

# Effect of Alkaline / Alkaline-Earth oxides on Viscous Behavior of Iron-making Slag system

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**Abstract:** Viscosity is the physical property of most interest to the majority of industrial processes. It is an important rheological parameter to be considered in dealing with fluid flow behavior and in understanding the hydrodynamics and the kinetics of reactions. Also, the rate of reactions between metal and slag can be determined by continuous measurement of the viscosity of composition. Moreover, viscosity is an indispensable quantity to predict other important transport coefficients, such as diffusivities, thermal conductivities and surface tensions of molten metals and slags. Thus, the viscosity is one of the most important factors to understand the thermodynamic properties of molten slag not only in the metallurgical community but also in chemical geology. Recently, BF operation in the ironmaking process includes the use of low grade iron sources and the pulverized coal injection, which have lead the increase of  $\text{Al}_2\text{O}_3$  in the typical iron-making slag system. Due to the amphoteric behavior of  $\text{Al}_2\text{O}_3$ , it would be necessary to have a new perspective for estimating the effects of major elements such as CaO,  $\text{SiO}_2$ , MgO and FeO significantly affecting on the viscous behavior of slag in the iron-making process. Although the alkaline oxide such as  $\text{Na}_2\text{O}$ ,  $\text{K}_2\text{O}$  accompanied with low grade material sources can also affect the viscosity and thus impact the stability of the BF operation, relatively little has been known for the effect of alkali oxides ( $\text{Na}_2\text{O}$ ,  $\text{K}_2\text{O}$ ) on the viscous behavior under conditions of high  $\text{Al}_2\text{O}_3$  concentrations. Furthermore, the contributions of  $\text{Na}_2\text{O}$  and  $\text{K}_2\text{O}$  toward the ionic charge compensation effect and structural changes in the BF type slags have not yet to be fully understood. The focus of present study is to understand the effect of not only major elements such as CaO, MgO but also alkaline oxide on the viscous behavior of iron-making slag system. To better understanding the viscous behavior, structural changes has been estimated using by Fourier Transform Infrared (FT-IR) spectroscopy, where the original Darken's excess stability function and ionic charge compensation effect was introduced in order to understand the thermo-physical phenomena. In addition, some effort has been also attempted to verify the relationship among the viscosity, primary phase and critical temperature.

**Key words:** Viscosity, Structure, Alkaline and Alkaline earth oxide, Stability, Ionic charge compensation, Critical temperature, Primary phase

## 1. Introduction

Viscosity is the physical property of most interest to the majority of industrial processes. It is an important rheological parameter to be considered in dealing with fluid flow behavior and in understanding the hydrodynamics and the kinetics of reactions. Significant contributions have been made to understanding viscosity using both modeling and experimental methods. Extensive work to predict the viscous behaviors by statistical<sup>[1]</sup>, thermodynamical<sup>[2],[3]</sup>, structural<sup>[4]</sup>, and empirical<sup>[5]</sup> approximations has been published. Experimental work has also been done on a wide

composition range of primary slags, tuyere slags, and taphole slags. Recent process changes in the BF operations including the increased use of Pulverized Coal Injection (PCI), utilization of low grade ore, and reduction of slag volume, have increased the concentration of  $\text{Al}_2\text{O}_3$  to nearly 20 wt% and alkali oxides ( $\text{Na}_2\text{O}$ ,  $\text{K}_2\text{O}$ ). The increases in  $\text{Al}_2\text{O}_3$  and alkali oxides ultimately change the relative concentration of the constituents in the typical BF type slag system, which can affect the viscosity and impact the stability of the BF operation. Studies on the effect of  $\text{Al}_2\text{O}_3$  in the  $\text{CaO-SiO}_2\text{-10wt.\%MgO-Al}_2\text{O}_3$  slag system have also been carried out in a previously published report where the viscosity increased with  $\text{Al}_2\text{O}_3$  additions up to 20 wt.%<sup>[6]</sup>.

Thus, it is necessary to understand the effects of major elements of the slag system such as  $\text{CaO}$ ,  $\text{SiO}_2$ ,  $\text{MgO}$ , and  $\text{Al}_2\text{O}_3$ . Of these components,  $\text{MgO}$  is of particular interest especially in the BF slag system.  $\text{MgO}$  is added not only for refractory protection, but also to lower viscosity to improve gas permeability, which enhances the reduction reaction and drainage. However, the phase diagram indicates that excessive  $\text{MgO}$  additions increase the viscosity by forming high temperature phases of periclase ( $\text{MgO}$ ) and spinel ( $\text{MgAl}_2\text{O}_4$ ), and an optimum concentration should exist due to the variation of melting temperature and liquid structure. Work by Kim *et al.* described the depolymerization of the slag network structure and subsequent decrease in the viscosity with  $\text{MgO}$  additions at basicity of 1.18.<sup>[7]</sup> An optimum concentration of 7 wt.%  $\text{MgO}$  was also suggested for a  $\text{CaO-SiO}_2\text{-13wt.\%Al}_2\text{O}_3\text{-MgO}$  slag system. Furthermore at higher concentrations of  $\text{Al}_2\text{O}_3$ , Park *et al.* showed the viscosity to increase until a certain amount of  $\text{Al}_2\text{O}_3$  content due to the amphoteric behavior of  $\text{Al}_2\text{O}_3$ . Therefore, the effect of  $\text{MgO}$  on the viscosity and its optimum concentration near 20 wt.%  $\text{Al}_2\text{O}_3$  is likely to behave differently.

In addition, relatively little has been known on the effect of alkali oxides ( $\text{Na}_2\text{O}$ ,  $\text{K}_2\text{O}$ ) under conditions of high  $\text{Al}_2\text{O}_3$  concentrations. Alkali oxide ( $\text{Na}_2\text{O}$ ,  $\text{K}_2\text{O}$ ) is of particular interest due to its recirculation in the BF, which can form scaffolds on the BF wall and hinder fluid flow. However, the contributions of  $\text{Na}_2\text{O}$  and  $\text{K}_2\text{O}$  toward the ionic charge compensation effect and structural changes in the  $\text{CaO-SiO-MgO-Al}_2\text{O}_3$  BF type slags have not yet to be fully understood. In this study, the viscosity of  $\text{CaO-SiO}_2\text{-20wt.\%Al}_2\text{O}_3\text{-MgO}$  quaternary slags from 0.8 to 1.2 basicity at 1773 K was measured. 5-13 wt.%  $\text{MgO}$  was added to these slags to determine the effect of  $\text{MgO}$  in the  $\text{CaO-SiO}_2\text{-20wt.\%Al}_2\text{O}_3\text{-MgO}$  slag system. With respect to alkali oxides, the viscosities of the  $\text{CaO-SiO}_2\text{-10wt.\%MgO-20wt.\%Al}_2\text{O}_3\text{-R}_2\text{O}$  (  $\text{R}=\text{Na, K}$  ) quinary slags from 0.8 to 1.2 basicity at 1773 K were also measured. 1-10 wt.%  $\text{Na}_2\text{O}$  or 1-5 wt.%  $\text{K}_2\text{O}$  was added to these slags to determine the effect of  $\text{Na}_2\text{O}$  and  $\text{K}_2\text{O}$  in the  $\text{CaO-SiO}_2\text{-10wt.\%MgO-20wt.\%Al}_2\text{O}_3\text{-R}_2\text{O}$  (  $\text{R}=\text{Na, K}$  ) slag system, respectively. Fourier Transform Infrared (FT-IR) spectroscopy was used to verify the changes in slag structure.

## 2. Experimental

### 2.1 Sample preparation

Slag samples were prepared using reagent-grade chemicals. In order to prepare the pre-melted slag, 110 g of mixed powder comprising CaO-SiO<sub>2</sub>-20wt.%Al<sub>2</sub>O<sub>3</sub>-5wt.%MgO (CaO/SiO<sub>2</sub>=0.8, 1.0, 1.2) in case of viscosity measurement for the effect of MgO and CaO-SiO<sub>2</sub>-10wt.%MgO-20wt.%Al<sub>2</sub>O<sub>3</sub> (CaO/SiO<sub>2</sub>=0.8, 1.0, 1.2) in case of measurement for effect of Na<sub>2</sub>O or K<sub>2</sub>O were pre-melted in graphite crucibles in an Ar (0.4 L/min) atmosphere at 1773 K. Moisture and oxygen in Ar gas were removed by passing the gas through a CaSO<sub>4</sub>, silica gel and a column of magnesium turnings heated at 753 K. The temperature was controlled within  $\pm 2$  K using a Pt-10wt.%Rh/Pt-13wt.%Rh thermocouple and a proportional integral differential controller. After homogenization, the slag melt was quenched and was then crushed for later experiments.

### 2.2 Measurement

The viscosity was measured using a rotating spindle connected to a rheometer. The experimental apparatus is shown in Figure 1. A calibrated Brookfield digital viscometer (model LVDV-II+) with a full-scale torque of  $6.737 \times 10^{-5}$  N·m was used. The viscometer head was connected to the working spindle by two Pt-10wt.%Rh hooks.

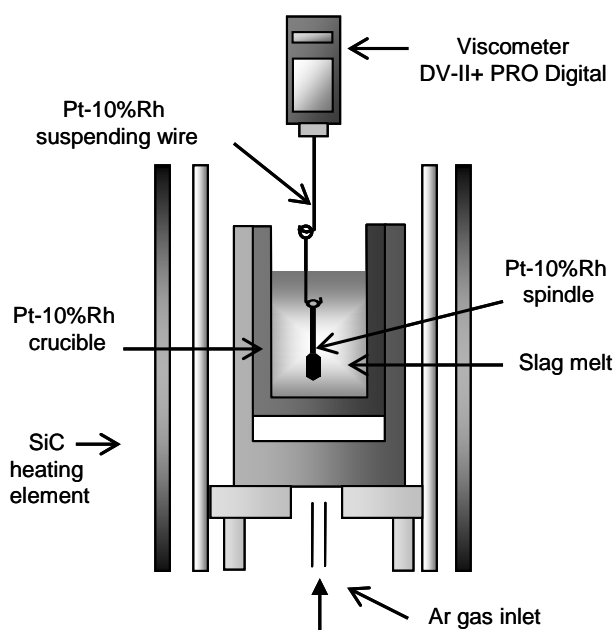


Figure 1. Schematic diagram of experimental apparatus for this study.

The crucible, suspension wire, and spindle used in the experiments were made of Pt-10wt.%Rh. 110 g of slag samples were prepared with additional MgO, Na<sub>2</sub>O, K<sub>2</sub>O powder to obtain the slag composition listed in Table 1. Small amount of other components were also added to maintain proper composition of CaO/SiO<sub>2</sub> and 20 wt.%Al<sub>2</sub>O<sub>3</sub>, CaO/SiO<sub>2</sub> and 20 wt.%Al<sub>2</sub>O<sub>3</sub>-10 wt.% MgO.

Table 1. Experimental compositions and measured values from present experiment.

No.	Experimental composition						unit : wt%	
	C/S	CaO	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	MgO	Na <sub>2</sub> O	K <sub>2</sub> O	
1	0.8	33.33	41.67	20	5			
2	0.8	32.44	40.56	20	7			
3	0.8	31.11	38.89	20	10			
4	0.8	29.78	37.22	20	13			
5	1.0	37.50	37.50	20	5			
6	1.0	36.50	36.50	20	7			
7	1.0	35.00	35.00	20	10			
8	1.0	33.50	33.50	20	13			
9	1.2	40.91	34.09	20	5			
10	1.2	39.82	33.18	20	7			
11	1.2	38.18	31.82	20	10			
12	1.2	36.55	30.45	20	13			
13	0.8	30.67	38.33	20	10	1		
14	0.8	29.78	37.22	20	10	3		
15	0.8	28.89	36.11	20	10	5		
16	0.8	26.67	33.33	20	10	10		
17	1.0	34.50	34.50	20	10	1		
18	1.0	33.50	33.50	20	10	3		
19	1.0	32.50	32.50	20	10	5		
20	1.0	30.00	30.00	20	10	10		
21	1.2	37.64	31.36	20	10	1		
22	1.2	36.55	30.45	20	10	3		
23	1.2	35.45	29.55	20	10	5		
24	1.2	32.73	27.27	20	10	10		
25	0.8	30.67	38.33	20	10		1	
26	0.8	29.78	37.22	20	10		3	
27	0.8	28.89	36.11	20	10		5	
28	1.0	34.50	34.50	20	10		1	
29	1.0	33.50	33.50	20	10		3	
30	1.0	32.50	32.50	20	10		5	
31	1.2	37.64	31.36	20	10		1	
32	1.2	36.55	30.45	20	10		3	
33	1.2	35.45	29.55	20	10		5	

The slag sample was placed into the reaction chamber and sufficiently purged with 400 sccm of Ar. The furnace was heated to 1773 K and held for more than 3 hours before immersion of the rotating spindle into the slag and centered within the melt. Each measurement was performed during the cooling cycle under an Ar atmosphere with an equilibration time of 30 minutes at each temperature to ensure sufficient thermal equilibration within the liquid slag. After viscosity measurements were completed, slag samples were reheated up to 1773 K and then quenched in flushing Ar stream in order to measure slag composition (by using X-ray Fluorescence: Bruker, S4 Explorer), slag structure (by using FT-IR spectroscopy: JASCO, FT/IR-300 E) and. According to the composition analysis of post-measurement slag

as well as pre-measurement slag, there was no significant change in the slag compositions (less than 1%).

### 3. Results and Discussion

#### 3.1 Effect of MgO on viscosity

Figure 2 shows the change of viscosity in the CaO-SiO<sub>2</sub>-20wt.% Al<sub>2</sub>O<sub>3</sub>-MgO slags as a function of basicity at various MgO concentrations and constant temperature of 1773 K.<sup>[8]</sup> At low basicities (C/S≤1.0), the viscosity is significantly affected by additions of MgO. At higher basicities (C/S=1.2), the effect of MgO on the viscosity is not as pronounced. The results of the viscosity with basicity and addition of MgO is compared with reported data by Machin *et al.* in the 13 wt.% MgO and 8 wt.% Al<sub>2</sub>O<sub>3</sub> containing slags.<sup>[9]</sup> The change in the viscosity with increased basicity is consistent with results from literature values, where CaO modifies the silicate network structure into simple ring and/or chain structure.<sup>[10]</sup> This depolymerization with CaO addition results in decreased viscosity.

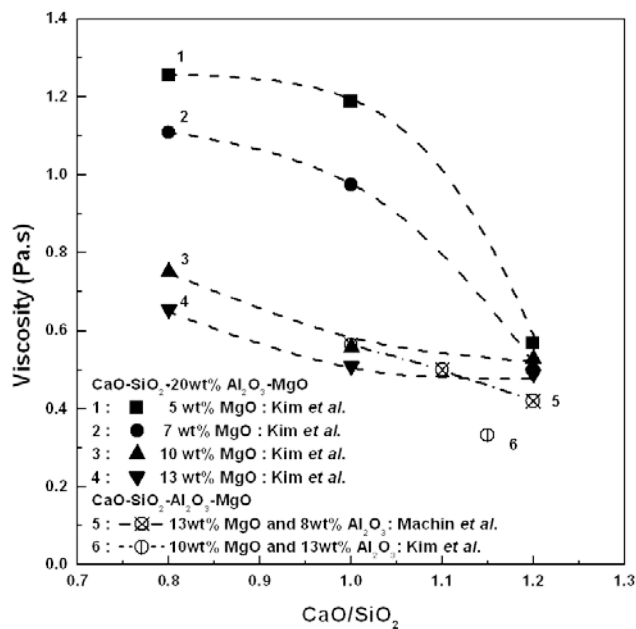


Figure 2. The viscosity of CaO-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>-MgO quaternary slag system at 1773 K as a function of CaO/SiO<sub>2</sub> ratio.

Structural analysis of the present slag system using FT-IR spectroscopy was applied to clarify the effect of MgO on the viscosity. The transmittance of the CaO-SiO<sub>2</sub>-20wt.% Al<sub>2</sub>O<sub>3</sub>-MgO at basicity of 0.8, 1.0, and 1.2 as a function of wave numbers at different MgO contents is shown in Figure 3.<sup>[8]</sup>

Four major Si-O IR bend peaks are observed at 1056 cm<sup>-1</sup>, 972 cm<sup>-1</sup>, 906 cm<sup>-1</sup>, and 862 cm<sup>-1</sup>, which correspond to the Non-Bridging oxygen (NBO) of 1, 2, 3, and 4, respectively. Although not observed in the present study, it should be noted that NBO=0 refers to a fully connected network with a wave number of 1200 cm<sup>-1</sup>. The silicate peaks are shifted to lower wave numbers with increasing MgO and suggest the silicate network is depolymerized to higher NBO's. The peak of [AlO<sub>4</sub>]-tetrahedra shown at the range of 740-610 cm<sup>-1</sup> dampens with increasing MgO. The peak almost disappears at 13 wt.%MgO. This could be a common behavior of MgO and its role as a basic oxide. The

[Al-O-Si]-bending peak is detected near  $500\text{ cm}^{-1}$  and dampens with increasing MgO. This suggests a decrease in the linkage between  $[\text{SiO}_4]$  and  $[\text{AlO}_4]$  in the aluminosilicate melt. With MgO concentrations near 13 wt.%, the flow units in the slag structure originated from the spinel phase, which is likely to differ with the flow units originating from the non-spinel phases. This change in flow unit may cause a change in the activation energy and the viscous behavior of the slag system.

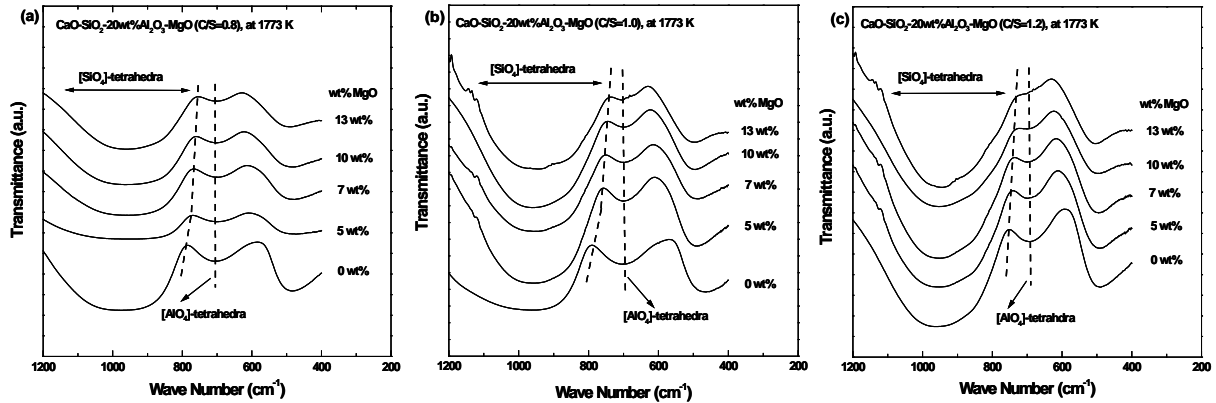


Figure 3. The FT-IR results of the CaO-SiO<sub>2</sub>-20wt% Al<sub>2</sub>O<sub>3</sub>-MgO slag sample as-quenched at 1773 K and a basicity of (a)0.8, (b)1.0, (c)1.2.

### 3.2 Effect of Na<sub>2</sub>O on the viscosity

Figure 4(a) shows the change of viscosity in the CaO-SiO<sub>2</sub>-10wt.%MgO-20wt.%Al<sub>2</sub>O<sub>3</sub>-Na<sub>2</sub>O quinary slags<sup>[11]</sup> as a function of basicity at various Na<sub>2</sub>O concentrations and constant temperature of 1773 K shown with the results by Sukenaga *et al.*<sup>[12]</sup> The difference of viscosity between Sukenaga *et al.* and the present study would be explained by the effect of MgO in slag.

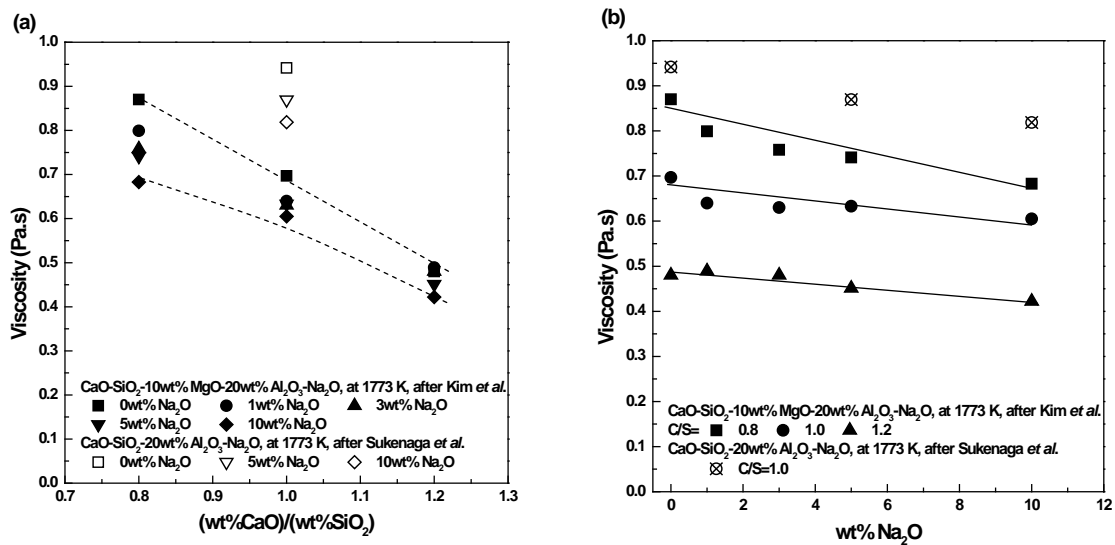


Figure 4. The Viscosity changes in the CaO-SiO<sub>2</sub>-10wt.%MgO-20wt.%Al<sub>2</sub>O<sub>3</sub>-Na<sub>2</sub>O system at 1773 K (a) as a function of C/S and (b) as a function of wt.%Na<sub>2</sub>O.

It can be observed that the magnitude of change in the viscosity with  $\text{Na}_2\text{O}$  addition decreases as the basicity (C/S) increases. This trend is similar to a basic oxide component acting upon a slag network structure. The effect of basicity on viscosity of slag is qualitatively consistent with results from literature values, where CaO modifies the silicate network structure into simple ring and/or chain structure.

In the perspective of  $\text{Na}_2\text{O}$  additions shown in Figure 4(b), the effect of  $\text{Na}_2\text{O}$  on the viscosity diminishes with higher basicity. As the basic components (CaO, MgO) in the slag outweigh the acidic components ( $\text{SiO}_2$ ), the networking structure of molten slag has already been depolymerized into simpler polymer type units. Thus, further additions of basic components ( $\text{Na}_2\text{O}$ ), when the slag structure has already been significantly depolymerized, have limited effect.

The transmittance of the  $\text{CaO-SiO}_2\text{-10wt.\%MgO-20wt.\%Al}_2\text{O}_3\text{-Na}_2\text{O}$  at C/S of 0.8 and 1.2 as a function of wave numbers at different  $\text{Na}_2\text{O}$  contents is shown in Figure 5(a) and 5(b), respectively.<sup>[11]</sup>

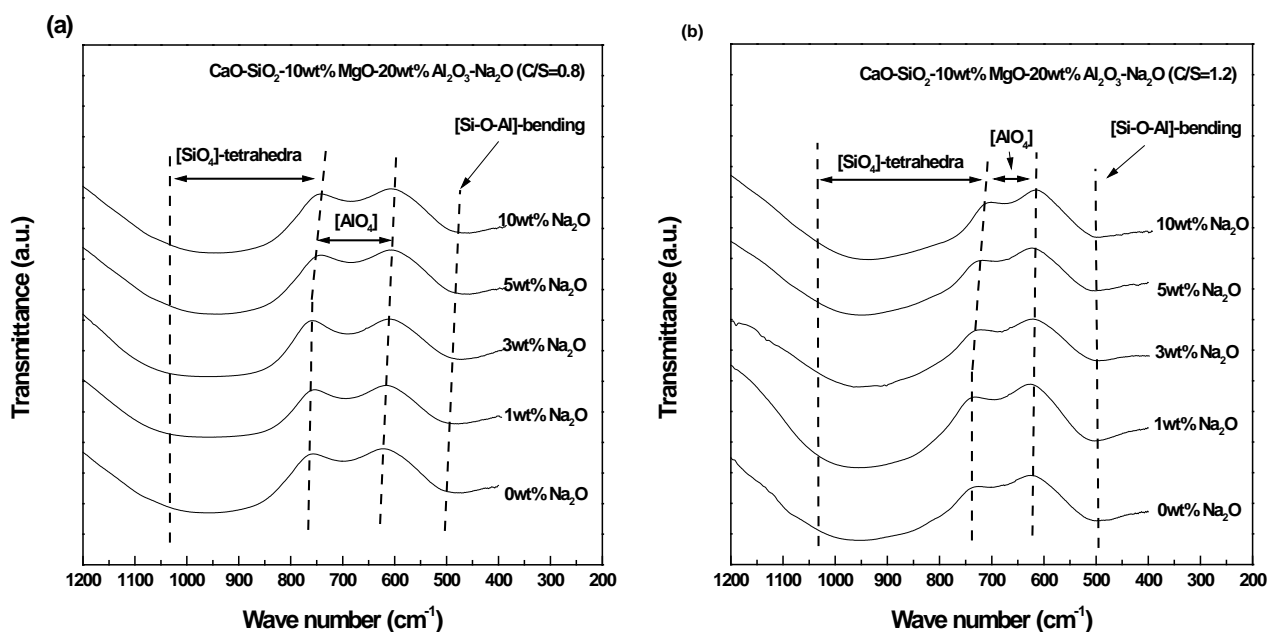


Figure 5. The FT-IR results of the  $\text{CaO-SiO}_2\text{-10wt.\%MgO-20wt.\%Al}_2\text{O}_3\text{-Na}_2\text{O}$  slag sample as-quenched at 1773 K and (a) a basicity of 0.8 (b) a basicity of 1.2.

In Figure 5(a), the transmittance of Si-O-Al bending and  $[\text{AlO}_4]\text{-tetrahedra}$  are changed continuously toward the low wave number while that of the  $[\text{SiO}_4]\text{-tetrahedra}$  band group remains unchanged below 5 wt.%  $\text{Na}_2\text{O}$ . A shift to the lower wave number means the distance between Si/Al and O has widened, *viz.*, the network structure is depolymerized. This indicates additional  $\text{O}^{2-}$  and  $\text{Na}^+$  provided by  $\text{Na}_2\text{O}$  modify the  $[\text{AlO}_4]^{5-}$  preferentially to satisfy the ionic charging compensation effect. In alumino-silicate melts similar to this study, the alkali element, which has a positive charge of +1 in the ionic state, has an ionic charge compensation effect.<sup>[13],[14]</sup> As the alumino-silicate network is formed by the substitution of  $\text{Si}^{4+}$  by  $\text{Al}^{3+}$  in the slag melt, it must maintain a charge-balance through the alkali cation,  $\text{Na}^+$ . The addition of  $\text{Na}_2\text{O}$  seems to stabilize the  $[\text{AlO}_4]\text{-tetrahedra}$  and induce the amphoteric oxide  $\text{Al}_2\text{O}_3$  to behave as an

acidic oxide. Thus, Na<sub>2</sub>O can preferentially interact with the [AlO<sub>4</sub>]-tetrahedra more readily than the [SiO<sub>4</sub>]-tetrahedra. In Figure 5(b), the range of silicate structure between 1030 and 750 cm<sup>-1</sup> at 1.2 basicity slightly shifted towards the lower wave number with additions of Na<sub>2</sub>O compared to 0.8 basicity shown in Figure 5(a). The peak of the [AlO<sub>4</sub>]-tetrahedra is not significantly shifted with addition of Na<sub>2</sub>O because at high basicity much of the [AlO<sub>4</sub>]-tetrahedra has already been depolymerized and additional O<sup>2-</sup> from Na<sub>2</sub>O will modify the residual [SiO<sub>4</sub>]-tetrahedra.

According to the abovementioned effect of Na<sub>2</sub>O on the viscosity and slag structure, increased concentration of basic oxides lowers the viscosity by breaking the network structure of the molten slag, and it is the cation that seems to affect the affinity with the particular acidic oxide group. Thus, the viscosity of CaO-SiO<sub>2</sub>-10wt.%MgO-20wt.%Al<sub>2</sub>O<sub>3</sub>-Na<sub>2</sub>O slags decreases with additions of Na<sub>2</sub>O by providing network breaking O<sup>2-</sup> and charge balance by Na<sup>+</sup> ion independently contributed to the depolymerization of the network structure of the molten slag.

### 3.3 Effect of K<sub>2</sub>O on the viscosity

Figure 6(a) and (b) shows the change of viscosity in the CaO-SiO<sub>2</sub>-10wt.%MgO-20wt.%Al<sub>2</sub>O<sub>3</sub>-K<sub>2</sub>O quinary slags as a function of basicity at various K<sub>2</sub>O concentrations and constant temperature of 1773 K shown with the results by Sukenaga *et al.*<sup>[12]</sup> The difference of viscosity between Sukenaga *et al.* and the this study<sup>[15]</sup> can be explained by the effect of MgO in slag.

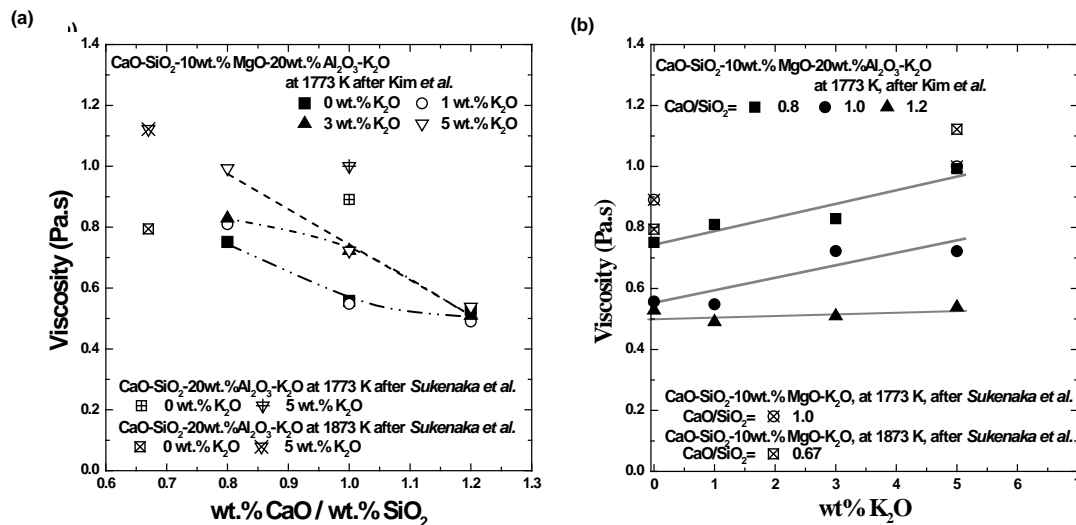


Figure 6. The viscosity change in the CaO-SiO<sub>2</sub>-10wt.%MgO-20wt.%Al<sub>2</sub>O<sub>3</sub>-K<sub>2</sub>O system at 1773 K (a) as a function of C/S and (b) as a function of wt.% K<sub>2</sub>O.

The viscosity increases with K<sub>2</sub>O additions at various basicities (C/S). This trend is opposite to a basic oxide component acting upon a slag network. The effect of basicity(C/S) on viscosity of slag is qualitatively consistent with results from literature values, where CaO modifies the silicate network structure into simple ring and/or chain structure. (Figure 6(a)). With respect to K<sub>2</sub>O additions shown in Figure 6(b), the effect of K<sub>2</sub>O on the viscosity is more



significant at lower basicity. As the acidic component ( $\text{SiO}_2$ ) in the slag outweigh the basic components ( $\text{CaO}$ ,  $\text{MgO}$ ), the networking structure of molten slag has already been polymerized into complicated units. Thus, further additions of network forming components ( $\text{K}_2\text{O}$ )<sup>[16]</sup>, when the slag structure has already been significantly polymerized, have the enlarged effect.

Structural analysis of the present slag system using FT-IR spectroscopy was applied to clarify the effect of  $\text{K}_2\text{O}$  on the viscosity.<sup>[15]</sup> The transmittance of the  $\text{CaO-SiO}_2$ -10wt.% $\text{MgO}$ -20wt.% $\text{Al}_2\text{O}_3$ - $\text{K}_2\text{O}$  at C/S of 0.8 and 1.2 as a function of wave numbers at different  $\text{K}_2\text{O}$  contents is shown in Figure 7. The band group of Si-O bonds was found between 1030 and 750  $\text{cm}^{-1}$  which corresponds to the NBO of 1 to 4. The band group shown in the range of 750-630  $\text{cm}^{-1}$  is related to the asymmetric stretching vibration of  $[\text{AlO}_4]$ -tetrahedra and the peak at 500  $\text{cm}^{-1}$  indicates the Si-O-Al bending.

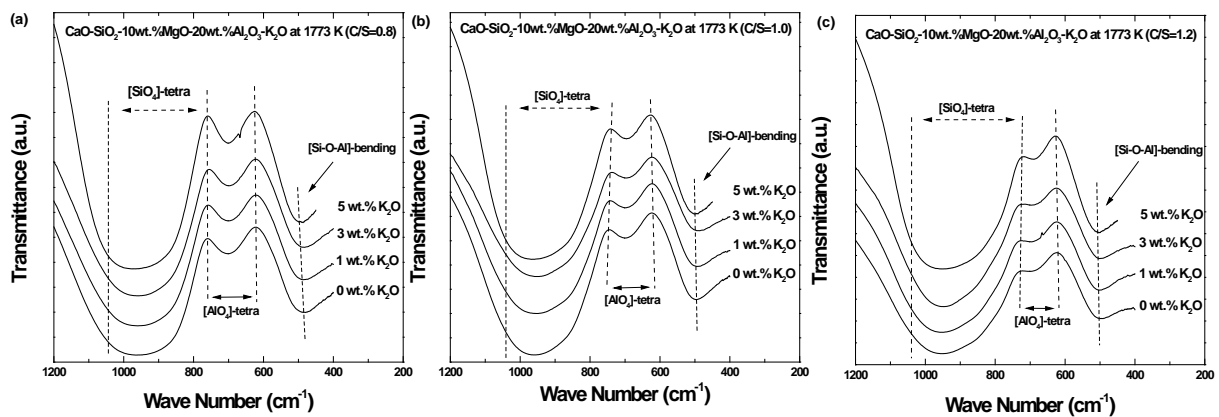


Figure 7. The FT-IR results of (a) the  $\text{CaO-SiO}_2$ -10wt.% $\text{MgO}$ -20wt.% $\text{Al}_2\text{O}_3$ - $\text{K}_2\text{O}$  slag sample as-quenched at 1773 K and a basicity of 0.8 (b) a basicity of 1.0 (c) a basicity of 1.2.

In Figure 7(a), the peak of the IR bands for the  $[\text{AlO}_4]$ -tetrahedral units become greater as addition of  $\text{K}_2\text{O}$  is increased. And the relative transmittance at higher limit of the  $[\text{AlO}_4]$ -tetrahedral bands is also increased with higher  $\text{K}_2\text{O}$ . Thus, the addition of  $\text{K}_2\text{O}$  into  $\text{CaO-SiO}_2$ -20wt.% $\text{Al}_2\text{O}_3$ - $\text{MgO}$  slag system would increase the relative fraction of  $[\text{AlO}_4]$ -tetrahedral units. Consequently, the viscosity of the melts increases, due to the polymerization of aluminate structure by the formation of  $[\text{AlO}_4]$ -tetrahedral units. And the band of Si-O-Al bending is changed to the higher wave number, which also indicates the distance between Si/Al and O has become narrow, *viz.*, the network structure is polymerized. This suggests  $\text{K}_2\text{O}$  make the  $[\text{AlO}_4]$ -tetrahedral units to satisfy the ionic charging compensation effect. The change of IR bands for the Si-O bonds shown at about 1030 to 750  $\text{cm}^{-1}$  was negligible. The reason for the negligible change in Si-O bonds can be attributed to the reaction of  $\text{O}^{2-}$  with  $\text{Al}_2\text{O}_3$  to form  $[\text{AlO}_4]$ -tetrahedral units. Consequently, the role on the aluminate structure is opposite to the effect of  $\text{Na}_2\text{O}$  on the slag structure. In this study, it is reasonable to assume that the role of  $\text{K}_2\text{O}$  on the aluminate structure is more dominant than that of  $\text{K}_2\text{O}$  on the silicate. These variations of the structure in the melts with  $\text{K}_2\text{O}$  addition could explain the role of  $\text{K}_2\text{O}$  as a network former in the viscous flow of the slags.

In alumino-silicate melts similar to this study, the alkali element, which has a positive charge of +1 in the ionic state, has an ionic charge compensation effect. As the alumino-silicate network is formed by the substitution of  $\text{Si}^{4+}$  by  $\text{Al}^{3+}$  in the slag melt, it must maintain a charge-balance through the alkali cation,  $\text{K}^+$ . The addition of  $\text{K}_2\text{O}$  seems to stabilize the  $[\text{AlO}_4]$ -tetrahedra and induce the amphoteric oxide  $\text{Al}_2\text{O}_3$  to behave as an acidic oxide. Thus,  $\text{K}_2\text{O}$  can preferentially interact with the  $[\text{AlO}_4]$ -tetrahedra more readily than the  $[\text{SiO}_4]$ -tetrahedra. In Figure 7(c), the relative intensity of the IR bands for the  $[\text{AlO}_4]$ -tetrahedral units at a basicity of 1.2 is less than that at a basicity of 0.8, which indicates the structure of the melts has already been depolymerized and the effect of  $\text{K}_2\text{O}$  on the structure is limited as shown in Figure 6(b). However, it was also founded that the changes of the  $[\text{AlO}_4]$ -tetrahedral units and Si-O-Al bending are similar to that of a basicity of 0.8. Consequently, viscosity of the slag is increased with higher  $\text{K}_2\text{O}$  even if the increase in viscosity is less than that of a basicity of 0.8.

#### 4. Conclusions

The aim of the present study was to understand the effect of  $\text{MgO}$ ,  $\text{Na}_2\text{O}$ ,  $\text{K}_2\text{O}$  oxides on the viscous behavior at a high concentration of  $\text{Al}_2\text{O}_3$  which are the major or minor components affecting on the ironmaking process.

1. The slag viscosity at 1773 K decreased with additions of  $\text{MgO}$  due to the basic oxide characteristic of this component, the effect of  $\text{MgO}$  dampened at a high basicity of 1.2. The FT-IR spectroscopic results showed the modification of the slags network structure with additions of  $\text{MgO}$  in the present slag system.

2. The slag viscosity at 1773K decreased with addition of  $\text{Na}_2\text{O}$ . From the FT-IR spectroscopic analysis, it was founded that the  $[\text{AlO}_4]$ -tetrahedra was depolymerized more readily than  $[\text{SiO}_4]$ -tetrahedra due to the ionic charge compensation effect which has a tendency to be attracted  $[\text{AlO}_4]$ -tetrahedra.

3. The slag viscosity at 1773K increased with addition of  $\text{K}_2\text{O}$ . From the FT-IR spectroscopic analysis, it was founded the role on the aluminate structure is a network former through making  $[\text{AlO}_4]$ -tetrahedral units, while the role on the silicate structure is not apparent. Thus, it is reasonable to assume that the role of  $\text{K}_2\text{O}$  on the aluminate structure is more dominant than that of  $\text{K}_2\text{O}$  on the silicate structure, which would be originated the consumption of  $\text{O}^{2-}$  by the formation of  $[\text{AlO}_4]$ -tetrahedral units. And it is also founded that Si-O-Al bending became more complicated.

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#### References

- [1] H. D. Weymann: *Kolloid Z. Polymer*, 1962, **181**, p. 131.
- [2] S. Seetharaman, Du Sichen: *Metall. Mater. Trans. B*, 1994, **25B**, p. 589.
- [3] F.-Z. Ji, S. Seetharaman, Du Sichen, *Metall. Mater. Trans. B*, 1997, **28B**, p. 827.
- [4] M. Nakamoto, T. Tanaka, J. Lee, T. Usui, *ISIJ Int.*, 2004, **44**, p. 2115.
- [5] J. H. Park, Ph.D. Thesis, Yonsei University, Department of Metallurgical engineering, Seoul, Korea, 2001.
- [6] J. H. Park, H. Kim, D. J. Min, *Metall. Mater. Trans. B*, 2008, **39B**, p. 150.

- [7] J. R. Kim, Y. S. Lee, D. J. Min, S. M. Jung, and S. H. Yi, *ISIJ Int.*, 2004, **44**, p. 1291.
- [8] H. Kim, W. H. Kim, I. Sohn, and D. J. Min, *Steel Research Int.*, 2010, **81**, p. 261.
- [9] J. S. Machin, T. B. Yee, and D. L. Hanna, *J. Am. Ceram. Soc.*, 1952, **35**, p. 322.
- [10] L. Zhang and S. Jahanshahi, *Metall. Mater. Trans. B*, 1998, **29B**, p. 177.
- [11] H. Kim, W. H. Kim, J. H. Park, and D. J. Min, *Steel Research Int.*, 2010, **81**, p. 17.
- [12] S. Sukenaga, N. Saito, K. Kawakami, K. Nakashima, *ISIJ Int.*, 2006, **46**, p. 352.
- [13] Y. Sasaki, K. Ishii, *Tetsu-to-Hagané*, 2002, **88**, p. 419.
- [14] Bjorn Mysen, *Contrib Mineral Petrol*, 1997, **127**, p. 104.
- [15] W. H. Kim, I. Sohn, and D. J. Min, *Steel Research Int.*, 2010, **81**, p. 735.
- [16] M. Nakamoto, Y. Miyabayashi, L. Holappa, T. Tanaka, *ISIJ Int.*, 2007, **47**, p. 1409.