VISCOUS PROPERTIES OF SYNTHETIC HIGH ALUMINA BLAST FURNACE SLAG

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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CERTIFICATE

This is to certify that the thesis entitled **"Viscous Properties of Synthetic High Alumina blast Furnace Slag"** submitted by **VIKASH CHANDRA DINKAR,** Roll No.**-212MM2454** 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 viscosity of the blast furnace slag, which is greatly influenced by its composition, has to be low at the operating temperature in order to make the slag easy flowing. Such a slag encourages an acceleration of the rate of slag metal reactions/exchanges, thus influencing the efficiency of the blast furnace process. The present project aims at measuring the viscosity of synthetic high alumina Indian blast furnace slags in agreement with the slag compositions encountered in the industries using inner-cylinder-rotating type viscometer (VIS 403). It is observed that the viscosity is greatly influenced by the CaO/SiO2 (C/S) ratio, MgO and TiO2 contents. The measured and the calculated values of viscosity using different models show that the Iida model yields values most close to the measured value. An attempt is made to comment on the structure of the slag based on estimated values of Activation Energy of viscous flow.

Key words – Synthetic High Alumina B/F Slag, Viscosity, Activation Energy of Viscous Flow, Viscometer

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CHAPTER – 1

INTRODUCTION

1.1. Introduction

In a blast furnace the viscosity of the slag governs the reaction rates in the furnace by its effect on diffusion of ions through the liquid slag to and from the metal slag interface. Therefore it is substantial effect on the speed and completeness of reduction reactions, heat transfer etc.

The viscosity of the slag is very much dependent on composition and temperature on the other hand the variation of viscosity with temperature and composition helps in understanding the structure of the slag. An understanding of the structures of the slag leads to compositional adjustments for suitable modifying the structures so as to give an optimum viscosity under the operating temperature. It can be stated with emphasis that the slag if highly viscous intervenes with the reactions and heat and mass transfer and if very fluid it brings in an imbalance in the heat distribution of blast furnace.

The blast furnace slag in addition to being free flowing must have appreciable affinity for the gangue constituents to facilitate the production of metal of choice. The quality of metal produced cannot be better than the quality of slag produced. One of the most important factor influencing the quality of the slag being its viscosity which is primarily composition dependent under the operating condition of temperature and pressure. Therefore it is useful to measure and analyses the viscosity of the blast furnace slag in terms of its composition.

In the present work an attempt is made towards this goal looking to the high alumina content of Indian blast furnace slags synthetic slags are prepared in the laboratory in agreement with high alumina industrial blast furnace slags. The viscosity measured using a high temperature viscometer at different temperatures is analyze in terms of its composition also the viscosity values are calculated by using three different models vis- Iida model, Ray's model and NPL model. It is found that the Iida model yields most close to the measured viscosity values.

We have also estimated the activation energy of viscous flow from the log(μ) vs. 1/T plots and examine it in terms of the composition of slag to comment down the basic structure of the slag.

In this thesis chapter 1 contents a detailed introduction to the thesis explaining the aim of the project.

Chapter 2 is dedicated to a detailed literature survey housing previous work done by several experimental.

Chapter 3 is on equipment’s used and the experimental procedure adopted describe in details.

In chapter 4 the results are tabulated and also plotted against the basic factor like composition and temperature. The results are discussed by the help of the plots to throng live on the relationship of the responds, i.e. the viscosity as related to temperature and compositions.

Chapter 5 houses conclusions drawn on the basis of the results obtained.

1.2. Objective

To study the variation of viscosity of high Alumina blast furnace slag is encountered in Indian industries with respect to temperature and composition and analyzes the variation of viscosity on the basis of structure of slag.

CHAPTER – 2

LITERATURE SURVEY

2.1. Blast furnace

A blast furnace is a type of metallurgical furnace used for smelting to produce industrial metal. In iron making the purpose of a blast furnace is to chemically reduce and physically convert iron oxide into liquid iron. The blast furnace has circular cross-sections of different diameter and around 30m height. The outer shell is made of steel. Inside the shell, there is a refractory lining. Lump iron ore (above 10mm in size) in the form of hematite (Fe_2O_3)or magnetite(Fe_3O_4) or iron oxide in the form of pellets or sinter prepared from iron ore fine are the source of iron units in blast furnaces. To meet the thermal as well as the chemical energy requirements and to support the burden during melting of the iron bearing burden, coke along with coal and oxygen primarily as air, are feed to blast furnaces. In order to separate the gangue in the feed materials from liquid iron, flux in the form of limestone/lime/dolomite is added either independently or through sinter. The raw materials require 6 to 8 hours to descend to the bottom of the furnace to finally give slag and liquid iron as the final product. These final products are drained at regular intervals.

Once the blast furnace is started it will continuously run for several years till it is shut down for repairs and modifications.

2.2. Blast Furnace process

In the blast furnace solid charge materials like iron ore (or agglomerate ore), coke and limestone are charged in a vertical shaft of furnace from the top and hot air blast is blow down through tuyeres located at the bottom level. The oxygen from the preheated blast combines with the carbon of coke and generates heat and carbon monoxide. The gas phase containing mainly nitrogen and carbon monoxide ascends upwards through the charge, which reacts with charge and extracts heat from the gas phase. Eventually the charge melts and metal and slag thus produced get stratified and separated to obtain metal. Fundamentally therefore the blast furnace is a counter current reactor.

The main chemical reactions are the reduction of iron oxide to iron and burning of coke. The iron oxide (iron ore, pellets and sinter) get reduced as follows:-

$$3Fe_2O_3 + CO = CO_2 + 2Fe_3O_4 \qquad (2.1)$$

$$Fe_3O_4 + CO = CO_2 + 3FeO \qquad (2.2)$$

$FeO + CO = CO_2 + Fe$ (2.3)

$FeO + C = CO + Fe$ (2.4)

Since the iron oxide is reduced directly by carbon as in equation (2.4), it has been referred to as ‘direct reduction’ of iron oxide. The carbon monoxide generated by burning of the fuel at the tuyeres or by direct reduction of iron oxide reduces iron oxide is in equations (2.1, 2.2, 2.3) is referred to as ‘indirect reduction’. The carbon monoxide required for indirect reduction is essentially generated at the tuyere level where carbon of coke burns as follow:-

$2\ C + O_2 = CO_2 + Heat$ (2.5)

Limestone and dolomite, if added as a flux in the charge, get calcined in the temperature zone of 800-1000°C as follows:-

$CaCO_3 = CaO + CO_2$ (2.6)

$MgCO_3 = MgO + CO_2$ (2.7)

The resulting basic oxides combine with the gangue oxides to form the slag. As the charge descends in the furnace its temperature is increased and finally it is melted in the bosh region. Two liquid phase forms as a result of melting, one is the iron phase and the other is molten oxide phase called slag. Those oxides which are not reduced join the slag phase and those which are reduced to elemental state join the metal phase.

The furnace is conveniently being divided into four main zones with respect to the physical process occurring in the furnace [1]. Which are as follows:-

2.2.1. Stack or shaft

It is extended from the Stocklime down to the mental level and in which burden is completely solid. The temperature range of the stack is from 200°C at the stocklime level to 1100-1200°C by the time it descends to bottom of the stack. To ensure free fall of the charge material, the cross- section of the stack is uniformly increased to almost double the size from stocklime to the mental level [1]. Much of the iron oxide reduction occurs in the stack.

2.2.2. Bosh

At the bottom of the stock the charge materials begin to soften and fuse. The next lower zone is called Bosh in which melting of burden, except that of coke, takes place. The gangue and flux combine to form the slag in this region. The furnace walls in this region are parallel to some extent and then taper down. The burden permeability in this region is mainly maintained due to solid coke. Any degradation of coke, leading to decreased permeability in the bosh region is bound to affect the blast furnace operation adversely.

2.2.3. Tuyeres or combustion zone

By the time the charge descends into the area near the tuyeres, except the central column of coke, the entire charge is molten. In this region the oxygen of the blast burns coke to carbon monoxide and a number of combustion zones, one in front of each tuyere, exist in the tuyere zone. There exists a runway or raceway in front of each tuyere and through which the flame runs and the gas flow smoothly expands over the entire cross-section of the furnace. The temperature in this zone is known as ‘raceway adiabatic flame temperature’ (RAFT).

2.2.4. Hearth

Almost most of the coke burns at the tuyere level, a small fraction descends even into the hearth (to form the ‘deadman’, which either sits on the hearth or floats just above it), where it dissolve in the metal to its near saturation. The entire charge is molten and tends to stratify into slag and molten metal layers in the hearth from where these are tapped separately. The walls of the hearth are parallel and smallest in cross-section.

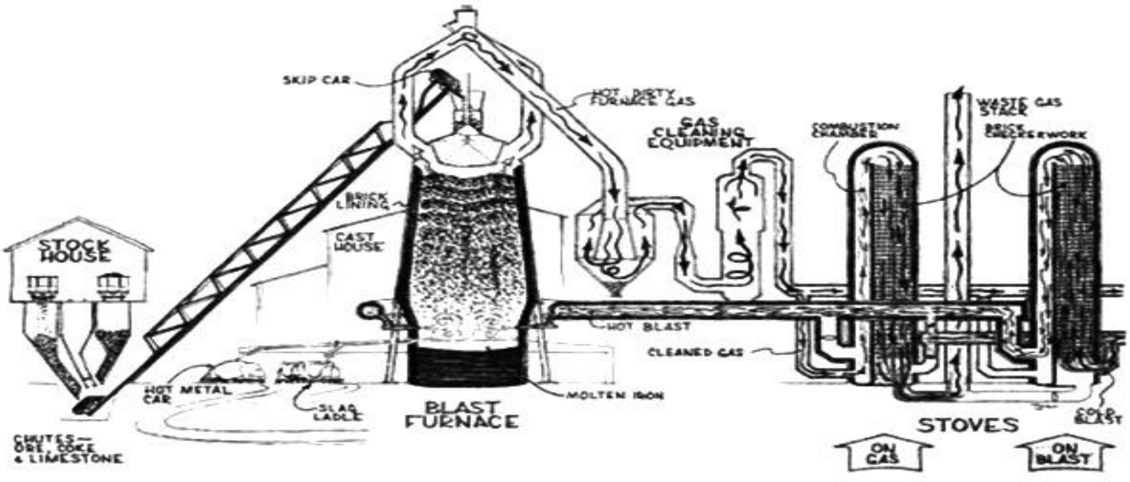


Fig.2.1. A schematic diagram showing Blast Furnace Process

In summary, the blast furnace is a counter-current reactor where the charge materials descend and gases ascend. There are several chemical and physical reaction occurs and produce the desired final product which is hot metal. Typically hot metal compositions are as follows [2]:-

Table.2.1. Typical composition of produced hot metal

SI No.	Elements	Percentage
1.	Iron (Fe)	93.5 – 95.0 %
2.	Silicon (Si)	0.30 – 0.90 %
3.	Sulphur (S)	0.025 – 0.050 %
4.	Manganese (Mn)	0.55 – 0.75 %
5.	Phosphorous (P)	0.03 – 0.09 %
6.	Titanium (Ti)	0.02 – 0.06 %
7.	Carbon (C)	4.1 – 4.4 %

2.3. Blast Furnace Reaction

The reduction and smelting of iron ore is done mainly in the blast furnace. The burden charged at the top of the furnace consists primarily of iron ore, flux and coke. The reducing gas carbon monoxide and the heat required for the smelting of the ore are generated at the bottom of the furnace by blowing preheated air into the coke bed. The blast furnace can be divided into three zones for a study of the physical and chemical reaction. These zones are as follows:-

(a) The upper or preheating zone
(b) The middle or indirect reduction zone
(c) The lower or melting or direct reduction zone

2.3.1. Reaction in the upper zone

The reactions of primary concern in the iron blast furnace are the reduction reactions of iron oxides. The formation of product layers during the reduction of the iron ore is well known. The greater the driving forces for reduction and the faster the rate of chemical reaction, the more pronounced is the formation of the product layer.

$$3\ Fe_2O_3 + CO = CO_2 + 2\ Fe_3O_4 + 10.33\text{kcal} \qquad (2.8)$$

$Fe_3O_4 + CO = CO_2 + 3\ FeO\ -8.75kcal$ (2.9)

$FeO + CO = CO_2 + Fe\ +3.99kcal$ (2.10)

During the reduction process of the iron oxide, the iron oxides are also beginning to soften. About 700 - 900°C the magnetite is reduced to wustite. In this zone there are some carbon deposition takes place followed by the following reaction:-

$2CO = CO_2 + C + 41.21kcal$ (2.11)

The deposition of carbon occurs in a narrow temperature range 400 - 600°C, the presence of iron catalyses' this reaction. There is also a chance of reduction of H_2O with the help of carbon monoxide.

$CO + H_2O = CO_2 + H_2 + 9.68Kcal$ (2.12)

The decomposition of carbonates also takes place at the temperature around 400°C. Now a days carbonates decomposition has very little importance because in modern furnace pellets and sinter are used and the carbonates are calcined from outside.

2.3.2. Reaction in the middle zone

The temperature range of this zone is in between 800 - 1000°C. Mainly the indirect reduction of wustite takes place in this zone. In this zone the CO/CO_2ratio is about 2 – 3, a value exhibiting equilibrium with Fe – FeO. If the length of the middle zone larger, the longer the gas - solid contact time and hence the degree of indirect reduction is more. Similarly the rapid reduction takes place if the reducibility of the ore is high. Hence the rate of reduction of the ore in the middle zone does not directly dependent on the optimum coke rate.

$FeO + CO = Fe + CO_2 + 3.99\ K\ cal.$ (2.13)

2.3.3. Reaction in the lower zone

The temperature range of this zone is I between 900 - 1000°C. There are several physical and chemical process takes place in this zone. Direct reduction of iron oxide takes place at the temperature above 1000°C according to the equation:-

$FeO + C = Fe + CO$ (2.14)

The reduction of Si and Ti takes place at very high temperature. While the oxide of Ca, Mg and Al are reduced to very less extant. The extant of reduction depends upon the temperature and the slag basicity. Cr, V and Mn are also reduced at very high temperature.

$MnO + C = Mn + CO$ (2.15)

$SiO_2 + 2C = Si + 2CO$ (2.16)

$S + CaO + C = CaS + CO$ (2.17)

P is present as tri or tetra phosphate of Ca, Si helps in breaking phosphate bond.[3]

$3CaO.P_2O_5 + 3SiO_2 = 3(CaO.SiO_2) + P_2O_5$ (2.18)

$P_2O_5 + 5C = 2P + 5CO$ (2.19)

2.4. Different internal zones of blast furnace

In seventies, quenched an experimental blast furnace, sectioned it vertically, collected samples from various zones and analyzed them. This led to a valuable insight into the internal state of the blast furnace in terms of the existence of various zone, their structure and composition, as well as the reaction mechanism involved. After the several pioneering investigation, especially by Japanese the blast furnace can be broadly divided into six zones as shown in fig.2.2. These six zones are as follows:-

- **Granular zone** - Where the entire charge is solid i.e. the stack.
- **Cohesive zone** – Where, except coke, the rest of the charge is semi- solid or is softened and at the lower zone end the slag is molten. This slag is rich in FeO and hence melts at much lower temperature.
- **Active coke zone** – Where coke activity takes part in the reaction involving direct reduction of iron oxide from the trickling slag and its own interaction with carbon dioxide. i.e. mainly bosh region.
- **Tuyere zone** – It is the zone where coke burns in front of the tuyere by combining with the hot blast (oxygen) effectively to CO.

- **Stagnant coke zone** –Where the coke is still solid and that supports the overlying entire burden and through which the slag and the metal trickles and metal gets saturated with carbon.
- **Hearth zone** – Where the slag and the metal clarify into two layers and they interact with each other with respect to the chemistry to move, as far as possible, towards equilibrium.

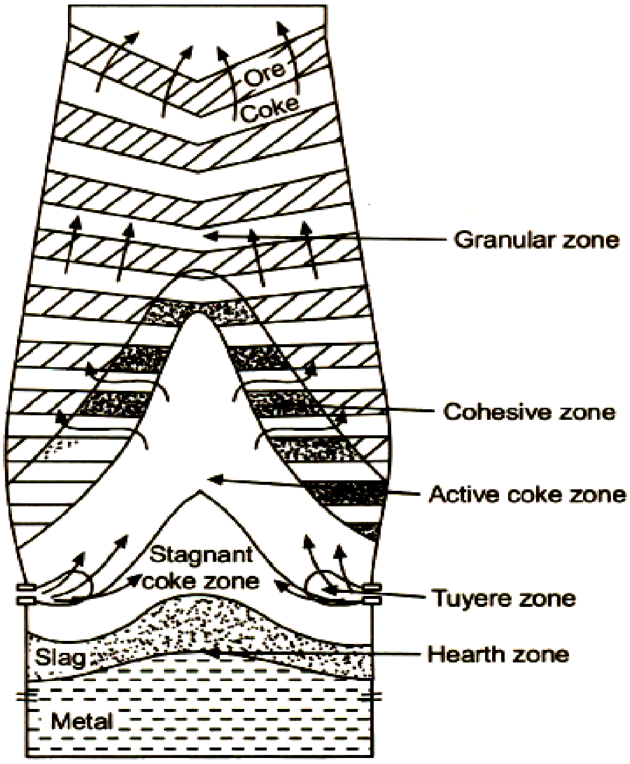


Fig.2.2. Schematic sectional diagram of the internal zones in a blast furnace

In all the above zone the most important finding was observed in the cohesive zone has a temperature range of 1000 - 1500°C. The shape and location of the cohesive zone has profound impact on blast furnace productivity, fuel consumption, hot metal quality, operational stability and lining life.

2.4.1. Cohesive Zone

The softening and melting of charge material takes place in the cohesive zone. This is also the region where most of the solid volume disappears, driving the solid flow. The performance of the blast furnace also depends on the position of the cohesive zone and also on the thickness of the cohesive zone. The things which are affected by the position and thickness of the cohesive zone are as follows:-

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

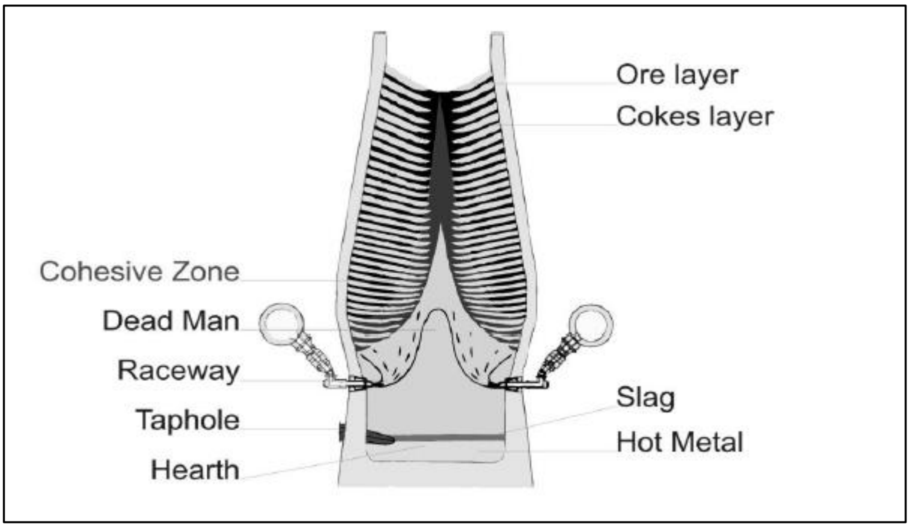


Fig.2.3. Cohesive Zone

- **Gas permeability** – It is related to the thickness of the cohesive zone. If the thickness of the cohesive zone is less, the more and more gases are allowed to pass, under a given pressure difference, through the short length of coke slit. But the gas volume not depend only on the length of the coke slit, but also on the viscosity band volume of the melt and their resulting influence on the bed permeability.
- **Extant of indirect reduction** – It depends on the position of cohesive zone. If the cohesive zone move down into the blast furnace, the volume of the granular zone is increased and hence the ascending carbon monoxide gas reduce more iron oxide indirectly because the charge material spend more time in granular zone. Therefore the relatively lower position of the cohesive zone increases the extant of indirect reduction of iron oxide and hence decreases the coke consumption rate.
- **Si content of pig iron** – The main source of Si in pig iron is the reduction of SiO present in the ash after burning the coke near raceway. The reduction of SiO occurs in the dipping zone just below the cohesive zone, the volume of dipping zone is decreased and SiO gets less chance to reduce and hence the Si content in pig iron is decreased.

$SiO_2 + C = SiO + CO$ (2.20)

$[Fe] + SiO = [Si] + (FeO)$ (2.21)

$(FeO) + CO = [Fe] + CO_2$ (2.22)

$C + CO_2 = 2CO$ (2.23)

2.5. Blast Furnace Slag

When iron ore, sinter, pellets, coke and different type of fluxes are smelted in a blast furnace, hot metal is produced and the impurities in the feed get separated as slag. Thus slag is an unavoidable by-product along with the useful hot metal. The chemistry and the volume of the slag thus produce depends upon the burden chemistry in particular the gangue constituents and their actual proportion in the ore and flux and, the chemistry and amount of coke ash. These dictate the type and amount of flux to be added to finally obtain thin and free- flowing slag at the working hearth temperature. The more is the gangue contents of the ore/sinter and more is the ash of coke the higher will be the slag volume.

The best practices and high productivity blast furnaces produce less than 300 kg of slag per ton of hot metal (thm) produced. It can be bad as 700-800 kg per thm because of very poor quality of burden materials. Major practices produce 400-500 kg of slag per thm produced.

Whatever be its exact composition, molten slag at over 1300°C is cooled, either by air or water/steam, to near room temperature. If the cooling of the blast furnace slag is rapid enough, glassy phase are formed. This type of quenched blast furnace slag becomes a valuable material for further processing, particularly as an additive to clinker in cement production. Therefore all modern blast furnaces are provided with slag quenching facilities.

2.5.1. Types of Slag

(a) Air-cooled blast furnace slag – It is defined in ASTM C125[4] as- “The material resulting from solidification of molten blast furnace slag under atmospheric conditions, subsequent cooling may be accelerated by application of water to the solidified surface”. The solidified slag has vesicular structure contain many non-connected cells.

(b) Expanded or formed blast furnace slag– This type of blast furnace slag is obtained by cooling and solidification of molten slag with the help of controlled quantities of water, air or steam. This process of cooling and solidification accelerate the cellular nature of the slag and gives a lightweight expanded or formed product. It has high porosity and low bulk density.

(c) Pelletize blast furnace slag – It is obtained when a molten blast furnace slag stream is passed over a vibrating feed plate where it is quenched by water. Due to addition of water the slag gets expanded. Now this expanded pyroplastic state slag stream feed into a rotating finned drum. As the drum rotates, the slag repeatedly strikes with fins and converted into spherical droplets. These droplets freeze rapidly to solid state as they are launched through the air away from the pelletizer. Pelletize slag has a unique internal cellular structure is contained within a smooth spherical skin. Hence it has low density aggregate and it is used as construction material. [5]

(d) Granulated blast furnace slag – If the molten slag is cooled and solidified with the help of high water volume and high pressure water jets to a glassy state, little or no crystallization occurs. And the formation of sand size fragments usually with some friable clinker like material. When it is crushed or milled to very fine particle, it has cementious properties, which make a suitable replacement for or additive to Portland cement.

2.5.2. Slag Structure

Blast furnace slags consisting of oxides of silicon and other elements. It has homogenous in nature in liquid form. It shows electrical properties. It contains simple and complex ions. Crystal structure of silica is tetrahedron in which silicon occupies the center of tetrahedrons and oxygen is at each of four corners. These tetrahedrons are link together and form a three dimensional crystalline network. Upon melting of pure SiO_2, short range order remains, but the long range order is destroyed. Molten slags are polymeric ionic melts. The cations (Ca^{2+},Na^{+},Mg^{2+}, Mn^{2+}, Fe^{2+},etc) are free and mobile, whereas anions (SiO_4^{4-}, AlO_4^{5-}, PO_4^{3-}, etc) are complex and less mobile. Therefore basic oxides are called network breakers. They break the SiO_2 network. Based on this classification the acidic oxides (SiO_2, etc.) are network formers.

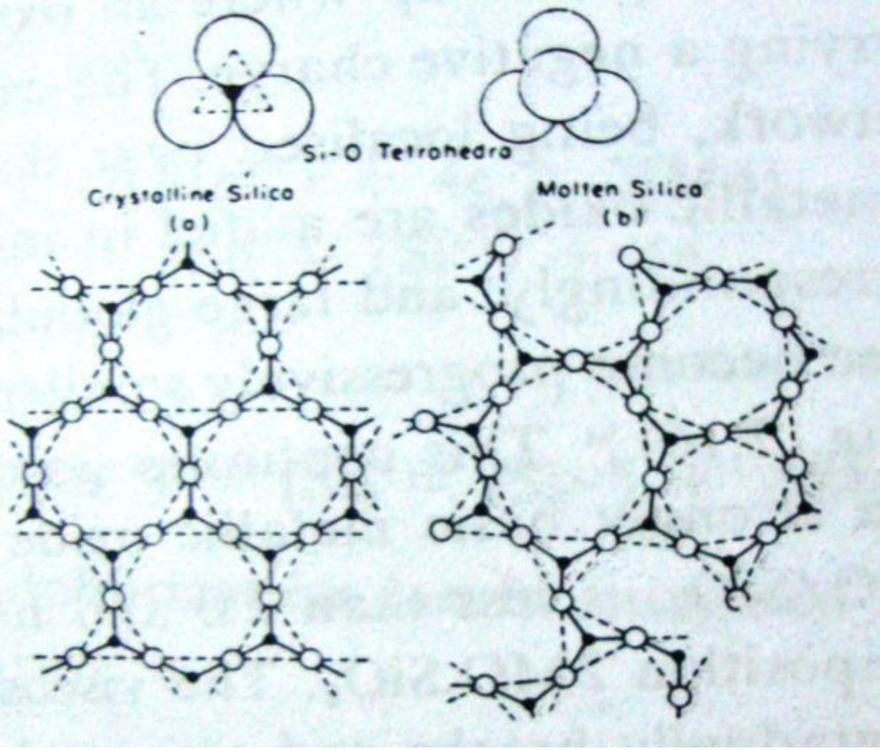


Fig.2.4. Schematic representation of the silicate tetrahedron

2.5.3. Slag Composition

The blast furnace slag cannot be of any specific chemistry. Its composition depends on the chemistry of the burden, coke rate, fuel injection and temperature of furnace operation. The charge contains alumina, silica, magnesia and lime as the main constituents. The minor oxides may be Cr_2O_3, TiO_2, FeO, MnO, etc.

Out of these nearly 15% of silica gets reduced and Si joins the metal phase, balance 85% joins the slag. Temperature has a decisive role in deciding this proportion. Nearly 60% of silica in the slag comes from iron bearing materials and remaining 40% comes from coke ash **[6].**Practically all the phosphorus in the charge, except the blown out as dust, is reduced and joins the metal phase. Nearly 60-70% of phosphorus in the metal comes from iron bearing charge materials and remaining 30-40% comes from coke. Nearly 90% input of Manganese finds its way into the metal, only 10% may present in the slag. Up to 40% of input Sulphur may join the slag and balance may join the metal phase. A typical composition of blast furnace slag shown in table 2.2.

Table.2.2. Typical composition of blast furnace slag

Major elements	Percentage	Minor elements	Percentage
SiO_2	32 – 42 %	S	1 – 2 %
Al_2O_3	7 – 16 %	FeO	1 – 1.5 %
CaO	32 – 45 %	MnO	0.2 – 1.0 %
MgO	5 – 15 %	TiO_2	1.01 %
		$K_2O + Na_2O$	1 %
		Trace oxides	0.5 %

2.5.4. 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.

Silicate slags are built up of Si4+ cations which are surrounded by 4 oxygen anions arranged in the form of a regular tetrahedron. TheseSiO_4^{4-} tetrahedra are joined together in chains or rings by bridging oxygen. Viscous flow in slag depends on the mobility of ionic species in the system, which, in turn depends upon the nature of the chemical bond and the configuration of ionic species. The interionic forces in the case of slags depend on the sizes and charges of ions involved. Thus, it is natural to expect that stronger interionic forces lead to an increase in viscosities. In the case of silicate melts with high silica contents, the polymeric anions cause a high viscosity. With increase of the metal oxide concentrations, the Si-O bonds progressively breakdown and size of network decreases accompanied by lowering of the viscosity of slags. Mackenzie[8] has shown that the addition of alkali oxides up to 10-20 mole % leads to a drastic fall in the viscosities due to depolymerization**.**

In blast furnace slag alumina is also present and the AlO_4^{5-} groups from polymer units withSiO_4^{4-}. The slag containing CaO – MgO – SiO_2 – Al_2O_3, alumina increase the viscosity as silica does. Lime and magnesia, the suppliers of oxygen, has the opposite effect on the viscosity.

The chemical composition and the temperature of the slag mainly affect the viscosity. Low viscosity helps to govern reaction rates by its effect on the transport of ions in the liquid on the slag – metal reacting interface and also provide a smooth running of the blast furnace. According to Turkdogan and Bills [9], for CaO – MgO – SiO_2 – Al_2O_3 system, both alumina and silica increase the viscosity of the melts.

The blast furnace slag is very complex in nature but for the calculation of viscosity we consider it as a Newtonian fluid due to presence of range shear stresses application on the slag.[10,11] The viscosity of the molten slag is determined by the Arrhenius equation[12],

$$\mu = A \exp\left(\frac{E}{RT}\right) \tag{2.24}$$

Where, μ = Viscosity

A = Pre exponential constant.

E = Activation Energy of viscous flow

T = Absolute Temperature

2.5.5. 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.

Iida Model

As we know that molten slag has a three dimensional network structure hence the viscosity is very sensitive to their structure. Therefore the structure of the molten slag must take into consideration for the model development, which predicts the viscosity.

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

$$\mu = A\mu_{\circ} \exp\left(\frac{E}{B_i^*}\right) \tag{2.25}$$

Where, $\mu_{\circ}$ is depends upon the chemical composition, melting point and molar volume. E and A depends upon the temperature and B_i^* depends upon chemical composition.

$$A = 1.745 - 1.962 \times 10^{-3}\,T + 7.000 \times 10^{-7}\,T^2 \tag{2.26}$$

$$E = 11.11 - 3.65 \times 10^{-3}\,T \tag{2.27}$$

$$\mu_{\circ} = \sum \mu_{\circ i} X_i \tag{2.28}$$

Where,

$\mu_{\circ}$ = Viscosity of non-network forming (hypothetical) melts.

$$\mu_{\circ_i} = 1.8 \times 10^{-7} \frac{[M_i (T_m)_i]^{1/2} \exp(H_i / RT)}{(V_m)^{2/3} \exp[H_i / R(T_m)_i]} \tag{2.29}$$

$$H_i = 5.1 (T_m)_i^{1/2} \tag{2.30}$$

Where,

M = Molecular weight of the oxide

V_m = Molar volume the oxide at melting point, T_m

R = Gas constant

X = Mole fraction

i= Subscript refers to the oxide

B_i^* = modified basicity index

$$B_i^* = \frac{\sum(\alpha_i W_i)_B + \alpha^*_{Fe_2O_3} W_{Fe_2O_3}}{\sum(\alpha_i W_i)_A + \alpha^*_{Al_2O_3} W_{Al_2O_3} + \alpha^*_{TiO_2} W_{TiO_2}} \tag{2.31}$$

Where

W = mass percentage of oxide

α_i = Specific coefficient of i^{th} oxide

α^* = Modified specific coefficient

$$\alpha^*_{Al_2O_3} = aB_i + bW_{Al_2O_3} + c \tag{2.32}$$

Where

$$a = 1.2\times10^{-5}T^2 - 4.3552\times10^{-2}T + 41.16 \tag{2.33}$$

$$b = 1.4\times10^{-7}T^2 - 3.4944\times10^{-4}T + 0.2062 \tag{2.34}$$

$$c = -8.0\times10^{-6}T^2 + 2.5568\times10^{-2}T - 22.16 \tag{2.35}$$

$$B_i = \frac{\Sigma(\alpha_i W_i)_B}{\Sigma(\alpha_i W_i)_A} \tag{2.36}$$

Where, subscripts A and B represent acidic and basic oxide respectively. Therefore with the help of equation (2.25) to (2.36) viscosity of the blast furnace slag can be estimated.

NPL model

On the basis of Arrhenius equation Mills and Sridhar **[14]** have also proposed a viscosity model which is expressed as:

$$\ln \mu = \ln A + \frac{B}{T} \tag{2.37}$$

Where,

$$\ln A = -233.69(\wedge^{corr})^2 + 357.32\wedge^{corr} - 144.17 \tag{2.38}$$

$$\ln \frac{B}{1000} = -1.77 + \frac{2.88}{\wedge^{corr}} \tag{2.39}$$

Where,

$\wedge^{corr}$ = Corrected optical basicity [39]

$$\wedge^{corr} = \frac{\sum_{i=1}^{n} x_i^{'} n_i \wedge_i}{\sum_{i=1}^{n} x_i^{'} n_i} \tag{2.40}$$

Where,

$x_i^{'}$ = Corrected mole fraction

n_i = No. of oxygen atom in the oxide of component i

$\wedge_i$ = Optical basicity of i^{th} oxide

Hence with the help of equation (2.37) to (2.40) we can estimate the viscosity of the blast furnace slag.

Ray's model

With the help of Weymann – Frenkel equation for viscosity Ray and Pal[15] also develop a model for the estimation of viscosity of the blast furnace slag, which depends upon the chemical composition and optical basicity of the oxides. The equation of Ray's model is expressed as follows:

$$\ln \frac{\mu}{T} = \ln A + \frac{1000}{T} \tag{2.41}$$

Where,

$$-\ln A = 0.2056B + 12.492 \tag{2.42}$$

$$B = 297.14(\wedge^{corr})^2 - 466.69\wedge^{corr} + 196.22 \qquad (2.43)$$

$\wedge^{corr}$ = Corrected optical basicity

Hence with the help of equation (2.41) to (2.43) we can estimate the viscosity of the blast furnace slag.

2.5.6. Flow characteristics of slag

Flow characteristics of the blast furnace slag are estimated with help of high temperature microscope. There are four characteristics temperature, **[16]** which describe the fusion behaviour of the slag, are as follows:

- Initial deformation temperature (IDT)
- Softening temperature (ST)
- Hemispherical temperature (HT)
- Flow temperature (FT)

Initial deformation temperature (IDT) - It is the temperature at which the initial rounding up of the edge of the sample starts. The shape of the sample is taken cubical for this experiment. Rheologically it is the temperature which indicates the stickiness of the surface of slag sample.

Softening temperature (ST) – It is the temperature at which the outline of the shape starts changing and is reported as the temperature at which the sample shrink by one division on the experiment pattern or we can say that it is the temperature at which the distortion of the sample starts. Rheologically this temperature indicates the start of plastic distortion.

Hemispherical temperature (HT) – It is the temperature at which the specimen attains a hemispherical shape and is measured as the temperature at which the height of the specimen is equal to half of its base length. In German industrial standards 51730, it is defined as the fusion point or the melting point. Rheologically this temperature indicates the sluggish flow of the slag starts.

Flow temperature (FT) – It is the temperature at which the specimen liquefies and is reported as the temperature at which the height of the specimen is equal to one-third of the height that it had at the hemispherical temperature. Rheologically this temperature indicates the liquid mobility of slag i.e. free flow of the slag.

2.6. Activation Energy

Activation energy is a term introduced by a Swedish scientist Svante Arrhenius in 1889. It is defined as the minimum energy that must be required to a chemical process, containing potential reactant, so that a chemical reaction occurs. It may also be defined as the minimum energy required to starting a chemical reaction. It is generally denoted by E_a and its SI unit is Kilojoule per mole.

In metallurgical point of view, the minimum energy required to break the relative bond within the molecule to start the reaction is known as activation energy. In other word, Activation energy is an energy barrier which opposes the chemical reaction to occur.

Svante Arrhenius derives an equation which gives the relationship between the activation energy and the rate of reaction of a chemical reaction. [17] This equation is expressed as:

$$k = Ae^{-E_a/RT} \tag{2.44}$$

Where K is the reaction rate coefficient, R is the universal gas constant, A is the frequency factor of the reaction and T is the absolute temperature. [18]

2.6.1. Activation energy of blast furnace slag

Activation energy of the blast furnace slag is an important parameter during the production of pig iron. It gives the following idea about blast furnace process:

- It play important role in adhesion of ash particles to the walls of a reactor.
- It gives an idea about solidification of slag.
- It gives the slag and metal separation temperature and time calculation.
- Calculation of heat content change of slag.
- Representation of endothermic and exothermic reaction.[19]
- It gives the idea about recrystallization temperature.[19]
- Energy barrier of slag flowing properties.
- Movement of flow units involves breaking of Si-O bonds (Heat of dissociation)[20]
- Time taken to the reaction of slag formation.[18]
- Viscosity property of slag. [21]

- The energy required to move one layer of silicate group with respect to the other layer .i.e. the number of ionic bonds which have to be broken or distorted in order to enable the group to move,
- It gives the melting point of slag. [22]
- It gives the idea about nucleation and grain growth.[23]

2.6.2. Factor affecting the activation energy

Activation energy of the blast furnace affected by the following factor:

1. **Temperature** – The region of furnace where the temperature is high, slag is highly active, the slag containing more energy and hence it required less amount of activation energy. Similarly the region of low temperature, slag containing less energy and hence it required more activation energy. This happens because we know that as we increase the temperature, the kinetic energy of the molecules increases and hence the probability of successful collision for reaction is also increases therefore the activation energy requirement is less.
2. **Concentration and pressure**–If a slag has high concentration or pressure, the number of molecules in a particular region will be more, the probability of collision of molecule will be more and hence the rate of reaction will be more and finally the requirement of activation energy will be less.
3. **Physical state –** Here particle state means the size of the slag particle. The size of slag particle for the estimation of activation energy must be in power shape. i.e. small in size. If the size of slag particle is in large shape then the reaction occurs on the solid surface due to which the value of activation energy calculated is not correct. And if the size of slag particle is small then the surface area for the reaction is more and hence the reaction takes place easily and faster.
4. **Composition of the slag** – As we know that the different oxides (oxide of Mg, Al, Ca, Si) have different network breaking ability and hence if there is a variation in the composition of slag, it gives different value of activation energy.
5. **Percentage of CaO –** If the CaO content in the slag is more, the basicity of slag is more, [22] and hence the liquidus temperature is more. [17] Therefore the amount of slag formation is less and the value of activation energy of the slag is more.

2.7. Available literature related to viscosity of the blast furnace slag.

Slag viscosity is a transport property that relates to the reaction kinetics and the degree of reduction of the final slag. [7] It determines the impurity removal capacity, slag-metal separation efficiency and the metal yield. The slag viscosity is increases due to the presence of a strong three dimensional network of silicate; hence we can say that the slag viscosity is sensitive to its ionic and molecular structure. If the slag viscosity is less, the slag could be tapped easily and the furnace operation is smooth. Hence it is related to energy requirement and the productivity of the blast furnace operation. The quality of the raw material and coke available in our country, generally a high Alumina slag is generated thus the study related to the effect of Alumina on the slag viscosity is necessary. The viscosity of the slag increases as we increase the Alumina content. The effect of Alumina on slag viscosity depends on the lime content, because Si^{4+} is replace by Al^{3+} in silicate network only if it is associated with $\frac{1}{2}Ca^{2+}$ to preserve electrical neutrality. [10]

Y.S.Lee et al [24] studied that viscous behaviour of CaO-SiO_2-Al_2O_3-MgO slag condition of basicity (C/S) 1.15 – 1.6. The mass percentage of Al_2O_3, MgO and FeO are 10-13%,5-10% and 0-20% respectively. They found that at a fixed basicity of slags, if we increase the FeO percentage the viscosity of the blast furnace slag decreases. At low FeO percentage (< 7.5 % FeO), by increase the MgO percentage, they found a minimum value of viscosity. If the FeO percentage is greater than 7.5%, addition of MgO does not affect the slag viscosity. A minimum value of slag viscosity is observed at about 7% MgO with 5% FeO.

Viscosity of the slag decreases if we increase the slag basicity up to 1.3 but after that if we increase the slag basicity from 1.3 to 1.5 they observed that the slag viscosity increases. Hence they conclude that, as we increase the slag basicity, the driving force for the decrease of slag viscosity would be increases in depolymerization of silicate network at $C/S \leq 1.3$. While the driving force which increase the slag viscosity at $C/S > 1.3$ is an increase in the chemical potential of solid compounds such as dicalcium silicate.

Kohei Sunahara et al [25] studied the effect of high Al_2O_3 the blast furnace operations. They found that the tapping of slag from the furnace hearth is a fluidization phenomenon dominated by viscosity. As the slag viscosity increases the slag drainage rate decreases. Hence to maintain slag drainage under high Al_2O_3, for instance, an addition of the MgO content in the slag is effective. They also found that the effect of the slag crystallization temperature on the slag drainage rate is relatively less in comparison to the effect of viscosity.

As the Al_2O_3 concentration in slag increases the pressure drop in the dripping zone increases. Pressure drop in dripping zone is also increase if CaO/SiO_2 increases. The pressure drop is mainly caused by the effect of wettability as a result of the slag static hold-up, and little due to effect of slag crystallization temperature and viscosity. To suppress the increase of pressure drop in the dripping zone, in the high alumina slag, it is effective that the decrease of hold-up by decreasing the slag basicity (CaO/SiO_2).

Amitabh Shankar et al **[10]** studied the viscous behaviour of $CaO\text{-}SiO_2\text{-}MgO\text{-}Al_2O_3$ and $CaO\text{-}SiO_2\text{-}MgO\text{-}Al_2O_3\text{-}TiO_2$ system by varying the C/S ratio between 0.72 and 1.23 in the temperature range of 1573-1873K. The percentage of Alumina was varied between 21-28%, Titanium was varied between 0-2% and magnesia was varied between 2-8%. They found that the slag viscosity decreases with increase in basicity (C/S). They have also found that the slope of the viscosity vs. temperature curve is steeper for low basicity. The slag viscosity is decreased if the basicity is increases, because the silicate three dimensional networks discrete into anionic group containing sample chains or rings as basic oxides are increased.

J. Muller et al **[7]** estimated the effective viscosity for typical blast furnace slag, has different basicity, FeO content and Al_2O_3 content, at 1873K. They found that the slag viscosity decreases with the increase of slag basicity. As we increases the slag basicity i.e. the CaO and MgO content, which acts as a network breakers and hence the slag viscosity decreases.

Effect of temperature on viscosity is more pronounced for low basicity slags; therefore generally the slag in the basicity range of 0.95-1.05 should be used. Further increase in basicity may result in an increase in slag viscosity as reported by ***Y.S.Lee et al*** **[24].**

Noritaka Saito et al **[26]** studied the effect of MgO on the viscosity of $CaO\text{-}SiO_2\text{-}Al_2O_3$ (40-40-20) slag system. They found that the viscosity of this slag system decreases with increase in MgO percentage. They proposed that MgO acts as a network modifier and hence decreases the slag viscosity. They also found that the activation energy of viscous flow decreases on the addition of MgO.

Yasuji Kawaiet al **[27]** studied about the viscosities of $CaO\text{-}SiO_2\text{-}Al_2O_3\text{-}MgO$ slags and the viscosities of molten slags. When the percentage of MgO is increases in $CaO\text{-}SiO_2\text{-}MgO$ slags, up to 20%, the viscosity decreased but beyond 20% if we increase the MgO content the viscosity increased. The region of low viscosity was greater than that in CaO-SiO2-Al2O3 slag.

***Masashi Nakamoto et al*[28]** studied the viscosity of molten slags has low melting point on the way to develop an enhanced blast furnace operation at lower temperature, about 1673 K. They estimate the viscosity of molten CaO- SiO_2-MgO-Al_2O_3 slag by rotating cylinder method and compared this result with the results of the model developed. They found that slag system 35% Al_2O_3-43.1% CaO-7.5% MgO-14.4% SiO_3 has melting point below 1673 K and has viscosity less than 0.6 Pa-s below 1673 K.

***Seong-Ho Seok et al* [29]** studied about the viscous behaviour of CaO-SiO_2-FeO-MgO melts saturated with dicalcium silicate and 8% MgO at 1873 K and also the CaO-SiO_2-FeO-Al_2O_3-MgO slags under highly basic environments. They found that the slag viscosity depends more strongly on Alumina than on Magnesia content because the fraction of solid phases present is more in the case of deviation in alumina percentage.

***J.Y. Jia et al* [30]** studied the calculation models for the viscosity of CaO-SiO_2-TiO_2 slag system. They established the mass action concentration calculation model and viscosity calculation model, on the basis of the coexistence theory of slag structure. The values of viscosity are measured under different temperatures and compositions for the CaO-SiO_2-TiO_2 ternary slag system. They have found that if TiO_2 percentage in slag is increases, the viscosity of slag system decreases.

***D. Ghosh V.A. Krishnamurthy, et al* [31]** studied the use of optical basicity to viscosity of high alumina blast furnace slag. They have found that experimental measurement of slag viscosity requires high temperature equipment and is time consuming. The slag Viscosity is strongly influenced by the chemical composition, structure and the temperature. And they also found that the basic oxides namely lime, magnesia, titania are the oxygen providers, which act as network breakers and result in depolymerisation of the melt.

2.8. Available literature related to Activation Energy of Blast Furnace Slag.

The estimation and the important of activation energy is always a topic for animated discussions at thermal analysis summit. After the several meeting and research analysis the researchers found that the value of the activation energy can predict about the thermal stability, optimum reaction conditions and the expected lifetime of a blast furnace slag at a certain temperature.

Borham, B. M. et al [18] studied the activation energy of urea nitrate by means of differential thermal analysis (DTA) curves using the Murray and White equation and several other reaction rate equations. They have found the average value of activation energy was 31.7 ±10.0 kcal/mole and they have also shown that these results illustrate the noticeable effect of self-heating on the estimation of activation energies. The Kissinger method of estimating the reaction order developed for endothermic DTA peaks provide good results when it was applied to the present DTA study.

Moynihan, C. T., et al [21] studied the activation energy ΔE of slag for the structural relaxation in the glass transition region, which is determined with the help of heating rate dependence of the glass transition temperature T_g or the cooling rate dependence of the limiting fictive temperature T_f measured using DSC or DTA.

Keuleers, R. R., J. F. Janssens, et al [32] studied the effective methods for the estimation of activation energy which deals the thermal decomposition of chemical compounds. They compare the different measurement and calculation techniques for the thermal decomposition of $Mn(Urea)_2Cl_2$.

Starink, M. J, et al [33] studied the model-free iso-conversion methods which were most effective methods for the calculation of activation energies of thermally activated reactions. A large number of iso-conversion methods have been proposed in this literature. Type A methods such as Friedman methods has no mathematical approximations, and Type B methods, such as the generalised Kissinger equation [4sanjay]. And they found that there is a limited accuracy of determination of transformation rates, and type B methods will be more accurate than type A methods.

Homer E. Kissinger et al [19] studied the variation in Peak Temperature by Differential Thermal Analysis with different heating rate. They have found that Changes in heat content of the active sample are indicated by deflections in a line representing the differential temperature. By convention an endothermic effect is represented by negative deflection and an exothermic effect by a positive deflection. These positive or negative deflections are called peaks.

Wang, Zhong-jie, et al [34] studied about the crystallization process of glass ceramics which was prepared by a mixture of blast furnace slag, nickel slag and a small amount of quartz sand. The crystallization behaviour of this mixture was studied by differential scanning calorimetry (DSC), X-ray diffraction (XRD) and field emission scanning electron microscope (FESEM). They have found that the radial crystals were detected when the glass was heated up to820 °C. By XRD analysis, they conform the spherical crystals and radial crystals were likely to be the crystals of Diopside ($CaMg(Si,Al,Fe)_2O_6$) and Hedenbergite ($CaFe(Si,Al,Fe)_2O_6$) respectively.

Gan, Lei, et al[35]studied the continuous cooling crystallization kinetics of molten blast furnace slag. They observed that Activation Energy obtained during cooling is much higher than that yielded during heating. They also shown that akermanite and gehlenite are the most important minerals in the continuous cooled crystalline blast furnace slag were investigated by means of X-ray diffraction.

CHAPTER – 3

EXPERIMENTAL

3. EXPERIMENTAL

3.1. Materials and its composition

In the present work the analysis of composition of slags, from different blast furnace of different steel plants of India, was done and on the basis of that we determined an average slag composition. After getting an average slag composition we prepared nine numbers of synthetic slags, keeping fixed Al_2O_3, MnO, Na_2O, K_2O and Fe_2O_3 content and varying the C/S ratio (basicity), MgO and TiO_2 content, in the laboratory. The materials used are, reagent grade oxides with more than 99% purity, listed in the table 3.1 and the composition of synthetic slags prepared in laboratory are listed in table 3.2.

Table.3.1. Percentage purity of oxides used for the preparation of synthetic slags

Materials	Purity
Aluminum oxide (Al_2O_3)	99.90%
Manganese oxide (MnO)	98.50%
Sodium oxide (Na_2O)	99.50%
Potassium oxide (K_2O)	99.40%
Iron oxide (Fe_2O_3)	98.00%
Magnesium oxide (MgO)	98.53%
Titanium oxide (TiO_2)	99.50%
Silicon oxide (SiO_2)	99.50%
Calcium carbonate ($CaCO_3$)	98.50%

3.2. Sample preparation

We are making 100 gram of each sample and follow the table 3.3 for the composition of synthetic slag sample. After collected the different oxide has almost 99% pure, the sample preparation involved following process:

- **Weighing** – The required amounts of each oxide were weighed by using Contech digital weighing machine accurately.
- **Mixing** – After weighing the required amount of different oxides, proper mixing is required in order to achieve a homogeneous mixture for better result. The received oxide powder of different classes was very fine, therefore to achieve a homogeneous

mixture we gone through ball milling. Ball milling consists two ceramic containers in which 50 gram oxide mixture was kept in each of container for two hours. Three such sessions are required for required mixing.

- **Pelletization** – After mixing we obtained a required homogeneous mixture which was pelletized between the dies in the compression machine under the load of 4 ton. We were taken the amount of sample mixture in such a way that each pellet formed having almost same dimension. The process of pelletization was done because the platinum crucible used for the melting of the oxides was very small and cannot contain all powdered sample at a time so making into pellets it become compacted and will take less space and hence less time for melting the 100 gram sample. This process generally takes 5 hours continuously for converting the 100 g of sample powder into pellets. After the formation of pellets it must be kept away from open atmosphere to avoid moisture absorption and hence it was stored in oven before the melting process.
- **Melting** – The obtained pellets were then melted at around 1550°C in the rising hearth furnace to the formation of synthetic blast furnace slag. This temperature is selected because this is the temperature that the slag undergoes when comes out of the blast furnace. The pellets are put in a platinum crucible and this crucible was kept inside the furnace. After the temperature is achieved, the slag sample was hold at that temperature for one hour for the complete melting.
- **Quenching** –After complete melting, quenching was done in the water at room temperature. During this process the platinum crucible is removed from the furnace and put it down immediately into the water.
- **Grinding** – After quenching the prepared slag was kept in the oven, at 150°C to remove the moisture content, for one day. Then the dried slag, ready for grinding, was kept in the ball mill for grinding operation. This grinding operation was taken one hour to obtain desired fine powder.
- **Re-melting –** The obtained fine power was again pelletized between the dies before melting. The re-melting operation was done in the same rising hearth furnace, which was used for melting purpose. This operation was done to obtain a required homogeneous synthetic slag.

- **Quenching** – After complete re-melting of synthetic slag, quenching was done in water at room temperature. The prepared sample was the kept inside the oven, at 150°C, for one day, so that the moisture from the sample is completely removed.
- **Grinding** – The dried sample was again gone for grinding operation. The grinding operation was done by ball milling machine. After ball milling we obtained a homogeneous synthetic slag powder for our present work.

On the basis of sample preparation method described above the compositions of synthetic slags prepared in laboratory are listed in table 3.2.

Table.3.2. The composition of synthetic slag prepared in laboratory

Slag No.	**Al_2O_3**	**MnO**	**Na_2O**	**K_2O**	**Fe_2O_3**	**MgO**	**TiO_2**	**SiO_2**	**CaO**	**C/S**
1.	20.0	0.1	1.0	0.5	1.0	9.0	0.55	31.56	36.29	1.15
2.	20.0	0.1	1.0	0.5	1.0	12.0	1.0	26.83	37.57	1.40
3.	20.0	0.1	1.0	0.5	1.0	6.0	0.1	29.71	41.59	1.40
4.	20.0	0.1	1.0	0.5	1.0	12.0	0.1	34.37	30.93	0.9
5.	20.0	0.1	1.0	0.5	1.0	6.0	1.0	37.05	33.35	0.9
6.	20.0	0.1	1.0	0.5	1.0	6.0	1.0	29.33	41.07	1.40
7.	20.0	0.1	1.0	0.5	1.0	12.0	1.0	33.89	30.50	0.9
8.	20.0	0.1	1.0	0.5	1.0	6.0	0.1	37.53	33.77	0.9
9.	20.0	0.1	1.0	0.5	1.0	12.0	0.1	27.21	38.09	1.40

3.3. Experimental Apparatus

3.3.1. Planetary Ball mill

It is used for size reduction and classical mixing process. With the help of this mill we can achieve any degree of required fineness. Apart from that it also meets all the technical requirements for colloidal grinding and it has sufficient energy input for the process of mechanical alloying. The mills have very high centrifugal forces which produce very high pulverization energy and hence the time required for grinding is less.

In the present work this mill is used for mixing and grinding the sample. The samples are kept in both the ceramic crucibles containing 6-7 balls. These crucibles are then mounted on the machine properly. Here we used 300 rpm of revolution and taken 30 minutes for each session.

Fig.3.1. A two station Planetary Ball Mill

3.3.2. VIS 403 Rotating Viscometer

The high temperature viscometer, VIS403, measures the dynamic viscosity of materials with Newtonian behavior such as glasses, slags or mold powder. The working principle of this viscometer is measuring the shear stress and shear rate of a rotating bob immersed in a sample (in fluid form) filled crucible under controlled temperature. Two different bob and crucible configurations are available based on the viscosity of the test fluid. Tests may be conducted in controlled stress or controlled rate conditions, and under isothermal or temperature ramp programs.

In the present work with the help of viscometer we were calculate the viscosity of the synthetic slag and also estimated the Activation energy by the available data of viscometer.

The Specification of this equipment is:

Viscosity range:	$10^1 – 10^8$ dPas
Measurement accuracy:	± 3°C
Measuring principle:	rotating rotor (Searle type)
Temperature range: max.	1700°C

Crucible material: PtAu5% Crucible volumes: 13,8 or 9,2cm^3

Speed: max. 800 rpm

Torque range: 0 – 150mNm

Atmosphere: air, inert gas as purge gas

Fig.3.2. VIS 403 Rotating High Temperature Viscometer

3.3.3. High Temperature Furnace

Furnace is an instrument which is used for heating purpose. The energy source of any furnace is fuel or electricity. In the present work we used a rising hearth furnace for the melting of pellet to obtain a desired synthetic slag. The source of energy of this furnace is electricity. The maximum temperature range of this furnace is 1750°C. In our work we were chosen a maximum temperature of 1550°C, this temperature is selected because this is the temperature that the slag undergoes when comes out of the blast furnace. The pellets are put in a platinum crucible and this platinum crucible was kept inside the furnace. After the temperature is achieved, the slag sample was hold at that temperature for one hour for the complete melting.

Fig.3.3. Rising hearth high temperature Furnace

3.4. Experimental procedure

The experimental procedure of the present work is divided into mainly in three parts, the aims at measuring the viscosity of high alumina Indian blast furnace slags in agreement with the slag compositions encountered in the industries. The three parts of experimentation are as follows:

3.4.1. Calibration of Viscometer

For the calibration of viscometer data submitted by the manufacturer for variation of viscosity with temperature for standard sample number 717a is used. The viscosity data in Pa.s is presented below in the table no. 3.3 for temperature variations from 1623K to 1853K (the range of temperature for which viscosity was measured for our sample). Measurement shows that a multiplying factor of 5.5 has to be chosen for the calibration of the instrument.

Table.3.3. Variation of viscosity with temperature for standard sample no. 717a (supplied by the manufacturer of the equipment)

Temperature, K	**Viscosity, Pa.s**
1623	428.18
1624	424.63
1625	421.11
---	---
---	---
---	---
1851	87.65
1852	86.95
1853	86.45

3.4.2. Testing of Viscometer

For testing purposes a standard slag of 40:40:20 (CaO : SiO_2 : Al_2O_3) is chosen. The viscosity of the slag is measured five times and an average value is compared with the viscosity values as reported in literature. [38] The comparison between the measured value and the value as obtained literature is reported in the table no. 3.4.

Table.3.4. Comparison of measured viscosity and viscosity value from literature of standard slag

Temperature, K	Viscosity (μ), Pa.s From literature	Viscosity (μ), Pa.s From experiment	% Deviation
1678	2.253	2.162	4.02
1718	1.519	1.421	6.45
1758	1.028	1.066	3.70
1798	0.693	0.715	3.13

Since the experimental value is very close (within 5%) to the value available in literature [38] hence our viscometer is calibrated and it generates accurate values of viscosity under the experimental conditions adopted in the present case.

3.4.3. Viscosity measurement procedure

In the present work 'VIS 403' Rotating High Temperature Viscometer is used for the measurement of viscosity. The platinum crucible field with slag sample was kept inside the furnace. The bob was lowered and placed at a level of 10 mm above from the slag layer. It is very necessary to keep both the bob and the crucible are properly aligned with the axis of the viscometer because a slight deviation from the axis could create experimental error. The furnace was heated up to experimental temperature and was held at that temperature for 30 minutes, so that the sample attained the thermal equilibrium. After the equilibrium reached the bob was fully dipped into the liquid sample. All the viscosity measurements were recorded during the cooling cycle ascertaining the homogeneity of the slag melt. Five reading are taken for each sample at different temperature and the average is presented. The temperature range for each experiment between 1400°C to 1550°C, cooling rate 3K/min and the bob was rotated at speed between 50 to 100 rpm. After the measurement, the platinum crucible taken out and it was cleaned subjected to chemical analysis.

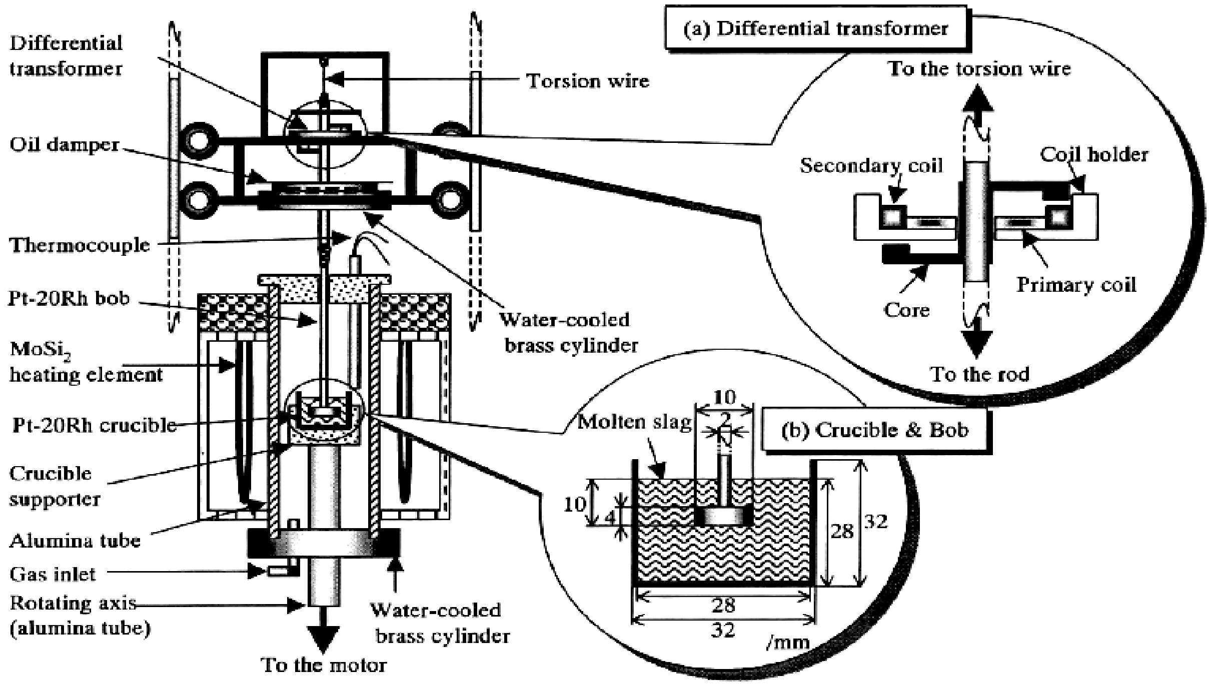


Fig.3.4. Schematic illustration of the apparatus for viscosity measurement

CHAPTER – 4

RESULT AND DISCUSSION

4. Result and Discussion

4.1. Validation of the models – The standard slag ($CaO:SiO_2:Al_2O_3$ :: 40 : 40 :20) and two other slags (slag no.1 and slag no.2) are chosen for validation of model. For this the viscosity was measured using high temperature viscometer (VIS 403 Rotating Viscometer) and also calculated using the respective models. The calculation details are provided in appendix 1. In the present we were chosen three models for the calculation of viscosity which are Iida Model, Ray and Pal Model and NPL Model. The detailed measured and calculated values of viscosity are presented in the following tables:

Table.4.1. Comparison of measured and calculated viscosity values of Standard slag

Model for calculation	Temperature, K	Calculated Viscosity (Pa.s)	Measured Viscosity (Pa.s)	% Deviation
Iida Model	1673	1.4883	2.0168	26.20
	1723	0.9474	1.2114	21.79
	1773	0.6533	0.8013	18.46
	1823	0.4841	0.5926	18.30
Ray’s Model	1673	0.9244	2.0168	54.16
	1723	0.6895	1.2114	43.08
	1773	0.5233	0.8013	34.69
	1823	0.4035	0.5926	31.91
NPL Model	1673	0.009435	2.0168	Very High
	1723	0.007332	1.2114	
	1773	0.005780	0.8013	
	1823	0.004616	0.5926	

Table.4.2. Comparison of measured and calculated viscosity values of Synthetic slag No.1.

Model for calculation	Temperature, K	Calculated Viscosity (Pa.s)	Measured Viscosity (Pa.s)	% Deviation
Iida Model	1673	1.2725	1.6123	21.07
	1723	0.7688	0.9687	20.63
	1773	0.5271	0.6325	16.67
	1823	0.3889	0.4723	17.65
Ray's Model	1673	0.4909	1.6123	73.27
	1723	0.3325	0.9687	65.68
	1773	0.2605	0.6325	58.81
	1823	0.2069	0.4723	56.17
NPL Model	1673	0.008755	1.6123	Very High
	1723	0.007583	0.9687	
	1773	0.005799	0.6325	
	1823	0.004014	0.4723	

Table.4.3. Comparison of measured and calculated viscosity values of Synthetic slag No.2

Model for calculation	Temperature, K	Calculated Viscosity (Pa.s)	Measured Viscosity (Pa.s)	% Deviation
Iida Model	1673	1.7076	2.1345	20.00
	1723	0.9623	1.2025	19.97
	1773	0.6119	0.7465	18.03
	1823	0.4598	0.5617	18.14
Ray's Model	1673	0.2808	2.1345	86.84
	1723	0.2207	1.2025	81.64
	1773	0.1761	0.7465	76.40
	1823	0.1423	0.5617	74.66
NPL Model	1673	0.008263	2.1345	Very High
	1723	0.006836	1.2025	
	1773	0.005715	0.7465	
	1823	0.004112	0.5617	

Therefore by observing the above tables (Table No.4.1, 4.2 and 4.3) we can say that the Iida model gives the closest value. From literature [36] it is seen that Iida model rendering a difference of about 22% is accepted as an accurate model therefore in the present case the Iida model rendering a difference of up to 21% is accepted for yielding accurate viscosity values.

4.2. 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 further slags (Slag No. 3 to slag No.9). The calculation of viscosity using this model is based on the equations 2.25 to 2.36 described in the section 2.2.5. The detailed calculated values of viscosity are presented in the table 4.4.

Table.4.4. Calculated values of viscosity of different slag using Iida Model

Viscosity (Pa.s) at temperature (K)				
Slag No.	1673 K	1723 K	1773 K	1823 K
Slag No. 1	1.2725	0.7688	0.5271	0.3889
Slag No. 2	1.7076	0.9623	0.6119	0.4598
Slag No. 3	1.2004	0.7194	0.4862	0.3657
Slag No. 4	1.3246	0.8263	0.5713	0.4273
Slag No. 5	1.4357	0.8987	0.6642	0.4561
Slag No. 6	1.3392	0.7831	0.5219	0.3858
Slag No. 7	1.4095	0.8604	0.6111	0.4324
Slag No. 8	1.3901	0.8872	0.6212	0.4625
Slag No. 9	1.4834	0.8591	0.5675	0.4246

These calculated viscosities are plotted against temperature, C/S ratio, MgO and TiO_2 content. With the help of these plots we analyzed the effect of these variables on viscosity. It is observed that the viscosity is greatly influenced by the C/S ratio, MgO and TiO_2 contents.

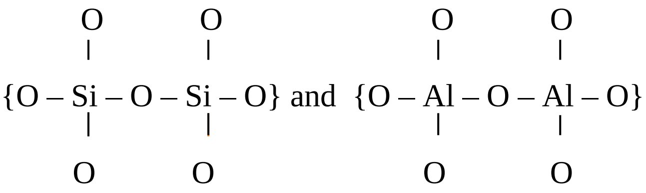
4.2.1. Effect of C/S ratio on Viscosity

As evident from Fig.4.1, the viscosity of the high alumina blast furnace slag decreases with increase of C/S (CaO/SiO_2) ratio when the MgO content of slag is low irrespective of the high /low levels of TiO_2. Also it is evident from the figure that when MgO level is high, highest level of C/S ratio, irrespective of the high/low level of TiO_2, increase the viscosity of the slag.

The viscosity of a slag is structure oriented. The viscosity of blast furnace slag is affected by the network breaking cations like Ca^{2+}, Mg^{2+} and the degree of polymerization of the silicate network. As explained by Lee et al. **[40]** CaO and MgO, the basic monoxides lower the viscosity by destructing the silicate network i.e, by depolymerizing while SiO_2 and Al_2O_3, which are highly covalent oxides contribute to the increase of the slag viscosity. Thus it is expected that increase of C/S ratio should decrease the slag viscosity at all levels.

However, detailed analysis would reveal the following:

(i) Al_2O_3 in the silicate melts can act both as a network former and a network modifier depending on the amount of other oxides present. When sufficient basic oxide is present in the melt, i.e., when sufficient oxygen is available in the melt, Al adopts a four-fold co-ordination with oxygen. In this case the melt would contain AlO_4^{5-} and SiO_4^{4-} ions.**[41]** In this situation polymeric ions like



$$\{O-\underset{\underset{O}{|}}{\overset{\overset{O}{|}}{Si}}-O-\underset{\underset{O}{|}}{\overset{\overset{O}{|}}{Si}}-O\}\text{ and }\{O-\underset{\underset{O}{|}}{\overset{\overset{O}{|}}{Al}}-O-\underset{\underset{O}{|}}{\overset{\overset{O}{|}}{Al}}-O\}$$

will be present in the melt to a higher extent, contributing towards the increase of the viscosity.

(ii) On the other hand when the amount of basic oxides like CaO and MgO is less, i.e., when sufficient oxygen is not available in the melt, Al would assume a six fold co-ordination (AlO_6). Here these AlO_6 groups would enter the interstices in the structure and cause depolymerisation reducing the percent of polymeric ions presented above and would contribute to the decrease of the slag viscosity.

The above explains the decrease of the viscosity with increase of C/S ratio at lower levels of MgO. This is because here the CaO and MgO combination would be low, lower extents of oxygen would be available in the melt. Al would adopt six-fold co-ordination and result in reduction of slag viscosity disintegrating the structure into smaller anionic units.

The reverse is also true. When C/S ratio is increased at higher levels of MgO the CaO, MgO combination would be high, higher oxygen would be available; Al would assume a four-fold co-ordination and the polymeric ions would be available in higher extents in the melt, increasing the viscosity of the slag.

Here, high and low M means MgO is 12 and 6 wt %respectively and high and low T means $TiO_2$1.0and 0.1 wt % respectively.

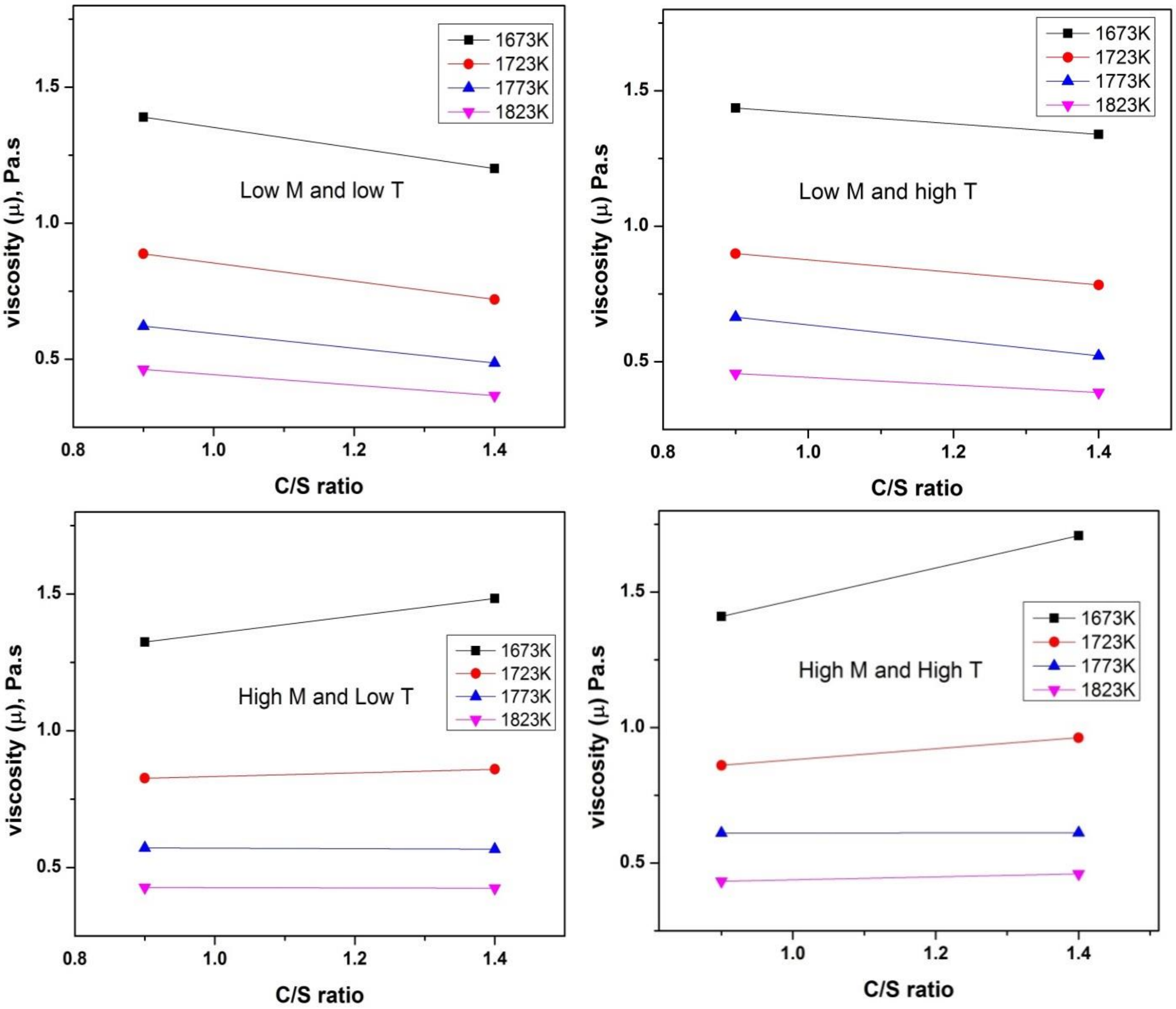


Fig.4.1. Influence of C/S ratio on viscosity

4.2.2. Effect of MgO on Viscosity

The variation of viscosity with MgO variation is presented in Fig.4.2. As evident from the figure, at higher level of C/S ratio increasing MgO increases the viscosity. Also at lower levels of C/S ratio increase of MgO levels decrease the viscosity. This trend of viscosity variations with MgO variations can be explained on the basis of four or six fold co-ordination of Al with oxygen. When the C/S ratio is high increased MgO levels increase the availability of oxygen thus favoring a four-fold co-ordination of Al with oxygen. This development increases the percentage of polymeric ions in the melt as explained above and is responsible for the increase of viscosity. On the other hand at lower levels of C/S ratio even an increase of MgO level does not provide sufficient amount of oxygen to melt, Al assumes a six-fold co-ordination with oxygen and breaks the anionic network decreasing the viscosity.

Here, high and low R means C/S ratio is 1.4 and 0.9 respectively and high and low T means TiO_2 is 1.0 and 0.1 wt% respectively.

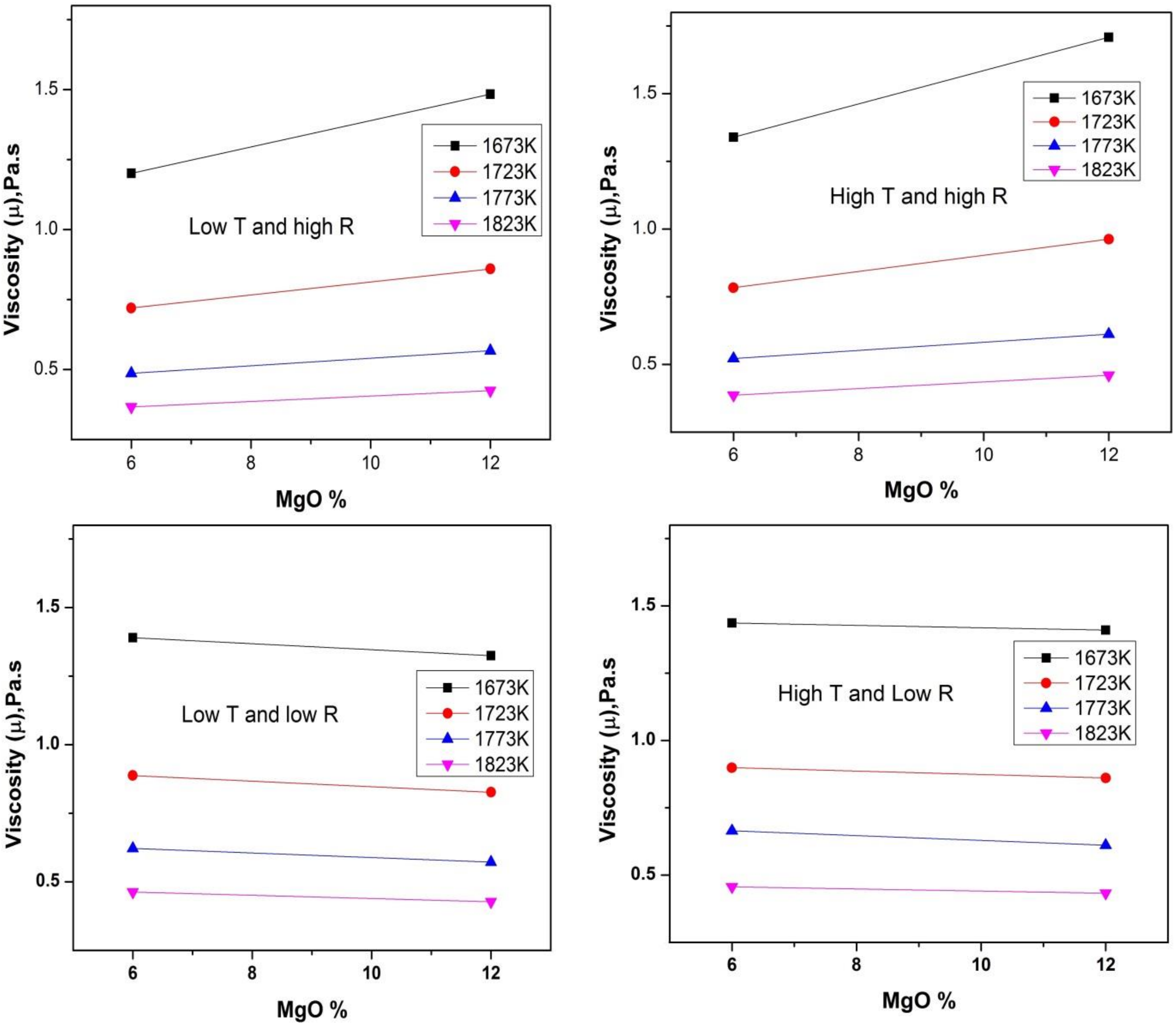


Fig.4.2. Influence of MgO on Viscosity

4.2.3. Effect of TiO_2 on Viscosity

Fig.4.3 represents the variation of viscosity with TiO_2 variations. It is observed that TiO_2, under the two levels of 0.1 and 1.0 wt % in the slag, has minimal effect on the viscosity. The viscosity of the slag seems to increase slightly with the increase in the TiO_2 levels. The rate of increase of viscosity, however, is seen to be the highest at high levels of both MgO and C/S ratio variations with increasing levels of TiO_2 content. This trend may be attributed to the availability of higher oxygen in the melt with high C/S ratio and MgO content. Such a situation would favour a four-fold co-ordination of Al with oxygen and assist faster polymerization of the silicate network.

Here, high and low R means C/S ratio is 1.4 and 0.9 respectively and high and low M means MgO is 12 and 6 wt % respectively.

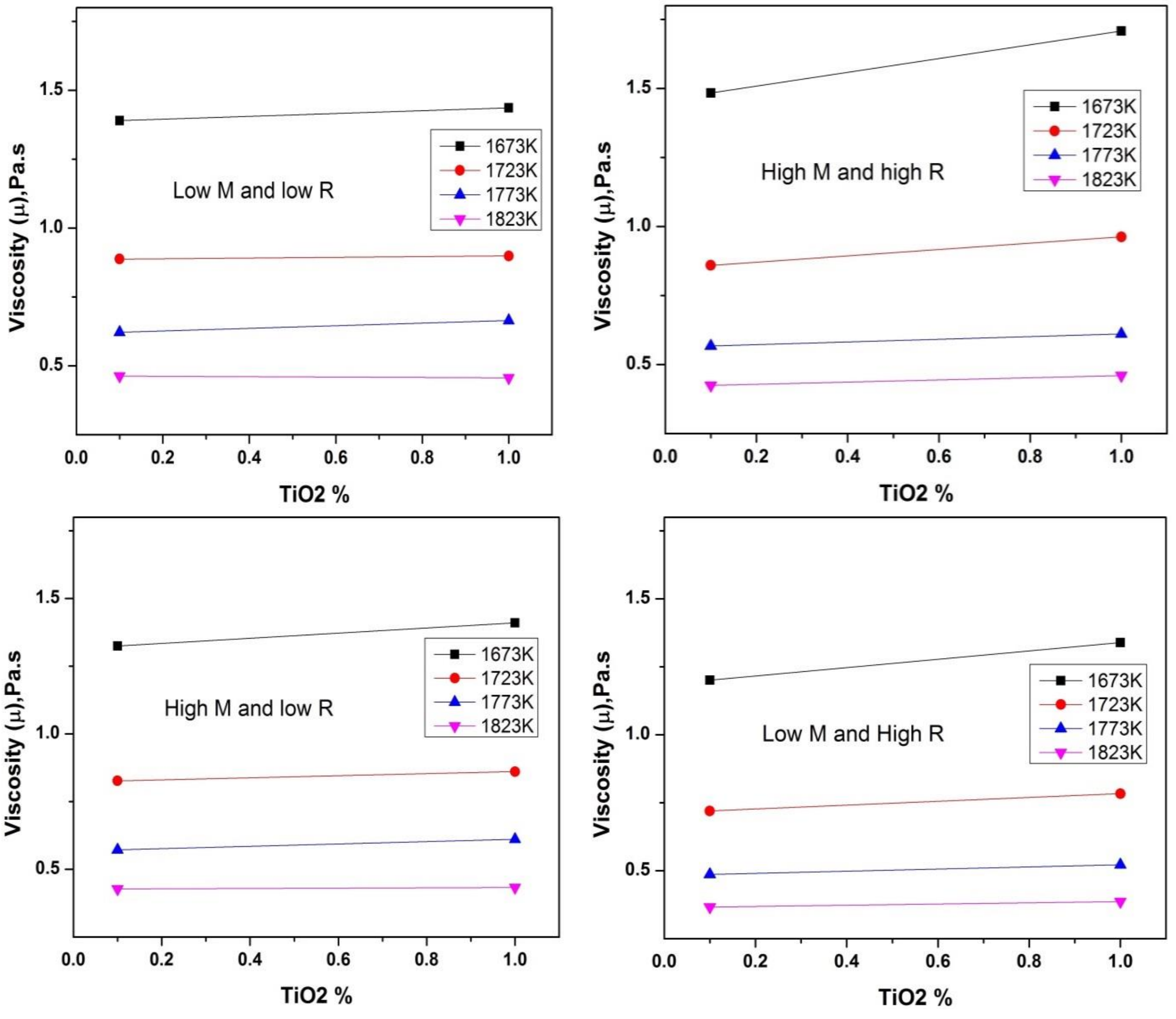


Fig.4.3. Influence of TiO_2 on Viscosity

4.2.4. Effect of Temperature on Viscosity

The viscosity of the slag continuously decreases with the increase in temperature; this is because temperature works as stimulant energizes the ions and makes the slag better flowing or making it more fluid. Fig.4.4 illustrates the same result graphically. This evident that slag no.2 is a short slag; here the viscosity increases abruptly with a small decrease in temperature. This slag has the highest C/S ratio at 1.4. This rise of viscosity may be due to the precipitation of a solid phase, namely Dicalcium Silicate (2CaO.SiO2) [37]. The literature states that Dicalcium Silicate precipitation out of the melt when the C/S ratio exceeds 1.3.

In such slag the temperature needs to be closely monitored and should not be allowed to fall below a certain value. If the temperature falls down below a certain value the slags becomes viscous hindering the slag metal separation, slag metal reaction rate and the slag metal exchanges.

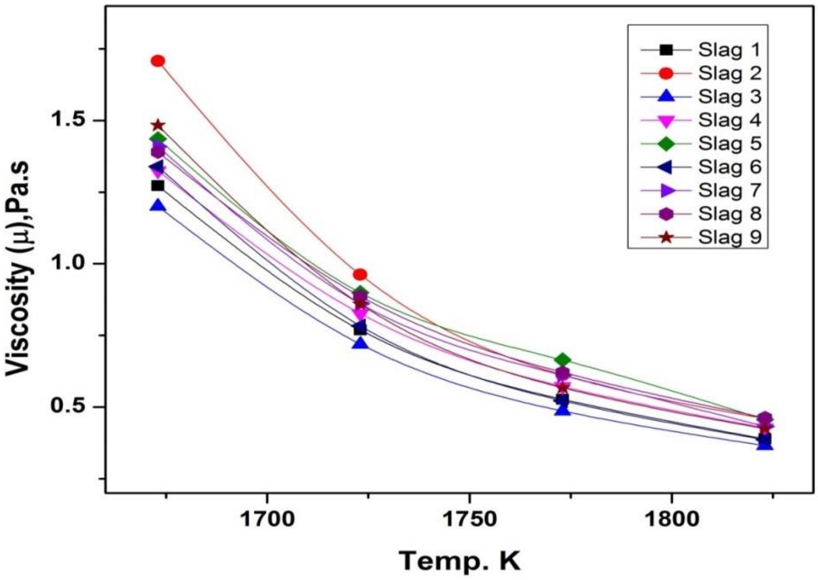


Fig.4.4.Effect of temperature on Viscosity

4.3. Activation Energy of Viscous Flow

Activation energy of viscous flow, E_{μ}, represents the energy barrier which must be exceeded to make the slag free-flowing. It depends on the composition of the slag which influences the structure of the slag and thus the extent of polymerisation/depolymerisation, reflecting on the energy requirements for rendering it free-flowing. The activation energy of the slags have been estimated from the slope of the plots between $\log \mu$ and 1/T on the basis of Arrhenius equation-

$$\mu = A\exp(\frac{E_\mu}{RT}) \tag{4.1}$$

$$\log \mu = \log A + \frac{E_\mu}{2.303RT} \tag{4.2}$$

Where,

μ is Viscosity (Pa.s), R is universal gas constant (8.314 J/mole-K), A is constant, E_μ is Activation energy and T is absolute Temperature.

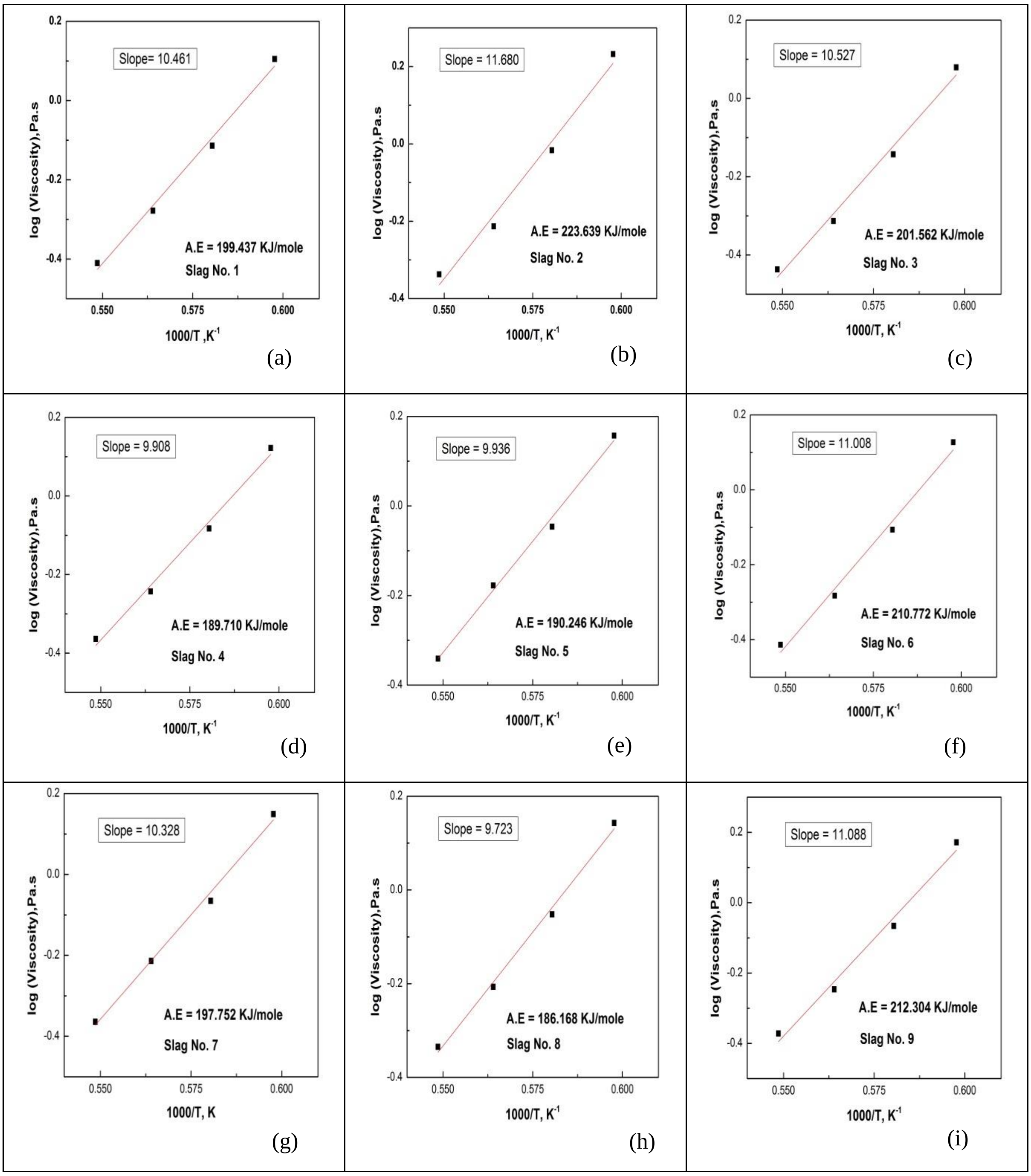
Now for the estimation of activation energy a graph is plotted between $\log \mu$ on Y-axis and 1/T on X-axis. The slope of this plot gives the value of $\frac{E_\mu}{2.303RT}$, from which we estimate the value of Activation energy.

The plots are presented in Fig.4.5.and the activation energy of viscous flow values are tabulated in the Table.4.5. Fig. no.4.6 through 4.8represent the variations of activation energy values of the slag compositions investigated with the variation of composition, C/S ratio, MgO wt % and TiO_2 wt %.

Table.4.5. Estimated values of Activation Energy of Viscous Flow of different slags

Slag No.	Activation Energy, $E\mu$, KJ/mole
1.	199.437
2.	223.639
3.	201.562
4.	189.710
5.	190.246
6.	210.772
7.	197.752
8.	186.168
9.	212.304

4.3.1. Log (Viscosity) vs Inverse Temperature (1/T) Plots



(a) (b) (c)

(d) (e) (f)

(g) (h) (i)

Fig.4.5. log (Viscosity) vs Inverse Temperature (1/T) plots

The plots presented in Fig.4.5 (a) through Fig.4.5 (i) established the fact that viscosity of slags obeys the relationship $\mu = A\exp(\frac{E_\mu}{RT})$ in general.

Further these plots show that viscosity decreases with an increase of temperature. The straight line relationship between $\log\mu$ and 1/T establishes a constant slope and hence constant E_μ

values, i.e., it shows that the activation energy of the slags investigated, does not change with temperature. From the above, it can be inferred that the decrease of viscosity with the increase 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_μ, 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.

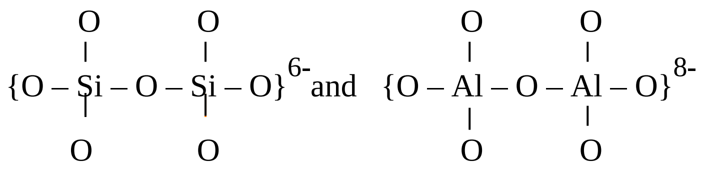
4.3.2. Effect of slag composition on Activation Energy of viscous flow

Fig.no.4.6 through Fig.no.4.8 presents the variation of E_μ with the variation of the composition of the slag.

As evident from Fig.4.6, the activation energy assumes the maximum value at all values of C/S ratio when the other two significant variables MgO and TiO_2 are at their higher levels. However even here the E_μ assume lower values at lower levels of C/S ratio.

From this it can be inferred that at higher level of all the significant variables C/S ratio, MgO wt% and TiO_2 wt% the melts contains higher percentages of polymeric ions and would require to exceed relatively higher levels of energy barriers to break the discrete silicate anions. This can be attributed to the availability of higher extents of oxygen in melt, rendering Al to adopt a four-fold co-ordination with oxygen. In such a situation Al substitutes silicon in the tetrahedral structure and contributes to the formation of higher percentage of polymeric ions.

Fig.4.6 also reveals that the E_μ values are lowest at the combined lower level of MgO wt% and TiO_2 wt%. Under these conditions, when sufficient metal oxides are not present in the melts and thus sufficient oxygen is not available, Al adopts a six-fold co-ordination with oxygen and the percentage of polymeric ions is reduced in the melt. Machine and Hanna **[42]** suggest that the polymeric ions as presented below are encouraged when CaO and /or MgO content increases in the melt. On the other hand the percentage of these polymeric ions decreases when the Al_2O_3 or SiO_2 increases.



$\{O - \underset{O}{\overset{O}{Si}} - O - \underset{O}{\overset{O}{Si}} - O\}^{6-}$ and $\{O - \underset{O}{\overset{O}{Al}} - O - \underset{O}{\overset{O}{Al}} - O\}^{8-}$

The above clarifies that when CaO wt%, MgO wt%, TiO_2 wt% decrease in the melt, i.e, when Al_2O_3 or SiO_2 content in the melt assumes relatively higher values, the polymeric ions are present in lower percentages and thus E_μ would assume lower values.

Similar conclusions can be arrived at on careful analysis of Fig.4.7 and Fig.4.8. When oxygen in the melts is high a four-fold co-ordination for Al with oxygen is encouraged, forming higher percentage of the polymeric ions whereas the reverse is true when oxygen is not sufficient the lesser extents of the cations present in the melt. When the percentages of polymeric ions will be decreased in the melt the E_μ assumes higher values in the former case and lesser values in the latter case. (F.g4.7, Fig.4.8)

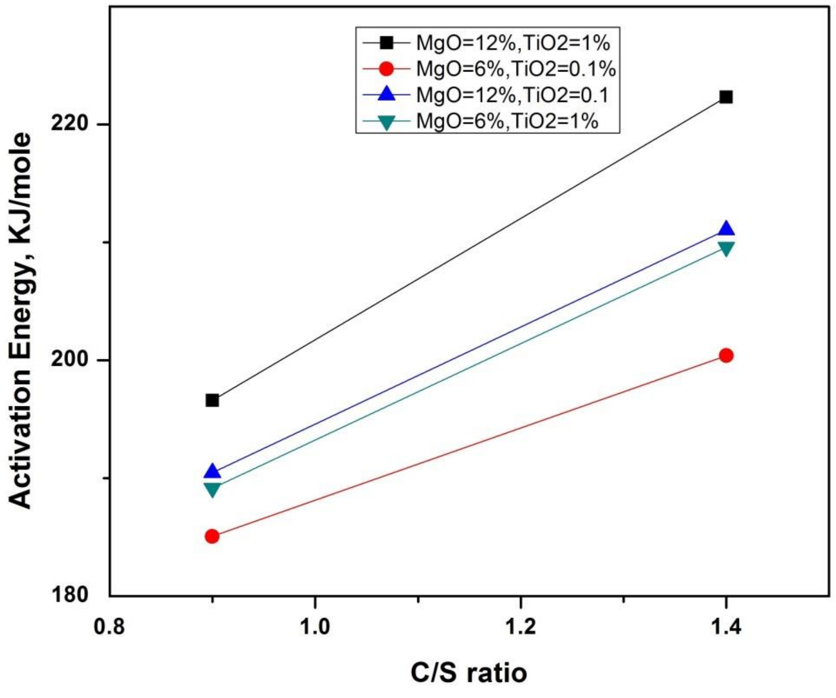


Fig.4.6. Effect of C/S ratio on Activation Energy

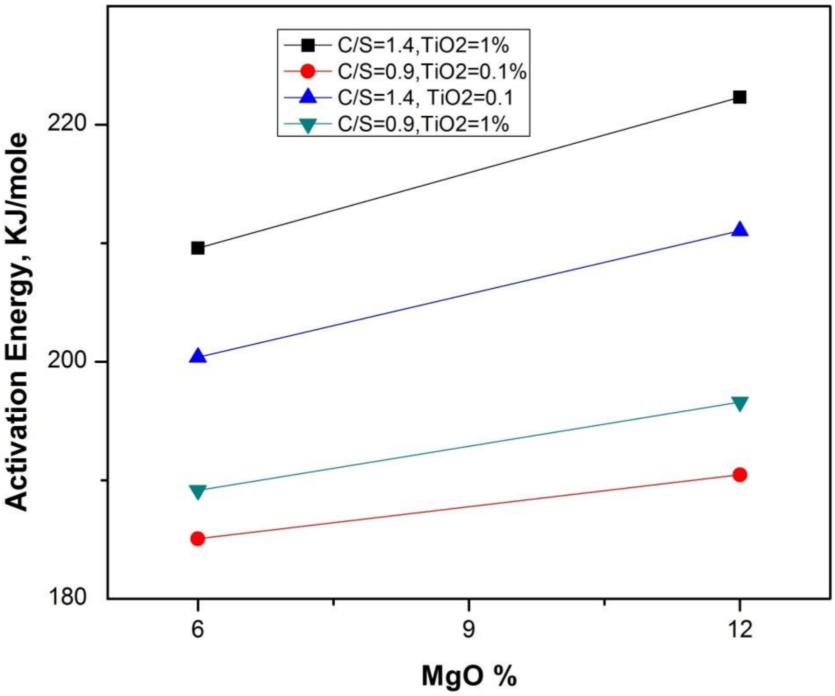


Fig.4.7. Effect of MgO on Activation Energy

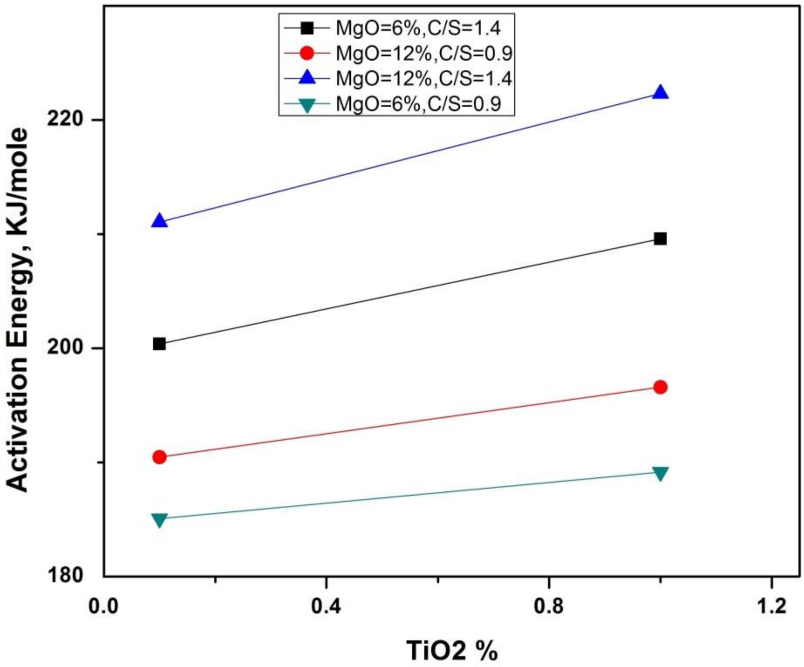


Fig.4.8. Effect of TiO_2 on Activation Energy

CHAPTER 5

CONCLUSION

5.1. Conclusion

- The Iida Model seems to be the most accurate one as it yields viscosity values of the slag most close to the measured viscosity values.
- It is established that being amphoteric in nature Alumina works both as a network former and a network breaker.
- With the presence of higher quantities of basic oxide, i.e., when higher amount of oxygen are available in melt aluminum adopts a four-fold co-ordinations and work as a network former.
- When the basic oxides are low in quantities, oxygen levels are not sufficient, Al assumes as six-fold co-ordination with oxygen and works as a network breaker.
- The Activation Energy of viscous flow does not change with temperature alone.
- For changing of Activation Energy, in addition to temperature compositional adjustments are a must.

5.2. Limitations

A further number of slags with greater extent of compositional variations may be examined to comment on the findings of this project work more emphatically.

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APPENDIX-I

Calculation details of viscosity using different Models

1. Calculation of viscosity using Iida Model (For slag no.1)

First we calculate the value of μ_{o_i} with the help of equation 2.29 and 2.30. The calculated values are tabulated in table.1 here. In this table the value of α_i is also presented.

Table.1. Calculated Values of μ_{o_i} of different oxides at different Temperature

		Value of μ_{o_i} at different temperature (mPa.s)			
Component	α_i	1673K	1723K	1773K	1823K
Al_2O_3	0.1	8.016041	7.139087	6.399756	5.771498
MnO	1.03	6.241512	5.645219	5.134892	4.695038
Na_2O	1.94	0.82723	0.785041	0.747206	0.713124
K_2O	1.37	0.531176	0.509664	0.490165	0.472422
Fe_2O_3	0.08	3.60259	3.299342	3.036643	2.807609
MgO	1.51	40.45228	34.37035	29.47242	25.4865
TiO_2	0.36	6.239331	5.62501	5.100908	4.650521
SiO_2	1.48	3.773945	3.423802	3.12325	2.863476
CaO	1.53	24.23027	20.84916	18.09256	15.82305

Table.2. Composition of slag no.1

Component	Wt %	Molecular Wt.	Mole Fraction(X_i)
Al_2O_3	20	102	0.120213
MnO	0.1	71	0.000863
Na_2O	1.0	62	0.009888
K_2O	0.5	94	0.003261
Fe_2O_3	1.0	160	0.003832
MgO	9.0	40	0.137944
TiO_2	0.55	80	0.004215
SiO_2	31.56	60	0.322483
CaO	36.29	56	0.397301

Now we calculate the value of μ_o with the help of equation 2.28. The calculated Values of μ_o at different temperature are given below.

Table.3. Calculated values of μ_o at different temperature

Temperature	1673	1723	1773	1823
μ_o (mPa.s)	17.443	15.038	13.077	11.463

Then we calculate the value of B_i with the help of equation 2.36 and the calculated value is 1.538.

Now with the help of equations 2.25 to 2.36 and the above calculated value we calculated the viscosity of the slag no.1 at different temperature. The calculated values are tabulated below.

Table.4. Calculated values of viscosity of slag no.1 at different Temperature

Temperature (K)	Viscosity (Pa.s)
1673	1.2725
1723	0.7688
1773	0.5271
1823	0.3890

Similarly we calculated the viscosity of all the slags using Iida model.

1. Calculation of viscosity using Ray's Model (For slag no.1)

Table.5. Values of Optical Basicity of different oxides

Component	Al_2O_3	MnO	Na_2O	K_2O	Fe_2O_3	MgO	TiO_2	SiO_2	CaO
Optical basicity ($\wedge$)	0.6	1.0	1.15	1.4	0.75	0.78	0.61	0.48	1.0

Now we calculated the value of $\wedge^{corr}$ with the help of equation 2.40. The calculated value of $\wedge^{corr}$ is 0.648. After that we calculated the value of B with the help of equation 2.43 and the calculated value is 18.601. Then we calculate the value of $\ln A$ with the help of equation 2.42, the calculated value is – 16.3162.

Now with the help of equation 2.41 and the above calculated value, viscosity is calculated at different temperature and the calculated value is tabulated below.

Temperature (K)	Viscosity (Pa.s)
1673	0.4309
1723	0.3325
1773	0.2605
1823	0.2207

Similarly we calculated the viscosity of rest of the slags.

2. Calculation of Viscosity using NPL Model (for slag no.1)

Calculation of viscosity using this model is similar to Ray's model, only the difference in equations.