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MODELLING OF HIGH ALUMINA BLAST FURNACE SLAG RHEOLOGY[1]

Kakali Mukherjee[2]
Swatantra Prakash[2]

Abstract

Blast furnace performance depends primarily on the performance characteristics of input/ raw materials viz. iron ore, coal, fluxes etc in the furnace. Iron ore quality is increasingly deteriorating with respect to high alumina-silica ratio, occasionally alumina in iron ore becomes even higher than 20%. It causes the blast furnace operations to maintain high heat levels (>1530 C) to ensure good hearth drainage performances and consequently improving the blast furnace stability and productivity. Besides, high alumina affects the slag viscosity; it adversely affects the blast furnace operation both in terms of enhanced energy consumption and CO_2 emission. It is, therefore, inevitable to carry out a systematic research work to optimize blast furnace slag chemistry at high alumina contents. BF slags systems generally comprising Al_2O_3, SiO_2, CaO, Fe_nO, MgO, MnO etc. possess network structure. It greatly influences the rheological characteristics of the slag system. In this work the effect of alumina on the slag rheology and its flow characteristics is presented in the paper. The paper also presents a rheological model of blast furnace slag system containing high alumina.

Key words: Blast furnace (BF), High alumina Slag, Flow behaviour, Network structure, Rheological model.

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[2] *CSIR-Scientist, CSIR-National Metallurgical Laboratory, Jamshedpur, India – 831007.*

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1 INTRODUCTION

Blast furnace slag viscosity and its flow characteristics affects the hot metal quality, furnace operation in the cohesive and hearth zone, fuel consumption, hearth drainage performance, etc. The slag characteristics invariably depends on the quality of raw /inputs materials viz. Iron ore, flux, coke / coal, sinter, lump, pellets etc. In high temperature processes, mass transport being the rate-controlling factor, the viscosity of the slag system determines the kinetics of the refining reactions. It is accompanied by mass and heat transfer at the slag metal interface. The viscosity and flow behaviour of the slag depends on its internal structure and on the chemical composition of the slag system. Any changes in the chemical composition of slag essentially affects its overall characteristics. The typical blast furnace slag systems comprising Al_2O_3, SiO_2, CaO, Fe_nO, MgO, MnO etc. form complex internal structure. The dependence of these structures on composition and temperature lead to an abrupt and complicated viscosity changes of the slag systems [1].
The furnace operations thus depend on the liquidus temperature, viscosity, and fluidity of the slag system. Several investigators [2-6] indicated that the lower liquidus temperature and corresponding viscosity can cause stability of various slag constituents viz., MgO, Al_2O_3 for the range of composition at a given basicity. The slag fluidity gets affected mainly by increasing/ decreasing Al_2O_3 content depending on the composition of the slag constituents. The viscosity of the slag affects the gas permeability in addition to the heat transfer, and the reduction of SiO_2, FeO etc.. it is therefore necessary to optimize the rheology of the slag system for a given BF input materials that can provide good fluidity even at low temperatures. There are several data reported on viscosity of blast furnace slags. But most of the data are mainly for slags with low alumina content in the range of 10-15% [2-6]. Molten slags produced during metal extraction normally exhibit a network structure of oxides of various elements. Each oxygen atom is bonded to various atoms of these elements in a three dimensional network. It can generally be referred to the weakly ordered regions within the slag volume. This network structure of molten slag in-turn influences their physico-chemical properties.
Viscous flow in slag depends on the mobility of ionic species in the system, which in turn depends upon the nature of the chemical bond and the configuration of ionic species. The inter-ionic forces in the case of slags depend upon the sizes and charges of ions involved. Thus the stronger inter-ionic forces may lead to an increase in viscosities. In the case of silicate melts with high silica contents the polymeric anions cause a high viscosity. With increase of the basic oxide concentrations, the Si-O bonds progressively breakdown and size of network decreases accompanied by lowering of the viscosity of slags. However, the addition of alkali oxides up to 10-20 mol% leads to a drastic fall in the viscosities due to depolymerization [7].
The blast furnace slag invariably contains alumina, and the AlO_4^{5-} group form polymer units with SiO_4^{4-}. In the slag containing CaO-MgO-SiO_2-Al_2O_3 alumina normally increase the viscosity as silica does. Whereas CaO and MgO being the suppliers of oxygen exhibits the opposite effect on viscosity. Both an increase of basic oxides and that of temperature above liquidus of the slag decrease viscosity. For CaO-MgO-SiO_2-Al_2O_3 system, alumina and silica are normally not equivalent on molar basis in their effect although both increase the viscosity of their melts. The effect of the former on viscosity depends on the lime content of slag. This is because Al^{3+} can replaceSi^{4+} in the silicate network only if associated with ½ Ca^{2+} to preserve electrical neutrality.The slag viscosity models must take the network structure into

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account. It is, therefore, desirable to have a quantitative description of the slag which can represent the network structure reliably and characterise the slag rheology more precisely. It can adequately be adopted by including the treatment of the non-Newtonian behaviour as exhibited by some molten slag systems prevailing in real processes. Iida et al. [8] defined the network structure of the slag using a parameter Ψ,

$$\Psi = \log \left[\frac{\mu}{\mu_0}\right]^2 \quad (1)$$

and formulated a model equation[2,9,10] employing the slag components and relating the structure to the parameters representing the basicity of the slag:

$$\mu = A\,\mu_0\,\exp\left[\frac{E}{Bi^*}\right] \quad (2)$$

Iida et al. measured the viscosity experimentally and validated the results of different models for different slag systems at various temperatures. The empirical equations used in their paper help determine the slag viscosity by using a parameter (Ψ) derived from the ratio of the viscosity of the non-network to network fluids. The parameters (Ψ,E,Bi*etc) are derived from the ratio of the viscosities of the slags possessing network and non-network structures and are, therefore, relative in nature. These may not necessarily define the network structure of the slag. The discrepancies in the results can perhaps be minimized by defining the network structure of the slag in terms of system parameters. The paper, besides defining slag viscosity/consistency index, presents such parameters, that are able to characterize the flow behaviour and its dependence on the network structure of the slags containing high alumina.

2 EXPERIMENTAL

The experimental programme involved a high temperature rheometer essentially consisting of two concentric cylinders: the inner of which rotates while the outer is held stationary. Viscosity is determined by measuring the rate of rotation of the inner cylinder under the application of a known torque.

2.1 Apparatus

Figure 1 shows the experimental apparatus employed in the present study. It exhibits some essential features of a commercial high temperature viscometer (Model: DV-III) based on rotating cylinder method and controlled by a PC. It comprised 32 bit instrument control and data acquisition software facilitates, temperature programming, instrument calibrating and verification tests, temperature data correction. The viscosities were calculated from the torque and corresponding rpm on line using the software. The working formula for the Rotational viscometer is given below.

$$\left[\frac{\tau\left(\frac{1}{r_i^2}-\frac{1}{r_o^2}\right)}{8\pi^2 h}\right] = \mu\,(\mathrm{N}) \quad (3)$$

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Where,

- τ = Torque, Nm; N= No. of revolution per sec,(sec^{-1}); h= height of Rotor, m;
- r_i, r_o = radius of rotor and crucible respectively, (m); μ = viscosity

The viscometer comprised alumina crucible (height 65mm, outer diameter 35 mm, inner diameter 29 mm, alumina rotor, and a resistance furnace employing long hairpin $MoSi_2$ heating element rated for 1700^{0}C with super B control thermocouple. The heating element is provided with protection tube and with three axis positioning adjustment. The rotor bob (16 mm diameter and 16 mm in height) is hinged with the shaft of 4 mm diameter and length 50 mm. The crucible could be moved with two supporting and one movable stand along the vertical direction to the furnace by a hydraulic moving system. The temperature of the slag was measured by Pt-Rh thermocouple.

2.2 Synthetic Slag Preparation

Synthetic slags (12 nos.) were formulated based on the typical Indian blast furnace slag system as shown in Table 1.

Table 1 Chemical composition ranges of the typical Indian blast furnace slag

Comp.	SiO_2	CaO	MgO	Al_2O_3	FeO	TiO_2	S	LOI
%	23-37	24-37	19-20	10-33	0.02-1.05	0.026-1.59	0.18-0.22	1.75

Twelve synthetic slags, each weighing about 1.0 kg, were prepared in the graphite crucible of dimension (ID=55mm, OD=75mm,. Height $_{External}$.= 175mm, and bottom thickness = 15mm). The synthetic slags mainly comprised SiO_2, CaO, MgO, Al_2O_3, FeO. These slag samples were prepared by using reagent-grade chemicals. According to their compositions, these were weighed poured and melted in the graphite lined induction furnace of (5 kg) capacity in the temperature range of (1750°C–1870°C). The molten material was then poured in another graphite crucible to cool down. The fused slag was ground to -10 mesh size then crushed in the Denver ball mill to -32+35 mesh size. Of this material, around 50 gm sample was further ground to -100 mesh size in the planetary ball mill for chemical analysis. The chemical analyses of twelve no. of synthetic slag (12 nos.) are given in Table 2.

2.3 Viscosity Measurement

Alumina beakers/crucibles and alumina rotors (comprising a bob and a shaft) were employed in all the experiments, as shown in Figure 1. About 3/4th of the alumina crucible was filled up with the solid slag. The crucible containing the slag was placed in between the three stands of beaker holder rods mounted vertically from the top of the viscometer and can go inside the furnace as and when required.

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Table 2: Chemical Analysis of BF type synthetic slag

Comp. %	Slag Samples											
	1	2	3	4	5	6	7	8	9	10	11	12
SiO2	36.97	34.51	34.79	32.63	31.08	28.62	23.5	24.12	23.76	33.58	27.37	27.73
CaO	35.89	36.2	35.32	24.67	29.65	31.53	32.72	34.66	31.53	35.8	29.64	27.77
MgO	14.69	14.22	13.28	19.07	15.24	14.36	13.17	11.83	10.55	10.6	9.65	9.65
Al2O3	10.18	13.27	14.27	18.23	20.07	20.45	28.19	27.06	30.61	18.4	29.97	32.36
FeO	0.53	1.05	0.77	0.76	0.81	0.82	0.02	0.92	0.66	0.52	0.53	1.05
TiO2	0.03	0.028	0.026	0.77	1.58	1.59	0.027	0.027	0.027	0.027	0.026	0.028
S	0.18	0.19	0.19	0.21	0.2	0.21	0.22	0.22	0.21	0.19	0.22	0.2
Basicity	0.97	1.049	1.015	0.938	0.954	1.102	1.392	1.437	1.327	1.066	1.083	1.001

The whole assembly is clamped in the viscometer bottom base by the crucible holders in between these holders using two fixed and one movable alumina rolds. The alumina bob was connected to the rotor by the suspending wire connection. To keep the rotor bob always rotating in the centre of the crucible, a triangular platinum wire base was also used to further supporting the crucible and ensuring the bob entering and rotating centrally into the middle of the beaker. It thus rotates by the application of torque, within the molten slag in the given annular space between the rotor and crucible, at the corresponding rpm. The viscosity of the synthetic slag was determined at various shear stresses and corresponding raten of deformation in the temperature range of 1450°C – 1550°C.

3 RESULTS AND DISCUSSION

Figure 2 shows the network structure of silicate slag. Silicate slags are built up of Si^{4+} cations which are surrounded by 4 oxygen anions arranged in the form of a regular tetrahedron. These SiO_4^{4-} tetrahedral are joined together in chains or rings by bridging oxygen. It comprises the bonding of SiO_4^{4-} units. These SiO_4^{4-} ions are combined with each other through bridging oxygen with the vortex oxygen in tetrahedron structure of SiO_4^{4-} units. Fig. 3 shows when some basic oxides are added in the silicate slag to maintain its basicity. The network structures are partially cut off by oxygen ions. These are decomposed from basic oxides to produce a few numbers of non-bridging (O^-) oxygen and free oxygen ions (O^{2-}). Figs. 4 and 5 show the cutting off points. These points assumingly exist adjacent to non-bridging oxygen and the free oxygen ions in the network structure of slag [11].

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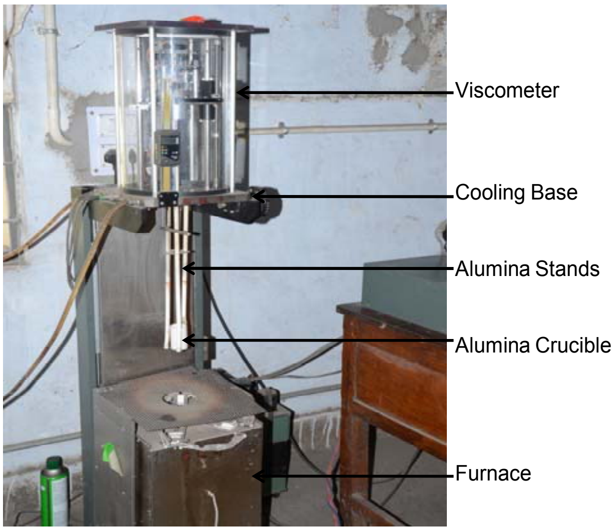

Fig. 1: High Temperature Viscometer Brookfield DV-III

Oxygen ions adjacent to cutting off points thus have large mobility. It can be attributed to the weakened bonding in the network structure at these points. When shear stress applied to the molten slag, oxygen ions adjacent to cutting off points move and break the networks around the cutting off points to produce new cutting off points. The cutting off points are transmitted in the network structure by repeating these processes and their movements cause a viscous flow. It can therefore be considered that the viscosity of molten slag is dependent on the frequency of occurrences of cutting off points in the network structure. The frequency of producing non-bridging oxygen and free oxygen ions need to be expressed by one of the rheological parameters of molten slags. These models shown in Figs. 4-6, however, indicate that the viscosity of molten slags depends on the network structure of the slag. It changes owing to the addition of basic oxides. The increased breaking of the silicate network steadily changes oxygen to silicon ratio irrespective of the system and the temperature. These figures (Figs. 4-6) depict that the degree of de-polymerization of the molten slag affect its flow mechanism. It appears that as the degree of polymerization of melts diminishes, owing to the cutting off of the network structure, the viscosity of the slag correspondingly changes.

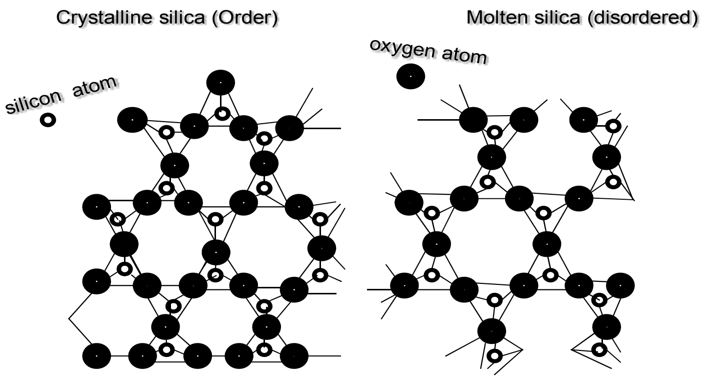

FIG. 2: SCHEMATICS OF SLAG NETWORK STRUCTURE

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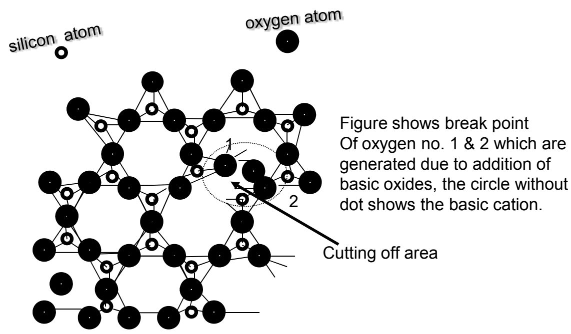

FIG. 3: SCHEMATICS OF BREAK POINTS SLAG NETWORK STRUCTURE DUE TO ADDITION OF BASIC OXIDES

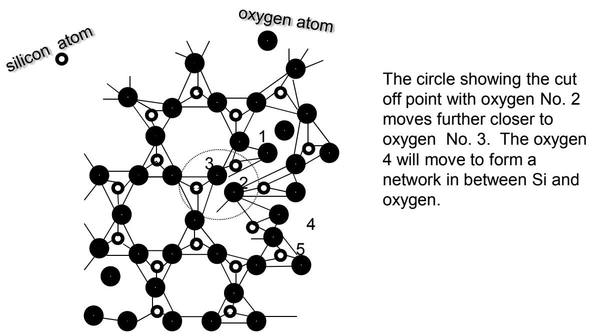

FIG. 4 : SCHEMATICS OF CUTOFF POINTS WITH OXYGEN MODIFYING SLAG NETWORK STRUCTURE IN BETWEEN SILICON AND OXYGEN

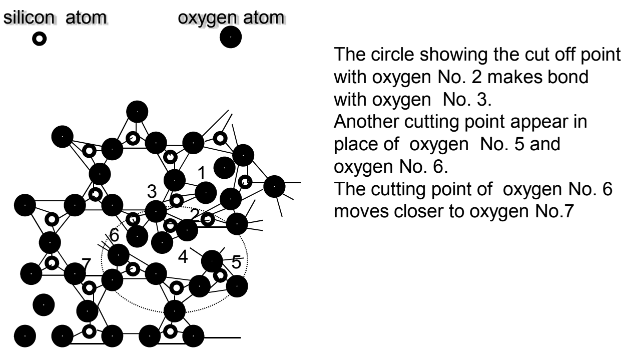

FIG. 5: SCHEMATICS OF CUT OFF POINTS MAKING BONDS WITH AN OTHER OXYGEN ATOMS IN SLAG NETWORK STRUCTURE

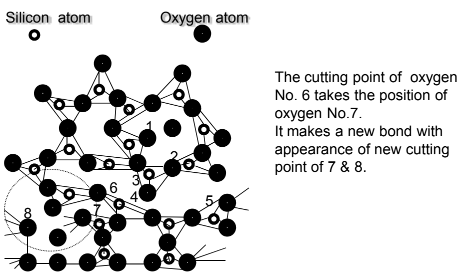

FIG. 6: SCHEMATICS OF CUTTING OFF POINTS MAKING BONDS WITH NEW CUTTING OFF POINTS IN SLAG NETWORK STRUCTURE

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Mills [12] expressed the slag network structure in terms of two parameters as the ratio of non-bridging oxygen(NBO) to tetragonally bonded oxygen (TBO). These can be used to calculate the structurally dependent property, viz. Viscosity, NBO/TBO, and the optical basicity Λ. The optical basicity (Λ) essentially incorporates network structure features by measuring fully bonded oxygen i.e. bridging,(O^o) partially bonded oxygen i.e. non-bridging (O^-) and free oxygens (O^{2-})in silicates and alumino-silicate melts. It is basically defined as the electron donor power of slag with respect to the electron donor power of CaO. Mills [12], however, corrected the optical basicity for the number of cations needed to charge balance the Al^{3+} ions incorporated into the Si^{4+} chain or ring. The relationship is as below:

$$\ln \eta = \left[\frac{1}{0.15 - 0.44\Lambda}\right] - \left[\frac{1.77 + 2.88\Lambda^{-1}{}_{Corr}}{T}\right] \quad 4$$

However, the measured viscosities of synthetic slag nos. 1, 11, and 12 by the High temperature viscometer are in good agreement with the viscosities calculated using the Eq. 4. The viscosities of the synthetic slags were calculated using commercial software viz. Factsage 6.2. but the range of viscosities found much lower which is not in good agreement with experimental. Figure 7 describes the comparison of the model and measured slag viscosities.

Most viscosity models often fail to simulate the slag behavior prevailing in real processes. The discrepancies in the results can perhaps be minimized by defining the network structure of the slag in terms of parameters characterizing the rheological behavior of slag system. These parameters, besides defining the slag viscosity/consistency index, should be able to characterise the flow behaviour and its dependence on the network structure of the slags. These models indicate that the viscosity of molten slags depends on its network structure. It changes with the addition of basic oxides and affects its flow mechanism. An attempt has therefore been made to use a novel concept to study the flow behaviour by describing the blast furnace slag system by the Ostwald-De-Waele model (Eq. 5).

$$\tau_{yx} = k'\left(\frac{dv_x}{dy}\right)^{n'-1} \times \left(\frac{dv_x}{dy}\right) \quad \ldots.5$$

τ_{yx} = shear stress, k' = consistensy index and n' = flow behaviour index;

$\left(\frac{dv_x}{dy}\right)$ = rate of deformation. For Newtonian fluids k' = μ and n'=1

The above model [Eq.5] can be expressed in terms of experimentally determined shear stress and rate-of deformation values by using high temperature concentrically rotating viscometer described as above for fluids exhibiting Newtonian behaviour. It is accordingly described by using equation [Eq.3]. The Eq.3 represents the rheological model for the fluids following Newtonian behavior, where the shear viscosity is independent of the shear rate.

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$$\left[\frac{\tau\left(\frac{1}{r_i^2}-\frac{1}{r_o^2}\right)}{8\pi^2 h}\right] = \mu\,(N) \qquad 5$$

Where,

τ = Torque, Nm; N= No. of revolution per sec,(sec^{-1}); h= height of Rotor, m;

r_i, r_o = radius of rotor and crucible respectively, (m); μ = viscosity ,(Pa.s)

In the present rheological studies of blast furnace slag systems it was, however, found that with the variation of the shear stress i.e. changing the rpm= 10, 20, 30, 40 the viscosity does not remain independent of the shear strees applied in the form of torque.

$$\left[\frac{\tau\left(\frac{1}{r_i^2}-\frac{1}{r_o^2}\right)}{8\pi^2 h}\right] \neq \mu N \qquad ....6$$

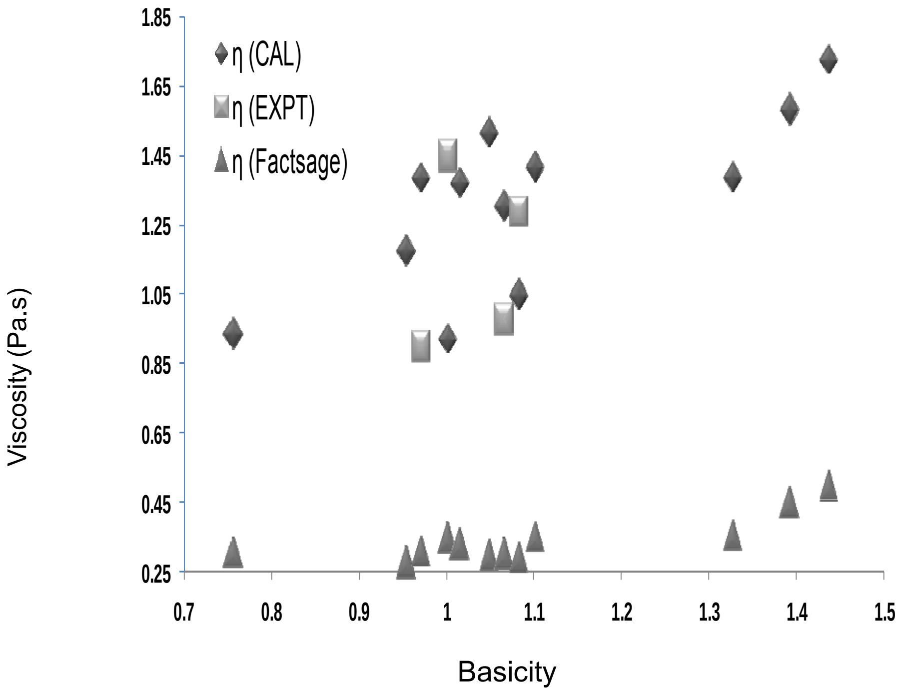

Fig. 7: Comparison of Model and Measured Slag Viscosities

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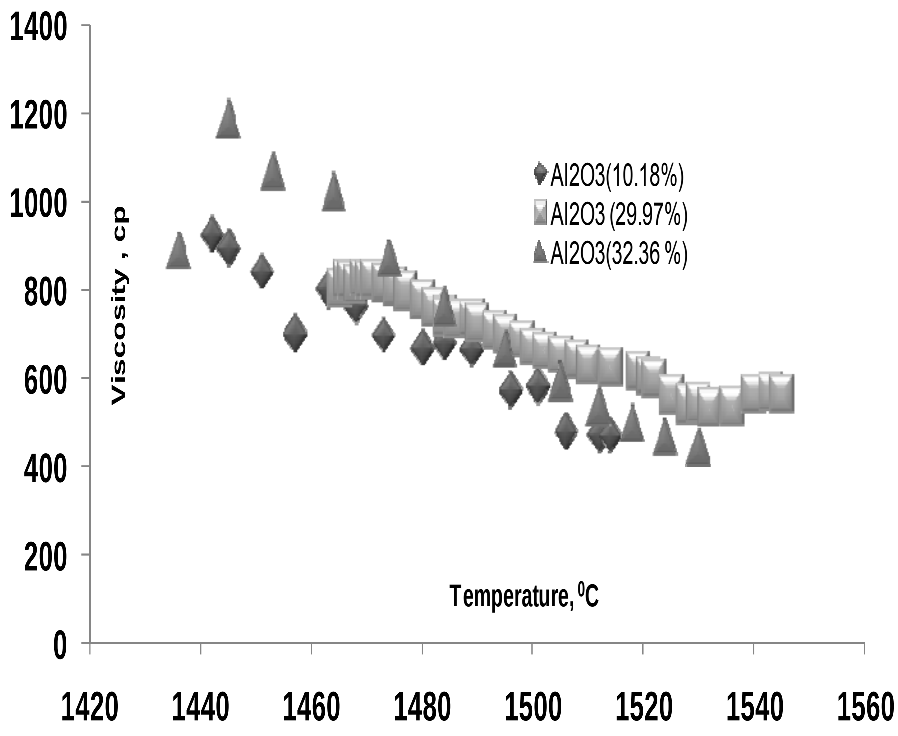

Fig. 8: Effect of Al_2O_3 on BF slag viscosity

Fig. 8 shows that the effect of Al_2O_3 content on the viscosities of SiO_2–CaO-MgO-Al_2O_3 slag as a function of temperature under the conditions of B2= 0.97, 1.083, 1.001 and MgO= 14.69, 9.65, 9.65 respectively and these experimental results indicated that the slag viscosity increases with decreasing slag temperatures. The viscosity variation tendency is observed in the temperature viscosity curves of slag with different Al_2O_3 contents of 10.18%, 29.97% and 32.36%. Fig. 8 also shows that with higher percentage of Al_2O_3 cotent in the BF slag shows higher viscosity for a particular temperature and it falls down with increasing temperature.
The slag systems, however, need to be characterised by using such parameters that would essentially incorporate the network structure features reliably and more precisely in determining the slag rheological behaviour. The approach has been taken to develop a model incorporating these parameters and express the momentum transport phenomena in dimensionless form and to validate the model for real slag systems. For that the Eq. 3 is modified in the form of Power law model (Eq.5) as described below.
It incorporates two parameters (k' and n') as expressed in Eq.7. Eq. 7, for n' =1,, reduces to Newton's law of viscosity with k' = μ , thus the deviation of n' from unity indicates the degree of deviation from Newtonian behaviour. The rheological characteristics of the BF type synthetic slag is expressed by using these parameters. As these parameters are quantitatively derived to determine the slag viscosities, they very well express the rheological characteristics of the given slag system. It would essentially incorporate the network structure features reliably and more precisely in respect of characterising the slag rheology.

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$$\left[\frac{\tau\left(\frac{1}{r_i^2}-\frac{1}{r_o^2}\right)}{8\pi^2 h}\right] = k'(N)^{n'} \quad \ldots\ 7$$

4 CONCLUSIONS

As the alumina affects the Blast furnace operation adversely both in terms of enhanced energy consumption and CO_2 emission, the paper presented a systematic research work to optimize blast furnace slag chemistry at high alumina contents aiming at decreasing its melting point and improving its fluidity. The rheological behaviour of a few typical BF slag systems of alumina contents of 29.97%, 32.36% and 10.18% within the temperatures range 1450-1550°C has been investigated with high temperature viscometer. The measured viscosities of these slags are in good agreement with the viscosities calculated using optical basicity concept. The viscosities of the synthetic slags calculated using commercial software viz. Factsage 6.2. are not found to be in good agreement with its corresponding experimental values. The rheological studies of blast furnace type synthetic slag using high temperature viscometer show that with the variation of the shear stress (torque) incorporated by changing the rate of deformation (rpm), the viscosity does not remain same. It shows the dependence of slags viscosity on shear stress and thus its deviation from the Newtonian behaviour.

The slag systems generally possess a random network structures comprising internal regions of weak ordering and the presence of these regions may result in non-Newtonian behaviour of the slag. As the viscosity of the slag is very sensitive to their structure, it is expressed by power law model normally applicable for fluids exhibiting non-Newtonian behavior. It involves two parameters (k' and n') which help determine the rheological characteristics of the fluids relating with its network structure. These parameters describe flow behaviour and the consistency index of the slag system. There is, however, an interdependency between n' and k'. Both may vary simultaneously depending on the rheological characteristics as well as the structural behaviour of the slag.

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