Activities of Na₂O in CaO-based Slags Used for Dephosphorization of Steel

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The activity of Na₂O in CaO-based slags has been measured employing a galvanic cell technique with a β -Al₂O₃ solid electrolyte. The iso-activity lines for Na₂O were obtained over the liquidus composition range in the CaO–Na₂O–SiO₂ system at 1 400°C. The activity of Na₂O in CaO-based slag is strongly controlled by the SiO₂ content in slag and the activity coefficient of Na₂O increases as the CaO content increases. The activity of Na₂O in a 50%CaO–40%Al₂O₃–10%SiO₂ (typical ladle slag composition) is extremely high. At a Na₂O concentration of about 8 wt% in this slag, the activity of Na₂O is nearly equal to that of 50wt%Na₂O–SiO₂ slag at the same temperature. The Richardson solution model fits the experimental data well and this model was used to compute the activity of CaO in these systems. The addition of Na₂O significantly increases the activity of CaO.

KEY WORDS: activity; dephosphorization; soda; lime; β -alumina; slag model.

1. Introduction

Sodium oxide plays a significant role on dephosphorization and desulfurization reaction in steelmaking processes.^{1–3)} It has been shown that a small addition of Na₂O to the CaO-based slags increases the removal of phosphorus and sulfur from liquid steel. However, Na₂O vaporization is high at the temperatures involved and CaO increases the activity of Na₂O which further increases the vapor pressure of Na₂O. Although it is of practical importance to know how Na₂O behaves in steelmaking slags, its activity in these slags is unknown.

The activity of Na₂O in slags has been measured by various techniques. Recently, Yamaguchi *et al.* employed a galvanic cell technique,⁴⁾ Rego *et al.* used a transpiration technique⁵⁾ and Tsukihashi *et al.* measured the Na distribution between Pb–Na alloys and slags⁶⁾ to measure the activity of Na₂O in binary silicate melts. The results from these independent techniques are in good agreement with respect to the activity of Na₂O. Combining these results, information is available over wide ranges of composition and temperatures for the Na₂O–SiO₂ system. Neudorf *et al.*⁷⁾ measured the effect of CaO additions on the activity of Na₂O at 1 070°C by adding up to 11 mol% of CaO to each of the binary silicate containing 24.4, 29.4 and 34.3 mol% of Na₂O. Rego⁸⁾ measured the iso-activity compositions for Na₂O in the Na₂O–CaO–SiO₂ system at 1 400°C. Their results indicated that the addition of CaO to Na₂O–SiO₂ melts increased the activity coefficient of Na₂O, and the results agreed well with Richardson's ideal mixing model^{9,10)} with appropriate modifications. It has also been found that the replacement of SiO₂ by Al₂O₃ increases the activity of Na₂O.¹¹⁾ However, their experiments

were limited to low temperature⁷⁾ and acidic slag compositions (high SiO₂ content),^{7,8)} which may not be directly applicable to practical steelmaking processes.

In the present study, the activity of Na₂O in the CaO–Na₂O–SiO₂ system has been measured at 1 400°C using a galvanic cell technique. A Na⁺ ion conductor β -Al₂O₃ solid electrolyte was employed in this study. The activities of Na₂O in four binary Na₂O–SiO₂ melts were measured with reference to a 40Na₂O–60SiO₂ (mol%) melt for which the activity was measured by Yamaguchi *et al.*⁴⁾ using a similar technique at the same temperature. Using these four binary melts as references, CaO was then added up to 42 mol% at fixed Na₂O/SiO₂ ratios. The activity of Na₂O in a typical ladle slag (50%CaO–40%Al₂O₃–10%SiO₂; wt%) which is one of the important metallurgical slags, was also measured at 1 500°C. The measured Na₂O activity data have been compared with those calculated by the Richardson's ideal mixing model. Using this model, the CaO activities in these slag systems have also been estimated.

2. Experimental

A concentration-type galvanic cell utilizing β -Al₂O₃ as a solid electrolyte was used to measure the activity of Na₂O in CaO–Na₂O–SiO₂ and CaO–Al₂O₃–SiO₂ systems at 1 400 and 1 500°C, respectively. The electrochemical cell employed in this work can be represented as:

where the reversible electromotive force, EMF, is given by

Fig. 1. Schematic of the galvanic cell to measure the activity of Na_2O in sample melts.

$$\text{EMF (V)} = \frac{RT}{4F} \ln \frac{P_{\text{O}_2}(\text{sample})}{P_{\text{O}_2}(\text{reference})} - \frac{RT}{2F} \ln \frac{a_{\text{Na}_2\text{O}}(\text{sample})}{a_{\text{Na}_2\text{O}}(\text{reference})} \quad \text{.....(1)}$$

A schematic of the galvanic cell used in these experiments is shown in Fig. 1. In the present experiment, air was used for both electrodes and thus the electromotive force is simply determined by the ratio of the activities of Na_2O in the two melts separated by the $\beta\text{-Al}_2\text{O}_3$ electrolyte.

In the case of $\text{CaO-Na}_2\text{O-SiO}_2$ system, four binary reference $\text{Na}_2\text{O-SiO}_2$ slags ($\text{Na}_2\text{O/SiO}_2 = 1/4, 1/2, 1$ and $3/2$; molar ratio) were prepared and the activities of Na_2O in these binary melts were measured at 1 400 and 1 500°C, with reference to a 40 $\text{Na}_2\text{O-60SiO}_2$ melt (mol%). The activity of this melt was measured by Yamaguchi *et al.*⁴⁾ using a similar technique at the same temperature. Using those four binary melts as references, activity of Na_2O was determined in $\text{CaO-Na}_2\text{O-SiO}_2$ slags in which the concentration of CaO increased up to 42 % slag fixed $\text{Na}_2\text{O/SiO}_2$ ratio. In the case of $\text{CaO-Na}_2\text{O-Al}_2\text{O}_3\text{-SiO}_2$ system, a typical ladle slag composition (50% $\text{CaO-40%Al}_2\text{O}_3\text{-10%SiO}_2$; wt%) was chosen and Na_2O was added up to 20 wt%. The reference melt for this system was $\text{Na}_2\text{O} \cdot 2\text{SiO}_2$ for which the activity of Na_2O was measured at 1 500°C beforehand.

The reference melts were prepared by melting accurately weighed and blended mixtures of reagent grade Na_2CO_3 and SiO_2 powders in a platinum crucible for 8 h at 1 100~1 300°C depending on melt composition. The melt was quenched to a glass on

a stainless steel plate, crushed and stored in a desiccator until used. The sample melt was prepared just before each experiment, by melting the blended mixtures of reagent grade CaO , Na_2CO_3 , SiO_2 and Al_2O_3 powders in a platinum crucible at the experimental temperature for 4 h followed by cooling the melt to room temperature. Chemical analysis of some samples confirmed that the melt compositions were the same as charged.

The $\beta\text{-Al}_2\text{O}_3$ electrolyte (90.4% $\text{Al}_2\text{O}_3\text{-8.85%Na}_2\text{O-0.75%Li}_2\text{O}$) tubes obtained from Ceramtec, Inc. were used in these experiments. The $\beta\text{-Al}_2\text{O}_3$ tubes were 10.5 mm OD $\times$ 7.5 mm ID $\times$ 100 mm long. In all experiments, the reference melt was held in the $\beta\text{-Al}_2\text{O}_3$ tube. As shown in Fig. 1, the anode and cathode consisted of platinum wires within alumina tubes. The tips of the alumina tubes were positioned approximately 2 cm above the surface of the melts. The entire system was open to the air and air was not blown onto the melts. The temperature of the cell was measured with a Pt/Pt-10%Rh thermocouple positioned just beside the platinum crucible.

The cell EMF was read by a digital multimeter and recorded continuously on a Honeywell stripchart recorder. The EMF of the cell was measured until a steady potential was obtained. A steady cell potential was usually obtained 1 to 4 h after lowering the electrolyte tube into the molten slag. The reversibility of the cells was tested by passing a small external current between the cell electrodes for approximately 10 s, and the EMF returned to the original values within a few minutes. Any possible external current was checked by shutting off the furnace instantly, and no change of EMF was observed. The EMF value was taken if it remained steady within 0.5 mV for at least 1 h. After each experiment, it was observed that a small amount of $\beta\text{-Al}_2\text{O}_3$ had dissolved into the melt during the experiment. The effect of Al_2O_3 on the activity of Na_2O did not appear to be large because the cell potential did not drift with time.

3. Results and Discussion

3.1. $\text{CaO-Na}_2\text{O-SiO}_2$ System at 1 400°C

The experimental results of EMF measurements for $\text{Na}_2\text{O-SiO}_2$ and $\text{CaO-Na}_2\text{O-SiO}_2$ melts are summarized in Table 1. From the EMF measurement, the activities of Na_2O in sample melts were calculated from Eq. (1) and tabulated in Table 1. The activities of Na_2O in four binary $\text{Na}_2\text{O-SiO}_2$ melts ($\text{Na}_2\text{O/SiO}_2 = 1/4, 1/2, 1$ and $3/2$) were measured with a 40mol% $\text{Na}_2\text{O-60mol%SiO}_2$ melt as the reference melt; the activities of Na_2O at 1 400 and 1 500°C are shown in Fig. 2. Using these four binary melts as reference melts, CaO was then added up to 42 mol% along constant $\text{Na}_2\text{O/SiO}_2$ ratio of $1/4, 1/2, 1$ and $3/2$. Lime was added in such a way that Na_2O content varied along constant CaO/SiO_2 ratio. In this manner, measurements were made over a wide range of compositions. Fig. 3 shows the slag compositions studied in this experiment. The compositions in this

Table 1. EMF value and $a_{\text{Na}_2\text{O}}$ in CaO-Na₂O-SiO₂ system.

Sample	Temp. (°C)	Reference (mol%)	Sample (mol%)			EMF (mV)	-log $a_{\text{Na}_2\text{O}}$
			Na ₂ O	CaO	SiO ₂		
A0	1 400	40N·60S*	60		40	-437	3.241
A0	1 500	40N·60S*	60		40	-450	2.963
B0	1 400	40N·60S*	50		50	-183	4.771
B0	1 500	40N·60S*	50		50	-188	4.454
C0	1 400	40N·60S*	33.3		66.7	102	6.488
C0	1 500	40N·60S*	33.3		66.7	115	6.177
D0	1 400	40N·60S*	20		80	317	7.784
D0	1 500	40N·60S*	20		80	353	7.528
A1	1 400	60N·40S	52.03	13.29	34.68	-130	2.458
A2	1 400	60N·40S	54.79	8.68	36.53	-100	2.639
B1	1 400	50N·50S	39.30	21.40	39.30	-171	3.740
B2	1 400	50N·50S	41.94	16.12	41.94	-116	4.072
B3	1 400	50N·50S	44.60	10.80	44.60	-63	4.391
C1	1 400	33N·67S	22.76	31.71	45.53	-136	5.669
C2	1 400	33N·67S	24.49	26.53	48.98	-98	5.898
C3	1 400	33N·67S	26.58	20.26	53.16	-61	6.120
C4	1 400	33N·67S	28.69	13.93	57.38	-28	6.320
C5	1 400	33N·67S	30.96	7.11	61.93	-12	6.416
D1	1 400	20N·80S	11.63	41.83	46.54	-167	6.781
D2	1 400	20N·80S	13.93	30.38	55.70	-93	7.227
D3	1 400	20N·80S	15.30	23.72	60.98	-56	7.445
D4	1 400	20N·80S	16.76	16.20	67.04	-23	7.648

N: Na₂O S: SiO₂*: log $a_{\text{Na}_2\text{O}}$ = -5.874 and -5.521 at 1 400 and 1 500 °C,⁴⁾ respectively. Fig. 2. Activity of Na₂O in the Na₂O-SiO₂ system at 1 400 and 1 500°C.

figure are the initial compositions charged into the crucible. The EMF's were always very stable for a long period of time and the dissolution of the solid electrolyte into the melt was relatively slow.

Fig. 4 shows the activity of Na₂O as a function of CaO addition at fixed Na₂O/SiO₂ ratios at 1 400°C. The results indicate that additions of CaO increase the activity of Na₂O even though the concentration

Fig. 3. Composition of slags for the Na₂O activity measurement for the CaO-Na₂O-SiO₂ ternary system at 1 400°C.

of Na₂O decreases. The activity of Na₂O increases more rapidly, as the CaO concentration increases; therefore, one can expect that the activity of Na₂O in highly basic slags (high CaO/SiO₂ ratio) is relatively high. In Rego's work,⁸⁾ the Richardson's ideal mixing model worked well for the prediction of the Na₂O activity in his rather acidic (high SiO₂ content) ternary system. According to Neudorf *et al.*,⁷⁾ this model works better in the acidic ternary melts because the changes in anionic structure which oc-

curs on mixing of two binary silicates, *i.e.*, $\text{Na}_2\text{O}-\text{SiO}_2$ and $\text{CaO}-\text{SiO}_2$, may not be very large at high SiO_2 concentrations. In this work, the Na_2O activities were measured over a wide range of compositions (low SiO_2 content) and the results were compared with the Richardson's ideal mixing model to be discussed later.

Fig. 5 plots the activity of Na_2O as a function of Na_2O content at fixed CaO/SiO_2 ratios at 1400°C .

Fig. 4. Effect of additions of CaO to $\text{Na}_2\text{O}-\text{SiO}_2$ melts on the activity of Na_2O at 1400°C .

Fig. 5. The activity of Na_2O as a function of Na_2O content at fixed CaO/SiO_2 ratios at 1400°C in $\text{CaO}-\text{SiO}_2-\text{Na}_2\text{O}$ melts.

The lines shown in Fig. 5 were drawn to aid in the interpolation of values of Na_2O activity at intermediate compositions. These interpolated values have been plotted as iso-activity lines for Na_2O in the $\text{CaO}-\text{Na}_2\text{O}-\text{SiO}_2$ ternary system at 1400°C , as shown in Fig. 6. The essential features of the iso-activity lines are that the Na_2O activity is strongly influenced by the SiO_2 content and that the activity coefficient of Na_2O increases as the CaO/SiO_2 ratio increases.

3.2. Activity of CaO in $\text{CaO}-\text{Na}_2\text{O}-\text{SiO}_2$ Ternary System

Since $\text{CaO}-\text{Na}_2\text{O}-\text{SiO}_2$ system will be used for dephosphorization and desulfurization, the activity of CaO is as important as that of Na_2O . In principle, the activity of CaO can be calculated from the measured iso-activity curve of Na_2O shown in Fig. 6 using Gibbs-Duhem integration for ternary system.¹²⁾ The activity of SiO_2 was calculated using this method by Rego.⁹⁾ However, this ternary system has very narrow composition range saturated with respect to CaO . Therefore, the Gibbs-Duhem integration method can not be applied directly to calculate CaO activity because the lower bound of integration is not known for the compositions studied. However, it is possible to estimate the activity of CaO using a mathematical model of the thermodynamics of molten slag. Although several sophisticated slag models are proposed, the application of the models to $\text{CaO}-\text{Na}_2\text{O}-\text{SiO}_2$ system is difficult because of the lack of the interaction parameters concerning Na_2O .

Richardson proposed a model for ternary silicate slags,^{9,10)} which treats $\text{XO}-\text{YO}-\text{SiO}_2$ ternary silicate as an ideal mixture of $\text{XO}-\text{SiO}_2$ and $\text{YO}-\text{SiO}_2$ binaries. Neudorf and Elliott⁷⁾ proved that this model can be applied to $\text{CaO}-\text{Na}_2\text{O}-\text{SiO}_2$ ternary system to calculate the activity of Na_2O at 1070°C . Since the ternary slag is an ideal mixture of two binaries and the activities in each binary satisfy the Gibbs-Duhem

Fig. 6. Iso-activity lines for Na_2O in the $\text{CaO}-\text{Na}_2\text{O}-\text{SiO}_2$ system at 1400°C .

relationship, the activities in ternary must satisfy Gibbs–Duhem relationship.¹³⁾

Modifying the Richardson's equation, the activity of Na₂O and CaO in the ternary are given in Eqs. (2) and (3), respectively.⁷⁾ Since this model is based on ideal mixing of the pseudo-binary components, $x\text{Na}_2\text{O}-\text{SiO}_2$ and $x\text{CaO}-\text{SiO}_2$, the slag composition lies on the $x\text{Na}_2\text{O}-\text{SiO}_2-x\text{CaO}-\text{SiO}_2$ join.

$$a_{\text{Na}_2\text{O}}(t) = N_{\text{Na}^{+}}^2 \cdot a_{\text{Na}_2\text{O}}(b) \left[\frac{a_{\text{SiO}_2}(\text{Na}_2\text{O}-\text{SiO}_2)}{a_{\text{SiO}_2}(\text{CaO}-\text{SiO}_2)} \right]^{\frac{N_{x\text{CaO}-\text{SiO}_2}}{x}} \quad (2)$$

$$a_{\text{CaO}}(t) = N_{\text{Ca}^{++}} \cdot a_{\text{CaO}}(b) \left[\frac{a_{\text{SiO}_2}(\text{CaO}-\text{SiO}_2)}{a_{\text{SiO}_2}(\text{Na}_2\text{O}-\text{SiO}_2)} \right]^{\frac{N_{x\text{Na}_2\text{O}-\text{SiO}_2}}{x}} \quad (3)$$

where, subscripts t, b : ternary and binary, respectively

$N_{\text{Na}^{+}}$: the Temkin ion fraction of Na⁺

$N_{x\text{CaO}-\text{SiO}_2}$: the mole fraction of $x\text{CaO}-\text{SiO}_2$ based on the pseudo-binary system

x : the molar ratio of basic oxide and SiO₂ in pseudo-binary.

For the Na₂O–SiO₂ binary, the activity of Na₂O measured in this study at 1 400°C was used and the SiO₂ activity was calculated by the Gibbs–Duhem integration with the solid tridymite (SiO₂) as a standard state. For the CaO–SiO₂ binary, the data measured at 1 500 and 1 600°C¹⁴⁾ was extrapolated to 1 400°C using their temperature dependencies. The calculated results for the Na₂O activity are compared with those measured in Fig. 4 to verify the model. Excellent agreement was obtained over the entire compositions especially in acidic (*i.e.*, high SiO₂) slags. Small positive deviations from ideal mixing for the slags with a high Na₂O/SiO₂ ratio may be attributed to the structural changes in the anionic matrix, and to cationic interactions resulting from the competition to achieve coordination with oxygen ions.⁸⁾

The iso-activity lines of CaO calculated using Eq. (3) is shown on the ternary diagram in Fig. 7. The CaO activity is strongly influenced by the SiO₂ content and the activity coefficient of CaO increases as Na₂O/SiO₂ ratio increases.

3.3. CaO–Na₂O–Al₂O₃–SiO₂ System at 1 500°C

In order to measure the activity of Na₂O in a highly basic steelmaking slag, Na₂O was added to a typical ladle slag (50%CaO–40%Al₂O₃–10%SiO₂: wt%). The reference melt for this experiment was Na₂O·2SiO₂. The activity of Na₂O in this slag is plotted and compared with other slag systems in Fig. 8. As indicated in the figure, about 8 wt% of Na₂O in this slag has the same activity value as in the 50wt%Na₂O–SiO₂ slag.

If it is assumed that the effect of Al₂O₃ on the activities of basic oxides is equivalent to that of SiO₂ on a molar basis, the basicity of 50%CaO–40%Al₂O₃–10%SiO₂ ternary is equal to that of 60%CaO–40%SiO₂ binary slag. The optical basicities¹⁵⁾ of these two slags were calculated and they have almost the same values. Therefore, the change of Na₂O activity

Fig. 7. Iso-activity lines for CaO in the CaO–Na₂O–SiO₂ system at 1 400°C.

Fig. 8. The Na₂O activities in various types of slags at 1 500°C.

in 60%CaO–40%SiO₂ slag at 1 500°C was calculated as a function of Na₂O concentration using Richardson's model. The result is shown as a dotted line in Fig. 8. Reasonably good agreement was obtained despite the rather crude assumption. The activity of CaO was calculated using the model and it increases from 0.03 for the CaO–Al₂O₃ binary¹⁴⁾ to 0.15 by adding 10 % Na₂O to this slag. Furthermore, 20 % addition of Na₂O increases the CaO activity to 0.7, which means that the ladle slag will increase its refining ability by the addition of Na₂O in two ways. First the Na₂O has a high activity, and secondly the activity of CaO is increased.

4. Summary and Conclusions

The activities of Na₂O in CaO–Na₂O–SiO₂ and

CaO–Na₂O–Al₂O₃–SiO₂ slags have been measured at 1400 and 1500°C, respectively. The iso-activity lines for Na₂O are obtained over the liquidus composition range in the CaO–Na₂O–SiO₂ system at 1400°C. The activity of Na₂O is strongly controlled by the content of SiO₂ and the activity coefficient of Na₂O increases as the CaO increases. The activity of Na₂O in a 50%CaO–40%Al₂O₃–10%SiO₂ (typical ladle slag composition) is extremely high. At a Na₂O concentration of about 8 wt% in this slag, the activity of Na₂O is nearly equal to that of 50wt%Na₂O–SiO₂ at the same temperature. The systems fit the Richardson solution model well and using the model the activity of CaO in the slags were calculated. The addition of Na₂O significantly increases the activity of CaO.

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