EXPERIMENTAL DETERMINATION OF THE EFFECT OF NA_2O ON THE VISCOSITY OF MOLTEN SLAGS

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ABSTRACT

It is well known that Na_2O accumulates in the blast furnace refractory. In spite of its harmful effects, Na_2O has been added due to its capacity as a strong network modifier. The addition of Na_2O into the BF type slag system has the effect of controlling the fluidity of high Al_2O_3 containing slag. Although these physical effects on the blast furnace slag have been reported, there are few viscosity data of slags containing Na_2O. In this study, the viscosities were measured with a rotating cylinder technique. The viscosities in various Na_2O (0 to 15 wt %) containing slags were measured to clarify the effect of Na_2O on the viscosity in blast furnace type slags. The content of MgO and Al_2O_3 were fixed at 10 and 20 wt%, respectively, and the range of basicity (CaO/SiO_2) was varied between 0.8 and 1.2. Furthermore, the structural role of Na2O was discussed based on results obtained by FT-IR spectrometry.

INTRODUCTION

In recent times, the addition of slag modifiers such as CaO has been reduced, mostly to lower the energy consumption in iron making processes. As a result, the slag quantity has been reduced, leading to an increase in the concentration of all constituents except CaO. In addition, in order to lower the unit cost of the product, there has been a trend to use lower quality ores; as a result, the slag compositions have trended towards lower basicity and higher alumina contents. Moreover, high pulverized coal ratio (PCR) is recommended in view of environmental issues, also causing changes in basicity and alumina content of blast furnace slags.

The viscous behavior of BF type slags has already been studied by several researchers [1, 2, 3], but only a few studies have dealt with low basicity- high alumina and higher viscosity slags [4]. For such slag systems, Na_2O additions could be an effective solution to decrease the viscosity; however, few data are available.

In this study, the effect of Na_2O on the viscosities of $CaO-SiO_2-MgO-Al_2O_3-Na_2O$ slags in the range of C/S=0.8-1.2, 10 wt% MgO, 20 wt% Al_2O_3 and 0-15 wt% Na_2O were measured. Furthermore, the viscous behavior was investigated by structural analysis employing FT-IR measurement technique.

METHODOLOGY

Preparation of Materials

Slag batches were prepared by mixing regent grade CaO, SiO_2, MgO and Al_2O_3 and melted in graphite crucibles under an argon (0.5 L/min) atmosphere at 1773 K. To prevent the presence of moisture and oxygen in the argon, the gas was passed through columns of drierite, silica gel and magnesium turnings at 753 K. The slag melts were kept at temperature for 3 hours for homogenization and then quenched and crushed for the experiments. Crushed, pre-melted slags were analyzed by XRF to confirm compositions.

Apparatus and Procedure

Melts were carried out in a SiC vertical resistance furnace; temperatures were measured with an R-type thermocouple and controlled with a P.I.D. devise. The bottom of the mullite reaction tube was closed with a silicon stopper while the top was partially sealed with a metallic flange permitting the insertion of a wire suspension. Viscosity measurements were carried out with the rotating cylinder technique. In the present study, the rotational torque was read by a viscometer (model LVDV-II+, Middleboro, MA) and computer recorded. The viscometer was connected to the working spindle by two suspending wires with a hook-type-joint to retard the fluctuations caused by the rotating wire. The working spindle was immersed in the center of 100 g slag melts contained in Pt-10wt%Rh crucibles. The reaction tube was flushed with argon (0.5 L/min) at 1773 K. Viscosities of the melt were measured at decreasing 25 K temperature intervals, attained by slowly cooling at a rate of -K/min.and holding them until the viscosity reached a constant value. Experiments were stopped when the viscosity reached 80 poise. After measuring the viscosities, the slag sample were reheated to 1773 K and quenched in an argon stream, analyzed for composition (X-ray Fluorescence, Bruker, SRS3400) and the structure determined by FT-IR (Spectra100, Perkin-Elmer inc., MA, USA). Compositional change before and after the test less than 1 wt%. The measurement procedure was described in detail elsewhere [3, 5].

RESULTS AND DISCUSSION

Viscosities of the CaO-SiO_2-MgO-Al_2O_3-(Na_2O) slag system were measured. Slag compositions ranged between 0.8 and 1.2 in terms CaO/SiO_2 in order to simulate blast furnace type slag systems.

Table 1: Experimental compositions

No.	CaO	SiO_2	MgO	Al_2O_3	Na_2O	CaO/SiO_2
1	31.11	38.89	10	20	0	0.8
2	30.67	38.33	10	20	1	0.8
3	29.78	37.22	10	20	3	0.8
4	28.89	36.11	10	20	5	0.8
5	26.67	33.33	10	20	10	0.8
6	24.44	30.56	10	20	15	0.8
7	35	35	10	20	0	1
8	34.5	34.5	10	20	1	1
9	33.5	33.5	10	20	3	1
10	32.5	32.5	10	20	5	1
11	30	30	10	20	10	1
12	27.5	27.5	10	20	15	1
13	38.18	31.82	10	20	0	1.2
14	37.64	31.36	10	20	1	1.2
15	36.55	30.45	10	20	3	1.2
16	35.45	29.55	10	20	5	1.2
17	32.73	27.27	10	20	10	1.2
18	30	25	10	20	15	1.2

The MgO content was fixed at 10 wt% as a standard composition and 20 wt% of Al_2O_3 was added. Preliminary viscosity values are presented in Figure 1; they compare well with previous data, as determined by other researchers.

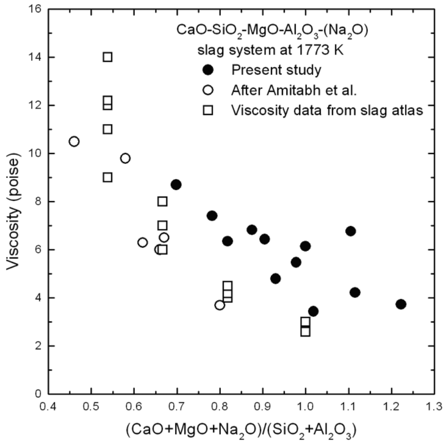

Figure 1: Viscosity changes as a function of (CaO+MgO+Na_2O)/(SiO_2+Al_2O_3)

Effect of Basicity

The effect of the ratio of (wt%CaO+wt%MgO+wt%Na_2O)/(wt%SiO_2+wt%Al_2O_3) (=B) is shown in Figure 1. Because the electro negativity of Na^+ is much larger than for Ca^{2+}, Na_2O behaves as a basic oxide and the mole ratio Al_2O_3/RO (RO: basic oxide) is smaller than unity so that Al_2O_3 was treated as acidic oxide. The viscosities decreased with increasing values of B. In general, added O_2- ions modify the polymerized silicate structure so that the network becomes simpler and includes short range ordered groups. [6] The viscosity decreases linearly until the activity of 2CaO•SiO_2 is definitely increased [3, 5]. Figure 2, 3 and 4 show the change of viscosities as a function of reciprocal temperature at each ratio of CaO/SiO_2 (=B). As shown in Figure 2, 3 and 4, the viscosities at 1773 K decreased with increasing B. Also, because of the difference of primary phase, Tcr was changed and the shape of viscous changes gets flatter with increasing B.

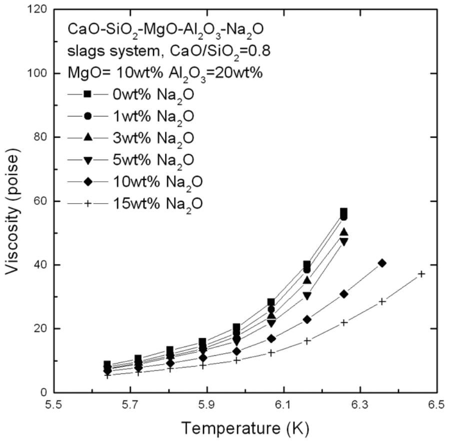

Figure 2: Viscosity changes as a function of reciprocal temperature at CaO/SiO_2 = 0.8

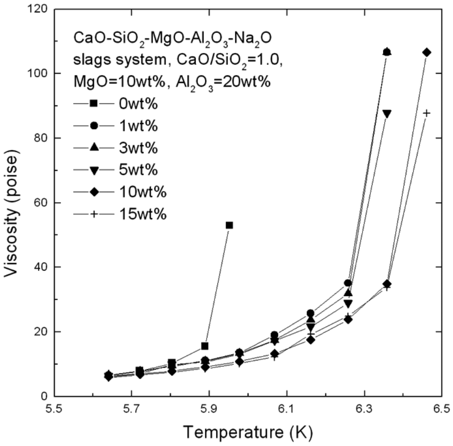

Figure 3: Viscosity changes as a function of reciprocal temperature at CaO/SiO_2 = 1.0

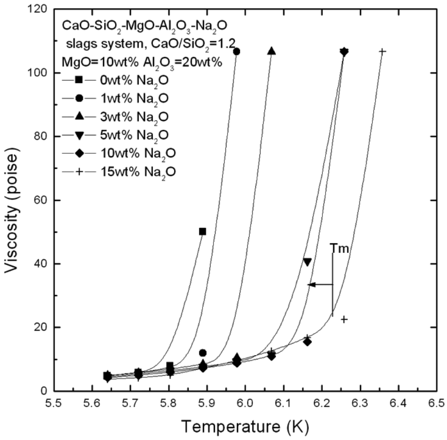

Figure 4: Viscosity changes as a function of reciprocal temperature at CaO/SiO_2 = 1.2

Effect of Na_2O

The dependence of slag viscosity on reciprocal temperature at different Na_2O and CaO/SiO_2 values = 0.8, 1.0 and 1.2, is shown in Figure 2, 3 and 4. The Na_2O content does not significantly affect viscosity in the fully liquid region at B = 1.0 and 1.2, but has a remarkable influence on the crystallization temperature. The crystallization temperature is shifted to lower temperature with increasing Na_2O contents.

Figure 5, 6 and 7 shows the effect of Na_2O on viscosity of CaO-SiO_2-MgO-Al_2O_3-Na_2O slags system at 1673 K, 1723 K and 1773 K. The slag viscosity decreases with increasing basicity from 0.8 to 1.2 and contents of Na_2O at fixed MgO. In case of the fully liquid region, the effect of Na_2O was negligible; however, the effect of Na_2O is significant in the temperature range near crystallization. It is believed that this phenomenon is caused by the contribution of Na_2O to decreasing melting temperature of slag.

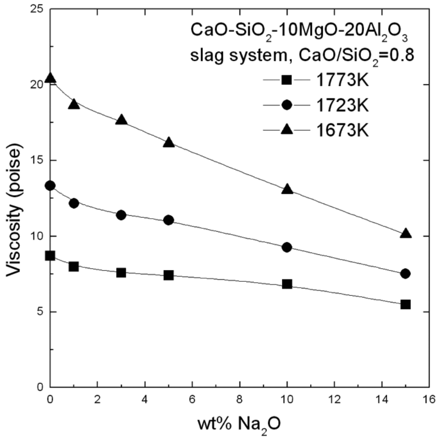

Figure 5: Dependence of Na_2O content on the viscosity at CaO/SiO_2 = 0.8

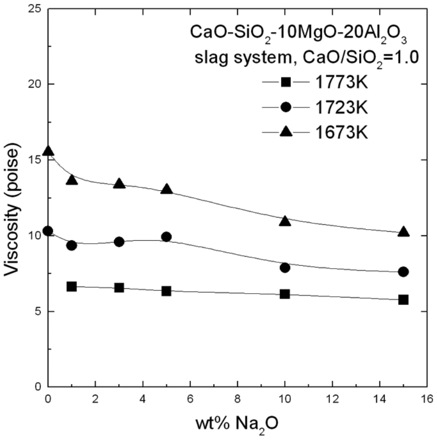

Figure 6: Dependence of Na_2O content on the viscosity at CaO/SiO_2 = 1.0

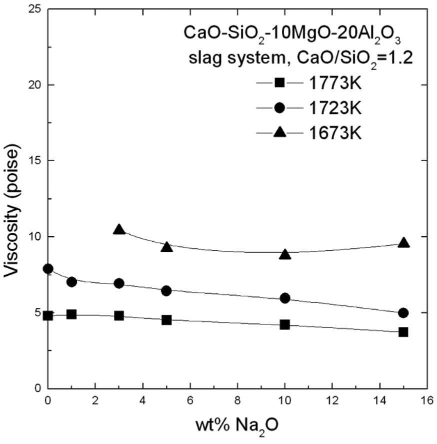

Figure 7: Dependence of Na_2O content on the viscosity at CaO/SiO_2 = 1.2

Activation Energy

In general, the temperature dependence of liquid viscosity is approximately expressed by an Arrehenius type relationship (1).

$$\eta = A\,exp\left(\frac{H_\eta}{RT}\right) \tag{1}$$

where A and R are the pre-exponential term and gas constant, respectively, and $H\eta$ is the activation energy for viscous flow. The activation energy can be calculated from the relationship between $\ln\eta$ and 1/T, which represents the change of frictional resistance for viscous flow and may indicate that the structure of liquid has changed.

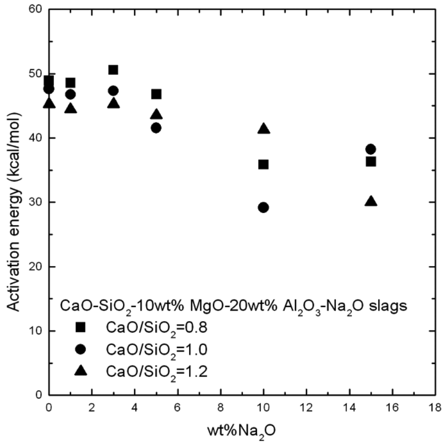

Figure 8: Changes of activation energy with various Na_2O contents

The variation of activation energy as a function of Na_2O content is shown in Figure 8. The activation energies are calculated above the crystallization temperature in order to exclude the effect of precipitated solid particles in the melt. The activation energy decreases as both of basicity and Na_2O contents increase. In general, basic oxide makes the slag structure simple by modifying the network structure of silicates. CaO and Na_2O are basic oxides so that the units for viscous flow are getting smaller and the frictional resistance is reduced.

Structural Analysis

Figure 9 shows the IR spectra of CaO-SiO_2-10 wt% MgO-20 wt% Al_2O_3-Na_2O (CaO/SiO_2=0.8) slag systems as a function of wave number (cm^{-1}) at different Na_2O contents. The peak of Si-O bonds were found between 1030 and 850 cm^{-1} which indicates NBO/Si is 1 to 4 [7, 8, 9, 10] Two kinds of band groups were shown in the range of 720-630 cm^{-1} and 500 cm^{-1} which are assigned asymmetric stretching vibration of [AlO_4]-tetrahedra and the Si-O-Al bending, respectively [10, 11, 12].

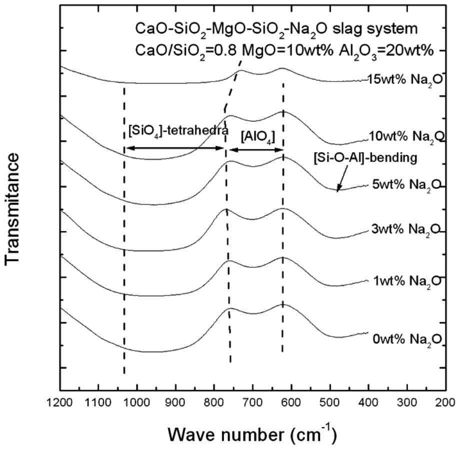

Figure 9: FT-IR spectra in CaO-SiO_2-MgO-Al_2O_3-Na_2O slag system at CaO/SiO_2 = 0.8

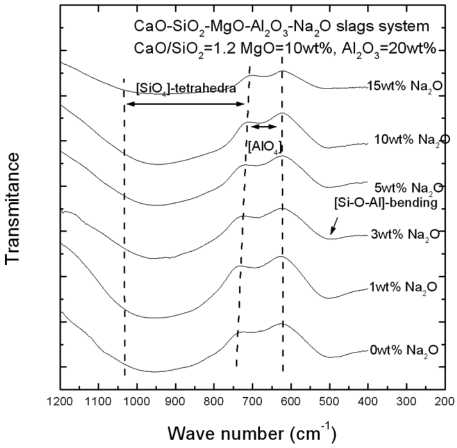

Figure 10: FT-IR spectra in $CaO-SiO_2-MgO-Al_2O_3-Na_2O$ slag system at $CaO/SiO_2 = 1.2$

In Figure 9, the absorption of Si-O-Al bending did not change significantly since the ratio of SiO_2/Al_2O_3 was not changed. However, with increasing Na_2O contents, the range of the network former $[AlO_4]$- tetrahedra become wider with the short wave number. This means that the bond tetrahedral structure has a different electric charge. $[AlO_4]$-tetrahedra has a negative charge of -1, and the dissociated anions in the slags are tend to locate near $[AlO_4]$-tetrahedra. The Na^+ from Na_2O modifies the aluminate network structure preferentially [13]. When the contents of Na_2O is 20 wt%, $[AlO_4]$-tetrahedra are fairly depolymerized so that the silicate peak is shifted to the short wave number because the silicate structures are modified by the remaining anions.

Figure 10 shows the IR spectra of $CaO-SiO_2$-10wt%MgO-20wt%$Al_2O_3-Na_2O$ (CaO/SiO_2=1.2) slags system as a function of wave number (cm^{-1}) at different Na_2O contents. In this slag system, CaO contents are relatively higher than that shown in Figure 9. The range of silicate structure between 1030 and 850 cm^{-1} is significantly wider than for low basicity slag sytems. The viscosity at CaO/SiO_2=1.2 (Figure 5(c)) slightly decreased with increasing Na_2O contents and the silicate peak is also lightly wider toward the short wave number. The peak of $[AlO_4]$-tetrahedra is not significantly shifted because the sufficient dissociated anions, such as Ca^{2+} and Na^{2+}, modify aluminate structure preferentially, and then silicate structure is modified with increasing the Na_2O content.

CONCLUSIONS

The effect of adding Na_2O on viscosity of $CaO-SiO_2$-10wt%MgO-20wt%$Al_2O_3-Na_2O$ (CaO/SiO_2=0.8-1.2) slags system was been measured by the rotating cylinder method.

- The viscosity decreased when the basicity increased in the rage from 0.8 to 1.2
- In the low basicity region, the effect of Na_2O on the viscosity is significant since $[AlO_4]$-tetrahedra have a negative charge. This causes the $[AlO_4]$-tetrahedra to modify in preference to the silicate structure
- In the high basicity region, anions for modifying $[AlO_4]$-tetrahedra are sufficient so that the silicate structure changes in the short-range order.

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