Evaluation of Blast Furnace Slag Procured from Adhunik Metallics Limited With Respect to Its Flow Characteristics

Thesis submitted in partial fulfillment of the requirements for the award of the degree of

Master of Technology

in

Mechanical Engineering

[Specialization: Steel Technology]

Submitted by

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Department of Metallurgical and Materials Engineering
National Institute of Technology Rourkela-769008, (India) May 2015

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CERTIFICAE

This is to certify that the thesis entitled "Evaluation Of Blast Furnace Slag Procured from Adhunik Metallics Limited With Respect to Its Flow Characteristics" submitted by VINAY KISHNANI, Roll No.-213MM2483 in partial fulfillment of the requirements for the award of the degree of Master of Technology in Mechanical Engineering with Specialization of Steel Technology at National Institute of Technology, Rourkela is an authentic work carried out by him under my supervision and guidance.

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

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ABSTRACT

The one of the crucial property which affects the blast furnace operation is viscosity, which is directly affected by the composition of the slag, viscosity of the slag should be low for the operation purpose at the operating temperature for making an easily free flowing slag. Such a slag boosts reaction rate of slag metal and influence the efficiency of the blast furnace operation. The present project aims at measuring the viscosity of blast furnace slag procured from Adhunik Metallics Limited, Industrial slag which is different from synthetic slag by various means. Both theoretical models and experimental apparatus will be used to predict the viscosity of blast furnace slag at different temperature. The activation energy of different slag will also be estimated from viscosity Vs temperature plots. The effects of chemical composition mainly C/S ratio, MgO content & Al₂O₃ content will be analyzed in the present study and their effect on the production and energy consumption. In this way an attempt is made to comment on the structure of the slag based on estimated values of Activation Energy of viscous flow and proper conditions and burden material used in the blast furnace to improve the production rate and quality of the product.

Key words – Industrial Slag, Viscosity, Activation Energy of Viscous Flow.

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CHAPTER-1 INTRODUCTION

1.1 Introduction

In present scenario of iron making industry main purpose is to increase the production and reduce the cost of operation or increase the production by using same burden material. There are many researches going on to get the answer how to increase the production by using same burden material. We get a proper explanation to increase the production by changing charging condition, amount of burden used, condition of blast furnace etc.

The important part of blast furnace is cohesive zone, this part have a major impact on flow behavior of blast furnace slag. The shape, size and location of cohesive zone in the furnace determine the flow characteristics of blast-furnace slag.

The main constituent of blast furnace burden consists of gangue minerals and coke ash in combination with fluxes usually lime and magnesia. There are some oxides in iron blast furnace and these principal oxides of the minerals are alumina and silica and these oxides are removed by the addition of flux, by the reaction of oxides of the minerals and flux a liquids solution is formed which is called slag, this liquid slag is low in density in comparison to the molten iron so it's being insoluble and lighter, due to lower density slag is floating on the molten iron by forming a separate layer. Flux also plays an important role in the slag forming, there are two types of flux one is basic flux and another is acidic flux. Basic flux is important not only to reduce the melting points of the acidic constituents and there by obtain a liquid or sufficiently fluid slag but it also play an important role in the slag-metal reaction & controls the metal quality, as follows the Si-, Mn-, and S- contents except from the four main non ferrous oxides (magnesia, alumina, lime and silica) which form 95-96% of the total slag, there are other compounds present in minor quantities depending upon the raw material and the type of iron smelted in the blast furnace. They generally are: FeO, MnO, FeS, CaS, alkali silicats etc.

Although an ideal slag could possibly never be achieved, furnace performance its efficiency and fuel consumption depend on a proper slag. An ideal slag depend on the metal temperature, slag quality directly depends on the metal quality i.e., the content of C, Si, Mn, S and FeO, it also depend on the homogeneity, absence of crystalline phase, i.e., the melt should not undergo variations in physical properties.

Furnace performance also improve by slag by absorbing the shocks generated by the tolerance of fluctuation in temperature and physical and chemical properties of the burden which constantly occur even under the best condition of the furnace operation, and by this cushion effect of the slag material properties is not affected.

Slag quality also depends on sulphur retention potentiality, i.e., a high (S)/[S] ration under the operating condition.

Blast furnace operation also depend on the viscosity of the slag, low viscosity .i.e. the slag should have ability to run out from the furnace freely and rapidly at the operating temperature is affected; as the coke rate is affected by the 'critical temperature' which will enable the slag to flow the free running characteristics of the slag will affect fuel economy.

Also the free movement of the stock and furnace gases; these are determined by the physical properties and zones of function of the primary and bosh slag's which directly affects the productivity of furnace and quality of the products.

The operating and other conditions, namely flame temperature, distribution of material is at the top, ore reducibility, burden yield (i.e., slag bulk), sinters and pellets(acid, fluxed or super fluxed), softening temperature of the ferrous charge ,coke ash content, furnace lines etc. affect the formation of primary and bosh slag. The use of a slag of optimum composition may result in a maximum production and minimum of slag bulk, metal-sulphur and fuel costs and all these achieved when all operating conditions are conductive to a smooth and regular furnace movement.

The FeO content also affect the flow characteristics of the slag. The higher amount of FeO in slag is disadvantageous for blast furnace, due to higher content of FeO, slag descends inadequately heated and prepared and disturbs the thermal state of the hearth. The formation of a pasty mass at a higher level of the furnace which hinders gas through flow and causes an erratic stock descent is promoted by the wide fusion range and high fusion temperature .If the FeO content is low, it promotes a high production rate and the adequate preheating ensures a stable furnace operation and metal quality because if the FeO content is low its being very reducible

and its acquires a high fluidity as soon as it melts and it does so at a high temperature and in a short zone in the belly or upper bosh.

In the following thesis work we are trying to get the best slag compositions which enhance the production and working condition of the blast furnace.

1.2. Objectives

- The objective of this work is to analyze a industrial slag which is procured from Adhunik Metallics Limited.
- To study the flow characteristics of industrial slag by measuring its Initial Deformation Temperature(IDT), Softening Temperature(ST), Hemispherical Temperature and Flow Temperature(FT).
- To find the Activation Energy and Viscosity of the slag and analysis.
- To increase the production rate on the giving condition which is already use in the industry and suggesting them about the quantity of burden material by which they improve the production rate by analyzing the slag.

CHAPTER-2 LITERATURE SURVEY

2.1. Blast Furnace

Pig iron is form by the use of a blast furnace, it's a type of metallurgical furnace and main purpose is smelting. The production of pig iron in the blast furnace ranks for most amongst all the iron making process. This is not only because of the very rich production rate but also because of the great degree of heat utilization that can be obtained in such furnace.

The iron ores exists commonly as oxides either as hematite Fe₂O₃ or magnetite Fe₃O₄ or sometimes in small proportion of hydroxides and carbonates. All iron bearing material used for blast furnace smelting.

It has circular cross section of different diameter and height approximately 30 m. Inner core of blast furnace is covered by the refractory lining according to the temperature profile of blast furnace and outer shell is made of steel. The charging source of iron units in blast furnace are lumpy iron ore (above 10 mm in size) in the form of hematite (Fe₂O₃) or magnetite (Fe₃O₄) and iron oxides in the form of pellets or sinter prepared from iron ore fines, for thermal and chemical energy and for happening of desired process of ore melting, we used coke and oxygen (air) feeding of blast furnace, for separating the gangue materials from the feed materials and liquid iron, flux is used in the form of dolomite/lime/limestone is added either independently or with sinter. The total time required for descending the raw materials is 6 to 8 hours from top to bottom of the furnace and finally gives liquid iron as the main product and slag as byproduct and those drained at regular time of intervals.

Blast furnace operation is a contentious operation once it started it runs for several years. It's shut only for repair work and modifications.

2.2. Blast Furnace Operation and Control

The burden materials are drawn out from the storage bins in required amounts and in desired sequence and are weighed as accurately as is feasible without impairing the rate of feed. The weighed materials are put in the charging skips which raise them to the furnace top and discharge them through the distribution chute. The ore coke and lime stone are never premixed.

On the contrary, these are charged separately, one skipful at a time, and depending at a time, and depending upon the requirements that many skips of the required material are charged.

Its operation is controlled from the top by trying to distribute the solid charge more uniformly in the furnace. Blast furnace simultaneously controlled from the bottom by the temperature and driving rate of the blast. In order to exercise this control a series of instruments are provided at various levels in the blast furnace complex to measure and control various parameters.

In a blast furnace operation the macro things which affect the flow and operation of the blast furnace are coke rate, burden distribution, hot air and flux, for getting 1 tone of hot metal 0.8 to 0.6 tone of coke, 0.5 to 0.6 tons of lime stone and 1.7 to 1.8 tone of hematite is required. Numerically it requires 2500 m^3 of hot air which provide 1 ton of hot metal 0.6 ton of molten slag and $3200 \text{ m}^3 + 80 \text{ kg}$ of dust.

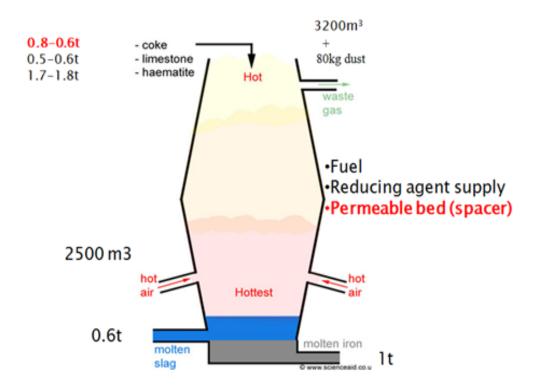


Fig-2.1 Simplified Material Flow In and Out Of Blast Furnace

2.2.1. Reduction of Iron Oxides

There are three forms of iron oxides hematite (Fe₂O₃), magnetite (Fe₃O₄) and wustite (FeO). These oxides are reduced in stages. Their reaction with CO, the equilibrium CO/CO₂ ratios and Co utilization factor η_{co} at 900° are given below. The extent of utilization, i.e., the fraction percentage of co converted to CO₂ is denoted as-

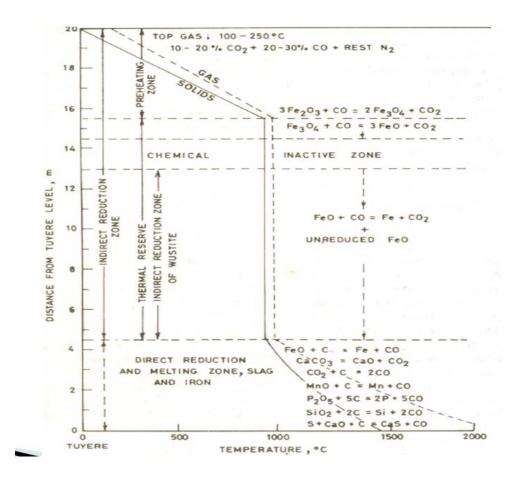


Fig- 2.2. Systematic diagram of iron oxides reduction in the blast furnace

Reactions	Equilibrium at	Equilibrium at 900°c	
	CO/CO ₂	η _{Co%}	
$3Fe_2o_3 + CO = 2Fe_3O_4 + CO_2$	0	100	
$Fe_3O_4 + CO = 3FeO + CO_2$	0.25	80	
$FeO + CO = Fe + CO_2$	2.3	30	

Table 2.1- Reduction reaction of iron ore

The burden material like ore/sinter/pellet (or agglomerated ore), coke and limestone/dolomite/lime are charged through top of the furnace and hot air blown through tuyeres which is located at the bottom of the blast furnace. Heat and carbon monoxide is generated by the reaction of oxygen and carbon, oxygen come from the preheated blast and carbon come from the coke. The burden material reacts with nitrogen and carbon monoxide and absorbs heat from the gas phase. The burden material melts down and metal and slag produced as the product which is in the layer form due to the density deference between molten metal and slag, slag float over the molten metal and separated to obtain the metal. As we know blast furnace is a counter current process, the hot blast coming through tuyere which contains high CO amount comes in to contact with wustite which required very high reduction potential for conversion to Fe. The resulting lower potential gas reacts with magnetite and hematite which need much smaller equilibrium CO/CO₂ ratios for reduction to lower oxides. Hence reduction of wustite is prime importance in iron oxides reduction, especially because about 70 % of hematite oxygen is present as wustite.

If any wustite remains unreduced in a zone where temperature is higher than 1000°c, the CO₂ produced rapidly reduced by carbon according to

$$CO_2 + C = 2CO (2.2)$$

$$FeO + C = Fe + CO (2.3)$$

These reactions which produced CO₂ called indirect or gaseous reduction. The overall reaction is mildly exothermic.

Reaction (2.2) is called direct reduction and is endothermic, contrast to indirect reduction but consumes less carbon for every mole of oxygen removed because the product CO can take part in further gaseous reduction.

If the flux material is added in to the burden material, it get calcined as-

$$CaCO_2 = CaO + CO_2$$
 (2.4)

$$MgCO_3 = MgO + CO_2$$
 (2.5)

In the blast furnace between the temperatures range of 800-1000°c basic oxides combine with the gangue materials to form the slag, reduction of oxides of iron is practically over while it is in solid state. This reduced iron shall be impure because of associated gangue constituents of the ore. Separation of iron from the associated gangue can only be brought about by melting the whole charge. The charge material get melt in the bosh region as it descend from the top. Here forms two liquid phases as result of melting, one is the iron phase called molten metal and other slag as the byproduct. The unreduced oxides join the slag phase and metal which is in elemental state join the metal phase.

Slag thus contains mainly silica, alumina, alkali -alkaline earth oxides, etc. with some minor other oxides and sulphides. A part of the SiO₂, MnO, P₂O₅, etc. get reduced and hence the metal is contaminated by Si, P, Mn, S etc. the metal also gets saturated with carbon because of its direct contact with coke inside the furnace. On the whole therefore the iron melt may contains anything up to 8 wt% of the total impurities like C, Si, Mn, P, S etc. as the metallic product. The slag may contain mainly SiO₂, Al₂O₃, CaO and other minor oxides and sulphides. Stratifications of metal and slag is best achieved if the slag is thin that is of low viscosity. Addition of flux in the charge helps, to a large extent, in achieving the correct nature of the slag.

The gas composition and the temperature vary smoothly over the vertical as well as the horizontal cross section of the furnace. The chemical processes are therefore continuous from bottom to top, as per the physical aspects the blast furnace is divided in to the four zones main zones.

2.3.Blast Furnace Zones with respect to the physical processes-

2.3.1. Stack or Shaft-

Stack or shaft lies between the stock line and mantle level in this region burden material is in solid form. The temperature range lies between 200°c to 1100-1200°c from stock line level to the bottom of the stack. The cross section of the furnace is increases progressively to almost double to the stock line to the mantle level for easily falling of charge material as the temperature rises gradually the charge material got loose or slightly molten so the volume of the charge material increases in mantle level in comparison to stock line.

2.3.2. <u>Bosh</u> –

As the charge material came down to the bottom of the stack it's begin to soften and fuse in physical state. The zone in which melting of burden occurred is called bosh zone, except of coke at that place. The gangue material and flux used in the process combine to form the B.F slag. In this region furnace walls are parallel to some extent and after that tappers down or are completely tapering down for the purpose reducing the cross sectional area by about 20-25 percentage for the channelization of the resultant decreased in the original volume of the burden material. The B.F operation directly affected by degradation of coke which leading to the decreased in permeability at the bosh region.

2.3.3. Tuyere or combustion zone –

At the tuyere zone except the coke column all the charge descends down and all the charge material is in molten state. The oxygen came from the hot blast reacts with the coke and produces CO and several combustion zones, in front of every tuyere, exists in the tuyere zone. In the tuyere zone there is a presence of a 'raceway' or 'runway' in front of every tuyere from which the flame and gas flows smoothly and these flame and gas spread over the entire C/S of the blast furnace. Over the entire C/S of the blast furnace raceway changes its direction firstly it is in horizontal and after that smoothly changes to its vertical direction while expanding over the entire C/S of the blast furnace.

2.3.4. <u>Hearth</u> –

At the tuyere level most of the coke burn out but it is believed that a fractional amount is came over in to the hearth zone where it comes at saturation state by dissolving in to the hot metal. The entire molten oxides came in to two different layer of molten slag and molten metal, molten slag floats over the molten metal because of its lower density in the hearth from where these slag and metal are tapped separately. The C/S of the blast furnace below the tuyere level decreases since no permeability is required further; it can be maintained in the liquid charge. The walls of the well are parallel and have smallest C/S of the furnace exists in the hearth.

2.4. <u>Different internal zones of blast furnace</u>

The internal zones of blast furnace are divided in vertical section. In seventies, there was many experiments done to find the internal attitude and behavior of blast furnace, to find that various sample collected from various zones and analyzed them. By these experiment and analysis scientist got an insight view on the behavior and attitude of the internal condition of the B.F in terms of the availability of various zone, their composition and structure, as well as the reaction mechanism involved in that zone. The B.F can be classified into six zones as shown in fig.2.3. These six zones are as follows:-

- **Granular zone** The zone at which the whole burden material is in solid form called granular zone.
- <u>Cohesive zone</u> The zone at which charge material are in semi-solid form except coke and lowering in this zone the slag got melted and form a slag which is rich in FeO content, hence it melts at much lower temperature.
- Active coke zone In this particular zone coke have a vital role, the coke travel for long in the B.F due to its high permeability and at this zone coke reacts with iron oxides which is called direct reduction, from the dripping slag and its own interaction with CO₂ i.e. mainly bosh region.

- <u>Tuyere zone</u> It is the zone at which hot blast coming through tuyere reacts with coke and burns in front of each tuyere by this carbon monoxide gas is formed after burning of coke in front of tuyere.
- <u>Stagnant coke zone</u> Due to the high permeability of coke it is still in solid form in this zone and entire molten material overlying on that coke. The metal and slag gets saturated by carbon while trickling down over that coke.
- <u>Hearth zone</u> It is the zone where the molten slag and metal collected and due to lower density of the slag it floats over the molten metal and splits in to two different layer and they react with each other till they separated by drainage.

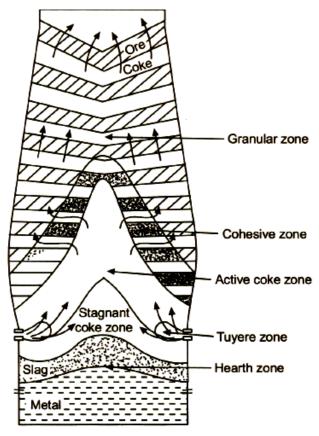


Fig.2.3. Diagram shows the sectional internal zones in a B.F.

It is seen that between entire zones present in B.F it is found that cohesive zone plays a vital role it has a temp. range of 1000 - 1500°C. It is found that thickness and location of the cohesive zone directly affect the productivity of blast furnace, quality of hot metal, consumption of fuel; stability of operation in the B.F and life of lining present in B.F.

2.4.1. Cohesive Zone

The zone at which charge material are in semi-solid form except coke and lowering in this zone the slag got melted and form a slag which is rich in FeO content, hence it melts at much lower temperature. At this zone softening and melting of the burden material started and solid volume disappears mostly in this zone. The location and the thickness have a direct effect on the blast furnace performance, its productivity, consumption of fuel and quality of hot metal. Following things are affected by the location and thickness of cohesive zone:-

- Gas permeability
- Extant of indirect reduction
- Silicon content of pig iron

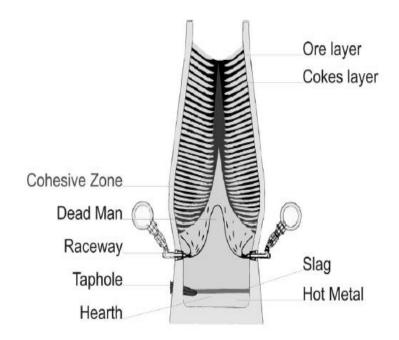


Fig.2.4. Cohesive Zone

2.4.1.1. Gas permeability — It's directly depending on the thickness of cohesive zone. It describes about the gas passing through the coke layer. For a given pressure difference in a B.F, gas flow is more through the thin layer of the coke, if the cohesive zone is narrow. Gas volume also depends upon the viscosity and volume of the melt produced through which bed permeability affected.

2.4.1.2. Extant of indirect reduction – Indirect reduction is affected by the place or position of the cohesive zone. The length of the granular zone get increased if cohesive zone moves down into the B.F, hence the utilization of CO gas get increased due to the increase in volume of the granular zone that means more iron ore get reduced by the CO gas because the time period of burden get increase in the granular zone. So we can say that more iron ore get reduced at a limiting amount of coke, hence coke consumption rate get decreased.

2.4.1.3 Si content of pig iron – the coke is burnt near about raceway which is the prime source of heat and Si content in hot metal, Si comes from reduction of SiO which is present in coke ash. If the cohesive zone get low in the B.F that means the volume of dripping zone is get reduced, at this zone SiO reduced and form Si, found in to the hot metal. So by decreasing the volume of dripping zone reduction of SiO get reduced so that less amount of Si found in hot metal.

$$SiO2 + C = SiO + CO$$
 (2.6)
[Fe] + SiO = [Si] + (FeO) (2.7)

$$(FeO) + CO = [Fe] + CO2$$
 (2.8)

$$C + CO2 = 2CO (2.8)$$

2.5. Blast Furnace Slag

Slag is basically referred as a waste material of the blast furnace or it is a by-product. The formation of slag is unavoidable. The slag quality and quantity rule over the main product of the blast furnace slag that is hot metal. Slag mainly defined as "the non-metallic product consisting essentially of silicates and alumino-silicates of calcium and other mean that is produced in a molten condition with iron in a B.F". Slag is mainly affected by the acid and basic flux. The

work of basic flux is not only to decrease the melting point of the acidic minerals for the purpose of an easily flow slag but also it controls the hot metal quality by taking part in the reactions.

The components present in the slag are lime, magnesia, alumina, silica and in minor fractions of FeO, MnO, FeS, CaS, alkali silicates etc. these minor components in slag depend on the raw material.

Slag plays an important role in the blast furnace it protects the hot metal and removes undesirable impurities present in the raw material. Usually a liquid slag layer covers the molten metal and carries out the following functions ^[47].

- (i) It prevents oxidation of the metal by sealing.
- (ii) It removes dangerous and undesirable elements like sulphur and phosphorous from the metal which is present in raw material.
- (iii) By flotation it removes non-metallic inclusions.
- (iv) It reduces the heat losses from the metal surface and prevents the "skull formation" and
- (v) It provides the lubrication and control of the heat extraction in the continuous casting of steel liquid slag.

2.5.1. Types of Slag

- a) <u>Air-cooled blast furnace slag</u> ACBF slag is defined in ASTM C125[4] as- "The solidified molten B.F slag under the required atmospheric conditions can also be Subsequent cooled by water to accelerate the solidification of surface." The structure of solidified slag practically shown with many non-connected cells. A greater surface area is found for slag texture which provides good bond strength with Portland cement and provides a high stability in bituminous mixtures.
- **b)** Expanded or formed blast furnace slag— when steam or air, water is used in a control quantity for the cooling purpose of the B.F slag so this type of slag is obtain and gives a formed product which is light in weight and this is happened due to its acceleration of cellular nature by using this type of solidification process.

- c) Pelletize blast furnace slag The pelletize blast furnace slag stand for, when the molten slag is quenched by a water jet in a vibrating inclined plate. After the vibrating feed plate slag is lead by a rotating drum where it reacts with water droplets to form spherical droplets. After getting the spherical shape with aid of water it loses its heat and get freeze and came out from the pelletizer. Each slag pellet has a special internal cellular structure. The cellular structure contained a smooth spherical skin which has voids can be visualize by microscope. [5]
- d) Granulated blast furnace slag there is no or little crystallization occurs if the molten B.F slag is cooled and being solidified with the help of high pressure and volume of a water jets when slag is in glassy state and by this phenomena there is formation of very fine sand grade fragments clinker like material. It also have the cementious property by which it is used for additive as a Portland cement after crushing and milling of the slag in the fine particle.

2.5.2. Slag Structure

It consist homogeneous oxides of silicon and other elements. It also consists of complex and simple ions and electrical properties. Crystal analysis of solid silica shows that silicon occupies the centre of a tetrahedron surrounded by 4 oxygen atoms, one at each of the 4 corners. The substance formed will have an overall stoichiometric formula of SiO_2 . The SiO_4 group carries 4 negative charges i.e. $(SiO_4)^{4-}$. The viscosity of molten silica is very high (= 10^5 P), the corners being linked tightly in all direction in a vast network^[48].

The (SiO₄) group can be assumed to exist as ion in the complex silicates. Measurement of the energy of activation for electrical conductance and other results indicate that the addition of CaO, MgO or other metal oxides to molten silica results in the breakdown of the 3D silicon oxygen network in to silicate ions. The driving force for the breakdown process is the attraction between silicon and oxygen. This depends on their relative valencies and ionic radii.

$$\equiv Si - O - Si \equiv +CaO = \equiv Si - O - + -O - Si \equiv +Ca^{2+}$$
 (2.10)

The cations distribute in the interstices of the network, being localized near the charged oxygen^[48]. As the metallic oxides are added in increasing amount, the Si-O bond break correspondingly, and large globular or ring type silicate ions are formed. These become progressively smaller as the metal oxide content increases^[48]. The viscosity of the acidic melt falls as the network gradually breaks and ultimately a stage is reached when no corners are shared^[48]. At this stage the slag reaches the orthosilicate composition (MO/SiO2 ratio equal to 2.0). The slag is deemed to be neutral and consists of discrete (SiO₄)⁴⁻ ions. On attaining the stoichiometric composition of 2MO.SiO₂, further additions of base would give oxygen ions and equivalent number of cations, i.e., when the MO/SiO2 ratio exceeds 2.0.

$$2(\equiv Si - 0 -) = \equiv Si - 0 - Si \equiv +0^{2-}$$
(2.11)

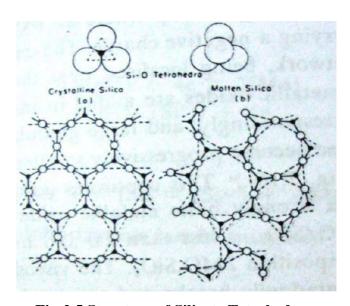


Fig-2.5.Structure of Silicate Tetrahedron

2.5.3 Electro-chemical Nature of Slag-Metal Reactions

Although direct exchange of two atoms or ions are possible between metal and slag, the introduction of the concept of an electro-chemical mechanism of slag -metal reaction becomes a

necessity since metal is non-polar and molten slag ionic in character. Hence any transfer of an element from metal to slag is accompanied with an anodic reactions, e.g.,

$$[Mn] = (Mn^{2+}) + 2e$$
 (2.12)

To preserve electro-neutrality of the slag, a cathodic reactions must occur with the deposition of an element in the metal, e.g.,

$$(Fe^{2+})$$
 + 2e = [Fe] (2.13)

$$[Mn] + (FeO) = (MnO) + [Fe]$$
 (2.14)

We may write,

$$[Mn] + (Fe^{2+}) = (Mn^{2+}) + [Fe]$$
 (2.15)

$$[C] + (O^{2-}) = CO_{(g)} + 2e$$
 (2.16)

$$[S] + 2e = (S^{2-})$$
 (2.17)

$$[Si] = (Si^{4+}) + 4e$$
 (2.18)

[Al] =
$$(Al^{3+}) + 3e$$
 (2.19)

2.5.4. Slag Basicity

The acid oxides are those oxides, which form anion complexes by accepting oxygen in melts for example SiO₂, Al₂O₃. Anion complex is break by the basic oxide by donating oxygen molecule basic oxides defined as, MnO, MgO, CaO and FeO. In practice, the ratio of the sum of the concentration of the bases to that of the acids is called basicity of the slag. In iron-making the ratio is usually depicted as CaO/SiO₂ or (CaO + MgO)/ (SiO₂ + Al₂O₃) although there are variations in their usage, concentration of MgO and CaO are sometimes taken as equivalent on molar basis. In terms of Wt% the CaO equivalence of MgO becomes %CaO= (56/40) % MgO=1.4%MgO.

2.5.5. Slag viscosity

Viscosity is the properties of a fluid which offers resistance to the movement of one layer of fluid over another adjacent layer of fluid i.e. flow phenomena. In blast furnace there are several important phenomena occurs such as heat transfer, mass transfer and the chemical reaction between the slag and metal, and it depends on the flow phenomena of the slag therefore the study about slag viscosity is very important.^[7]

In the blast furnace, slag formation and the mineralogical transformation that the slag undergoes during descend of charge; influence the quality of the hot metal. As we know that the silica and Al present in slag increases the viscosity of whereas the presence of calcium oxide decreases the viscosity. The melting zone of slag determines the cohesive zone and hence the melting characteristics and fluidity of the slag play a major role on the productivity of the blast furnace. Viscosity of the slag also affects the coke consumption, degree of desulphurization, gas permeability, smoothness of operation, heat transfer and many more.

$$\mu = Ae^{\frac{E}{RT}} \tag{2.20}$$

Where, $\mu = Viscosity$

A = Pre exponential constant.

E = Activation Energy of viscous flow

T = Absolute Temperature

2.5.6. Available viscosity models

For the estimation of viscosity there are several models available in the literature. Out of the available models the most relevant model for blast furnace slag has been discussed below.

- 1. Iida Model
- 2. NPL Model
- 3. Ray's Model

Iida Model

The viscosity of slag is structure sensitive it is known that slag has a 3-D network so that structure affects the B.F slag viscosity. This is the reason to consideration of structure of the slag for prediction of slag viscosity.

Iida's model ^[13] is based upon relating the structure to parameters representing the basicity of the slag and is expressed as:

$$\mu = A\mu_0 e^{\frac{E}{Bi^*}} \tag{2.21}$$

 μ_0 - Directly depends on the molar volume, composition of chemical and slag melting point.

E & A depends upon temperature (T) while Bi* depend on composition of chemical.

$$A = 1.745 - 1.962 \times 10^{-3}T + 7.000 \times 10^{-7}T^2$$
 (2.22)

$$E = 11.11 - 3.65 \times 10^{-3} T \tag{2.23}$$

$$\mu_{0=\sum \mu_{0i}X_i} \tag{2.24}$$

Where,

 μ_0 =Viscosity of hypothetical melts.

$$\mu_{0i} = 1.8 \times 10^{-7} \frac{[M_i(T_m)_i]^{1/2} e^{(\frac{H_i}{RT})}}{V_m^{2/3} e^{[\frac{H_i}{R(T_m)i}]}}$$
(2.25)

$$H_i = 5.1(T_{mi})^{1/2} (2.26)$$

M= Oxides molecular weight

 V_m = Molar volume of oxide considering at the melting point T_m

R= Universal gas constant

X= Mole Fraction of the substituent.

i= subscript refers to oxide

 $B_i^* = modified basicity index$

$$B_i^* = \frac{\sum (\alpha_i W_i)_B + \alpha_{Fe \, 203}^* W_{Fe \, 203}}{\sum (\alpha_i W_i)_A + \alpha_{Al \, 203}^* W_{Al \, 203} + \alpha_{Ti0 \, 2}^* W_{Ti0 \, 2}}$$
(2.27)

Here,

 $\alpha_i = Specific coefficient of i_{th} oxide$

 $\alpha^* = modified specific constant$

$$\alpha_{Al2O3}^* = aB_i + bW_{Al2O3} + c (2.28)$$

Where,

$$a = 1.2 \times 10^{-5} T^2 - 4.3552 \times 10^{-2} T + 41.16$$
 (2.29)

$$b = 1.4 \times 10^{-7} T^2 - 3.4944 \times 10^{-4} T + 0.2062 \tag{2.30}$$

$$c = -8.0 \times 10^{-6} T^2 + 2.5568 \times 10^{-2} T - 22.16 \tag{2.31}$$

$$B_i = \frac{\sum (\alpha_i W_i)_B}{\sum (\alpha_i W_i)_A} \tag{2.32}$$

Word A and B represent acidic oxide and basic oxide. So viscosity of the slag measured with help of the equation (2.20) to (2.31).

2.5.7. Flow characteristics of slag

High temperature microscope is helpful in finding the flow characteristics of B.F slag. Flow characteristic temperature is classified in to 4 types. ^[16] Which explains fusion behavior of B.F slag.

- Initial deformation temperature (IDT)
- Softening temperature (ST)
- Hemispherical temperature (HT)
- Flow temperature (FT)
- (1) <u>Initial deformation temperature</u> (IDT) Here the prepared sample of slag which have a cube shape is placed in heating microscope which have a completely six by six grid pattern as per the viewing from the microscope. The deformation temperature at which roundness of the edge of slag sample started called initial deformation temperature, at that temperature stickiness of the sample started.
- **Softening temperature** (ST) Temperature at which B.F slag sample get called softening temp, practically shape of cubical outline of slag sample starts changing it shrinks one grid out of the six grid, practically at that temperature slag got soften or we can say that plastic distortion started at that temperature.
- (3) <u>Hemispherical temperature (HT)</u> Temperature at which slag sample convert in to a hemispherical shape called hemispherical temperature practically its noted as the temperature at which the total height of the slag sample is equal to half of its base length.
- **Flow temperature** (FT) The temp. at which the slag sample attains liquids state, practically this temperature noted as the temperature at which height of the slag sample is equal to 1/3 rd of the total height of the slag sample which it had at

the hemispherical temp., or we can say at that temp. The liquid mobility of slag is shown i.e. free flowing of the slag.

2.6. Activation Energy

The minimum energy required for a chemical process called activation energy, basically it's a potential energy which starts up chemical reaction. It is a minimum energy required for start up of a chemical reaction. The symbol of activation energy generally expressed by Ea and it's have SI unit in KJ/ mole.

It is the minimum energy required for breaking of a molecular bond for start up of the reaction as metallurgical point of view, It also known as an energy barrier which is needed to startup the chemical reaction.

There is a relationship between the activation energy and the rate of reaction of a chemical reaction. ^[17] This equation is expressed as:

$$K = A e^{-\frac{E_a}{RT}} (2.33)$$

Where

K= Coefficient of reaction rate

R=Universal gas constant

A =Frequency factor of the reaction

T= Absolute temperature. [18]

2.6.1. Activation energy of blast furnace slag

Activation energy of B.F slag plays crucial role during the formation of pig iron. These are the points which affect the blast furnace slag from activation energy point of view:

- It affects the adhesion of the ash particle behavior towards walls of reactor.
- It effects solidification time of slag.
- It affects the separation temp. of B.F slag and hot metal. As well as time required.
- It manages the amount of heat required to molten the slag material.
- Endothermic and exothermic reaction can be notify by the activation energy. [19]
- Recrystallization temperature can be found by the activation energy. [19]
- Energy required for the flowing property of the slag.
- Energy required for breaking of Si-O bonds which is called Heat of dissociation. [20]
- Time taken to complete slag formation reaction. [18]
- It also describes the property of slag which shows it viscous behavior. [21]
- Melting point of the slag can be found by the activation energy. [22]
- Nucleation and grain growth of the slag material can be found by the activation energy.^[23]

2.6.2. Factor affecting the activation energy

Activation energy of the B.F is directly affected by the following factor:

1. <u>Temperature</u> – The slag is highly active at that region where the temp. of furnace is high, also it is highly active, containing more energy so the less amount of activation energy is required. Similarly the more activation energy is required where the temp. of blast furnace is low, B.F slag containing less energy. It directly depends on kinetic energy of the molecules as the temperature increases simultaneously kinetic energy increases so the collision rate of molecule increases and hence less activation energy is required.

- **2.** <u>Concentration and pressure</u>— the physical condition also affects the activation energy of a slag. If at a region no. of molecule is high due to the high pressure so the region becomes dense and the inter-molecular space becomes less so the chance of collision of molecule increases. So rate of reaction automatically increases due to high pressure and requirement of activation energy decreases.
- **3.** <u>Physical state</u> Slag particle affects the activation energy of the slag. Power shape (small size of particle) is needed for the effective founding of the activation energy, for the calculation of activation energy it is needed to reaction should be completed at both places at the surface as well as the inner side of the molecule. For large size particle reactions is completed only on the surface so that the resulting energy is not correct and for the small size particle reaction occur inside and outside so the resultant result is accurate because small size particle has large surface area for reaction.
- **4.** <u>Composition of the slag</u> It is known that for every composition they have different bond strength and to break that bond strength there is need of different energy. As per this law if we use different composition of slag, means the slag used have different oxides(oxides of Ca, Si, Al, Mg), it required different activation energy.
- **5.** <u>Percentage of CaO</u> –The amount of CaO plays an important role in activation energy; basicity of slag is dependent on the CaO content. Basicity is higher for the higher CaO ^[22] and there for the temperature of the liquid is more. ^[17] Relative of that slag formation decreases and the activation needed is more.

2.7. Methods of increasing the productivity-

The coke consumed for a unit of iron is termed as coke consumption rate or simply coke rate in kg or tones per THM. The production rate, also known as smelting rate or output is denoted as^[1]

$$P = Q / K \tag{2.34}$$

Where.

P = Productivity, THM per day

Q = coke burned, tones per day

K = coke consumed, tones per THM

From Eq.1 blast furnace production can be increased by measures which would increase the coke throughput and decrease the coke consumption rate. The methods for achieving a high production rate are summarized below.^[2]

The coke throughput can be increased by:

- 1. Increased oxygen supply (increased blast volume, oxygenated blast, humidified blast, high top pressure);
- 2. Decreased volume, viscosity and increased density, surface tension of slag;

The coke rate can be decreased as:

- a) Preparation and concentration of charge materials;
- b) Increase in blast temperature;
- c) Blast modification;
- d) Super(metalized) burden;
- e) Stack gas injection
- f) Fuel additives

2.7.1. Increase in coke throughput (Q)

The coke burning rate can be increased by an increased oxygen supply. Since most furnaces blown with normal blast an increase gas through flow would depend upon the aerodynamics of the bed ^[3].

2.7.2. Increased in blast volume-

An increased blast volume rate means an increase oxygen input in unit time which result in an increased coke burning rate. The coke burning rate is approximately proportional to oxygen input. A large blast volume will be accepted by the furnace if the permeability of the stock column is increased simultaneously so that the material descent and gas distribution are uniform throughout the vertical and horizontal cross section.

Although the driving rate can be increased greatly with large particle size because of the high rate of gas flow permitted, two other factors governing the coke rate are affected, viz., reduction and heat transfer rates.

2.8. Literature studied on Viscosity of B.F slag and Activation Energy

Slag viscosity plays a vital role in the quality and quantity of hot metal produced, it affects the kinetic energy of B.F slag material as well as degree of reduction of final slag produced.^[7] It also affects the impurity removal capacity which is describe as the separation of slag and hot metal. The slag contains the 3-D network of the silicate which increases the viscosity of the slag, it shows that the viscosity of slag is highly sensitive towards the molecular and ionic structure of slag material. In the furnace operation slag viscosity needed is low because of easily tapping of the slag. This is directly related to energy needed and B.F productivity. In our country due to the medium grade of iron ore and coke material the slag generated is high in the alumina contain. So it's necessary to take an interest towards the analysis of high alumina contain slag. The slag viscosity increases as the alumina contain in the slag increases, which directly depend on the lime content., because Si⁴⁺ is replace by Al³⁺ in silicate network only if it is associated with Ca²⁺ to preserve electrical neutrality. ^[10]

Y.S.Lee et al ^[24] – studied that the viscosities of slag's which contain CaO-SiO₂-Al₂O₃-MgO-FeO under a specific condition of C/S ratio between 1.15-1.6, Al₂O₃ % 10-13, MgO-5-10% and FeO % 5-20. They found that at a fixed C/S ratio condition of slag if we increased FeO content the slag viscosity get decreased, slag containing low FeO(<7.5% FeO) on by slightly

increasing MgO amount they got a minimum value of viscosity. The slag viscosity decreased with increase in C/S ratio up to 1.3 while it increased as the C/S ratio increased from 1.3 to 1.5. thus it was conclude that the decreased in slag viscosity would be achieve by increase in depolymerisation of silicate network at $(CaO/SiO_2) \le 1.3$. While the viscosity increases at $(CaO/SiO_2) > 1.3$ by increasing the chemical potential of primary solid phase. Thus it was confirmed that slag viscosity in basic slag system $(CaO/SiO_2) > 1.3$ could be determined by the chemical potential of dicalcium silicate.

Kohei Sunahara et al ^[25] studied about the effect of high alumina on blast furnace. They found that the viscosity dominate the tapping behaviour of slag coming out from the furnace which is a fluidization phenomena. They found that the slag viscosity directly affect the drainage of slag, it decreases on increasing viscosity to maintain that under high alumina condition small amount of MgO is added. They also found that viscosity of slag has more effect on drainage rate in comparison to crystallization temperature. The pressure in dripping zone is directly affected by C/S ratio and Alumina contain in slag. It decreases by increasing concentration of alumina and increasing C/S ratio separately. It also effect by wet ability, viscosity, and slag crystallization temperature.

Amitabh Shankar et al ^[10]-they studied about effects of C/S ratio, temperature, silica activity of slag and TiO2 on viscosity of slag by experiment on two different slag composition CaO-SiO₂-MgO-Al₂O₃-TiO₂ quinary system and CaO-SiO₂-MgO-Al₂O₃ quaternary system in between temperature range of 1377°c to 1400°c. They found that viscosity got decreased for the condition of high Al₂O₃ slag for C/S range of 0.46 to 0.8. At higher C/S ratio more than 0.8, the slag viscosity still decreases even with addition of small amount of TiO₂ approximately 2%, the slag viscosity increases with increase in silica activity between 0.1 to 0.4, below the liquids temperature the increase being steeper.

J. Muller et al ^[7] they studied that viscosity is an important term for blast furnace operation its affect the rate of molten metal as well as slag, it's also affect the reaction of the furnace as per the location occurring inside the blast furnace. To optimize these processes, it is required to get accurate liquids temperature and viscosity data.

Noritaka Saito et al [26] studied that for a composition of slag (CaO-SiO₂-Al₂O₃) which had mass percentage of40-40-20, on increasing the % of MgO, Fe₂O₃ or TiO₂, viscosity of the slag decreases. They also found that with increased in content of Al₂O₃ or SiO₂ viscosity of calcium ferrite slag get increased and for the same content of oxides, Al₂O₃ is also play an important role for increasing the viscosity.

Yasuji Kawaiet al ^[27] studied about the effect of content % of MgO on viscosities of molten slags. They found that as MgO % increased in CaO-SiO₂-MgO slags, viscosity decreased up to 20% but if we increase the MgO % beyond the 20% viscosity increased. The low viscosity region was found greater than in comparison to CaO-SiO₂-Al₂O₃ slag.

Masashi Nakamoto et al[^{28]} studied about a slag with low melting point and low viscosity at a high concentration regions of CaO and Al₂O₃ for a molten slag CaO-SiO₂-Al₂O₃-MgO. They found that at 1400°c viscosity of a molten slag was less than 0.6 Pa.s for a slag composition of Al₂O₃-CaO-MgO-SiO₂ at a mass percentage of (35-43.1-7.5-14.4) which full fill the condition of fluidity in BF operation.

Seong-Ho Seok et al ^[29] studied about the effect of Al₂O₃ and MgO content on BF slag viscosities, slag CaO-SiO₂-FeO-MgO which is saturated with di-calcium silicate and 8% MgO at 1673°c and slag CaO-SiO₂-FeO-Al₂O₃-MgO under highly basic environment. They found that the slag viscosity strongly depends on Al₂O₃ than on Magnesia content, reason of that behaviour is that solid phases present is more in the case of deviation in alumina percentage.

- *J.Y. Jia et al* [30] studied the effect of titania on slag system. They analyze slag system at different temperature and different % of TiO₂ for refrenced viscosities of a slag system CaO-SiO₂-TiO₂. They found that by increasing the % of TiO₂, action concentration of TiO₂ also increases but viscosity decreases.
- **D.** Ghosh V.A. Krishnamurthy, et al $^{[31]}$ studied about the effect of high Al_2O_3 slag within the range of 15 to 30% on viscosity of blast furnace slag. They used chemical parameters to find the change in viscosity as a function of chemical composition. They found that high Al_2O_3 slag have more viscosity and less sulphide capacity in comparison to low Al_2O_3 slag's. In

this work they interpreted the effect on viscosity by the chemical composition and ionic structure by using chemical parameter of optical basicity.

Hino, Mitsutaka, et al.^[43] studied about the effects of Fe_tO, Al₂O₃ and C/S ratio on weight of slag and dripping temperature in 5 slag system with the help of funnel. They found that the sinter which is formed by eutectic melt have a great importance in the dripping behavior of the B.F slag which is due to the porosity of the ore particles and reduced iron. By increasing the percentage of Al₂O₃, weight of the slag is also increased which remain in the funnel and its directly effects acidic slag and slag which contain low amount of Fe_tO. They also found that increase in percentage of Al₂O₃ has harmful effect on indirect reduction rate and permeability resistance in the B.F due to the increase in weight of slag remaining in the funnel.

Akbarnejad, S.,et al.^[44] studied the effect of time and hydration on blast furnace slag which is used as self cementing road base material. They found that after long time the road base material got hydrated and they also had different composition than that of the normal cement, for analyzing purpose XRD and XRF spectrometry techniques were used.

Higuchi, Kenichi, et al. [45] studied about the blast furnace productivity which requires improved reduction behavior and enhanced reducibility at high temp. of sintered ore. They found that the reduction behavior of sinter directly depended on their chemical composition and pore structure which affects the amount of liquid phase, slag viscosity and smelting rate of that slag which contain 'FeO'. They also found that the sinter which contain porosity below than15μm, rich in Fe content, basicity range b/w (1.5-2.0), low content of alumina had more reduction behavior and concluded that low SiO₂, low MgO, and low alumina is favorable for B.F operations.

WATAKABE et al. [46] they studied about high ratio coke mixed charging technique. They found that by précising control on burden distribution and with the help of flow control gate charging method mixed coke ratio was improved and they found by these technique they got higher production and low RAR operation by the use of lowest grade of sinter.

Moynihan, C. T., et al ^[21] discuss about the shear viscosity activation energy. They found that for determining the activation energy of structure in glass transition region. We must know

about heating rate dependence of the glass-transition-temperature or the cooling rate dependence of the limiting-fictive-temperature which is found by DSC or DTA.

Keuleers, R. R., J. F. Janssens, et al ^[32] studied about the effective methods for the calculation of activation energy which gives the thermal decomposition of chemical compounds. They compare the different measurement and calculation techniques for the thermal decomposition of Mn (Urea)₂Cl₂.

Homer E. Kissinger et al [19] studied about the Variation of Peak Temperature with Heating Rate by Differential Thermal Analysis and found that variation in heat content of the active sample which is indicated by deflections and line representing the differential temperature. The negative deflection shows an endothermic affect and positive deflection shows an exothermic affect. The deflections in temperature are called peaks whether positive or negative.

Wang, Zhong-jie, et al ^[34] discussed about a crystallization process of glass ceramics which was prepared from a composition of nickel slag, BF slag and a few amount of quartz sand. The slag was analyzed by differential scanning calorimetry (DSC), field emission scanning electron microscope (FESEM) and X-ray diffraction (XRD) for getting the crystallization behaviour. They found that the radial crystals were found when the glass was heated up to 1093 K, with the help of XRD analysis, the spherical crystals and radial crystals were likely to be the crystals of Diopside (CaMg(Si,Al,Fe)₂O₆) and Hedenbergite (CaFe(Si,Al,Fe)₂O₆) respectively.

Gan, Lei, et al^[35] studied about the behaviour of throughout cooling crystallization of molten BF slag. They found that activation energy (Ea) obtained during cooling is much higher than that of during heating. They also observe that during continuous cooled crystalline of BF slag and then analyze them by X-ray diffraction they found that akermanite and gehlenite are crucial minerals.

CHAPTER-3 EXPERIMENTAL

3.1. Materials and Composition Procured from the industry

In this experimental work analysis the composition of slag which was procured from Adhunik Metallics Limited, the analysis was done on slag samples on the basis of that we determined an average slag composition by which we get the quantity of optimum burden material by which we get a higher hot metal and by which the production of the company increases, in these slag samples content of SiO₂, Al₂O₃, CaO, MgO, FeO is different in each sample.

We have data of 10 sample of slag and their composition with burden distribution and their metal composition, data was provided by Adhunik Metallics Limited. The following data is listed in following table. Burden used in different casting table.3.1, slag composition table.3.2, metal composition of hot metal table.3.3.

Table.3.1. Burden used in different casting.

Burden(Kg)/Sample	1	2	3	4	5	6	7	8	9	10
(Cast No)	(211)	(223)	(237)	(197)	(232)	(289)	(10)	(48)	(82)	(226)
Coke	2500	2500	2500	2500	2500	2500	2500	2500	2500	2500
Iron Ore	2800	2000	1900	1800	1800	700	1500	0	500	0
Sinter	4000	4500	4900	5600	5700	5300	5600	5700	5200	5900
Lime Stone	175	275	250	175	150	250	100	0	0	50
Dolomite	0	0	0	75	75	0	0	0	0	0
Pellet	0	0	0	0	0	1000	0	1500	1500	1500

Table.3.2. Slag Composition.

	1	2	3	4	5	6	7	8	9	10
SiO ₂	33.24	34.58	32.40	34.08	32.80	31.90	33.24	32.10	31.90	33.54
Al ₂ O ₃	16.87	19.24	15.90	18.84	18.84	19.83	18.87	19.24	19.52	19.76
CaO	36.19	32.11	36.89	35.0	35.0	35.08	33.90	33.92	35.63	34.16
MgO	10.61	10.28	11.53	9.8	9.8	10.16	11.12	11.18	9.58	8.94
FeO	0.41	0.78	0.57	1.56	1.56	0.53	0.63	0.51	0.48	0.72
B ₁	1.089	0.928	1.138	1.06	1.06	1.019	1.032	1.057	1.117	1.018
B_2	1.408	1.226	1.495	1.36	1.36	1.418	1.371	1.405	1.417	1.285

Table.3.3. Metal composition of hot metal.

	1	2	3	4	5	6	7	8	9	10
С	4.39	4.15	4.36	4.01	4.07	4.39	4.40	4.34	4.38	4.42
Si	0.80	0.92	0.89	1.17	1.0	1.22	1.31	0.79	0.84	0.74
S	0.007	0.012	0.008	0.039	0.015	0.011	0.017	0.027	0.007	0.03
Mn	0.168	0.192	0.09	0.146	0.186	0.126	0.110	0.088	0.102	0.087
P	0.081	0.171	0.089	0.129	0.147	0.126	0.126	0.108	0.128	0.135
Ti	0.074	0.110	0.083	0.116	0.133	0.150	0.176	0.104	0.122	0.072
В	0.0009	0.0008	0.0009	0.0005	0.0009	0.0011	0.0010	0.0007	0.0010	0.0004
Fe	94.4	94.3	94.4	94.3	94.4	93.9	93.8	94.5	94.3	94.4

3.2. Sample Preparation

3.2.1. <u>Crushing</u>

The slag material procured from the industry is in block form like concrete, for preparation of the sample it is necessary to crush the sample in fines. This is further deal by milling machine.

3.2.2. Milling of the sample

Crushed sample further milled to convert small pieces of slag in to powder form. This powder form of slag is suitable for the analyzing in heating microscope.

3.2.3. Coning and Quartering

It is simple technique to mix the powder and form a homogeneous mixture because of industrial slag also content some amount of ash and other material.

It is a continuous processor by forming a conical heap and then is spread out into a circular or flat cake. The cake is divided into ¼ of the original cake size and two opposite 1/4 are combined. The other two 1/4 are discarded. This process is repeated again and again till we find the desired quantity for final use.

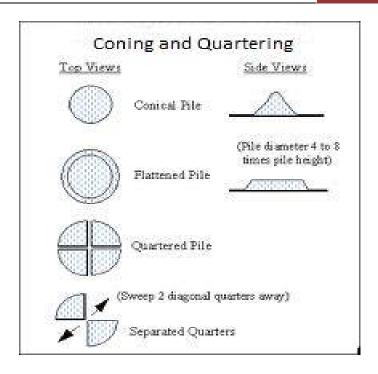


Fig.3.1.coning and Quartering technique

3.3. Experimental Apparatus

3.3.1 Planetary Ball Mill

Planetary ball mill is an apparatus which is used for the getting the fine material in the powder form. It is also used for the proper mixing of the sample material; from planetary ball mill we can achieve a required fineness in the material. It generates very high centrifugal force by which the material turn in to the fine powder. Its contain two ceramic vessel and ceramic balls, charge is keep in to the vessel and some balls are inserted, number of ball and number of rotation is choose according to the requirement of degree of fineness of the charge material. The vessel container should be air and liquid tight for the purpose of milling. It is called planetary ball mill because of the separate rotation of the vessel, the vessels are free to move in any circular direction and base on which the vessel are lying rotating clockwise so its create a planet movement system. In the present work system we used 7 balls in each vessel and 15 min. for milling purpose at 300 rpm.

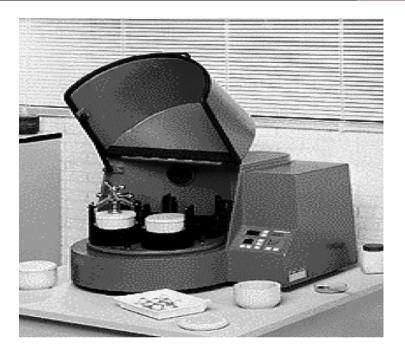


Fig- 3.2. Planetary ball mill

3.3.2. <u>Heating Microscope</u>

Heating microscope is used for analysis the behavior of slag towards the temperature. The temperatures characteristics can be recorded by heating microscope, fig. and the plan diagram of heating microscope given in fig.3.3

The samples form in the cube of 3 mm, and heated in an electric furnace incorporated in heating microscope and the stage of change of size of slag cube according to the temperature changement has be noted.

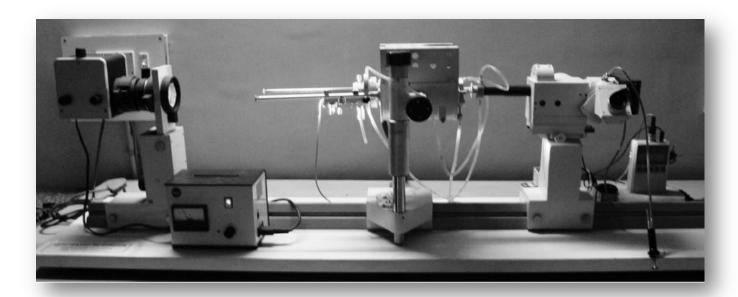


Fig.3.3. Leitz Heating Microscope

Following are the four characteristic temperatures which are studied in the experiment of heating microscope.

- (1) Initial Deformation Temperature(IDT)
- (2) Softening Temperature(ST)
- (3) Hemispherical Temperature(HT)
- (4) Flow Temperature(FT)
- <u>Initial Deformation Temperature</u> (IDT) Here the prepared sample of slag which have a cube shape is placed in heating microscope which have a completely six by six grid pattern as per the viewing from the microscope. The deformation temperature at which roundness of the edge of slag sample started called initial deformation temperature, at that temperature stickiness of the sample started.
- <u>Softening Temperature</u> (ST) The temperature at which distortion of the slag sample starts called softening temperature, practically shape of cubical outline of slag sample starts changing it shrinks one grid out of the six grid, practically at that temperature slag got soften or we can say that plastic distortion started at that temperature.

- <u>Hemispherical Temperature</u> (HT) The temperature at which the slag sample convert in to a hemispherical shape called hemispherical temperature practically its noted as the temperature at which the total height of the slag sample is equal to half of its base length.
- Flow Temperature (FT) The temp. at which the slag sample attains liquids state, practically this temperature noted as the temperature at which height of the slag sample is equal to 1/3 rd of the total height of the slag sample which it had at the hemispherical temp., or we can say at that temp. the liquid mobility of slag is shown i.e. free flowing of the slag.

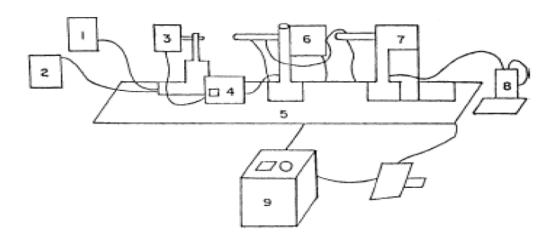


Fig- 3.4.Lay Out Of Heating Microscope

3.3.3. Rising Hearth Furnace

Rising heart furnace is used for quenching and melting purpose of the slag sample for getting solid sample for further experimental purpose. For the desire requirement powder slag was than kept in to the furnace and melted at flow temp. for the formation slag sample like of B.F slag. We choose particularly flow temperature for the experiment purpose because at that particular temperature slag comes out from the BF.

In this process fine powder slag sample is put in to the crucible which is made of platinum and then crucible was kept in to the rising hearth furnace for the desired temperature after getting the desired temperature, the sample was hold till one hour for complete melting of the slag sample. After finishing of melting quenching is done at room temperature in water for getting the required crystal structure and property as per getting from the BF.



Fig.3.5. Rising Hearth Furnace

CHAPTER-4 RESULT AND DISCUSSION

4.1. Flow characteristics of blast furnace slag

The slag procured from Adhunik Metallics Limited, after milling it used for getting the flow characteristic of the slag, in this the slag sample loaded in heating microscope in a cubical shape and we analyses the behavior of slag as the temperature rises, it initially deforms ,soften, getting hemispherical shape and finally it gets flowing property as the temperature rises. The following table 4.1.shoes the temperature distribution.

Table.4.1. Flow characteristics of blast furnace slag.

Sample No.	Cast No.	IDT(K)	ST(K)	HT(K)	FT(K)	FT-ST(K)
1	237	1575	1641	1659	1681	40
2	223	1077	1489	1609	1683	194
3	232	1495	1647	1657	1693	46
4	211	1558	1636	1651	1677	41
5	289	1074	1584	1643	1693	109
6	48	1564	1640	1684	1738	98
7	82	1469	1615	1642	1683	68
8	197	1479	1564	1651	1673	109
9	10	1546	1636	1671	1693	57
10	226	1076	1495	1619	1671	176

As per the requirement of a good blast furnace working condition the ST should be high as much as possible so that the granular zone is large and utilization of CO gas is high hence the more iron ore get reduced due to indirect reduction because the charge material spend much time in the granular zone. So the charge reduced is more at the same condition of blast furnace and due to this the coke consumption gets reduced.

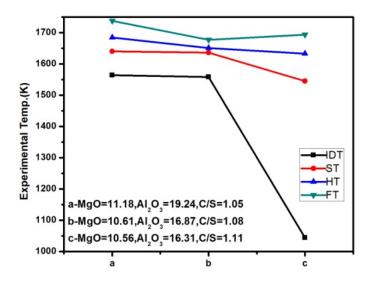
Another condition for the ideal blast furnace is that the thickness of cohesive zone should be low as much as possible or the temperature difference between flow temperature (FT) and softening temperature (ST) should be minimum this condition is needed because of gas permeability, narrow cohesive zone allowed more gas under the given pressure difference through a small coke layer.

So as per the result obtain by the heating microscope experiment we got result as given in table no.4.1. the data shows that Softening temperature(ST) is high for sample number.1,3,4,6,9(1641,1647,1636,1640,1636 all temperature are in Kelvin) and the difference between ST and FT is low for sample number.1,3,4,9(40,46,41,57 all temperature are in Kelvin). It shows that the particular sample shows the ideal condition in comparison to other slag sample.

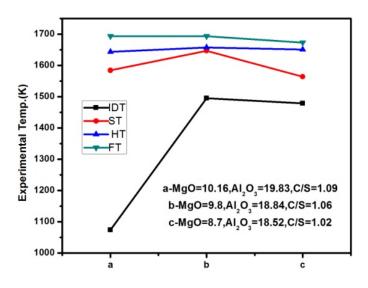
That's means Cast No-237, 232, 211, 48, 10 shows good result for high ST. and Cast No-237, 232, 211, 10 shows good result for low temperature difference for FT and ST.

4.2. <u>Effect on Flow characteristics of Blast Furnace Slag by variation of MgO, Al₂O₃ and C/S ratio-</u>

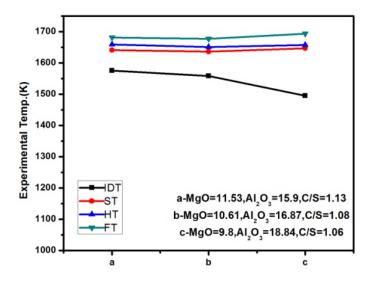
For testing the behavior of flow characteristics of blast furnace slag by variation of MgO,Al₂O₃ and C/S ratio, we are taking some slag with different combination by varying content of MgO,Al₂O₃ and C/S ratio by this we get eight combination of the slag these are (1) MgO decreases, Al₂O₃ decreases, C/S increases(2) MgO decreases, Al₂O₃ decreases, C/S decreases (3) MgO decrease, Al₂O₃ increases, C/S decreases (4) MgO decrease, Al₂O₃ increases, C/S increases (5) MgO increases, Al₂O₃ decreases, C/S decreases (6) MgO increases, Al₂O₃ increases, C/S decreases (7) MgO increases, Al₂O₃ increases, C/S increases (8) MgO increases, Al₂O₃ decreases, C/S increases, C/S increases, C/S increases, C/S increases, Al₂O₃ decreases, C/S increases, C/S increases, C/S increases, C/S increases, Al₂O₃ decreases, C/S increases, C/S increases, C/S increases, Al₂O₃ decreases, C/S increases, C/S increases, C/S increases, C/S increases, Al₂O₃ decreases, C/S increases, C/S in



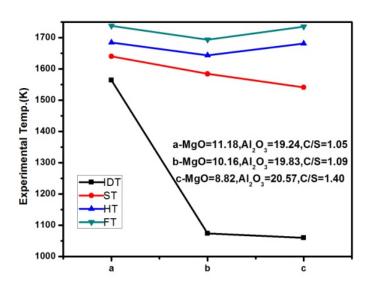
(1)



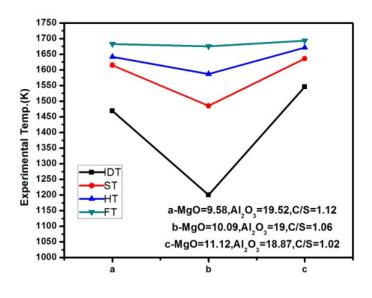
(2)



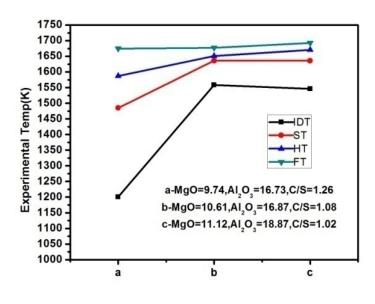
(3)



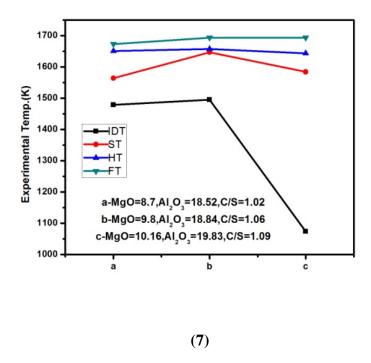
(4)



(5)



(6)



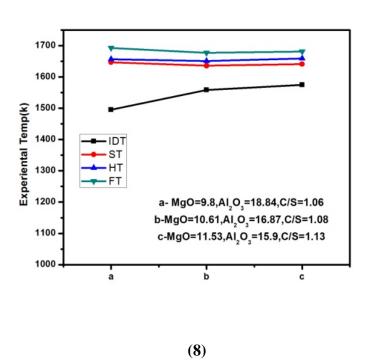


Fig.4.1. Effect on Flow characteristics of Blast Furnace Slag by variation of MgO, Al_2O_3 and C/S ratio

- As shown in graph (1) for the slag composition (b) MgO-10.61, Al₂O₃-16.87, C/S-1.08 shows high ST while Low FT and S.T difference.
- In graph (2) slag no (b) MgO-9.8, Al₂O₃-18.84, C/S-1.06 shows high ST while Low FT and S.T difference.
- In graph (3) slag no (b) MgO-10.61, Al₂O₃-16.87, C/S-1.08 shows high ST while Low FT and S.T difference.
- In graph (4) slag no (a) MgO-11.18, Al₂O₃-19.24, C/S-1.05 shows high ST while Low FT and S.T difference.
- In graph (5) slag no (c) MgO-11.12, Al₂O₃-18.87, C/S-1.02 shows high ST while Low FT and S.T difference.
- In graph (6) slag no (b) MgO-10.61, Al₂O₃-16.87, C/S-1.08 shows high ST while Low FT and S.T difference.
- In graph (7) slag no (b) MgO-9.8, Al₂O₃-18.84, C/S-1.06 shows high ST while Low FT and S.T difference.
- In graph (8) slag no (a) MgO-9.8, Al₂O₃-18.84, C/S-1.06 shows high ST while Low FT and S.T difference.

And we get the following composition of slag which shows the better condition-

- MgO-10.61, Al₂O₃-16.87, C/S-1.08
- MgO-9.8, Al₂O₃-18.84, C/S-1.06
- MgO-11.18, Al₂O₃-19.24, C/S-1.05
- MgO-11.12, Al₂O₃-18.87, C/S-1.02

4.3. Effect of chemical composition on Viscosity

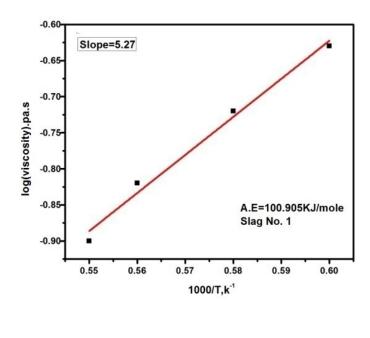
Since the Iida model gives the closest value of viscosity with respect to experimental value, therefore in the present work we used the Iida model for the calculation of viscosity of slags. The calculation of viscosity using this model is based on the equations 2.21 to 2.32 as described in the section 2.2.6. The detailed calculated values of viscosity are presented in the table 4.2.

Table.4.2. Calculated values of viscosity of different slag using Iida Model

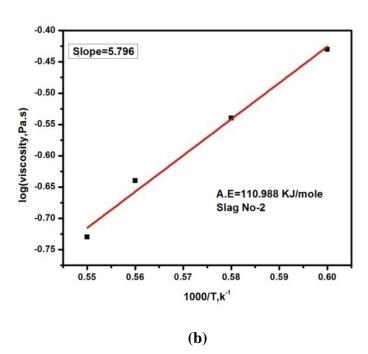
Vis	Viscosity(Pa.s) at Temperature(K.)								
Slag No.	1673 K	1723 K	1773 K	1823 K					
Slag No.1.	0.2368759	0.18888624	0.15274875	0.12506425					
Slag No.2.	0.36880072	0.2891013	0.22982905	0.18498471					
Slag No.3.	0.19863165	0.15948269	0.12986304	0.1070642					
Slag No.4.	0.3069517	0.24226569	0.19390569	0.1571257					
Slag No.5.	0.24118372	0.19211294	0.15518661	0.12691745					
Slag No.6.	0.22675374	0.18108835	0.14666002	0.12025564					
Slag No.7.	0.26650986	0.21155239	0.1703045	0.138808871					
Slag No.8.	0.238231347	0.189923313	0.153554302	0.12569833					
Slag No.9.	0.225914181	0.180431024	0.146138534	0.119835375					
Slag No.10.	0.305107362	0.240865089	0.192829817	0.156291255					

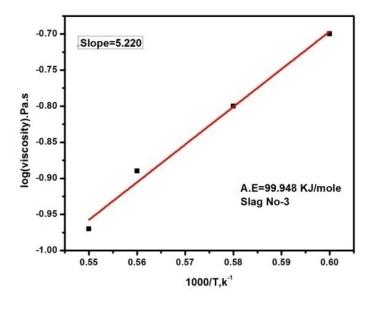
As per the table.4.2 we see that as the temperature increase the viscosity of the slag decreases. These calculated velocity further used for finding the activation energy of the slag. By which we analyze the slag on the basis of activation energy.

4.4. Log (Viscosity) Vs Inverse Temperature Graph

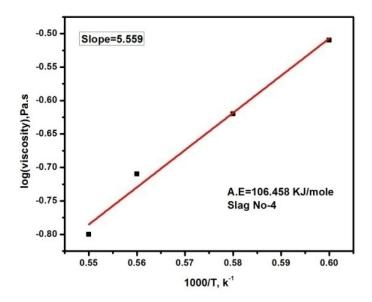


(a)

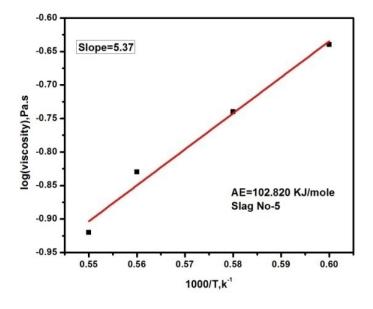




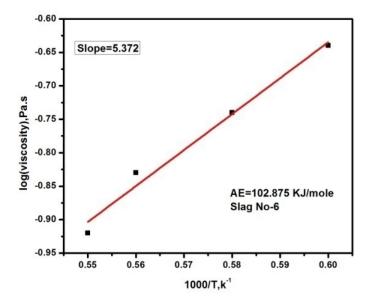
(c)



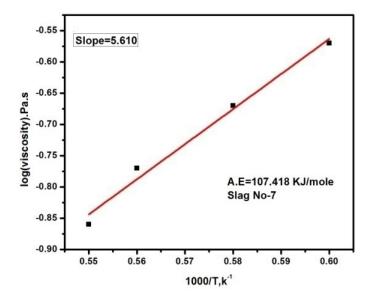
(d)



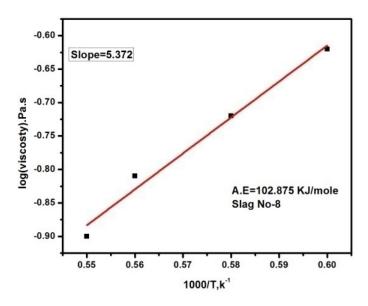
(e)



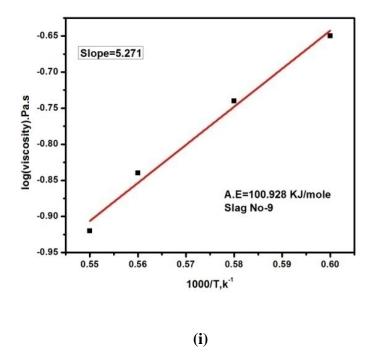
(f)



(g)



(h)



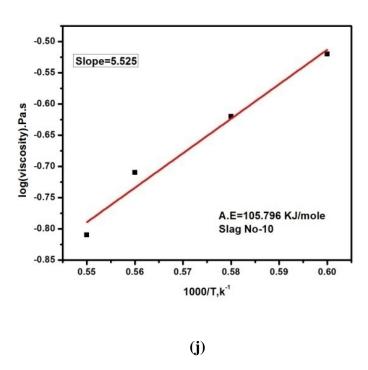


Fig.4.2. Log (Viscosity) Vs Inverse Temperature Graph

From the following graph of log (viscosity) Vs inverse temperature, we found that slop between viscosity and temperature, i.e., the effect of temperature on viscosity. Now from that slope we are trying to find the activation energy of the slag sample.

The graphs presented in Fig.4.4 (a) to Fig.4.4 (j) shows that the viscosity of slags obeys the relationship $\mu=Ae^{\frac{E_{\mu}}{RT}}$ in general.

These graphs also show that by increase in temperature, viscosity of slags decreases. The straight line shows that there is a constant slope between $\log \mu$ and 1/T, hence constant activation energy ($E\mu$) values, i.e., it shows that temperature does not effects the activation energy of the analyzed slags. From the above, it shows that the decrease in viscosity with the rise in temperature is only due to a general weakening of the bond between the cations (Ca^{2+} , Mg^{2+}) and the discrete silicate anions. As there is no change in $E\mu$, the activation energy of viscous flow, the degree polymerisation/depolymerisation is practically constant for a given slag, with a given composition at different temperatures. This establishes that discrete anions do not breakdown to small units with the increase of temperature.

Table-4.3. Estimated values of Activation Energy of Viscous Flow of different slags

Slag No.(Cast No)	Activation Energy, Eμ, KJ/mole
1 (211)	100.905
2.(223)	110.988
3.(237)	99.948
4.(197)	106.458
5.(232)	102.820
6.(289)	102.875
7.(10)	107.418
8.(48)	102.875
9.(82)	100.928
10.(226)	105.796

After getting the viscosity from Iida model which is a theoretical model, we may found the activation energy of the slag sample. Determination of activation energy is quite necessary because it's a key factor of flow, energy required, coke consumption, time taken in braking of bond. It is the minimum energy required for starting the reaction that means it is a barrier energy which is necessary to startup of a reaction or breaking the molecular bond. It is like a potential barrier which separates two minima of potential energy.

From Arrhenius Equation we got the Activation energy of the slag sample.

$$\mu = Ae^{\frac{E_{\mu}}{RT}}$$

$$log\mu = logA + \frac{E_{\mu}}{2.303RT}$$

$$Slope = \frac{E_{\mu}}{2.303RT}$$

Where,

Eμ= activation Energy

R= Universal gas constant

T= Temperature

Table no-4.3, show the activation energy getting by analyzing, as we know low activation energy is beneficial for the blast furnace operation to breakage of bond so from the following table we take a threshold activation energy barrier below which we consider the process, we take below 102 KJ/Mole for our analysis from these we found that cast no-211, 237, 232, 289, 48, 82 are support our condition. Which show lower energy consumption for breaking of bond.

CHAPTER-5 CONCLUSION

By all of this analysis we get following results-

- From activation energy we get cast no. 211, 237, 232, 289, 48 and 82 have low activation energy which is useful for the process.
- From flow graph we get cast no.211, 232, 48 and 10 have better performance skills for the blast furnace operations.
- From difference between FT and ST temperature we get cast no. 237, 232, 211 and 10 have low temperature difference
- ➤ By concluding all of these data and result we found that cast no 211 and 232 give best result in comparison to others. So from back data analysis we suggest that the burden material (Table.1) used in cast no 211 and 232 gives higher production rate, low consumption in energy, which is beneficial for Adhunik Metallics Limited. So we suggest that they use-

Cast No	Coke(Kg)	Iron Ore(Kg)	Sinter(Kg)	Lime Stone(Kg)	Dolomite(Kg)
211	2500	2800	4000	175	00
232	2500	1800	5700	150	75

CHAPTER-6 REFRENCES

REFERENCES

- 1. Tupkary R.H. and Tupkary V.R., _An Introduction to Modern Iron Making', Khanna Publication.
- 2.http://www.steel.org/AM/Template.cfm?Section=Articles3&TEMPLATE=/CM/ContentDisplay.cf m&CONTENTID=25317, retrieved on 04:05:10.
- 3. Gupta S. S., and Chatterjee A., —Blast Furnace Iron Makingl, SBA Publication.
- 4. Behera R. C., Mohanty U. K., and Mohanty A. K., High Temperature Materials and Processes, 9, 1990, pp. 57-75.
- 5. Khanna O.P. —material science and metallurgical |, dhanpat rai publications.
- 6. A. Ghosh and A. Chatterjee, _Iron making and Steel Making' Theory and Practice, PHI Learning Private LTD.
- 7. Muller J. and Erwee M., Southern African Pyrometallurgy, 2011.
- 8. J.D. Mackenzie: Adv. Inorg. Chem.. Radiochem, 4 (1962),p.293.
- 9. J.D. Mackenzie: Adv. Inorg. Chem.. Radiochem, 4 (1962),p.293.
- 10. Shankar Amitabh, Gornerup Marten, Lahiri A.K, Seetharaman S., Experimental Investigation of the Viscosities in CaO-SiO2-MgO-Al2O3 and CaO-SiO2-MgO-Al2O3-TiO2 Slags, Metallurgical and Materials Transactions B, 38 (6), pp. 911-915.
- 11. Jose M franco and pedro partal. Campus de —El karmen I. 21071. Huelva spain.
- 12. Bottinga, Yan, and Daniel F. Weill. "The viscosity of magmatic silicate liquids; a model calculation." American Journal of Science 272.5 (1972): 438-475.
- 13. T. Iida, H. Sakai, Y.Kita and K.Shigeno, ISIJ International, Supplement2000, Vol. 40, pp. S110-S114.
- 14. K. C. Mills and S. Sridhar, Ironmaking and Steelmaking, 1999, 26, pp.262-268.
- 15. H. S. Ray and S. Pal, Ironmaking and Steelmaking, 2004, 31, pp.125-130.
- 16. German Industrial Standard 51730.
- 17. H.E. Kissinger, J. Res. Nat. Bur. Stand. 57 (1956) 217.

- 18. Borham, B. M., and F. A. Olson. "Estimation of activation energies from differential thermal analysis curves." Thermochimica Acta 6.4 (1973): 345-351.
- 19. Kissinger, Homer E. "Reaction kinetics in differential thermal analysis." Analytical chemistry 29.11 (1957): 1702-1706.
- 20. Mohanty U.K., Thermo physical properties of some metallothermic slags, Ph.D. Dissertation, R.E. College, Rourkela, 1998.
- 21. Moynihan, C. T., et al. "Estimation of activation energies for structural relaxation and viscous flow from DTA and DSC experiments." Thermochimica acta 280 (1996): 153-162.
- 22. Mittemeijer EJ (1992) J Mater Sci 27:397.
- 23. Ki 12. Ozawa T (1970) J Therm Anal 2:301.
- 24. Lee Y.S., Kim J.R., Yi S.H. and Min D.J., VII International Conference on Molten Slags Fluxes and Salts, The South African Institute of Mining and Metallurgy, 2004.
- 25. Sunahara Kohei, Nakano Kaoru, Hoshi Masahiko, Inada Takanobu, Komatsu Shusaku and Yamamoto Takaiku, ISIJ International, Vol. 48, No. 4, 2008, pp. 420-429.
- 26. Noritaka Saito, Naoto Hori, Kunihiko Nakashima and Katsumi Mori, Metallurgical and Materials Transactions, Volume 34B, October 2003.
- 27. Kawai Yasuji, Viscosities of CaO-SiO2-Al2O3-MgO Slags.
- 28. Nakamoto Masashi, Tanaka Toshihiro, Lee Joonho and Usui Tateo, ISIJ International, Vol. 44, No. 12, 2004, pp. 2115-2119.
- 29. Seok Seong-Ho, Jung Sung-Mo, Lee Young-Seok and Min Dong-Joon, ISIJ International, Vol. 47, No. 8, 2007, pp. 1090-1096.
- 30. Jia J.Y., Bai C.G., Qiu G.B., Chen D.F. and Xu Y, VII International Conference on Molten Slags, Fluxes and Salts, the South African Institute of Mining and Metallurgy, 2004.
- 31. D. Ghosh, V.A. Krishnamurthy and S.R. Sankaranarayanan, J. Min. Metall. Sect. B-Metall. 46 (1) B (2010) 41 49.

- 32. Keuleers, R. R., J. F. Janssens, and H. O. Desseyn. "Comparison of some methods for activation energy determination of thermal decomposition reactions by thermogravimetry." Thermochimica acta 385.1 (2002): 127-142.
- 33. Starink, M. J. "Activation energy determination for linear heating experiments: deviations due to neglecting the low temperature end of the temperature integral." Journal of materials science 42.2 (2007): 483-489.
- 34. Wang, Zhong-jie, et al. "Crystallization behavior of glass ceramics prepared from the mixture of nickel slag, blast furnace slag and quartz sand." Journal of Non-Crystalline Solids 356.31 (2010): 1554-1558.
- 35. Gan, Lei, et al. "Continuous cooling crystallization kinetics of a molten blast furnace slag." Journal of Non-Crystalline Solids 358.1 (2012): 20-24.
- 36. Shankar Amitabh, _Studies on High Alumina Blast Furnace Slags' Doctoral Thesis, Royal Institute of Technology,Sweden 2007.
- 37. S. Seetharaman and D. Sichen: ISIJ International, 37 (1997), 109.
- 38. S. Noritaka, et al. _Viscosity of Blast Furnace Type Slags' Metallurgical and materials transations, 510—Volume 34B, OCTOBER 2003.
- 39. K. C. Mills, ISIJ International, vol.33, 1993, No.1, pp.148-155.
- 40. Lee, Y.S.; Jung, S.M.; Yi, S.H. Influence of basicity and FeO content on viscosity of blast furnace type slags containing FeO. ISIJ International 2004, 44, 1283 1290.
- 41. Wely, W.A., The significance of the co-ordination requirements of cations in the constitution of glass. Society of Glass Technology 1951, 35, 421 447.
- 42. Machine, J.S. and Hanna, D.L. _Journal of the American ceramic society', 28, 310 316(1945) 43-Hino, Mitsutaka, et al. "Simulation of primary-slag melting behavior in the cohesive zone of a blast furnace, considering the effect of Al2O3, Fe t O, and basicity in the sinter ore." *Metallurgical and Materials Transactions B* 30.4 (1999): 671-683.
- 44- Akbarnejad, S., and L. J. M. Houben. "CHEMICAL AND MINERALOGICAL CHARACTERIZATION OF BLAST FURNACE SLAG AS A ROAD BASE MATERIAL."

- 45- Higuchi, Kenichi, et al. "Quality Improvement of Sintered Ores in Relation to Blast Furnace Operation." *SHINNITTETSU GIHO* 384 (2006): 33.
- 46- WATAKABE, Shiro, Akinori MURAO, and Shigeaki GOTO. "Application of high ratio coke mixed charging technique to blast furnace." *JFE Technical Report* 13 (2009): 21-27.
- 47- O.P.Khanna "material science and metallurgical", dhanpat rai publications
- 48-RICHARDSON, F.D.: Phys. Chemistryof Steelmaking, Etd. J.F.ELLIOTT, MIT, MASS., 1958, p.55-62.