

# VISCOSITY MEASUREMENTS OF SYNTHETIC HIGH ALUMINA BLAST FURNACE SLAGS IN THE LABORATORY

This thesis is submitted in the partial fulfillment of the requirement

for the degree of Bachelor of Technology in

**Metallurgical and Materials Engineering**

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**NATIONAL INSTITUTE OF TECHNOLOGY, ROURKELA**

**2014**

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## **CERTIFICATE**

This is to certify that the thesis entitled 'Measurement of Synthetic High Alumina Blast Furnace Slags in the laboratory' submitted by Prachi Pragnya (110MM0373) and Simanta Sarma (110MM0379) in partial fulfillment of the requirements for the award of Bachelor of Technology degree in Metallurgical and Materials Engineering at the National Institute of Technology, Rourkela, is an original work carried out by them under my supervision and guidance.

The matter embodied in the thesis has not been submitted to any other University/institute for the award of any degree or diploma.

Date: 7<sup>th</sup> May, 2014

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## **ACKNOWLEDGEMENT**

We would like to express our sincere gratitude to Prof. B. C. Ray, Head of the Department, Metallurgical and Materials Engineering, NIT Rourkela for giving us an opportunity to work on this project and provide the valuable resources of the department.

With great pleasure, we would like to express our deep sense of gratitude and indebtedness to our guide, Prof. U. K. Mohanty, Department of Metallurgical and Materials Engineering, NIT Rourkela, for his valuable guidance, constant encouragement and kind help throughout the project work and the execution of the dissertation work.

We would like to convey our thankfulness to Prof. S. K. Sahoo, Department of Metallurgical and Materials Engineering, NIT Rourkela, for his support and timely guidance during the project work.

We would also like to extend our sincere thanks to Mr. Uday Kumar Sahu, Department of Metallurgical and Materials Engineering, NIT Rourkela, for providing valuable insight and assistance during the experimental work.

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## **ABSTRACT**

Viscosity of synthetic high alumina blast furnace slags prepared in the laboratory in line with compositions of the slag encountered in the related industry is measured using inner cylinder rotation type viscometer.(Model: VIS403-HF)

The measured values are compared with values of viscosity calculated using IIDA model. The measured and the calculated values are in good agreement. The analysis of results show that increased C/S ratio and MgO contents of the slag decrease the viscosity while TiO<sub>2</sub> additions have a minimal effect on the viscosity measurements, under the compositional ranges examined.

Keywords: synthetic blast furnace slag, viscosity, IIDA model, C/S ratio

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# **CHAPTER-1**

## **INTRODUCTION**

## 1. Introduction:

The blast furnace iron-making process is one of the most dominant processes for the production of iron, for steel-making. The blast furnace is a furnace used to carry out smelting operations for metal production (here, iron). It works on a counter current principle where the ascending gases or the blast meet the descending burden and carry subsequent reduction of the iron oxides in the iron bearing materials while progressively heating it, owing to the prevailing temperature and pressure conditions. The result of production is liquid metal, slag and blast furnace gas of high calorific value. The blast furnace charge consists of iron bearing materials in the form of lump ores, pellets and sinters, flux in the form of limestone and dolomite, and coke. Coke plays a very important role in the blast furnace operations since it is the only substance that remains solid, to provide mechanical support to the overlying burden. It is also responsible for providing permeability for proper gas flow in the tuyere zone. The efficiency of the process depends on the permeability of the burden which is responsible for efficient gas flow and influences the heat transfer and the slag metal reactions in the furnace [1], [2]. The blast furnace comprises of zones like the granular zone, cohesive zone, active coke zone, hearth etc. of which the cohesive zone plays the most important role. It is the cohesive zone where the softening and melting of the iron bearing materials start under the influence of fluxing agents. This softening and melting, in turn, affects the permeability in the zone hampering gas flow. A high softening temperature and subsequent low flow temperature would lead to the thinning of the cohesive zone. This narrow cohesive zone would decrease the distance travelled by liquid in the furnace, thus, lowering Si pick-up. The final slag, which is formed lower down the bosh, should flow as soon as it softens.

The major constituents in the Indian blast furnace slag are CaO, MgO, Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, etc. which play an important role in controlling the characteristic properties of the slag [4]-[13]. It is however the Al<sub>2</sub>O<sub>3</sub> in the slag which is more important in the evaluation of the characteristic properties because of its amphoteric nature. In case of basic slag, increase in the SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> contents in the slag increase the viscosity as they act as network formers, where Al and Si occupy similar sites in the lattice [13]. However, in case of

acidic slag,  $\text{Al}_2\text{O}_3$  acts as a network breaker and decreases the viscosity of the slag.  $\text{CaO}$  and  $\text{MgO}$ , which are basic in nature, release  $\text{Ca}^{+2}$  and  $\text{Mg}^{+2}$  ions. These cations are randomly distributed in the silica network and they weaken the Si-O bond thus decreasing the overall viscosity of the slag [5], [6].  $\text{CaO}$  is a stronger base as compared to  $\text{MgO}$  and its presence makes the slag sufficiently basic to retain S. however, the presence of strongly basic  $\text{CaO}$  beyond a certain limit leads to increase in the chemical potential of some primary solid phases and thus leads to an increase in viscosity. Thus it is necessary to maintain an optimum basicity and this can be achieved by adding  $\text{MgO}$  or other less basic oxides. This would also assure that the depolymerization responsible for lowering viscosity is not affected.

Considering all the above factors, it is aimed at formulating a method to calculate the viscosity of the slag samples. The viscometer to be used for viscosity measurements in the laboratory is to be standardized using 40%  $\text{CaO}$ , 40%  $\text{SiO}_2$  and 20%  $\text{Al}_2\text{O}_3$  slag sample. It is also aimed to arrive at a theoretical method for the calculation of viscosity of the slag samples. Once the viscosity measurements have been made, both theoretically and in the laboratory, the obtained values are to be compared and the effects of different components on the viscosity are to be studied.

# **CHAPTER-2**

## **LITERATURE SURVEY**

## 2.Literature Survey:

### 2.1 Blast Furnace:

Because of its high production rate and very high extent of heat utilization, the blast furnace iron making process is the most used process of all iron making processes. The blast furnace works on a counter current principle and is very highly efficient. Production as high as 12000 tonnes hot metal per day has been reported for some high capacity furnaces [1]. The raw materials charged in the blast furnace basically comprises of iron ore, coke and flux. Along with the fore mentioned materials, hot blast is also purged from the tuyeres.

Iron ore is charged in the form of lump ores, pellets and sinters, which basically contain iron oxides such as hematite ( $\text{Fe}_2\text{O}_3$ ) and magnetite ( $\text{Fe}_3\text{O}_4$ ). Though hematite and magnetite theoretically contain 70% and 72.4% iron respectively, in actuality the iron ore content ranges from 50-65% for rich ores and 30-50% for lean ores. This lowering in percentage of iron is because of the association of the iron bearing materials with gangue in the form of silica, alumina, etc.

Flux is added as a raw material in the form of limestone and dolomite. The gangue materials possess very high melting point and are insoluble in the liquid iron. The flux added however helps by forming low melting compound with the gangue materials. This low melting mixture is called slag. The lime and magnesia added are basic in nature because the gangue materials silica and alumina (although amphoteric) act as acidic oxides. The ratio of basic oxides to acidic oxides is said to be the basicity [1]-[14]. Several reactions take place inside the blast furnace and lead to the formation of molten metal, slag and blast furnace gas of sufficiently high calorific value. Slag and molten metal can be separated only in the liquid form where they are tapped out at different positions owing to the differences in their relative density. To maintain the slag and liquid metal in the molten form, sufficient amount of heat is required. This brings coke into the picture. The function of coke is manifold. Not only does it provide the required amount of heat energy, coke also acts as a reducing agent for the reduction of iron oxides to iron. Coke is the only material that remains in the solid state throughout the process and provides mechanical support to the overlying burden. Coke also helps in lowering the

melting temperature of iron by 200-300°C depending upon the amount of coke carbon the iron picks. The solid coke grid provides permeability for the gases to ascend. Coke contains ash, which is the storehouse of impurities or gangue in the form of S, P, silica, alumina, etc. and their removal requires further addition of flux.

The heat energy that the coke provides is however a result of coke combustion and hence it makes air/oxygen an essential input. Air is blasted into the furnace in preheated condition so as to supply some sensible heat externally. The air is preheated in coke ovens which utilizes the blast furnace off gas. The top gas exiting the furnace contains some amount of CO whose chemical heat is used in the firing of the checkered bricks of coke oven. The heat, stored in the bricks, is then taken up by the air passing through the bricks. The preheated blast is introduced into the furnace through tuyeres located at the lower part of the furnace. The oxygen leads to the combustion of coke carbon just in front of the tuyeres, producing CO<sub>2</sub>. This results in immense heat energy, which raises the temperature in this region to 1800-2000°C. The CO<sub>2</sub> produced immediately converts to CO because of its instability in presence of C. This CO then ascends to carry out the reduction of iron oxide. The hot blast that enters through the tuyeres reaches the top after 6-8 seconds, undergoing several reactions. The blast furnace process is a continuous process and it takes about 8 hours for one tapping.

## **2.2 Blast furnace internal zones:**

In an ideal case, the temperature and composition of gas inside the furnace is supposed to vary along with the height, i.e. it can be assumed constant along a horizontal line.

However, in practice, there are significant variations in the horizontal direction as well.

The temperature isotherms or the gas composition are not along the horizontal. This can be attributed to two reasons:

- i) The hot air blast which is introduced through the tuyeres carries out localized combustion. The gases thus produced travel upwards and are unable to penetrate uniformly up to the furnace centre.



- ii) The burden charged from the top is heterogeneous. The densities as well as the size ranges vary which lead to non uniformity from the centre to the periphery.

All these lead to the formation of internal zones in the blast furnace. These zones play a very important role in influencing the performance of the furnace. The structure of each zone depends on the physical, chemical and physiochemical properties of the burden.

A blast furnace can be broadly divided into six zones [2]. These are:

- i) Granular zone
- ii) Cohesive zone
- iii) Active coke zone
- iv) Stagnant coke zone
- v) Tuyere zone
- vi) Hearth zone

Right at the upper part of the furnace is the granular zone. This zone contains the coke and the iron bearing materials charged with some amount of limestone and other fluxes. Towards the lower end of the granular zone, the iron bearing oxides get reduced to wustite and metallic iron. In this zone, it is basically the indirect reduction by carbon monoxide that plays a major role.

With the descent of the burden, the temperature rises and this leads to the softening and melting of the iron bearing materials. This region is called the cohesive zone. The cohesive zone plays a very important role in the blast furnace operations. The shape, size and extent of the cohesive zone affect the gas flow pattern. The burden loses its permeability in this region and gas flow occurs only through the coke grid. The cohesive zone consists of alternate layers of coke and impenetrable, viscous, semi fused mass of iron and slag. The cohesive zone should possess a low thickness as a thinner cohesive zone is expected to allow more gas passage and this can be achieved by a low temperature difference between the softening and melting temperatures. The cohesive zone should form lower down the furnace so as to get an extended granular zone and this can be achieved by a high softening temperature of the burden material.

Just below the cohesive zone lies the active coke zone. In this zone, direct reduction of iron bearing materials takes place. The stagnant coke zone is the only zone in the furnace which remains in the solid state. It is the only source of support to the overlying burden. This zone also enhances the flow of ascending gases as well as the descending iron bearing materials and slag. This zone also enhances the carbon pickup of the iron.

Barring the stagnant coke zone, the entire charge is molten by the time it reaches the tuyere zone. In this zone, the oxygen of the hot blast reacts with coke and causes its combustion. There are several tuyeres and each has its own combustion zone. The raceway in front of each tuyere is first horizontal. It then continuously expands over the entire cross section of the furnace and becomes vertical gradually.

By the time the metal and slag reach the hearth, they get separated into two layers. The hearth zone is basically responsible for the slag metal interface reactions. Both the slag and the metal tend to achieve equilibrium conditions. The hot metal and slag are then tapped out of the furnace.

Considering all the zones and the reactions occurring in those, along with the considerations of gas and burden flow, it can be said that the cohesive zone plays the important role. Productivity of the blast furnace, fuel consumption, hot metal quality, etc. depends on the extent and location of the cohesive zone.

### **2.2.1 The cohesive zone:**

It is the region where the solid mass starts getting converted to liquid form. Softening of the burden takes place in this region followed by melting. The extent and location of the cohesive zone directly affect the parameters such as gas permeability, extent of indirect reaction and silicon content in the pig iron.

**Gas permeability:** in the cohesive zone, the molten iron and slag flow downwards through the bed of coke. Thus, the cross section available for gas flow reduces, thereby increasing the resistance to gas flow and the pressure drop. It may so happen at times that the gas flowing at high velocity prevents the downward flow of liquid metal and slag called loading. A further increase in the gas velocity causes flooding, where the liquid

gets carried upwards. Lesser the thickness of the cohesive zone, better it is for gas permeability.

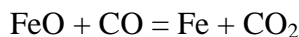
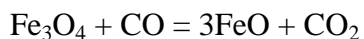
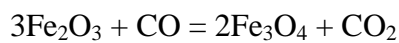
**Extent of Indirect reduction:** indirect reduction, or the reduction by carbon monoxide, takes place at the granular zone, located just above the cohesive zone. If the cohesive zone is formed lower down the furnace, it would lead to an extension in the granular zone thereby leading to an increase in the extent of indirect reduction. It leads to better utilization of carbon monoxide. The lowering of cohesive zone thus leads to a decrease in the coke consumption.

**Silicon content in hot metal:** Due to the favorable reducing conditions in the blast furnace, silica also gets reduced to Si and is incorporated in the hot metal. Silica first gets reduced to SiO and later to Si through a series of reactions in the bosh. Thus, if the cohesive zone is lowered down, the chances of Si pick up also lowers.

## 2.3 Reactions in the blast furnace

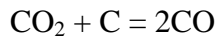
The iron oxide that gets reduced to pig iron in the blast furnace undergoes reduction in stages. The three forms of oxide hematite, magnetite and wustite are formed in the order.

**The reactions taking place with CO are [1]:**

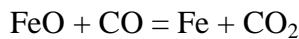


The tuyere gas, which has very high carbon monoxide content, first comes in contact with wustite. Wustite, which is subsequently converted to Fe, requires a very high reduction potential for conversion. The resulting gas is a low potential gas. As it ascends, it reduces magnetite and hematite to lower oxides, as they require smaller reduction potentials. The reduction of wustite, thus, is of prime importance. Better utilization of the thermal and chemical energies of carbon will take place if the extent of indirect reduction increases.

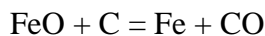
Wustite, if remains unreduced at a temperature higher than 1000°C, then the following reactions cause the reduction:



i.e. carbon dioxide, which is unstable above 1000°C in the presence of carbon, gets converted to carbon monoxide. This reaction is called the carbon gasification or the Boudouard reaction. The CO then reduces the wustite as per the reaction:



**The overall reaction can be written as:**

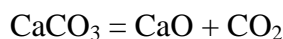


This reaction is termed as the direct reduction of iron oxide. Though this reaction is endothermic compared to indirect reduction of carbon, it consumes less carbon per mole of oxygen removed. The heat requirements in the blast furnace are supplied by the ascending gases and the blast furnace can be divided into 3 distinct temperature zones: lower zone, middle zone and upper zone.

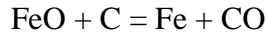
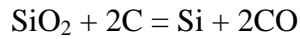
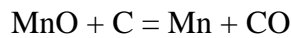
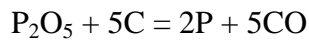
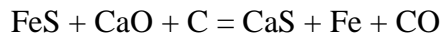
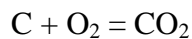
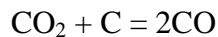
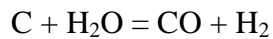
### **2.3.1 Reactions in the lower zone:**

This zone extends up to 3-5 meters from the tuyere level. The temperature of the gases comes down to 800-1000°C whereas that of the molten materials reaches 1400-1450°C. burning of coke near the tuyeres creates empty space continuously which allows the charge materials to flow downwards. The gangue and the flux start fusing in the belly region. Two immiscible phases, primary slag and primarily carburized iron, are formed at temperatures above 1200°C. the primary slag, formed earlier, picks up lime and forms the bosh slag. The bosh slag transforms to the hearth slag once the coke ash at the tuyeres is released. The reactions taking place at the lower zone are: [1]

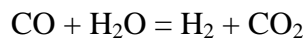
**Endothermic calcinations of limestone:**



**Endothermic direct reduction of FeO:**

**Endothermic direct reduction of SiO<sub>2</sub>:****Endothermic direct reduction of MnO:****Endothermic direct reduction of P<sub>2</sub>O<sub>5</sub>:****Endothermic sulphur removal:****Exothermic combustion of carbon:****Endothermic reduction of CO<sub>2</sub>:****Endothermic reduction of moisture:****2.3.2 Reactions in the Middle zone:**

The thermal reserve zone is the zone where the temperatures of the gases and the solids are near identical, 800-1000°C. It is also called the indirect reduction zone because most of the indirect reduction occurs here. The extent of this zone is important as higher the extent more is the chance of indirect reduction. A very important reaction in this zone is the water gas shift reaction. Hydrogen generated in this reaction is a more active reductant than CO.



### 2.3.3 Reactions in the upper zone:

This zone is referred to as the preheating zone. The ascending gases attain a temperature of 100-250°C and the burden 800°C. The main reactions in this zone are:

Decomposition of carbonates other than calcium carbonate

Vaporization of moisture of the burden

Carbon deposition  $2\text{CO} = \text{C} + \text{CO}_2$

Partial or complete reduction of hematite and magnetite to their lower oxides

### 2.4 Blast Furnace Slag:

Oxygen being abundantly present in the atmosphere and the oxide state being relatively more stable, metals are generally present in the oxide forms. Slag is a low melting product formed by the eutectic reaction between the gangue particles present in the iron bearing materials and coke with the flux added in the form of limestone, dolomite, etc. The basic impurities in the iron ore and coke ash are acidic silica and alumina. Since the impurities silica and alumina are acidic in nature, the flux added should have basic characteristics so as to bring down the melting point of the impurities, thus making it lighter and easier to remove. The major constituents of blast furnace slag are the acidic oxides  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  and the basic oxides  $\text{CaO}$  and  $\text{MgO}$ . Some minor constituents are also formed apart from the fore mentioned oxides. These include  $\text{FeO}$ ,  $\text{MnO}$ ,  $\text{FeS}$ ,  $\text{CaS}$ ,  $\text{TiO}_2$ ,  $\text{Na}_2\text{O}$ ,  $\text{K}_2\text{O}$ , etc. The functions of blast furnace slag are manifold and those can be achieved only with a slag of desired composition so that it has low viscosity, can control metal quality and metal temperature, has a high sulphur retention potential, etc.

The viscosity and the fusion characteristics of the slag are the major parameters that define the efficiency of the blast furnace. At a certain operating temperature a low viscosity slag is always desirable which would reduce the coke rate and enable more economic fuel usage. The slag should be able to absorb all unreduced non volatile components of the burden, retain the sulphur and unleash the iron oxide to the liquid metal. The slag should be of low volume and viscosity maintaining temperature stability

at times of physical and chemical alterations of the burden. The slag also regulates the furnace gases and the stock movement for a smooth operation. In an overall sense it maintains metal quality and its homogeneity. Finally, the slag should be converted to salable material such as use in cement manufacture road ballast etc.

The basicity of the slag is also an important criteria which is basically determined by the ratio of  $\text{CaO}/\text{SiO}_2$  or  $(\text{CaO} + \text{MgO})/\text{SiO}_2$ , which is required to be maintained between 1.2 and 1.4 for smooth functioning of the blast furnace.

The slag formation in the blast furnace occurs in a sequence and is divided into three zones:

- i) Primary slag zone
- ii) Bosh slag zone
- iii) Final or hearth slag zone

The silica and alumina in the blast furnace comes from the ore and coke ash whereas lime and magnesia from the fluxes. The mutual interaction of these components is very slow in the solid state. At higher temperatures, sintering of alumina and silica occurs, and this forms a much more stable alumino silicate. Also, sufficient lime is not picked up unless it is in the liquid form. At lower temperatures, lime dissolution depends on solid state diffusion and this leads to a very slow rate. Thus fluxing of alumino-silicate by iron oxides leads to the formation of the first slag. This easily fusible eutectic thus formed is called the primary slag. Formation of this slag takes place above the bosh region. This slag has a high FeO content due to the partial reduction of oxides by then. With the descent of the slag, however, the FeO content decreases and lime pickup starts. Reduction of FeO and subsequent lime pickup increases the basicity of the slag. The lime pickup basically occurs in the hot zones, i.e. down the furnace, by the tuyeres. The bosh slag has a higher basicity than the final slag because the acidic silica from the coke ash is incorporated only after the tuyere level. The bosh slag must possess a high fluidity as it would then ensure free movement of gases through the coke grid. The slag should also have a high basicity. The final or the hearth slag is formed when the lime that was not already incorporated by the tuyere level dissolute into the slag and coke ash released after combustion is absorbed by the slag. It runs down with the molten metal and a pool is

formed in the hearth with metal underneath. As iron droplets progress through the slag, slag metal reactions occur and transfer of Si, Mn, S, etc occur to and from the metal. The slag composition, nature and the slag volume is very important in determining the hot metal quality, composition and production. All these factors combine to determine the blast furnace efficiency. It must be aimed to achieve an optimum slag composition so that S content in hot metal is minimal and we get a lower slag volume.

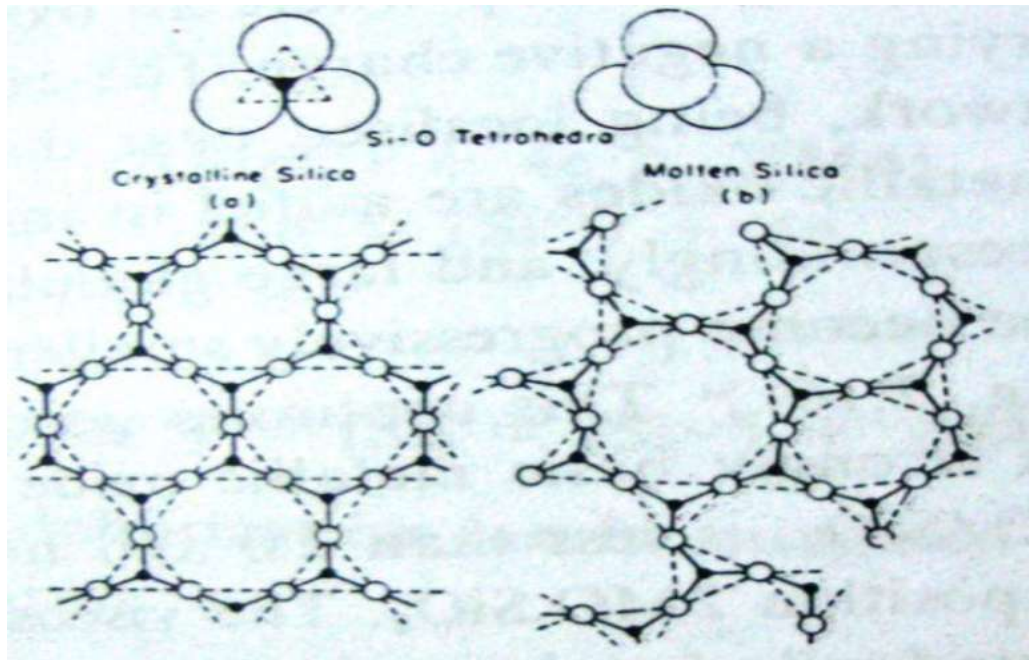
## 2.5 Blast Furnace Slag Structure:

Crystal analysis of solid silica shows that silica occupies the centre of the tetrahedron surrounded by four oxygen atoms. Each oxygen atom is bonded to two silica atoms and the network is continuous in three dimensions. In the crystalline state the tetrahedral shape remains intact. In molten silica the structure becomes distorted, but most of the corners remain shared. Studies indicate that addition of CaO or MgO or other metal oxides to molten silica results in the breakdown of the three dimensional silica-oxygen network and formation of silicate ions. The driving force for the breakdown process is attraction between silicon and oxygen.

Two silicon oxygen bonds are opened up when lime or magnesia is added to molten silica. As we go on increasing the amount of metallic oxides, the SiO bonds go on breaking and form large globular silicate ions, which decrease in size with further addition of metal oxides. A stage will finally be reached when there will be no more shared corners. After this, any more addition of metal oxides would lead to formation of oxygen anions and equivalent cations.

As the strong silicate networks break, the viscosity of the melt decreases drastically as viscosity of a material depends not only on its composition but also on its structure. The more relaxed the structure is the less is the viscosity [1].





## 2.6 Blast Furnace Slag viscosity:

Slag viscosity is a transport property that correlates the reaction kinetics and the degree of reduction of the final slag. The slag viscosity controls the aerodynamics and the heat of the blast furnace.

The presence of a range of applicable shear stresses on the blast furnace slag makes it behave as a Newtonian fluid. It is the ionic and molecular structure that regulates the viscosity of the blast furnace slag. Various important phenomena such as the heat transfer, mass transfer and the chemical reactions depend on the flow phenomena of the slag and hence on its viscosity [15]. The free flow nature of the slag at operating temperatures controls the comprehensive slag-metal separation. From the point of view of the available heat in the hearth the blast furnace slag should be neither too viscous nor too fluid. The extent of ion diffusion between the slag and the metal is dependent on the viscosity of the slag which influences the rates of the reaction. A depolymerisation process lowers the viscosity of the slag. As due to this process the increase in basicity results in the breaking down of the 3-dimensional silicate network into discrete anionic groups leading to the decrease in the viscosity of the slag. However, the blast furnace slag viscosity cannot be explained only by the enhanced degree of depolymerisation. Beyond

certain basicity level the chemical potential of certain solid phases increases which leads to an increase in the viscosity of the slag. The ease of slag removal depends on its viscosity and the energy requirement and ultimately affects the profitability of the process.

## 2.7 Liquidus temperature:

The liquidus temperature can be defined as the temperature at which the heated slag takes up a hemispherical shape, according to the German Industrial Standards 51730. This temperature can also be nominated as the temperature at which the first crystal is formed when the melt is cooled down as indicated by Osborn [16] and Snow [17]. While Ohno *et al* [18] indicated that all the crystal structures disappear when the slag is heated to the temperature of Liquidus temperature. It directly influences the effective width and positioning of the cohesive zone, thus directly influencing productivity.

## 2.8 Effect of Slag basicity on Viscosity:

Y.S. Lee *et al* [19] examined and noted the viscous behaviour of CaO-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>-MgO-FeO slag under controlled conditions of C/S = 1.15-1.6, 10-13mass% Al<sub>2</sub>O<sub>3</sub>, 5-10mass% MgO and 0-20% FeO. The inferences drawn are that there is depolymerization of silicate network and hence increase of viscosity of the slag above the C/S ratio of 1.3 and less than the ratio of 1.5. Till the ratio of 1.3 viscosity decreases due to the increasing chemical potential of the dicalcium silicate which is a primary solid phase. The thermodynamic approach for finding the activity of primary solid components provides a good correlation between the viscosity and the slag components. So it was confirmed that slag viscosity in highly basic slags (C/S>1.3) can be approximated by the chemical potential of dicalcium silicate.

The study also deduced that for a low value of FeO content (< 7.5%) the slag viscosity showed minimum value with increasing MnO content, but with FeO content (> 7.5%) with increasing MnO content no particular effect on the slag viscosity is observed. The study also concluded that the BF slag viscosity decreases with increasing FeO content for a fixed CaO/ SiO<sub>2</sub> ratio. The variation in the slag basicity as well as the Si content in the

metal can be minimized by less reduction of  $\text{SiO}_2$  into Si. This can be achieved by injection of flux in the blast furnace according to some tests conducted by some Japanese companies.

**Y.S.Lee, J.R.Kim, S.H.Yi and D.J.Min:** “Viscous behavior of  $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3\text{-MgO-FeO}$  slag”. Proceedings of VIII international conference on molten slag, fluxes and salts, The South African Institute of Mining and Metallurgy, 2004, p.225.[20]

Their studies showed that the heat transfer, mass transfer,  $\text{SiO}_2$  and FeO reduction and gas permeability is controlled by the flow characteristics of the slag. This implied the effect of the viscous nature of slag on the efficiency and productivity of the blast furnace. The viscous behavior of  $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3\text{-MgO-FeO}$  slags was studied under the conditions of  $\text{CaO/SiO}_2 = 1.15\text{-}1.6$ , 10-13 %  $\text{Al}_2\text{O}_3$ , 5-20% MgO, 5-20% FeO.

Up to the  $\text{CaO/SiO}_2$  ratio of 1.3, slag viscosity decreased with increasing slag basicity. The FeO content in slag if increases the viscosity of the slag decreases so when the FeO decreases from 10-15% so the viscosity of slag at basicity of  $\text{CaO/SiO}_2 = 1.5$  increases from about 2.5 to 10 dPa.s with increase in FeO content as mentioned above.

**Amitabh Shankar et al [9]** for the  $\text{CaO-SiO}_2\text{-MgO-Al}_2\text{O}_3$  and  $\text{CaO-SiO}_2\text{-MgO-Al}_2\text{O}_3\text{-TiO}_2$  system by varying the C/S ratio between 0.72 and 1.23 in the temperature range of 1573-1873 K. Alumina content ( 21-28%), Magnesia( 2-8%) and Titania (0-2%). They have shown that viscosity decreases with increase in basicity. It was also shown that the slope of the Viscosity vs. Temperature curve is steeper for low basicity slags. An increase in basicity decreases the slag viscosity, because silicate structure changes from network to discrete anionic groups containing simple chains or rings as basic oxides are increased.

**J.-Y. JIA, C.-G. BAI, G.-B. QIU, D.-F. CHEN and Y. XU [21]** based on the studies of the ternary slag system of  $\text{CaO-SiO}_2\text{-TiO}_2$ , it established a calculation model. Thus, they were able to outline a mass action concentration calculation model and viscosity calculation model based upon the existing theories and documented data at different temperatures of the ternary slag system at different compositions.

With increasing  $\text{TiO}_2$  content the mass action concentration also increases. Viscosity of slag decreases with increasing  $\text{TiO}_2$  content in the slag. With the rise in temperature viscosity decreases and running quality is improved.

### 2.8.1 Effect of $\text{MgO}$ and $\text{Al}_2\text{O}_3$ content on viscosity of the slag:

**Seong-Ho Seok et al [22]** the viscous behavior of  $\text{CaO-SiO}_2\text{-FeO-MgO}$  and  $\text{CaO-SiO}_2\text{-FeO-Al}_2\text{O}_3\text{-MgO}$  melts were studied which were saturated with dicalcium silicate with a  $\text{MgO}$  content of 8% under conditions of high basicity and temperature of around 1873K. The inferences drawn is that the viscosities of slag depend relatively more on the alumina content as the solid phases present is more in case of alteration in alumina content than that of  $\text{MgO}$ .

**Y.S. Lee et al[23]** studied the influence of  $\text{MgO}$  and  $\text{Al}_2\text{O}_3$  alteration on the viscosities of BF slag. The viscous behavior of  $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3\text{-MgO-FeO}$  slag was studied and the viscosity under conditions of C/S ratio 1.35-1.45, 10-18% Alumina, 3.5-10%  $\text{MgO}$  and 5%  $\text{FeO}$  was measured. For a fixed  $\text{MgO}$  content and basicity, the viscosity increases with increase in the Alumina content. The slag also showed a minimum value of viscosity at around 7% of  $\text{MgO}$  at over the temperature of 1723K. The  $\text{MgO}$  content variation did not significantly change the slag viscosity.

**Yasuji Kawai [24]** studied on the viscosities of molten slags and on the viscosities of  $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3\text{-MgO}$  slags. When  $\text{MgO}$  was added to  $\text{CaO-SiO}_2$  slags, the viscosities decreased with increasing amount of  $\text{MgO}$  only up to about 20%, beyond which, however, it increased. The region of low viscosity was greater than that in  $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3$  slag.

**Noritaka Saito et al [25]** studied the effect of  $\text{MgO}$  on the viscosity of 40  $\text{CaO}$ -40  $\text{SiO}_2$ -20 $\text{Al}_2\text{O}_3$  slags. Through their studies they proposed that magnesia acts as a network modifier and also that the activation energy for viscous flow also decreases with  $\text{MgO}$ .

**Masashi Nakamoto et al [26]** to measure the viscous behavior of molten CaO- SiO<sub>2</sub>-MgO-Al<sub>2</sub>O<sub>3</sub> they used the rotating cylinder method and compared the result with its model that was created. Their purpose of study was to obtain a specific composition of slags that would melt at low temperatures (1673K) to improve the blast furnace. **J. Muller et al [27]** calculated the effective viscosities for typical blast furnace slags with different basicity at 1500°C with different FeO and Al<sub>2</sub>O<sub>3</sub> contents. They noticed that slag viscosity goes on decreasing with increase in slag basicity. An increase in slag basicity or an increase in CaO and MgO content which act as silicate bond breakers, thus accounts for the decrease in viscosity. **Kohei Sunahara et al [28]** studied the effect of high Al<sub>2</sub>O<sub>3</sub> slag on the blast furnace operations. They found that the slag drainage phenomenon in the furnace hearth is a fluidization phenomenon dominated by viscosity. The slag drainage rate decreases as the slag viscosity increases. To maintain slag drainage under high Al<sub>2</sub>O<sub>3</sub>, for example, an increase of the MgO concentration in the slag is effective. Also, in this experiment range, the effects of the slag crystallization temperature on the slag drainage rate are relatively small in comparison to the effects of viscosity. **Amitabh Shankar et al [9]** studied the effect of TiO<sub>2</sub> on the viscosity of blast furnace slags in the temperature range of 1573-1873 K. TiO<sub>2</sub> decreases the slag viscosity marginally for low basicity slag (~0.5). But for high basicity slags (~0.8), slag viscosity decreases even with 2% addition of TiO<sub>2</sub>. The slag viscosity increases with increase in silica activity of the slags. The increase in basicity is more pronounced below the liquidus temperature due to presence of solid particles. The correlation between the silica activity and activation energy is relatively better for TiO<sub>2</sub> containing slags. With increase in silica activity, the Arrhenius activation energy for viscous flow increases.

## 2.9 Slag viscosity measurements:

Slags perform the act of refining metal, removing detrimental oxides and sulfides, protecting the metal from oxidizing atmosphere along with providing thermal insulation. For the slag to perform the above functions satisfactorily, it would require particular properties of the slag, and thus some particular composition. Viscosity, one of the important physical properties, has a direct effect on the kinetic conditions of the process.

While slag of low viscosity enhances heat and mass transport and the separation of metal and slag on one hand, it affects the refractory lining tremendously. [29] [30]

It is generally very difficult to precisely measure the slag viscosity through empirical methods and practical methods are expensive. Extensive studies have been made on the viscosities of multi component oxide systems and have led to the development of several models.

### 2.9.1 Definition:

When a layer of fluid moves over another, an opposing friction force acts on the layers. The measure of the internal friction of fluid is termed as viscosity. Higher the frictional forces between the layers, more will be the force required to move them. The S. I. unit of dynamic viscosity is Pa.s. A non S. I. unit generally used is poise. 1 poise is equal to 0.1 Pa.s. Many scenarios require the use of a quantity called kinematic viscosity, which is the dynamic viscosity divided by the density.

### 2.9.2 Temperature dependence of viscosity:

The viscosity of molten slag is very sensitive to temperature and composition changes. The Arrhenius relationship gives the temperature dependence of viscosity.

$$\eta = A e^{(E_a/RT)}$$

$\eta$  is the viscosity, A is the pre exponential factor, T is the absolute temperature,  $E_a$  is the activation energy and R is the universal gas constant.

Increasing the temperature loosens up the structure leading to a decrease in viscosity. It is generally seen that viscosity is proportional exponentially to the inverse temperature.

### 2.9.3 Effect of slag composition on viscosity:

Silica slags contain  $\text{Si}^{+4}$  ions which are surrounded by four oxygen anions in a regular tetrahedron. These tetrahedrons are joined together by oxygen bridges. These polymeric anions lead to a high viscosity in silicate melts. However, it is known that the entry of oxide ions from metal oxides results in breaking of the Si-O bonds progressively and this

leads to a decrease in the network size. All these are accompanied by a decrease in viscosity of the molten slags.

Alumina plays a role similar to that of silica in a CaO-MgO-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> system. Alumina is present as AlO<sub>4</sub><sup>5-</sup> and forms polymer units with SiO<sub>4</sub><sup>4-</sup>. Thus the effect of alumina is the same as that of silica, i.e. both act as network formers and increase the viscosity. On the other hand, oxygen suppliers such as CaO and MgO, which are network breakers, lead to a decrease in the slag viscosity.

### 2.9.4 Viscometer:

A **viscometer** is an instrument employed to measure the viscosity of a fluid. Viscosity is the measure of fluid friction which can be considered as the internal friction effecting when a layer of fluid is made to move relatively to another layer. Viscosity is a measure of the ratio of shearing stress to rate of shear. Viscometers measure only under unidirectional flow condition. Generally, either of the fluid or the object remains stationary and the other moves through it. The drag produced by the relative motion of the fluid and the surface is a measure of the viscosity.

$$\text{Shear Stress (dynes)/ Rate of Shear (cm/sec) = Poise}$$

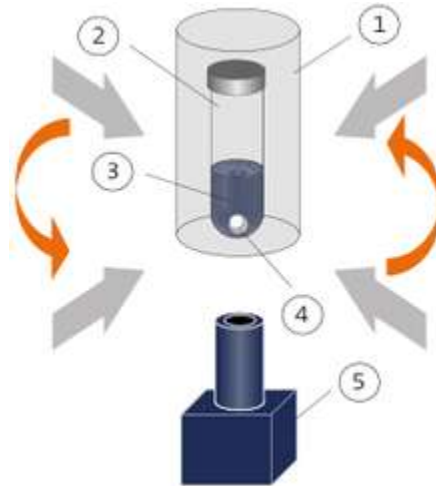
At 20.00 degrees Celsius the viscosity of water is 1.002 mPa·s and its kinematic viscosity (ratio of viscosity to density) is 1.0038 mm<sup>2</sup>/s. These values are used for calibrating certain types of viscometer

### Rotational viscometers:

Rotational viscometers exploit the concept that the torque required to turn an object in a fluid is a function of the viscosity of that fluid. Generally viscometers measure the torque required to rotate a disk or bob in a fluid at a known speed. 'Cup and bob' viscometers work by outlining the exact volume of a sample which is to be sheared within a test cell; the torque required to achieve a certain required rotational speed is computed and

graphed. There are two classical geometries in "cup and bob" viscometers, known as either the "Couette" or "Searle" systems, differentiated by whether the cup or the bob rotates. 'Cone and Plate' viscometers utilize a cone of very shallow angle in bare contact with a flat plate. A plot of shear stress (torque) against shear rate (angular velocity) yields the viscosity in a straightforward manner.

### Electromagnetically Spinning Sphere Viscometer (EMS Viscometer)



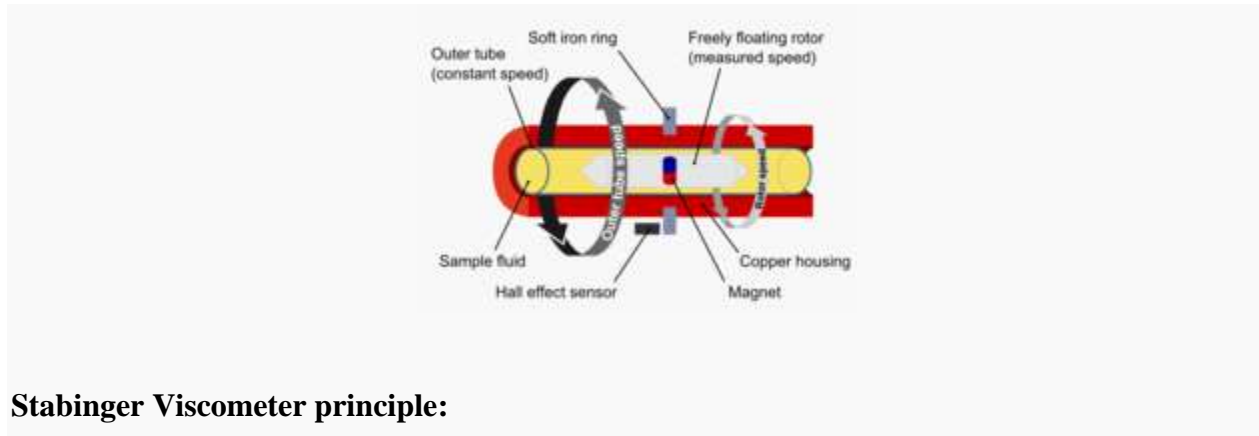
#### Measuring Principle of the Electromagnetically Spinning Sphere Viscometer:

The EMS Viscometer computes the viscosity of liquids through detection of the rotation of a sphere which is driven by electromagnetic interaction: A magnetic field is created between two magnets attached to a rotor. The sample to be measured is kept in a small test tube, inside which is an aluminium sphere. The tube is placed in a temperature controlled chamber and rested such that the sphere is situated right at the centre of the two magnets. The rotating magnetic field induces eddy currents in the sphere. The resulting Lorentz interaction between the magnetic field and these eddy currents produces torque that rotates the sphere. The rotational speed of the sphere depends on the rotational velocity of the magnetic field, the magnitude of the magnetic field and the viscosity of the sample around the sphere. The sphere motion is monitored by a video camera. The EMS viscometer is different as it requires very small sample quantities, sealed sample



vessel is required for measurements and all the parts of the viscometer are disposable and inexpensive

### Stabinger viscometer



#### Stabinger Viscometer principle:

It is the modification of the classic Couette type rotational viscometer, where combination of accuracy of kinematic viscosity determination with a wide measuring range is achieved. The outer cylinder is a tube that rotates at constant speed in a temperature-controlled copper housing. Due to centrifugal forces the hollow, light internal cylinder shaped as a conical rotor floats freely within them. The rotor is driven by the rotating fluid's shear forces, while a magnet inside the rotor forms an eddy current brake with the surrounding copper housing. An equilibrium rotor speed is achieved between driving and retarding forces, which is an unambiguous measure of the dynamic viscosity.

$$\nu = \frac{\eta}{\rho}$$

where:

$\nu$  is the kinematic viscosity ( $\text{mm}^2/\text{s}$ )

- $\eta$  is the dynamic viscosity ( $\text{mPa}\cdot\text{s}$ )
- $\rho$  is the density ( $\text{g}/\text{cm}^3$ )

#### Basic Procedure:

1. Preheat spindle, sample chamber, and viscometer environmental chamber to  $135^\circ\text{C}$  or  $408\text{K}$ .

2. Heat the standard slag sample (40%CaO-40%SiO<sub>2</sub>-20%Al<sub>2</sub>O<sub>3</sub>) so as to make a fluid enough to pour. Stir the sample, being careful not to entrap air bubbles.
3. Pour appropriate amount of slag into sample chamber. The sample size varies according to the selected spindle and equipment manufacturer.
4. Insert sample chamber into RV temperature controller unit and carefully lower spindle into sample.
5. Bring sample to the desired test temperature (typically 408 K (135°C)) within approximately 30 minutes and allow it to equilibrate at test temperature for 10 minutes.
6. Rotate spindle at 100 RPM, making sure the percent torque as indicated by the RV readout remains between 2 and 98 percent.
7. Once the sample has reached temperature and equilibrated, viscosity readings are taken for different temperatures. Several readings are taken at a particular temperature and the average of those is considered the viscosity at any particular temperature.

### 2.9.5 Viscosity models:

Due to the large number of variables involved, the measurement of viscosity of industrial slag is a complicated task.[31] This difficulty and the corresponding high cost involved have led to the development of several viscosity models. A number of models are available in literature for measurement of viscosity: Urbain model, NPL model, Iida model, Riboud model, Ray and Pal model, etc. out of which the Iida model was chosen for the current study.

#### IIDA model:

Molten slags have a random structure in general, and viscosity is a structure sensitive property. Iida's viscosity model is based on Arrhenius type of equation where the basicity index ( $B_i$ ) is used to take the network structure into account.

$$\eta = A \cdot \eta_0 \cdot \exp(E/B_i^*)$$

where E and A are functions of temperature,  $B_i^*$  is a function of chemical composition and  $\eta_o$  is function of composition, molar volume and melting point.

$$A = 1.745 - 1.962 \cdot 10^{-3} T + 7.00 \cdot 10^{-7} T^2$$

$$E = 11.11 - 3.65 \cdot 10^{-3} T$$

The value of  $\eta_o$  can be calculated from the mole fractions and a quantity called  $\eta_{oi}$  where value of  $\eta_{oi}$  can be calculated from the formula

$$\eta_{oi} = 1.8 \cdot 10^{-7} \cdot [(M_i \cdot (T_m)_i)^{0.5} \exp(H_i/RT)] / [(V)^{2/3} \exp(H_i/RT_m)]$$

where M is the molecular weight of the components, V is the molar volume,  $T_m$  is the melting point and R is the universal gas constant.

and

$$H_i = 5.1 \cdot (T_m)^{1/2}$$

The value of  $\eta_o$  can then be calculated as

$$\eta_o = \sum \eta_{oi} \cdot X_i$$

$B_i^*$  can be calculated readily using the equation

$$B_i^* = [\sum (\alpha_i W_i)_B + \alpha^*_{Fe_2O_3} W_{Fe_2O_3}] / [\sum (\alpha_i W_i)_A + \alpha^*_{Al_2O_3} W_{Al_2O_3} + \alpha^*_{TiO_2} W_{TiO_2}]$$

Where W and  $\alpha$  is the mass percentage and specific coefficient. The values of  $\alpha$  are as given in the table:

Component		$\alpha_i$
Acidic Oxide	SiO <sub>2</sub>	1.48
	B <sub>2</sub> O <sub>3</sub>	1.12
	P <sub>2</sub> O <sub>5</sub>	1.23
Amphoteric Oxide	Al <sub>2</sub> O <sub>3</sub>	0.10
	Fe <sub>2</sub> O <sub>3</sub>	0.08
	TiO <sub>2</sub>	0.36
Basic Oxide	CaO	1.53
	MgO	1.51
	K <sub>2</sub> O	1.37
	Na <sub>2</sub> O	1.94
	Li <sub>2</sub> O	3.55
	MnO	1.03
	FeO	0.96
	Cr <sub>2</sub> O <sub>3</sub>	0.13
CaF <sub>2</sub>	1.53	

**Table No 1:  $\alpha$  values for different components (IIDA model)**

For the oxides amphoteric in nature, the values of  $\alpha$  become modified to  $\alpha^*$  which is given by the relation:

$$\alpha_i^* = a \cdot B_i + b \cdot W_i + c$$

where a, b and c are temperature dependent quantities and  $B_i$  and  $W_i$  are basicity index and weight percentage respectively. [32] [33]

$$a = 1.2 \cdot 10^{-5} \cdot T^2 - 4.3552 \cdot 10^{-2} \cdot T + 41.16$$

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

$$c = -8 \cdot 10^{-6} \cdot T^2 + 2.5568 \cdot 10^{-2} \cdot T - 22.16$$

Calculating all the values and putting them in the equation, we can easily attain the theoretical viscosity for a slag system.

# **CHAPTER-3**

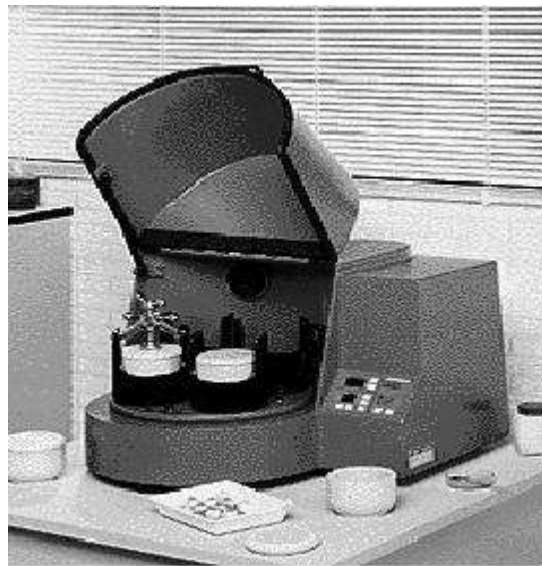
## **EXPERIMENTAL DETAILS**

### 3. Experimental details:

#### 3.1 Experimental apparatus:

##### 3.1.1 Planetary ball mill:

The planetary ball mill also known as centrifugal mill is used to grind or mix the sample. It is used to grind quenched hard samples for our experimentation. The mill has various components or parts. The container used to feed the sample and the balls used to grind are made up of zirconia. A rotatable platform is used to mount the container. The direction of rotation of the container is opposite as to the rotation of the rotator platform. Once the containers are mounted and the lid has been closed the machine becomes operational and generates huge amount of energy. The material is grinded into colloidal fineness. The rotational speed of the machine is 300RPM. In order to achieve the desired fineness for our experimental work the sample is subjected to the grinding action for 1 hour. A planetary ball mill of the Gilson Company is shown below.



*A planetary mill with two stations*

Due to the inverse rotation of the container and the rotator platform these opposite centrifugal forces are cancelled and the balls in the container roll midway around the container. Then the balls fall from the halfway mark. To create a very high impact the balls are thrown across to the opposite wall with very high speeds. Thus an acceleration around 20g is reached due to this kind of a planetary action and as compared to the time

taken by simple centrifugal mills to grind the sample the observed time is reduced by a factor of 2/3.

### 3.1.2 Viscometer:

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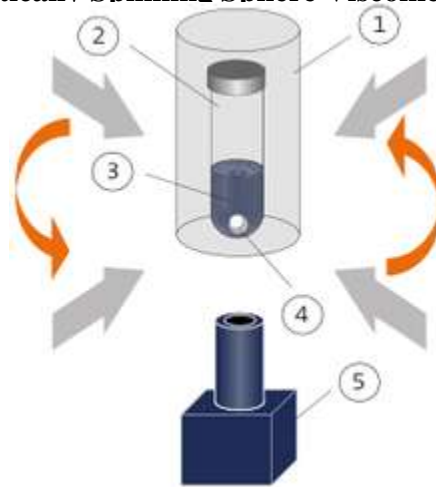
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### Basic Procedure:

1. Preheat spindle, sample chamber, and viscometer environmental chamber to 135°C or 408K.
2. Heat the standard slag sample (40%CaO-40%SiO<sub>2</sub>-20%Al<sub>2</sub>O<sub>3</sub>) so as to make a fluid enough to pour. Stir the sample, being careful not to entrap air bubbles.
3. Pour appropriate amount of slag into sample chamber. The sample size varies according to the selected spindle and equipment manufacturer.
4. Insert sample chamber into RV temperature controller unit and carefully lower spindle into sample.
5. Bring sample to the desired test temperature (typically 408 K (135°C)) within approximately 30 minutes and allow it to equilibrate at test temperature for 10 minutes.
6. Rotate spindle at 100 RPM, making sure the percent torque as indicated by the RV readout remains between 2 and 98 percent.
7. Once the sample has reached temperature and equilibrated, viscosity readings are taken for different temperatures. Several readings are taken at a particular temperature and the average of those is considered the viscosity at any particular temperature.

### 3.2 Experimental Process:

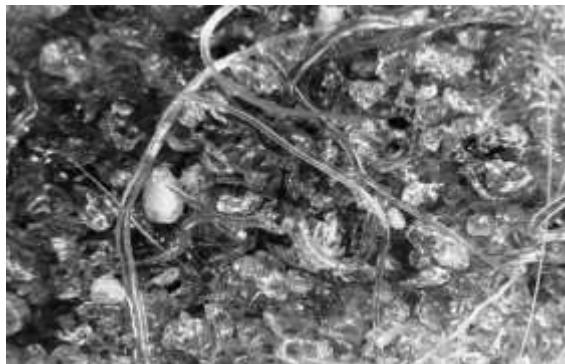
An average slag composition was selected by varying the different constituents in the slag. Slag samples collected from different Indian blast Furnaces were analyzed and the compositional details recorded. A standard 40% CaO, 40% SiO<sub>2</sub> and 20% Al<sub>2</sub>O<sub>3</sub> slag composition was chosen to standardize the high temperature viscometer to be used for measuring viscosity of the slag samples. The compositions of the slag samples considered for the study were varied in terms of C/S ratio, MgO content and TiO<sub>2</sub> content, keeping all the other components constant. Slag compositions were chosen where the C/S ratio was varied from 0.95 to 1.35, the MgO content from 6.5% to 11.75% and the TiO<sub>2</sub> content from 0.2% to 0.95%. The viscosity of the slag samples were also calculated using the IIDA model and compared to those measured. The effect of compositional changes on the viscosity of slags was studied.

### 3.2.1 Sample Preparation:

The oxides used for sample preparation were commercial oxides with 99% purity. The process involved heating the oxides first at about 150°C in an oven to remove moisture content. After oven heating, the oxides were properly weighed in the weighing machine as per the required percentage composition and were mixed thoroughly in the planetary ball mill. The oxides mixed were in the powder form and they cannot be fired as such. So the powders were made into small pellets, thus making them compact and easier to charge. The pellets obtained were heated in the oven for some time to remove any moisture content in it. They were then introduced in to the furnace at 1600°C in platinum crucibles, and held for duration of 30 minutes. The molten sample was then readily water quenched. The slag sample thus obtained was then ground in the ball mill for duration of 30 minutes. The sample was then again introduced into the furnace at 1600°C for duration of 30 minutes for remelting. It was subsequently water quenched and the synthetic slag obtained was again ground. The sample was then stored for further experimentation.

### 3.2.2 Sample analysis:

In coning and quartering, the powder is laid on a surface to form a conical heap, and this heap is divided into four quarters. Two opposite quarters, 1<sup>st</sup> and 3<sup>rd</sup> or 2<sup>nd</sup> and 4<sup>th</sup>, are selected and the other two discarded. This process is carried out until we obtain the desired amount of powder required for experimentation. After the process of coning and quartering, the desired amount of sample is selected and its viscosity studies are carried out up to a temperature of 1773K.



**Synthetic slag sample prepared in the laboratory**

# CHAPTER-4

## **RESULTS AND DISCUSSION**

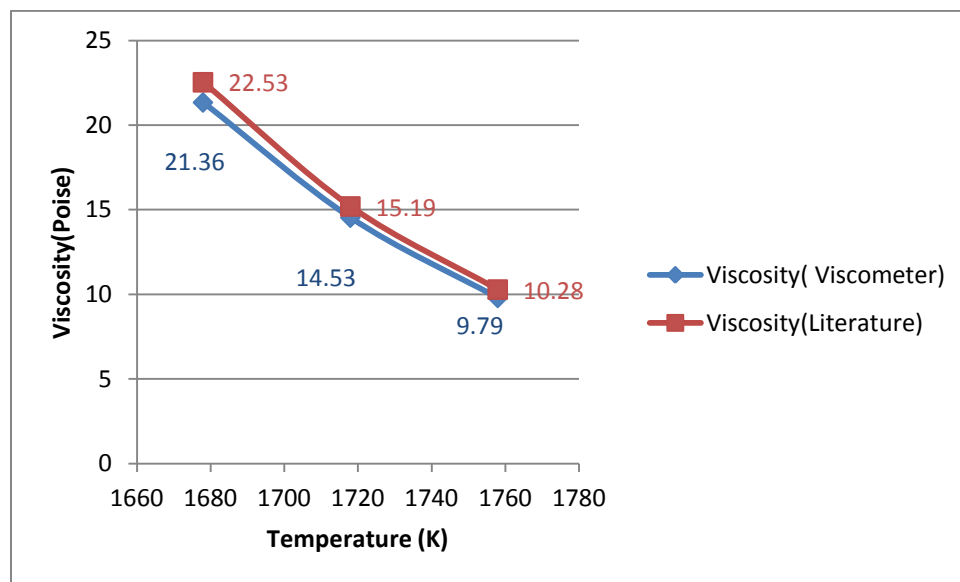
## 4.Results and Discussion:

### 4.1 Standardization of the viscometer:

For this purpose, a 40:40:20 (CaO:SiO<sub>2</sub>:Al<sub>2</sub>O<sub>3</sub>) slag was chosen. The viscosity was measured at three preset temperatures. The readings obtained for this standard slag were compared with those available in literature. The following table shows the details:

Sl. No.	Temperature (K)	Viscosity(Poise) From Viscometer	Viscosity(Poise) From Literature	% Difference
1	1678	21.36	22.53	5.3
2	1718	14.53	15.19	4.36
3	1758	9.79	10.28	4.82

**Table No 2: Measured Viscosity values of the 40:40:20 (CaO:SiO<sub>2</sub>:Al<sub>2</sub>O<sub>3</sub>) slag v/s literature**



**Figure No 1: Plot between viscosity values of 40:40:20 slag found in laboratory and the in literature**

Therefore, it was concluded that the measurement of viscosity with the instrument under the experimental conditions is standardized.

## 4.2 Measurement of viscosity:

### 4.2.1 Measurement with the High temperature Viscometer:

Three synthetic slag samples of the composition as given in the table below were considered for viscosity measurement in the high temperature viscometer.

	Al <sub>2</sub> O <sub>3</sub>	MnO	MgO	Na <sub>2</sub> O	K <sub>2</sub> O	Fe <sub>2</sub> O <sub>3</sub>	TiO <sub>2</sub>	CaO	SiO <sub>2</sub>	C/S
<b>Slag1</b>	20	0.01	6.5	1.1	0.5	1	0.2	34.44	36.25	0.95
<b>Slag2</b>	20	0.01	9.5	1.1	0.5	1	0.65	35.22	32.02	1.10
<b>Slag3</b>	20	0.01	11.5	1.1	0.5	1	0.9	36.73	28.26	1.30

**Table No 3: Composition of the slag samples used for viscosity measurement in the viscometer**

The viscosity was measured at three temperatures: 1673K, 1723K, and 1773K. The measured values are reported in the table below:

	Viscosity(Poise)		
	1673K	1723K	1773K
<b>Slag1</b>	15.33	9.61	6.60
<b>Slag2</b>	12.98	8.26	5.65
<b>Slag3</b>	13.37	9.13	5.97

**Table No 4: Viscosity of the three different slag samples measured at three preset temperatures**

### 4.2.2 Calculation of viscosity using IIDA model:

Mills et al [34] performed several tests and concluded that the KTH and the Iida models for viscosity estimation are the most reliable. The Iida model was ranked one of the most reliable models for estimation of viscosity. [34] Therefore, we considered the Iida model for viscosity estimation theoretically.

The same three samples considered for viscosity measurement in the high temperature viscometer are used for calculation here.

The calculated viscosity is shown in the tabulated form below:

	Viscosity(Poise)		
	1673K	1723K	1773K
<b>Slag1</b>	12.96	8.23	5.71
<b>Slag2</b>	11.07	7.53	5.15
<b>Slag3</b>	11.45	8.05	5.39

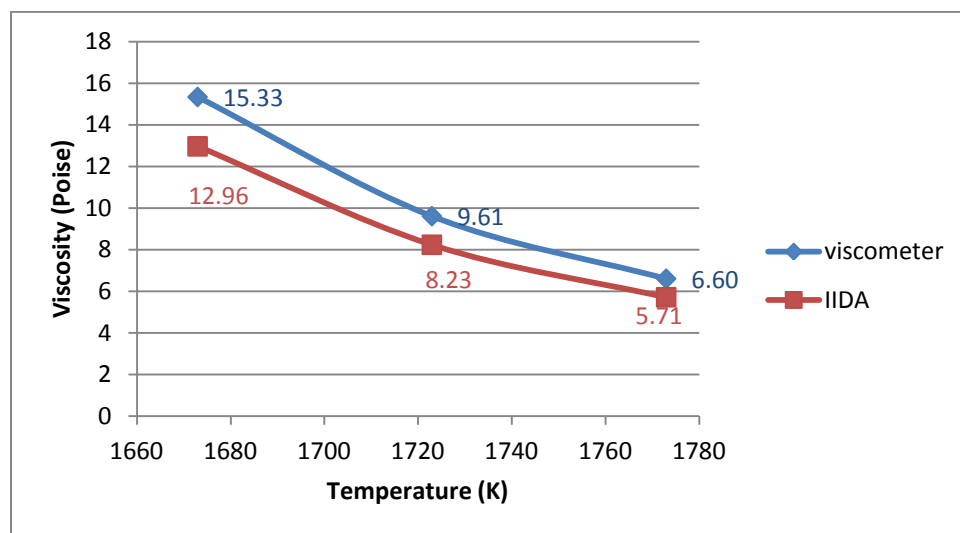
**Table No 5: Viscosity of the three slag samples calculated by the IIDA model**

#### 4.2.3 Comparison of the measured and calculated values:

The values of viscosity measured in the high temperature viscometer and those calculated with the IIDA model were compared. They are shown below:

SLAG1	Temperature(K)	Viscosity(Poise)		%Difference
		Viscometer	IIDA	
	1673	15.33	12.96	15.47
	1723	9.61	8.23	14.32
	1773	6.60	5.71	13.48

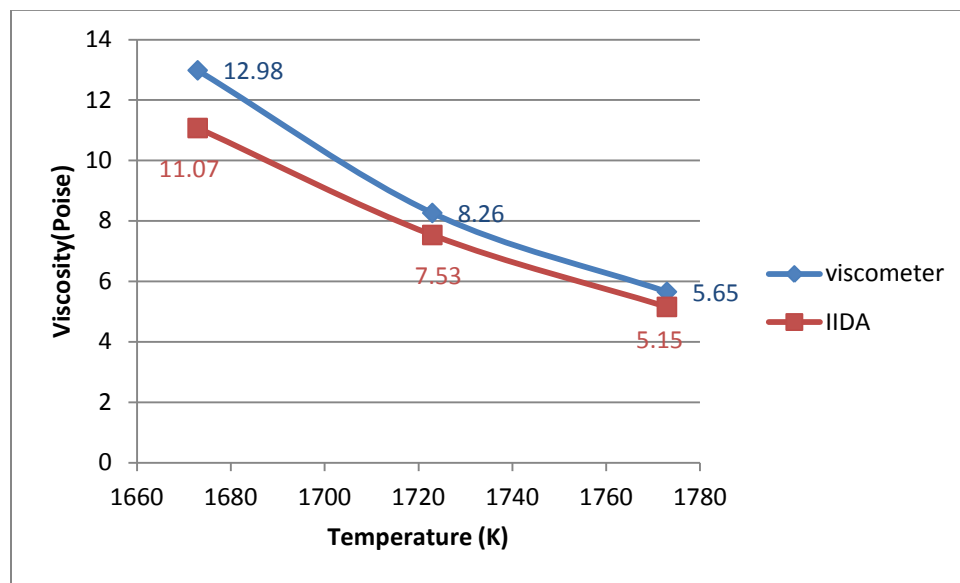
**Table No 6: Comparison of the viscosity values of slag1 measured in the viscometer and with the IIDA model**



**Figure No 2: Plot between Viscosity and Temperature for slag1 for measured and calculated values**

SLAG2	Temperature(K)	Viscosity(Poise)		%Difference
		Viscometer	IIDA	
	1673	12.98	11.07	14.71
	1723	8.26	7.53	8.84
	1773	5.65	5.15	8.85

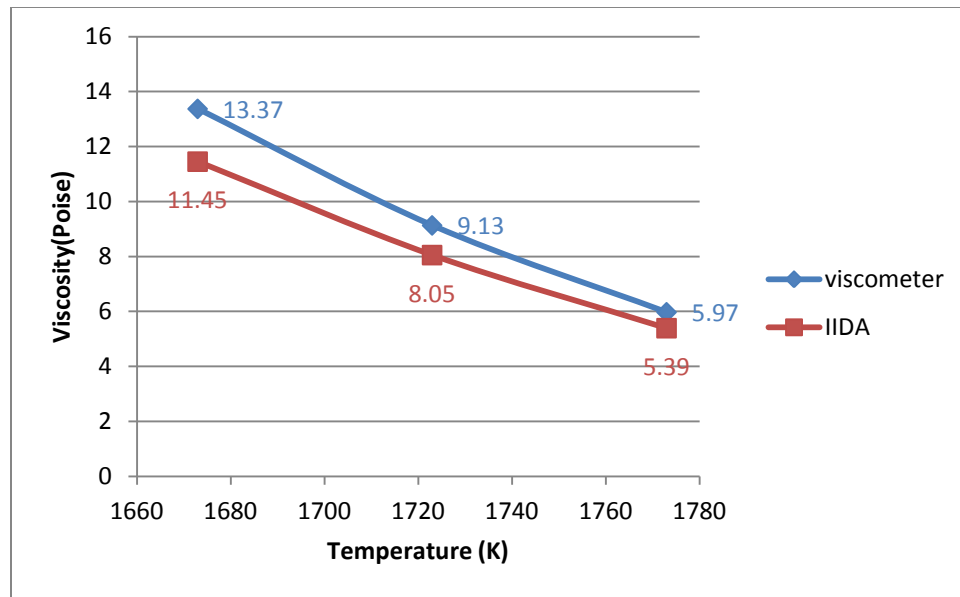
**Table No 7: Comparison of the viscosity values of slag2 measured in the viscometer and with the IIDA model**



**Figure No 3: Plot between Viscosity and Temperature for measured and calculated values of slag2**

SLAG3	Temperature(K)	Viscosity(Poise)		%Difference
		Viscometer	IIDA	
	1673	13.37	11.45	14.36
	1723	9.13	8.05	11.83
	1773	5.97	5.39	9.72

**Table No 8: Comparison of the viscosity values of slag3 measured in the viscometer and with the IIDA model**



**Figure No 4: Plot between Viscosity and Temperature for measured and calculated values for slag3**

Thus the model used renders an acceptable value of the viscosity. Literatures have shown that a deviation of 22% of the calculated value from the measured value is acceptable [9]

Therefore, for further slags, viscosity is calculated using the IIDA model and the effect of composition on viscosity was analyzed. The slag compositions and the viscosities are given below:

	Al <sub>2</sub> O <sub>3</sub>	MnO	MgO	Na <sub>2</sub> O	K <sub>2</sub> O	Fe <sub>2</sub> O <sub>3</sub>	TiO <sub>2</sub>	CaO	SiO <sub>2</sub>	C/S
slagM1	20	0.01	6.5	1.1	0.5	1	0.2	34.44	36.25	0.95
slagM2	20	0.01	9.5	1.1	0.5	1	0.2	32.98	34.71	0.95
slagM3	20	0.01	11.5	1.1	0.5	1	0.2	32.00	33.69	0.95
slagT1	20	0.01	6.5	1.1	0.5	1	0.2	34.44	36.25	0.95
slagT2	20	0.01	6.5	1.1	0.5	1	0.65	34.22	36.02	0.95
slagT3	20	0.01	6.5	1.1	0.5	1	0.9	34.09	35.89	0.95
slagC1	20	0.01	6.5	1.1	0.5	1	0.2	34.44	36.25	0.95
slagC2	20	0.01	6.5	1.1	0.5	1	0.2	37.02	33.66	1.10
slagC3	20	0.01	6.5	1.1	0.5	1	0.2	39.95	30.73	1.30

**Table No 9: Composition of the slags used to study the effect of different constituents**



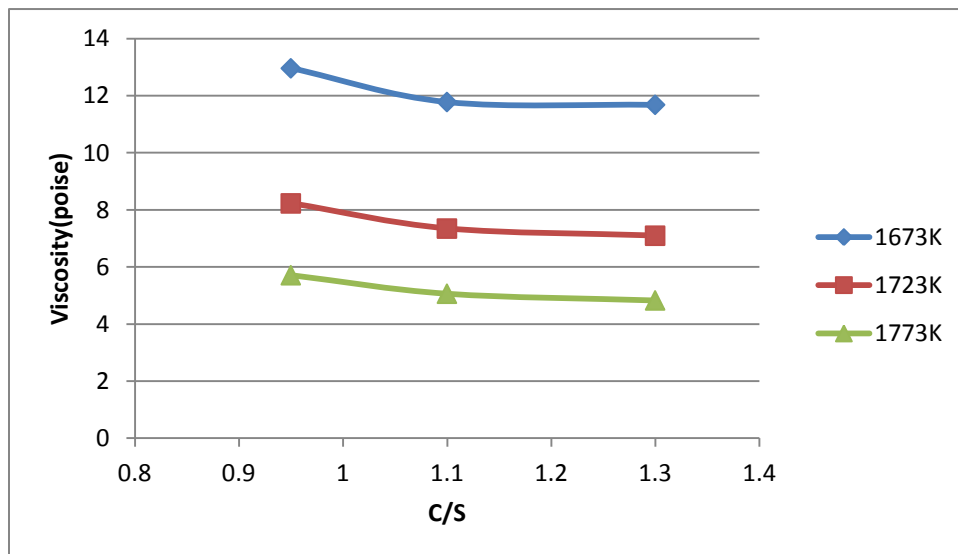
	Viscosity (Poise)		
	1673K	1723K	1773K
slagM1	12.96	8.23	5.71
slagM2	12.78	8.02	5.54
slagM3	12.82	7.98	5.49
slagT1	12.96	8.23	5.71
slagT2	13.04	8.27	5.74
slagT3	13.08	8.30	5.76
slagC1	12.96	8.23	5.71
slagC2	11.78	7.35	5.06
slagC3	11.68	7.10	4.83

**Table No 10: Viscosity of the slag samples used to study the effect of constituents**

In the samples marked M1, M2 and M3, the MgO content was varied, keeping the TiO<sub>2</sub> and C/S ratio constant. Similarly, in the samples marked T and C, the TiO<sub>2</sub> and the C/S ratio were varied respectively. This was carried out so as to study the effect of composition on the viscosity of the slag.

### 4.3 Effect of the constituents on slag Viscosity:

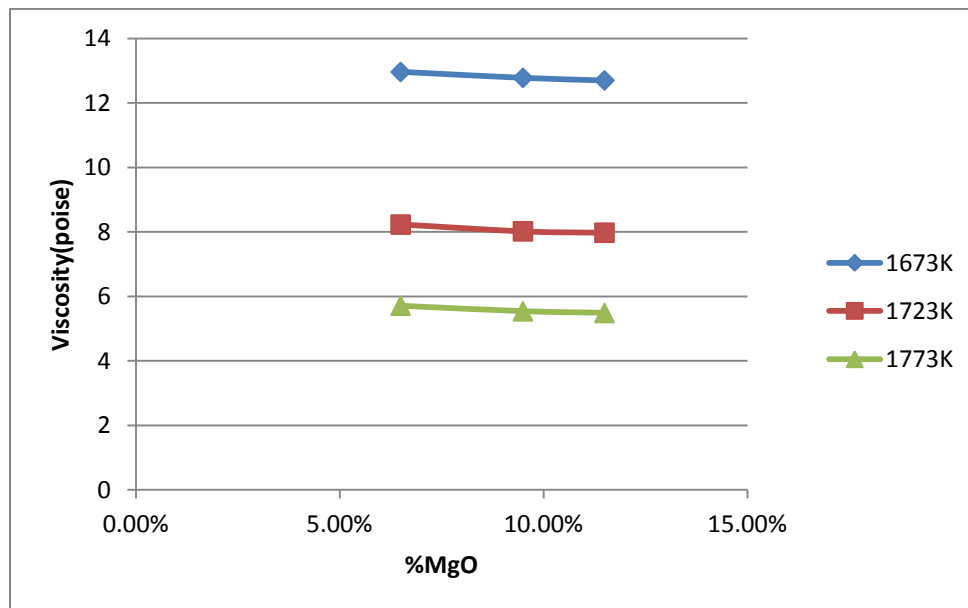
#### 4.3.1 Effect of C/S ratio on slag viscosity:



**Figure 5: Effect of C/S ratio on Viscosity**

The C/S ratio affects the slag viscosity greatly. The graph clearly shows a decreasing trend with the increase in C/S ratio. This is because, with the increase in C/S ratio, the CaO increases and it acts as a network breaker. It breaks the silica tetrahedron and makes the flow easy, thus decreasing the viscosity. The silicate structure changes from network to discrete anionic groups in the form of simple chains or rings [9]. The decreasing effect is, however, more prominent when the C/S ratio is low, i.e. when the C/S ratio increases from 0.95 to 1.1 the drop in viscosity is higher than when it increases from 1.1 to 1.3. The decreasing effect of C/S ratio on the viscosity is seen only up to a C/S ratio of 1.3. This may be because of the depolymerization of silicate network and because of the increase in chemical potential of certain solid phases, which in turn increases the viscosity. Thus for the smooth functioning of the furnace, the C/S ratio should be between 1.2-1.4.

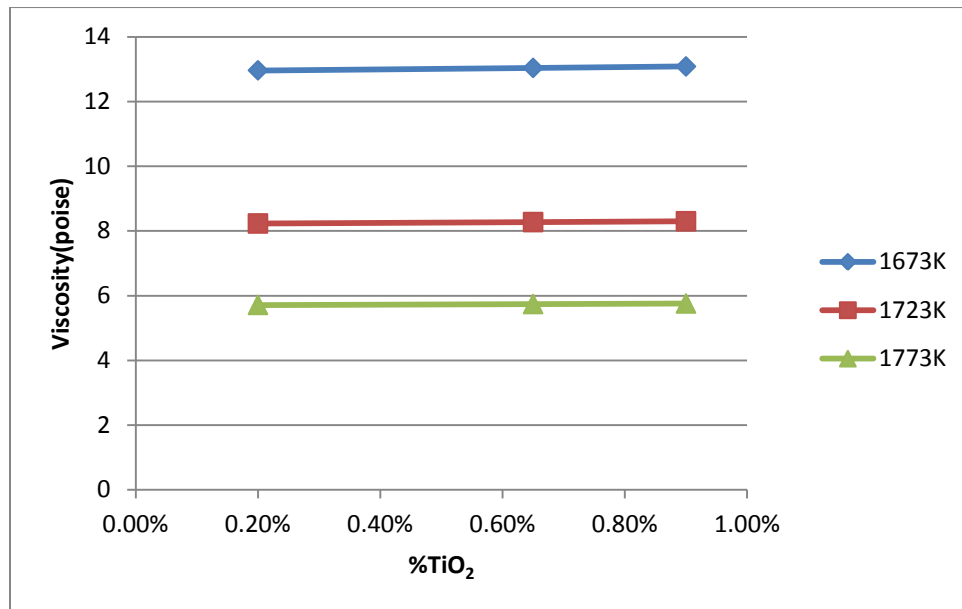
#### 4.3.2 Effect of MgO on slag viscosity:



**Figure No 6: Effect of MgO content on Viscosity**

Although, the increase in MgO content of the slag decreases the slag viscosity, the variation in the slag viscosity is not much significant. However, the decrease in slag viscosity by increase in MgO content is seen only up to 20% MgO. Beyond that, the viscosity of slag increases [24].

### 4.3.3 Effect of TiO<sub>2</sub> on slag viscosity:



**Figure No 7: Effect of TiO<sub>2</sub> content on viscosity**

As can be seen from the graph, the effect of TiO<sub>2</sub> is slightly increasing with increase in its percentage. This increase is a very low amount, ranging from 0.01-0.04 poise. TiO<sub>2</sub> is a minor constituent. Its effect is however studied because of the factor NBO/T, the non bridging oxygen per tetragonally bonded oxygen. This factor is a measure of the degree of depolymerization, which is responsible for modifying the slag structure. Thus, this factor influences the slag viscosity. TiO<sub>2</sub> contributes considerably towards the NBO/T factor [35], [36].

# **CHAPTER-5**

## **CONCLUSIONS**

## 5. Conclusions:

The basic conclusions that can be drawn from the experimental results are given below:

(i) The high temperature viscometer can be used satisfactorily to measure the viscosity of the synthetic high alumina blast furnace slags.

(ii) Under the compositional ranges considered, increase in the C/S ratio has a beneficial effect as it decreases the slag viscosity. The decrease in the slag viscosity increases its ability to flow, thereby exposing newer surfaces for further reactions.

(iii) MgO has the same effects as C/S in decreasing the slag viscosity with the increase in its content.

(iv) However, the C/S and the MgO content should not be increased beyond a certain level as it increases the slag viscosity by increasing the chemical potential of some solid phases.

# **CHAPTER-6**

## **FUTURE SCOPE**

## **6. FUTURE SCOPE:**

The high temperature viscometer has been standardized to measure the viscosity of high alumina synthetic blast furnace slag and can be used for measuring viscosity of different slag samples ranging from highly basic to highly acidic.

The IIDA model has been validated and shown that it can be used to calculate the viscosity of the slag samples theoretically without actually measuring them and thus can be used to predict the viscosity for slag samples of widely varying compositions.

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