OPTIMIZATION OF FLOW CHARACTERISTICS OF BLAST FURNACE SLAG

THIS THESIS IS SUBMITTED IN THE PARTIAL FULFILMENT OF THE REQUIREMENT FOR THE DEGREE OF **BACHELOR OF TECHNOLOGY**

IN

METALLURGICAL AND MATERIALS ENGINEERING

 $\mathbf{B}\mathbf{Y}$

NACHIKETA MOHANTY

(Roll No. 108MM037)

&

SUPRATIK DASH

(Roll No. 108MM040)



NATIONAL INSTITUTE OF TECHNOLOGY, ROURKELA

2012

OPTIMIZATION OF FLOW CHARACTERISTICS OF BLAST FURNACE SLAG

THIS THESIS IS SUBMITTED IN THE PARTIAL FULFILMENT OF THE REQUIREMENT FOR THE DEGREE OF **BACHELOR OF TECHNOLOGY**

IN

METALLURGICAL AND MATERIALS ENGINEERING

BY

NACHIKETA MOHANTY

(Roll No. 108MM037)

&

SUPRATIK DASH

(Roll No. 108MM040)

Under the guidance of

Prof. U. K. Mohanty



NATIONAL INSTITUTE OF TECHNOLOGY, ROURKELA



NATIONAL INSTITUTE OF TECHNOLOGY ROURKELA

CERTIFICATE

This is to certify that the thesis entitled "Optimization of Flow Characteristics of Blast Furnace Slag" submitted by Nachiketa Mohanty (108MM037) and Supratik Dash (108MM040) 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 (Deemed University) 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: 9th May, 2012

Prof. Dr. U.K. Mohanty Department of Metallurgical and Materials Engineering, National Institute of Technology Rourkela - 769008

ACKNOWLEDGEMENT

We 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 allowing us access to valuable facilities in the department.

We avail this opportunity to express our 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 at various stages for the execution of this dissertation work.

We would like to convey our heartfelt gratitude to Mr. A.S. Reddy and Mr. Amitabh Shankar, TATA Steel, Jamshedpur to whom we are indebted for their relentless support and timely guidance during our project work.

We are also grateful to Mr. Uday Kumar Sahu, Department of Metallurgical and Materials Engineering, NIT Rourkela for providing valuable assistance and insight during the experimental process.

Date: 9th May, 2012

Nachiketa Mohanty (108MM037) Supratik Dash (108MM040) Department of Metallurgical and Materials Engineering, National Institute of Technology, Rourkela Rourkela-769008

ABSTRACT

A study of the flow characteristics of blast furnace slag is important to record the softening and melting phenomena in blast furnace which greatly influence the extent and location of the cohesive zone having a direct say on the blast furnace operation, quality of hot metal and the coke consumption. In the present work, a noble technique (heating microscope) is adopted to determine the flow characteristics of blast furnace slags obtained from different blast furnaces. It is seen that the results so obtained agree very closely with the values obtained from adopting conventional methods of determining the same using the slag atlas. It is also seen that the characteristics temperature are altered with the alteration of C/S ratio and also the MgO content of the blast furnace slag.

Keywords: Cohesive zone, Characteristic temperature, Quality of hot metal, C/S ratio

CONTENTS

ABSTRACT	III				
INTRODUCTION	1				
1. Introduction	2				
LITERATURE SURVEY					
2. Literature Survey					
2.1. Blast Furnace Iron Making					
2.1.1. Reduction of iron oxides	7				
2.1.2. Reactions in the lower one	8				
2.1.3. Reactions in the middle zone	10				
2.1.4. Reactions in the upper zone	11				
2.2. Blast Furnace Slag					
2.3. Characteristic Properties of Blast Furnace Slag					
2.3.1. Slag Viscosity	15				
2.3.2. Slag Liquidus Temperature	16				
2.4. Softening and Melting Phenomena	17				
2.4.1. Shortness of a Slag	19				
2.4.2. Flow Characteristics of Blast Furnace Slag	19				
2.5. Methods for Measuring Liquidus Temperature					
2.5.1. Pressure Drop Technique	21				
2.5.2. Slag Atlas	22				

2.6. Effect of Slag Constituents on Viscosity	23
2.7. Effect of Slag Constituents on Liquidus Temperature	29
EXPERIMENTAL	31
3. Experimental	32
3.1. Sampling	32
3.2. Testing	32
RESULTS AND DISCUSSION	36
4. Results and Discussion	37
4.1. Liquidus Temperature Measurement	37
4.2. Effect of Basicity (C/S ratio or B_2) on characteristics temp.	39
4.3. Effect of MgO content on characteristic temperatures	41
CONCLUSION	43
5. Conclusion	44
FUTURE SCOPE	44
REFERENCES	45

LIST OF FIGURES

Figure 1	Softening and Melting characteristics of Pressure Drop technique	22
Figure 2	Slag Atlas for liquidus temperature estimation for slag with 20% Al_2O_3	23
Figure 3	Coning and Quartering	32
Figure 4	High Temperature Microscope	33
Figure 5	Line Diagram of High Temperature Microscope	34
Figure 6	Flow Characteristics of Blast Furnace slag sample	37
Figure 7	Comparison of liquidus temp. values from present work and slag atlas	38
Figure 8	Variation of different characteristic temperatures with C/S ratio	40
Figure 9	Variation of (FT – ST) with C/S ratio	40
Figure 10	Variation of different characteristic temperatures with MgO content	41

LIST OF TABLES

Table 1	Liquidus temp of slag samples obtained from present work and slag atlas	38
Table 2	Composition and flow characteristics of blast furnace slags	39

Introduction

1. Introduction

The iron-making blast furnace is a complex high temperature counter current reactor in which iron bearing materials (ore, sinter/pellet) and coke are alternately charged along with a suitable flux to create a layered burden in the furnace. The iron bearing material layers start softening and melting in the cohesive zone under the influence of the fluxing agents at the prevailing temperature which greatly reduces the layer permeability that regulates the flow of materials (gas/solid) in the furnace. It is the zone in the furnace bound by softening of the iron bearing materials at the top and melting and flowing of the same at the bottom.^[1] A high softening temperature coupled with a relatively low flow temperature would form a narrow cohesive zone lower down the furnace.^[2] This would decrease the distance travelled by the liquid in the furnace there by decreasing the Silicon pick- up.^[3,4] On the other hand the final slag, that trickles down the Bosh region to the Hearth in the furnace, should be a short slag that starts flowing as soon as it softens. Thus fusion behaviour is an important parameter to evaluate the effectiveness of the B.F. slag.

Fusion behaviour is described in terms of four characteristic temperatures ^[5]; IDT, the initial deformation temperature symbolising surface stickiness, important for movement of the material in the solid state; ST, symbolising plastic distortion, indicating start of plastic distortion; HT, the liquidus temperature, symbolising sluggish flow, playing a significant role in the aerodynamics of the furnace and heat and mass transfer; and FT, the flow temperature, symbolising liquid mobility.

The slag formed in the cohesive zone is the primary slag formed with FeO as the primary fluxing constituent; the solidus temperature, fusion temperature, solidus-fusion interval being significantly affected by FeO ^[6]. This slag is completely different from the final slag where the fluxing is primarily caused due to the presence of basic constituents like CaO or MgO.

While it is not possible to obtain primary slag from the industrial blast furnace, it is always possible to prepare a synthetic slag in the laboratory resembling the primary slag and study its flow characteristics. We have kept this venture for future studies and the present study limits itself to the study of flow characteristics of the final slag as obtained from the industry. However, it must be noted that from the process point of view the final slag should be a 'Short Slag', a slag with a small difference between the ST and FT. Such a slag acquires liquid mobility and trickles down the furnace away from the site where it starts distorting plastically, as soon as possible. This action exposes fresh sites for further reaction and is supposedly responsible for enhanced slag-metal reaction rates, influencing the blast furnace operations and the quality of the metal.

Keeping the above in mind, in addition to employing two different experimental techniques for measurement of the flow characteristics of industrial blast furnace slags and comparing the liquidus temperatures so obtained the present work also involves itself with analysis of the data on the basis of the chemical composition of the slag.

Literature Survey

2. Literature Survey

2.1. Blast Furnace Iron Making

Blast furnace iron making process is the most used process among all the iron making processes. This is because blast furnace iron making has a high production rate and a very high degree of heat utilization (85-90%). This is because the blast furnace is an extremely efficient counter current heat exchange apparatus. Modern high capacity furnaces are producing as much as 12000 tonnes of hot metal per day. ^[34]

The sources of iron are its ores in which iron is contained mainly as its oxides such as hematite (Fe₂O₃) or magnetite (Fe₃O₄) and sometimes in small proportions as hydroxides and carbonates. Hematite constitutes the largest portion of all the ores used for blast furnace iron making. When pure, hematite contains about 70% and magnetite about 72.4% of iron. But in actuality, the iron content of the ores ranges from 50-65% for rich ores and 30-50% for lean ores and the remainder is gangue which consists mostly of silica and alumina as well as minor amounts of moisture and chemically- combined water. The ores are normally charged as sinters or pellets. Sintering and pelletizing are processes by which iron ore fines are agglomerated into larger pieces with or without incorporation of lime and magnesia as fluxes. The gangue materials are insoluble in liquid iron and possess very high melting points. However they fuse at lower temperatures in the presence of fluxes and form a slag. Magnesia are basic in nature and silica and alumina are acidic in nature and their ratio is known as basicity. ^[34, 35]

The slag and the iron can only be separated completely from each other when they are in the liquid state which requires them to be heated to above their fusion temperatures. The heat is

usually supplied by burning of coke. The reduction of iron oxides also needs sufficiently high temperatures as well as adequate amounts of reducing agents (coke carbon). The iron also picks up 2-4.5% carbon from the coke which lowers its melting temperature from 1534°C by 200-300°C depending upon the carbon content. The coke contains ash which is mainly constituted of silica and alumina which require a further amount of lime and magnesia for fluxing. The ore, coke and flux contain compounds of Si, Mn, P, S and small amounts of other impurities like Pb, Sn, Cu, Ni, Cr, Ti, alkali metals, etc., which get partly or wholly reduced and get taken up by iron. Manganese ores are usually deliberately added for manganese's beneficial effect on iron making.^[34]

The oxygen required for the burning of coke is supplied by air (blast). This air is preheated in order to supply sensible heat from outside, hereby reducing coke expenditure. Because preheating of the air is performed by the burning of the blast furnace gas (which come out of the furnace top and usually contains 20-30% CO and 10-20% CO₂, nitrogen and a little hydrogen and moisture), a part of the chemical heat, i.e. unused CO, is utilized indirectly. The blast is introduced above the bottom of the furnace through water-cooled tuyeres whereas the burden materials are charged from the top. ^[34]

Coke is the only component of the charge materials which descends as a solid to the tuyere level. Apart from supplying the reducing agent and heat for processing the burden into finished products, the coke provides mechanical support to the burden especially where it is needed most, i.e. in the bosh region where the metal and slag are liquid. These liquids flow down to the hearth through the interstices of the coke particles (coke grid). The coke rate in the blast furnace per tonne of pig iron varies from 1000kg to as low as 45-500kg. Low coke rates are obtained with pre-fluxed sinters and pellets, high blast temperatures and uniform gas distribution. The hot blast of air entering the furnace through the tuyeres burns the coke carbon to CO_2 immediately in front of them. The intense heat produced gives a flame

temperature (tuyere gas temperature) of $1800-2000^{\circ}$ C, depending upon the blast temperature. Since CO₂ is unstable in the presence of carbon above 1000° C, CO is produced. The tuyere gas, therefore, consists only of CO and nitrogen, their contents being about 35% and 65% respectively when dry blast is used. The coke does not fall continuously but only periodically into the tuyere zone from above. The hot reducing gas rises through the active coke bed to the bosh, belly and the shaft and reduces the iron oxides. ^[34, 35]

2.1.1. <u>Reduction of Iron Oxides:</u>

There are three forms of iron oxide: hematite (Fe₂O₃), magnetite (Fe₃O₄) and Wustite (FeO). These oxides are reduced in stages. Their reactions with CO, the equilibrium CO/CO₂ ratios and CO-utilization factors at 900°C are given below. The extent of CO utilization, i.e. the fraction or percentage of CO converted to CO₂ is denoted as, ^[34]

$$CO-utilization = 100 \text{ x } CO_2 / (CO_2 + CO)$$
 Eq. 1

Reactions

Equilibrium at 900°C

	CO/CO_2	%CO-utilization		
$3Fe_2O_3 + CO = 2Fe_3O_4 + CO_2$	0	100	Eq.2	
$Fe_3O_4 + CO = 3FeO + CO_2$	0.25	80	Eq.3	
$FeO + CO = Fe + CO_2$	2.3	30	Eq.4	

The blast furnace is a counter current process. Thus, the tuyere gas with high CO-content comes into contact with the Wustite which needs a very high reduction potential for conversion to Fe (Eq. 4). The resulting lower potential gas, as it ascends, encounters magnetite and hematite which require much smaller equilibrium CO/CO_2 ratios for reduction

to lower oxides. Hence, the reduction of Wustite is of prime importance in iron oxide reduction, especially because about 70% of hematite oxygen is present as Wustite.

Since CO_2 represents the end combustion product of carbon, the utilization of the chemical and thermal energies of carbon will be more complete if higher amount of oxygen is removed by reactions Eq.2 to Eq.4. These reactions are called indirect or gaseous reduction and the reaction product is CO_2 . The overall reaction from Eq.2 to Eq.4 is mildly exothermic. ^[34]

If any Wustite remains unreduced in a zone where temperatures are higher than 1000° C, the CO₂ produced by reaction 4 is rapidly reduced by carbon according to:

$$CO_2 + C = 2CO - 41210$$
 cal Eq.5

Combining equations 4 and 5,

$$FeO + C = Fe + CO - 37220$$
 cal Eq.6

Reaction 5, known as Boudouard or solution loss or carbon gasification reaction is highly endothermic and also deteriorates CO-utilization. Reaction 6 is called direct reduction and is endothermic in contrast to indirect reduction but consumes less carbon for every mole of oxygen removed because the product, CO, can take part in further (gaseous) reduction. ^[34]

2.1.2. <u>Reactions in the lower zone:</u>

The lower or melting zone extends from the tuyere level to 3-5m above. The temperature of the molten materials reaches 1400-1450°C in this zone and the gas cools down to 800-1000°C. The burning of coke in front of the tuyeres results in a continuous creation of an empty space around the hearth periphery which permits the flow of the charge materials downwards. This combustion zone constitutes an active area as a ring of 1-2m depth and is called the raceway. Beyond the raceway, there is a closely-packed central column of coke

called dead man's zone. The coke column either floats on the liquid iron in the hearth or reaches as far as the hearth floor. Some slag and iron remain entrapped in the interstices of the coke pieces and are drained out during tapping.^[34]

The gangue in association with the flux starts to fuse in the belly region where two immiscible phases (partly carburized primary iron and FeO-SiO₂-Al₂O₃-MnO primary slag containing some CaO) begin to form at temperatures above 1200°C. Further down, these liquid phases separate from each other, infiltrate through the coke grid above the raceway and collect in the hearth well from where they are tapped periodically. Since the tuyere gas also rises through the voids of the coke bed, the raceway resembles a counter-current liquid-gas exchanger, the coke providing the mechanical support. ^[34]

The minimum hearth temperature necessary for free running of the slag is termed as critical hearth temperature which is about 1500-1550°C in order to provide some superheat in the hearth and ensure that both slag and iron are in the liquid state under all operating conditions. The more important chemical reactions occurring in this zone are: ^[34]

1. Endothermic calcinations of limestone; $CaCO_3 = CaO + CO$

- 2. Endothermic direct reduction of FeO; FeO + C = Fe + CO
- 3. Endothermic direct reduction of SiO_2 ; $SiO_2 + 2C = Si + 2CO$
- 4. Endothermic direct reduction of MnO; MnO + C = Mn + CO
- 5. Endothermic direct reduction of P_2O_5 ; $P_2O_5 + 5C = 2P + 5CO$
- 6. Endothermic sulphur removal; FeS + CaO + C = CaS + Fe + CO

7. Exothermic combustion of carbon; $C + O_2$ (air) = $CO_2 + N_2$

8. Endothermic reduction of CO_2 ; $CO_2 + C = 2CO$ (>1000°C)

9. Endothermic reduction of moisture in blast; $C + H_2O = CO + H_2$ (>1000°C)

The final temperature of iron is about 1350-1450°C and that of slag about 50-100°C higher. Depending upon the raw materials and finished products, the heat requirement in the lower furnace including radiation and cooling losses may range from 0.7 to 1.0 million kcal per THM. This results in rapid cooling of the tuyere gas from about 2000°C to 800-1000°C since all the above heat devouring reactions occur above 900°C. ^[34]

2.1.3. <u>Reactions in the middle zone:</u>

This zone, where the temperatures of the solids and the gas are near identical (800-1000°C), is called isothermal or reserve zone. Since, most of the indirect reduction, especially of Wustite, occurs in this zone, it is also referred to as indirect reduction zone. This zone may occupy 50-60% of the furnace volume. A major proportion of indirect reduction of iron oxides according to Eq.2-4 occurs in this zone. ^[34] The extent of this zone is important because the Wustite should be given as much opportunity as possible for getting reduced indirectly.

Insertion probes into modern blast furnaces show the presence of a chemically inactive zone inside the middle zone where very little exchange of oxygen between the ore and the gas occurs and the gas composition suffers very little change. The CO/CO_2 ratio of the gas in the inactive zone is about 2.3. This zone becomes pronounced in cases where the coke consumption per THM is very low. Another reaction of importance which occurs in the middle zone is the water-gas shift reaction:

$$CO + H_2O = CO_2 + H_2$$
 Eq.7

This reaction generates hydrogen which is a more active reductant than CO. The moisture is generated from reduction of iron oxides with hydrogen which itself comes from humid air or when steam and hydrocarbons are used as blast additives. ^[34]

2.1.4. <u>Reactions in the upper zone:</u>

In the upper or preheating zone, the temperature of the gas ascending from the middle zone falls rapidly from 800-1000°C to 100-250°C and that of solids rises from ambient to 800°C. The main reactions that occur in this zone are:

- 1. Decomposition of carbonates other than that of calcium
- 2. Vaporization of moisture and hydrated water of the burden
- 3. Carbon deposition, $2CO = CO_2 + C$
- 4. Partial or complete reduction of hematite and magnetite to their lower oxides

It takes about 6-8 hours for the burden to descend from the top to the tuyere level depending upon the rate of production. ^[34]

2.2. Blast Furnace Slag

When raw materials i.e. iron ore, sinter, pellets coke and different types of fluxes are charged in a blast furnace, hot metal is produced and the impurities in the charge get separated as slag. Thus, slag is a product formed by chemical combination of fluxes (usually lime and magnesia) with aluminates, silicates and other gangue constituents in iron oxide and coke ash. The molten slag is insoluble in hot metal and is lighter than the liquid iron, resulting in a separate layer of its own. Basic flux is essential to lower the melting points of the acid constituents and thus obtain a liquid and sufficiently fluid slag. Basic flux also takes part in the slag-metal reactions and controls the metal quality. Apart from the four main non-ferrous oxides (lime, magnesia, alumina and silica) which form about 95-96% of the total, there are other compounds present in minor quantities depending upon the raw materials and the type of iron smelted in the blast furnace viz. FeO, MnO, FeS, CaS, alkali silicates, etc. ^[34]

A proper slag should perform various functions in order to achieve maximum fuel efficiency and maximum furnace performance. The slag should have low viscosity so that it flows freely and rapidly at operating temperatures. The coke rate influences this flowing temperature and hence this affects the eventual fuel economy of the process. The slag should facilitate free movement of stock and furnace gases. It should also have a high sulphur retention potential i.e. (S)/[S]. The slag also controls the metal temperature, metal quality and homogeneity. The slag should tolerate and cushion the fluctuations in the temperature and physical and chemical properties of the burden. And finally, the slag should be suitable for use in cement manufacture, road ballast, etc. On the other hand, the formation of slag is a subject to the operating conditions and other factors like flame temperature, distribution of materials at the top, ore reducibility, burden yield, sinters and pellets, softening temperatures of the ferrous charge, coke ash content, furnace lines, etc. When all the operating conditions are conducive to a smooth and regular furnace movement, the use of a slag of optimum composition may result in a maximum production and minimum of slag bulk, metal-sulphur and fuel costs. ^[34]

It is generally accepted that for smooth blast furnace operation, the basicity ratio, CaO/SiO₂ or (CaO + MgO)/SiO₂, should be maintained at about 1.2 or 1.4 respectively and the alumina content of the slag should not exceed 18% and neither fall below 12%. High alumina slags have high viscosity, which hampers desulphurization. In such a situation, MgO is normally added to reduce the viscosity but this results in an increase in slag volume which lowers the furnace productivity and increases the coke rate. A study of the viscosities of blast furnace slags reveals that acceptable viscosities are obtained with either 5% or 10% MgO in the slag, for slags containing up to 20% alumina. ^[34]

The sequence of slag formation in a blast furnace can be divided into three zones:

- (a) Primary slag fusion zone
- (b) Bosh slag fusion zone
- (c) Final slag or hearth slag zone

In raw ore and limestone burden, the calcinations and assimilation of the latter occur slowly and are complete only when very high temperatures are reached, i.e. in the bosh, tuyere and hearth zones. Thus, the initial slag formed is acidic in nature as it consists mostly of unreduced FeO and gangue silica and alumina with some MnO, the fusion temperature depending on the FeO content. If the ore is lean and highly reducible, the FeO content in the slag is less and the fusion temperature is high (1200-1350°C) and if the ore is rich with low slag bulk, the FeO content is comparatively higher even if its highly reducible and the fusion temperature is low (about 1200°C). The %FeO decreases due to direct reduction and the fusion temperature rises as the primary slag flows down. The presence of MnO and absorption of lime and magnesia keep the slag molten during its passage to the hearth. ^[34]

The absorption of lime may be slow but it is continuous and is complete only in the hottest parts, i.e. at the tuyere level. The reduction of FeO in the lower, hotter zones is very fast and is almost complete above the tuyeres. The resulting bosh slag is much more basic than the final slag because the acid constituents of the coke ash are only absorbed when released at the tuyeres. Bosh slag composition may vary widely depending on the furnace movement as well as on the individual materials charged, namely, iron ore, manganese ores, sinters or fines, or limestone. Iron oxide is usually low (5 percent) but maybe as high as 10-20 percent. The bosh slag basicity is higher with richer ore, greater coke rate, greater sulphur load, greater metal-silicon, and greater coke ash content. ^[34]

The hearth slag is formed on dissolution of lime which was not incorporated in the bosh and on absorption of coke ash released during combustion. The formation is more or less complete in the combustion zone. This slag runs along with the molten iron into the hearth, accumulates there and forms a pool with the liquid metal underneath. During the passage of iron droplet through the slag layer, the slag reacts with the metal and a transfer of mainly Si, Mn and S occurs from or to the metal, tending to attain equilibrium between themselves. The nature, composition and bulk of the hearth slag ultimately control the composition of the pig iron and the productivity of the blast furnace. The most important purpose of slag control is the control of sulphur, since sulphur is the key to iron quality. The use of optimum slag composition would give minimum sulphur in metal and minimum slag volume, resulting in maximum production and minimum fuel costs. ^[34]

2.3. Characteristic Properties of Blast Furnace Slag

In blast furnace, formation of slag and the mineralogical transformation that the slag undergoes during descend of burden inside the furnace influence the quality of hot metal. The components of slag namely silica and alumina increase the viscosity whereas the presence of calcium oxide reduces the viscosity. The melting zone of slag determines the cohesive zone of blast furnace and hence the fluidity and melting characteristics of slag play a major role in determining the blast furnace productivity. Initially iron rich slag is formed and thereafter due to assimilation of CaO and MgO from flux, the composition of slag varies. As the slag moves down, it assimilates silica and alumina of ash, generated from combustion of coke.

The various characteristic properties of slag play a vital role in ironmaking as this influence the final hot metal quality and the process economy. These properties not only influence the blast furnace operations but also increase the value of the slag as a by-product. The impurities entering the blast furnace in the form of their various compounds are removed in the slag phase. The presence of these compounds of the impurity items affects the slag structure and other properties. The slag must ensure efficient removal of impurities along with smooth running of the blast furnace processes. From this point of view, the slag characteristics are of prime importance in ironmaking operations. The most important characteristic properties of slag, which have attracted the attention of many metallurgists, are: Slag Viscosity, Slag Liquidus Temperature, and Sulphide Capacity of the Slag and Alkali Capacity of the Slag.

2.3.1. Slag Viscosity:

Slag viscosity is a transport property that relates to the reaction kinetics and the degree of reduction of the final slag ^[8]. Slag viscosity also determines the slag-metal separation efficiency, and subsequently the metal yield and impurity removal capacity. In operation, the slag viscosity is indicative of the ease with which slag could be tapped from the furnace, and therefore relates to the energy requirement and profitability of the process. The slag viscosity is sensitive to its iconic and molecular structure.

The concept of viscosity was introduced by Poiseuille. Blast furnace slags are considered to be Newtonian liquids for the range of shear stress commonly encountered during blast furnace operation. The viscosity of Newtonian liquids is independent of the shear stress. Blast furnace slag viscosity is sensitive to its iconic and molecular structure. In a blast furnace the flow phenomenon of the slag, as dictated by its viscosity, greatly influence the heat transfer, mass transfer and chemical reactions between the slag and the metal. The blast furnace slag should be a free flowing one at the operating temperatures to ensure efficient slag-metal separation. It must have appreciable affinity for the gangue constituents to facilitate the production of metal of choice. Yet, from the available heat (in the hearth) point of view ^[7] the blast furnace slag should be neither very viscous nor very fluid. The viscosity of the blast furnace slag governs the reaction rates in the furnace by its effect on the diffusion of ions

through the liquid slag to and from the slag metal interface. It also affects the operation efficiency of the blast furnace by its influence on the aerodynamics of the furnace since the flow pattern of the molten slag significantly influences the gas permeability and heat transfer in the furnace.

A process of depolymerisation lowers the viscosity of the slag. An increase in basicity decreases the viscosity of the blast furnace slag breaking the three dimensional silicate network in to discrete anionic groups thereby causing depolymerisation. However, the blast furnace slag viscosity cannot be described only by the enhanced degree of depolymerisation. Beyond certain level of basicity the viscosity actually increases, despite the enhanced degree of depolymerisation as such an increase in the basicity may also result in an increase in the chemical potential of some primary solid phases.^[7]

2.3.2. <u>Slag Liquidus Temperature:</u>

The liquidus temperature influences the effective positioning and width of the cohesive zone which directly controls the productivity of the blast furnace operation. The positioning and width of the cohesive zone controls the gas permeability, Si content in the hot metal and the extent of indirect reduction inside the furnace. Thus the determination of liquidus temperature of the slag is of vital importance.

The liquidus temperature has been reported by various nomenclatures by various investigators. Osborn ^[9] and Snow ^[10] reported liquidus temperature as the temperature at which the first crystal forms during cooling down the melt whereas Ohno *et al* ^[11] reported it as the temperature at which the last crystal disappears during heating. The liquidus temperature or fusion point in German Industrial Standards 51730 has been defined as the hemispherical temperature, *i.e.*, the temperature at which a small mass of the slag assumes the

shape of a hemisphere on heating. The heating microscope method is adopted to measure this hemispherical temperature.

In industrial melts, *i.e.*, when a pyrometallurgical process is carried out in a furnace, it is the fusion behaviour of the non-metallic melts (*i.e.*, the mixture of oxides which would combine to make the slag) which is more important than the exact fusion temperature. The fusion behaviour is described in terms of four characteristic temperatures.^[5] These are; the initial deformation temperature (IDT), symbolising the surface stickiness; the softening temperature (ST), symbolising the plastic distortion; the hemispherical temperature (HT), which is also the liquidus temperature, symbolising sluggish Flow; and the flow temperature (FT), symbolising liquid mobility.

2.4. Softening and Melting Phenomena

The softening of the burden refers to the change in the state of ferrous materials such that it causes an increase in its rate of deformation and decreases the bed permeability. The voids between the materials can be occupied by the exuded liquid and/or fragmented solid pieces. Therefore the deformation of phases and formation of liquid can be the two primary causes which will accelerate the loss of strength of the material under the action of mechanical forces. ^[12]

In cohesive zone or mushy zone, different phenomenon occur at the same time, the softening and melting of the oxide phase and the softening and melting of the metallic iron phase. The strength of the metal phase will depend on the amount of carbon present whereas the strength of the oxide phase depends on the amount of non-ferrous oxides or slag formers present, along with their distribution, morphology and chemistry. It will also depend upon the reduction degree as it affects the availability of iron oxide as a slag former.^[13]

The softening and melting phenomenon of the ferrous burden is a complex phenomenon and thus can be subdivided into various steps. The first oxide melt is formed at the interface with lowest melting point, usually between and iron oxide particle and another oxide. It thus is heavily dependent on the phases present and their distribution. The first melt formed will subsequently wet the ore particles due to reduction in interfacial energy. This liquid film will slow he reduction kinetics as it inserts another resistance to the reaction, i.e. an additional step of transportation through the liquid slag film. This is often referred as reduction retardation. It has been observed that in majority of the blast furnaces, the metallic burden reaches its softening temperature with a reduction degree higher than 50 percent. Hence we can assume that there is a porous solid iron shell confining the solid and liquid oxides. As the liquid phase covers the solid oxide particles, it becomes a semi-solid material, where the liquid slag layer acts as a lubricant for the remaining particles. As a result of the wetting of the ore particles by the liquid slag, the core has a much reduced mechanical strength and the resistance to deformation will be determined by iron shell. The ability of the metallic shell to hold the molten oxides together will depend on its strength and reduction degree. With increase in liquid volume fraction with increase in temperature, subsequently a point will be reached when the iron oxide will not be able to hold the liquid. This will cause the dripping of the liquid slag from the burden material. In the meanwhile, the reduced iron shell is being carburised, and the temperature is continuously rising. As the liquid oxide fraction increases, it will also tend to transferred from the core to metallic shell. This is due to reduction of overall free energy as the interfacial energy between liquid and Wustite is larger than that between liquid and metallic iron. This however does not cause exudation of the burden.^[13]

Softening is defined as the moment when the metallic burden can no longer withstand the action of mechanical forces. This generally coincides with the dripping of material from the burden component. The dripping will be a competition between increase in liquid slag

volume which increase the pressure on the shell, and the carbon content of the iron shell, which reduces its strength. Both these parameters tend to increase with temperature. The reduction degree will remain constant during this, because the reduction kinetics is slow after the reduction retardation. Thus, the dripping is triggered by the onset of melting in the oxide region, which in equilibrium occurs at the solidus temperature. The burden then subsequently melts and moves down to hearth where the hot metal layer and slag layer get separated due to the difference in their density. ^[13]

2.4.1. Shortness of a Slag:

The softening and melting phenomena of blast furnace slag is of vital importance in BF operation as it has a direct say over the productivity and efficiency of the process. The characteristic temperatures obtained from the flow characteristics of blast furnace slag includes: Initial Deformation Temperature (IDT), Softening Temperature (ST), Hemispherical Temperature (HT) and Flow Temperature (FT). The ST and FT rheologically signify the plastic distortion and liquid mobility of the blast furnace slag respectively. The difference between the flow temperature and softening temperature is termed as the 'shortness' of the slag. In a blast furnace operation, a short-slag is desirable as it trickles down the furnace as soon as it is formed thus exposing further reaction sites for better slagmetal reaction rates. Shortness of the slag has a direct impact over the furnace productivity as it controls he slag-metal reaction rates.

2.4.2. Flow Characteristics of Blast Furnace Slag:

High temperature microscope is used to determine flow characteristics of slag sample. It has got four characteristics temperatures to be studied:

- ✓ Initial deformation temperature (IDT)
- ✓ Softening temperature (ST)

- ✓ Hemispherical temperature (HT)
- ✓ Flow temperature (FT)

The followings are defined as per German Industrial Standards 51730.^[5]

Initial Deformation Temperature (IDT):

Initial deformation temperature is the temperature at which the first rounding up of the edges of the cube-shaped sample specimen takes place. In fact this is the temperature at which the first sign of the change in shape appears. Rheologically this temperature symbolizes the surface stickiness of the slag.

Softening Temperature (ST):

It is the temperature at which the outline of the shape of the sample starts changing and is reported as the temperature at which the sample shrinks by one division or the temperature at which the distortion of the sample starts. Rheologically this temp symbolizes the start of plastic distortion.

Hemispherical Temperature (HT):

It is the temperature at which the sample has fused down to hemispherical shape and is measured as the temp at which the height of the sample is equal to the half of its base length. This is defined as the fusion point or the melting point in Germen Industrial Standards 51730^[5]. Rheologically this temperature symbolizes the sluggish flow of the slag.

Flow Temperature (FT):

It is the temperature at which the sample liquifies and is reported as the temperature at which the height of the sample is equal to one-third of the height that it had at HT (hemispherical temperature). Though some books reported as the temperature at which the height becomes one third of the initial height. The former is more accurate and is universally accepted. Rheologically this temperature symbolizes the liquid mobility of the slag.

2.5. Methods for measuring Liquidus Temperature

2.5.1. Pressure Drop Technique:

The softening-meltdown properties of ferruginous material have very important bearing on the furnace operation including pressure drop, distribution of hot ascending gas, fuel rate, hot metal quantity etc. Accordingly, it is desirable to assess the suitability of the iron bearing raw material, prior to their use in the blast furnace, in the laboratory, under simulated conditions. The basic purpose of the softening-melting test is to evaluate the softening-melting characteristics of iron ore and sinter sample taken in a small cylindrical graphite crucible by simulating the physical and chemical conditions in the shaft till the cohesive zone of blast furnace. This simulation study under laboratory conditions is carried out by subjecting the sample to pre-programmed time dependent variation of temperature, reducing gas composition and load. Behaviour of the sample in the test can be characterized by measuring changes in the sample bed height, gas-pressure drop across the sample bed, bed shrinkage, identifying softening and melting temperatures and calculating degree of reduction and percentage non-dripped material (NDM).^[14]

The parameters that are programmed/ set/ controlled in the apparatus for each experiment is as follows:

- ✓ Rate of heating, that is, Time Vs Temperature: using the programmable temperature controller
- \checkmark Gas mass flow rate: using the mass flow controller
- Temperature at which reducing gas enters the reaction tube: using the programmable temperature controller
- \checkmark Load applied on the sample bed using the pressure regulator

✓ Temperature at which the melt collection chamber changes its position using the programmable temperature controller



Figure 1. Softening and melting characteristics of Pressure Drop technique

2.5.2. Slag Atlas:

In the present work, Slag Atlas is used as an important tool for estimation of liquidus temperature of BF slags. For example let us consider the following iso-liquidus diagram for CaO-SiO₂-MgO-Al₂O₃ system with a fixed Alumina content of 20%. The left end of the horizontal axis signifies 100% CaO and the right end of the horizontal line signifies 100% MgO. For estimation of liquidus for a slag system with x% CaO and y% MgO we proceed as follows. For MgO content we start from the opposite side of its end and we draw a line parallel to the side of the triangle situated at that end at y%. Similarly, for CaO content, we start from the opposite end of its end and draw a line 1t 35%. The intersection point of these two lines defines the slag chemistry. And the liquidus line closest to this point estimates its value. We can also consider SiO₂ content and MgO content or CaO content and SiO₂ content for the estimation and we will get the same result. ^[15]



Figure 2. Slag atlas for liquidus temperature estimation for slag with 20% Al₂O₃

2.6. Effect of Slag Constituents on Viscosity:

Slag viscosity is a transport property that relates to the reaction kinetics and the degree of reduction of the final slag ^[16]. It determines the slag– metal separation efficiency, and then the metal yield and impurity removal capacity. The slag viscosity is sensitive to its ionic and molecular structure because the strong network in the vast silicate structure present in the slag results in an increase in viscosity. In operation, the slag viscosity indicates the ease with which slag could be tapped from the furnace, and therefore relates to the energy requirement and profitability of the process. In India, generally a high Alumina slag is generated due to

the quality of raw materials and coke available in the country. Thus it is necessary to study the effect of Alumina on slag viscosity. An increase in Alumina content of the slag leads to an increase in its viscosity and moreover, the effect of Alumina on slag viscosity depends on the lime content of the slag, because Al^{3+} can replace Si^{4+} in the silicate network only if it is associated with $\frac{1}{2}Ca^{2+}$ to preserve electrical neutrality.^[17]

Y.S. Lee et al ^[18] studied the viscous behaviour of CaO-SiO₂-Al₂O₃-MgO-FeO slag under conditions of C/S = 1.15-1.6, 10-13 mass% Al₂O₃, 5-10mass% MgO and 0-20% FeO. Viscosity of the slag decreased with increasing slag basicity up to 1.3 while it increased in the range 1.3 to 1.5. The driving force for the decrease in slag viscosity could be an increase in depolymerisation of silicate network at C/S≤1.3, while the viscous behaviour at C/S>1.3 could be increased with increase in the chemical potential of primary solid phase *e.g.* dicalcium silicate. It was confirmed that slag viscosity in highly basic slags (C/S>1.3) can be estimated by the chemical potential of dicalcium silicate.

Amitabh Shankar et al ^[17] studied the viscous behaviour of CaO-SiO₂-MgO-Al₂O₃ and CaO-SiO₂-MgO-Al₂O₃-TiO₂ system by varying the C/S ratio between 0.72 and 1.23 in the temperature range of 1573-1873 K. Alumina content was varied between 21-28%, Magnesia was varied between 2-8% and Titania was varied between 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. Muller et al ^[16] calculated the effective viscosities for typical blast furnace slag with different basicity at 1500°C with different FeO and Al_2O_3 content. They found that slag viscosity goes on decreasing with increase in slag basicity. An increase in slag basicity means

increase in CaO and MgO content which act as silicate bond breakers, thus accounting for the decrease in viscosity.

As the temperature dependence of viscosity is more pronounced for low basicity slags and the working temperature inside the furnace is pretty high, generally slags in the basicity range of 0.95-1.05 should be used. Increasing the basicity further may result in an increase in viscosity as reported by Y.S. Lee *et al* ^[18].

Noritaka Saito et al ^[19] studied the effect of MgO on the viscosity of 40CaO-40SiO₂-20Al₂O₃ slags. They have shown that viscosity of this slag system decreases with increase in MgO content. It has been suggested that MgO works as a network modifier and thus decreases the viscosity. The activation energy for viscous flow also decreases on the addition of MgO.

Y.S. Lee et al ^[20] studied the influence of MgO and Al₂O₃ contents on the viscosities of blast furnace slags containing FeO. The viscosities of CaO-SiO₂-Al₂O₃-MgO-FeO slag were measured under conditions of C/S 1.35-1.45, 10-18% Alumina, 3.5-10% MgO and 5% FeO. They found that on increasing Al₂O₃ content, the viscosity of the slag increased at fixed C/S and MgO content. The viscosity of the slag showed a minimum value at around 7% MgO at temperatures above 1723 K. However, it was not significantly changed with varying MgO content.

Kohei Sunahara et al ^[21] studied the effect of high Al₂O₃ 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 Al₂O₃, 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. *Yasuji Kawai* ^[22] studied about the viscosities of molten slags and the viscosities of CaO-SiO₂-Al₂O₃-MgO slags. When MgO was added to CaO-SiO₂ slags, the viscosity decreased with increasing amount of MgO up to about 20%. However, beyond 20%, the viscosity increased. The region of low viscosity was greater than that in CaO-SiO₂-Al₂O₃ slag.

Masashi Nakamoto et al ^[23] studied the viscosity of molten slags with low melting point to develop an improved blast furnace operation at lower temperature such as 1673 K. They measured the viscosities of molten CaO- SiO₂-MgO-Al₂O₃ slag by rotating cylinder method and compared with the results of the model developed. They showed that slag with composition 35% Al₂O3-43.1% CaO-7.5% MgO-14.4% SiO₂ has melting temperature below 1673 K and has a viscosity less than 0.6 Pa.s below 1673 K.

Seong-Ho Seok et al ^[24] studied the viscous behaviour of CaO-SiO₂-FeO-MgO melts saturated with dicalcium silicate with 8% MgO at 1873 K and of CaO-SiO₂-FeO-Al₂O₃-MgO slags under highly basic conditions. They showed that the viscosities of the slags depend more strongly on Alumina content than on Magnesia content as the fraction of solid phases present is more in the case of variation in alumina content.

J.Y. Jia et al ^[25] studied the calculation models on the viscosity of CaO-SiO₂-TiO₂ slag system. The mass action concentration calculation model and viscosity calculation model are established, according to the coexistence theory of slag structure. Values are recorded under different temperatures and compositions for the CaO-SiO₂-TiO₂ ternary slag system. They have found that with increasing TiO₂ per cent in slag, viscosity of slag decreases.

Amitabh Shankar et al ^[17] studied the effect of TiO_2 on the viscosity of blast furnace slags in the temperature range of 1573-1873 K. TiO_2 decreases the slag viscosity marginally for low basicity slag (~0.5). But for high basicity slags (~0.8), slag viscosity deceases even with 2%

addition of TiO_2 . 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_2 containing slags. With increase in silica activity, the Arrhenius activation energy for viscous flow increases.

The viscosity of molten slag in blast furnace operations is an important process variable, influencing the rate and location of reactions inside the furnace. It also influences the ease with which the final slag could be removed from the furnace. In order to optimize these processes, it is necessary to estimate the slag viscosity and liquidus temperatures accurately, and know the target values. Some models to predict viscosities and liquidus temperatures, incorporating phase equilibrium calculations, have been developed and validated with measured data. ^[16]

The models developed are based on phase equilibrium calculations, using thermodynamic data set up for specific metallurgical systems. In the models developed, FactSage software was used to perform phase equilibrium calculations, using the contained thermodynamic data mostly from the FToxid and FACT53 databases, as per the metallurgical system.

The effective viscosity is the liquid viscosity of the slag, also considering the precipitated solids from the liquid slag. The phase equilibrium calculation results are subsequently used to determine the volume percentage of all the solid phases forming. This is used to correct the liquid viscosity for possible solids by using the Roscoe equation:

$\eta_{\text{liq}} = \eta_{\text{eff}} (1 - 1.35 \phi)^{-2.5}$

Where η_{liq} is the liquid viscosity (Poise), η_{eff} the effective viscosity (Poise), and ϕ is the volume fraction of solids predicted in the molten slag.^[16]

The liquidus temperature model also uses phase equilibrium calculations by minimizing the Gibbs free energy in the FactSage software. The viscosity model was used to estimate the slag temperature required for a specified viscosity of a slag composition.

Considering all control objectives, a global optimum has to be found in which costs are minimized while all the other controlled variables fall within their limits.

Model Results:

- ✓ First the validation of the model was done by comparing it with the data available from various literatures and the error (if any) was found out. The relation between the predicted and measured viscosities is better at lower viscosities at higher temperatures than at higher viscosities.
- ✓ A plot of the Roscoe Equation was plotted which shows the strong exponential effect of solids on the viscosity of the slag. The difference between the predicted liquid viscosity and the measured viscosity is found to be higher at low temperatures as the solid precipitation is greater.
- ✓ For pictorial representation, ternary diagrams for effective viscosity, liquidus temperature and volume factions of solids present were constructed for the quaternary system of SiO₂- MgO- CaO- Al₂O₃ with 12.5% Al₂O₃.
- ✓ Effective viscosities were calculated for typical blast furnace slag with different basicity at 1500°C with different FeO and Al₂O₃ content. The slag viscosity decreases with increasing FeO content as FeO acts as a silicate bond breaker. Viscosity goes on decreasing with higher basicity due to the same effect of CaO and MgO but this happens up to the point where the solids in the slag phase start to precipitate. When this happens, the viscosity increases. Viscosity increases with Al₂O₃ content when the temperature is below the liquidus temperature.

- ✓ Effective viscosities were calculated for typical BF slags with a fixed basicity of 1.5 at different temperatures for varying Al₂O₃ and FeO content. With FeO content fixed, viscosity increases with increase in Alumina content. The liquidus temperature also increases due to significant increase in viscosity at low temperatures due to formation of solids.
- ✓ Effective viscosities were calculated for typical BF slags with a fixed Alumina content of 10% at different temperatures with different basicity and FeO content. It was observed that with a fixed Alumina content, the viscosity is lower and the liquidus temperature is higher for higher basicity.
- ✓ The models were applied to historical data for analysing the performance based on Viscosity and Liquidus Temperature, and also target values were calculated for process optimisation. ^[16]

2.7. Effect of Slag Constituents on Liquidus Temperature:

The liquidus temperature influences the position and width of the cohesive zone which directly controls the productivity of the blast furnace operation. The positioning and width of the cohesive zone controls the gas permeability, Si content in the hot metal and the extent of indirect reduction inside the furnace. Thus the determination of liquidus temperature of the slag is of vital importance.

The liquidus temperature has been mentioned by different terms by different scientists. *Osborn* ^[9] and *Snow* ^[10] reported liquidus temperature as the temperature at which the first crystal forms during cooling down the melt. *Ohno et al* ^[11] reported it as the temperature at which the last crystal disappears during heating. German Industrial Standards 51730 defines it as the hemispherical temperature, *i.e.*, the temperature at which a small mass of the slag assumes the shape of a hemisphere on heating. The heating microscope method is adopted to measure this hemispherical temperature. When a pyrometallurgical process is carried out in a furnace, it is the flow characteristics of the non-metallic melts (*i.e.*, the mixture of oxides which would combine to make the slag) which is more important than the exact fusion temperature. The flow characteristics are defined in terms of four characteristic temperatures. These are; the initial deformation temperature (IDT), symbolising the surface stickiness; the softening temperature (ST), symbolising the plastic distortion; the hemispherical temperature (HT), which is also the liquidus temperature, symbolising sluggish flow; and the flow temperature (FT), symbolising liquid mobility.

R.K. Verma et al ^[26] studied the effect of basicity on the solidus and liquidus temperature of the blast furnace type slags. They have found that, generally liquidus and solidus temperatures are high for higher basicity slags. They have also studied the effect of Al_2O_3 on the solidus and liquidus temperature of blast furnace type slags. They have concluded that the solidus temperature is the lowest in the range of 30-33% Alumina content for both high and low basicity slags. For higher basicity slags (B-1.66), addition of Alumina initially increases the liquidus temperature but later decreases. Liquidus temperature of lower basicity slags (B-0.82) decreases marginally up to 32-33% Alumina content and then increases. For the intermediate basicity slags (B-1.38), solidus and liquidus temperature increase with Alumina content.

H.A. Fine et al ^[27] studied the effect of minor constituents on the liquidus temperature of blast furnace slags determined at an oxygen potential of 10^{-15} atm. The slag samples contained 10% Alumina and had V ratios between 0.94 and 1.13. They have found that the effect of Titania on the liquidus temperature of the slag is strongly dependent on the oxygen potential. At low oxygen potentials, Titanium Oxide increases the liquidus temperature of the slag, while at high oxygen potentials; it decreases the liquidus temperature of the slag.

Experimental

3. Experimental

3.1. <u>Sampling:</u>

Coning and quartering sampling technique is used, which is the reduction in size of a granular or powdered sample, by forming a conical heap which is spread out into a circular, flat cake. The cake is divided radially into quarters and two opposite quarters are combined. The other two quarters are discarded. The process is repeated as many times as necessary to obtain the quantity desired for some final use (e.g. as the laboratory sample or as the test sample). If the process is performed only once, coning and quartering is no more efficient than taking alternate portions and discarding the others. ^[28]



Figure 3. Coning and Quartering ^[29]

3.2. Testing:

High temperature microscope is used to determine flow characteristics of slag sample. It has got four characteristics temperatures to be studied:

• Initial deformation temperature (IDT)

- Softening temperature (ST)
- Hemispherical temperature (HT)
- Flow temperature (FT)

These temperatures have already been defined as per German Industrial Standards 51730.

The Heating Microscope method is adopted for recording the characteristic temperatures. A picture of the Leitz heating microscope is shown in Fig.4. Schematic diagram of the instrument is presented in Fig.5. The sample, in the form of a 3 mm cube, is heated in an electric furnace in the microscope assembly. The shape change of the sample as a result of heating is photographed by a camera. A grid-division which is simultaneously photographed with the sample and the temperature to which the sample is being heated facilitate identification of the four characteristic temperatures. The four temperatures are reported as follows by following the German Industrial Standard 51730.



Figure 4. High Temperature Microscope



Figure 5. Line diagram of High Temperature Microscope

- 1. Cooling water tank
- 2. Cooling water recirculating tank
- 3. Light source
- 4. Regulating transformer for light source
- 5. Optical bench
- 6. High temperature electrical furnace with specimen carriage
- 7. Observation and photo microscope
- 8. Digital thermometer
- 9. Regulating transformer for high temperature electrical furnace

The different steps for determining the flow characteristics are as follows.

- ✓ The sample, in the form of a 3 mm cube, is heated in an electric furnace in the microscope assembly.
- \checkmark The shape change of the sample as a result of heating is photographed by a camera.
- ✓ A grid-division which is simultaneously photographed with the sample and the temperature to which the sample is being heated facilitate identification of the four characteristic temperatures.
- \checkmark The temperature, at which the sample just starts to deform a bit, is reported as IDT.
- ✓ The temperature, at which the sample has already shrunk by exactly one division or at which the cube starts to swell, is reported as ST.

- ✓ The temperature, at which the sample takes the shape of a hemisphere with its height to diameter ratio 1:2, is reported as HT.
- ✓ The temperature, at which the height of the sample reduces to one-third of the height measured at HT, is reported as FT.

In present work, each slag has been tested twice (once each for each one of the alternate quarters).

Results and Discussions

4. <u>Results and Discussion</u>

The flow characteristics of 14 blast furnace slag samples were measured using the high temperature microscope. The flow characteristics four characteristics temperature, viz. Initial Deformation Temperature (IDT), Softening Temperature (ST), Hemispherical Temperature (HT) and Flow Temperature (FT). The flow characteristics of the samples are represented in table 2 and figure 6.



Figure 6. Flow Characteristics of Blast furnace slag sample

4.1. Liquidus Temperature Measurement:

The difference between liquidus temperature measured through the two methods reported above are presented in Table 1 and Fig 7.

Sample No	HT from Present	HT from Slag	Difference	% Error
	work in °C (X)	Atlas in °C (Y)	Abs(X-Y)	$(\frac{X-Y}{X}*100)$
1	1318	1325	7	0.53
2	1274	1290	16	1.25
3	1345	1350	5	0.37
4	1266	1280	14	1.11
5	1335	1330	5	0.37
6	1363	1350	13	0.95
7	1307	1310	3	0.23
8	1362	1380	18	1.32
9	1310	1300	10	0.77
10	1324	1310	14	1.06
11	1331	1320	11	0.83
12	1323	1320	3	0.23
13	1326	1320	6	0.45
14	1324	1320	4	0.30

Table 1 - Liquidus temperatures of slag samples as obtained from present work and slag atlas



Figure 7. Comparison between liquidus temperature values obtained from present work and slag atlas

It is clearly established that the average difference between liquidus temperatures measured by the hot stage microscopy method and that estimated using slag atlas agree closely. The difference is $\pm 0.66\%$ maximum, the minimum deviation being 0.22% and the maximum being 1.32%.

Thus the high temperature microscopy method adopted in the present work renders comparable results in relation to the age-old slag atlas method and can be considered as a novel method for estimating characteristic temperatures of the blast furnace slag.

4.2. Effect of basicity (C/S ratio or B₂) on characteristic temperatures:

The variation of ST, HT and FT with C/S ratio is presented in Table no 2 and Figure 8. The flow temperature decreases with increase in the C/S ratio, the rate of decrease of the flow temperature decreasing with increase in the C/S ratio.

Serial	CaO %	SiO ₂ %	MgO%	$AI_2O_3\%$	C/S	IDT	ST	HT	FT	FT-ST
No						°C	°C	°C	°C	°C
1	34.04	32.05	10.09	19	1.062	1203	1271	1318	1383	112
2	33.25	30.84	11.01	20.89	1.078	1220	1240	1274	1330	90
3	35.1	32.24	10.4	18.77	1.089	1210	1324	1345	1400	76
4	33.4	31.3	10.4	19	1.067	1204	1245	1266	1368	123
5	32.55	31.58	10.4	20.28	1.031	1225	1315	1335	1423	108
6	33.61	32.05	10.09	20.05	1.049	1217	1330	1363	1410	80
7	30.85	30.85	9.79	18.54	1.000	1200	1251	1307	1388	137
8	36.2	34.6	7.05	17.9	1.046	920	1220	1362	1376	156
9	34.57	36.72	6.51	19.04	0.941	827	1148	1310	1420	272
10	34.15	34.06	6.5	18.07	1.003	810	1224	1324	1370	146
11	31.9	33.5	10.4	20.8	0.952	817	1217	1331	1373	156
12	31.9	33.7	10.5	20.6	0.947	820	1195	1323	1392	196
13	31.6	33.9	10.6	20.6	0.932	813	1216	1326	1390	174
14	31.8	33.8	10.5	20.6	0.941	818	1224	1324	1393	169

Table 2 - Composition and flow characteristics of blast furnace slags



Figure 8. Variation of different characteristic temperatures with C/S ratio

This is because the addition of the basic oxide CaO to the silicate network breaks down the network resulting in formation of smaller silicate groups known as anionic units or flow units.^[30] The net effect is reduction of viscosity. However, since smaller and smaller flow units require relatively higher oxygen, rendered by the addition of higher amounts of basic oxide, the progressive increase in metal oxide content is less and less effective in decreasing the flow unit size. This explains the decrease of flow temperatures at a decreasing rate with increase of the C/S ratio.^[31]



Figure 9. Variation of (FT – ST) with C/S ratio

It is further observed that the ST increases with the C/S ratio. The net result is that with the increase in the C/S ratio the difference between FT and ST decreases (Figure 9). It may be appreciated that in the blast furnace it is necessary to have a narrow softening-flowing range rather than a sharp low liquidus temperature. Such a situation would generate a 'Short Slag', i.e. , as soon as the slag softens, though the volume shrinks and the permeability of the bed is adversely affected, such a slag trickles down away from the site without necessarily requiring any higher availability of thermal energy. From this point of view alone it may be concluded that under the experimental conditions and within the range of compositions studied, higher values of C/S ratios are beneficial to the blast furnace process.

4.3. Effect of MgO content on the characteristic temperatures:

The variation of the characteristic temperatures with the MgO content is presented in Table 2 and Figure 10.



Figure 10. Variation of different characteristic temperatures with MgO content

It is observed that the ST increases with increase in MgO content and though the trend is not very clear, the FT decreases with the increase in the MgO content in general. Thus, higher MgO contents within the range of compositions examined tend to generate 'Short Slags', decreasing the difference between the FT and ST in general. Under the blast furnace conditions if we consider slags with softening-flowing range to be less than 100°C, it can be seen form Table 2 that slag nos. 2, 3 and 6, having a combination of high C/S ratio and high MgO content result in short slags. This is in line with the work done by V.K. Gupta et al and R.N Singh ^[32, 33]. They observed that a high MgO combined with a high C/S ratio results in a short slag.

Conclusion

5. Conclusion

The basic conclusions that are drawn from the analysis of the experimental data can be enumerated as follows:

- 1. The high temperature microscopy is a novel method for determining the characteristic temperatures (flow characteristics) of blast furnace slag.
- Under the range of compositions examined a high C/S ratio is beneficial for the blast furnace process as it ensures the formation of a 'Short Slag'.
- Increased MgO content combined with a high C/S ratio form 'Short Slags' which is advantageous to blast furnace process

Future Scope:

In the present work the final slag i.e. hearth slag has been tested and analyzed. The future scope would include the study of flow characteristics of the primary slag i.e. the slag generated in the cohesive zone. Such a study would predict the location and extent of the cohesive zone having a direct bearing with the coke consumption, quality of metal produced and operation of the blast furnace process; indirectly addressing the greenhouse problem to a great extent.

<u>References</u>

References

- Nogueira Paulo F. and Fruehan Richard J., Metallurgical and Materials Transactions B, 35 B, 2004, p 829
- Kaushik P. and Fruehan Richard J., Ironmaking & Steelmaking, 33, No. 6, 2006, pp. 507-519
- Clixby G., Softening & Melting of super fluxed sinters and acid pellets, BSC, Ironmaking Session, Tesside Laboratories, International Report, 1979
- 4. Potebnyaj et al, Steel USSR 3, 1973
- 5. German Industrial Standard 51730
- Taskanen P.A., Huttunen S.M., Mannila P.H. and Harkki J.J., *Ironmaking & Steelmaking*, 29, 2002, pp. 281-286
- Gupta S.S. and Chatterjee A., Iron Making and steel making theory & practice, SBA Publication, 1995
- 8. Muller M. Erwee, Southern African Pyrometallurgy, 2011
- Osborn E. F. et al., Process Blast Furnace, Coke Oven and Raw Materials Conference, 1953
- 10. Snow R. B., Proc., AIME, 1962
- 11. Ohno A. and Ross H. U., Can. Metall. Q., 2, 1963, p 243.
- 12. Kaushik P. and Fruehan R.J, Iron Making and Steel Making, 2004
- Kaushik P. and Fruhen J., Mixed Burden Softening and Melting, Iron Making and Steel Making, Volume 33(Issue 6), 2006, pp. 507-519
- 14. Roy P.K., Mishra U.N. and Pal S., R&D Centre for Iron and Steel, SAIL, Ranchi
- 15. Slag Atlas
- 16. Muller J. And Erwee M., Southern African Pyrometallurgy, 2011

- Shankar Amitabh, Gornerup Marten, Lahiri A.K, Seetharaman S., Experimental Investigation of the Viscosities in CaO-SiO₂-MgO-Al₂O₃ and CaO-SiO₂-MgO-Al₂O₃-TiO₂ Slags, Metallurgical and Materials Transactions B, 38 (6), pp. 911-915
- Lee Y.S., Kim J.R., Yi S.H. and Min D.J., VII International Conference on Molten Slags Fluxes and Salts, The South African Institute of Mining and Metallurgy, 2004.
- Noritaka Saito, Naoto Hori, Kunihiko Nakashima and Katsumi Mori, Metallurgical and Materials Transactions, Volume 34B, October 2003
- 20. Lee Y.S., Kim J.R., Yi S.H., Min D.J. and Jung S.M., ISIJ International, Vol. 44, No.8, 2004, pp. 1291-1297
- 21. Sunahara Kohei, Nakano Kaoru, Hoshi Masahiko, Inada Takanobu, Komatsu Shusaku and Yamamoto Takaiku, ISIJ International, Vol. 48, No. 4, 2008, pp. 420-429
- 22. Kawai Yasuji, Viscosities of CaO-SiO₂-Al₂O₃-MgO Slags
- Nakamoto Masashi, Tanaka Toshihiro, Lee Joonho and Usui Tateo, ISIJ International, Vol. 44, No. 12, 2004, pp. 2115-2119
- 24. Seok Seong-Ho, Jung Sung-Mo, Lee Young-Seok and Min Dong-Joon, ISIJ International, Vol. 47, No. 8, 2007, pp. 1090-1096
- 25. Jia J.Y., Bai C.G., Qiu G.B., Chen D.F. and Xu Y, VII International Conference on Molten Slags, Fluxes and Salts, the South African Institute of Mining and Metallurgy, 2004
- 26. Verma R.K., Ray H.S., Ghosh A., Singh R.N and Dharnipalan S., Transactions of Indian Institute of Metals, Vol. 32. August 1979
- 27. Fine H.A. and Arac S., Ironmaking and Steelmaking, 1980
- 28. IUPAC Compendium of Chemical Terminology, 2nd Edition, 1997
- 29. http://www.cwc.org/glass/gl_htm/gl979rpt.htm/12-02-2012

- Mohanty U.K., Thermo physical properties of some metallothermic slags, Ph.D.
 Dissertation, R.E. College, Rourkela, 1998
- 31. Behera R. C., Mohanty U. K., and Mohanty A. K., High Temperature Materials and Processes, 9, 1990, pp. 57-75
- 32. Gupta V.K. and Sheshadri V., Transactions of Indian Institute of Metals, 26, 1973, pp. 55-64
- 33. Singh R.N., Steel India 7, 1984, pp. 73-83
- Biswas A.K., Principles of Blast Furnace Ironmaking, Calcutta: SBA Publications, 1984
- 35. Ghosh Ahindra and Chatterjee Amit, Ironmaking and Steelmaking Theory and Practice, New Delhi: PHI Learning Private Limited, 2010