Foaming Characteristics of BOF Slags

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Slag foaming measurements were carried out for BOF type slags that exist during the first half of the blowing period in order to better understand slopping of slag. The foam index (Σ) decreases with increasing FeO up to about 20 % FeO content and is almost constant for FeO from 20 to 32 % FeO. This is believed to be because above about 25 % FeO, the viscosity is nearly constant. The foam index shows a minimum value at basicity $[(\text{CaO} + \text{MgO})/(\text{SiO}_2 + \text{Al}_2\text{O}_3)]$ of 1.4 at 1713 K; it increases at higher basicities due to the precipitates such as 2CaOSiO_2 or $(\text{Fe}, \text{Mg})\text{O}$ which stabilizes the foam. The effect of TiO_2 and MgO on foam index was also evaluated. An empirical equation for the foam index obtained by the previous researchers was applied to the present experimental results. The foaming during the first half of the blowing in BOF process was described based on the empirical relationship and the foam height was estimated for a BOS converter as a function of decarburization rate.

KEY WORDS: slopping; BOF Slags; foam index; viscosity of slags; bubble size.

1. Introduction

Slopping remains one of the major concerns in oxygen steelmaking (OSM). Slopping results from excessive amounts of gas being generated in a highly foamable slag. Most of the previous work on foaming has been done for limited conditions, primarily relevant to iron smelting. For example, FeO contents were less than 5 % in a limited temperature range. For steelmaking slags most measurements have been for latter in the process, close to tap conditions. These conditions do not reflect those present during the first part of oxygen steelmaking (OSM) when slopping occurs. Therefore, it is important to understand the fundamental features of slag foaming occurring during the first half of the blow in the BOF process.

In recent investigations on slag foaming in the metallurgical processes, foams were often generated and maintained at steady state by using a constant rate of production of gas bubbles. Zhang and Fruehan¹⁾ injected argon gas into liquid slag contained in an cylindrical alumina crucible at 1773 K through an alumina nozzle (1.75 mm I.D.) and examined foaming by a X-ray video technique. The results showed that the whole foam column was composed of polyhedron shaped bubbles, and no initial transitional spherical bubbles could be seen. In studying the kinetics of the reaction between FeO in the slag and carbon in the liquid iron, Zhang and Fruehan¹⁾ observed foams dominated by spherical bubbles of much smaller size using the same X-ray video technique. The later type of foam was much more stable than that observed by Jiang and Fruehan,²⁾ although the slag compositions and temperatures were almost identical in both experiments. The more stable foam resulted from smaller bubbles generated by the chemical reaction.

The dynamic measurement of foamability was first pro-

posed by Bikerman³⁾ in which an equilibrium between formation and collapse of the foam was established by the generated gas bubbles of definite size at a constant rate. The unit of “foaminess” was defined as the foam index (Σ), given by

$$\Sigma = \frac{V_f}{Q_g} \dots\dots\dots(1)$$

where V_f is the volume of the foam at steady state and Q_g is the gas flow rate. The parameter Σ has the unit of the time and can be roughly interpreted as the average traveling time of gas in the foamed liquid. Bikerman³⁾ found that Σ is independent of the amount of the liquid and the cross-sectional area of the cylindrical container.

In the study of slag foams, Ito and Fruehan⁴⁾ modified Bikerman's definition of the dynamic measurement of foam stability and referred to it as the foam index,

$$\Sigma = \frac{\Delta h}{\Delta v} = \frac{\Delta H_f}{\Delta v_s} = \frac{H_f}{v_s} \dots\dots\dots(2)$$

where h is the height of the foam layer at steady state, H_f is the foam height defined as the difference of the level of foamed liquid surface to the level of the liquid at rest, v is the linear gas velocity in the foam and v_s the superficial gas velocity which is defined by,

$$v_s = \frac{Q_g}{A} \dots\dots\dots(3)$$

Here A is the cross-sectional area of the container. Ito and Fruehan⁴⁾ also showed that the measured foam index is independent of the size of the container above a certain

size when the effect of the container is negligible. They measured the foam index for a slag of composition $\text{CaO}/\text{SiO}_2=0.67$; $\text{FeO}=30\%$ at 1573 K in four different sized crucibles (diameter: 25, 32, 38, 50 mm). The results showed that foam indexes obtained were the same for all the crucibles greater than that of the 32 mm diameter. They also showed that in a $\text{CaO-SiO}_2\text{-FeO}$ system, Σ decreased with increasing basicity up to 1.22 at 1673 K. When CaO/SiO_2 was greater than 1.22, Σ increased due to the presence of second-phase particles (CaO or 2CaOSiO_2). Second-phase particles have a large effect on foam stability because they increase the bulk viscosity of the slag. Jiang and Fruehan²⁾ also conducted a larger scale experiment for their slags at 1773 K in which the diameter of the crucible was 92 mm; Their results for the same slag at the same temperature were similar.

It has been shown that the foam index is closely related to the physical properties of the liquid slag by dimensional analysis.^{1,2)} In a recent study, Zhang and Fruehan¹⁾ measured the foam index for the bath-smelting type of slags ($\text{CaO-SiO}_2\text{-Al}_2\text{O}_3\text{-FeO}$) with small bubbles generated by argon gas injection through the nozzle of multiple small orifices. An improved correlation was obtained by using more accurate data for the slag viscosity, density, surface tension, and bubble diameter in the dimensional analysis. The correlation developed is expressed by

$$\Sigma = 115 \frac{\mu^{1.2}}{\sigma^{0.2} \rho D_b^{0.9}} \quad (4)$$

where Σ is the foam index (sec), μ is the viscosity (N s/m^2), σ is the surface tension (N/m), ρ is the density (kg/m^3), and D_b is the bubble diameter (m).

It is the objective of this research to understand the fundamental features of slag foaming for $\text{CaO-SiO}_2\text{-FeO-MgO}$ slags relevant to steelmaking processes during the first half of the blowing in the converter. Also Ti is often in blast furnace hot metal which enters the slag. Therefore the effect of TiO_2 on slag foaming was examined. The effect of MgO was also measured. Another focus of this research is to confirm if the correlation recently developed by Zhang and Fruehan¹⁾ can be applied to the BOF slags.

2. Experimental

A schematic diagram of the experimental apparatus is shown in Fig. 1. An electric resistance furnace with a 150-mm hot zone length was used for the experiments to establish an isothermal condition. The slag sample weighed about 150 g, which corresponded to a slag depth of about 4 cm for a crucible diameter of 4.5 cm. This slag depth is sufficient to eliminate the effect of the amount of the liquid on foaming, as indicated by Bikerman.³⁾ It took about 30–60 min to take each set of measurements during which the dissolution of MgO from the crucible resulted in the final slag composition containing 6–22% MgO. The argon gas was introduced into the molten slag through a pure iron pipe with a knife edged nozzle (2.1-mm ID, 3.2-mm OD) which was placed about 0.5–1.0 mm above the bottom of the crucible. When the foam height reached a stable level, the surface position of the slag was detected with an electric probe

Fig. 1. Schematic diagram of the experimental apparatus.

Fig. 2. Foam height of $\text{CaO-SiO}_2\text{-FeO-MgO}_{\text{sat}}$ slags as a function of superficial gas velocity at 1713 K.

made of a pure iron rod. In the present study, the foam height was measured as the difference between the top foam surface position and the liquid slag position at rest. In order to obtain an accurate value for the foam index, a series of measurements at various gas flow rates were conducted for each slag composition studied, and the foam index was determined from the slope of the line in a foam height vs. superficial gas velocity plot, as shown in Fig. 2.

The master slag composed of CaO , SiO_2 , and MgO was pre-melted in a MgO crucible using an induction furnace. CaO , SiO_2 , and FeO was added to the master slag to adjust the slag compositions for actual experiments. FeO was prepared by sintering Fe_3O_4 powder in an iron crucible under Ar gas atmosphere at 1573 K for about 12 hr. After the measurement was finished, the slag samples were chemically analyzed.

3. Results and Discussions

3.1. Bubble Size

It has been pointed out that the foam stability of liquid

depends not only on its physical properties but also on the bubble size.⁵⁾ In foams produced in the present foaming experiment, the following relationship between the volume of bubbles (V_B), bubble frequency (f), the gas flow rate (V_g) can be deduced by Eq. (5).

$$V_B = V_g / f \quad (5)$$

Assuming that bubbles are perfect spheres, Eq. (5) can be rewritten as follows.

$$D_b = \left(\frac{6V_g}{\pi \cdot f} \right)^{1/3} \quad (6)$$

As indicated in Eq. (6), the equivalent spherical bubble diameter (D_b) can be calculated by measuring the bubble frequency (f) at a given gas flow rate. **Figure 3** shows the measured bubble diameter as a function of gas flow rate. Bubble frequency measurements, which were obtained using a pressure transducer installed between the gas flow controller and the gas lance in Fig. 1 which would indicate when a bubble was released. The measured bubble diameter is larger than that calculated from the equation proposed by Sano *et al.*⁶⁾ shown as a straight line. In the calculation of

Fig. 3. The relationship between mean bubble size and gas flowrate at 1713 K.

bubble diameters using Sano's equation,⁶⁾ the surface tension and density values of the slag system designated by CSFM-4 in **Table 1** were used. Because the consideration of viscosity effect on the bubble size was not taken into in Sano's equation, there may be some discrepancy between the measured bubble size and the calculated one. Compared to the average bubble diameter (about 12 mm) measured by Ito and Fruehan⁴⁾ for CaO–SiO₂–FeO–Al₂O₃ system, the average bubble diameter for the CaO–SiO₂–FeO–MgO slag system shows higher values (about 17 mm). A second reason might be resulted from the difference of the shape of the nozzle tips used in the present work and in the experiment performed by Ito and Fruehan.⁴⁾ While the gas lance in the work by Ito and Fruehan⁴⁾ was made of stainless pipe with knife edged nozzle (O.D.=2.1 mm), the lance in the present research was made of iron pipe with flat edged nozzle. According to the research by Sano *et al.*,⁶⁾ the bubbles produced through flat edged nozzle may be larger than those through knife edged nozzle because the bottom part of the bubble sticking to the flat edged nozzle may expand to the external surface of the nozzle tips.

3.2. The Effect of FeO Content on Foam Index

The experimental results for determining foam index (Σ) along with the analytical results for the slag compositions are presented in Table 1. Σ is plotted in **Fig. 4** as a function of FeO content. It is indicated that the foam index Σ decreases with increasing FeO up to about 20 % FeO content. This phenomena was also observed for bath smelting slag systems (CaO/SiO₂=1 and 1.25) measured by Jiang and Fruehan²⁾ and for Nippon steel's bath smelting slag.²⁾ Jiang and Fruehan²⁾ attributed the higher foaming index observed for the lower basicity slag (CaO/SiO₂=1) to the fact that viscosities for the bath smelting slags are higher. One interesting point found in the measurement by Jiang and Fruehan²⁾ is that a maximum foaming index occurred at around 2 % FeO. From their experimental observations, it is concluded that CaO–SiO₂ slags do not foam when no FeO is present in the slag, because it is too viscous to foam significantly. That is, the slags with low FeO contents have a high melting point and viscosity, and no true foam is formed due to the channeling of the gas bubbles through

Table 1. BOF Slag Foaming Measurement for CaO–SiO₂–FeO–MgO_{sat} system.

Sample No.	Temp (K)	Basicity (C/S ratio)	%CaO	%SiO ₂	%FeO	%MgO	%TiO ₂	Foam Index	Density (g/cm ³)	Surface tension (N/m)	Viscosity (N·s/m ²)
CSFM-01	1673	0.93	29.61	31.95	20.47	17.97		1.10	2.922	0.509	0.293
CSFM-03	1713	1.0	34.78	33.76	22.52	8.94		0.59	2.958	0.502	0.270
CSFM-04	1713	1.1	37.39	35.57	20.87	6.17		0.53	2.936	0.493	0.291
CSFM-05	1713	1.1	30.96	29.39	24.16	15.69		0.54	2.978	0.521	0.226
CSFM-06	1713	1.1	29.11	27.73	31.52	11.64		0.68	3.093	0.524	0.221
CSFM-07	1713	0.93	30.00	32.13	18.09	17.78		0.57	2.892	0.511	0.248
CSFM-08	1713	0.86	28.67	33.42	17.57	20.34		0.87	2.874	0.510	0.250
CSFM-09	1713	0.61	23.02	37.73	15.23	24.02		0.98	2.824	0.497	0.283
CSFM-10	1713	0.42	17.21	40.99	13.68	28.12		1.70	2.786	0.489	0.309
CSFM-11	1823	1.0	34.08	32.77	15.11	18.04		0.50	2.851	0.516	0.213
CSFM-12	1773	0.93	29.12	31.32	20.96	18.60		0.75	2.925	0.525	0.178
CSFM-13	1713	1.0	38.18	38.94	10.24	12.38		0.37	2.784	0.486	0.310
CSFM-14	1713	1.0	28.07	27.53	27.98	14.10		0.87	3.045	0.524	0.220
CSFM-21	1713	1.0	31.67	31.73	17.68	15.95	2.66	0.87	2.905	0.507	0.239
CSFM-22	1713	1.0	29.31	29.05	18.48	16.61	4.96	1.1	2.936	0.510	0.219
CSFM-23	1713	1.0	27.95	27.63	19.37	16.44	7.17	1.2	2.964	0.510	0.207
CSFM-24	1713	1.0	27.01	26.55	20.15	16.47	9.44	1.4	2.987	0.510	0.196

Fig. 4. The change of the foam index for CaO–SiO₂–FeO–MgO_{sat} slags as a function of FeO content at 1713 K.

Fig. 5. The relationship between the viscosity of slag and FeO contents at 1713 K.

the slag layer. This phenomena has also been observed in the previous research about the addition effect of P₂O₅ on foaming of CaO–SiO₂ slags by Cooper and Kitchener.⁷⁾ They have shown that foaming is absent with binary CaO–SiO₂ melts but is marked when P₂O₅ in the range of 0 to 1.8 % is added to melts containing more than 50 % of SiO₂.

The tendency in Fig. 4 can be explained on the basis of Fig. 5 plotting viscosity as a function of FeO content. The viscosities of both bath smelting slags and BOF slags decrease with increasing FeO content. In Fig. 5, the viscosities of the slags were estimated using Urbain's model⁸⁾ based on the slag compositions shown in Table 1. From the result in Fig. 5, it is believed that the decrease of viscosity is the major contributor to foam instability of slags.

The apparent result for the bath smelting slags and BOF slag is that foam index Σ decreases with increasing the FeO content up to about 20 % FeO. However, the foam index Σ is almost constant with increasing FeO content higher than 20 % FeO in the slag. As indicated in Fig. 5, the viscosity does not decrease significantly above 25 % FeO which is the most likely reason for the foam index being constant.

Fig. 6. The change of foam index Σ with basicity index $[(\text{CaO}+\text{MgO})/(\text{SiO}_2+\text{Al}_2\text{O}_3)]$ of the CaO–SiO₂–FeO–MgO_{sat} slags at 1713 K.

3.3. The Effect of Slag Basicity on Foam Index

Figure 6 shows the foam index for CaO–SiO₂–FeO–MgO slags at 1713 K as a function of basicity index defined as $(\text{CaO}+\text{MgO})/(\text{SiO}_2+\text{Al}_2\text{O}_3)$ in weight percent. The foam index decreases with increasing $(\text{CaO}+\text{MgO})/(\text{SiO}_2+\text{Al}_2\text{O}_3)$ up to 1.4, which is expected to be the liquidus composition. In general the surface tension increases and viscosity decreases with increasing basicity. Therefore, low surface tension and high viscosity is expected to favor the stability of slag foam. However, the foam index increases with increasing basicity when the basicity index is higher than 1.4. A similar tendency can be seen in the data of foam index measured by Ito and Fruehan⁴⁾ for CaO–SiO₂–FeO–Al₂O₃ slag system. The critical basicity indexes reaching the minimum foam index are about 1.20 at 1573 K and 1.22 at 1673 K, which correspond to the liquidus temperature of CaO–SiO₂–FeO–Al₂O₃ slag system. They⁴⁾ reported that this is because solid particles such as 2CaOSiO₂ precipitate at higher CaO contents, and the particles significantly increase foam stability. The similar finding can be seen in other previous research.⁷⁾ When SiO₂ is low and CaO high, the slags may crystallize at the steelmaking temperatures, the crystallizing substance being in most cases the orthosilicate Ca₂SiO₄, as can be confirmed in the CaO–SiO₂–FeO phase diagram.⁹⁾ From the CaO–SiO₂–FeO phase diagram, even basic slags are not saturated with CaO, but rather with Ca₂SiO₄ or, in some cases, with 3CaOSiO₂. If the slag is high enough in magnesia content as in the present slags saturated with MgO, magnesio-wustite[(Fe,Mg)O] may be the phase which crystallizes first. Therefore, the increase of foam index caused by the precipitation of second-phase particles may be due to the role of the particles like 2CaOSiO₂ or (Fe,Mg)O which increase the bulk viscosity. Of course, high viscosity is required both to stop the drainage of the liquid from the thin films separating the bubbles in foams and the coalescence of bubbles approaching each other in gas bubbles. It should be noted that precipitated second phase particles which are smaller than the foam bubbles stabilize the foam. The increase in the bulk viscosity reduces the slag foam bubble drainage rate.

Fig. 7. The change of the foam index for CaO-SiO₂-FeO-MgO_{sat} slags as a function of TiO₂ content at 1 713 K.

However, large pieces of undissolved lime do not stabilize the foam.

The slight difference of the basicity index for the minimum foam index between CaO-SiO₂-FeO-Al₂O₃ and CaO-SiO₂-FeO-MgO slag may be attributable to the fact that MgO and Al₂O₃ are regarded as basic and acidic oxide, respectively. CaO and MgO are being dealt with as the same oxide for convenience in defining basicity index in Fig. 6. The minimum is actually the liquidus composition and therefore is not necessarily related to the basicity.

3.4. The Effect of TiO₂ Content on Foam Index

Figure 7 shows the effect of TiO₂ on the foam index for the BOF slags. As the content of TiO₂ increases, the experimentally measured foam index increases. According to the previous research,¹⁰⁾ TiO₂ increases the viscosity and lowers the surface tension of FeO just as SiO₂ does. However, it was pointed out that TiO₂ was not a networkbuilder because Ti⁴⁺ cations are too large. It is known that TiO₂ introduced in an acid silicate melt lowers its viscosity in the same manner as CaO or FeO. From the experimental tendency in Fig. 7, it may therefore be speculated that TiO₂ added combines with MgO dissolved from the crucible wall to form 2MgOTiO₂ ($T_m = 1\,756^\circ\text{C}$) precipitates. In reality, the calculation of predicted foam index based on several models which do not take the presence of precipitates into consideration. Although the viscosity in the calculation decreased along with the increase of TiO₂ content, the actual viscosity affected by the formation of precipitates may increase, which is believed to be the crucial reason for the increase of foam index observed in Fig. 7.

3.5. The Effect of MgO on Foam Index

Figure 8 shows the influence of MgO content on the foaming behavior for a 35%CaO-35%SiO₂-30%FeO slag to which a proper amount of MgO was added for each measurement. In order to facilitate the control of MgO content, an Fe crucible was used for the slag container for these measurements. It is shown that the foam index decreases with increasing MgO additions. In Fig. 8, the foam index obtained for 28CaO-28SiO₂-28FeO-14MgO_{sat} slag is in relatively good agreement with the results at lower MgO

Fig. 8. The change of the foam index for CaO-SiO₂-FeO-MgO_{sat} slags as a function of MgO content at 1 713 K.

Fig. 9. The temperature dependence of the foam index for CaO-SiO₂-FeO-MgO slag.

contents measured using an iron crucible. The tendency in Fig. 8 has been reported by Ren *et al.*¹¹⁾ who reported a reduction in foaming intensity with increasing MgO contents at 1 623 K for basic compositions (CaO/SiO₂ ≥ 1).

3.6. The Effect of Temperature on Foam Index

Figure 9 shows the temperature dependence of the foam index for a 35%CaO-35%SiO₂-30%FeO-10%MgO slag. It is indicated that the logarithm of foam index decreases with increasing temperature in the temperature range of 1 673 to 1 823 K. Generally since the temperature coefficient for surface tension¹²⁾ is positive and that for viscosity¹³⁾ is negative, decreasing temperature would favor the increase of the foam index. From the data in Fig. 9, the temperature dependence of the foam index can be expressed by Eq. (7).

$$\log \Sigma = \frac{6\,610}{T} - 3.90 \quad \text{.....(7)}$$

The temperature dependence given by Eq. (7) can be used to predict the foam index at other temperature for the slag and experimental conditions employed in this study. From

Fig. 10. The result of the dimensional analysis considering the effect of the bubble size. $N_z = \Sigma \mu g / \sigma$, $Mo = \mu^4 g / \sigma^3 \rho$; and $Ar = \rho^2 D_b^3 g / \mu^2$

Eq. (7), the apparent activation energy for the decay of the foam can be estimated to be 126.5 kJ/mol. For this value, Ito and Fruehan⁴⁾ obtained 160 kJ/mol as the activation energy for the decay of the foam for 35%CaO–35%SiO₂–30%FeO slag in the temperature range of 1 523 to 1 673 K. And Ozturk and Fruehan¹⁴⁾ reported the value of 139.6 kJ/mol as the apparent activation value for foam decay for 48%CaO–32%SiO₂–10%FeO–10%Al₂O₃ slag in the temperature range of 1 723 to 1 873 K. It was found that there was no significant difference between the activation energy for the foam decay and that for the viscous flow in the case of both present result and their results.^{4,14)}

3.7. Application of the Existing Correlation to the Present Experimental Results

It has been proved that the foam index for bath smelting slags by Ito and Fruehan,¹⁵⁾ Jiang and Fruehan²⁾ and ladle slags by Roth *et al.*¹⁶⁾ has the quantitative relationship with the slag physical properties. According to the previous research,¹⁾ it is obvious that the foam stability of slags are affected by viscosity, surface tension, density, and the average bubble diameter. For the case where the bubbles were produced by injecting gas from an orifice, the average bubble diameter can be estimated by the viscosity, surface tension, nozzle geometry, and gas flow rate or simply measured as in the present study. One of the objectives of this research is to confirm if the experimentally determined foam indexes in the present work agree with those calculated by the equation derived by Zhang and Fruehan.¹⁾

Zhang and Fruehan¹⁾ described the following equation which reflects the dependence of the foam index on the viscosity, surface tension, density, and the average bubble diameter by the dimensional analysis. The estimation of the slag properties is given in Appendix. As can be seen in Fig. 10, the correlation (4) developed by Zhang and Fruehan predicts the foam index for BOF slags during the first half

Fig. 11. The calculated foam index for CaO–SiO₂–FeO–MgO slag during the course of the blowing time in the BOS process.

Table 2. The slag composition in the BOS process defined approximately during the first half of the blowing.

stage in the entire blowing time	Temperature(K)	CaO/SiO ₂	mass% FeO	mass% MgO
17%	1633	0.8	35	2
33%	1693	1.2	32	4
50%	1753	1.5	23	6

of the blowing reasonably enough. Equation (4) indicates that viscosity is the most important physical properties in determining foam index with surface tension, density, and bubble size also being important. That is, the foam stability increases with increasing viscosity and decreasing the bubble size, surface tension and density of slags, as was previously mentioned. In applying Eq. (4) to the present results, the average measured value in Fig. 3 was used to estimate the size of the bubbles produced by injecting gases through an orifice into liquid slags.

4. Foaming in Steelmaking Process

Understanding slag foaming in the converter is crucial not only for the prevention of slopping but also for the control of the reactions occurring in the BOS process. The slag foaming in the BOS process can be estimated using the foaming index formula previously derived as a function of the physical properties of BOS slags. Based on the estimated foam index, the foam height in the converter during the first half of the blowing can be calculated using the following Eq. (8) derived by Ito and Fruehan.¹⁵⁾ Here V_g^* is a superficial gas velocity and h^* height before foaming begins.

$$h = \Sigma(V_g^s - V_g^*) + h^* \dots \dots \dots (8)$$

Figure 11 shows the estimated foam index for CaO–SiO₂–FeO–MgO slags as a function of the blowing time quantified by percentage with respect to the entire processing time in BOS process. The three slag compositions were selected to simulate the stages 1, 2, and 3 which correspond to the 17 % stage, 33 % stage, and 50 % stage of the entire blowing time in the BOS operation, respectively based on the real process data supplied by Inland Steel

Fig. 12. The expected foam height of BOF slag during the first half of the blowing as a function of the decarburization rate.

Company. Because BOF slags usually contain 6 to 8% MgO at the end of the BOS operation, the MgO content in Table 2 was approximately defined by the solubility of MgO.¹⁷⁾ It was indicated that the MgO content of just a few percent intensifies the foaming action of acidic and neutral slags.¹⁸⁾ The predicted foam index decreases as the BOS operation proceed in the range of 0.8 to 1.5 which corresponds to the basicity change of BOF slags by the addition of burnt lime (CaO) during the blowing in BOS process. From the point of view of the only physical properties of the BOF slags studied, the slopping can be predicted at the initial stage where the slag composition lies in the low basicity, high FeO content, and low temperature.

Figure 12 shows the expected foam height of the slags during the first half of the blowing in the BOS process. The foam height was calculated for a 200-ton converter (Diameter=6.0m) as a function of decarburization rate under the assumption that the CO gas generated by the decarburization reaction dominated the superficial gas velocity in the vessel. During the first half of the blowing, the change of stage 1 to stage 2 led to larger decrease of foam height than that of stage 2 to stage 3. This figure indicates why slopping occurs during the first 50 % of the blow.

5. Summary and Conclusions

Slag foaming was qualitatively investigated for BOF type slag during the first half of the blowing period in the process in order to improve our understanding on slopping. The foam index Σ decreases up to about 20 % FeO content. This is believed to be due to the effect of viscosity which decreases as FeO content increases. At FeO contents higher than 20 % FeO, foam index is almost constant. In a CaO-SiO₂-FeO-MgO_{sat} system, the foam index decreases with increasing basicity up to 1.4 at 1713 K; when (CaO+MgO)/(SiO₂+Al₂O₃) was greater than 1.4, foam index increased due to the precipitates like 2CaOSiO₂ or (Fe,Mg)O. As the content of TiO₂ increases, the experimentally measured foam index increases. It is expected that TiO₂ added combines with MgO from the crucible wall or the slag to form 2MgOTiO₂ ($T_m=2029$ K) precipitate. It is indicated that the logarithm of foam index decreases with

increasing temperature in the temperature range of 1673 to 1823 K for 35%CaO-35%SiO₂-30%FeO-10%MgO slag. This is primarily because the foam index is inversely proportional to viscosity the foam index decreases and the temperature coefficient for viscosity is negative. The foam index decreases with increasing MgO additions to 35CaO-35SiO₂-30FeO slag.

The correlation developed by Zhang and Fruehan predicts the foam index for the present BOF slags during the first half of the blowing reasonably well. The measured foam indexes are slightly larger than those calculated. This may be because the uncertainty in viscosity estimation for BOF slags is relatively larger than that for bath smelting slags and ladle slags based on Urbain's model. The foam height was estimated for a 200-ton converter (Diameter=6.0m) as a function of decarburization rate. The calculations indicate that slopping is more likely early in the blow if the decarburization rate is high.

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Appendix. Estimation of Physical Properties

In order to estimate the foam index using Eq. (7), it is necessary to estimate slag properties. Due to the experimental difficulties at high temperatures, accurate measurement of the physical properties of slags in many cases has not been made. Therefore, models were developed to estimate the values for the properties such as density, surface

Table A1. Recommended values for partial molar volume $\bar{V}$ of various slag constituents at 1773 K.¹⁹⁾

Constituent	CaO	SiO ₂	FeO	MgO	TiO ₂
$\bar{V}$, cm ³ mol ⁻¹	20.7	19.55+7.966 X_{SiO_2}	15.8	16.1	24.0

Table A2. Recommended values for partial surface tension $\bar{\sigma}$ of various slag constituents at 1773 K.¹⁹⁾

Constituent	CaO	SiO ₂	FeO	MgO	TiO ₂
$\bar{\sigma}$, mNm ⁻¹	625	260	645	635	360

tension, and viscosity. The uncertainties vary according to the physical property being estimated so that experimental uncertainties are about $\pm 2\%$ for density, about $\pm 10\%$, and about $\pm 25\%$ for viscosity measurements. It is unreasonable to expect any predictive model to produce data which are more accurate than those obtained experimentally, for the models use experimental results to derive values for the various partial molar parameters.

An additive method for the estimation of densities in alloys and slags has been widely used. In this method, the molar volume V , can be obtained from Eqs. (A-1) and (A-2) below where M , x , and $\bar{V}$ are the molecular weight, mole fraction, and the partial molar volume, respectively, and the subscripts 1, 2, and 3 denote the various oxide constituents of the slag.

$$\rho = \frac{x_1 M_1 + x_2 M_2 + x_3 M_3}{V} \quad \text{.....(A-1)}$$

$$V = x_1 \bar{V}_1 + x_2 \bar{V}_2 + x_3 \bar{V}_3 \quad \text{.....(A-2)}$$

The partial molar volume is usually assumed to be equal to the molar volume of the pure component V° .¹⁹⁾ The recommended values for V° for the various oxides at 1773 K are given in **Table A1**. In order to calculate the values for the molar volume of CaO, SiO₂, FeO, MgO, and TiO₂ based on those obtained in Table A1, 0.01 % K⁻¹ was used as the temperature dependence of the molar volume.¹⁹⁾

Methods for estimating the surface tension of slags based on the addition of the partial molar contributions $\bar{\sigma}$ of the individual constituents have been reported by Appen *et al.*,²⁰⁾ Boni and Derge²¹⁾ and Popel.²²⁾ All these methods make use of Eq. (A-3)

$$\sigma = x_1 \bar{\sigma}_1 + x_2 \bar{\sigma}_2 + x_3 \bar{\sigma}_3 \quad \text{.....(A-3)}$$

where the subscripts 1, 2, 3, *etc.*, denote the various slag constituents. Values of $\bar{\sigma}_i$ are often taken to be the surface tension of the pure component σ_i° . This method of estimating the surface tension works well for certain slag mixtures but breaks down when surface-active constituents, such as P₂O₅, are present. Surface-active components migrate preferentially to the surface and cause a sharp decrease in the surface tension and only very small concentrations are required to cause an appreciable decrease in σ . The recommended values for σ° for the various oxides at 1773 K are given in **Table A2**. In order to calculate the values for the surface tension of CaO, SiO₂, FeO, MgO, and TiO₂ based on those shown in Table A2, 0.15 mNm⁻¹ K⁻¹ was applied as the temperature dependence of the surface tension ($d\sigma/dT$) of the present slag system.¹⁹⁾

Several models exist for the estimation of viscosities of

Table A3. Equations for B -parameters in Urbain model for viscosity.

B_i	$B_i = a_i + b_i \alpha + c_i \alpha^2$
B_0	$13.8 + 39.9355\alpha - 44.049\alpha^2$
B_1	$30.481 - 117.1505\alpha + 129.9978\alpha^2$
B_2	$-40.9429 + 234.0486\alpha - 300.04\alpha^2$
B_3	$60.7619 - 153.976\alpha + 211.1616\alpha^2$

slags based on their chemical composition. The applicability of these models has been reviewed and it was concluded that the models developed by Urbain *et al.*⁸⁾ and Riboud *et al.*¹⁸⁾ were in closer agreement with the experimentally measured viscosities than the others. However, it was found that the Urbain model gives a slightly better fit than the Riboud model. In the present study, Urbain's model was used for the estimation of slag viscosities. Both of these models use the Frenkel equation, as given in Eq. (A-4), where A and B are viscosity parameters, T is the temperature K, and μ is in N m⁻² s,

$$\mu = A \cdot T \cdot \exp(B/T) \quad \text{.....(A-4)}$$

In this model the parameters A and B are calculated by dividing the slag constituents into three categories.

$$\text{glass former: } x_G = x_{\text{SiO}_2} + x_{\text{P}_2\text{O}_5} \quad \text{.....(A-5)}$$

$$\text{modifier: } x_M = x_{\text{CaO}} + x_{\text{MgO}} + x_{\text{FeO}} + 2x_{\text{TiO}_2} + x_{\text{K}_2\text{O}} + 3x_{\text{CaF}_2} + x_{\text{MnO}} + 2x_{\text{ZrO}_2} \quad \text{.....(A-6)}$$

$$\text{amphoterics: } x_A = x_{\text{Al}_2\text{O}_3} + x_{\text{Fe}_2\text{O}_3} + x_{\text{B}_2\text{O}_3} \quad \text{.....(A-7)}$$

The normalized values x_G^* , x_M^* , and x_A^* are obtained by dividing the mole fractions, x_G , x_M , and x_A by the term $(1 + 2x_{\text{CaF}_2} + 0.5x_{\text{FeO}_{1.5}} + x_{\text{TiO}_2} + x_{\text{ZrO}_2})$.

$$x_G^* = \frac{x_G}{1 + 2x_{\text{CaF}_2} + 0.5x_{\text{FeO}_{1.5}} + x_{\text{TiO}_2} + x_{\text{ZrO}_2}} \quad \text{.....(A-8)}$$

$$x_M^* = \frac{x_M}{1 + 2x_{\text{CaF}_2} + 0.5x_{\text{FeO}_{1.5}} + x_{\text{TiO}_2} + x_{\text{ZrO}_2}} \quad \text{.....(A-9)}$$

$$x_A^* = \frac{x_A}{1 + 2x_{\text{CaF}_2} + 0.5x_{\text{FeO}_{1.5}} + x_{\text{TiO}_2} + x_{\text{ZrO}_2}} \quad \text{.....(A-10)}$$

Urbain proposed that the parameter B was influenced both by the ratio α and by x_G^* . The parameter B can be expressed in the form of Eq. (A-12) where B_1 , B_2 , and B_3 can be obtained by Eq. (A-13).

$$\alpha = \frac{x_M^*}{x_M^* + x_A^*} \quad \text{.....(A-11)}$$

$$B = B_0 + B_1 x_G^* + B_2 (x_G^*)^2 + B_3 (x_G^*)^3 \quad \text{.....(A-12)}$$

$$B_i = a_i + b_i \alpha + c_i \alpha^2 \quad \text{.....(A-13)}$$

B_0 , B_1 , B_2 , and B_3 can be calculated from the equations listed in **Table A3** and these parameters are then introduced into Eq. (A-12) to calculate B .

The parameter A can be calculated from B by Eq. (A-14) and the viscosity of the slag (in N m⁻² s) can then be determined by using Eq. (A-15).

$$-\ln A = 0.2693B + 11.6725 \quad \text{.....(A-14)}$$

$$\mu = 0.1[AT \exp(10^3 B/T)] \quad \text{.....(A-15)}$$