ii) From the result of chemical analysis of Fe $^{+2}$, % of FeO was calculated.

iii) The oxygen percentage in FeO was 22.23 % and Fe $^{+2}$ was 77.78%.

iv) The oxygen weight percentage (22.23%) was multiplied with the calculated value of FeO, to give the value in given weight of mill scale.

v) The same procedure was adopted in case of oxygen in Fe_2O_3

Result of oxygen present with iron oxides in mill scale; shown in table 3.6

Table-3.6: Result for result of oxygen present in mill scale

O_2 in FeO (%)	**O_2 in Fe_2O_3 (%)**	**Total O_2 iron oxides of mill scale (%)**
11.88	10.58	22.46

3.4 Formulae for degree of reduction (DOR or α)

Degree of reduction: The degree of reductions means to weight of oxygen removed in direct reduced iron to weight of oxygen present in the iron ore or mill scale before reduction. If the sample in the form of pellets reduced by solid carbonaceous material like coal, coke, char etc., or the sample reduced by gaseous reductant only, the degree of reduction can be simply understood by calculating the loss in weight of the sample after reduction. But in case of reduction of sample in form of lump, then loss in weight due to removal of oxygen and carbon during the reduction can't be easily calculated. So a simple formula suggested by Chernyshev and Gonzales is most prominently used in this kind of situations.

$$\mathbf{DOR}(\boldsymbol{\alpha}) = \mathbf{K}\,\frac{\boldsymbol{Fe(t)^{DRI} - Fe(t)^{MS}}}{\boldsymbol{Fe(t)^{DRI} \times Fe(t)^{MS}}} \times \mathbf{100}$$

Here, DOR (α) = Degree of reduction, Fe (t) ^{DRI} = Percentage of total iron in direct reduced iron, Fe (t) ^{MS} = Percentage of total iron in mill scale before reduction, K = ratio of weight of total iron to the weight of total oxygen present in given amount of mill scale before reduction.

Calculation for value of K in above formula (given weight of mill scale =15gram):

$$\boldsymbol{K = \frac{Weight\ of\ total\ iron\ in\ 15 gram\ of\ mill\ scale}{Weight\ of\ total\ oxygen\ in\ 15\ gram\ of\ mill\ scale}}$$

i) Weight of total iron present in 15 gram of mill scale before reduction = 15 x 0.673 = 10.09 g, (because total in mill scale = 67.3%)

ii) Weight of total oxygen present in 15 gram of mill scale before reduction = 15 x 0.2246 = 3.36 g (because total oxygen in mill scale = 22.46%)

iii) K = 10.09/3.36 = 3 (approximately)

3.5 Stoichiometric calculation for low grade coal

As the reduction proceeds from higher order of iron oxide to lower so for calculating the stoichiometric amount required to reduce 15 gram of mill scale, all the oxides present in mill scale was considered to be hematite (Fe_2O_3) and the reaction considered for stoichiometric calculation shown below:

$$\mathbf{Fe_2O_3 + 3C \rightarrow 2\,Fe + 3CO} \qquad \mathbf{(3.1)}$$

So for the 15 gram mill scale, the low grade coal having 25% approx. fixed carbon required to be 13.5 gram, which was 0.9 times the mill scale weight

3.6 Characterization study techniques

Analysis of mill scale before reduction and after reduction were characterized using XRD, EDX, and SEM

3.6.1 XRD (X-Ray Diffractometry) [44]

XRD studies were carried out on unreduced and reduced samples of mill scale before and after the reduction, to identify the phases of iron present in the samples. The I vs 2θ for the given samples was determined by X-ray diffraction (XRD, X'Pert Powder PAN analytical) automated X-ray diffractometer within the angle range of 20-90° with the Cu target with $\lambda k\alpha = 1.540$ A°.

3.6.2 SEM (Scanning Electron Microscopy)

The SEM characterization technique was done to understand the surface morphology of unreduced and reduced mill scale samples. Samples viewed at different level of magnifications (From 5X to 5000X) to show the effect occurred at the micro structural level on the sample after reduction. The samples were always kept in air tight container to avoid dust particles

3.6.3 EDX (Energy-Dispersive X-Ray Spectroscopy

Energy dispersive X-ray spectroscopy (EDS) detector (Bruker, Germany) was employed for phase composition and elemental mapping for phase identification on the unreduced and reduced samples of mill scale.

3.7 Experimental

Reduction of mill scale carried out in different steps like material cleaning, sample preparation, sample size determination, furnace heating, time-temperature and particle size variation. After sample heating, characterization study were carried out to reveal the degree of reduction with the help of chemical analysis

3.7.1 Apparatus used in the experiment:

- Alumina Crucible
- Weighing Balance
- Vibratory Sieve Shaker
- Electric Muffle Furnace
- Ring magnet

3.7.2 Experimental Procedure

i) The mill scale and coal obtained were washed in water two-three times to remove the dirt attached on their surface. The lubricants present in mill scale also got washed out by such attempt.

ii) Among the raw materials (mill scale, limestone & coal, shown in figure 3.1), the mill scale and coal were allowed to get dried up in open sun to remove the moisture which come during their washing.

(a) Mill Scale **(b) Low grade coal** **(c) Limestone**

Figure-3.1: Raw materials used in the research work

iii) Mill scale and limestone were individually crushed by rod crusher (shown in figure 3.2) to bring into powder form.

Figure-3.2 Rod Crusher

iv) Similarly, coal is also converted into powder form by jaw crusher and roller crusher, as shown in figure 3.3.

(a) Coal **(b) Jaw crusher** **(c) Roller crusher**

Figure-3.3: Jaw and Roller Crushers

v) Partially crushed coal coming out of the roll crusher was feed into rod crusher to obtain in powdered form, as shown in figure 3.4.

(a) Semi crushed coal **(b) Coal in Rod Crusher** **(c) Powdered Coal**

Figure-3.4: Powdering of Coal

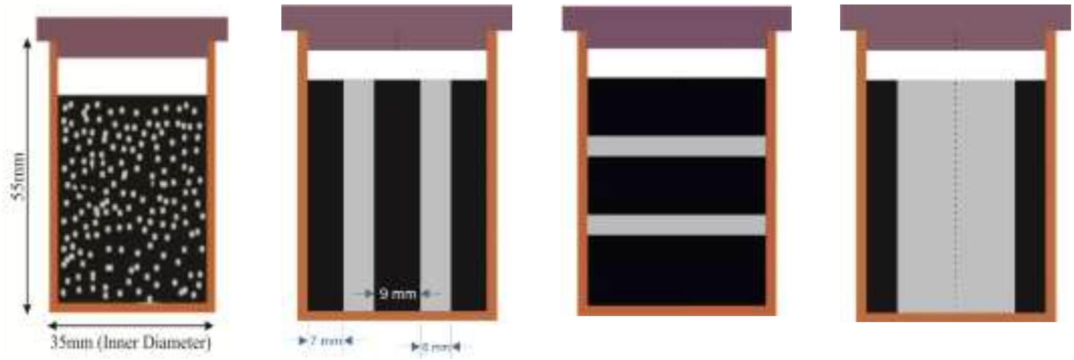
vi) Individually raw materials in powder form was then passed through various sieves by using sieve shaker (figure 3.5) and collect different-different sieved sample respectively: 30-90, 90-120, 120-150, 150-180, 180-210 and 210-270 microns in packets (fig.3.6). Run time of vibratory sieve shaker is 45 minutues.

Figure-3.5: Vibratory Sieve

Figure-3.6: Powdered mill scale/coal in packets

vii) To increase the reducing ability of coal, 10 % limestone powder (in wt. % of mill scale) mixed with the coal to give coal mixture (coal + limestone)

viii) The mill scale and coal mixture arranged in the crucible as per the study. Each crucible after the arrangement of mill scale, coal mixture (coal + limestone) covered with refractory brick made lid covers and insulation by glass wool. The various arrangements of mill scale and coal mixture (coal + limestone) in crucible for which the final study was carried out shown below and labelling shown separately in centrally arranged crucible.



(a) (b) (c) (d)

Figure-3.7: Arrangement of mill scale and coal mixture: (a) mixed, (b) alternate concentric (c) layered (d) layered (e) labelling of crucible and sample shown in central arrangement.

ix) Furnace Heating for Reduction : Programmable Muffle Furnace was used to the reduction of all sample which has been prepared; Reduction temperature parameter was 850°C, 900°C, and 950°C and period of reduction parameter was 15, 30, 60, 90, 120, 150 minutes. First the temperature of muffle furnace at particular temperature was adjusted. On reaching of the concerned temperature the furnace was kept unloaded for 30 to 40 min for obtainment of uniform temperature gradient and genuine temperature. Then the charging and discharge crucible was done with the help of laboratory tong to avoid any harmful injury. The picture of muffle furnace shown in figure 3.8.

(a) **(b)**

Figure-3.8: Electric Muffle Furnace (a & b)

x**)** The closed crucibles were taken out from the furnace, after predetermined time of reduction and allowed to cool for 1 to 2 hours below the running fan.

xi) Magnetic separation was done by using ring magnet (shown in figure 3.9) for removal all non-magnetic material after the reduction of mill scale and then the samples sent for chemical analysis and characterization study.

Figure- 3.9: Ring magnet

\

3.8 Experimental work-flow chart

Flow chart of experimental work

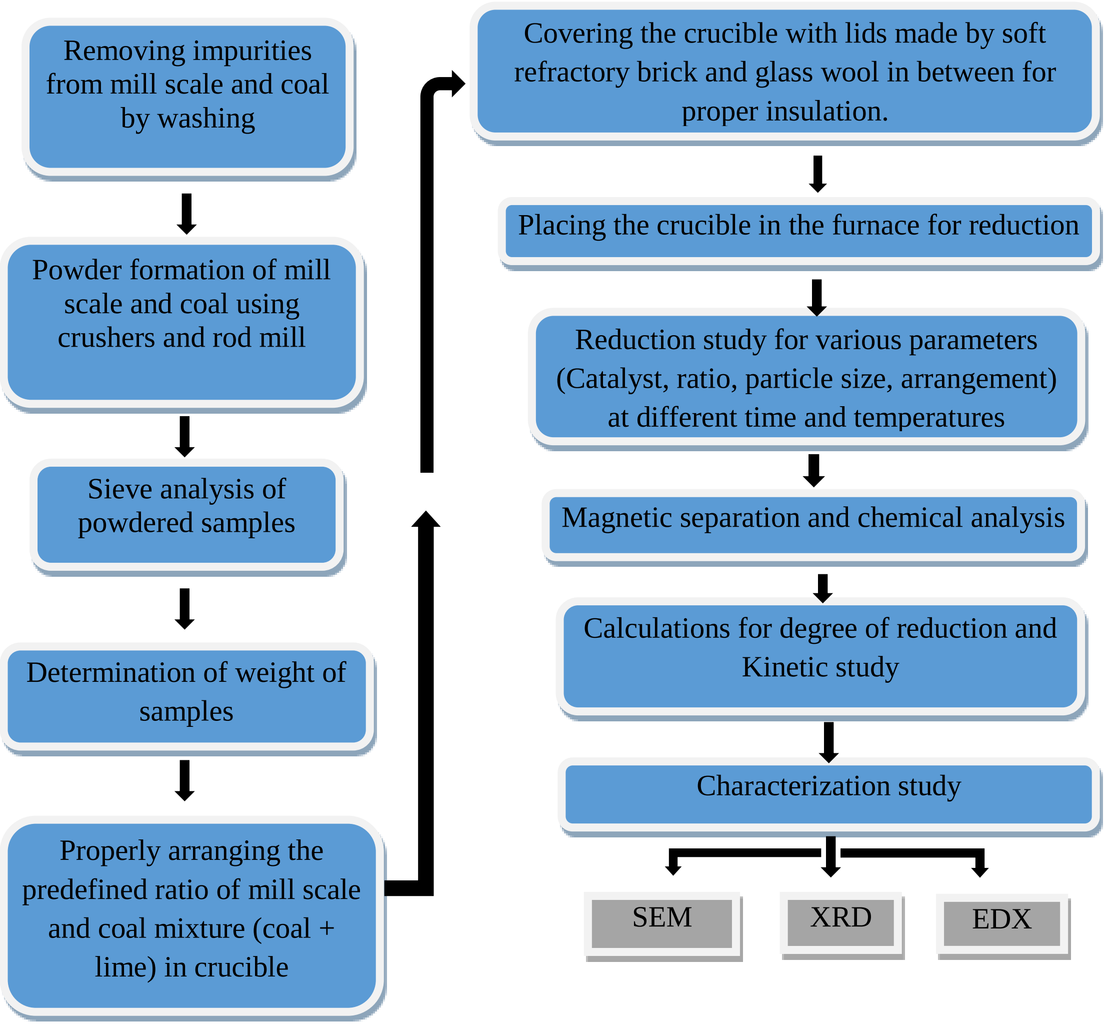


Figure-3.10: Experimental flow chart of research work

CHAPTER - 4

PRELIMINARY STUDY

In this chapter the result of reduction of mill scale by low grade coal for certain parameters have been discussed. The aim of this chapter was to optimize the reduction parameters for the final study. The data collected from the chemical analyses of the samples reduced for different parameters were employed to describe the progress of degree of reduction of the samples during the course of study. By comparing the result of progressions from experiments conducted with different parameters, the influence of the respective parameters were determined and discussed. The optimized value of parameters were accepted as constant variable in the final study.

4.1 Preliminary study work:

The preliminary studies were carried at fixed time (150 minutes) and temperature (950°C). The result obtained from the first preliminary study was accepted as constant parameter for the second study and same way passed down by second preliminary study to the third. The overall optimized parameter values accepted as constant parameters in the final study. The parameters study done in part of preliminary study work includes:

1. **Preliminary study (PS) 1: Effect of particle size of mill scale and coal**
   (Particle size = 30-90, 90-150, 150-210 and 210-270μm)
2. **Preliminary study (PS) 2: Effect of ratio of ratio of mill scale and coal**
   (Ratio = 1:0.9, 1:1, 1:1.1, 1:1.2, 1:1.3, 1:1.4 and 1:1.5)
3. **Preliminary study (PS) 3: Effect of addition of limestone**
   (Percentage of limestone mixed with coal w.r.t weight of mill scale = 0, 5, 10, 15, 20 %).

4.1.1 PRELIMINARY STUDY (PS) 1: EFFECT OF PARTICLE SIZE

About the study: Among the various parameters which effect the degree of reduction or percentage reduction, particle size of raw materials plays a vital role. In different reduction situations like fixed bed, fluidized bed, rotary kiln reduction, different particle size show different value of reduction. So the particle size range which shows maximum reduction in given set of conditions is necessary to determine. Here, as per standard settings (told in previous chapter) the fixed weighted mill scale mixed with stoichiometric calculated weighted low grade coal placed in alumina crucible for reduction, shown in figure 4.1. The constant and variable values of parameters for the first study was given in table 4.1. The result of this study was understandable by graph shown in figure 4.2.

Table-4.1: The constant and variable parameters for preliminary study 1

Constant parameter	Variable parameter
i) Arrangement of mill scale and coal mixture (coal + limestone) in alumina crucible: Mixed	Particle size of mill scale and coal used (in microns) : i) 30 – 90 ii) 90 – 150 iii) 150 – 210 iv) 210 – 270
ii) Furnace temperature : 950^{o}C	
iii) Time for reduction in furnace: 150 minutes	
iv) Ratio of mill scale and coal = 1:0.9, calculated stoichiometrically. Here, mill scale = 15 gram, coal = 13.5 gram	

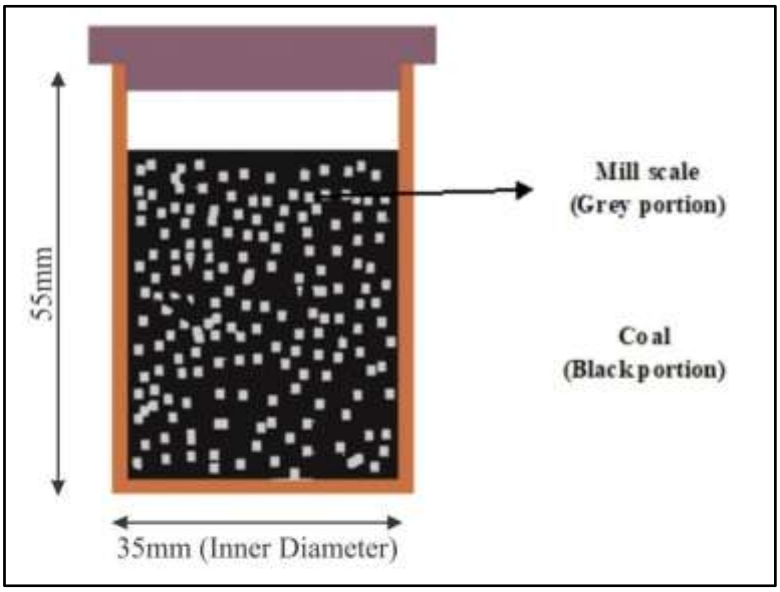


Figure-4.1: The diagram of mill scale and coal placed in alumina crucible in mixed arrangement.

Graph for preliminary study (PS) 1

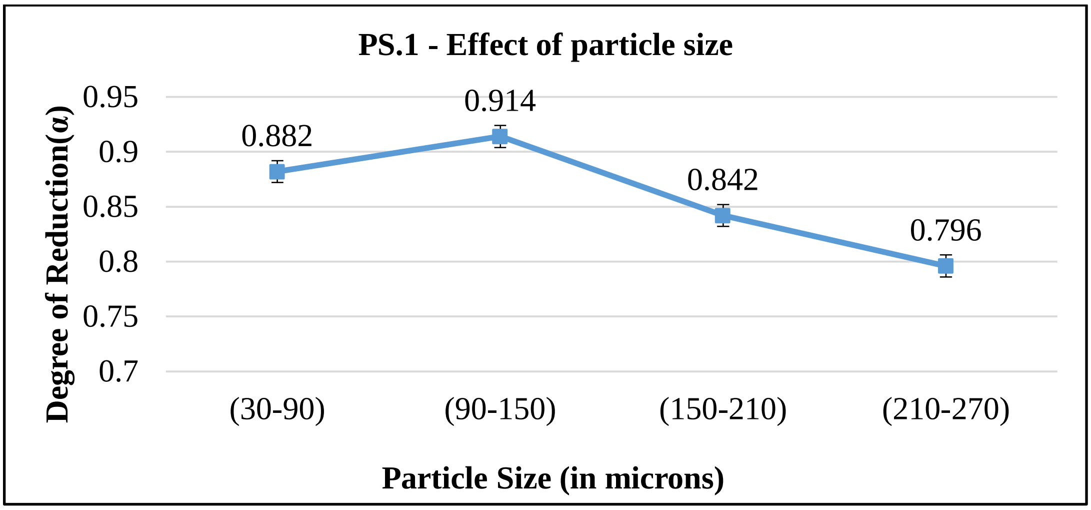


Figure-4.2: The graph for study 1 between degree of reduction and particle size

Result and discussion of preliminary study 1: The study clearly shows that samples of particle size 90-150 microns shows the highest reduction (α = 0.914), followed by samples having 30-90 microns particles (α = 0.882), then 150-210 microns (α = 0.842), and at last 210-270 microns particle (α = 0.796) samples. As per literature the finer particles possess more surface area, so the reduction in them should be more. Same happens in this study also except of sample having particle size 30-90 microns. The reduction of mill scale in crucible was due to both solid carbon present in coal as well as by carbon mono-oxide (CO) produced during reduction. However the maximum reduction was due to carbon monoxide which was produced in intermediate stage. It was because the gaseous reductant (CO) becomes more available at all surface of particles than the solid coal. So in this case the sample, having particle size 30-90 microns were very fine, due to which the permeability between the particles becomes very less. So the CO gas can’t able to pass freely between the pores and diffusion of carbon monoxide becomes difficult. Here, the sample of particles 90-150 microns of appropriate size. It possess optimum porosity and surface area for diffusion by carbon and CO, so the reduction found to be highest (α = 0.914).In samples of particle size 150-210, 210-270 microns were large enough, so less reduction took place. The sample with particle size 90-150 microns was selected for further study.

Result of PS1:
Maximum reduction (α = 0.914) in sample of 90-150 microns particle size

4.1.2 PRELIMINARY STUDY (PS) 2: EFFECT OF RATIO BETWEEN MILL SCALE AND COAL MIXTURE

About the study: The mill scale and coal mixture should be mixed together in right ratio. Correct ratio provides the appropriate interaction between reducible matter (mill scale) and reducing agent (carbon and carbon monoxide), during the direct reduction process. More or less addition of coal may decrease the reduction of mill scale, as understandable by the result of this study. To understand the correct ratio, this study was necessary to carried out. The constant and variable parameters of this study given in table 4.2 and its result understandable by graph in figure 4.3

Table-4.2: The constant, variable parameters and their values, as per preliminary study 2

Constant Parameter	Variable parameter(here, gram = g, Mill scale = MS and Coal = C)
i) Particle size: 90- 150 microns ii) Arrangement of mill scale and coal mixture in alumina crucible: Mixed iii) Furnace temperature : 950^{o}C iv) Time for reduction in furnace: 150 minutes	Ratio of mill scale and coal i)1: 0.9,MS = 15 g and C = 13.5 g ii)1: 1 ,MS = 15 g and C = 15 g iii)1: 1.2,MS = 15 g and C = 18 g iv)1: 1.3,MS = 15 g and C = 19.50 g v)1: 1.4,MS = 15 g and C = 21 g vi)1: 1.5,MS = 15 g and C = 22.5 g

Graph for Preliminary study (PS) 2

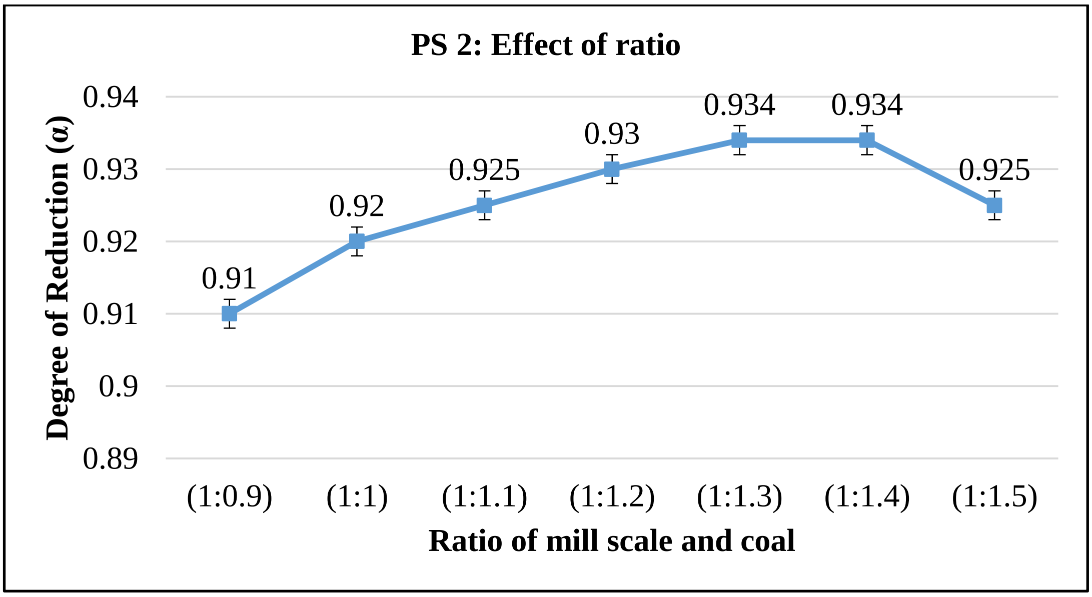


Figure-4.3: The graph for PS 2, between degree of reduction and ratio of mill scale and coal

Result and discussion of preliminary study (PS) 2: The study was done by keeping different ratio of coal mixture with mill scale. This study was done by putting coal from 0.9 to 1.5 % w.r.t. mill scale. In every sample 0.1% difference of coal was kept. It was clear from above graphs that with increase in percentage of coal mixture, the reduction increases up to a limit, becomes constant and then decreases. The 1:0.9 ratio of mill scale and coal was stoichiometric calculated amount, but still it can’t be claimed that, all 100% coal mixture would get fully utilize in the process. Some coal mixture at the bottom and corners of crucible remain unburnt or unused, so some extra amount of coal required to fully reduce the present mill scale than the stoichiometric required ratio (sample of 1:0.9 ratio). Here, the highest reduction was found in sample containing ratio 1:1.3 ($\alpha = 0.934$). On further increase of coal in crucible (sample of 1:1.4 ratio), there is no further increase in reduction found. In fact, the reduction starts decreasing in sample which contains ratio 1:1.5. It happens may be due to the free space available in crucible which was required for gases (carbon mono-oxide and carbon dioxide) produced during reduction decreases, due to further addition of coal in crucible. The extra coal makes hindrance in the movement of reducing gas (CO) to approach the mill scale particle. As the result of which, the reduction decreases on further addition of coal after a certain limit. In fact, it was found during series of experiments, the lid cover of the crucible gets open if the coal percentage is increased in the crucible. It happens due to the high pressure of carbon monoxide and carbon dioxide produced during the reduction process in crucible. So correct ratio of mill scale and coal is required. The maximum reduction found in sample containing 1:1.3 and 1: 1.4 ratio ($\alpha = 0.934$). For safety point and maximum reduction value, sample with ratio 1:1.3 taken reference for further study.

Result of PS 2-
Maximum reduction ($\alpha = 0.934$) found in sample of 1:1.3 ratio

4.1.3 PRELIMINARY STUDY (PS) 3: EFFECT OF ADDITION OF LIMESTONE

About the study: Limestone consist calcium carbonate ($CaCO_3$) which works as catalyst for the reduction reaction and also helps in scavenging sulphur present in coal. Its effect was studied in this. From this study, it was tried to identify the percentage of limestone required to be added for reduction of mill scale by low grade coal. The constant and variable parameter of this study was given in table 4.3 and result was understandable from graph, shown in figure 4.4

Table-4.3: The initial constant and variable parameters for preliminary study 3

Constant Parameter		Variable parameter
i)	Particle size: 90- 150 microns	Limestone (in weight % of 15 g mill scale) added with 19.5 g coal i) 0 %= 0 g ii) 5 %= 0.75 g iii) 10% = 1.5 g iv) 15% = 2.25 g v) 20% = 3 g
ii)	Arrangement of mill scale and coal mixture (coal + limestone) in alumina crucible: Mixed	
iii)	Ratio of mill scale and coal = 1: 1.3Here, Mill scale = 15 g and Coal = 19.50 g	
iii)	Furnace temperature : 950°C	
iv)	Time for reduction in furnace: 150 minutes	

Graphs of Study 3

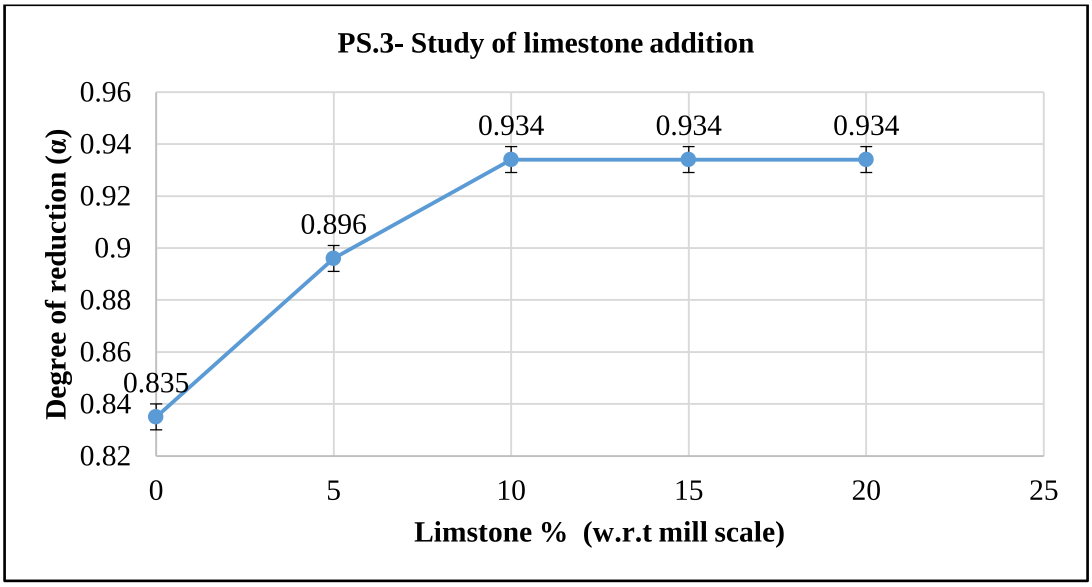


Figure-4.4: The graph for preliminary study 3, between DOR and % limestone in crucible w.r.t mill scale

Result and discussion of preliminary study 3: The study clearly revels that addition of limestone boost the reduction from the starting of the experiment. During the reduction at high temperature (above 600^oC), the $CaCO_3$ present in limestone breaks down into CaO and CO_2, which enhances the gasification reaction. The reaction occurs during the process shown below:

$$CaCO_3 \rightarrow CaO + CO_2;$$

$$CO_2 + C \rightarrow 2CO$$

This CO_2 formed during the process, produces CO (carbon mono-oxide) in absence of air, which works as reducing agent and increases the reduction. It should be noted that limestone (catalyst) addition just increases the rate of reaction, within the given period of time, due to which the reduction increases. If the limestone was not added, the direct reduction process would require more energy (i.e. Time and temperature) for the same result. It means the limestone act as the catalyst which decreases the activation energy required during the process. With increase in addition of limestone from 0 to 20%, the reduction increases, reaches to highest value ($\alpha = 0.934$, in sample containing 10% limestone) and then becomes constant. After 10% addition, there is no subsequent change found in reduction. It means 10% addition of limestone in crucible is appropriate amount. The result (10% limestone) of this study was similar to that obtained by A.K.M.M.Rahman [92] for reduction of mill scale by coal in mild steel crucible. However, the reduction was in central arrangement, particle size was 2.3 mm and the coal used was having higher percentage of fixed carbon (52.6%). The result of that study was also 10 % limestone, as obtained in this study. So, here the 10% limestone addition was taken reference for final study. When the limestone mixed with coal in crucible, it was referred as coal mixture in this research work. So total weight of coal mixture required for reduction 15 gram mill scale will be 19.5 g coal + 1.5 g limestone, which equals to 21g coal mixture. In final study, in all samples 21 g coal mixture (19.5 g coal + 1.5 g limestone) was used.

Result of PS 3
Maximum reduction ($\alpha = 0.934$) found in sample containing 10% limestone

CHAPTER - 5

FINAL STUDY

The chapter deals with main (final) study of the research work on – Effect of mill scale reduction by low grade coal for different arrangements in crucible. The value of kinetic parameters were calculated for the given study. For calculating the kinetic parameters, the final study was carried out at different time and temperatures. The kinetic parameters include the rate constant, activation energy and identification of rate control equation for the samples reduced in different arrangement. The optimized results of the preliminary study work were used as constant parameters in the final study. The parameters for the final study shown below:

Final Study

(i) Arrangements = Mixed, central, alternate concentric and layered.

(ii) Temperatures = 850, 900 and 950°C

(iii) Timings = 15, 30, 60, 90, 120 and 150 minutes.

FINAL STUDY: EFFECT OF ARRANGEMENT OF MILL SCALE AND COAL MIXTURE IN ALUMINA CRUCIBLE.

5.1 About the study: In the rotary kiln the reduction the raw materials moves with the motion of kiln, so the arrangement of materials can’t play any significant role. However, when carrying out direct reduction in crucible, the raw materials remain in static condition, so they can be arranged and their effects can be check out. In this study, it was tried to implement all possible arrangements of mill scale and coal mixture that could possible in crucible. The various arrangement of mill scale and coal mixture for the final study were shown in figure 5.1. The optimized parameter values accepted in the final study. To understand the kinetics of work the study was done at different time and temperatures. This study will also verify the effect of time and temperature on reduction of mill scale by low grade coal. The constant and variable parameters of the final study, shown in table 5.1. The result of reduction was shown by graphs in figures 5.2 to 5.5 and 5.6 to 5.8.

Table 5.1: The constant, variable parameters and their values, as per final study

Constant parameter	Variable parameter
i) Limestone mixed with coal: 10%. Here, mill scale =15 g, coal mixture (19.5 g coal + 1.5 g limestone) = 21 g Total raw material (mill scale + coal mixture) in crucible = 15 + 21 = 36 g	i) Arrangement of mill scale and coal mixture in crucible : - Mixed arrangement - Centrally aligned (Central) - Alternate concentric - Layered
ii) Ratio of mill scale & coal mixture:1: 1.3	ii) Temperature: 800,900, 950 ^{o}C
iii) Particle size: 90- 150 microns	iii) Time: 60, 90, 120 minutes

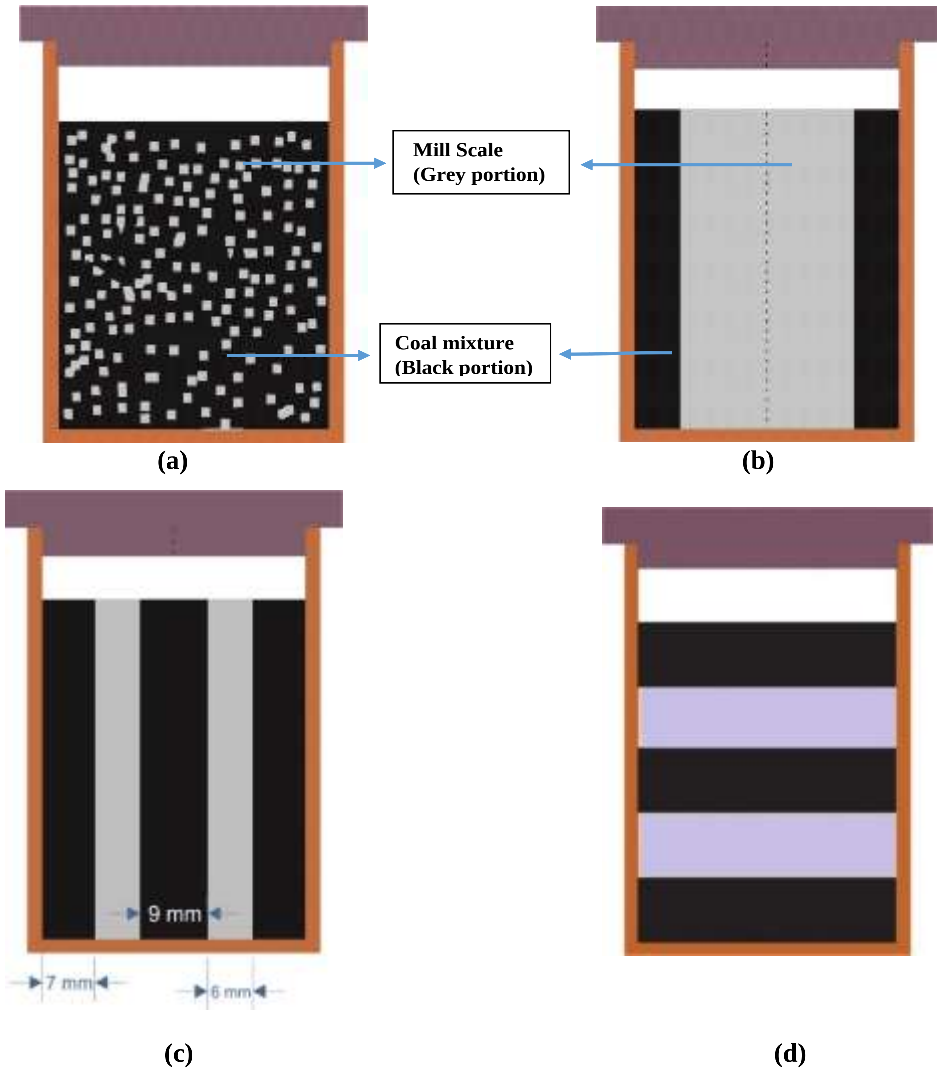


Figure-5.1: The various arrangements of mill scale and coal mixture (coal + limestone) in crucible for which the final study was carried out -(a) Mixed arrangement (b) Central arrangement (c) Alternate concentric (d) Layered Arrangement

5.2 Graphs of degree of reduction for the final study

5.2.1 Graph for DOR of Mixed arrangement at different temperatures

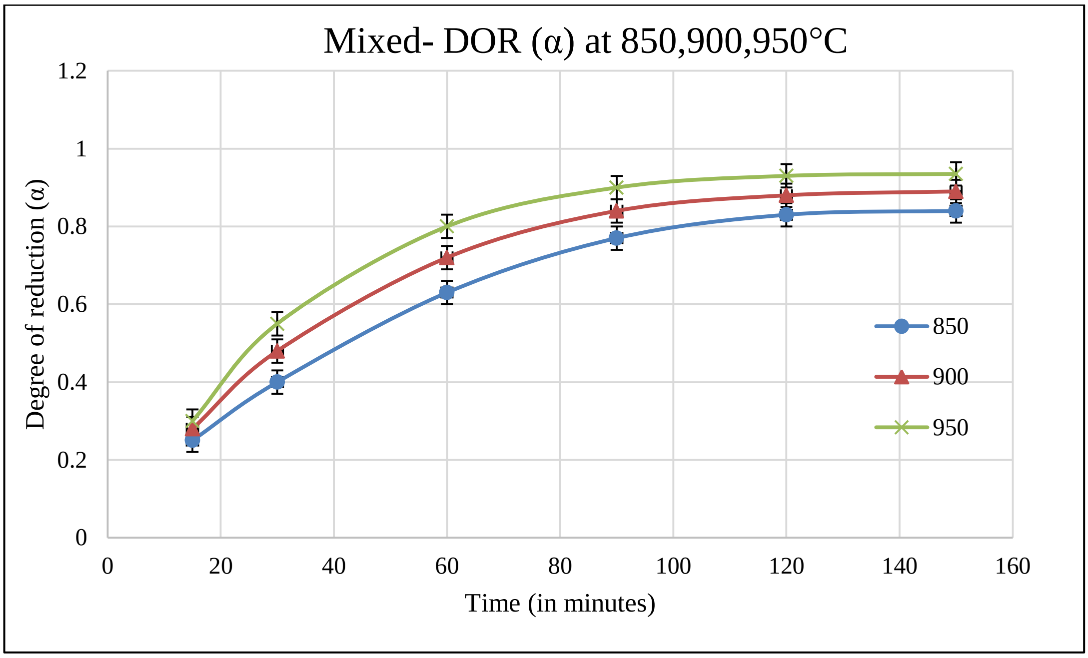


Figure 5.2: Graph of DOR at different time and temperatures for mixed arrangement

Note: The error bar was not shown in further graphs. It obscures the symbols used in graph & readings become unreadable, as graph lines are quite close to each other.

5.2.2 Graph for DOR of Central Arrangement at different temperature.

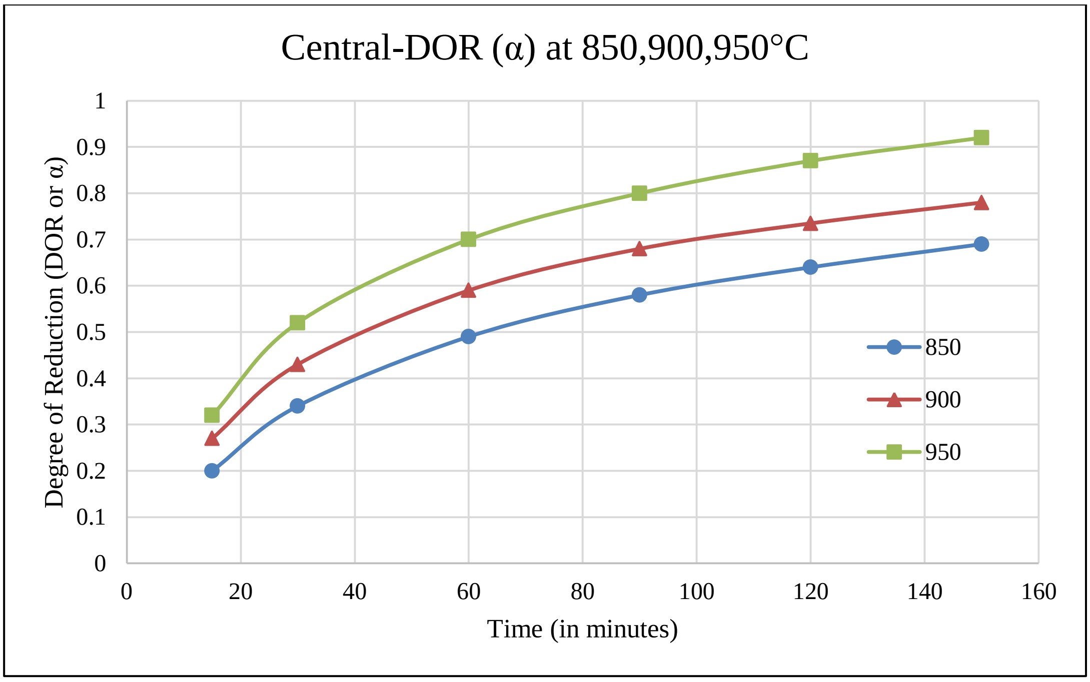


Figure 5.3: Graph of DOR at different time and temperatures for central arrangement

5.2.3. Graph for DOR of Alternate concentric arrangement at different temperatures

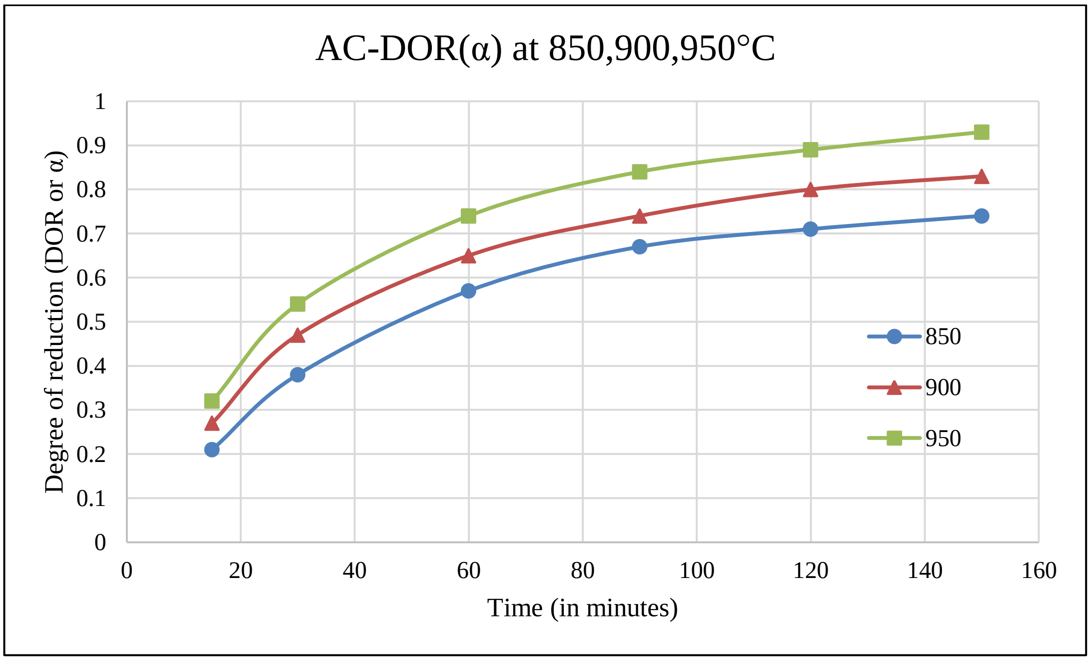


Figure-5.4: Graph of DOR at different time and temperatures for AC. Arrangement

5.2.4 Graph for DOR of Layered arrangement at different temperature.

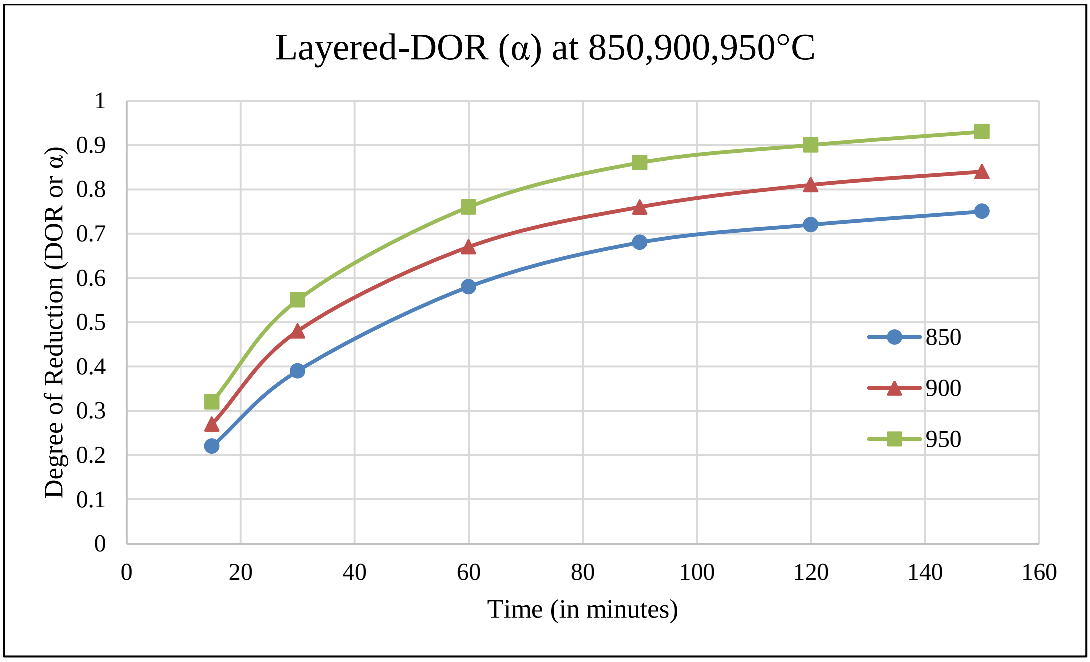


Figure-5.5: Graph of DOR at different time and temperatures for layered arrangement

The above graphs (fig 5.2 to 5.5) shown the effect of temperatures on reduction in different arrangements. To compare the result of reduction in all arrangements, the DOR graphs were also sketched at individual temperatures (fig. 5.6 to 5.8).

Graphs for comparison of DOR of samples in different arrangements at particular temperature.

5.2.5 Graph for comparison of DOR of all arrangements at 850°C

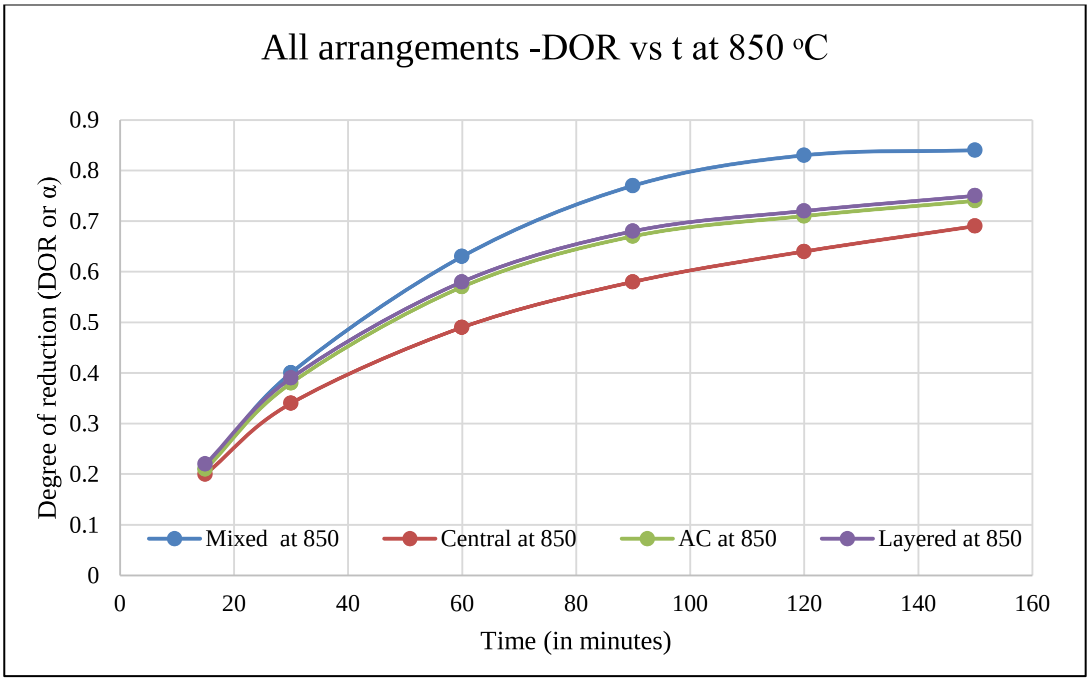


Figure-5.6: Graph for degree of reduction of all arrangements at 850°C

5.2.6 Graph for comparison of DOR of all arrangements at 900°C

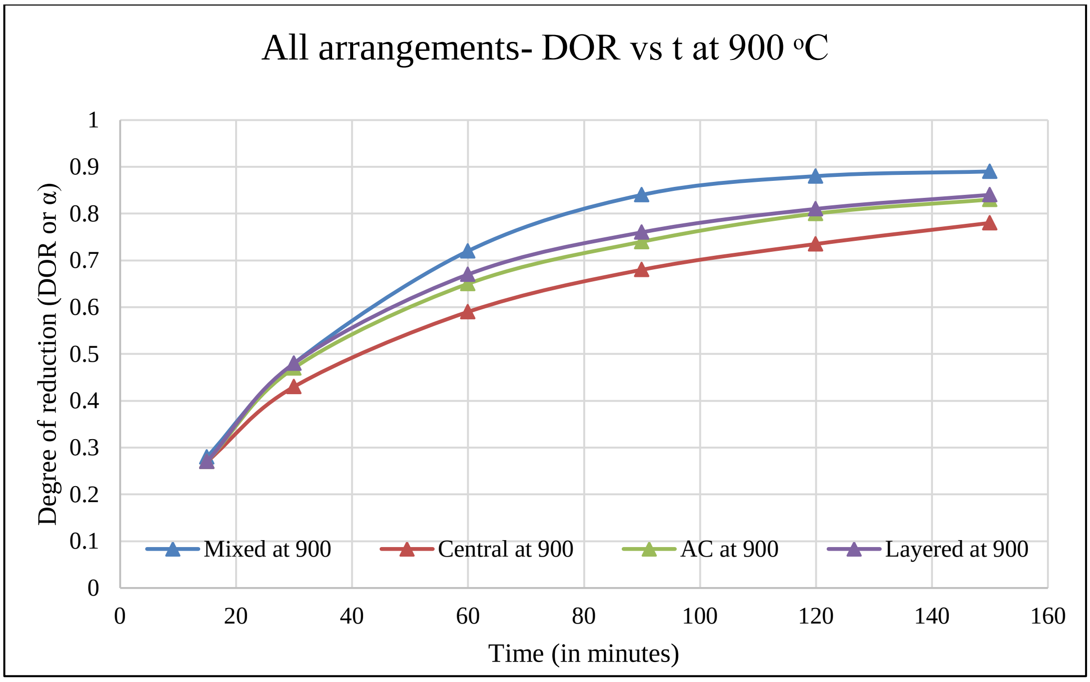


Figure-5.7: Graph for degree of reduction of all arrangements at 900°C

5.2.7 Graph for comparison of DOR of all arrangements at 950°C

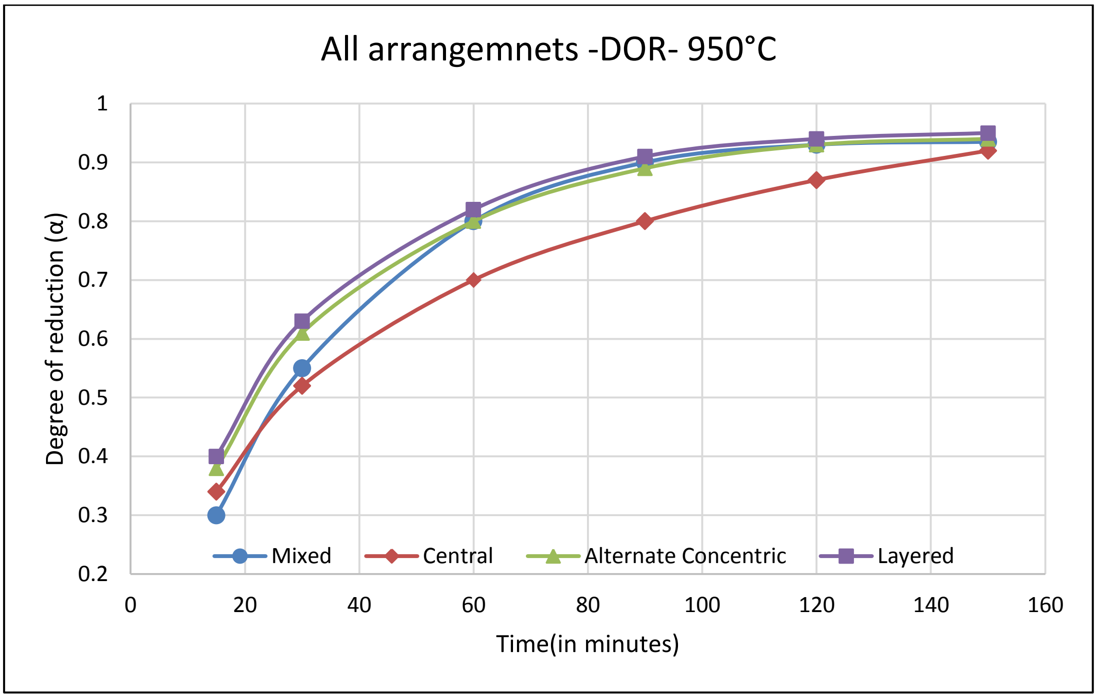


Figure-5.8: Graph for degree of reduction of all arrangements at 950°C

Result and discussion for degree of reduction graphs:

It was clear from all the graphs (figures 5.6 to 5.8) that all the arrangements possess different rates of reaction during the reduction process. The maximum reduction among all arrangements found in mixed arrangement, followed by layered arrangement, similar to that in alternate concentric arrangement and last in centrally arranged samples. There were differences in values of reduction at temperature 850 and 900°C, in last reduction timing-150 minutes of all arrangement samples. It means further increase in reduction was possible in all arrangements. But, when the samples reduced at 950 °C, all the sample in different arrangements crosses the 90 % reduction (i.e. 0.90 degree of reduction) up to 150 minutes, as visible in comparison graph of all arrangements- DOR vs. t at 950°C (figure 5.8). This was clear from the data that effect of arrangement on reduction diminishes till 150 minutes at 950 °C. But if the reduction calculated at different timings and different temperatures, the reduction was found to be different because of different rates of reaction acting in different arrangements. The layered and alternate concentric arrangement almost followed the same trajectory at all temperatures reduction. The central arrangement started following the moderate rate and reached to 90% reduction gradually till 150 minutes. The mixed arrangement seemed to have highest rate during the process among others. But nothing can be certainly said in terms of numerical value, nor can't the reaction mechanism be get cleared up from these combined degree of reduction graphs. There are various approaches to understand the rate mechanism, but the best method to get clearly understand the reaction mechanism is by reduced (dimensionless- $t/t_{0.5}$) time method.

5.3 Standard reduced time plots for different reaction mechanism equations

The Standard reduced time plots for mostly used reaction mechanism mathematical equations in direct reduction of iron ore -shown by graph in figure 5.9.

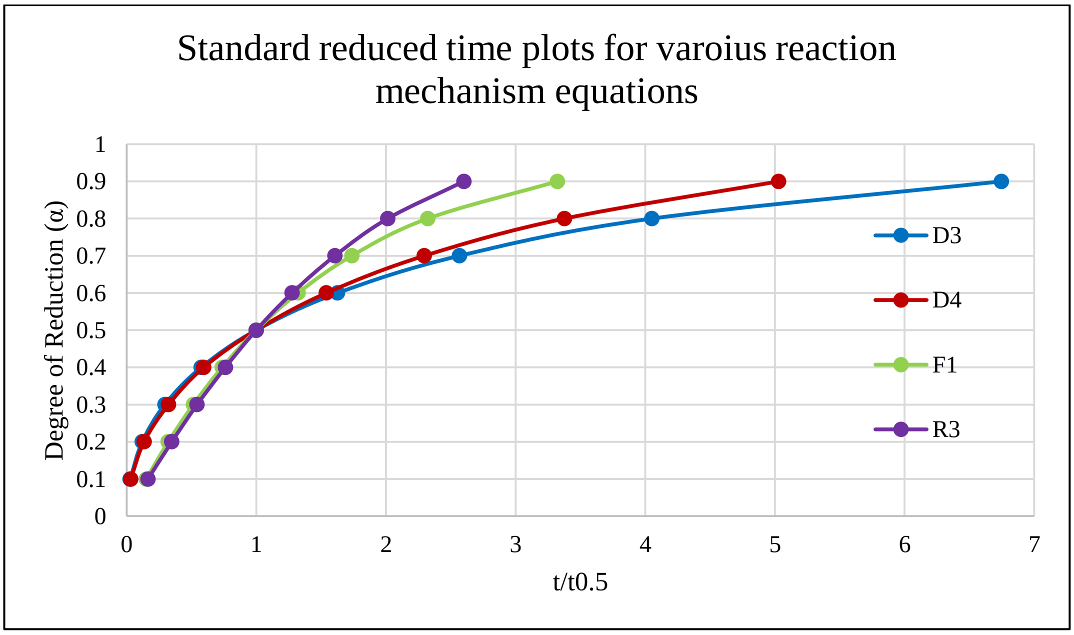


Figure 5.9: The degree of reduction (α) vs. $t/t_{0.5}$ standards plots of various rate mechanisms

Here, the alphabets with numbers used in graph represents the equations $G(\alpha)$of different rate control mechanisms, applicable in different conditions, shown below:

1) $G(\alpha) = D3 = \left[1-(1-\alpha)^{\frac{1}{3}}\right]^2$ = Diffusion controlled

2) $G(\alpha) = D4 = (1-\frac{2}{3}\alpha) - (1-\alpha\Big)^{2/3}$ = Diffusion controlled

3) $G(\alpha) = R3 = 1-(1-\alpha)^{1/3}$ = Chemically controlled

4) $G(\alpha) = F1 = -\ln(1-\alpha)$= Chemically controlled

The experimentally calculated DOR values of final study were put on standard reduced time plots & thereby the reaction control mechanisms were identified.

5.3.1 Graphs of reduced time plots for mixed arrangement (fig 5.10 to 5.12)

5.3.1.1 Graph of reduced time plots for mixed arrangement at 850°C

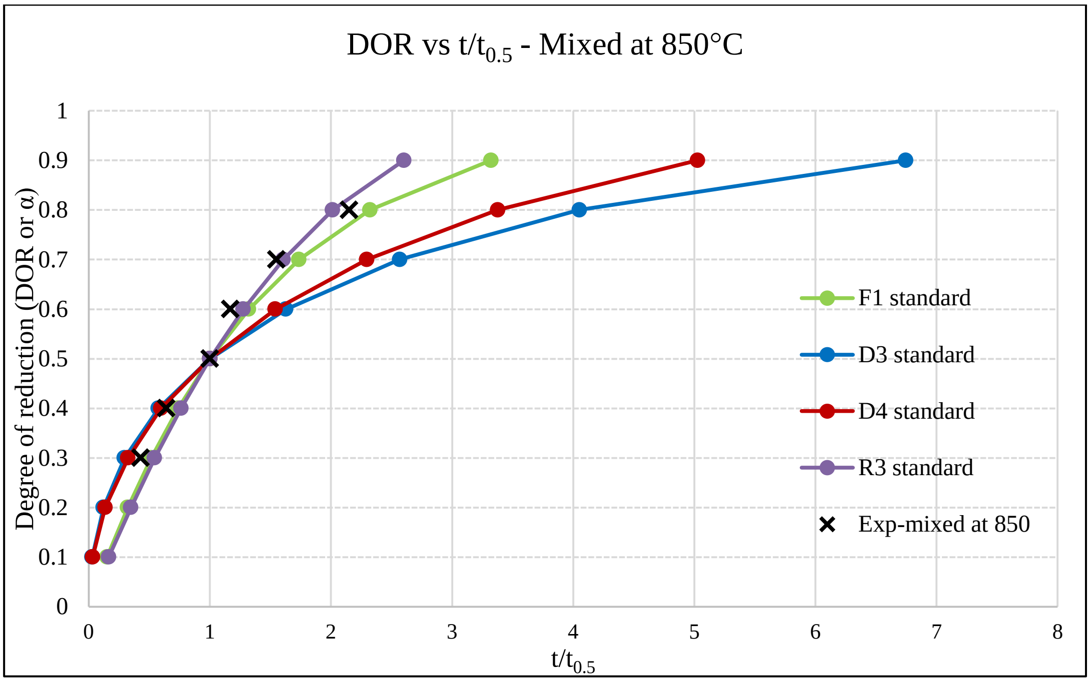


Figure-5.10: The degree of reduction (α) vs. $t/t_{0.5}$ plot of mixed arrangement sample at 850°C with standards plots of various rate mechanisms

5.3.1.2 Graph of reduced time plots for mixed arrangement at 900°C

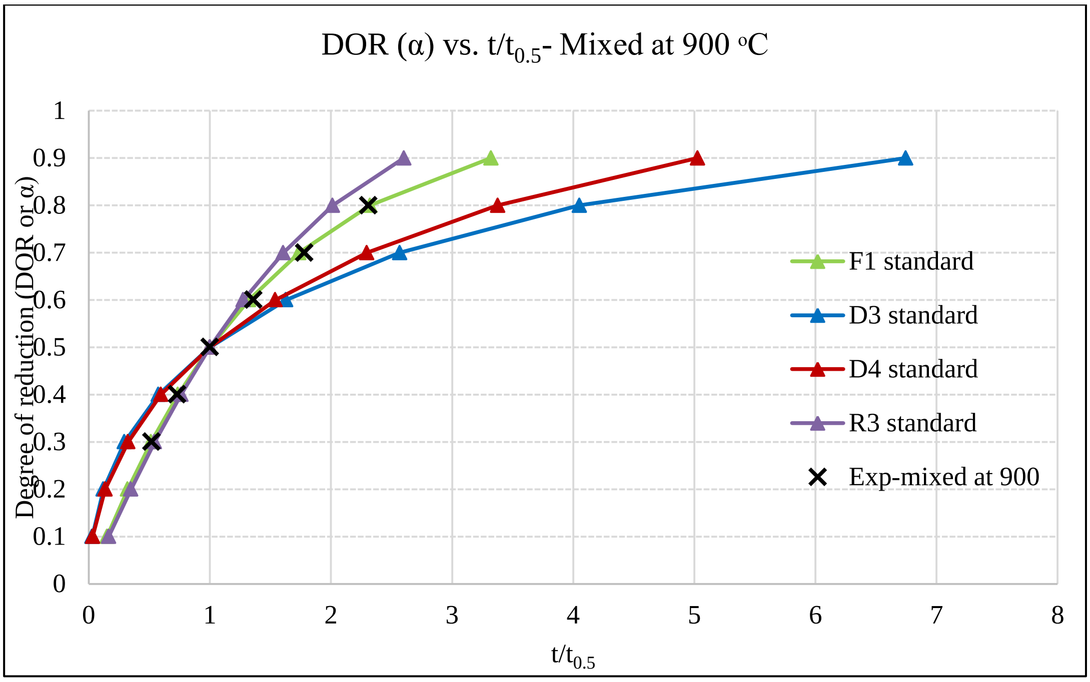


Figure 5.11: The degree of reduction (α) vs. $t/t_{0.5}$ plot of mixed arrangement sample at 900°C with standards plots of various rate mechanisms

5.3.1.3 Graph of reduced time plots for mixed arrangement at 950 °C

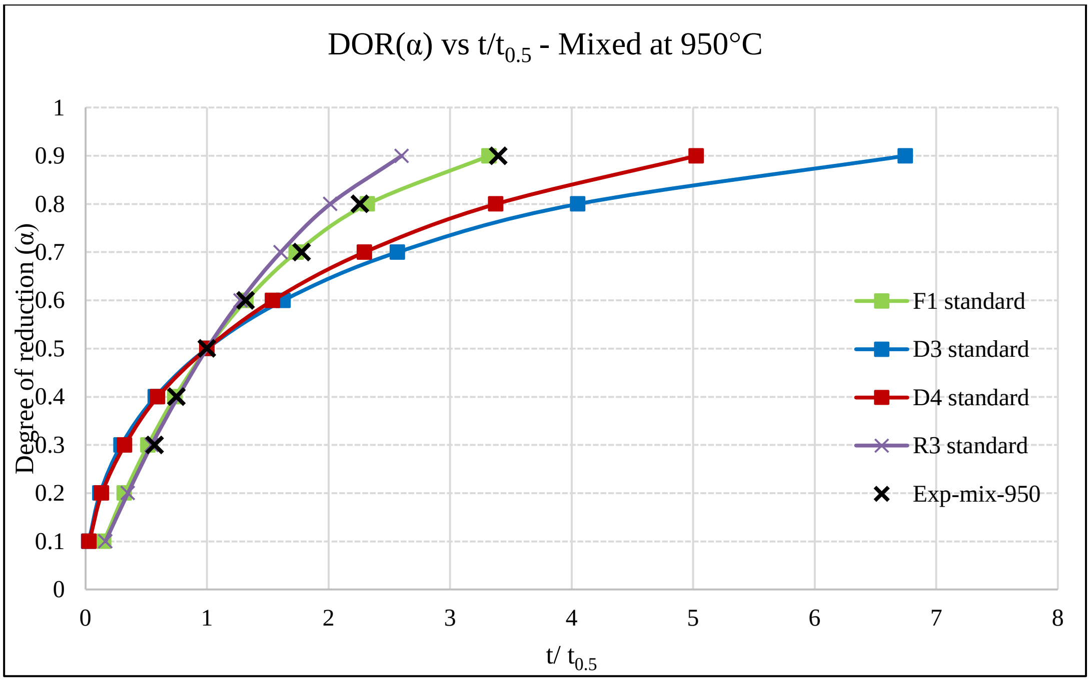


Figure -5.12: The degree of reduction (α) vs. $t/t_{0.5}$ plot of mixed arrangement sample at 950°C with standards plots of various rate mechanisms

Result obtained from reduced time plot of mixed arrangement:

The samples reduced in mixed arrangement seems to chemically control. The experimental kinetic data follows the first order equation (F1) as visible from graphs shown in figure 5.10 to 5.12. There was little discrepancy at 850°C of experimental data from the F1 equation plot, but clearly matches at temperature 900 and 950°C. The catalyst effect in the sample also merged in the same alignment of the rate mechanism. The rate controlling steps effective in this arrangement is found to be chemical reaction. Never the less the sample in mixed arrangement follow the chemical controlled mechanism equation:

$$\textbf{Result}: \textbf{Mixed arrangement was chemically controlled}: \mathbf{G(\alpha) = F1 = -ln(1-\alpha)}$$

5.3.2 Graphs of reduced time plots for Central Arrangement (fig. 5.13 to 5.15)

5.3.2.1 Graph of reduced time plots for the Central Arrangement at 850°C

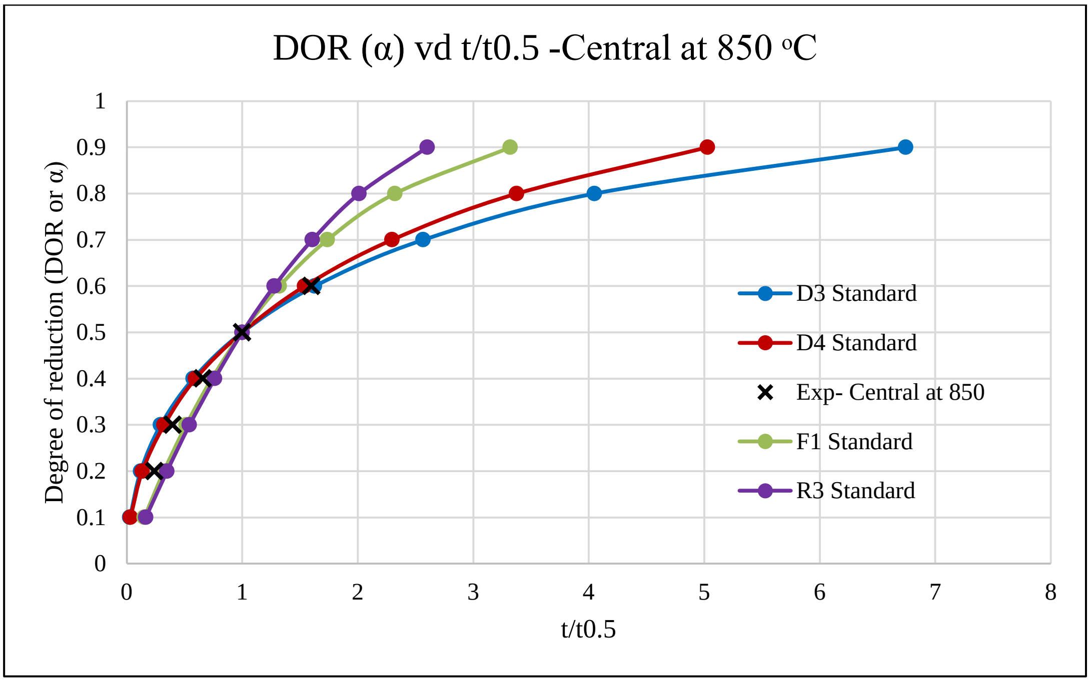


Figure 5.13: The degree of reduction (α) vs. t/$t_{0.5}$ plot of central arrangement sample at 850°C with standards plots of various rate mechanisms

5.3.2.2 Graph of reduced time plots for the Central Arrangement at 900° C

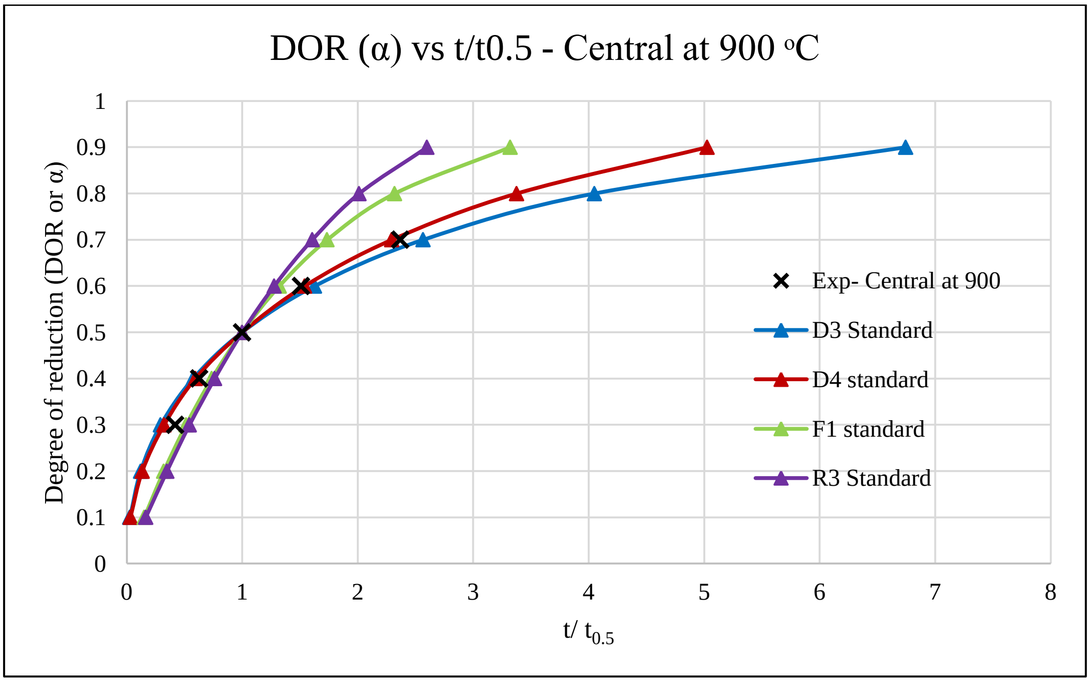


Figure-5.14: The degree of reduction (α) vs. t/$t_{0.5}$ plot of central arrangement sample at 850°C with standards plots of various rate mechanisms

5.3.2.3 Graph of reduced time plots for the Central Arrangement at 950°C

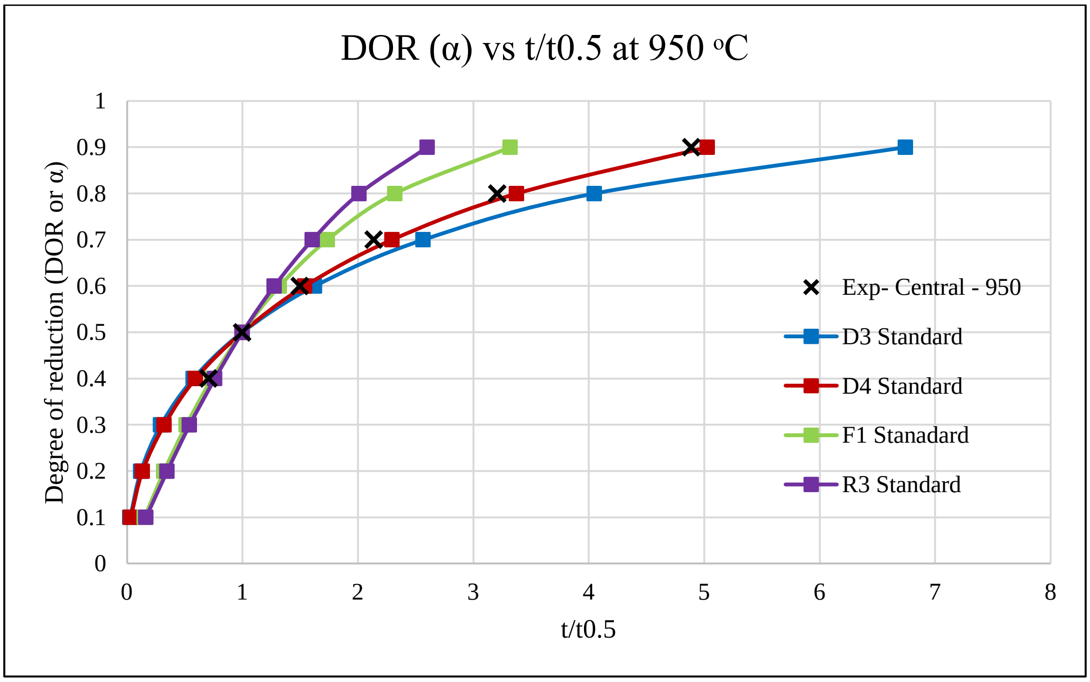


Figure -5.15: The degree of reduction (α) vs. $t/t_{0.5}$ plot of central arrangement sample at 950°C with standards plots of various rate mechanisms

Result obtained from reduced time plot of central arrangement:

The samples reduced in central arrangement seems to diffusion controlled. The experimental kinetic data follows the Ginstling−Brounshtein equation (D4) as visible from graphs shown in figure 5.13 to 5.15. There was little discrepancy in following of the experimental data from the D4 equation plot. It may be due to the effect of catalyst, which increases the gasification reaction in the process. However the most nearest reaction mechanism mathematical line from the kinetic data was D4 at all temperatures. So the overall process considered to be diffusion controlled following the diffusion controlled rate law equation:

$$\mathbf{Result: Central\ arrangement\ was\ diffusion\ contrlloed: D4 = \left(1 - \frac{2}{3}\,\alpha\right) - (1 - \alpha)^{2/3}}$$

This result of reduction mechanism (Ginstling−Brounshtein equation = D4) was similar to that obtained by S.Mukherjee *et al*.[88] who reduced the iron ore by coal in central arrangement and also by A.K.M.M Rahman *et al*.[92] who reduced the mill scale by coal in central arrangement.

5.3.3 Graphs of reduced time plots for the Alternate concentric (AC) arrangement (fig. 5.16 to 5.18)

5.3.3.1 Graph of reduced time plots for the Alternate concentric arrangement at 850° C

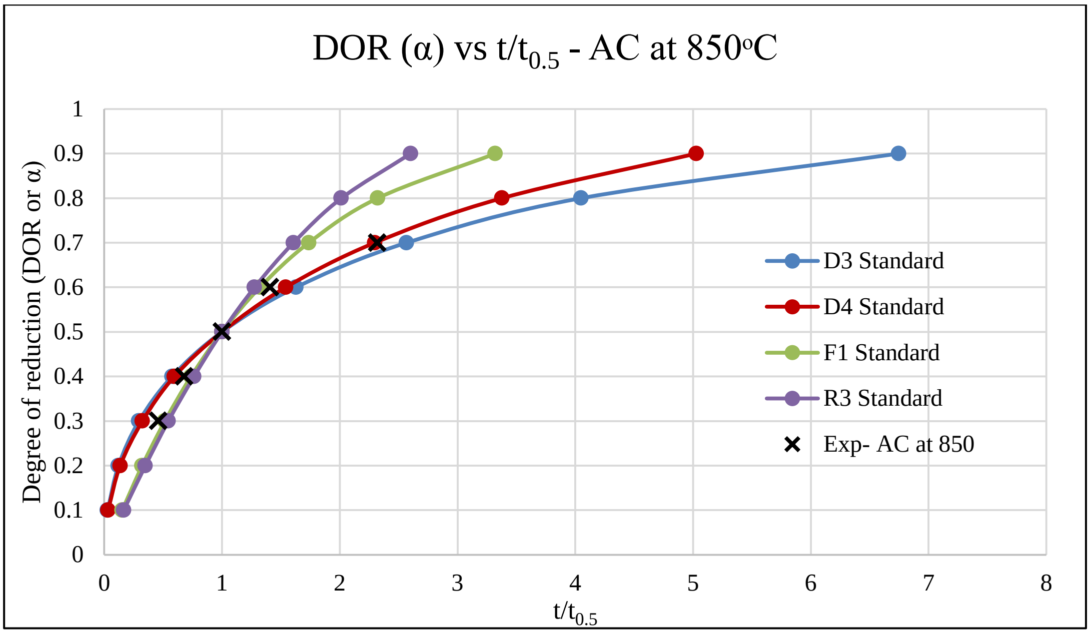


Figure-5.16: The degree of reduction (α) vs. $t/t_{0.5}$ plot of alternate concentric arrangement sample at 850°C with standards plots of various rate mechanisms

5.3.3.2 Graph of reduced time plots for the Alternate concentric arrangement at 900° C

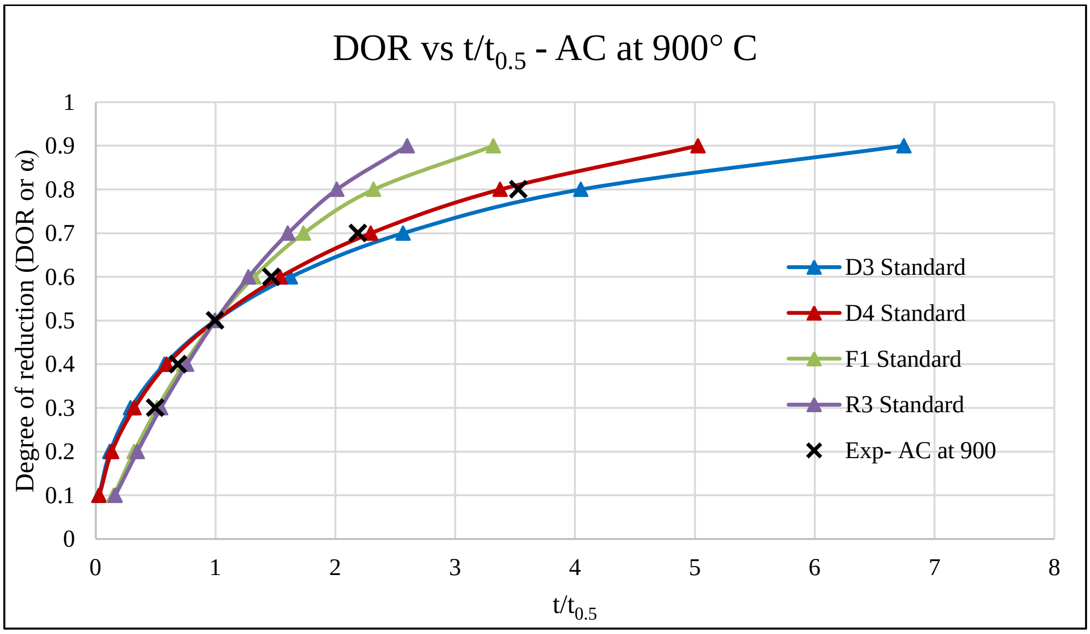


Figure 5.17: The degree of reduction (α) vs. $t/t_{0.5}$ plot of alternate concentric arrangement sample at 900°C with standards plots of various rate mechanisms

5.3.3.3 Graph of reduced time plots for the Alternate concentric arrangement at 950°C

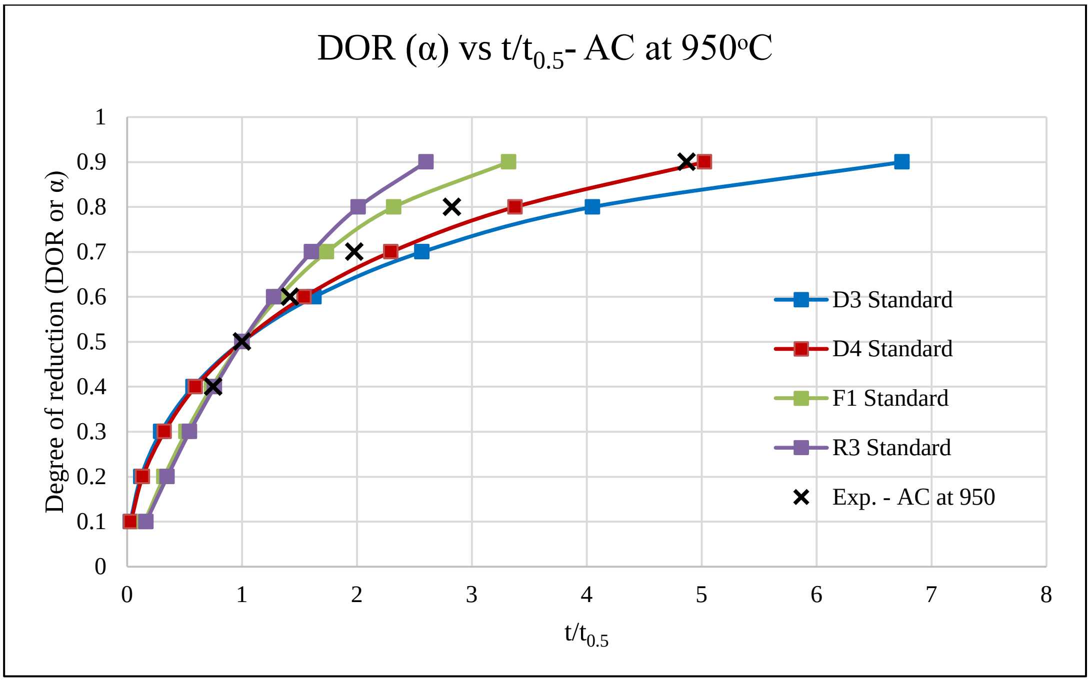


Figure-5.18: The degree of reduction (α) vs. $t/t_{0.5}$ plot of alternate concentric arrangement sample at 950°C with standards plots of various rate mechanisms

Result obtained from reduced time plot of alternate concentric arrangement

The samples reduced in alternate concentric (AC) arrangement seems to diffusion controlled. The experimental kinetic data follows the Ginstling–Brounshtein equation (D4) as understandable from graphs shown in figure 5.16 to 5.18. There was some discrepancy in following of the experimental data from the D4 equation plot. It may be due to the effect of catalyst, which increases the gasification reaction in the process. Due to the catalyst actions sometimes there was change in mechanism also found in literature. However the most nearest reaction mechanism mathematical line from the experimental data was D4 at all temperatures. So the overall process considered to be diffusion controlled following the diffusion controlled rate law equation:

$$\mathbf{Result: AC\ arrangement\ was\ diffusion\ contrlloed: D4} \\ = \left(1-\frac{2}{3}\alpha\right)-(1-\alpha)^{2/3}$$

5.3.4 Graphs of reduced time plots for Layered Arrangement (fig. 5.19-5.21)

5.3.4.1 Graph of reduced time plot for the Layered Arrangement at 850° C

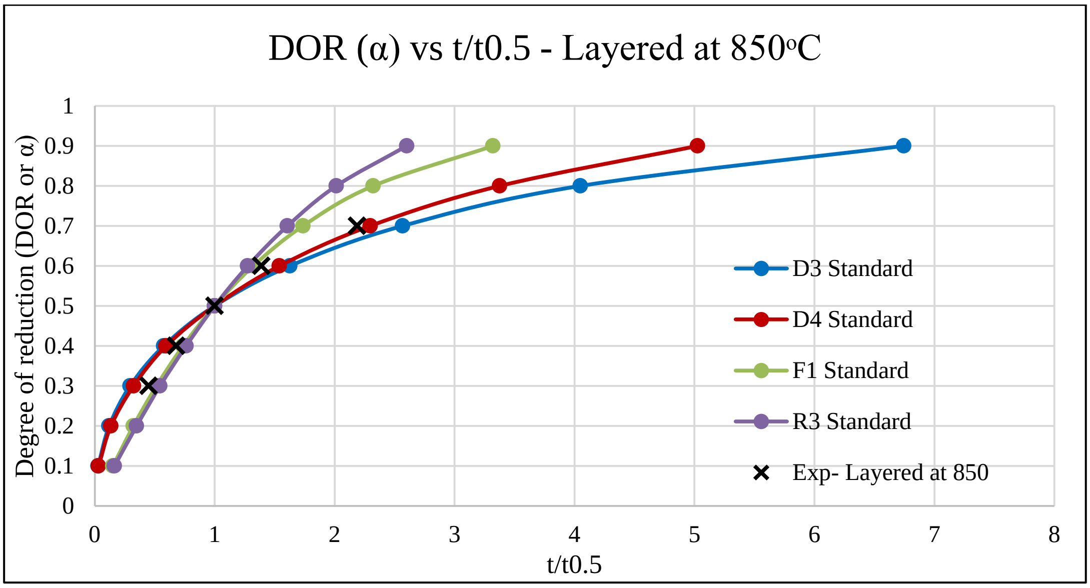


Figure 5.19: The degree of reduction (α) vs. t/$t_{0.5}$ plot of layered arrangement sample at 850°C with standards plots of various rate mechanisms

5.3.4.2 Graph of reduced time plot for the Layered Arrangement at 900°C

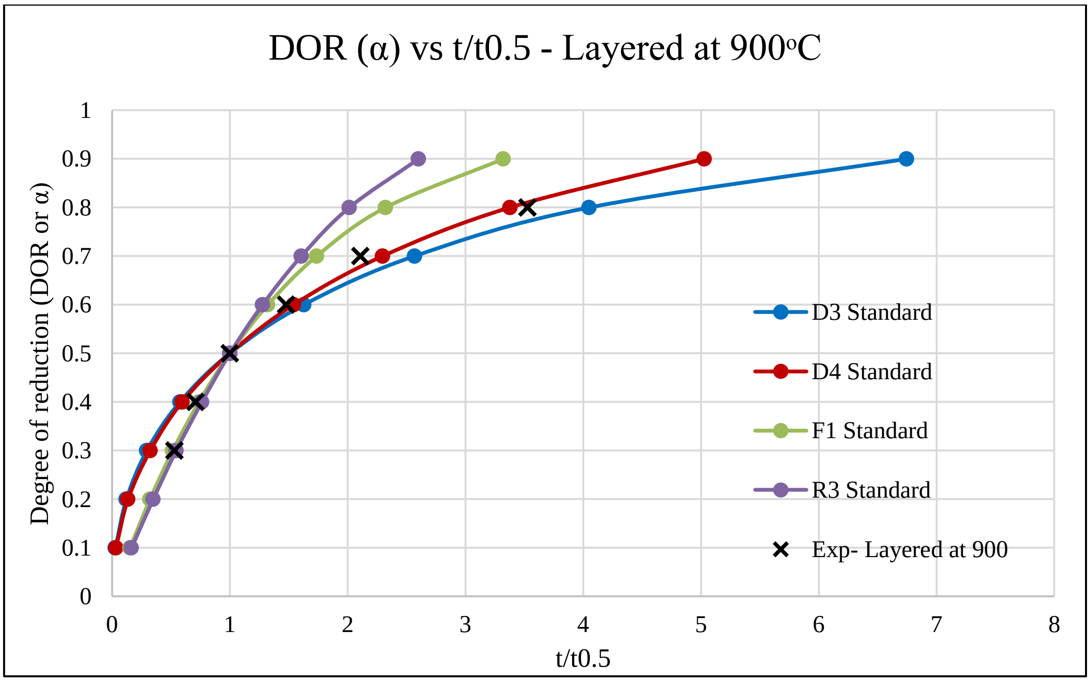


Figure 5.20: The degree of reduction (α) vs. t/$t_{0.5}$ plot of layered arrangement sample at 900°C with standards plots of various rate mechanisms

5.3.4.3 Graphs of reduced time plot for the Layered Arrangement at 950°C

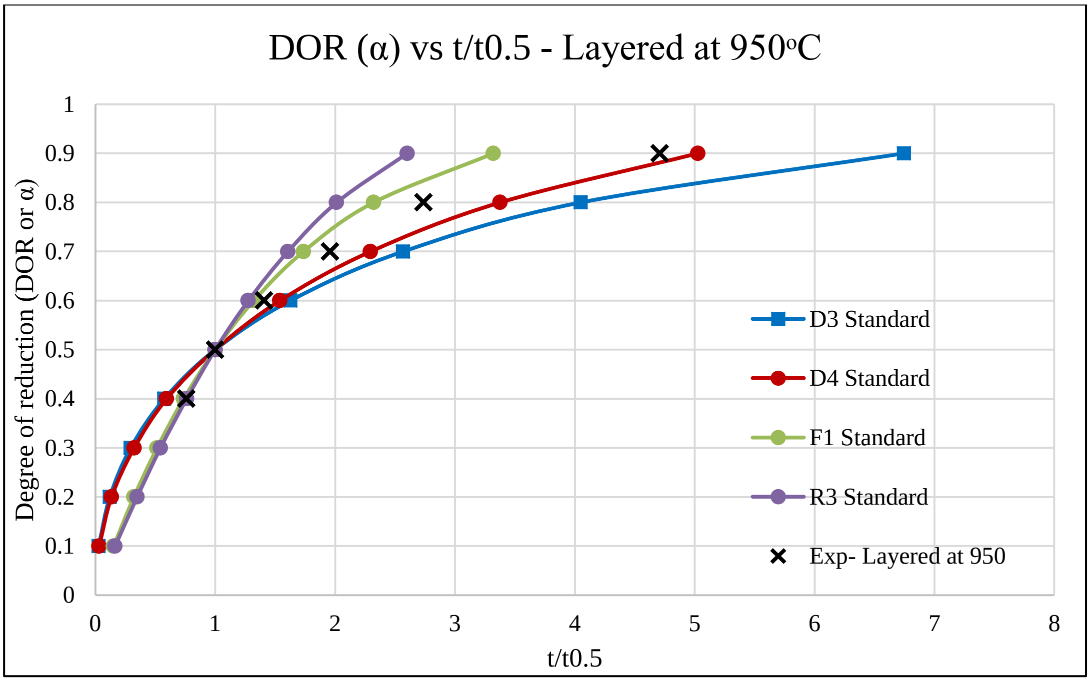


Figure 5.21: The degree of reduction (α) vs. t/$t_{0.5}$ plot of layered arrangement sample at 950°C with standards plots of various rate mechanisms

Result obtained from reduced time plot of layered arrangement:

The samples reduced in layered arrangement seems to be diffusion controlled. The experimental kinetic data follows the Ginstling−Brounshtein equation (D4), as visible from graphs shown in figure 5.19 to 5.21. There was some discrepancy in following of the experimental data from the D4 equation plot. It may be due to the effect of catalyst, which increases the gasification reaction in the process. Due to the catalyst actions sometimes there was change in mechanism also found in literature. However the most nearest reaction mechanism mathematical line from the experimental data was D4 at all temperatures, as visible in above graphs. The data also not coinciding with any other reaction mechanism equation at all temperatures. So the overall process was considered to be diffusion controlled following the diffusion controlled rate law equation:

$$\mathbf{Result: Layered\ arrangement\ was\ diffusion\ contrlloed: D4}$$
$$= (\mathbf{1} - \frac{\mathbf{2}}{\mathbf{3}}\,\boldsymbol{\alpha}) - (\mathbf{1} - \boldsymbol{\alpha})^{\mathbf{2/3}}$$

5.4 Isothermal kinetic plot, Rate constant, Arrhenius plot and Activation Energy

The value of degree of reduction of samples reduced in various arrangements were put into the rate law mechanism equation governed from the previous step. From the graphs of isothermal kinetic data the rate constants have been evaluated for different arrangements. The rate constants values put into the Arrhenius equation to obtain Arrhenius plot. The activation energy calculated from the slope of the Arrhenius plot. The approach to find the activation energy in this manner is called Integral method.

5.4.1 MIXED ARRANGEMENT

5.4.1.1 Isothermal kinetic plot for mixed arrangement: The rate constant (k) for mixed arrangement was evaluated from graph {G(α) vs. t}, as shown in figure 5.22. The rate control equation was G(α) governed in previous step.

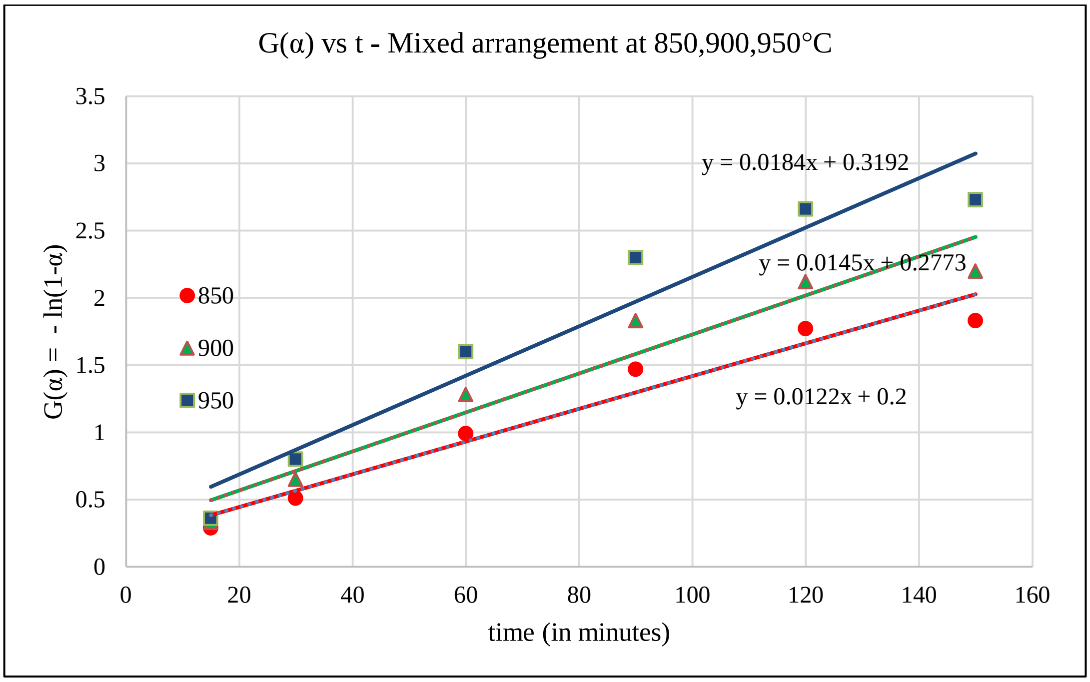


Figure-5.22: Isothermal kinetic plot for the sample in mixed arrangement following the equation G(α) = -ln (1-α)

5.4.1.2 Rate constant (k) values for mixed arrangement: Rate constant is temperature dependent function for the reaction. It is the slope of the linear line covering the maximum data in the above graph (figure 5.22) at a given temperature. Thereby value of ln k also calculated which is used in sketching Arrhenius plot (figure 5.23). The values of rate constant at different temperature calculated from the above graph (figure 5.22) of mixed arrangement shown in table 5.2.

Table-5.2: The value of rate constant (k) and ln k of mixed arrangement samples at different temperatures.

Mixed Arrangement		
Temperature (°C)	**Rate constant (k)**	**ln (k)**
850	0.0122	-4.4
900	0.0145	-4.23
950	0.0184	-4

5.4.1.3 Arrhenius Plot for mixed arrangement: Refer figure 5.23

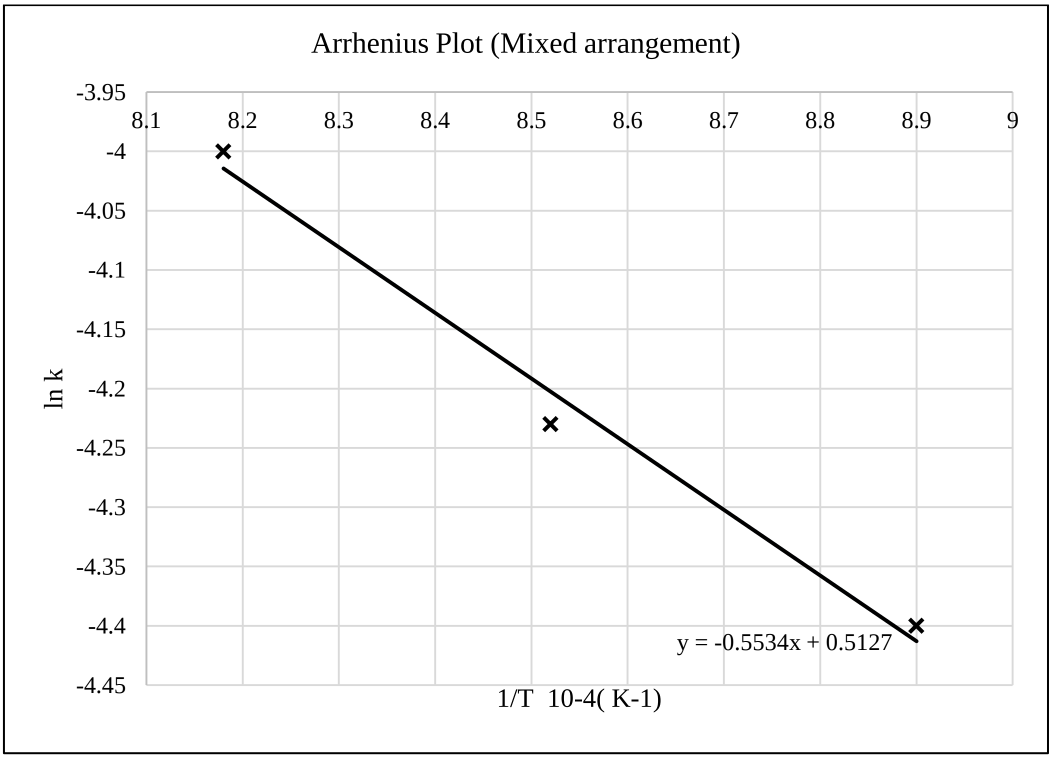


Figure-5.23: Arrhenius plot for the samples reduced in mixed arrangement

5.4.1.4 Activation energy (Ea) for mixed arrangement: Refer table 5.3

Table 5.3: The activation energy calculated of samples reduced in mixed arrangement.

Slope of Arrhenius plot (-Ea/R) **= - 0.5534 × 10^4**	**Activation energy (Ea)** **= 46 KJ/ Mole**

5.4.2 Central Arrangement

5.4.2.1 Isothermal kinetic plot for central arrangement: Refer figure 5.24

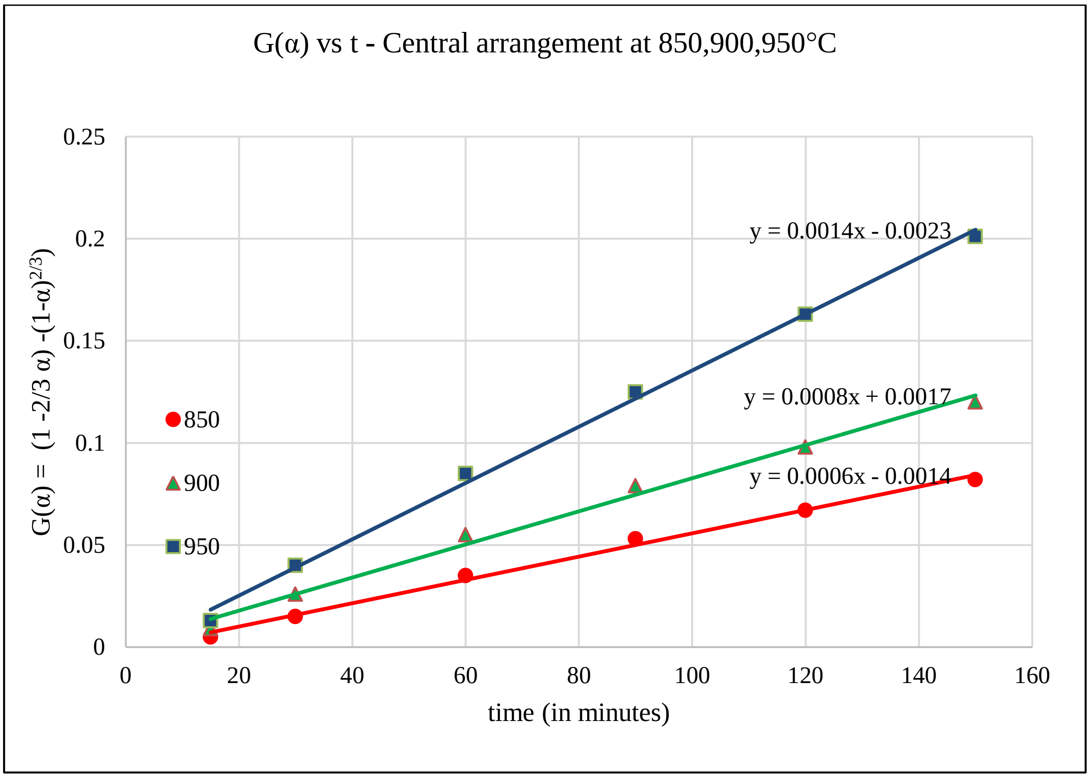


Figure-5.24: Isothermal kinetic plot of centrally arranged following the equation: $G\ (\alpha) = (1 - \frac{2}{3}\ \alpha) - (1 - \alpha)^{2/3}$

5.4.2.2 Rate constant (k) values for central arrangement: Refer table 5.4

Table-5.4: The values of rate constant (k) and ln k of samples reduced in central arrangement at different temperatures.

Central Arrangement		
Temperature (°C)	**Rate constant (k)**	**ln (k)**
850	0.0006	-7.42
900	0.0008	-7.13
950	0.0014	-6.57

5.4.2.3 Arrhenius plot for central arrangement: Refer figure 5.25

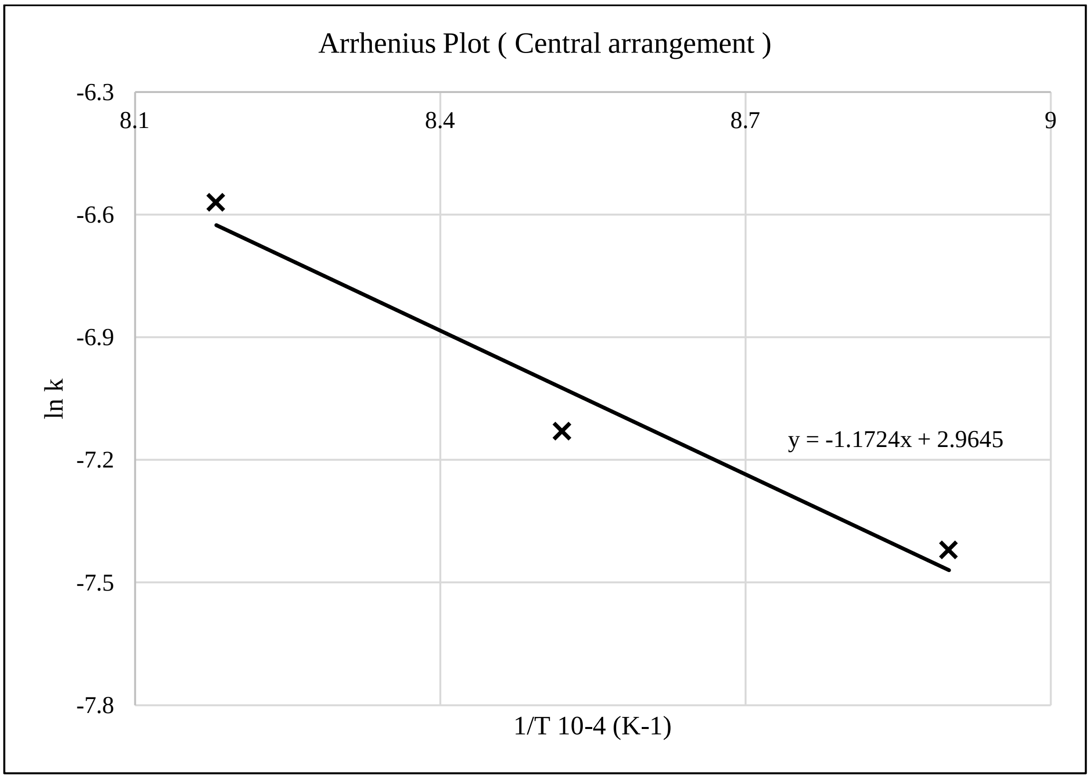


Figure-5.25: Arrhenius plot for the samples reduced in central arrangement

5.4.2.4 Activation energy (Ea) for central arrangement: Refer table 5.5

Table 5.5: The activation energy calculated from the slope of the Arrhenius plot of the samples reduced in central arrangement.

Slope of Arrhenius plot **(-Ea/R) = - 1.1724 × 10^4**	**Activation energy** **= 97.47 KJ/ Mole**

5.4.3 Alternate concentric arrangement: Refer figure 5.26

5.4.3.1 Isothermal kinetic plot for alternate concentric arrangement

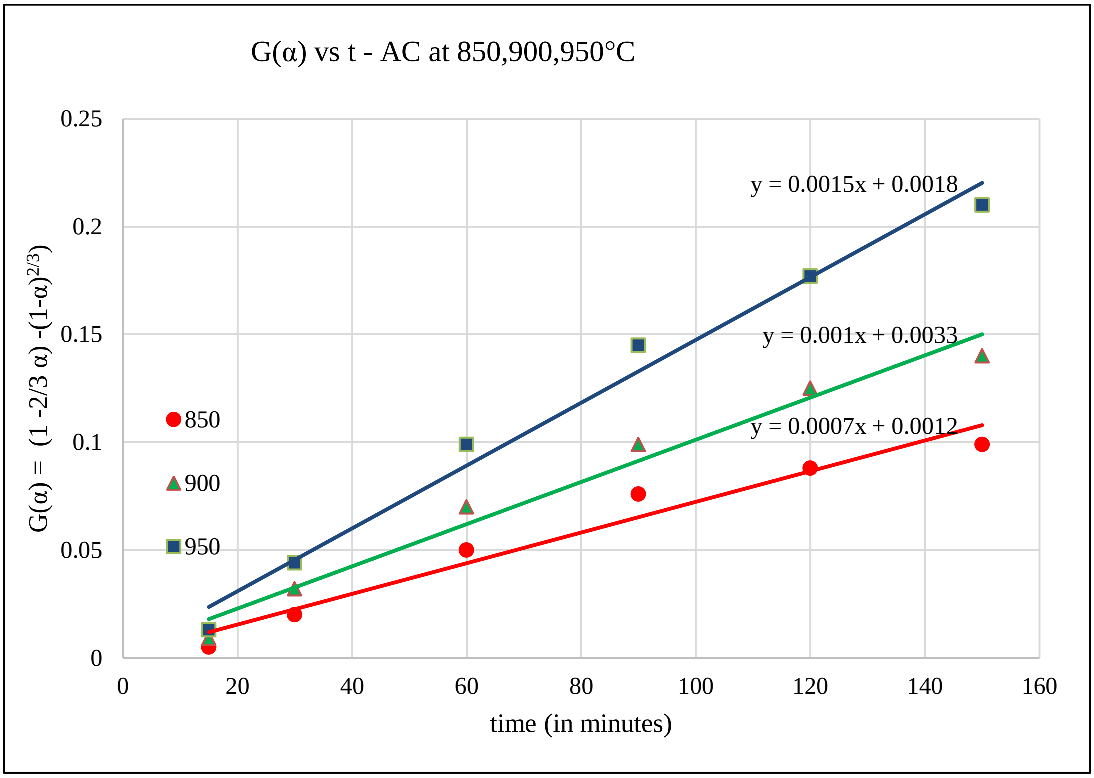


Figure-5.26: Isothermal kinetic plots for the samples reduced in alternate concentric arrangement following the rate control mechanism equation: $\mathbf{G\ (\alpha) = (1 - \frac{2}{3}\ \alpha) - (1 - \alpha)^{2/3}}$

5.4.3.2 Rate constant (k) values for alternate concentric arrangement: Refer table 5.6

Table 5.6: The value of rate constant (k) and ln k of samples reduced in alternate concentric arrangement at different temperatures.

Alternate concentric arrangement		
Temperature (°C)	**Rate constant (k)**	**ln (k)**
850	0.0007	-7.26
900	0.001	-6.91
950	0.0015	-6.5

5.4.3.3 Arrhenius plot for alternate concentric arrangement: Refer figure 5.27

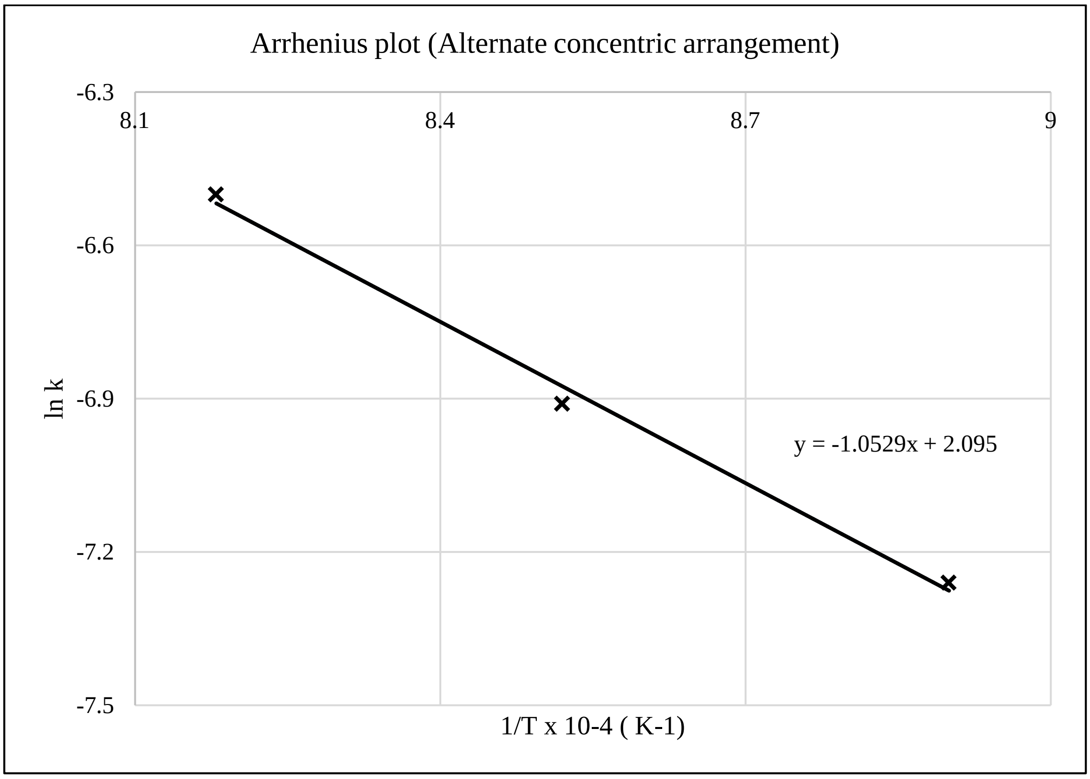


Figure-5.27: Arrhenius plot for the samples reduced in alternate concentric arrangement

5.3.3.4 Activation energy (Ea) for alternate concentric arrangement: Refer table 5.7.

Table 5.7: The value of activation energy calculated from the slope of the Arrhenius plot of the samples reduced in alternate concentric arrangement.

Slope of Arrhenius plot (-Ea/R) = - 1.0529 × 10^4	**Activation energy = 87.53 KJ/ Mole**

5.4.4 Layered arrangement

5.4.4.1 Isothermal kinetic plot for layered arrangement: Refer figure 5.28

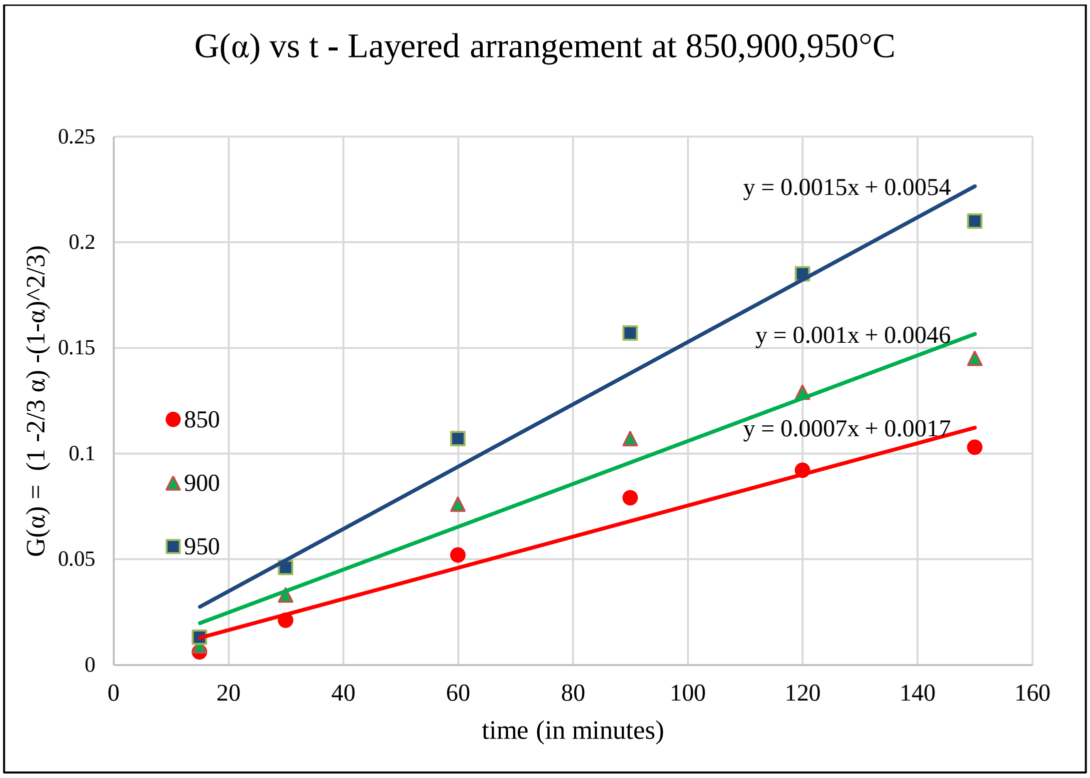


Figure 5.28: Isothermal kinetic plots for the samples reduced in layered arrangement following the rate control mechanism equation: $\mathbf{G}\,(\alpha) = (1 - \frac{2}{3}\,\alpha) - (1-\alpha)^{2/3}$

5.4.4.2 Rate constant (k) values for layered arrangement: Refer table 5.8

Table-5.8: The value of rate constant (k) and ln k of samples reduced in layered arrangement at different temperatures.

Alternate concentric arrangement		
Temperature (°C)	**Rate constant (k)**	**ln (k)**
850	0.0007	-7.13
900	0.001	-6.81
950	0.0015	-6.5

5.4.4.3 Arrhenius plot for layered arrangement: Refer figure 5.29

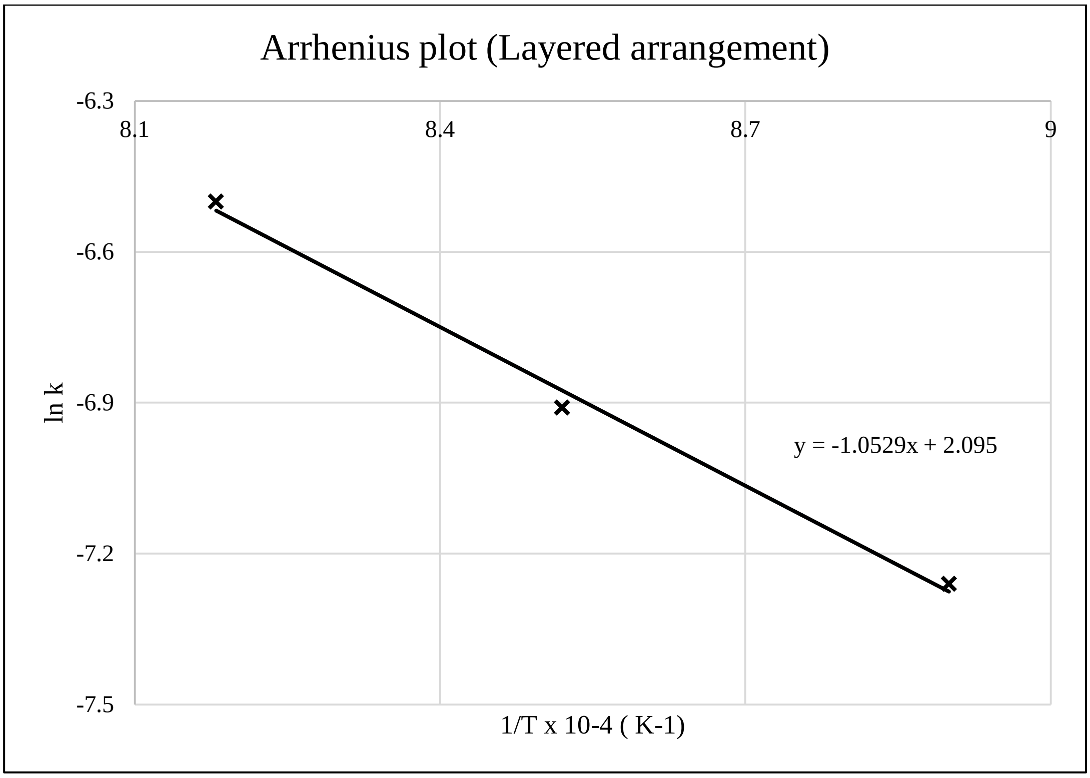


Figure 5.29: Arrhenius plot for the samples reduced in layered arrangement

5.4.4.4 Activation energy (Ea) for the layered arrangement: Refer table 5.9

Table 5.9: The activation energy calculated of samples reduced in layered arrangement.

Slope of Arrhenius plot (-Ea/R) = - 1.0529 × 10^4	**Activation energy = 87.53 KJ/ Mole**

5.4.5 Comparison of Activation energy (Ea) of all arrangements

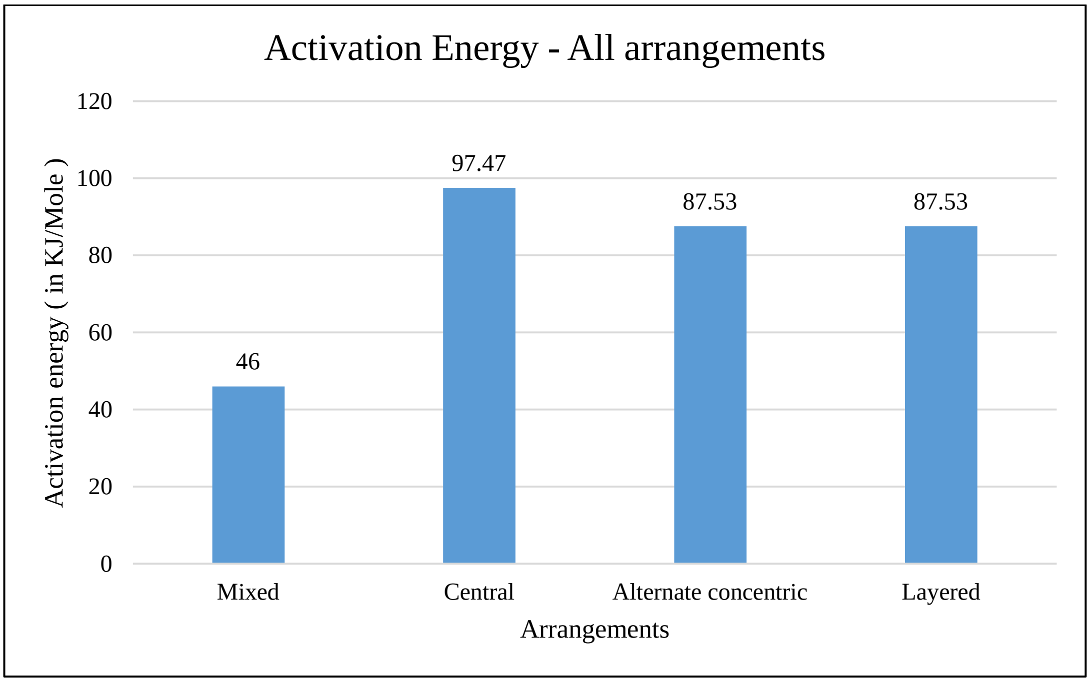


Figure-5.30: The value of overall activation energy in different arrangements.

***Result of Activation energy (Ea)*:** For any system to give product from the reactant or to start the chemical reaction requires energy (even in the exothermic process during starting). The activation energy is that energy which must be available to the system to start that chemical reaction. Some process may require less or some require high activation energy, according to the conducive conditions available for running the process. Here, in research work when the reduction of samples carried out in different arrangements the some arrangements possess better conditions to start the reduction reaction and some possess less. This easiness measured in terms of requirement of activation energy measured in terms of kilo joule per mole (KJ/Mole). The Arrhenius formula signifies higher the activation energy, slower the reaction be. Certainly the catalyst presence reduces the energy barrier or the activation energy required to run the reaction. But the catalyst is available in same amount in all the samples reduced in different arrangements. So the difference in activation energy will be due to the rate of reaction acting in different arrangements. In the final study, it was found out that the minimum activation energy for the system was required in samples reduced in mixed arrangement (46 KJ/Mole). The experimental data result of the alternate concentric and layered arrangement sample were near about same, so the activation energy for both systems were also found to be same (87.53 KJ/Mole). The highest activation energy found to be in central arrangement (97.47 KJ/Mole). So, the maximum rate of reaction was found in mixed arrangement, then in layered and alternate concentric and last in central arrangement. The discussion for the results obtained of final study are more elaborately explained in result and discussion chapter. Before that chapter, the samples condition before and after reduction in final study was tried to be understood by their instrument analysis.

5.5 Characterization studies.

It was found out during the characterization studies that the condition of the samples after the reduction was near about same when reduced in any arrangement. However, the presence of elements, their respective phases and surface conditions of sample particles becomes different due to the reduction. So to check the effect of reduction on mill scale, different characterization techniques such as SEM, XRD and EDS were employed in the research work.

5.5.1 SEM (Scanning electron microscope)

Samples of unreduced mill scale of particle size 90-150µm and reduced mill scale of mixed arrangement, reduced at temperature 950°C for 150 minutes of particle size 90-150µm are compared to each other at various degree of magnifications, shown in figures 5.31 to 5.33.

5.5.1.1. SEM micrograph of unreduced mill scale

Unreduced mill scale of particle size = 90-150 µm, at magnification = 5000X

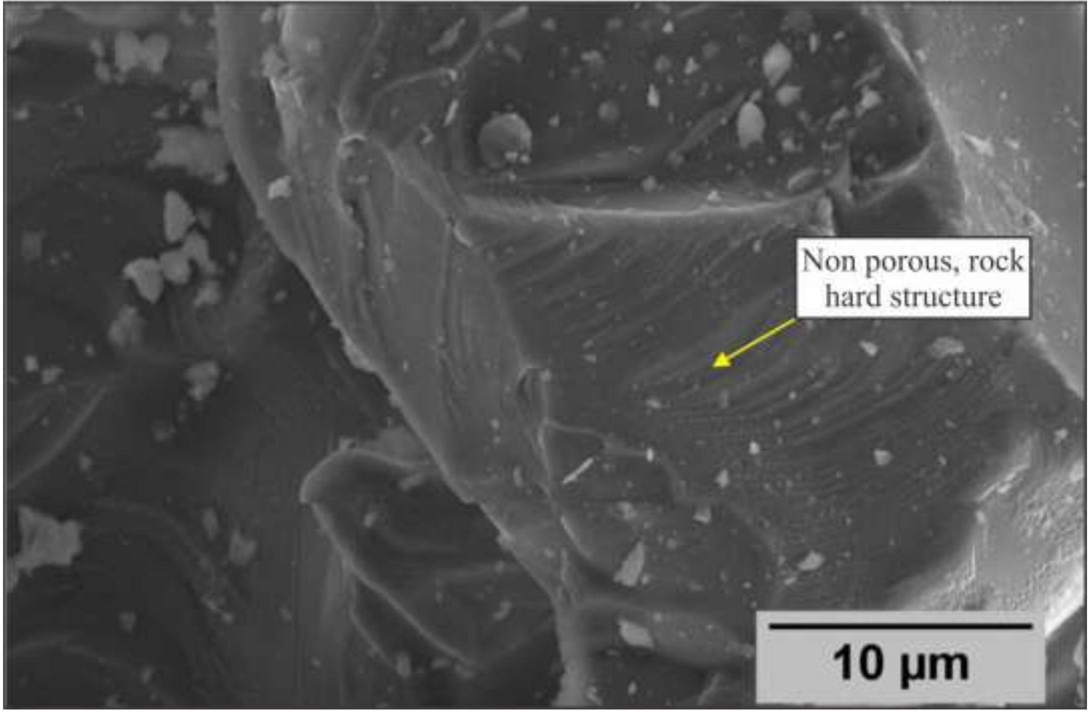


Figure-5.31: SEM micrograph of mill scale sample of particle size 90-150 microns at magnification of 5000X

5.5.1.2 SEM micrograph of reduced mill scale

Reduction parameters:

- Temperature (T) = 950°C,
- Time (t) = 150 minutes
- Particle size (P.S) = 90-150 microns
- Arrangement = Mixed

Reduced mill scale: T = 950°C, t = 150 min, P.S = 90-150 µm, Magnification = 5000X

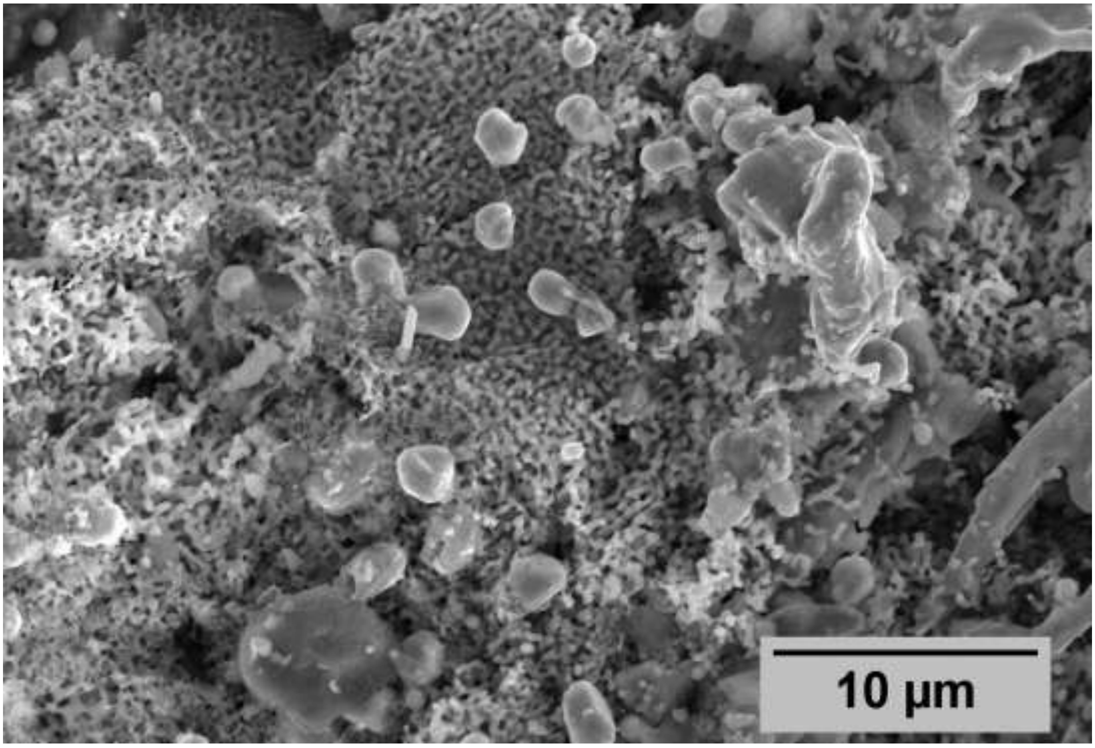


Figure 5.32: SEM micrograph of reduced mill scale sample of particle size 90-150 microns at magnification of 5000X. The sample was reduced at 950°C for 150 minutes

Result: SEM micrograph of unreduced and reduced mill scale

The micrograph of mill scale of particle size 90-150 microns (figure 5.31) shows clearly that the surface structure looks to be stone like hard and no porosity viewable on it. The micrograph of reduced mill scale sample (figure 5.32) clearly shows the changes occurs at the surface of mill scale after the reduction. Lots of porosity generated on the sample due to the removal of oxygen from the iron oxides, on account of reduction. The stone like hard structure of mill scale changes into fine spongy structure. The porous and spongy structure spread all over the micrograph.

5.5.1.3. SEM micrographs of mill scale and reduced mill scale at different magnifications.

The similar change in surface morphology observed by studying the same sample micrographs at different level of magnification. Effect of reduction can be seen by comparing the samples of unreduced (fig 5.33 i, iii and v) and reduced mill scale (figures 5.33 ii, iv, vi) at same magnification.

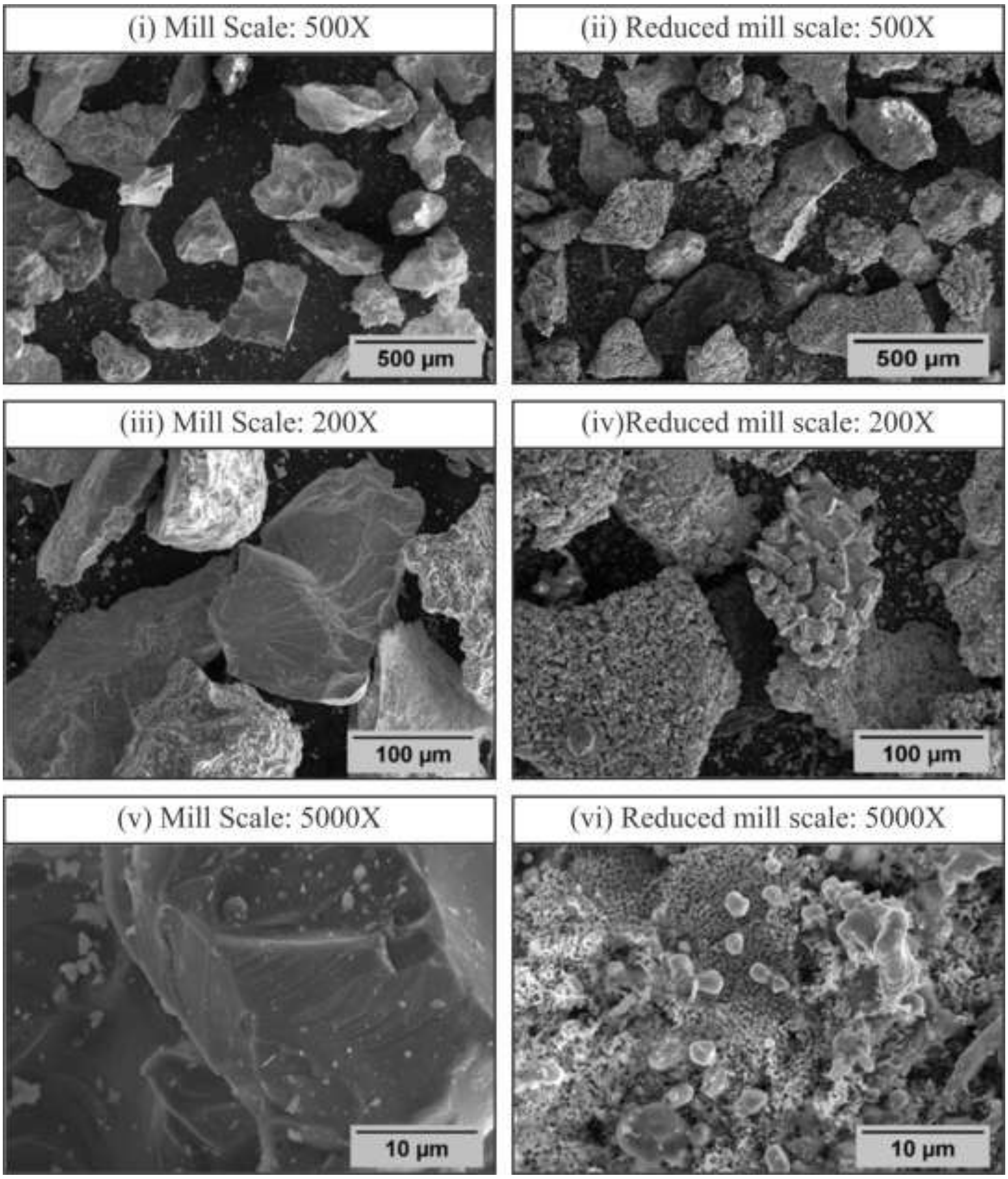


Figure-5.33: Micrographs of mill scale and reduced mill scale sample at different level of magnifications. Figure (i), (iii) and (v) micrographs of mill scale and (ii), (iv) & (vi) of reduced mill scale at magnification of 500, 200 & 5000X.

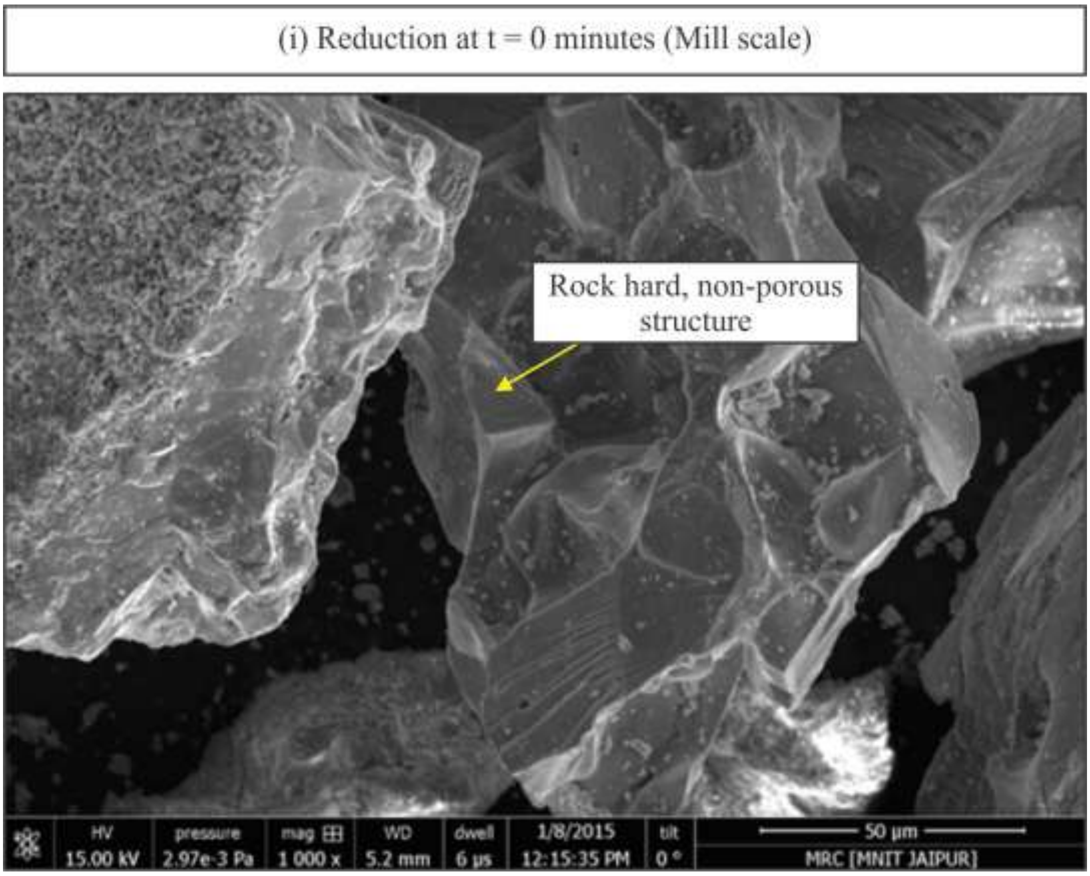
5.5.1.4. SEM micrographs for understanding the effect of reduction at different timings:

Reduction parameters:

- Temperature (T) = 950°C
- Arrangement = Mixed
- Particle size (P.S) = 90-150 microns
- Time (t) of study = 0, 30, 60, 90, 120 and 150 minutes

Note: In order to clearly view the effect of reduction at different timings on surface of same sample, the micrographs were taken at one fixed magnification (1000X) and scale (50µm) for different timings of reduction, as shown in figures 5.34 to 5.39.

(i) Reduction for t = 0 minutes (Mill scale)



(i) Reduction at t = 0 minutes (Mill scale)

Rock hard, non-porous structure

Figure 5.34: Micrographs of unreduced sample, i.e. reduced at t = 0 minutes

Result: SEM micrograph for reduction at time = 0 minutes (Mill scale):

The micrograph revels the surface condition of the sample for reduction at time at zero minutes, i.e. the sample is unreduced mill scale. The sample surface looks rocky hard with no porosity.

(ii) Reduction at t = 30 minutes

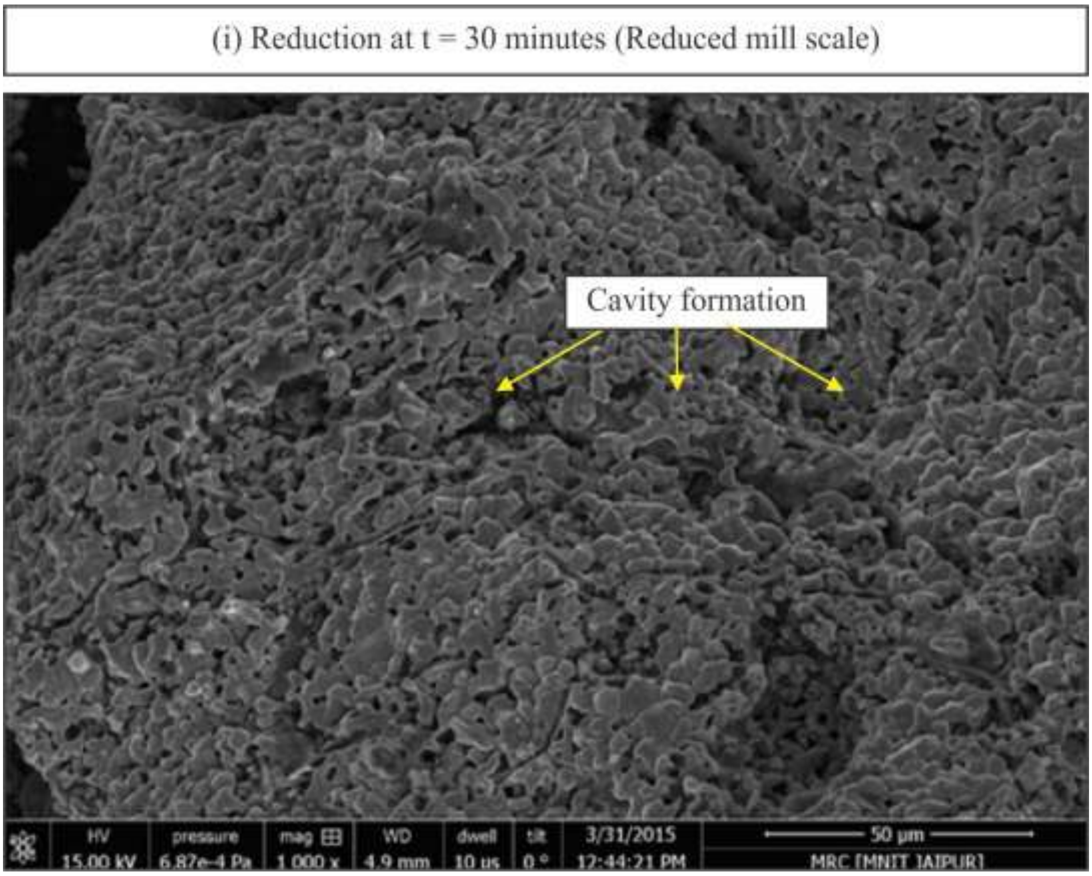


Figure-5.35: Micrographs of sample reduced at t = 30 minutes.

Result: SEM micrograph for reduction at t =30 minutes

The sample surface revels the changes occurred on reduction at time = 30 minutes. Cavities started forming at the surface of sample. The hard surface of the mill scale, started becoming porous. It was due to the removal of oxygen from the iron oxides present in mill scale due to the effect of reduction. The similar increment in cavities and porous structure seen when reduced carried out for higher timings.

(iii) Reduction at 60 minutes

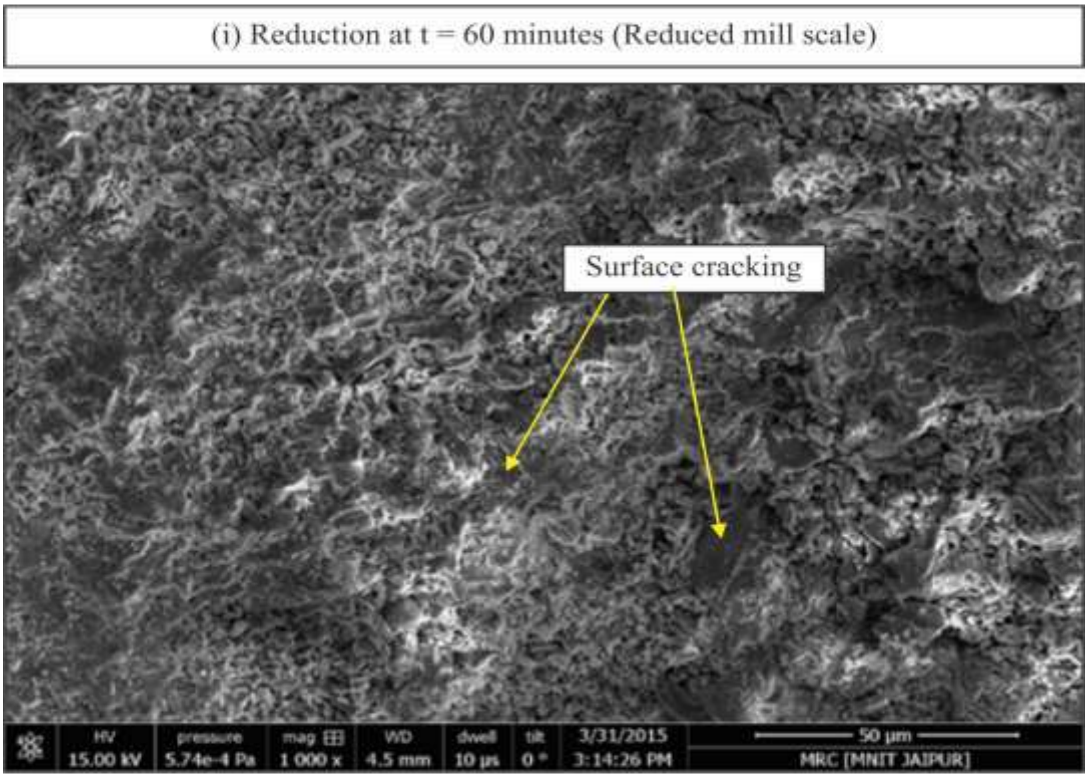


Figure-5.36: Micrographs of sample reduced at t = 60 minutes.

(iv) Reduction at 90 minutes

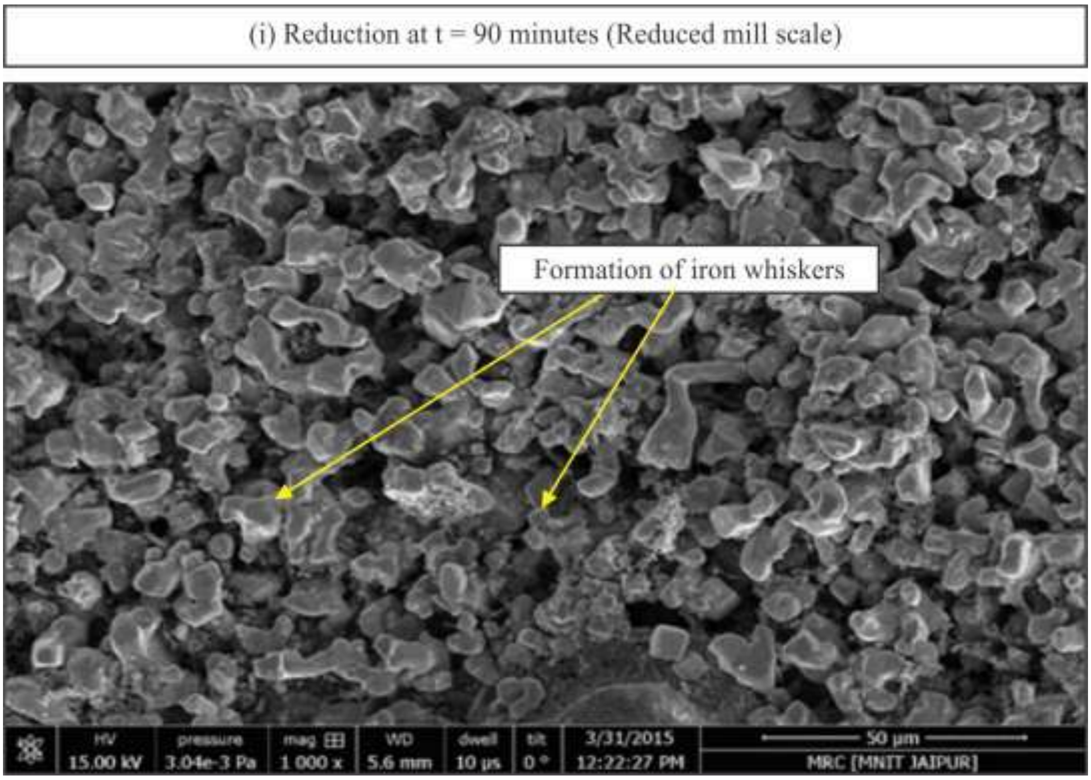


Figure-5.37: Micrographs of sample reduced at t = 90 minutes

Result: The rock hard surface of mill scale got broken, cracked into small fragmental parts, leads to the formation metallic iron whiskers, signifies thatiron oxides in the mill scale broken down into metallic iron with the removal of oxygen.

(v) Reduction at 120 minutes

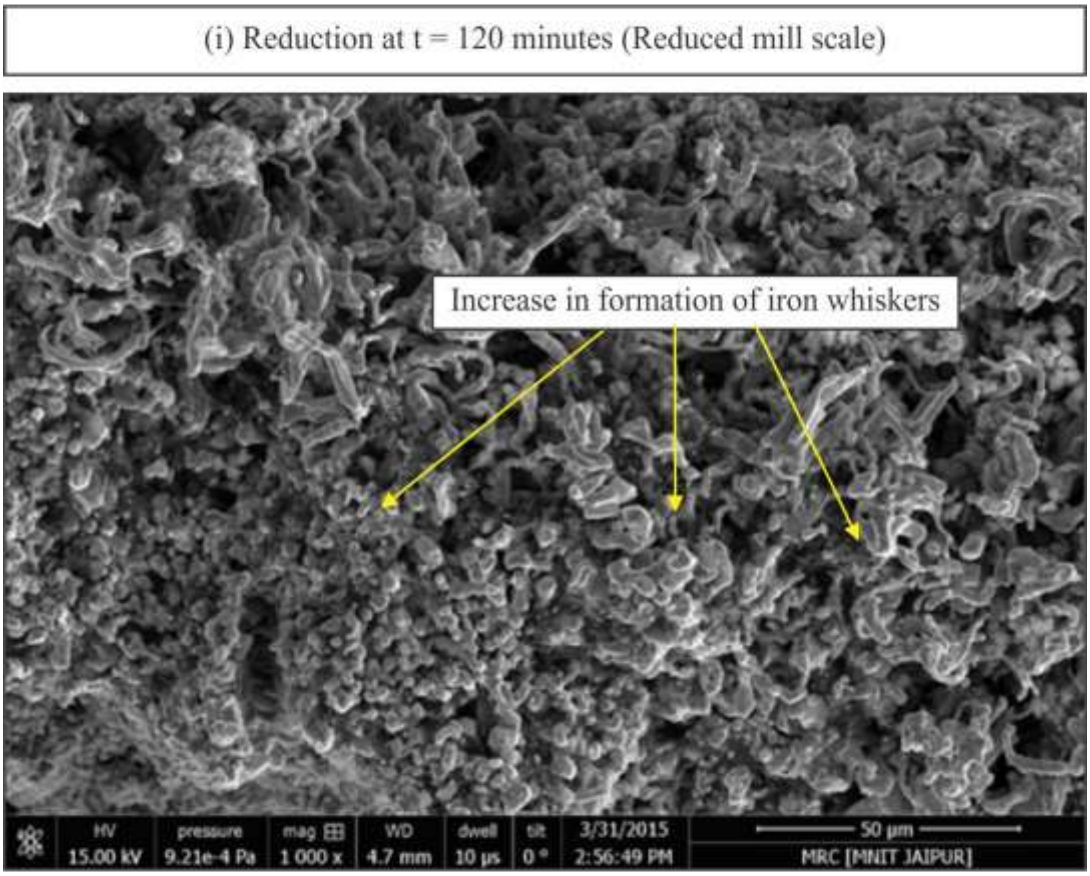


Figure-5.38: Micrographs of sample reduced at t = 120 minutes

(vi) Reduction at 150 minutes

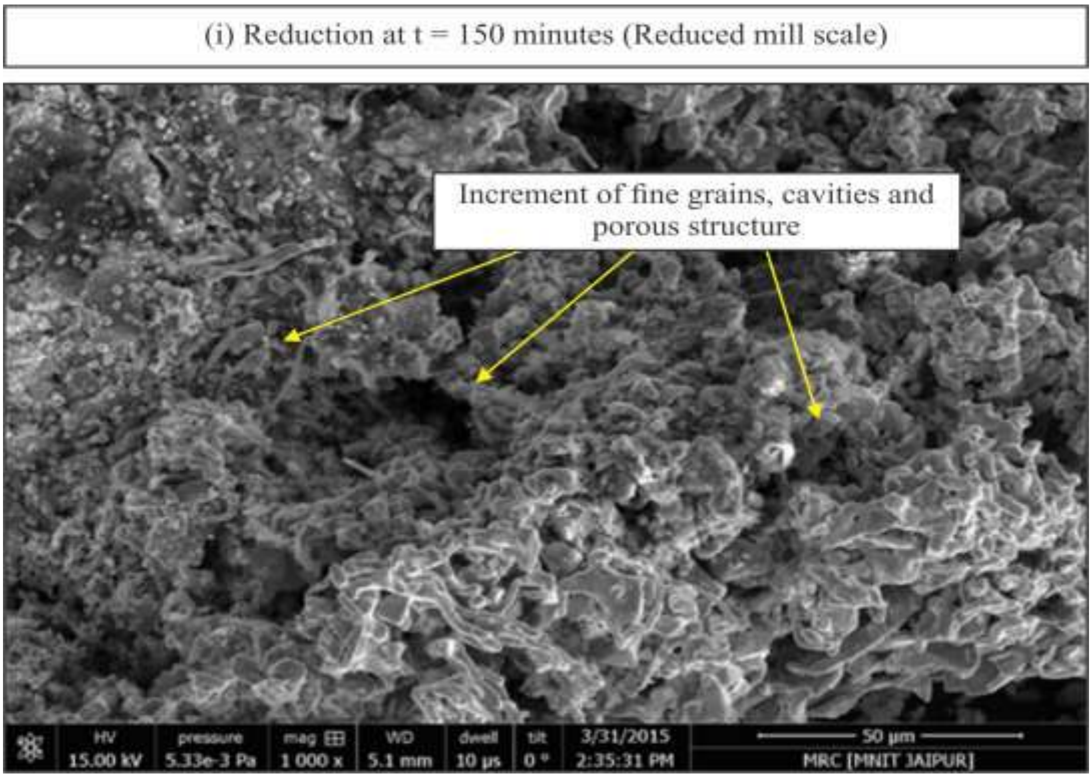


Figure-5.39: Micrographs of sample reduced at t = 150 minutes

Result: The similar increment in cavities, porous structure and fine grains was found in micrographs, when reduction carried out for higher timings (120 and 150 minutes).

5.5.2 EDX (Energy dispersive x-ray): Surface mapping

5.5.2.1 Surface mapping of mill scale sample (P.S: 90-150 microns) by EDX.

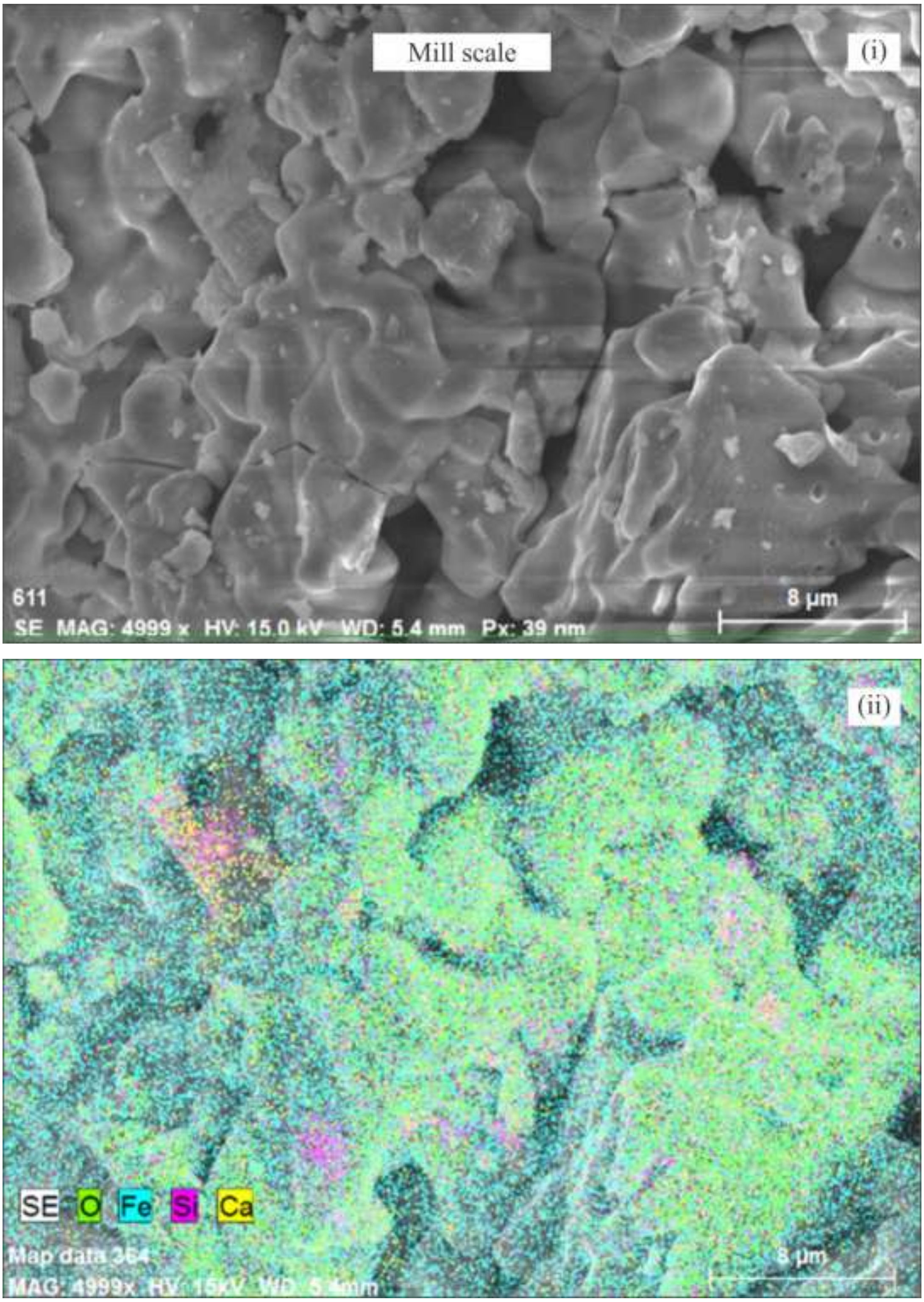


Figure-5.40: The surface mapping of the mill scale sample by EDX. (i) Micrograph of mill scale under study and (ii) combined concentration of elements in the area under consideration.

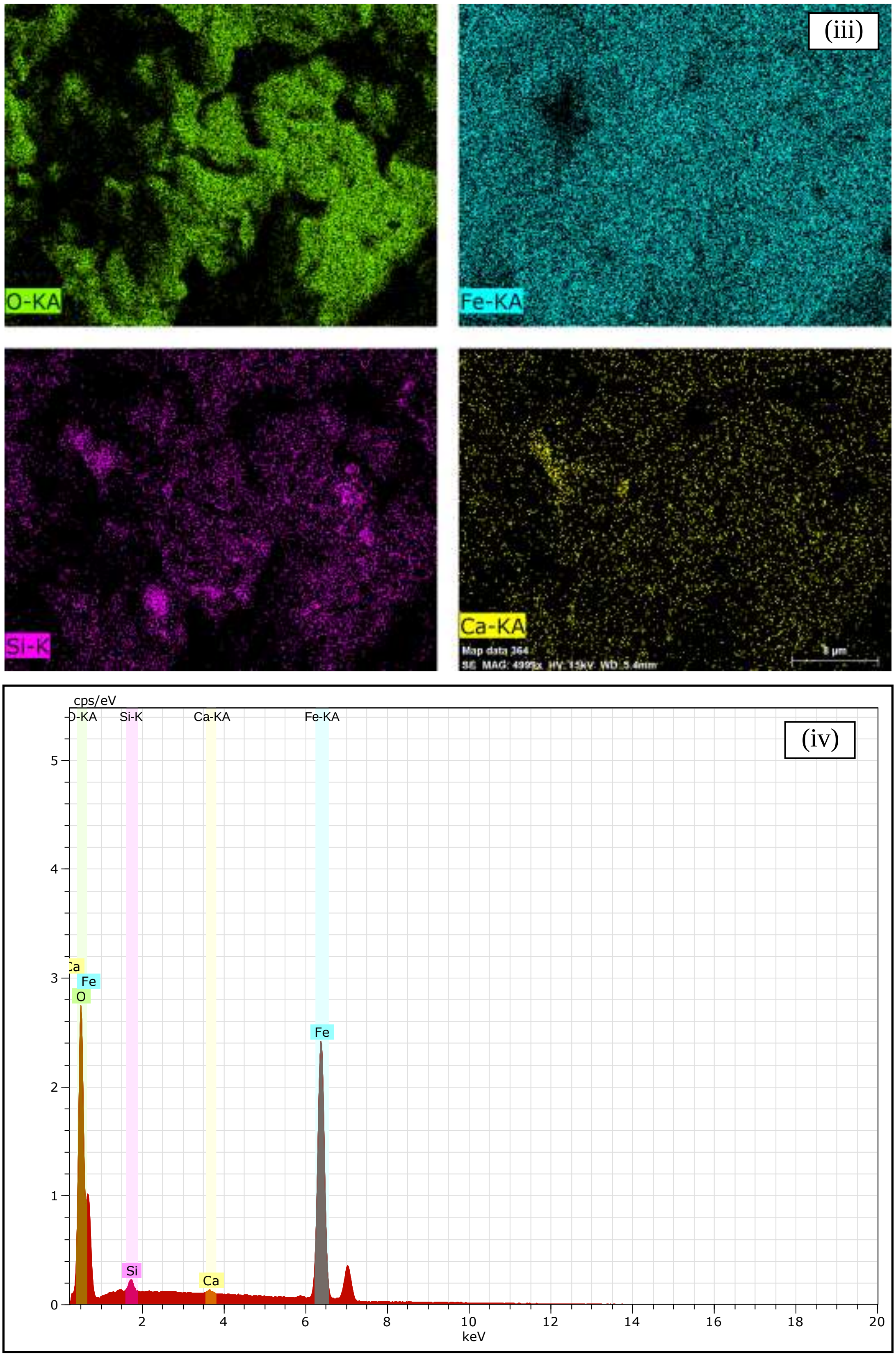


Figure 5.40: (iii) The individual concentrations of elements in the area under consideration and (iv) the intensity graph of various elements present at the surface mill scale done by EDX.

5.5.2.2 Surface mapping of reduced mill scale by EDX

Sample reduced of particle size 90-150 microns, at Temperature = 950°C, time = 90 minutes in mixed arrangement

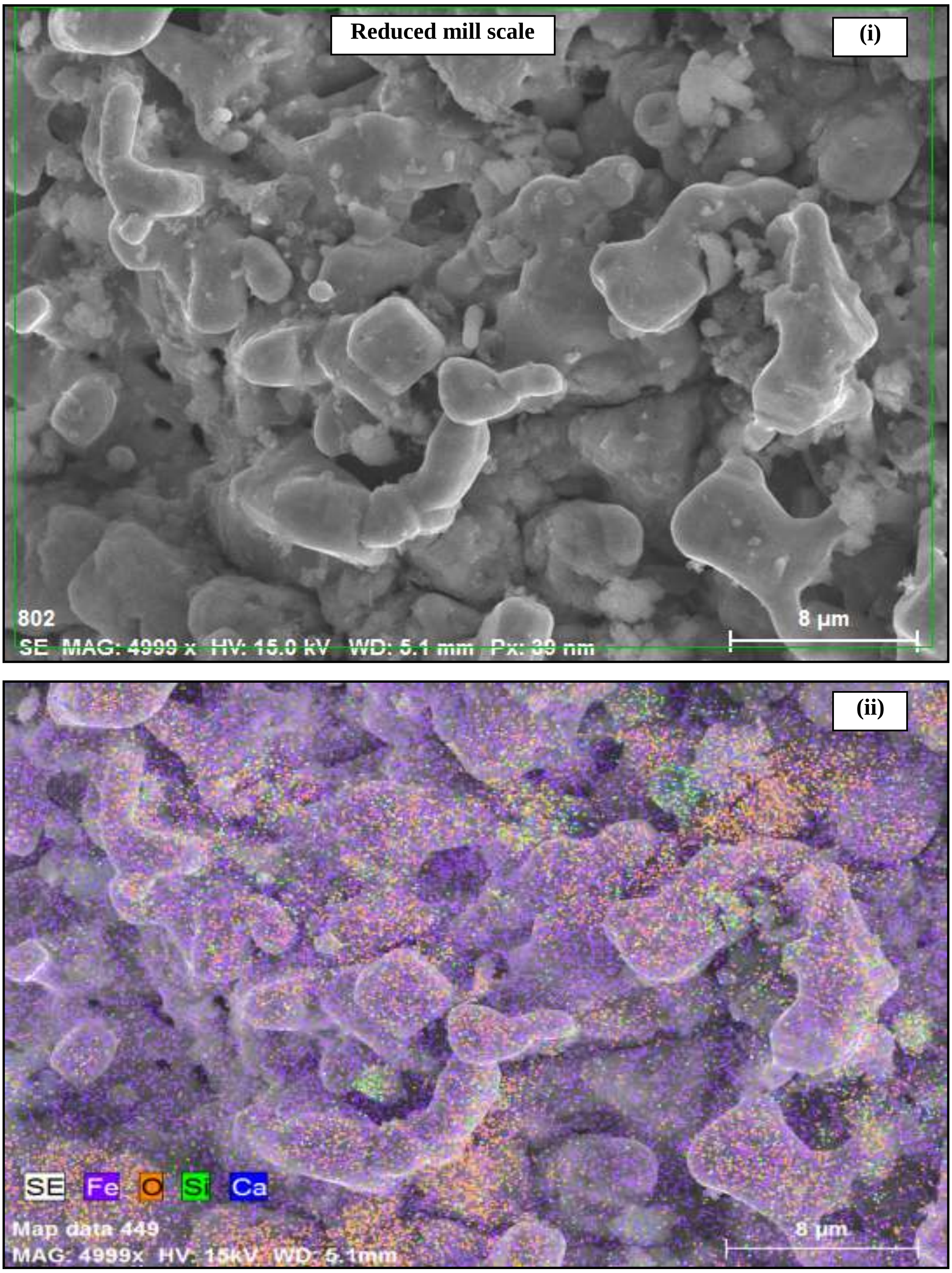


Figure 5.41: The surface mapping of the reduced mill scale sample by EDX. (i) Micrograph of reduced mill scale under study and (ii) combined concentration of elements in the area under consideration.

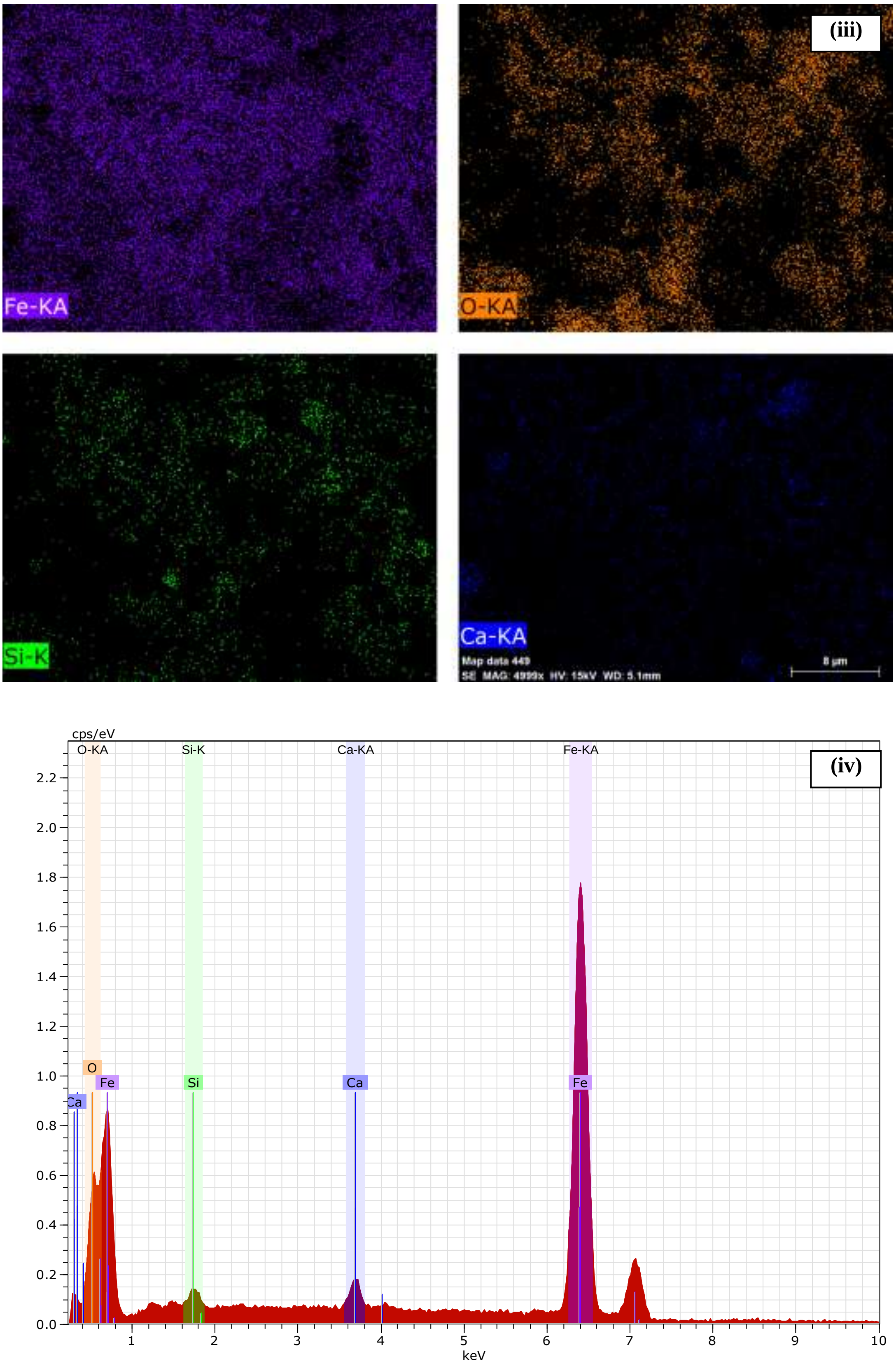


Figure 5.41: (iii) The individual concentrations of elements in the area under consideration and (iv) the intensity graph of various elements present at the micrograph of reduced mill scale done by EDX

Result of surface mapping by EDX: The surface mapping by EDX of unreduced and reduced mill scale sample clearly show the concentration oxygen got decreased from the surface of sample on account of reduction and the concentration of iron increased w.r.t other elements.

5.5.3 XRD (X- Ray Diffractometer)

5.5.3.1 Mill Scale: Sample (90-150µm)

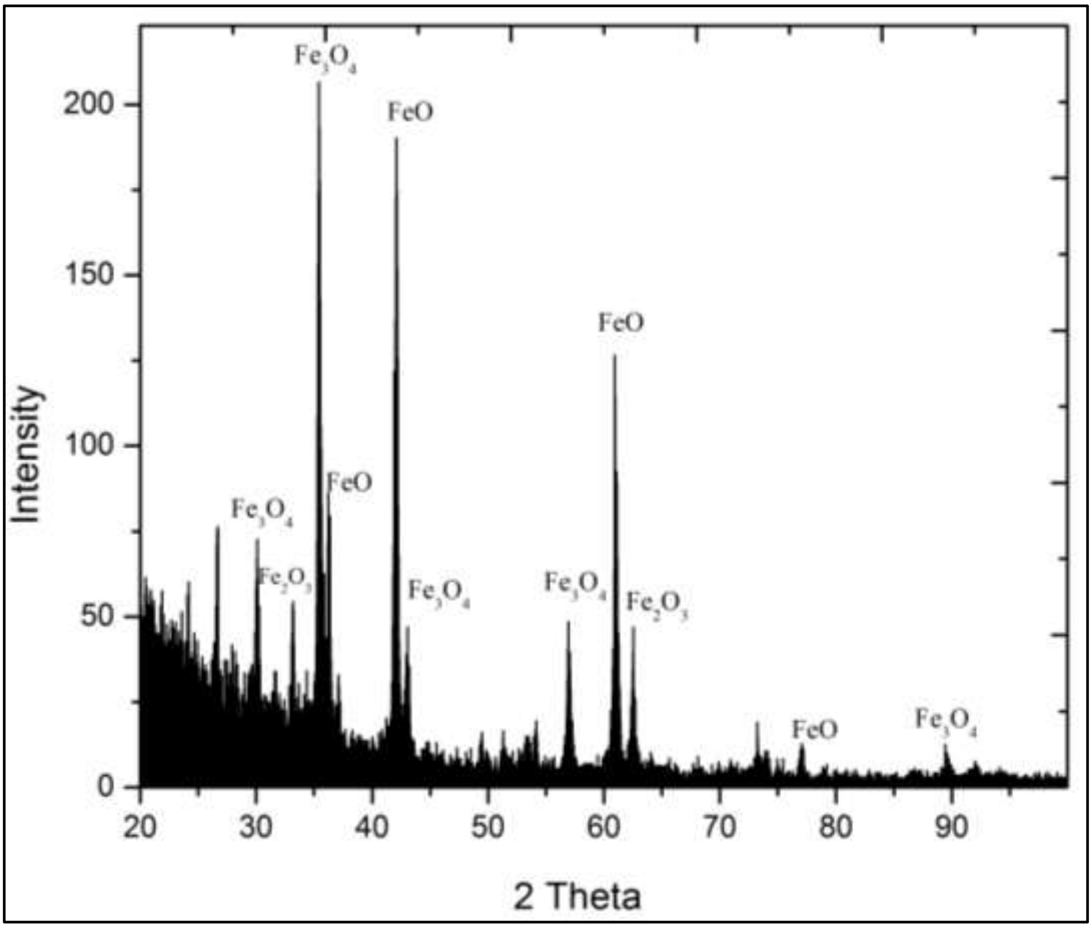


Figure-5.42: XRD plot of mill scale sample of particle size 90-150 µm, showing various peaks of different oxides of iron.

XRD- Mill Scale sample

The XRD plot of mill scale (figure 5.44) shows the presence of various oxides – hematite (Fe_2O_3), magnetite (Fe_3O_4) and wustite (FeO). The peaks of oxides confirmed from the standard JCPDF cards. Peaks of Fe_2O_3 confirmed by JCPDF no. – 00-033-0664, Fe_3O_4 by JCPDF no. - 01-071-6336 and 00-019-0629 and FeO by JCPDF no. - 00-046-1312 and 00-006-0711.

5.5.3.2 XRD of Reduced Mill Scale:

Sample (Mixed arrangement, particle size: 90-150µm, T= 950°C, t = 150 minutes)

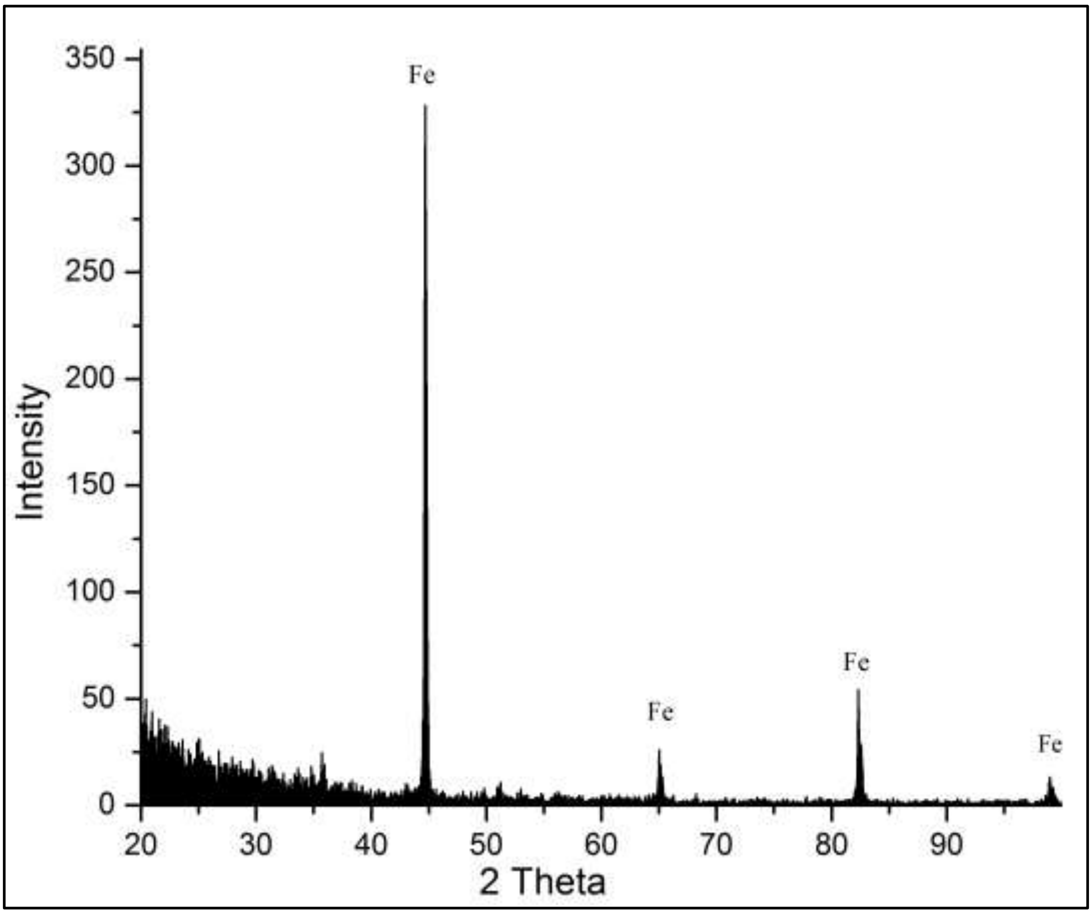


Figure-5.43: XRD plot of direct reduced iron sample reduced at 950°C, for 150 minutes in mixed arrangement.

XRD- Direct reduced iron sample

The XRD plot of mill scale sample reduced at 950°C, for 150 minutes in mixed arrangement, shown in figure 5.45. Samples reduced in any arrangement at 950 °C almost shows the same XRD plot, so a single XRD plot used to show the effect of reduction on appearance of metallic iron and disappearance of iron oxide phases. The reduced mill scale XRD plot clearly shows only metallic iron peaks at different position, confirmed by standard JCPDF card no. 00-006-0696, and all the iron oxides peaks got disappeared due to removal oxygen by reduction.

5.5.3.3 XRD for understanding the effect of reduction at different temperatures

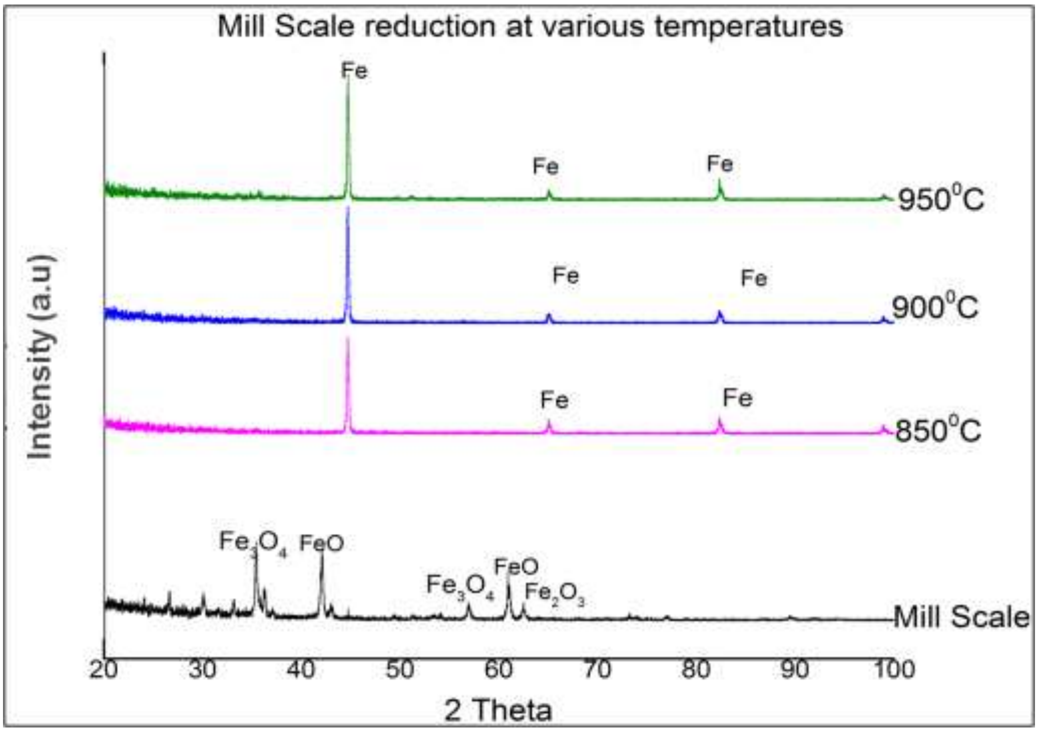


Figure-5.44: XRD plot of samples of mill scale reduced at different temperature.

Result of XRD: The stacked XRD plot (figure 5.46) shown the effect of temperature on reduction. The temperature effect on reduction of mill scale was similar in samples reduced in any arrangement, so XRD plot of any one arrangement was shown. The mill scale sample of particle size 90-150 microns at the bottom of the plot shows the peaks of various iron oxides. The peaks of iron oxides disappears on reduction and metallic iron peaks appears, and the peak intensity increases with increase in reduction temperature. It signifies that almost all iron oxides got reduced to metallic iron and represents good reduction. The peaks of Fe_2O_3 confirmed by JCPDF card no. - 00-33-0664, Fe_3O_4 by 01-071-6336 and FeO by 00-006-0711.

5.5 RESULTS AND DISCUSSION OF FINAL STUDY:

5.6.1. Effect of furnace holding time

With increase in furnace holding time, the reduction increases (understandable from figures 5.2 to 5.7). The reduction so happened, was by solid carbon in coal, and by carbon monoxide thus produced during the process. It was observed during the experimental work that whole mass in crucible takes around 15 minutes to reach to reduction temperature, because the degree of reduction in different arrangements samples are nearly same within starting 15 minutes of reduction. The reduction process at high temperatures becomes effective in lesser time and started reducing the mill scale by carbon in coal and carbon monoxide thus produced and by both. As the time increases, the carbon monoxide produced during the reduction, tries to cover all possible regions of mill scale and converts it into reduced mill scale. If the sufficient holding time remains available for reduction process, then most of the iron oxides present in mill scale gets converted into metallic iron. Certainly the reduction process remains fast initially, due to more concentration of coal- to give carbon and carbon monoxide for reduction and more surface availability of mill scale to be get reduced. Later with increase in holding time the reduction process slowly slows down as visible in the degree of reduction graphs of all arrangements. In all arrangements, up to 90 minutes holding time, the rate of reduction increases steadily but later from 120 to 150 minutes the reduction rate decreases. As all the arrangements follow different rate of reaction, so different values of reduction was obtained at different furnace holding time at any fixed temperature.

5.6.2. Effect of furnace temperature

With the increase in furnace temperature, the reduction increases. It was evident from all the degree of reduction graphs (shown in figures 5.2 to 5.4) that as the furnace temperature was increased from 850 to 950^{o}C, the reduction got increased in all samples. In all possible arrangements, the highest reduction was obtained in samples reduced at 950^{o}C.The higher temperature provides more energy to reactants to penetrate into core of mill scale particle and breaks the iron oxides into direct reduced iron. The reduction of iron oxides present in mill scale were carried out in series of steps. The hematite present in mill scale, reduces then into magnetite, then to wustite and finally to metallic iron. It means the oxygen present in iron oxides slowly and gently got removed from higher state of iron oxide to lower one. This process intensifies with increase in interface temperature between mill scale and coal mixture. The interface temperature gradually increases with increase in furnace temperature, thus reduction increases.

5.6.3. Effect of arrangement of mill scale and coal mixture in crucible

It was clear from the results of reduction of samples (shown in figure 5.6 to 5.8), reduced in different arrangement that the arrangement of raw materials in crucible effects the reduction of mill scale. The different arrangement provided different surface contact or interface area for reduction of iron oxides by carbon present in coal. Same as the different arrangements provided different ease for the carbon monoxide to flow inside the crucible and reduce the iron oxides present in mill scale. In same arrangement the reduction reaction dominated for chemical reaction between the iron oxide and reductant and in some arrangement the reduction dominated by the diffusion of reducing gas on the particle of mill scale.

1) **Central arrangement**: The minimum reduction, at all-time and temperatures found in samples reduced in central arrangement (figure 5.1 b) , it signifies that the reductants (carbon and carbon monoxide) approach to the iron oxides in central arrangement was slow as compared to the other arrangements. It was justified by the value of the activation energy, which was found to be maximum in central arrangement (shown in figure 5.30). The Arrhenius equation confirms, higher the activation energy, lower the rate constant or rate of reaction. It happened because the most of the reduction happens in centrally arranged sample was due to carbon monoxide, which was produced as the intermediate product by carbon gasification. It means the carbon gasification was the rate controlling step in the central arrangement. The reduction mechanism was diffusion controlled. It was confirmed by the result of kinetic data (shown in figures 5.13 to 5.15) which fits on the Ginstling-Brounshtein reaction model.
2) **Alternate concentric and layered arrangement**: As the result obtained in both the arrangements were almost equal, so discussed together. In the layered arrangement, two alternate layers of mill scale covered from the

layers of coal in crucible in horizontal direction (shown in figure 5.1 d) and same was there in the alternate concentric arrangement, but the layers in vertical direction (shown in figure 5.1 c). Here the surface contact or interface area of the mill scale particles with the coal were more as compared to the central arrangement. The reduction was both by carbon and as well as carbon monoxide. However the reduction reaction dominated by the diffusion of carbon monoxide, as confirmed by the result of kinetic data which fits on the Ginstling-Brounshtein reaction model (shown in figure 5.16 to 5.18 and figure 5.19 to 5.21). It means the carbon gasification was the rate controlling step. The reduction mechanism was diffusion controlled for both the arrangements. It was clear from the result of activation energy (87.3KJ/Mole) which was found to be equal in both arrangements (as shown in figure 5.30). However the reduction was found higher than central arrangement because the reduction surface contact area was more, as explained earlier.

3) **Mixed arrangement:** The highest reduction found in samples reduced in mixed arrangement at all time and temperature, as confirmed by the graphs of degree of reduction (shown in figure 5.5 to 5.7) and also from the result of activation energy (shown in figure 5.30). The activation energy was found minimum (46KJ/Mole). It signifies that the rate of reaction was fast in the given arrangement, which was justified by the values of rate constants. The kinetic data fits on the first order reaction model (as understandable from figures 5.10 to 5.12). It means the process was chemical controlled. Normally also the chemically controlled process possess higher rate of reaction as compared to diffusion controlled. The mixed arrangement provides the highest reduction among all arrangements.

4) **Overall comparison in terms of Activation energy:** The highest activation energy found to be in central arrangement (97.47 KJ/Mole). It was lesser than that obtained by A.K.M.M. Rahman *et al* [92] in similar (central) arrangement while reducing mill scale by better quality coal (having fixed carbon 52.6%). The other investigators like Ladin Camchi *et al*. [93] and Ornulap Yucel *et al*.[94] reduced the mill scale by coke (solid reductant) in form of pellets and the activation found in them were 48.5 and 55.2 KJ/Mole.

Their activation energies were greater than sample reduced in this research work in mixed arrangement having activation energy 46KJ/Mole. It means, the reduction was better than their findings, even utilizing low grade coal. So, the maximum rate of reaction was found in mixed arrangement, then in layered and alternate concentric and last in central arrangement.

5.6.4. Characterization study: The characterization study was carried out for the unreduced and reduced samples to check the effect of reduction on the samples. The SEM micrographs of mill scale shown the rock hard, non-porous surface (shown in figure 5.31) which was broken down into porous structure by the effect of reduction (shown in figure 5.32). Cavities, porous structure and formation of iron whiskers (shown in figures 5.35 to 5.38) concluded that the oxygen removed from iron oxides and metallic iron increased. The EDX surface mapping clearly shown (in figures 5.40 to 5.43), how the concentration of oxygen got decreased and iron got increased with respect to other elements the on to the surface of sample after reduction. The XRD analysis shows the decrease in peaks of iron oxides (or iron oxide phases) on account of reduction at different temperatures (shown in figure 5.46).

CHAPTER - 6

CONCLUSION AND FUTURE WORK

CONCLUSIONS:

1. The maximum value of reduction was found to be 93.5 % (or 0.935 degree of reduction) in sample reduced in mixed arrangement reduced at 950°C for 150 minutes (as shown in figure 4.4).
2. With increase in temperature and time, the reduction increases.
3. The rate of reduction increases steadily till 90 minutes and then the rate of reduction slow down or decreases from 90 to 150 minutes, as found in all arrangements.
4. All the arrangements possess different rates of reaction during the reduction process. The maximum reduction among all arrangements found in mixed arrangement, followed by layered arrangement, similar to that in alternate concentric arrangement and last in centrally arranged samples.
5. The activation energy was found minimum in mixed arrangement (46KJ/Mole) and highest in central arrangement (97 KJ/Mole).The alternate concentric arrangement and layered arrangement found to equal activation energy of 87.3 KJ/Mole.
6. The reaction mechanism in mixed arrangement was chemically controlled. The kinetic data fits on the first order equation: $G(\alpha) = F1 = -\ln(1-\alpha)$
7. The reaction mechanism in central, alternate concentric and layered arrangement was found to be diffusion controlled. Their kinetic data fits on with theGinstling-Brounshtein equation :$G(\alpha) = D4 = (1 - \frac{2}{3}\alpha) - (1-\alpha)^{2/3}$
8. With the decrease in particle size the reduction increases upto a limit, then decreases on extreme fineness of particle. In the part of preliminary study the highest reduction found in sample having particle size 90-150µm.
9. With increase in coal- mill scale ratio the reduction increases up to a limit becomes constant and then decreases.In the part of preliminary study the highest reduction found in sample having mill scale and coal ratio 1:1.3

10. With increase in percentage of limestone in crucible w.r.t weight mill scale the reduction increases up to limit and then becomes constant. In the part of preliminary study the highest reduction found in sample having 10% limestone and on further increase of coal the reduction remains constant.
11. The little deviation of the kinetic data of samples reduced in different arrangements from the standard rate control equations was due to the effect of addition of catalyst which increases the rate of reaction.

FUTURE WORK:

1. Effect of particle size for different arrangements can be studied.
2. Effect of reduction of mill scale, if reduced by both coal and gaseous reductant in two different steps.
3. Effect of increasing the layers of mill scale in layered arrangement.
4. Effect of reduction of mill scale on changing the height or volume of crucible.
5. Effect of reduction of mill scale in rotary kiln by low grade coal.

REFRENCES

[1] Erfan Sharifi Kiasaraei , Masters thesis on “Decarburization and Melting Behavior of Direct-reduced Iron Pellets in Steelmaking Slag, University of Toronto 2010, pp3

[2] R. J. Fruehan, "Future steelmaking technologies and the role of basic research," Metall Mat Trans A Phys Metall Mat Sci, vol. 28 A, pp. 1963-1973, 1997

[3] Amit Chatterjee, “ Sponge iron production by direct reduction of iron oxide” , Chapter 1, pp 14, 2012

[4] Temkin Abdlkader, “Production of iron and steel”, Material science slide of Addis Ababa University, 2015

[5] T. Rosenqvist, Principles of Extractive Metallurgy. New York: McGraw-Hill, 1983.

[6] B. Anameric and S. Komar Kawatra, "Properties and features of direct reduced iron," Miner. Process Extr Metal Rev, vol. 28, pp. 59-116, Jan.-Mar., 2007

[7] Julius H. Strassburger, “Blast Furnace - Theory and Practice”, Gordon and Breach Science Publishers, New York, 1969

[8] E. T. Turkdogan, Fundamentals of Steelmaking. London: Institute of Materials, 1996.

[9] M. Jellinghaus, Electric Steelmaking. Düsseldorf: Stahleisen, 1989

[10] Jeremy A. T. Jones. Electric arc furnace steelmaking. 2008.

[11] B.V.R.Raja, N.Pal, P.L.Talwar, N.P.Jayaswal “Technologies for cost reduction in EAFs AlloySteels Plant”, Steel Authority of India Ltd. : Steelworld, 2005.

[12] J. A. Lepinski, “Iron by Direct Reduction”,Kirk-Othmer Encyclopedia of Chemical Technology.4 DEC 2000, pp 1

[13] A. K. Vaish, S.D. Singh and K.N.Gupta, “Potentialities of alternative Charge materials forthe electric arc furnace”, eprints.nmlindia.org/2825/1/97-105

[14] Dutta, S.K.; Roy Chowdhury, P.J. IE(I) J.—MM 1986,66(2), 91.

[15] Prasad, K.K. Steel, Metall. 2004, 6(8), 29.

[16] D. J. Haris et.al. Continuous casting of steel, vol. 1. Iron and steel soc. AIME (1983)

[17] Mohammad Sadat, “The effects of casting speed on steel continuous casting process”,Heat and Mass Transfer, December 2011, Volume 47, Issue 12, pp 1601–1609

[18] A.Badri, T. T. Natarajan, C. Snyder, K. D. Powers, F. J. Mannion, A. W. Cramb, “A mold simulator for the continuous casting of steel: Part I. The development of a simulator”,Metallurgical and Materials Transactions B, June 2005, Volume 36, Issue 3, pp 355–371

[19] M.Debapriya, “Rolling of Metals: Process and Principles”, Rolling of Metals, Your online library, 9556, 2014.

[20] Akpan, Emmanuel Isaac and Haruna, Idoko Andrew, “Structural Evolution and Properties of Hot Rolled Steel Alloy”, Journal of Minerals & Materials Characterization & Engineering, Vol. 11, No.4, pp.417-426, 2012

[21] S. K. Dutta, “Utilization of Iron & Steel PlantWastes by Briquetting/Pelletization, Mining & Mineral Processing Vol. 60 No. 7,2016, pp.158-164

[22] Sushovan Sarkar, Debabrata Mazumder, “Solid Waste Management in Steel Industry -Challenges and Opportunities”, International Journal of Economics and Management EngineeringVol:9, No:3, 2015

[23] Chkravarty T. K. and Panigrahi S. K., “Strategies for solid wastemanagement in SAIL steel plants”, Proceedings: NS-EWM, pp. 52-62, 1996

[24] Das. S. K , Kumar Sanay and Ramachandrarao P, “Exploitationof iron ore tailing for the development of ceramic tiles”, Wastemanagement, 20, pp. 725-72, 2000

[25] International Seminar on Waste Management in Iron and Steel Industryjointly organized by SAIL and IIPE, 9-10 May’ 2008, pp 1-192.

[26] Kumar Sanjay, Kumar Rakesh and Bandopadhyay Amitava (2006),“Innovative methodologies for the utilisation of wastes frommetallurgical and allied industries”, Conservation and recycling, 48, pp.301-314

[27] Perrinea Chaurand, Jeromea Rose, Jean-Yvesa Bottero and JérémiebDomas, “Environmental impact of BOF steel slag reused in roadconstruction: a crystallographic approach”, pp.1-80.

[28] Ramakrishna Konduru R. and Viraraghavan, (1997),”Use of slag for dyeremoval”, Waste Management, Vol. 17, pp. 483-488

[29] Subhra Dhara1, Somnath Kumar , B. C. Roy, “Management of Solid Wastefor Sustainability of SteelIndustry”, International Journal of Technology Innovations and Research (IJTIR) Volume 16, pp. 1-5, July 2015

[30] Sushovan Sarkar, “Solid wastes generation in steel industry and their recycling potential”, Conference: Management & utilisation of wastes from metal processing industries and thermal power stations, Volume: pp 1-14, 2015

[31] Jiří Bažan, Ján Kret, “Iron and Steelmaking”,Academic materials for the Economics and Management of Industrial Systems study, Edition: first, pp 70-102, 2015

[32] Saral Dutta. B. Tech. (Hons.), Executive Director, ISP & RMD, SAIL (Retired), “HOT ROLLING PRACTICE – An Attempted Recollection”,

[33] Raaft Farahat, Mamdouh Eissa, Gamal Megahed, and Amin Baraka, “Reduction of mill scale generated by steel processing”, Steel grips, Journal of steel and Related Materials,2010

[34] M. Graf, R. Kawalla, “Scale development on steel during hot strip rolling”, International Conference, ROLLING 2013, June 2013, organized by AIM, Acciaio.

[35] M.I. Martín, F.A. López, W. Sun, A. K. Tieu, Z. Jiang, Jose M. Torralba, “Production of sponge iron powder by reduction of rolling mill scale”, 2011

[36] W. Sun, A. K. Tieu, Z. Jiang, C. Lu, H. Zhu, Jose M. Torralba “Journal of Materials Processing Technology”, Vol. 140 (2003), pp 76–83.

[37] L. Camci, S. Aydin, C. Arslan, “Reduction of iron oxides in solid wastes generated by Steelworks”, Turkish J. Engineering Environment Science, 2002, pp 37-40.

[38] J.W. Park, J.C. Ahn, H. Song, K. Park, H. Shin, J.S. Ahn, “Reduction characteristics of oily hot rolling mill sludge by direct reduced iron method”,2002, pp 129-140.

[39] Santosh Chacko, Suresh Vasani, A.K.Ray, “Scale formation and its removal in Hot Rolling Process”, Lechler (India) Pvt. Ltd., Thane, India, 2013

[40] H. Saiki, Y. Marumo, “Journal of Materials Processing Technology”, Volume 140 (2003), pp 25–29

[41] Rounak Sneh Anand, Prakash Kumar, Dr. D.N.Paswan, “Conversion of Sponge Iron From Low Grade Iron ore and MillScale Through Simulating Tunnel Kiln Condition”, ournal of Mechanical and Civil Engineering, Volume 13, pp. 49-54, 2016

[42] Anupam Singhal, Dipendu Bhunia, Bartik Pandel, “Effect of Sand Replacement by Mill Scale on the Properties of Concrete”, International Journal of Engineering Technology Science and Research, Volume 2 Special Issue, March 2015

[43] Dayanand Paswan, M. Malathi, R.K. Minj & D. Bandhyopadhayay, “Mill Scale: A Potential Raw Material for Iron and Steel Making, Steel world 2015

[44] Green house gases from major industrial sources- III, Iron and Steel production, Report No. PH3/30, pp. 13-32, 2000

[45] Hendrikus Mattheus Wessels Delport, Masters Thesis on “The Development of DRI Process For Small Scale EAF-Based SteelMills,University of Stellenbosch, March 2010

[46] Sujay Kumar Dutta , Rameshwar Sah, “Direct Reduced Iron: Production”, Encyclopedia of Iron, Steel, and Their Alloys DOI: 10.1081/E-EISA-120050996

[47] Donskoi.E And Mcelwain.D.L.S Estimation and Modeling of Parameters forDirect Reduction. Metallurgical and Materials Transactions B ,34pp 93-102,2003

[48] J.-W. Park, J.-C. Ahn, H. Song, K. Park, H. Shin, J.-S. Ahn: Reduction characteristics of oily hot rolling mill sludge by direct reduced iron method, Conserv. Recy., 2002, 34(2), 129-140

[49] Pelton, A. D., and C. W. Bale, Thermodynamics, Direct Reduction Iron, Iron and Steel society, Warrendale, USA, 1999, pp 29.

[50] F. Grobler and R.C.A. Minnitt, “The increasing role of direct reducediron in global steelmaking”, The Journal of The South African Institute of Mining and Metallurgy, pp. 111-116, 1999

[51] C. Di Cecca, S. Barella, C. Mapelli, A. F. Ciuffini, A. Gruttadauria, D. Mombelli, E. Bondi, “Use of DRI/HBI in ironmakingand steelmaking furnaces”, La Metallurgia Italiana - n. 4, pp. 32-44, 2016

[52] A.Ghosh, A.Chatterjee. Ironmaking and Steelmaking:Theory and Practice . New Dehli : PHI learning Privatelimited, 2011

[53] Anameric, B. and Kawatra, S. K., ‘‘Natural gas based direct reductionprocesses.’’ Mineral Processing and Extractive Metallurgy Review, 2006

[54] Anameric, B. and Kawatra, S. K., ‘‘Coal based direct reduction processes.’’ Mineral Processing and Extractive Metallurgy Review, 2006

[55] A. Chatterjee, R. Singh and B.D. Panday Steel India, 6,1983,57.

[56] I.A. Mozer and G.H. Laferriere: Midrex direct reductlon plant.,International symposlum an the iron and steel industry. Brazil,October, 1973.

[57] L.A. Te111er, I.A. Mozer and Turcotte: Direct reductlon andsteel maklng at sidbec- Dosco. Iron steel Eng., 1974, 33-39.

[58] W, Karf: A new way from ore to steel US Ug the Mldrex directreduction process. 7th Annual meeting of the IISI, Johannsburg,8-10, october, 1973.

[59] Dutta, S.K.; Sah, R. Alternate Methods of Ironmaking S. Chand & Co Ltd: New Delhi, India, 2012.

[60] Dutta, S.K.; Roy Chowdhury, P.J.; Gadgeel, V.L. IE(I) J.—MM (Spl) 1988, 68(2), 52.

[61] Vijayavergia, R.K.; Chauhan, G.I.S. Awakening of theIndian Steel Industry: 2005–2020; Chatterjee, A., Ed.;IIM: Jamshedpur, India, 2006; 27.

[62] Chatterjee, A.; Sathe, A.V.; Singh, R.; Chakravarty, P.K.InProceedings of Symposium on Direct Reduction Processesin Iron and Steelmaking, 36th ATM of IIM: Rourkela,India, 1982; 133

[63] Roman-Moguel, Guillermo Julio, PhD Thesis “Kinetics of direct reduction of unagglomerated iron-ore with coal char, The University of British Columbia, 1984

[64] Roy.G.G , Kumar Amit Application of the Genetic Algorithm to Estimate the, Parameters Related to the Kinetics of the Reduction of the Iron Ore, CoalMixture. Metallurgical and Materials Transactions B, 36 ,2005, pp. 901-904

[65] Sandeep Kr Baliarsingh. & Barun Mishra, “Kinetics of iron ore reduction by coal and charcoal”, Thesis, NITR, 2008

[66] Rashmi Ranjan Pati & Vinay M, “Reduction Behaviour of Iron Ore Pellets”, Thesis, NITR, 2008

[67] Subhasisa Nath, “Study of Reduction kinetics of Iron ore Pellets by Noncoking coal”, Thesis, NITR, 2009

[68] Samir Kumar Pal, “Study of Reduction behaviour of Iron ore Nugget”, Thesis Jadhavpur University, 2009

[69] A.K.M Rahman, “Reduction of Mill Scale By Coal: Kinetic study and Effect of Process Variables.”, Thesis BUET, 2009

[70] H.S. Ray: Proc. Int. Conf. on Advances in Chemical Metallurgy, Vol.2, ICMS-79, BARCBombay, 1979, 43/11/1.

[71] Rene cypress and Claire Soudan- Moinet: Fuel, 59, Jan. 1980, 48.

[72] Rene Cypress and Claire Soudan-Moinet: Fuel, 60, Jan. 1981, 33.

[73] S. Paul and S. Mukherjee: Non-isothermal and isothermal reduction kinetics of iron ore agglomerates. Iron making and Steelmaking W: J, No.3, vol. 19, 1992.

[74] J.R. Sharp, G.W. Brindley and B.N. Narharl A char: J, Amer. Ceram. sec. 46, 1963, 364.

[75] A. Giess: J. Amer. Ceram. Sec, 43, 1963, 364.

[76] H.S. Ray' Trans. IIM 36(11), 1983, 11.

[77] G.J. Keattach and D. Doillmore: An Introduction to Thermogravimetry. 2nd Ed. Heyden (London), Ch. 5. 1975.

[78] Y. K. Rao: Metau. Trans., 2(1971), 1439.

[79] N. S. Srinivasan and A. K. Lahiri: Metall. Trans. B, 8B (1977),175.

[80] K. Otsuka and D. Kunni: J. Chem.Engng. Jpn., 2(1969), 46.

[81] M. C. Abraham andA. Ghosh:IronmakingSteelmaking, I (1979),14.

[82] C. Bryk and W. K. Lu: Ironmaking Steelmaking, 13 (1986), 70.

[83] P. C. Ghoshand S. N. Tiwari: J, Iron Steel Insl., 208 (1970),255.

[84] C. E. Seaton, J. S. Foster and J. Velasco: Trans. Iron Steel Inst.Jpn., 23 (1983), 490.

[85] J. K. Wright, K. MCG Bowling and A. L. Morrison: Trans. IronSteel Inst. Jpn., 21 (1981), 149.

[86] S. B. Sarkar andH. S. Ray: Trans. Iron Steellnst. Jpn., 28 (1988),l006.

[87] P. Basu, S. B. Sarkar and H. S. Ray: Trans. Indian Inst. Met.,(1989) 165.

[88] S.Mookherjee, H. S. RayandA. Mookherjee: Thermochim.Acta,95 (1985), 235.

[89] Sajal KumarDey.Biswanath Jana and Amitava Basumallick, “Kinetics and Reduction Characteristics of Hematite-Noncoking Coal Mixed Pellets Under Nitrogen GasAtmosphere”, ISIJ International, Vol. 33 (1993), No. 7, pp. 735-739

[90] Hongsheng Chena, Zhong Zhenga,, Wanyuan Sh, “Investigation on the Kinetics of Iron Ore Fines Reduction by CO inMicro-fluidized Bed, Hongsheng Chen et al. / Procedia Engineering 102 (2015) 1726 – 1735

[91] K M K Sinha, T.Sharma, D D Haldar, “Reduction of Iron Ore with Non Coking Coal”, International Journal of Engineering and Advanced Technology (IJEAT), ISSN: 2249 – 8958, Volume-3, Issue-3, February 2014

[92] A.K.M Rahman, “Reduction of Mill Scale By Coal: Kinetic study and Effect of Process Variables.”, Thesis BUET, 2009

[93] Çamci, L., Aydin, S. and Arslan, C., Reduction of iron oxides in solid wastes generated by steelworks. Turkish Journal of Engineering and Environmental Sciences, Vol.6, No.1, pp.37-44, 2001.

[94] Onuralp Yucel, Fahri Demirci, Ahmet Turan and Murat Alkan, “Determination of Direct Reduction Conditions of Mill Scale”, High Temperature Materials and Processes., Vol.32, No.4, pp. 405-412, 2013.

[95] Maurício Covcevich Bagatini, Victor Zymla, Eduardo Osório and Antônio Cezar Faria Vilela., “Characterization and Reduction Behavior of Mill Scale”, ISIJ International, Vol. 51., No. 7, pp. 1072–1079., 2011.

[96] N. M. Gaballah, A. F. Zikry, M. G. Khalifa, A. B. Farag, N. A. El-Hussiny, M. E. H. Shalabi., “Production of Iron from Mill Scale Industrial Waste via Hydrogen”, Open Journal of Inorganic Non-Metallic Materials, Vol.3, pp. 23-28, 2015

[97] C. Joshi, N. B. Dhokey, “Study of Kinetics of Mill Scale Reduction: For PM Applications”, Transaction of Indian Institute of Metals Vol.68., No. 1., pp. 31–35, 2015

[98] R. Farahat, M. Eissa, G. Megahed, and A. Baraka, “Reduction of mill scale generated by steel processing,” Steel Grips, vol. 8, pp. 88–92, 2010.

[99] N. A. El-Hussiny, F. M. Mohamed and M. E. H. Shalabi,“Recycling of Mill Scale in Sintering Process,” Science of Sintering, Vol. 43, No. 1, 2011, pp. 21-31.

[100] M. I. Martini, F. A. Lopez, and J. M. Torralba, “Production of sponge iron powder by reduction of rolling mill scale,” Ironmaking & Steelmaking, Vol. 39, No. 3, pp. 155–162, 2012.

[101] Ünal H.İ., Turgut, E., Atapek, Ş.H. and Alkan, A., “Direct Reduction of Ferrous Oxides to form an Iron-Rich Alternative Charge Material”, High Temperature Materials and Processes, Vol. 34, No.8, pp.751-756, 2015.

[102] Mamdouh Eissa, Azza Ahmed, and Mohamed El-Fawkhry, “Conversion of Mill Scale Waste into Valuable Products via Carbothermic Reduction”, Journal of Metallurgy, Hindawi Publishing Corporation, Volume 2015.

[103] Benchiheub, O., Mechachti, S., Serrai, S. and Khalifa, M.G., 2010. Elaboration of iron powder from mill scale. Journal of Materials and Environmental Science, 1(4), pp.267-276.

[104] Dayanand Paswan, M. Malathi, R.K. Minj & D. Bandhyopadhayay, “Mill Scale: A Potential Raw Material for Iron and Steel Making –, Steel world 2015

[105] Rounak Sneh Anand , Prakash Kumar and Dr. D.N.Paswan., Conversion of Sponge Iron From Low Grade Iron ore And Mill Scale Through Simulating

Tunnel Kiln Condition. IOSR Journal of Mechanical and Civil Engineering, pp. 49-54, 2016.

[106] T. Umadevi, A. Brahmacharyulu, P. Karthik, P. C. Mahapatra, M. Prabhu, and M. Ranjan,“Recycling of steel plant mill scale via iron ore sintering plant,” Ironmaking and Steelmaking, Vol. 39., No.3., pp. 222–227, 2012.

[107] Flores, B.D., I.V., Bagatini, M.C., Osório, E. and Vilela, A.C.F., “Study on reducing and melting behavior of mill scale/petroleum coke blend”. Tecnol. Metal. Mater. Miner Vol. 10, No.4, pp.365, 2013.

APPENDIX-1

Preliminary study 1: Effect of particle size

Particle size (in µm)	Fe (t)	DOR	% Reduction
30-90	83.86	0.882	88.2
90-150	84.66	0.914	91.4
150-210	82.98	0.842	84.2
210-270	81.97	0.796	79.6

Total iron calculated by the chemical analysis and Degree of reduction (DOR) calculated by the formula below:

$$\mathbf{DOR}(\boldsymbol{\alpha}) = \mathbf{K}\ \frac{\boldsymbol{Fe(t)^{DRI} - Fe(t)^{MS}}}{\boldsymbol{Fe(t)^{DRI} \times\ Fe(t)^{MS}}} \times \mathbf{100}$$

Calculation for value of K in the above formula of DOR (given weight of mill scale =15gram):

$$\boldsymbol{K = \frac{Weight\ of\ total\ iron\ in\ 15 gram\ of\ mill\ scale}{Weight\ of\ total\ oxygen\ in\ 15\ gram\ of\ mill\ scale}}$$

iv) Weight of total iron present in 15 gram of mill scale before reduction = 15 x 0.673 = 10.09 g, (because total in mill scale = 67.3%)

v) Weight of total oxygen present in 15 gram of mill scale before reduction = 15 x 0.2246 = 3.36 g (because total oxygen in mill scale = 22.46%)

vi) K = 10.09/3.36 = 3 (approximately)

APPENDIX-2

Mixed Arrangement : Reaction mechanism calculation method:

Time (min)	DOR
15	0.3
30	0.55
60	0.8
90	0.9

Enlarged graph is plotted between DOR vs time, and value of time checked out decimal integral values of DOR, there by the vales in below table to calculate further kinetic values

DOR	TIME	ln t	$t/t_{0.5}$	round off $t/t_{0.5}$	F1	D3	D4	R3
0.3	15	2.708050201	0.566037736	0.57	0.515	0.295	0.324	0.544
0.4	20	2.995732274	0.754716981	0.75	0.737	0.576	0.595	0.762
0.5	26.5	3.277144733	1	1	1	1	1	1
0.6	35	3.555348061	1.320754717	1.32	1.322	1.628	1.541	1.277
0.7	35	3.850147602	1.773584906	1.78	1.737	2.568	2.297	1.607
0.8	47	4.094344562	2.264150943	2.26	2.322	4.051	3.378	2.014
0.9	60	4.49980967	3.396226415	3.4	3.322	6.747	5.028	2.602

The experimental $t/t_{0.5}$ vales matched with the standard rate control equations, FI, D3, D4 and R3 data. The experimental data matches any among the equation, is the rate control equation for the arrangement reduction process. Similarly all other arrangements reaction mechanism can be identified

APPENDIX-3

List of publications:

1. Rahul Sen, Aditya Maan, Ujjwal Goyal, Aditi Birdhaniya, Upender Pandel, “In Crucible Reduction of Mill Scale by Lean Grade Coal: Study of Time, Temperature and Arrangement for Optimum Reduction Conditions”, Materials Today: Proceedings 5 (2018), pp. 3256-3263, Elsevier Scopus Journal), available online at www.sciencedirect.com

2. Rahul Sen, Satender Dehiya, Upender Pandel, M.K.Banejee, “Utilization of Low Grade Coal for Direct Reduction of Mill Scale to Obtain Sponge Iron”, Procedia Earth and Planetry Science 11 (2015), pp.8-14, Elsevier Scopus Journal, available at www.sciencedirect.com

3. Nikitha Gade, Gaurav Verma, Rahul Sen, Upender Pandel, “ Effect of Calcium Carbonate on Reduction Behavior of Mill Scale ”, Procedia Earth and Planetry Science 11 (2015),pp. 319-324, Elsevier Scopus Journal, available at www.sciencedirect.com

4. Rahul Sen, Upender Pandel, “Direct Reduction of Mill Scale by Low Grade Coal: An Industrial Waste Recovery Approach” , International Conference, on Advances in Chemical Engineering and Technology, ICACE TKMCE 14, pp. 328–331 , organized by TKM College of Engineering, Kollam, Kerala on 16 to18 Oct., 2014 (Elsevier Publication) available at www.googlescholar.com

5. Nikitha Gade, Mayuri Nayak, Rahul Sen, Upender Pandel, “Study on the Reduction of Mill Scale by Low Grade Coal”, 52nd National Metallurgists Day & Annual Technical Meeting” at Pune on 12 to 15 Nov., 2014