Effect of CaO/SiO₂ Ratio on Surface Tension of CaO–SiO₂–Al₂O₃–MgO Melts

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The effect of the CaO/SiO₂ molar ratio on the surface tension of calcium aluminosilicate melts containing magnesia (CaO–SiO₂–Al₂O₃–MgO) has been explored using a ring method at 1 723–1 823 K; the Al₂O₃ and MgO contents were approximately 12 and 8 mol%, respectively. The CaO/SiO₂ molar ratio of the samples was varied in the range of 1.1–1.7. The surface tension of the CaO–SiO₂–Al₂O₃–MgO system simultaneously increased upon increasing the CaO/SiO₂ molar ratio. The present data were compared with the surface tension of the binary calcium silicate (CaO–SiO₂) and the ternary calcium aluminosilicate (CaO–SiO₂–Al₂O₃) melts reported in the literatures. The surface tension of the present CaO–SiO₂–Al₂O₃–MgO melts was higher than those of the binary calcium silicate melts and slightly lower than those of the ternary calcium aluminosilicate melts when the polymerization degrees of the melts were comparable. The change in the surface tension was considered from the viewpoint of the local structure of oxygen atoms at the melt surface. Oxygen atoms, which require higher coordination by cations in the bulk, may tend to lose their neighbors at the surface of the melts, which can result in the formation of unsatisfied bonds at the surface. An increase in the number of unsatisfied bonds can yield an increase in the surface tension.

KEY WORDS: surface tension; Mg–Ca aluminosilicate melts; blast-furnace-type slag; polymerization degree; negative charge on oxygen atoms.

1. Introduction

The MgO-containing calcium aluminosilicate (CaO–SiO₂–Al₂O₃–MgO) melt is one of the most important systems for numerous industrial processes at elevated temperature (*e.g.*, pyrometallurgical process, glass making).^{1,2)} In blast-furnace iron-making, the melts can be formed as a slag phase with the reduction of iron ore to metallic iron in the lower part of the furnace (*i.e.*, cohesive and dripping zone). The gas permeability in the lower part of the blast furnace is strongly related to the flow rate and holdup behavior of the molten slag in the coke-packed bed. The flow rate of the molten slag was controlled by its viscosity; in addition, the melt holdup in the coke bed can be dominated by the surface tension of the molten slag and its wettability with coke.^{3,4)} Sunahara *et al.*⁵⁾ reported that a lower surface tension of the molten slag and its better wettability with coke decrease the pressure decrease in the lower part of the blast furnace, which can result in an improvement in the efficiency of the blast furnace performance. Therefore, the surface tension of CaO–SiO₂–Al₂O₃–MgO melts is one of the important factors in estimating the slag holdup behavior in the furnace.

Typically, the CaO/SiO₂ molar ratio of a blast-furnace-type slag is in the range of 1.2–1.4; the Al₂O₃ and MgO con-

tents in the slag are normally approximately 10 mol% and 3–8 mol%, respectively.⁶⁾ In future blast furnace operation, an increase in the Al₂O₃ content (up to 13 mol%) has been predicted by a change in the chemical composition of the iron ore sinter.⁵⁾ Because the surface tension of molten slag is sensitive to the chemical composition, re-optimization of the CaO/SiO₂ molar ratio of the slag is an important first step to control the physical properties of the higher Al₂O₃-containing slags.

The surface tension of oxide melts has been studied not only for its industrial importance but also for scientific interest concerning the surface structure of oxide melts. Many studies have been conducted on the surface tension of binary and ternary oxide systems such as CaO–SiO₂,^{7,8)} and CaO–SiO₂–Al₂O₃.^{7–10)} For the CaO–SiO₂–Al₂O₃–MgO system, the measurements are very limited in the literature. Nesterenko¹¹⁾ measured the surface tension of the CaO–SiO₂–Al₂O₃–MgO system with a lower Al₂O₃ content of approximately 3 mol%, varying the CaO/SiO₂ molar ratio from 0.8 to 1.6. Their data suggested that the surface tension reaches a maxima when the CaO/SiO₂ molar ratio is between 1.0 and 1.3. However, the mechanism of the phenomena was not explained. For a higher Al₂O₃-containing system (Al₂O₃ = 12 mol%), the measurements are limited to the CaO/SiO₂ molar ratio range of 0.8–1.2.¹²⁾ Therefore, the effect of the CaO/SiO₂ molar ratio (= 1.1–1.7) on the surface tension for a higher Al₂O₃-containing (= 12 mol%) system

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remains to be investigated.

The conventional view holds that the structure of CaO–SiO₂–Al₂O₃–MgO melts consists of a three-dimensional aluminosilicate network formed by connections between the framework species, such as SiO₄^{4–} and AlO₄^{5–} tetrahedra.^{13,14} A defining characteristic of silicate and aluminosilicate melts is the degree of polymerization.¹⁵ Some of the bulk properties, such as the viscosity, have been discussed in relation to the polymerization degree.¹⁶ However, few studies have focused on its relation to the surface tension. Similarly, the contribution of Al³⁺ species on the surface tension of the silicate melts has not been understood well enough.

In the present paper, the effect of the CaO/SiO₂ molar ratio on the surface tension of selected CaO–SiO₂–Al₂O₃–MgO (CaO/SiO₂ molar ratio=1.1–1.7; Al₂O₃=12 mol%; MgO=8 mol%) quaternary melts has been measured using a ring method. The mechanism of the change in the surface tension with the chemical composition has been considered from the viewpoint of the polymerization degree of the network structure and the type of oxygen species in the melts; they proposed a new angle of understanding for the surface tension of aluminosilicate melts.

2. Experimental

2.1. Sample Preparation

The samples were prepared from reagent grade SiO₂, Al₂O₃, CaCO₃, and MgO powders (Sigma Aldrich, Inc.). The reagent powders were weighed with precision in the correct amounts to form melts with the target compositions and were thoroughly mixed in a mullite mortar. The powder mixture was placed in a Pt crucible and melted at 1 873 K in a resistance furnace for 15–20 min in air. Then, the melt was quenched on a copper plate. The quenched sample was crushed into a powder, and this powder was employed for the surface tension measurements.

The target compositions of the samples for the surface tension measurements are listed in **Table 1**. The samples were labeled according to the chemical compositions as CASM_x, with *x*=the CaO/SiO₂ molar ratio. The Al₂O₃ and MgO contents were approximately 12 mol% and 8 mol%, respectively. The molar ratio of CaO/SiO₂ changes from 1.1

to 1.7. **Figure 1** shows that liquidus temperature¹⁷⁾ of all the samples was below 1 773 K. The molar compositions of the samples (see Table 1) indicate that the molar fraction of Al₂O₃ and MgO changed only slightly with the CaO/SiO₂ molar ratio. The polymerization degree of the samples is expressed as the concentration of non-bridging oxygens (NBOs)¹⁸⁾ in Table 1 (see details in section 4.1) The NBO/total-O (%) values were calculated using the following Eq. (1).¹⁸⁾

$$\text{NBO / total - O (\%)} = 100 \cdot \{2 \cdot \text{O (at\%)} - 4 \cdot \text{Si (at\%)} - 4 \cdot \text{Al (at\%)}\} / \text{O (at\%)}, \dots (1)$$

where O, Si, and Al (at%) represent the atomic percentage of each of the atoms.

2.2. Surface Tension Measurements

The surface tension of the sample melts was measured using a ring method.^{19,20)} Detailed information on the apparatus and procedure were described in a previous paper.²¹⁾ A Pt crucible (inner diameter: 65 mm, height: 27 mm) and a ring made of 0.16 mass%ZrO₂ dispersion-strengthened Pt-10 mass%Rh alloy were used in the experiments. The outer and inner diameter of the ring were 14.4 mm and 12.2 mm, respectively. Determination of the surface tension, γ , is based on measurements of the maximum force, $W_{\max}$, exerted on a ring body as the ring is withdrawn from the surface of the liquid. The surface tension, γ , is expressed by Eq. (2):

$$\gamma = \frac{W_{\max} \cdot g}{4\pi R_0 (1 + \alpha \Delta T)} \cdot S, \dots (2)$$

where R_0 is the radius of the ring. S is an empirical correction factor known as Harkins and Jordan's correction factor,²²⁾ which depends on the $W_{\max}/\rho$ (m³) ratio, and ρ represents the density of the sample. In a previous study,²¹⁾ an empirical relationship between S and $W_{\max}/\rho$ was determined using molten salts (PbCl₂, KNO₃, KCl, NaNO₃, K₂SO₄ and Na₂SO₄) as reference samples.²³⁾ The relationship between S and the $W_{\max}/\rho$ ratio of these molten salts is expressed using the following Eq. (3):

Table 1. Initial chemical composition (mol%) of the samples for the surface tension measurements. The mass fractions (mass%) of each component are listed in parentheses. The basicity of the sample was expressed as the molar ratio of CaO to SiO₂ and listed in this table. The non-bridging oxygen (NBO) concentration (%) represents the nominal fraction of NBO to the total oxygen atoms.

Sample	CaO	SiO ₂	Al ₂ O ₃	MgO	CaO/SiO ₂	NBO(%)
CASM1.1	41.4 (37.5)	38.7 (37.5)	12.2 (20.0)	7.7 (5.0)	1.1	45.2
CASM1.3	45.1 (40.9)	35.1 (34.1)	12.1 (20.0)	7.7 (5.0)	1.3	51.1
CASM1.5	48.2 (43.8)	32.0 (31.2)	12.1 (20.0)	7.7 (5.0)	1.5	56.1
CASM1.7	50.8 (46.2)	29.5 (28.8)	12.1 (20.0)	7.6 (5.0)	1.7	60.2

Fig. 1. Initial chemical compositions of the samples plotted on the reported liquidus surface¹⁷⁾ at 1 773 K of CaO–SiO₂–MgO–20 mass%Al₂O₃ system.

$$S = 0.65 + 0.2229 \cdot 10^6 \cdot \frac{W_{\max}}{\rho}, \dots\dots\dots (3)$$

The sample powder was placed in the Pt crucible and heated up to 1 823 K in air. The ring touched the surface of the sample melt and then pulled it up slowly. The force exerted on the ring was detected as the potential difference using a strain gauge; $W_{\max}$ was calculated based on the reference relationship between the exerted force and the potential difference, which was obtained using various standard weights beforehand. The surface tension measurements were performed during the cooling of the melt for temperatures varying in steps of 25 K in air (temperature range: 1 623–1 823 K). $W_{\max}$ was measured 5 times at each of the examined temperatures. The repetitive error in the measured potential difference, *i.e.*, $W_{\max}$, was within $\pm 0.4\%$.

2.3. Density Estimation

The densities of the sample melts were needed to determine the surface tension of the melt using the ring method (see Eqs. (2) and (3)). In the present study, the densities of the samples were estimated from the partial molar volume of each component reported by Mills and Keene²⁴⁾ (Eqs. (4) and (5)).

$$V = \sum X_i V_i, \dots\dots\dots (4)$$

$$\rho = \frac{M}{V}, \dots\dots\dots (5)$$

where V and M are the molar volume and molecular weight of the sample, respectively. X_i is the partial molar volume of each component. The molar volumes at 1 773 K were estimated using the partial molar volumes of 20.7×10^{-6} and 16.1×10^{-6} (m³/mol) for the CaO and MgO components,²⁴⁾ while those of SiO₂ and Al₂O₃ were calculated using Eqs. (6) and (7):

$$V_{\text{SiO}_2} = 19.55 + 7.97 X_{\text{SiO}_2}, \dots\dots\dots (6)$$

$$V_{\text{Al}_2\text{O}_3} = 28.3 + 32 X_{\text{Al}_2\text{O}_3} - 31.45 X_{\text{Al}_2\text{O}_3}^2, \dots\dots\dots (7)$$

The calculated densities were adjusted to other temperatures by applying a temperature coefficient of $-0.01\%/K$ for other molar volumes.²⁴⁾ Namely, the temperature dependences of the molar volume were calculated using the following Eq. (8):

$$V = V_{1773\text{ K}} + V_{1773\text{ K}} \cdot (T - 1773) \cdot \frac{0.01}{100}, \dots\dots\dots (8)$$

where $V_{1773\text{ K}}$ is molar volume at 1 773 K and T is the absolute temperature. This model usually provides the calculated density within $\pm 2\%$ of the measured values.²⁴⁾

3. Results

3.1. Temperature Dependence of Surface Tension

Figure 2 and Table 2 show the temperature dependence of the surface tension for the CaO–SiO₂–Al₂O₃–MgO melts. The obtained values of the surface tension changed slightly with the temperatures. As seen in the phase diagram of the CaO–SiO₂–Al₂O₃–MgO system, the CASM1.5 and the CASM1.7 might have potential to be crystallized at 1 723 K, however, surface tension of the samples did not drastically changed during the measurements in the temperature range of 1 823–1 723 K. It indirectly indicated that these samples were super-cooled below their liquidus temperatures under this experimental condition. Because the temperature dependence of the density was assumed to be independent of the chemical composition, the temperature coefficient of the surface tension is not discussed in the present paper. It should also be noted that the surface tension increased upon increasing the CaO/SiO₂ molar ratio. This tendency is similar to that observed for CaO–SiO₂ and CaO–SiO₂–Al₂O₃ systems.^{7–11)}

Fig. 2. Temperature dependences of surface tension for the CaO–SiO₂–Al₂O₃–MgO melts.

Table 2. The surface tension of the CaO–SiO₂–Al₂O₃–MgO system determined in the present study. Estimated density values from the reported partial molar volume²⁴⁾ were also listed in the table.

Sample	Surface tension, $\gamma/\text{mN}\cdot\text{m}^{-1}$					Density, $\rho/\text{kg}\cdot\text{m}^{-3}$ at 1 773 K
	1 723 K	1 748 K	1 773 K	1 798 K	1 823 K	
CASM1.1	475.1	476.3	477.6	477.5	477.2	2.763×10^3
CASM1.3	499.8	499.7	500.1	503.1	503.5	2.778×10^3
CASM1.5	511.9	512.3	514.3	513.9	515.3	2.788×10^3
CASM1.7	533.2	535.1	534.6	533.0	536.5	2.796×10^3

3.2. Effect of CaO/SiO₂ Molar Ratio on the Surface Tension

Figure 3 shows the effect of the CaO/SiO₂ molar ratio on the surface tension of CaO–SiO₂–Al₂O₃–MgO melts at 1 823 K. The surface tension linearly increased upon increasing the CaO/SiO₂ molar ratio. Nesterenko¹¹⁾ reported the surface tension of the lower Al₂O₃ (=3 mol%) containing CaO–SiO₂–Al₂O₃–MgO system has a maxima when the CaO/SiO₂ molar ratio was in the range of 1.0–1.3, as demonstrated in Fig. 3. However, this tendency was not observed in the present system with a higher Al₂O₃ content of 12 mol%. The CaO–SiO₂–Al₂O₃–MgO system with 3 mol% Al₂O₃ has a higher liquidus temperature than that of the present system. A previous review paper²⁵⁾ reported that the surface tension measurements were performed below the liquidus temperature for some of the compositions in the literature.¹¹⁾ The liquid composition might be changed because of the precipitation of a solid phase in their study. Surface tension measurements above the liquidus temperature are required to confirm whether there is a surface tension maximum along the CaO/SiO₂ molar ratio in the lower Al₂O₃ containing system.

4. Discussion

4.1. Structural Implication

The surface tension of oxide melts can be a reflection of the difference between the structure of the bulk and that of the surface.²⁶⁾ Surface atoms have less neighboring atoms with which to bond than atoms in the bulk.²⁷⁾ In other words,

Fig. 3. Effect of CaO/SiO₂ molar ratio on the surface tension of CaO–SiO₂–Al₂O₃–MgO melts (CaO/SiO₂: 1.1–1.7, Al₂O₃ concentration: 12 mol%, MgO concentration: 8 mol%) at 1 823 K compared with those values measured by Nesterenko.¹¹⁾ In their study, the CaO/SiO₂ molar ratio ranged from 0.8 to 1.5, and the Al₂O₃ and MgO concentration were approximately 3 and 9 mol%, respectively.

surface atoms lack a few neighbors, which can stabilize the chemical environment around an atom, thereby resulting in many unsatisfied bonds with higher energy. The surface tension of a liquid is the force required to reduce the liquid surface area to decrease the number of unsatisfied bonds with higher energy on the melt surface. Therefore, normally, an increase in these unsatisfied bonds yields an increase in the surface tension of the melts.²⁸⁾

Kingery²⁸⁾ suggested that the liquid surface of oxides melts has been covered with oxygen atoms. An oxygen-centric view of alkaline-earth aluminosilicate melts presents three types of oxygen atoms in the system: Si–O_{BO}–Si, Si–O_{BO}–Al, and Si–O_{NBO}.^{*} **Figure 4(a)** presents schematic illustrations of the three types of oxygen atoms. Si–O_{BO}–Si is a bridging oxygen (BO), which connects two SiO₄^{4–} tetrahedra (Fig. 4(a)). Si–O_{BO}–Al represents a BO between SiO₄^{4–} and AlO₄^{5–} tetrahedra. Si–O_{BO}–Al, which is negatively charged³²⁾ because of the valence difference between Si⁴⁺ and Al³⁺, requires a positive charge from alkaline-earth ions to maintain the charge neutrality (Fig. 4(b)). In the melts with percalcic compositions (CaO/Al₂O₃ molar ratio > 1), there are enough alkaline-earth ions (*i.e.*, Ca²⁺ and Mg²⁺) to compensate for the negative charges on the Si–O_{BO}–Al. More alkaline-earth ions that are required for charge compensation are present, and these excessive ions break the connections between the framework species (*i.e.*, these ions act as network modifiers), resulting in the creation of non-bridging oxygens (Si–O_{NBO}) in the melts^{33,34)} (Fig. 4(c)). Si–O_{NBO} also requires the positive charge from network modifier cations. The nominal concentration of Si–O_{NBO} species (O_{NBO}/total-O) can be calculated from the chemical composition of the samples, as shown in Table 1. **Figure 5** shows the relationship between the NBO concentration and the surface tension of the present CaO–SiO₂–Al₂O₃–MgO melts compared with those of the calcium silicate and calcium aluminosilicate melts measured by Mukai and Ishikawa.⁸⁾ Some of the authors²¹⁾ measured the surface tension of selected CaO–SiO₂–Al₂O₃ melts; its surface tension was very close to the surface tension of the melts with similar composition measured by Mukai and Ishikawa.⁸⁾ This finding demonstrates that the authors'

Fig. 4. Schematic illustrations of the local structure for three types of oxygen atoms in the bulk and at the melt surface. The Al coordination is assumed to be tetrahedral. The coordination numbers of (a) Si–O_{BO}–Si, (b) Si–O_{BO}–Al, and (c) Si–O_{NBO} are drawn as 2, 3 and 4, respectively.

*The presence of Al–O_{BO}–Al was neglected because it is not main component in the present system.²⁹⁾ In addition, a previous study indicated a presence of fivefold coordination for Al³⁺ as a minor species;³⁰⁾ however, the coordination number of Si⁴⁺ and Al³⁺ can be assumed to be 4 for simplicity in Fig. 4. The presence of Al–O_{NBO} species was ignored in the present paper because this presence has not been detected in a similar type of glass in NMR spectra.³¹⁾

Fig. 5. Effect of NBO concentration (%) on the surface tension of CaO-SiO₂-Al₂O₃-MgO melts at 1 823 K compared with those of CaO-SiO₂ and CaO-SiO₂-Al₂O₃ melts at 1 823 K measured by Mukai and Ishikawa⁸⁾ and Sukenaga *et al.*²¹⁾ The Al₂O₃ concentration of the CaO-SiO₂-Al₂O₃ system is in the range of 10–13 mol%.

data may be comparable with those obtained by Mukai and Ishikawa.⁸⁾ Figure 5 indicates that the surface tension of all the systems increased with increasing NBO concentration. Figure 4 shows the coordination structure of oxygen atoms at the surface. In the typical bulk structure of the silicate melts, the coordination number of the Si-O_{BO}-Si species (normally 2) is less than that of the Si-O_{NBO} species (4 or 5).³⁵⁾ The atoms with lower coordination number can more easily satisfy the chemical bonds at the melt surface. Therefore, Si-O_{NBO} species lose their neighbor atoms more easily than the Si-O_{BO}-Si species at the melt surface, indicating that an increase in the NBO concentration can result in an increase in the number of unsatisfied bonds of oxide melts.

It should be also noted that the surface tensions of the calcium aluminosilicate melts were higher than that of calcium silicate when the NBO concentrations were comparable (see Fig. 5). This finding may result from the difference in the type of BOs: calcium silicate contains only Si-O_{BO}-Si, whereas calcium aluminosilicate contains both Si-O_{BO}-Si and Si-O_{BO}-Al. Here, Si-O_{BO}-Al requires the positive charge from the charge compensator cations. The data in Fig. 5 imply that some of the charge compensation was not satisfied at the melt surface, which results in an increase in the surface tension of the melts.

A comparison of the surface tension for the present CaO-SiO₂-Al₂O₃-MgO melts with those of the CaO-SiO₂-Al₂O₃ melts indicates a slight decrease in the surface tension with a substitution of CaO with MgO when the NBO concentration is approximately 45%. Similar phenomena in the higher SiO₂ concentration system (SiO₂ content=44–61.5 mol%) have been reported by Staronka and Piekarska.³⁶⁾ It has been reported the smaller cation has priority to act as a network

modifier, whereas the larger cation prefers to behave as a charge compensator.³²⁾ In CaO-SiO₂-Al₂O₃-MgO melts, there are two types of modifier cations: Ca²⁺ and Mg²⁺. In the present quaternary system, the Mg²⁺ cation is smaller than Ca²⁺, which prefers to link with Si-O_{NBO} and behave as a network modifier. Recent NMR studies experimentally demonstrated this phenomena.¹⁴⁾ Si-O_{NBO} linked with Ca²⁺ increases the melt surface tension more than the Si-O_{NBO} linked with Mg²⁺. This tendency is similar to the surface tension of the binary alkaline-earth silicate system.³⁷⁾ The reason has not yet been clarified. Because the bond length of Mg-O is smaller than that of Ca-O,³⁸⁾ there is a possibility of a decrease in the coordination number of Si-O_{NBO} resulting from the larger charge density on Si-O_{NBO} from Mg²⁺ than from Ca²⁺.³⁸⁾ An investigation of the local structure of magnesium and oxygen atoms is required to clarify the mechanism of the surface tension change with Ca-Mg substitution in CaO-SiO₂-Al₂O₃-MgO melts.

4.2. Effect of CaO/SiO₂ Molar Ratio in High Al₂O₃ Slag on Gas Permeability of Blast Furnace

From the viewpoint of slag surface tension, Sunahara *et al.*⁵⁾ reported that the lower surface tension of the molten slag provides a decrease in the slag holdup in the cokes bed. In the present study, the surface tension increased with increasing CaO/SiO₂ molar ratio. These data imply that the use of the lower CaO/SiO₂ molar ratio can improve the gas permeability of the dripping zone in the blast furnace unless the viscosity of the slag has sufficient fluidity to flow down the cokes bed smoothly. Some of the authors measured the viscosity of CaO-SiO₂-Al₂O₃-MgO with 12 mol% of Al₂O₃ for a CaO/SiO₂ molar ratio in the range of 0.7–1.3.³⁹⁾ The viscosity of the melts increased with decreasing CaO/SiO₂ molar ratio. A decrease in the CaO/SiO₂ molar ratio can produce a negative effect on the smooth slag flow in the blast furnace from the viscosity viewpoint. One additional important factor to control the slag holdup in the coke bed, namely the wettability of the slag with coke, which should also be explored in future work. It is necessary to optimize the slag composition with careful consideration of these physical properties.

5. Conclusion

The surface tension of magnesia-containing calcium aluminosilicate melts simultaneously increased with the CaO/SiO₂ molar ratio, and the surface tension did not reach a maxima for the CaO/SiO₂ molar ratio in the range of 1.1–1.7; this tendency did not agree with the literature data in a 3-mol%-Al₂O₃ containing system. The change in the surface tension can be explained by the increase in the Si-O_{NBO} species, which can create some unsatisfied bonds more easily than Si-O_{BO}-Si species at the melt surface. Si-O_{BO}-Al, which requires some positive charges from alkaline-earth cations, can also create many unsatisfied bonds at the surface. The surface tension of the silicate and aluminosilicate can be dominated by the difference in the coordination structure of oxygen atoms between the bulk and melt surface. Future studies on the local structure of oxygen atoms will provide a more in-depth understanding of the surface tension for silicate and aluminosilicate systems. In addition,

experimental studies on the wettability between the melt and solid phases (*i.e.*, solid iron or coke) are required to adjust the CaO/SiO₂ molar ratio of the slag for efficient blast furnace operation with higher Al₂O₃-containing slags.

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