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APPLICATION OF OPTICAL BASICITY TO VISCOSITY OF HIGH ALUMINA BLAST FURNACE SLAGS

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Abstract

The composition and properties of blast furnace slags greatly affect the furnace productivity and the quality of hot metal produced. Viscosity is an important physical property of slags, strongly influenced by the chemical composition, structure and the temperature. Experimental measurement of slag viscosity requires high temperature equipment and is time consuming. Therefore, chemical parameters are used to identify trends in viscosity as function of chemical composition. Limited information is available for High Alumina Blast Furnace Slags, since much of the open literature deals with Low Alumina Slags, with alumina content less than 15 weight percentage. High Alumina slags (alumina content in the range of 15% to 30%) are predominantly encountered in Indian Blast Furnaces. It appears that these slags have higher viscosity and lower sulphide capacity than the low alumina slags. The effect of chemical composition / ionic structure on viscosity has been interpreted in this work, using the chemical parameter of optical basicity. Data reported in the literature have been used, along with the values of liquidus temperature, for high alumina slags. Three slag systems, i.e., $CaO–Al_2O_3–SiO_2$, $CaO–Al_2O_3–SiO_2–MgO$ and $CaO–Al_2O_3–SiO_2–MgO–TiO_2$ have been considered in this work. The trends observed are discussed in the paper.

Keywords: *Optical basicity; Viscosity; Blast furnace; High alumina slags; Liquidus temperature.*

1. Introduction

Viscosity of a slag is strongly influenced by the chemical composition, structure and the temperature. In blast furnace iron making process, slag viscosity is a very important physical property, because it influences the furnace operation in many

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ways. The viscosity of the slag affects the degree of de-sulphurization, coke consumption, smoothness of operation, gas permeability, heat transfer etc. However, most of the data available are mainly for low alumina slags with alumina in the range of 10 to 15 %. Further, these viscosity data represent slags with high CaO/SiO_2 ratio, which is not common in blast furnace operation. Viscosity data for multi-component slag systems have been collected from literature - with a wide range of slag constituents and a wide range of temperatures Tunezo SAITO [1] & Shankar [2]. In the present work, viscosity of three slag systems, $CaO–Al_2O_3–SiO_2$, $CaO–Al_2O_3–SiO_2–MgO$ and $CaO–Al_2O_3–SiO_2–MgO–TiO_2$ have been considered. These slags are high alumina blast furnace slags. Alumina was varied between 18 and 30 %, MgO between 2 and 5 %, TiO_2 between 0 and 2 %, and CaO/SiO_2 between 0.56 and 1.45. The temperature range used in this investigation was between 1400 and 1600 °C. The present objective is to study the effect of optical basicity on the viscosity of slags and the trends observed are discussed in detail, in the paper.

2. Viscosity of slags

The temperature and the chemical composition of the slag are instrumental in determining the viscosity of the slag. Viscosity of a slag is calculated from the Arrhenius equation, which gives the temperature dependence of viscosity:

$$\eta = A\exp(\frac{E}{RT}) \qquad .....(1)$$

where η = viscosity of slag
A = Pre – exponential term
E = Activation energy for viscous flow
R = Gas constant
T = Temperature, in absolute scale

Silicate slags are built up of Si^{4+} cations, surrounded by 4 oxygen anions, in the form of a regular tetrahedron. These $(SiO_4)^{4-}$ tetrahedra are joined together in chains or rings by bridging oxygen. The mobility of ionic species present in the slag determines it viscosity. However, the mobility is, in turn, dependent on the nature of the chemical bond, inter-ionic forces of the ions involved. Hence, stronger inter ionic forces leads to higher viscosities. In high silica systems, the polymeric anions result in high viscosity. As the metal oxide concentrations increase, Si-O bonds break down and hence the viscosity of the slags subsequently decreases. In high alumina blast furnace slags; alumina is present as $(AlO_4)^{5-}$ forming polymeric units with $(SiO_4)^{4-}$; thus, alumina acting as a network former. The basic oxides namely lime, magnesia, titania are the providers of oxygen, act as network breakers and result in depolymerization of the melt – thereby decreasing the viscosity. Thus, for smooth furnace operation, it is always advisable to have a low viscosity slag which helps in smooth transport of ions from the slag/metal interface to the liquid slag.

3. Optical basicity

Duffy and Ingram first formulated the concept of “Optical Basicity“ [3]. The Optical Basicity scale, characterized by Λ, is used to classify oxides on a scale of acidity, which is referred to the same O^{2-} base. Optical Basicity of glasses and slags is derived from the Lewis acidity/basicity concept, which is built using the ICP, the Ionic Covalent Parameter. Also, Duffy and Ingram [4] noted that the shifts in frequency of the absorption band in the 6s–6s transaction observed in the ultraviolet (UV) region of the spectrum can be utilized to relate it to the chemical behaviour of glasses and slags. This frequency shift is considered as a ratio of the electron donor power and is expressed in terms of Optical Basicity (Λ) defined in equation (2). As pointed out by Masson [5], the optical basicity is a global measure of the concentrations of bridging (O°) non-bridging (O^-) and free oxygen (O^{2-}) in silicate and alumino–silicate melts and thus provides a measure of depolymerisation of the melt. The optical basicity values of different oxide systems considered in the given study is listed in Table 1.

$$\Lambda = \frac{\text{Electron donor power of slag}}{\text{Electron donor power of } CaO} \quad ...(2)$$

Table 1. Optical basicity of different oxide systems

Oxide	CaO	MgO	$Al_2 0_3$	SiO_2	TiO_2
Optical Basicity	1	0.78	0.6	0.48	0.61

4. Calculation of optical basicity

There are a number of models to calculate the optical basicity of slags. In this work the models formulated by Duffy [6] and Shankar [7, 8] have been considered. The details of the two models are discussed below:

4.1. Duffy model

Duffy [6] showed that the optical basicities of various glassy and slag systems (denoted Λ_{th}) can be determined from their Pauling electronegativities. These authors showed that optical basicity of a slag can be calculated from the optical basicity of individual oxides present in the slag using could be derived from equation (3)

$$\Lambda = \frac{\sum x_1 n_1 \Lambda_{th2} + x_2 n_2 \Lambda_{th2} + ...}{\sum x_1 n_1 + x_2 n_2 + ...} \quad .....(3)$$

where, Λ is the optical basicity of the slag; Λ_{th} is the optical basicity of individual oxides; as calculated from Pauling electronegativities. x is the mole fraction of individual oxides and n is the number of oxygen atoms associated with acidic and basic oxides, respectively.

4.2. A. Shankar model

Shankar et. al [7, 8] developed a new basicity ratio which was required for high alumina blast furnace slags, since such slags have a very wide range of viscosities when compared to optical basicity. Hence, even at different viscosities, the optical basicity of the slag remained constant. These authors considered basicity as a ratio of the optical basicities of basic to acidic oxides. The new basicity ratio is similar to optical basicity as it gives a measure of the 'availability' of free oxygen ions in the slags; which are the main network breakers; thus, this new basicity ratio can give us an indication of the degree of polymerization of the melts. The new basicity ratio can be derived from equation

(4).

$$\Lambda = \frac{\dfrac{\sum X_B n_B \Lambda_B}{\sum X_B n_B}}{\dfrac{\sum X_A n_A \Lambda_A}{\sum X_A n_A}} \quad .....(4)$$

where Λ - new optical basicity, Λ_A and Λ_B are the optical basicities of acidic and basic oxides respectively, X_A and X_B are the mole fractions of acidic and basic oxides respectively, and n_A and n_B are number of oxygen atoms associated with acidic and basic oxides, respectively.

5. Results

Three slag systems have been considered to study the effect of optical basicity on the viscosity and liquidus temperature of each of these slag systems. Also, the effect of MgO, Al_2O_3, TiO_2 on the viscosity and liquidus temperature of high alumina blast furnace slags are studied.

5.1. Viscosity of $CaO–Al_2O_3–SiO_2$ system

The viscosity values for six different slag compositions as shown in Table 2 are taken from literature at two different temperatures 1500°C and 1600°C. Five different slag compositions are studied. The Al_2O_3 content of the slag was varied between 18.5–30.4 weight % [1]. The optical basicity of the slag is calculated from the two models discussed above. The liquidus temperature for the given slag system was calculated using Slag Atlas [9].

The relationship between viscosity and Optical basicity is shown in Fig. 1 as proposed by Duffy. The trend observed is that viscosity decreases, when optical basicity increases. Thus, it is desirable to maintain a low silica and alumina content in the slag to get a slag with low viscosity. This can be achieved by adding excess lime, but this will in turn lead to an increase in the liquidus temperature of the slag. Alumina also increases the liquidus temperature of the slag but since alumina is increased in extremely low quantities it does not affect furnace operation.

The relationship between viscosity and Optical basicity is shown in Fig.2 as proposed by Shankar et al [7]. However, there is a variation in the manner Optical Basicity was calculated i.e. the authors considered optical basicity to be a ratio of basic and acidic oxides. In case of high alumina blast furnace slags, alumina is considered to be acidic in nature, as it acts as a network former in high basicity levels as observed in blast furnace operation. Thus, the nature of the curve is not the same as observed in the other two models. Thus, from the graph we can conclude that the lower the alumina content in the slag the lower is its viscosity. Hence, to decrease the

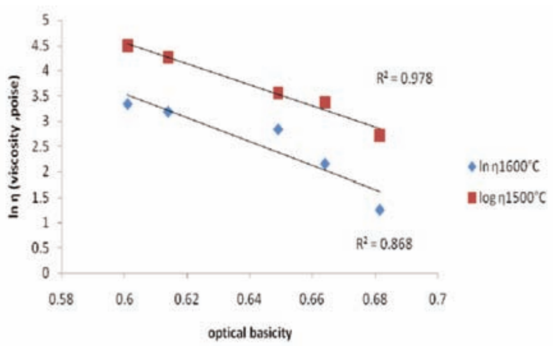

Fig.1. Effect of OB_{DUFFY} on viscosity.

Table 2. Viscosity of CaO- Al_2O_3–SiO_2 system

CaO	SiO_2	Al_2O_3	Liquidus temp(°C)	η1600°C (poise)	η1500°C (poise)	OB_{DUFFY}	OB_{AS}
46.7	31.9	21.4	1515	3.5	15	0.681	1.906
29.5	52	18.5	1300	28	90	0.601	1.965
39.9	29.7	30.4	1510	8.6	29	0.664	1.862
37.2	34	28.8	1450	17	35	0.65	1.882
29.3	42.7	28	1390	24	71	0.614	1.908

viscosity, lower alumina content is desirable which can be facilitated by higher lime addition in blast furnace operation which will also result in decrease in silica content in hot metal

The relationship between liquidus temperature of slag and OB_{Duffy} is shown in Fig.3; considering four out of the five compositions considered in the present study. It can be noted that we observe an increasing trend from the plot. Thus, with increasing Optical Basicity the liquidus temperature of the slag also increases. Hence, we can conclude that increasing lime addition may lead to a rise in liquidus temperature of the slag which is detrimental in operation of the furnace as more blast temperature may be required to maintain the increased liquidus temperature. The relationship between liquidus temperature of slag and OB_{AS} is shown in Fig. 4 considering four out of the five compositions considered in the present study. A decreasing trend is observed due to the manner in which OB_{AS} is calculated as already discussed above. The relationship between liquidus temperature & alumina content is shown in Fig. 5; while the effect of CaO addition on liquidus temperature of the slag is shown in Fig. 6. An

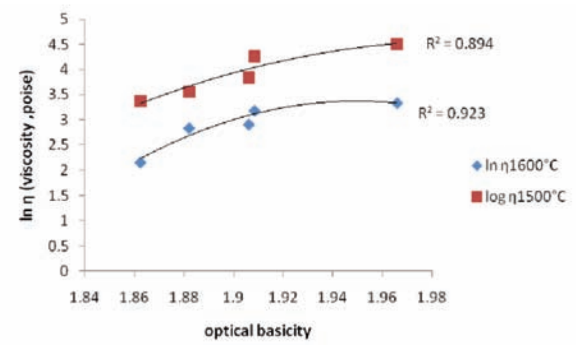

Fig.2. Effect of OB_{AS} on viscosity.

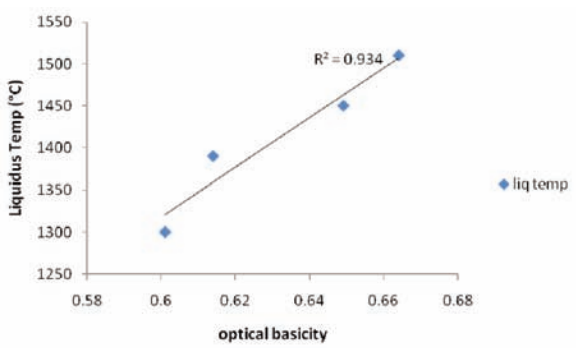

Fig.3. Effect of OB_{DUFFY} on Liquidus temp.

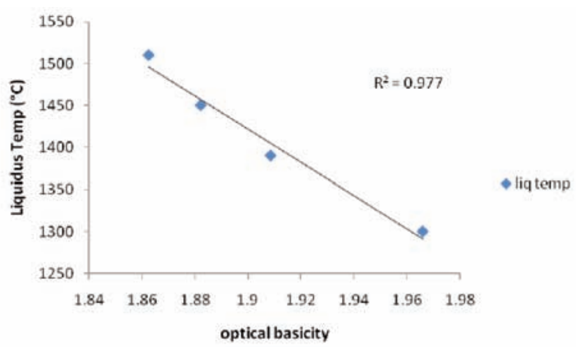

Fig.4. Effect of OB_{AS} on Liquidus temp.

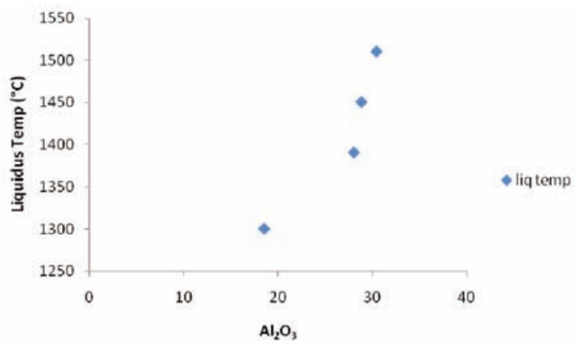

Fig.5. Effect of alumina on Liquidus temp.

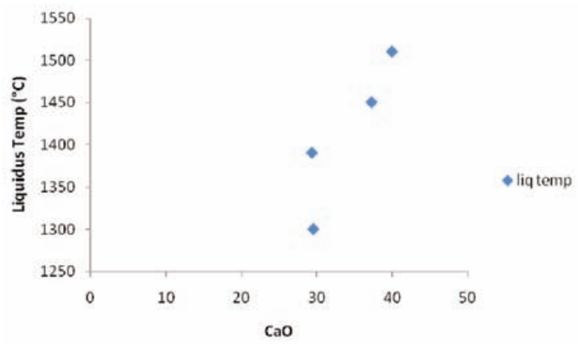

Fig.6. Effect of CaO on Liquidus temp.

increasing trend is observed in both cases, and hence, we can conclude that with increasing lime and alumina content, the liquidus temperature of the slag increases. Thus excess lime content in the slag is detrimental towards operation of the furnace.

5.2. Viscosity of $CaO–Al_2O_3–SiO_2–MgO$ system

The viscosity values for six different slag compositions as shown in Table 3 are taken from literature at four different temperatures between 1400°C and 1600°C [7]. The optical basicity of the slag is calculated from the two models discussed above. Five different slag compositions were considered with different levels of basicity ratio and three different MgO content. The basicity ratio was varied between 0.72-1.23 and the MgO was varied between 2-5 %. The liquidus temperature for the given slag system was calculated from the Slag Atlas [9].

The relationship between viscosity and OB_{Duffy} is shown in Fig. 7; a decreasing trend is observed suggesting that as the lower the optical basicity of the slag the lower is its viscosity. The relationship between viscosity and OB_{AS} is shown in Fig. 8. The trend

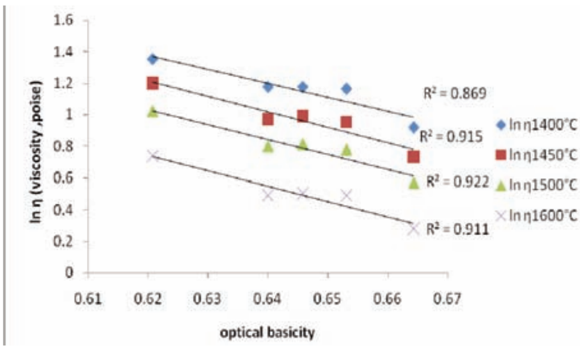

Fig.7. Effect of OB_{DUFFY} on viscosity.

Table 3. Viscosity of $CaO- Al_2O_3–SiO_2- MgO$ system

CaO	SiO_2	Al_2O_3	MgO	OB_{Duffy}	OB_{AS}	Liquidus temp(°C)	η1400 °C	η1450 °C	η1500 °C	η1600 °C
28.8	39.8	28.5	2.28	0.621	1.858	1365	22.5	15.9	10.5	5.5
33	37.8	23.7	4.94	0.64	1.84	1385	15	9.4	6.3	3.1
35.1	37.6	22.2	4.66	0.645	1.853	1404	15	9.8	6.5	3.2
37.3	34.4	25.3	2.16	0.653	1.865	1420	14.6	9	6	3.1
39.2	34.1	21.2	5.01	0.664	1.849	1430	8.3	5.4	3.7	1.9

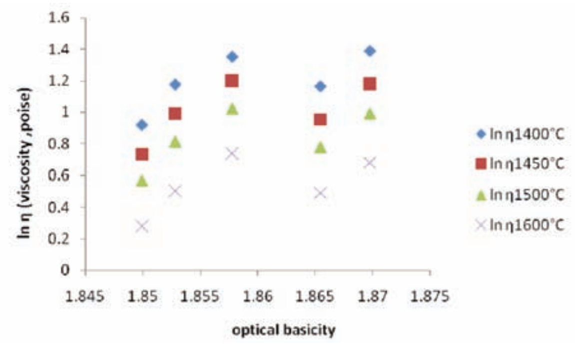

Fig.8. Effect of OB_{AS} on viscosity.

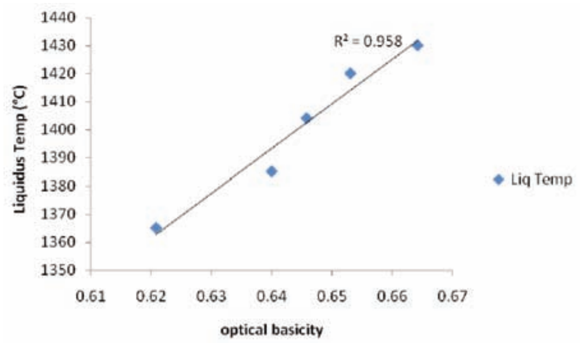

Fig.9. Effect of OB_{DUFFY} on Liquidus temp.

observed is a polynomial curve, but it becomes almost constant at 1.86. Thus from here we can conclude that the lower the alumina content in the slag the lower is its viscosity; thus, this further reiterates the fact that alumina acts as a network former in the slag and hence increases the viscosity of the slag.

The effect of optical basicity on the liquidus temp of the slag is shown in Fig. 9. An increasing trend is observed, suggesting that increasing optical basicity results in increase in viscosity of the slag. Thus, the alumina content of the slag should be maintained at a minimum to lower the liquidus temperature. The relationship between liquidus temperature and corrected basicity ratio is shown in Fig. 10. An increasing trend is again observed in this case which further establishes the argument that alumina acts as a network former for the given slag system. The effect of alumina on viscosity is shown in Fig. 11; the trend observed is increasing in nature clearly indicating that alumina acts as a network former in high alumina blast furnace slags.

5.3. Viscosity of $CaO–Al_2O_3–SiO_2–MgO–TiO_2$ system

The viscosity values for five different slag compositions as shown in Table 4 are taken from literature at three different temperatures between 1400°C and 1600°C [7]. Five

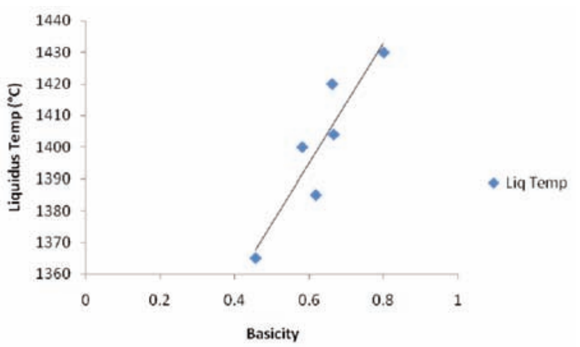

Fig.10. Effect of Basicity on Liquidus temp.

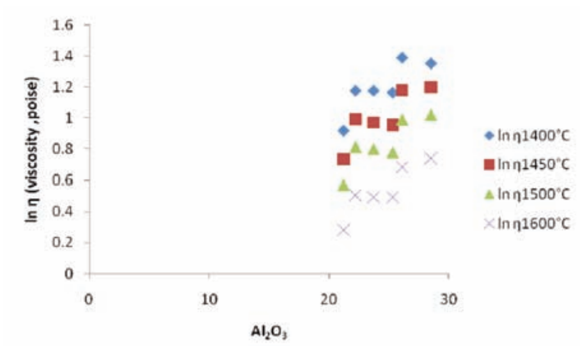

Fig.11. Effect of alumina on viscosity.

Table 4. Viscosity of CaO-SiO$_2$-Al$_2$O$_3$- MgO- TiO$_2$ system

CaO	SiO_2	Al_2O_3	MgO	TiO_2	OB_{Duffy}	OB_{AS}	η 1400°C	η 1500°C	η 1600°C
29.2	38.3	27.8	2.42	1.71	0.619	1.763	24.9	9.8	4.6
34.5	35.4	25.8	2.11	1.86	0.637	1.777	14.8	6.3	3.3
38	32	25.2	2.14	2.18	0.652	1.766	9.4	4.1	2.2
32	37.8	23.3	4.7	1.82	0.631	1.761	13.3	5.7	2.9
39.4	32	21.2	4.8	2.17	0.661	1.764	6.3	2.9	1.6

different slag compositions were considered; TiO_2 was varied between 1.7-2.3 %. MgO was varied between 2.11-4.8 % while alumina content was varied between 21.2–28.5 %. The optical basicity of the slag is calculated from the two models discussed above.

The effect of TiO_2 on the viscosity of high alumina blast furnace slags is shown in Fig. 12. A decreasing trend is noticed, which tells us that it acts as a basic entity in the slag and hence as a network breaker. Also it can be noted from here that a small increase in the TiO_2 % results in a sharp drop in the viscosity of the slag. The relationship between viscosity and OB_{Duffy} is shown in Fig. 13. A decreasing trend is observed from which we can conclude that the viscosity decreases with increasing optical basicity. Hence even in this system a low alumina content is favourable for furnace operations; which leads to low viscosity and hence enables the slag to flow out of the furnace freely.

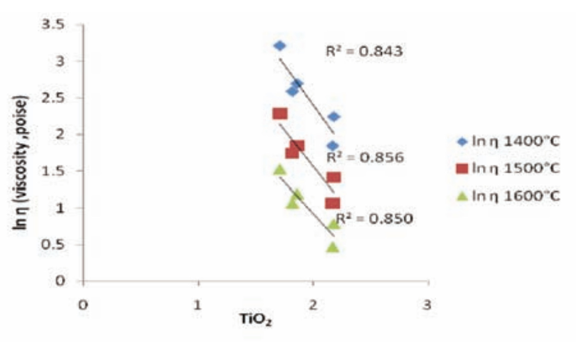

Fig.12. Effect of TiO$_2$ addition on viscosity.

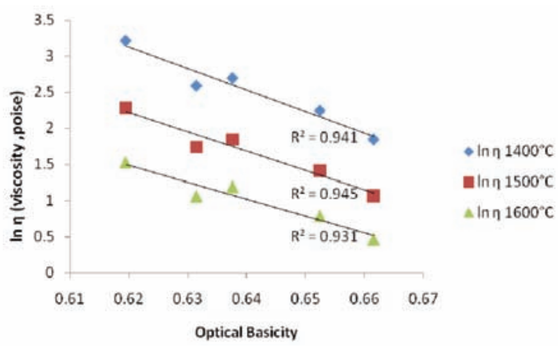

Fig.13. Effect of OB_{DUFFY} on viscosity.

6. Conclusions

A clear understanding of slags and the properties of slags is necessary for improved control in blast furnace iron making. Experimental data on viscosity of slags have been taken from the literature and the data analyzed in terms of Optical Basicity. The following systems have been taken for analysis: CaO–Al$_2$O$_3$–SiO$_2$, CaO–Al$_2$O$_3$–SiO$_2$–MgO and CaO–Al$_2$O$_3$–SiO$_2$–MgO–TiO$_2$.

The following observations could be made from the present investigation:

Viscosity of the slag system is lowered, with increasing Optical basicity.

The liquidus temperature of the slag is found to increase with increasing alumina and lime content.

Optical basicity has been successfully used to explain the trends covering 15 different slag systems.

Alumina is found to be a network former in high alumina blast furnace slags.

Work reported earlier [10] on the use of optical basicity to metallurgical slags could possibly be expanded to various specific cases / groups.

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References

[1] T. Saito and Y. Kawai.,The Research Institute of Mineral Dressing and Metallurgy. Received (1951), 492.

[2] A. Shankar, Marten Gornerup, A.K. Lahiri, and S. Seetharaman., Metallurgical and Materials Transactions B, 38 B (2007), 911.

[3] J.A. Duffy, Ingram, M.D., J.A.C.S., 93 (24) (1971) 6448.

[4] J.A. Duffy; Ingram, M.D., J. Non-Cryst. Solids., 21(1976) 373.

[5] C.R. Masson: Proc. of the Second Int. Symp. on Metallurgical Slags and Fluxes, ed. by H.A. Fine and D.R. Masson, TMS-RIME, Warrendale, 1984, 157.

[6] J.A. Duffy, M.D. Ingram., J. Inorg. Nuc. Chem., 37 (5) (1975) 1203.

[7] A. Shankar, M. Go¨rnerup, A.K. Lahiri and S. Seetharaman., Ironmaking and Steelmaking, 34 (6)(2007), 477.

[8] A. Shankar., Studies on High Alumina Blast Furnace Slags, Royal Institute of Technology., SE-100 44 Stockholm, Sweden, 2007, Doctoral Thesis.

[9] Slag Atlas; 2nd revised edition,Verlag Stahleisen, Germany, (1995) p.156.

[10] M. Kumar and S.R. Sankaranarayanan, Journal of Mining and Metallurgy Section B-Metallurgy, 44 (1) B (2008) 133.