REDUCTION OF MILL SCALE BY COAL-
KINETIC STUDY AND EFFECT OF PROCESS
VARIABLES.

A thesis submitted to the Department of
Metallurgical Engineering, Bangladesh University of
Engineering and Technology, Dhaka, in partial
fulfilment of the requirements for the degree of
Masters of Science in Engineering (Metallurgical).

A. K. M. Matiur Rahman

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DECLARATION

I do, hereby declare that this work has been carried out by the author under the supervision of Dr. A. A. Md. Rezaul Haque, Associate Professor, Department of Metallurgical Engineering, BUET, Dhaka, and it has not been submitted elsewhere for the award of any other degree or diploma.

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BUET, Dhaka.

The Author
Mill scale from Chittagong Steel Mills Ltd. (CSM), Bangladesh and coal from India were used to study the effects of reaction temperature, coal/mill scale ratio in the reduction mixture, average particle size of mill scale/coal and bed depth of the mixture on reduction kinetics. Isothermal studies were carried out at four different temperature levels from 1173 to 1323 K. The kinetic data of reduction fit the Ginstling-Brounstein reaction model

\[ G(\alpha) = (1-2/3 \alpha) - (1-\alpha)^{2/3}. \]

where \( \alpha \) is the degree of reduction.

An empirical integrated rate equation describing the relationship between the process variables was obtained which can be used conveniently to estimate the time for a particular degree of reduction in the range of 0.5 to 0.8. The activation energy for the reduction reaction was found to be 147 kJ/mol. Within the range of variables studied an increase in reaction temperature and coal/mill scale ratio of the mixture results in high reduction rate, whereas, an increase in average particle size and bed depth decreases the reduction rate.

Optical micrographs of the reduced masses show distinct appearance of the metallic phase and disappearance of wustite phase with time and temperature.
CHAPTER-1

INTRODUCTION

Generally iron is produced from iron ore in blast furnaces which is known as conventional method of ironmaking. Alternatively iron can be produced by direct reduction (DR) process. In this process, the metallic iron is produced by the reduction of iron ore or other iron oxide below the melting temperature of any of the materials involved. The product is known as direct reduced iron (DRI) or sponge iron because of its porous character, which results from the manner in which the reduction is performed.

Iron oxide can be reduced by solid carbon or by a gaseous intermediate, reformed natural gas or carbon monoxide formed by the gasification of carbon. The former process, called direct reduction, is said to begin at the points of contact between the iron oxide and carbon particles. As reduction proceeds the islets of iron, formed on the oxide surface, join together to form a shell around the oxide core. It is assumed that the reaction progresses further by solution of carbon in the metallic phase to the metal/oxide interface. However, it is now universally accepted that the latter process i.e, indirect reduction plays the major role of iron oxide reduction. 
In Bangladesh, there is no reserve of iron ore but large quantities of mill scale are produced in the re-rolling mills every year. Only in Chittagong Steel Mills Ltd. (CSM), 3600 tons of mill scale are produced every year. Most of these scales are wasted. Since the mill scale is a high grade iron oxide, there is a great scope to develop a process by which DRI can be produced from these mill scales. The reduced mass (DRI) can be used as a substitute of scrap in steelmaking.

Although in Bangladesh there is sufficient reserve of natural gas, it can not be used as a reducing agent without reforming. To avoid the difficulties of reforming, coal was used as a reducing agent in the present study. Coal used are fines, which are generally produced during transportation and storage. These fines are usually wasted. The present study is undertaken with a view to study the kinetic of reduction of mill scale by coal and to study systematically the effect of various process parameters on reduction kinetics and to optimise these parameters to maximise the extent of reduction. Another aim of the study is to establish an empirical correlation which can be conveniently used to estimate time for a range of the degree of reduction under different process variables such as temperature, coal/mill scale ratio, average particle size and bed depth. The data obtained from the study could be useful in the design and operation of large scale reduction reactors.
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CHAPTER-2

LITERATURE REVIEW

This chapter deals with relevant information of DR (Direct Reduction) processes and the analysis of Kinetic Data.

2.1. Direct reduction process:

Since 1920, about 100 DR processes have been developed. Some of the processes are coal based while others are based on natural gas or reformed gas. The gas based processes have certain advantages over coal based processes, namely, higher productivity, easier process control, better product, higher carbon content etc. Countries having resources of natural gas have gone only for gas based processes such as HYL, Midrex, Purofer, FTOR etc. On the other hand, gas starved countries have to depend on coal based processes such as SL/RN, ACCAR, Krupp etc. despite their limitations. Some of the important DR processes are described here.

2.1.1 Reformed natural gas based processes:

Iron oxide can be reduced by CO or H₂, which can be represented by the following equations:
The reformed gas, which is rich in CO and H₂, is produced by reforming natural gas primarily methane, in catalyst filled reformer tubes. The CO and H₂ are generated in CH₄-steam reforming processes according to the reaction:

\[
\text{CH}_4 + \text{H}_2\text{O} = \text{CO} + 3\text{H}_2 \quad \text{(2.7)}
\]

High steam/carbon ratios were once required to prevent carbon formation in the reformer tubes and catalyst deterioration. The resultant reducing gas then had to be cooled to remove excess water vapour and reheated, before the reducing gas could be used to reduce iron oxide. However, modern catalysts now permit operation with steam/carbon ratios approaching the stoichiometric ratio, this producing a mixture of H₂ and CO of 95% purity (wet basis). Thus energy saving is achieved by lower steam usage and elimination of reheating of the reducing gas.
2.1.1.1 Kidrex process (Midrex Corporation)

The principle of this process is the reduction of iron ore in a shaft furnace by reducing gases in accordance with the counterflow principle. The main components of the process are the shaft furnace, the gas reformer, and the cooling-gas system. Solid and gas flows are monitored so that the process variables can be controlled within operating limits. The temperature and composition of each gas stream to the shaft furnace are controlled within specification limits, to maintain bed temperature for reduction, degree of metallization, carburization level (Fe-C content), and to ensure the most efficient utilization of the reducing gas.

The furnace is a steel vessel with an internal refractory lining. The solids are charged continuously into the top of the furnace through seal legs. The reduction furnace is designed for uniform movement of the burden by gravity feed, through the preheat, reduction and cooling zones of the furnace. The cooled DRI is continuously discharged through seal legs at the bottom of the furnace. Insert gas is injected into the seal legs to prevent escape of process gases. On discharge from the shaft, the DRI is screened for removal of fines. The fines may be finally briquetted to make them a usable DRI product.
2.1.1.2 HYL (Hojalata Y Lamina, Steel company of Monetary Mexico)

In the HYL process, reducing gas (rich in CO and H\textsubscript{2}) is generated, typically by nickel-based catalytic reforming of natural gas, which is mixed with steam before entering the reformer. Commercial HYL operations use excess steam over stoichiometric requirements, as shown in equation 2.8, to prevent carbon formation and to promote long catalyst life.

\[ \text{CH}_4 + \text{H}_2\text{O} = \text{CO} + 3 \text{H}_2\text{O} \quad \text{(2.8)} \]

The reducing section consists of a set of four reactors, three of which are in operation, while the fourth is engaged in discharging and charging operations. The HYL process is a cyclical batch operation, and the three on-line reactors operate in series. The reduction of the charge is performed in two stages, an initial reduction stage and a main reduction stage. Cooling and carburization, and the final adjustment of metallization are performed in the third stage. Each stage of operation takes about three hours. An intricate system of valves permits the reactors to be connected in any desired order, so that any one reactor can be connected in its correct process stage.

2.1.1.3. The FIOR (Fluidized Iron Ore Reduction) Process

The FIOR process reduces iron ore fines in a series of four fluid-bed reactors. The two other major components of the FIOR process
are a reformer to produce the fresh reducing gas and a briquetted section in which the reduced iron ore fines are compacted. The ore is fed continuously into the preheating reactor, where residual water is driven off and the ore is heated to about 800°C. The combustion products are used to fluidize and heat the ore. As the ore level builds up in the preheater, it overflows into the first of the three reduction reactors. Compressed reducing gas enters the bottom of the lowest reactor and flows countercurrent to the descending ore. Reactor top gas leaves the first-stage reduction reactor and is scrubbed and cooled to remove dust and most of the water produced in the reduction reaction. Direct-reduced iron fines are discharged from the final reactor into the briquetting press.

2.1.1.4. The Purofer process (Thyssen Purofer, West Germany)

Countercurrent reduction of ores in a shaft furnace with gases obtained by reforming hydrocarbons with oxidizing gas is the basic principle of this process. The Purofer process utilizes a shaft furnace as the reduction reactor. The shaft furnace is charged with lump ore or pellet. The reducing gas is produced by reforming natural gas, coke oven gas or the like with recycled top gas in regenerative gas reformers and is fed directly into the shaft furnace. If fuel oil or coal is used the cold gas produced in a gasification plant is heated up in a recuperator.
2.1.2 Coal-based processes:

Rotary-kiln processes are the only commercially available coal-based DR processes currently operating. The main components of these rotary-kiln systems consist of a solid-feed system, the rotary kiln, a product cooler screen, magnetic separators, and off gas cleaners. The basic technology for rotary-kiln reduction emphasizes the importance of correct selection of raw materials. The iron oxide feed (lump ore or pellets) should fulfill certain requirements regarding chemical composition, size, distribution, and behavior under reducing conditions in the rotary kiln. The feed should have a high iron content (above 65% and preferably close to 67% for hematite ores), and correspondingly the gangue content should be low, so that cost for further processing in the electric furnace are kept as low as possible. Sulfur and phosphorus content should also be low. The minimum size of feed ore should be controlled also.

In rotary-kiln DR processes, the coal, any flux required, and the iron oxide are charged into the high end of the inclined rotary kiln. The burden travels through the rotary kiln by the rotation of the kiln and by gravity. The burden first passes through a preheating zone where devolatilization of coal occurs, flux is calcined and the charge is heated to the operating temperature for reduction. In the reduction zone, iron oxide is reduced either by solid carbon or CO gas as represented by the following reactions.
It is now universally accepted that the reduction of iron oxide takes place by CO rather than C.

At the elevated bed temperature, part of the CO reacts with the carbon in the char by the reaction:

\[ \text{CO} + \text{C} = 2\text{CO} \]  \\
\[ \text{CO} + \text{C} = \text{CO}_2 + \text{C} \]  \\

In an all-coal DR process, pulverized coal is supplied to the burner. Fuel oil and natural gas, however, are viable alternatives. The burner operates with a deficiency of air to maintain a reducing atmosphere in the kiln. Additional process heat is supplied by combustion of the volatile matter and CO emerging from the kiln bed. Combustion air is supplied through ports spaced along the length of the rotary kiln. The air flow is controlled to maintain a uniform temperature profile in the reduction zone and a neutral or slightly reducing atmosphere above the bed. The gas flow runs countercurrent to the flow of the solids. The solids discharged from the rotary kiln are cooled, then screened and separated magnetically.

\[ 3\text{Fe}_3\text{O}_4 + \text{C} = 2\text{Fe}_3\text{O}_4 + \text{CO} \]  \\
\[ \text{Fe}_3\text{O}_4 + \text{C} = 3\text{FeO} + \text{CO} \]  \\
\[ \text{FeO} + \text{C} = \text{Fe} + \text{CO} \]  \\
\[ 3\text{Fe}_2\text{O}_3 + \text{CO} = 2\text{Fe}_2\text{O}_4 + \text{CO}_2 \]  \\
\[ \text{Fe}_3\text{O}_4 + \text{CO} = 3\text{FeO} + \text{CO}_2 \]  \\
\[ \text{FeO} + \text{CO} = \text{Fe} + \text{CO}_2 \]
2.1.2.1. Krupp codir process (Krupp industries, West Germany)

The coal-ore, direct-iron-reduction (Codir) process, marketed by Krupp Industries of West Germany, is based on Krupp's experience in rotary-kiln reduction dating from the 1930s. Lump ore or oxide pellets, along with solid reductant, dolomite or limestone as flux if needed, and recycled char are charged from the bins into the rotary kiln. The feed size of the solids is closely controlled to expedite separation later in the process. Typically, the preheating zone extends from 25% to 40% along the Codir process kiln.

Primary heat is supplied to the kiln by the combustion of finely pulverized coal injected at the solid discharge end of the kiln. Secondary heat is supplied by supplied air into the kiln gas space through tubes spaced along the entire length of the kiln. The secondary air is introduced axially (along the kiln centerline) in the direction of the kiln gas flow and serves to burn combustibles released from the bed. In this way, a uniform charge-temperature profile between 950 and 1050°C is achieved in the reduction zone of the kiln.

The DRI, char, coal ash, and spent flux are discharged via an enclosed chute from the rotary kiln burner hood into a sealed rotary cooler. Cooling is accomplished by spraying a controlled amount of water directly on to the hot solids and by spraying additional water on the outside of the cooler shell. The reduced mass is separated from the char and ash by magnetic separation.
2.1.2.2. SL/RN (Stelco-Lurgi/Republic Steel-National Lead) Process

The SL/RN processes are based on research work carried out separately by two groups of companies. The SL process was originally developed with the aim of producing sponge iron for steel making furnaces, using ores rich in iron. If ores with a low iron content were present, the ferruginous material were separated from the gangue before reduction. In the RN process (Republic Steel-National Lead), the emphasis was on heat treatment of ores, with a low iron content which were divided into their constituents parts—metallic iron and gangue—after reduction. In this process, reduction of iron oxides takes place in a rotary kiln with a solid reducing agents.

The main unit is the rotary kiln, the characteristic feature of which is the series of shell burners disposed along the length of the kiln. These allow precise regulation of the reaction temperatures. The material discharged from the kiln is cooled indirectly or directly in a cooling drum. Screens and magnetic separators are required for the discharged material. A briquetted press is sometimes needed for compacting the finer particles of sponge iron.
2.1.2.3. The ACCAR process (Allis-Chalmers Corporation)\textsuperscript{16}

The Allis-Chalmers Controlled Atmosphere Reactor (ACCAR) produced highly metallized DRI in a ported rotary kiln. Liquid, solid and gaseous fuels, singly or in combination, are used directly in the kiln. The ACCAR kiln is equipped with an intricate port system and with valving arranged radially around the circumference of the kiln and spaced uniformly along its length, for liquid and/or gaseous fuel injection under the bed and for injection above it. The flow rates through the ports are closely controlled to maintain optimum temperature profile and gas composition along the length of the kiln. Coal and lump ore and/or oxide pellets are charged into the feed end of the rotary kiln. The solids are heated to reduction temperature by the countercurrent flow of hot gas. Volatile matter is released from the coal during heat-up and is carried out in the kiln exhaust gas. As the coal and iron oxide travel through the kiln, reduction is accomplished by the CO reduction mechanism. The final degree of reduction is achieved by introducing liquid and/or gaseous fuel through the kiln-shell ports near the product end of the kiln as they pass under the solid bed. In passing through the bed, this fuel is cracked to form \(H_2\) and \(CO\) to complete the iron oxide reduction and to provide a protective atmosphere for the highly metallized product. This method of fuel injection permits operation without the excess of coal required to maintain a reducing atmosphere in the bed in other coal based DR processes.
Thus char recycling is eliminated. Solids are discharged from the rotary kiln into a rotary cooler, where cooling is accomplished with external water spray. The DRI is separated from the coal ash by magnetic separation, and is then screened to achieve coarse and fine product separation.
2.2. ANALYSIS OF KINETIC DATA

2.2.1. Introduction

Kinetic studies are aimed to determine the influence of various process parameters on a reaction and also to explain the reaction mechanism. When a kinetic law is established and the variation of the rate constant with temperature is studied then it becomes possible to obtain a value of activation energy which is said to indicate the reaction mechanism. This, however, requires some mathematical procedures and some of these are summarized in this section.

2.2.2. Isothermal kinetics:

The main purpose of studying kinetics is to gain information on the mechanism of process and the associated kinetic parameters. Generally reaction rates increase exponentially with increase in temperature. At any instant, the value of the specific reaction rate constant k for a process is the weighted mean of the individual events that cause the transformation. If the contribution made by the individual events changes as the transformation proceeds then the value of k varies with the progress of transformation or with change in temperature. Provided that the temperature range is not too wide the temperature
dependence of the rates of most reactions obey the Arrhenius type exponential equation:

\[ k = A \exp^{-E/RT} \]  \hspace{1cm} (2.16)

This is often applicable to both homogeneous and heterogeneous reactions. While the so-called activation energy \( E \) is said to depend on the reaction mechanism, the pre-exponential factor \( A \) depends on many factors. \( R \) is the gas constant and \( T \) is the temperature in degree Kelvin.

2.2.3. Determination of kinetic parameters:

Integral Approach

During isothermal kinetic studies the progress of a reaction is generally measured in terms of degree of conversion which is expressed as \( \alpha \) and this \( \alpha \) varies from zero to unity. \( \alpha \), which is also known as degree of reduction means the ratio of oxygen removed from the feed to the total oxygen combined with iron in the feed. Values of \( \alpha \) are plotted against time \( t \) for the given temperatures. Subsequently these data are fitted into an appropriate form of integrated kinetic equation. Integral expression of kinetic equations for some reaction mechanisms are well known. In these laws an appropriate function of \( \alpha \), \( G(\alpha) \), is shown to be
proportional to time \( t \). The reaction rate constant \( k \) is obtained from the slope of the linear plot of \( G(\alpha) \) versus time.

Isothermal experiments are carried out at different temperatures to estimate the reaction rate constants for each of these temperatures. The temperature dependence of the rate constant is then expressed as:

\[
\ln k = \ln A - \frac{E}{RT} \quad \text{---2.17}
\]

Hence a plot of \( \ln k \) against \( 1/T \) should give a straight line whose slope will be \( E/R \). Thus, the slope of this linear plot gives the value of the activation energy. The pre-exponential factor is obtained from the intercept. This approach is called the integral approach because it makes use of an integrated form of kinetic equation.

**Differential Approach**

The integral approach calls for prior identification of the appropriate function \( G(\alpha) \), which can only be identified by trial and error methods. Then the reaction rate can be estimated after linearising the basic kinetic data. This difficulty is not encountered in another approach, where knowledge of the kinetic equation is not necessary. At any given time the reaction rate is a function of temperature \( T \) and \( \alpha \) and, therefore, the general differential form of the rate
expression is expressed as
\[ \frac{da}{dt} = k(T) \cdot f(a) \]  \hspace{1cm} \text{2.18}

where \( k(T) \) is the temperature dependent rate constant and \( f(a) \) is an appropriate function of \( a \).

Substituting for \( k(T) \) from Eq. 2.16 in 2.18 we get:
\[ \frac{da}{dt} = A \cdot \exp^{-\frac{E}{RT}} \cdot f(a) \]  \hspace{1cm} \text{2.19}

Equation 2.19 can be written as
\[ \int \frac{da}{f(a)} = k \int dt = A \int \exp^{-\frac{E}{RT}} dt \]  \hspace{1cm} \text{2.20}

For any given level of \( a \) the L.H.S. integral, with limits of zero and \( a \), has a constant value. The R.H.S. integral has the value \( t \), i.e. time required to obtain the given values of \( a \) at the given temperature. Thus it can be written as:
\[ a \cdot t_1 = \text{constant} / \exp^{\frac{E}{RT}} \]  \hspace{1cm} \text{2.21}

or
\[ \ln t_1 = \text{constant} + \frac{E}{RT} \]  \hspace{1cm} \text{2.22}

In other words plot of \( \ln t_1 \) against \( 1/T \) should be linear. Again there will be plots of various levels of \( a \) which make it possible to calculate the activation energy at various stages of reaction. It should be noted that in the above differential approaches the form of \( f(a) \) need not be known. However, \( f(a) \) itself may be used to describe the kinetics of reaction.
2.2.4. Reduced time plots

An important step in the analysis of kinetic data of many reaction systems is the identification of the reaction mechanism. In many cases a preliminary identification is possible using the so-called reduced time plots. Although such plots have widely been used in the analysis of solid state reactions, their application in the chemical metallurgy has been limited. This method can be used to ascertain the reaction mechanism and hence the appropriate function $G(\alpha)$.

In reduced time plots, the kinetic relationships are rewritten in terms of dimensionless time using the following procedure: we have

$$G(\alpha) = kt \quad \text{(2.23)}$$

Now let us suppose that, if $t_{0.5}$ is the time required to obtain 0.5 fraction reacted, i.e., $\alpha = 0.5$ then $g(0.5) = kt_{0.5}$. Dividing Eq. 2.23 by this, one obtains a modified form of Eq. 2.23

$$G(\alpha) = G(\alpha)_{t=0.5} \cdot \frac{t}{t_{0.5}} \quad \text{(2.24)}$$

$$G(\alpha) = B \left( \frac{t}{t_{0.5}} \right) \quad \text{(2.25)}$$

where $B$ is a constant dependent on the form of the function $G(\alpha)$. Eq. 2.25 is dependent on the kinetic rate constant and is dimensionless. Thus for a particular reaction mechanism, a single equation of the type of Eq. 2.9 represents all kinetic data irrespective of the nature of the system, temperature or other factors which affect the reaction. Thus each mechanism has a unique reduced time plot.
Keattach and Dollimore\textsuperscript{11} have described the method of using the reduced time plots and have given the values of $t/t_{0.5}$ for different $\alpha$ values for some of the reaction mechanism.

The method initially involved tabulation of the functional values $G(\alpha)$ for various reaction mechanisms for different $\alpha$ values. These $G(\alpha)$ values are used to calculate the $t/t_{0.5}$ values. Later plots of the various reaction mechanisms are obtained by plotting the $\alpha$ values against the calculated values of $t/t_{0.5}$. Reduced time plots of experimental data are superimposed on these master plots and the mechanism is identified by observing which one of the theoretical expression fit the experimental data.
CHAPTER-3

EXPERIMENTAL

3.0 Raw material and procedure:

Mill scale from Chittagong Steel Mills (CSM) Ltd., Bangladesh and coal from India were used in the study. The analysis of mill scale and coal are given in Table-1 and 2 respectively. All reduction experiments were carried out in mild steel crucibles of diameter 50mm and height 65 mm. Mill scale and coal of the same particle sizes were mixed thoroughly and the mixture poured into the crucibles. No load was applied for compaction, only three mild tappings were applied in each case. The crucibles containing the reduction mixture were heated in an electrically heated muffle furnace.

A reducing atmosphere was maintained by placing some crucibles full of coal in the furnace. The temperature was controlled within ±5°C. After predetermined times the samples were taken out from the furnace and the crucibles were quenched in a water tray by placing in such a way that they were half immersed. To prevent reoxidation the top of the crucibles were covered with mild steel sheets.

After cooling, the reduced masses were separated magnetically from the charge. The reduced mass may contain Fe₂O₃, FeO and Fe. Although
Fe₂O₃ and Fe are magnetic. FeO and Fe₂O₃ are non-magnetic. Fe₃O₄ was absent in the mill scale. Since all the different phases coexist in each particle, the iron bearing particles are easily separated from char and ash. It was then crushed to -150 micron size and analysed chemically to estimate the percentage of total iron using standard methods²⁴,²⁵.

Table 1

Chemical Analysis of Mill scale used.

<table>
<thead>
<tr>
<th>Element</th>
<th>Wt.%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>72.56</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>52.60</td>
</tr>
<tr>
<td>FeO</td>
<td>44.36</td>
</tr>
<tr>
<td>SiO₂</td>
<td>2.42</td>
</tr>
<tr>
<td>MnO</td>
<td>0.54</td>
</tr>
<tr>
<td>S and P</td>
<td>0.08</td>
</tr>
</tbody>
</table>

Mill scale and analysis supplied by Chittagong Steel Mills Ltd, Chittagong and RRL, Bhubaneswar, India, respectively.
The proximate analysis of coal used.

<table>
<thead>
<tr>
<th>Element</th>
<th>Wt.%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moisture</td>
<td>3.57</td>
</tr>
<tr>
<td>Volatile Matter</td>
<td>34.08</td>
</tr>
<tr>
<td>Fixed Carbon</td>
<td>52.60</td>
</tr>
<tr>
<td>Ash</td>
<td>9.75</td>
</tr>
</tbody>
</table>

3.1. Estimation of Total Iron:
Total iron was analysed by volumetric method using potassium dichromate as titrating agent and the results were verified by a method using potassium permanganate as titrating agent. Both methods yield similar results. The methods are described in Appendix-1.

3.2. Estimation of the Degree of Reduction:
Direct reduced iron (DRI) is generally characterized in terms of degree of reduction, which is the ratio of weight of oxygen removed to that of the initial total oxygen present in the oxide in combination with iron. When iron oxide is reduced by a gaseous reductant, the degree of reduction is obtained through simple
measurement of weight loss. However, when the reductant is a carbonaceous solid, the weight loss of the charge is due to the removal of oxygen from iron oxide as well as removal of carbon by gasification of the carbonaceous material. It is not easy to identify these weight losses separately and, therefore, it becomes necessary to analyse the reduced oxide for various valence states of iron.

Although standard volumetric methods for various valence states of iron are available, estimation of the degree of reduction using these methods suffer from several drawbacks. To avoid the difficulties associated with these multistep procedures, several workers have recommended some simple formula which can be used to obtain the degree of reduction.

Chernyshev et al. and Gonzales et al. have proposed a formula for the estimation of degree of reduction. The formula is

\[ \alpha = K \left( \frac{\% \text{Fe}^{\text{tot}} - \% \text{Fe}^{\text{red}}}{\% \text{Fe}^{\text{tot}} \times \% \text{Fe}^{\text{red}}} \right) \times 100 \]

Where \( \alpha \) is the degree of reduction, \( K \) is the ratio of weight of iron to weight of oxygen in mill scale, \( \% \text{Fe}^{\text{tot}} \) and \( \% \text{Fe}^{\text{red}} \) are the percentages of total iron in initial mill scale and the total iron in the reduced mass respectively. This equation was also successfully used by other workers.\(^{26,28}\)
CHAPTER-4

RESULTS AND DISCUSSIONS

4.0. Preliminary selection of process parameters:

The process parameters of the present experiments were temperature, mill scale and coal particle size, coal/mill scale ratio and bed depth. The experimental ranges were selected after some preliminary studies. As shown in Fig. 1(a) the rate of reduction decreases with an increase in average particle sizes, which is shown in Fig. 1(a). Fig.1(b) shows that an increase in coal/mill scale ratio increases the rate of reduction. Fig.1(c) shows that an increase in bed depth decreases the rate of reduction. From the above studies finally an average particle size of 2.03 mm, coal/mill scale ratio of 0.8 and bed depth of 38 mm were selected for the kinetic studies because a reasonable degree of reduction can be achieved after reducing the oxides under given parameters, at 1273 K for 2 Hours. Further decrease in particle sizes or increase in coal/mill scale ratios may not help to increase in degree of reduction significantly. The main aim of the study was to establish a kinetic law and calculate the activation energy of the reaction.
4.1. Kinetic study:

To establish the reaction mechanism, isothermal kinetic studies were carried out at four temperature levels namely, 1173, 1223, 1273 and 1323 K. The results are shown in Fig. 2. It shows plots of the degree of reduction (\( \alpha \)) in the mill scale-coal mixture against time (\( t \)).

It was observed that the reaction mass took about 10 to 25 minutes to reach the reaction temperatures. Although the temperature profile is not truly isothermal in the initial stage of reaction, the kinetic plots seem to be quite smooth passing through origin. This is due to the reason that from about 500°C onwards the coal begins to liberate volatile matter. It is well known that volatile matter contributes to some reduction of iron oxides even at low temperatures\(^\text{12}\). Due to this compensating effect the plots are quite smooth.

To get an initial idea about the kinetic law, reduced time plots (sec. 2.2.4) were used which is shown in Fig. 3. It can be seen that four commonly suggested models such as Spherical, Parabolic, First order reaction and Ginstling-Brounstein for iron oxide reduction, the Ginstling-Brounstein equation seems to be the appropriate one to fit the data obtained in these studies.

Based on the findings from the reduced time plots, the data of Fig. 2 were plotted according to the Ginstling-Brounstein equation:

\[
G(a) = (1-2/3 \alpha) - (1-a)^{2/3} = kt.
\]

The plots are shown in Fig. 4.
4.1.1. Evaluation of activation energy \((E)\) value:

It has been previously discussed in chapter-2 that the kinetic data can be analysed in two ways for the evaluation of the activation energy \((E)\). At first, the integral approach was used to estimate the value of \(E\). In this method, the reaction rate constants of various temperature were obtained from the linearised plots of Fig.4 and then were plotted according to the Arrhenious type equation. This is shown in Fig.5. The apparent activation energy of the process is thus estimated from the Arrhenious type plot \((\text{slope} = \frac{-E}{R})\) as 147 kJ/mol.

The apparent activation energies at different levels of reaction were also estimated using differential approach. For this purpose \(t_1\) values at different levels of \(\alpha\) were estimated from the plots of Fig.2. Then in \(t_2\) versus \(1/T\). \(K^{-1}\) plots were plotted, which are shown in Fig.6. The values of the apparent activation energies were in the range of 147 to 149 kJ/mol for \(\alpha\) values in the range of 0.5 to 0.8. It is thus found that apparent activation energy obtained by the different approaches are nearly identical. This may be taken as an evidence to support the kinetic law identified. It is also found that the variation of \(E\) values with \(\alpha\) is minor. This is due to the fact that the reaction mechanism remains practically unaltered as the reaction progress.
4.2 Effect of process variables:

In the present work, some additional experimental studies were carried out to establish quantitative relationship between time for a given range of degree of reduction and various process variables. The aim of the work is to develop an empirical correlation which can be used to estimate time for the range of 50% to 80% reduction under different process variables. The process variables studied in the present work are: reaction temperature (T), average particle size (P), bed depth of the mixture (H) and coal/mill scale ratio (C), similar approaches were used by other workers.15

4.2.1 Range of process variables:

Table 3 summaries the ranges of experimental conditions used in the work. It has already been mentioned that these ranges were selected on the basis of some preliminary experiments. Mill scale from Chittagong steel Mills Ltd. and coal from India were used in the experiments. Analysis of mill scale and coal used in the experiments are listed in Table 1 and 2 respectively.
Table-3

Ranges of Experimental Conditions:

<table>
<thead>
<tr>
<th>Parameter studied</th>
<th>Ranges</th>
<th>Fixed Parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature T,K</td>
<td>1173-1323</td>
<td>T = 1273 K</td>
</tr>
<tr>
<td>Coal/Mill scale Ratio, C</td>
<td>0.5-1.0</td>
<td>C = 0.8</td>
</tr>
<tr>
<td>Average Mill scale and coal particle size, P mm</td>
<td>0.51-2.87</td>
<td>P = 2.03 mm</td>
</tr>
<tr>
<td>Bed depth of mixture, H mm</td>
<td>25-51</td>
<td>H = 38 mm</td>
</tr>
</tbody>
</table>

4.2.2. Effect of reaction temperature:

For this series of experiment, mill scale of 2.03 mm average particle size were mixed with coal particles of same size to give a coal/mill scale ratio of 0.8. The mixtures were packed in the crucibles to a bed depth of 38 mm for each experiments. Reduction studies were carried out at four temperature levels namely, 1173, 1223, 1273 and 1323 K. Fig.2 shows a-t plots at different reaction temperatures. The times for various levels of a (a<sub>0.5, 0.8</sub>, t<sub>a</sub> were estimated from the plots of Fig.2 and are presented in Fig.7 according to Eqn 2.22 discussed earlier in chapter 2. Using linear regression, the time (min.) required for various levels of degree of reduction, a at the reaction temperature T (K) are given by the following equation:
The activation energy for degree of reduction in the range of 0.5-0.8 is found to vary from 147.03 to 149.67 kJ/mol over the temperature range of 1173 to 1323 K. However, the average value, 148.04 kJ/mol is taken for the development of an integrated rate equation. Fig.7 shows that the time required for a given $\alpha$ value decreases with increase of reaction temperature.

4.2.3 Effect of average particle size:

For this series of experiments, a reaction temperature of 1273 K and coal/mill scale ratio of 0.8 and bed depth of 38 mm were used. Fig.8 shows plot of $a$ as a function of $t$ for different particle sizes. Time for various degrees of reduction, $t_\alpha$ obtained from these plots are presented in Fig.9. From these log-log plots of $t_\alpha$ against the average particle size ($\bar{P}$), the following linear relationship can be obtained for various degrees of reduction.
Although the exponent of average particle size varies from 0.333 to 0.466, in developing the integrated rate equation, the average value, 0.41 has been taken. The results show that, within the range of variables under study, an increase of average particle size decreases the rate of reduction i.e., time for a particular degree of reduction increases, with increase in particle size.

4.2.4 Effect of coal/mill scale ratio:

For these series of experiments, a reaction temperature of 1273 K, an average particle size of 2.03 mm and a bed depth of 38 mm were used. Fig. 10 shows x-t plots for different coal/mill scale ratios. Time for various degrees of reduction, t, obtained from these plots are presented in Fig. 11. The data points on a log-log plot of t against coal/mill scale ratio lie on straight lines which can be expressed as:

\[ t_{d=0.5} = 23.21 \times e^{0.463} \quad \text{--------} \quad 4.5 \]

\[ t_{d=0.6} = 35.1 \times e^{0.412} \quad \text{--------} \quad 4.6 \]

\[ t_{d=0.7} = 50.63 \times e^{0.420} \quad \text{--------} \quad 4.7 \]

\[ t_{d=0.8} = 75.09 \times e^{0.431} \quad \text{--------} \quad 4.8 \]
4.11

The exponent of coal/mill scale ratio varies from -1.6 to -3.08 and an average value of -2.21 is taken for the development of the integrated rate equation. Within the range of coal/mill scale ratio studies, the results show that an increase of the ratio increase the rate of reduction of mill scale i.e the time required for a particular degree of reduction decreases with the increase in coal/mill scale ratio.

4.2.5 Effect of bed depth:

Experimental parameters, P = 2.03 mm, C = 0.8, T = 1273 K were used in this series. The required times for a values of 0.5-0.8 were obtained from the a-t plots shown in the Fig.12. These t_e values were found to correlate satisfactorily with the bed depth (H) of the reduction mixture. The following relationships are derived:

4.13

\[ t_{e=0.5} = 0.088 \, H^{1.66} \]

4.14

\[ t_{e=0.6} = 0.076 \, H^{1.82} \]

4.15

\[ t_{e=0.7} = 4.43 \, H^{0.125} \]

4.16

\[ t_{e=0.8} = 4.65 \, H^{0.37} \]
Fig. 13 shows a log-log plot of $t_\alpha$ against $H$. Although the exponent of bed depth varies from 0.725 to 1.820. Average value of 1.26 is selected for the development of the integrated rate equation. The above relationships show that within the range of variables studied, an increase of the bed depth decreases the rate of reduction.

4.2.6. Overall correlations:

From the above stated correlations, it is now possible to derive an empirical correlation that expresses the combined effect of different process variables for a fixed values of $\alpha$. Four such equations for four values of $\alpha$ ($\alpha = 0.5-0.8$) are stated below:

\[
t_{e=0.5} = 1.179 \times 10^{-7} \cdot M \\
t_{e=0.6} = 1.934 \times 10^{-7} \cdot M \\
t_{e=0.7} = 2.593 \times 10^{-7} \cdot M \\
t_{e=0.8} = 3.974 \times 10^{-7} \cdot M
\]

where $M$ represents the term $p^{0.41} \cdot H^{1.26} \cdot C^{1.21} \cdot e^{18443/M}$.

Fig. 14 shows the plots of $t_e$ ($\alpha = 0.5-0.8$) against $M$ for the experimental results obtained in four series of experiments. The four lines passed through the origin which indicates the validity of these equations.
An attempt was made to develop a general integrated rate equation from the above four equations. For this purpose, a relationship between various degree of reduction and respective $k$ values were obtained from the above four correlations. Fig. 15 shows the log-log plot of $k_i$ against degree of reduction. The relationship is as follows

$$k_i = 6.77 \times 10^{-7} \cdot a_i^{0.5}$$  \hspace{1cm} 4.21$$

Again based on the sixteen correlations obtained above namely, equations 4.1 to 4.16, an overall correlation was obtained and can be written as follows:

$$t_{a_i t a i \cdot 0.5} = 6.77 \times 10^{-7} \cdot a_i^{0.5} \cdot M, \hspace{1cm} 4.22$$

where $M = e^{1.4i} \cdot H^{1.76} \cdot C^{-1.31} \cdot e^{1.6942/27}$.

Fig. 16 gives the plot of $t_i$ against $(a_i^{0.5} \cdot M)$ for all experimental results obtained in the above four series of experiments. The value of $K$ was evaluated to be $6.77 \times 10^{-7}$, which is, as expected, equal to the $K$ value obtained by equation 4.21. This overall correlation is the empirical integrated rate equation.
4.3. Optical microscopy:

To study the phase changes of mill scale during reduction, some of the particles of reduced mass were examined microscopically. Some optical micrographs of the reduced mass are shown in Fig. 17 (a-d). The metallic phase is seen as white areas. The grey area is wustite (FeO). Pores are seen as dark areas. The increase of the white areas are due to gradual metallization can be observed from the micrographs. Metallic phase and wustite are present at the initial stages of reduction (Fig. a-c). At the later stages, there is little wustite and the micrograph shows mainly metallic phase and pores (Fig. d).
CHAPTER-5

CONCLUSIONS

The following conclusions can be drawn from the results of this study:

1. The kinetic data of reduction of mill scale by coal fits the Ginstling-Brounthein reaction model.

\[ G(a) = (1 - 2/3 \alpha) - (1 - \alpha)^{1/3} \]

2. The apparent activation energy for the reduction of mill scale coal mixture is 147 kJ/mol.

3. The time required for reduction of mill scale coal mixture for \( \alpha \) in the range of 0.5-0.8 is given by the expression

\[ t_{0} = 6.77 \times 10^{-7} \alpha^{0.51} P^{0.41} H^{1.25} R^{-2.8} e^{10045/RT} \]

This is valid for the experimental condition given in Table 3.

4. The time required for degree of reduction (\( \alpha \)) values in the range of 0.5-0.8 decreases with increasing temperature and coal/mill scale ratio whereas it increases with increasing average particle size and bed depth.

5. Optical micrographs of the reduced masses show distinct appearance of the metallic phase and disappearance of wustite phase with time and temperature.
Iron oxides reduced by gaseous reductant are of superior quality than that reduced by solid reductant. Bangladesh has an abundant supply of natural gas. However, first it must be reformed so that it can be used as a reducing agent. This reformed gas can be used for both packed bed and fluidized bed reduction of iron oxide. Study can be done on reduction kinetics of these reduction processes and the effect of process variables can also be studied. Finally, an overall comparative study between these two processes can be done.
REFERENCES:


VOLUMETRIC METHOD FOR ESTIMATION OF TOTAL IRON

1. Volumetric method using potassium dichromate:

0.5 gm sample was weighed out and dissolved in a 250 ml beaker with 25 ml (1:1) HCl. After one hour digestion the solution was cooled and diluted to a volume of 250 ml. 25 ml of the solution was taken out in a conical flask and few drops of HCl were added. The solution was then heated to boiling. Stannous chloride solution was added drop by drop with constant shaking till the yellow colour changes to almost colourless. It was then cooled quickly to avoid oxidation. 20 ml of HgCl₂ solution was added. A silky white precipitate was formed. Then again 20 ml acid mixture was added. 2-3 drops of diphenylamine indicator was added and the solution was titrated with 0.1N K₂Cr₂O₇ solution. The end point was indicated by the appearance of deep blue colour.

1 ml of 1M K₂Cr₂O₇ = 0.05585 gm of Fe.

% Fe(total) = 11.17 × V (ml)
The important reactions which take place during the determination of total iron by this method are as follows:

\[ 2 \text{FeCl}_3 + \text{SnCl}_4 = 2 \text{FeCl}_2 + \text{SnCl}_2 \]

\[ \text{SnCl}_2 + 2 \text{HgCl}_2 = \text{SnCl}_4 + \text{Hg}_2\text{Cl}_4 \]

\[ 6 \text{FeCl}_3 + \text{K}_2\text{Cr}_2\text{O}_7 + 14 \text{HCl} = 6 \text{FeCl}_2 + 2 \text{KCl} + \text{Cr}_2\text{Cl}_6 + 7 \text{H}_2\text{O} \]

Solution required:

1. 0.1M standard \(\text{K}_2\text{Cr}_2\text{O}_7\) solution.
2. \(\text{SnCl}_2\) solution: 50 gm \(\text{SnCl}_2\) was dissolved in 200 ml conc. \(\text{HCl}\) and then made upto 1 litre by adding water.
3. A saturated solution of \(\text{HgCl}_2\) in water at room temperature.
4. Diphenylamine indicator: 1 gm in 100 ml conc. \(\text{H}_2\text{SO}_4\).
5. Acid mixture: \(\text{H}_2\text{SO}_4 + \text{H}_2\text{PO}_4 + \text{H}_2\text{O}\) (15:15:70)

2. Volumetric method using potassium permanganate:

2 gms of sample was weighed out and dissolved it in 100 ml of dilute (1:1) HCl in a beaker of 250 ml. The solution was warmed gently and the heating was continued till the residue was free from coloured material. The solution was allowed to cool and filtered through a hardened quantitative filter paper. The filtrate was collected in a 250 ml volumetric flask. The solid residue on the filter paper was then washed with very dilute HCl and allowed the washing to pass into the flask. The solution was then made up to the mark and shaken. 50 ml of the solution was taken out into a
conical flask and heated to boiling. The solution was then treated
with stannous chloride to reduce into ferrous salt. The reduced
solution was poured into 400 ml of water containing 25 ml of the
Zimmermann-Reinhardt solution and titrated slowly with standard
c.1N Potassium permanganate to the first pink colour which was
stable for 15 seconds.

$1 \text{ ml of } 1\text{N } \text{KMnO}_4 = 0.05585 \text{ gm of Fe}.$

$8 \text{ Fe}_2 = 0.27925 \times V \text{ ml}$

The important reactions that take place during determination of
total iron by this method are as follows.

$2 \text{ FeCl}_2 + \text{SnCl}_2 = 2 \text{ FeCl}_2 + \text{SnCl}_4$  \hspace{1cm} \text{(3.4)}$

\text{Mn (III)} + e^- = \text{Mn(II)}$  \hspace{1cm} \text{(3.5)}$

$10 \text{ FeCl}_3 + 16 \text{HCl} + 2 \text{ KMnO}_4 = 10 \text{ FeCl}_2 + 2 \text{KCl} + 2 \text{ MnCl}_2 + 8 \text{ H}_2\text{O}$ \hspace{1cm} \text{(3.6)}$

Solution Required:

1. Standard 0.1N KMnO$_4$ solution.
2. Zimmermann-Reinhardt's solution: 50 gm of crystalline manganese
   sulphate in 250 ml of water, adding a cooled mixture of 100 ml
   of conc. $\text{H}_2\text{SO}_4$ and 300 ml of water followed by 100 ml of $\text{H}_3\text{PO}_4$.
3. SnCl$_2$ solution.
Fig. 1(a) Effect of average particle size on the degree of reduction

Fig. 1(b) Effect of coal/mill scale ratio on the degree of reduction

Fig. 1(c) Effect of bed depth on the degree of reduction
Fig. 2 Kinetics of isothermal reduction of mill scale by coal
Fig. 3 Reduced time plots for isothermal kinetic data shown in fig. 2

1. \( G(\alpha) = 1 - (1 - \alpha)^{1/3} \)
2. \( G(\alpha) = \alpha^2 \)
3. \( G(\alpha) = \ln(1 - \alpha) \)
4. \( G(\alpha) = (1 - 2^{1/3} \alpha) - (1 - \alpha)^{2/3} \)
Fig. 4 Plots for isothermal kinetic data according to Ginstling-Brounstein reaction equation.

Fig. 5 Arrhenius type plots for kinetic data of fig. 4.
Fig. 6 Plots for calculation of apparent activation energy using the differential approach.
Fig. 7 Time ($t$) for different values of degree of reduction ($\alpha$) as a function of temperature ($T$).
Fig. 8 Effect of average particle size ($P$) on degree of reduction ($\alpha$).

Fig. 9 Time ($t$) for different values of degree of reduction ($\alpha$) as a function of average particle size ($P$).
Fig. 10 Effect of coal/mill scale ratio (C) on degree of reduction ($\alpha$)

Fig. 11 Time ($t$) for different values of degree of reduction ($\alpha$) as a function of coal/mill scale ratio (C)
Fig. 12 Effect of bed depth (H) on degree of reduction (\( \alpha \))

Fig. 13 Time (t) for different values of degree of reduction (\( \alpha \)) as a function of bed depth (H)
Fig. 14 Correlation for $\alpha = 0.5, 0.6, 0.7$ and $0.8$
**Fig. 15** Plot of $K_{\infty}$ against degree of reduction

**Fig. 16** Overall correlation

\[ \alpha^2 \approx 0.41 - 1.26C - 2.21e^{-148043/RT} \]
Fig. 17. Optical micrographs of reduced masses produced at

(a) 900°C after 70 min. ($\alpha = 0.46$) x 600
(b) 1000°C after 50 min. ($\alpha = 0.64$) x 600
(c) 1050°C after 50 min. ($\alpha = 0.78$) x 600
(d) 1050°C after 140 min. ($\alpha = 0.96$) x 600