

# Thermodynamics of Na<sub>2</sub>O and K<sub>2</sub>O in The Molten CaO-CaF<sub>2</sub>-SiO<sub>2</sub> System

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## ABSTRACT

The effect of BaO and K<sub>2</sub>O addition to the CaO-CaF<sub>2</sub>-SiO<sub>2</sub> system on the phosphorus partition ratio between CaO-CaF<sub>2</sub>-SiO<sub>2</sub> system doubly saturated with CaO and 3CaO·SiO<sub>2</sub> and carbon saturated iron melts has been investigated at hot metal temperatures by a chemical equilibration technique. The addition of 7 mass% BaO or 0.4 mass% K<sub>2</sub>O enhances the partition ratio ten times.

The activity of a few percent of Na<sub>2</sub>O in the CaO-CaF<sub>2</sub>-SiO<sub>2</sub> system doubly saturated with CaO and 3CaO·SiO<sub>2</sub> has been determined between 1423 and 1623K. The temperature dependence of the activity coefficient of Na<sub>2</sub>O may be expressed as follows.

$$\log \gamma_{\text{Na}_2\text{O}} = -\frac{18,600(\pm 1,100)}{T} + 7.53(\pm 0.08)$$

The activity of a small amount of Na<sub>2</sub>O in the CaO-CaF<sub>2</sub>-SiO<sub>2</sub> flux is discussed in comparison with that for the Na<sub>2</sub>O-SiO<sub>2</sub> system in terms of their refining characteristics.

## 1. INTRODUCTION

A small addition of Na<sub>2</sub>O to the CaO bearing fluxes, which are widely in use for hot metal treatment, significantly increases their dephosphorization ability. The addition of as little as 2.5 mass% Na<sub>2</sub>O to the CaO-CaF<sub>2</sub>-SiO<sub>2</sub> system enhances the phosphate capacity approximately ten times.<sup>[1]</sup> Furthermore, it was shown by the authors that the yield of manganese increases and the recovery of niobium, vanadium, and titanium from hot metal to slag is improved by a small addition of Na<sub>2</sub>O to

CaO-CaF<sub>2</sub>-SiO<sub>2</sub> fluxes.<sup>[2]</sup>

In the present study, the effect of basic oxides such as BaO and K<sub>2</sub>O addition to the CaO-CaF<sub>2</sub>-SiO<sub>2</sub> system on the phosphorus partition ratio between CaO-CaF<sub>2</sub>-SiO<sub>2</sub> system doubly saturated with CaO and 3CaO·SiO<sub>2</sub> and carbon saturated iron melts was investigated at hot metal temperatures.

Furthermore, since the thermodynamic properties such as the activity of Na<sub>2</sub>O in the CaO-CaF<sub>2</sub>-SiO<sub>2</sub> system are not known, the activity coefficient of Na<sub>2</sub>O in the CaO-CaF<sub>2</sub>-SiO<sub>2</sub> flux doubly saturated with CaO and 3CaO·SiO<sub>2</sub> has been measured at temperatures of 1423 to 1623 K.

## 2. EXPERIMENTAL

### 2.1. Partition Ratio of Phosphorus

Five grams of CaO-(BaO or K<sub>2</sub>O)-CaF<sub>2</sub>-SiO<sub>2</sub> fluxes doubly saturated with CaO and 3CaO·SiO<sub>2</sub> (BaO: 0 to 26 mass%, K<sub>2</sub>O: 0 to 5 mass%, (P): 0 to 1 mass%) were equilibrated with 2 grams of carbon saturated iron in a CO atmosphere in a graphite crucible at temperatures of 1473 to 1623K. In order to maintain a constant sodium potential in the system, Pb-Na alloys (Na: 0 to 5 mass%) were used when CaO-K<sub>2</sub>O-CaF<sub>2</sub>-SiO<sub>2</sub> fluxes were used. The samples were equilibrated for 1 to 18 hours in a CO gas with a flow rate of  $2 \times 10^{-6}$  m<sup>3</sup>/s. After equilibration, the crucible was withdrawn from the furnace and samples were supplied for chemical analysis. The phosphorus contents of carbon saturated iron and CaO-(BaO or K<sub>2</sub>O)-CaF<sub>2</sub>-SiO<sub>2</sub> flux were analyzed by colorimetry. Barium and potassium in the fluxes were determined by gravimetric method and atomic absorption spectroscopy, respectively.

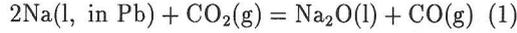
The flux samples were prepared from reagent grade CaF<sub>2</sub>, SiO<sub>2</sub>, BaO, Na<sub>2</sub>CO<sub>3</sub>, and CaCO<sub>3</sub>. The CaCO<sub>3</sub> chemicals were decomposed to CaO at 1273K in air before mixing the reagents to the desired CaO-CaF<sub>2</sub>-SiO<sub>2</sub> composition doubly saturated with CaO and 3CaO·SiO<sub>2</sub> (for example, CaO : CaF<sub>2</sub> : SiO<sub>2</sub> = 64 : 23 : 13 in mass% at 1573K). With an addition of BaO or K<sub>2</sub>O, the mixture was premelted in an argon atmosphere. Reagent grade lead and sodium were used for Pb-Na alloy preparation.

In order to ensure equilibration, equilibrium was approached from two sides, namely, the oxidation and the reduction of phosphorus.

## 2.2. Activity Coefficient of Na<sub>2</sub>O in CaO–Na<sub>2</sub>O–CaF<sub>2</sub>–SiO<sub>2</sub> flux

Twenty grams of Pb–Na alloy were equilibrated in a CO<sub>2</sub>–CO atmosphere at temperatures of 1423 to 1623K with 13 grams of CaO–Na<sub>2</sub>O–CaF<sub>2</sub>–SiO<sub>2</sub> fluxes doubly saturated with CaO and 3CaO·SiO<sub>2</sub> in a CaO crucible.

The reaction and its equilibrium constant are expressed by Eqs. (1) and (3).



$$\Delta G^\circ = -92,900 + 22.2T \quad \text{J/mol}^{[3]} \quad (2)$$

$$K = \frac{a_{\text{Na}_2\text{O}} \cdot P_{\text{CO}}}{a_{\text{Na}}^2 \cdot P_{\text{CO}_2}} = \frac{(\gamma_{\text{Na}_2\text{O}} \cdot X_{\text{Na}_2\text{O}}) \cdot P_{\text{CO}}}{(\gamma_{\text{Na in Pb}} \cdot X_{\text{Na in Pb}})^2 \cdot P_{\text{CO}_2}} \quad (3)$$

where  $a_i$  and  $\gamma_i$  are the activity and activity coefficient of component  $i$  relative to pure substance, respectively.  $X_i$  is mole fraction of component  $i$  and  $P_i$  is partial pressure of  $i$ .

In the present study the  $P_{\text{CO}_2}/P_{\text{CO}}$  ratio was kept constant. Therefore, according to Eq. (3), the activity coefficient of Na<sub>2</sub>O can be calculated by measuring Na contents of the Pb–Na alloy and fluxes. The activity coefficients of Na in a Pb–Na alloy are reported as 0.315 and 0.582 at 1473 and 1573K, respectively, by the authors.<sup>[4]</sup> The activity coefficients at 1423, 1523 and 1623K were estimated as 0.224, 0.432 and 0.769 at 1423, 1523, and 1623K, respectively, by interpolating or extrapolating the values at 1473 and 1573K using relationship of  $\ln \gamma_{\text{Na}} = A/T + B$  ( $A, B$ , constant).

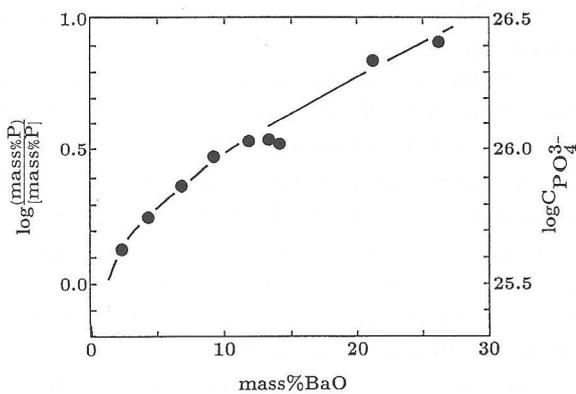


Fig.1. Effect of BaO addition to CaO<sub>satd.</sub>–CaF<sub>2</sub>–SiO<sub>2</sub> melts on the phosphorus partition ratio at 1573K with oxygen partial pressure of  $2.80 \times 10^{-12}$  Pa.

The samples in a CaO crucible (18mm ID, 23mm OD, 52mm height) were equilibrated for 40 to 60 minutes in a CO–CO<sub>2</sub> gas with a flow rate of  $2 \times 10^{-6}$  m<sup>3</sup>/s. After equilibration, the CaO crucible was withdrawn from the furnace and samples were quenched in an argon flow. The Na contents of Pb–Na alloy and CaO–Na<sub>2</sub>O–CaF<sub>2</sub>–SiO<sub>2</sub> flux were determined by atomic absorption spectrometry.

In order to ensure equilibration, equilibrium was approached from two sides, namely the oxidation of sodium and the reduction of sodium oxide.

## 3. RESULTS AND DISCUSSION

### 3.1. Partition Ratio of Phosphorus

The effect of BaO addition on the partition ratio of phosphorus between CaO–BaO–CaF<sub>2</sub>–SiO<sub>2</sub> fluxes doubly saturated with CaO and 3CaO·SiO<sub>2</sub> and carbon saturated iron at 1573K is shown in Figure 1. The partition ratio increases with increasing the BaO content. The addition of 7 mass% BaO enhances the partition ratio ten times.

The equilibrium partition ratios of phosphorus between CaO–K<sub>2</sub>O–CaF<sub>2</sub>–SiO<sub>2</sub> fluxes doubly saturated with CaO and 3CaO·SiO<sub>2</sub> and carbon saturated iron at 1473 to 1573 K are shown in Figure 2 as a function of K<sub>2</sub>O content added to the flux. The effect of basic oxide

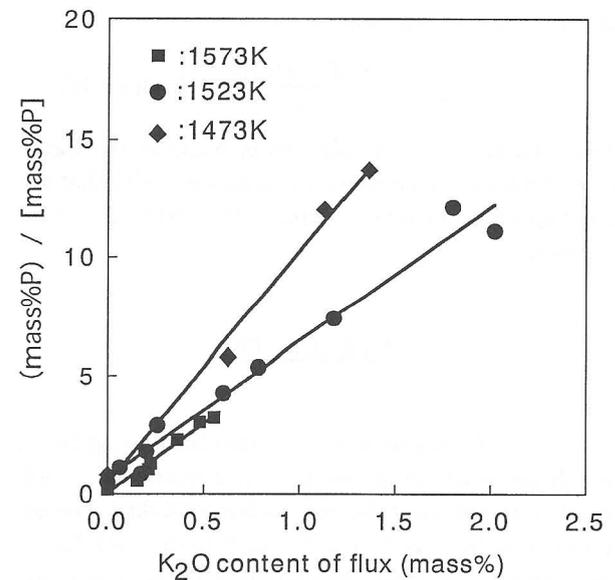
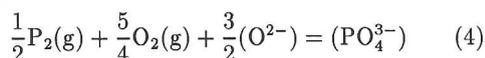


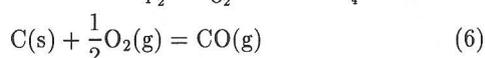
Fig.2. Effect of K<sub>2</sub>O addition to CaO<sub>satd.</sub>–CaF<sub>2</sub>–SiO<sub>2</sub> melts on the phosphorus partition ratio at 1573K with oxygen partial pressure of  $2.80 \times 10^{-12}$  Pa.

addition on the phosphorus partition ratio is shown in Figure 3 together with the effect of Na<sub>2</sub>O addition. [1] A small addition of K<sub>2</sub>O to the flux significantly enhances the dephosphorization ability of flux.

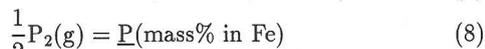
To compare the ability of dephosphorization of fluxes, it is convenient to use the phosphate capacity, C<sub>PO<sub>4</sub><sup>3-</sup></sub>, as a measure of dephosphorization ability.[5] The phosphate capacities of the CaO-(K<sub>2</sub>O, Na<sub>2</sub>O, or BaO)-CaF<sub>2</sub>-SiO<sub>2</sub> fluxes doubly saturated with CaO and 3CaO · SiO<sub>2</sub> fluxes are calculated as shown in Figure 4 by using following data.



$$C_{PO_4^{3-}} = \frac{(\text{mass}\%PO_4^{3-})}{P_2^{1/2} \cdot P_{O_2}^{5/4}} = \frac{K \cdot a_{O^{2-}}^{3/2}}{f_{PO_4^{3-}}} \quad (5)$$



$$\Delta G^\circ = -114,400 - 85.77T \quad \text{J/mol}^{[3]} \quad (7)$$



$$\Delta G^\circ = -157,700 + 5.4T \quad \text{J/mol}^{[6]} \quad (9)$$

$$\log f_P^C = -\frac{386}{T} + 0.891 \quad [7] \quad (10)$$

where  $a_{O^{2-}}$  is the activity of O<sup>2-</sup>,  $f_P^C$  is the activity coefficient of phosphorus in a carbon saturated iron relative to 1 mass%, and  $P_i$  is partial pressure of component i.

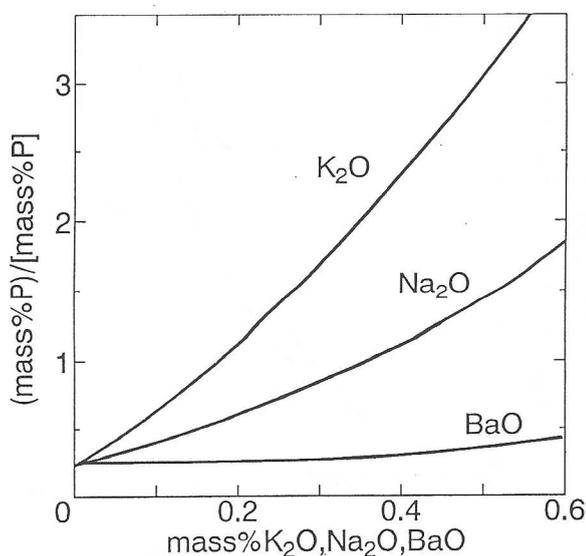


Fig.3. Comparison of the effects of K<sub>2</sub>O, Na<sub>2</sub>O, and BaO addition to CaO<sub>satd.</sub>-CaF<sub>2</sub>-SiO<sub>2</sub> melts on the phosphorus partition ratio at 1573K with oxygen partial pressure of  $2.80 \times 10^{-12}$  Pa.

### 3.2. Activity Coefficient of Na<sub>2</sub>O in the CaO -Na<sub>2</sub>O - CaF<sub>2</sub> -SiO<sub>2</sub> flux

The relationship between Na<sub>2</sub>O content of the CaO-4mass% Na<sub>2</sub>O - CaF<sub>2</sub>- SiO<sub>2</sub> flux and Na content of a Pb-Na alloy at 1573K with changing the  $P_{CO_2}/P_{CO}$  ratio from 0.01 to 3 is shown in Figure 5. Equation (11) is derived from Eq. (3).

$$\begin{aligned} \log \left( \frac{P_{CO_2}}{P_{CO}} \right) - \log X_{Na_2O} \\ = -2\log X_{Na} - 2\log \gamma_{Na} + \log \gamma_{Na_2O} - \log K \end{aligned} \quad (11)$$

Assuming Henry's law for Na<sub>2</sub>O and Na, the term  $(-2\log \gamma_{Na} + \log \gamma_{Na_2O} - \log K)$  may be constant at a constant temperature. Therefore, in accordance with Eq. (11), the relationship between  $(\log (P_{CO_2}/P_{CO}) - \log X_{Na_2O})$  and  $(\log X_{Na})$  is expected to be linear with the slope of -2. The observed slope of the line in Figure 5 is -2.1, which is close to the expected value.

The temperature dependence of the activity coefficient of Na<sub>2</sub>O of 4 mass% was measured from 1423 to 1623K as shown in Figure 6, varying the  $P_{CO_2}/P_{CO}$  ratio from 0.01 to 10 to control the sodium content of a Pb-Na alloy in a reasonable range for chemical analysis. The activity coefficient of Na<sub>2</sub>O is expressed by Eq. (12).

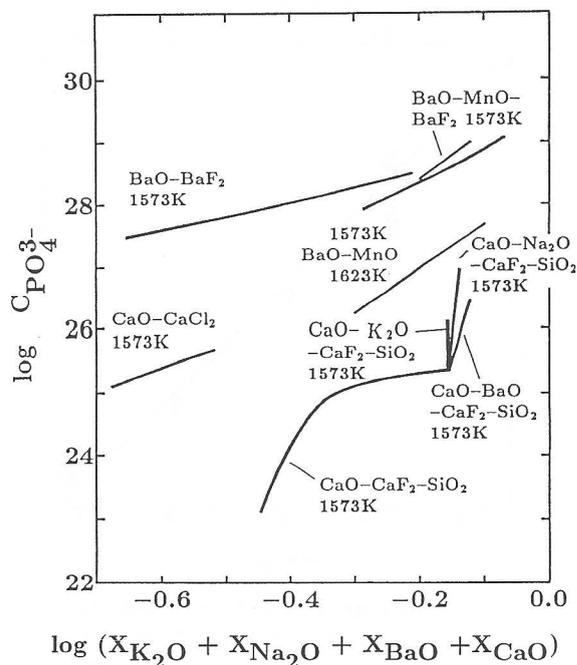


Fig.4. Phosphate capacities of various fluxes.

$$\log \gamma_{\text{Na}_2\text{O}} = -\frac{18,600(\pm 1,100)}{T} + 7.23(\pm 0.08) \quad (12)$$

The activity of Na<sub>2</sub>O from 0.48 to 5.33 mass% increases linearly with increasing the Na<sub>2</sub>O content at 1473K as shown in Figure 7. Therefore, it is confirmed that Henry's law is applicable up to 5 mass% Na<sub>2</sub>O of the CaO-Na<sub>2</sub>O-CaF<sub>2</sub>-SiO<sub>2</sub> flux doubly saturated with CaO and 3CaO·SiO<sub>2</sub>.

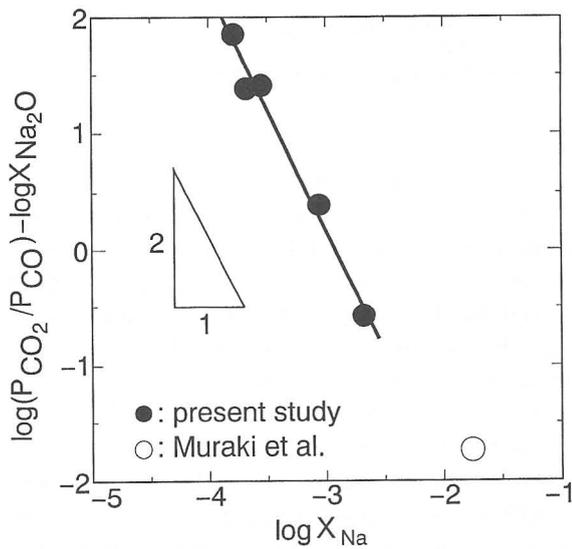


Fig.5. Relationship between  $\log X_{\text{Na}}$  and  $\log (P_{\text{CO}_2}/P_{\text{CO}}) - \log X_{\text{Na}_2\text{O}}$  at 1573K.

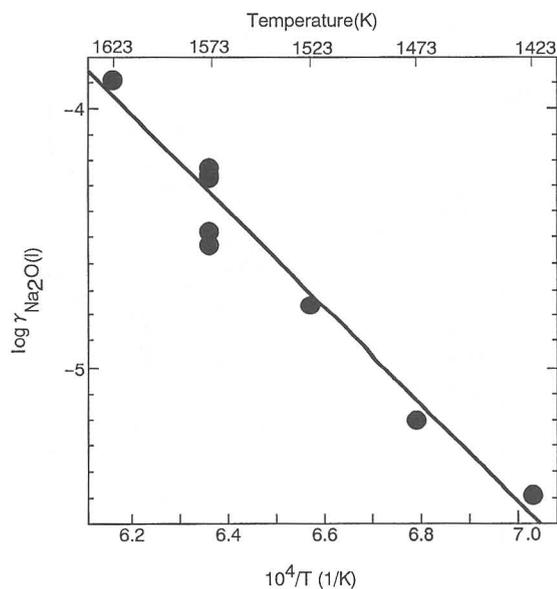


Fig.6. Temperature dependence of the activity coefficient of Na<sub>2</sub>O in the CaO-4 mass% Na<sub>2</sub>O-CaF<sub>2</sub>-SiO<sub>2</sub> system doubly saturated with CaO and 3CaO·SiO<sub>2</sub>.

The relationship between the Na<sub>2</sub>O contents of both Na<sub>2</sub>O-SiO<sub>2</sub> [4] and CaO-Na<sub>2</sub>O-CaF<sub>2</sub>-SiO<sub>2</sub> fluxes having the same Na<sub>2</sub>O activity at 1473 and 1573K are shown in Figure 8. For example, CaO-4 mass% Na<sub>2</sub>O-CaF<sub>2</sub>-SiO<sub>2</sub> flux doubly saturated with CaO and 3CaO·SiO<sub>2</sub> is equivalent to 44 mass% Na<sub>2</sub>O-SiO<sub>2</sub> flux at 1473K and is equivalent to 45 mass% Na<sub>2</sub>O-SiO<sub>2</sub> flux at 1573K in terms of the Na<sub>2</sub>O activity. This indicates that the saturation of the present slag with CaO significantly increases

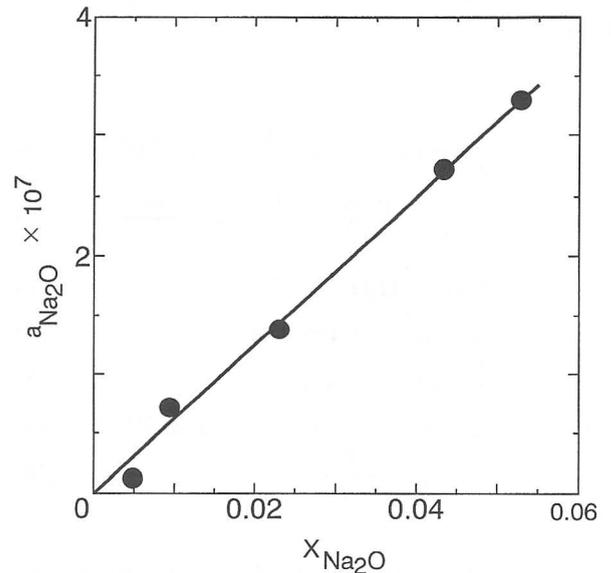


Fig.7. The activity of Na<sub>2</sub>O in the CaO-Na<sub>2</sub>O-CaF<sub>2</sub>-SiO<sub>2</sub> system doubly saturated with CaO and 3CaO·SiO<sub>2</sub> at 1473K.

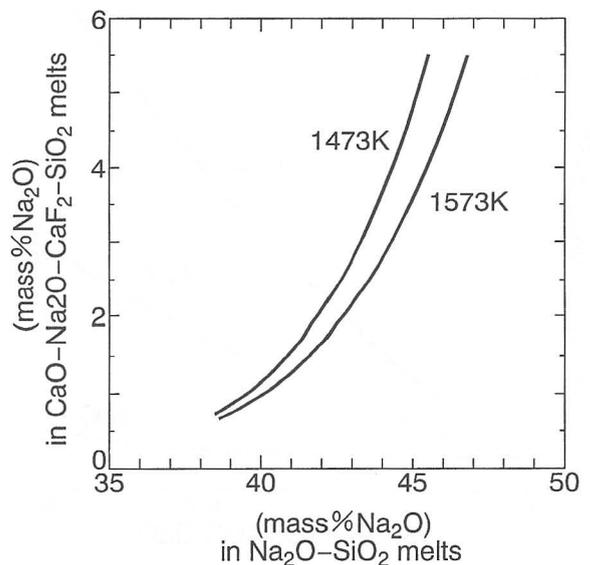


Fig.8. The relationship between Na<sub>2</sub>O content of CaO-CaF<sub>2</sub>-SiO<sub>2</sub> fluxes and that of Na<sub>2</sub>O-SiO<sub>2</sub> fluxes having the same activity of Na<sub>2</sub>O at 1473 and 1573K.

the activity coefficient of a small content of Na<sub>2</sub>O owing to strong repulsion between Na<sub>2</sub>O and CaO in the slag.

The sodium content of lead equilibrated with the CaO–2.3 mass% Na<sub>2</sub>O–CaF<sub>2</sub>–SiO<sub>2</sub> flux was 0.196 mass% at 1573K with the partial pressure of oxygen of 2.80×10<sup>-12</sup> Pa according to the results of Muraki et al.<sup>[1]</sup> Their result is in good agreement with the present results as shown in Figure 5.

Since the activities of Na<sub>2</sub>O for the Na<sub>2</sub>O–SiO<sub>2</sub> and CaO–Na<sub>2</sub>O–CaF<sub>2</sub>–SiO<sub>2</sub> systems were obtained, the phosphorus partition ratios between these fluxes and a carbon saturated iron were compared at the same activity value of Na<sub>2</sub>O in the fluxes as follows, although the activity coefficients of phosphorus of both fluxes were different.

The authors<sup>[8]</sup> investigated the temperature dependence of the phosphorus partition ratio between the Na<sub>2</sub>O–SiO<sub>2</sub> flux and a carbon saturated iron at the oxygen partial pressure controlled by the reaction C(s) + 1/2O<sub>2</sub>(g) = CO(g). For example, the CaO–2 mass% Na<sub>2</sub>O–CaF<sub>2</sub>–SiO<sub>2</sub> flux has the same activity of Na<sub>2</sub>O as 42 mass% Na<sub>2</sub>O–SiO<sub>2</sub> flux at 1473K according to Figure 8. The phosphorus partition ratio between this 42 mass% Na<sub>2</sub>O–SiO<sub>2</sub> flux and a carbon saturated iron measured by the authors is 4.0 at 1473K with the partial pressure of oxygen of 8.53×10<sup>-13</sup> Pa.<sup>[8]</sup> The extrapolated phosphorus partition ratio at 1573K according to the known temperature dependence is 0.54 at the oxygen partial pressure of 2.80 × 10<sup>-12</sup> Pa which is derived by the C–CO equilibrium as shown in Figure 9. On the other hand, Muraki et al.<sup>[1]</sup> observed that the phosphorus partition ratio between the CaO–2 mass% Na<sub>2</sub>O–CaF<sub>2</sub>–SiO<sub>2</sub> flux and a carbon saturated iron is 25 at the same oxygen partial pressure at 1573K. This value is much larger than that for the Na<sub>2</sub>O–SiO<sub>2</sub> system at the same Na<sub>2</sub>O activities for the both fluxes.

Therefore, the activity of Na<sub>2</sub>O is not a single factor to determine the phosphorus partition ratios and the effect of the activity coefficient of phosphorus in fluxes on the partition ratio should be considered.

#### 4. CONCLUSIONS

The effect of BaO and K<sub>2</sub>O addition to the CaO–CaF<sub>2</sub>–SiO<sub>2</sub> system on the phosphorus partition ratio between CaO–CaF<sub>2</sub>–SiO<sub>2</sub> system doubly saturated with CaO and 3CaO·SiO<sub>2</sub> and carbon saturated iron melts has been investigated at hot metal temperatures for comparison with that of Na<sub>2</sub>O obtained previously by a chemical equilibration technique.

The partition ratio of phosphorus increases ten times with the addition of 7 mass% BaO or 0.4 mass% Na<sub>2</sub>O.

The temperature dependence of the activity coefficient of Na<sub>2</sub>O in the CaO–4 mass% Na<sub>2</sub>O–CaF<sub>2</sub>–SiO<sub>2</sub> is expressed as follows.

$$\log \gamma_{\text{Na}_2\text{O}} = -\frac{18,600(\pm 1,100)}{T} + 7.23(\pm 0.08)$$

The relationship between the activity of Na<sub>2</sub>O in both CaO–CaF<sub>2</sub>–SiO<sub>2</sub> fluxes doubly saturated with CaO and 3CaO·SiO<sub>2</sub> and Na<sub>2</sub>O–SiO<sub>2</sub> fluxes is determined. Not only the activity of Na<sub>2</sub>O but also the activity coefficient of phosphorus in fluxes have an effect on the partition ratio of phosphorus.

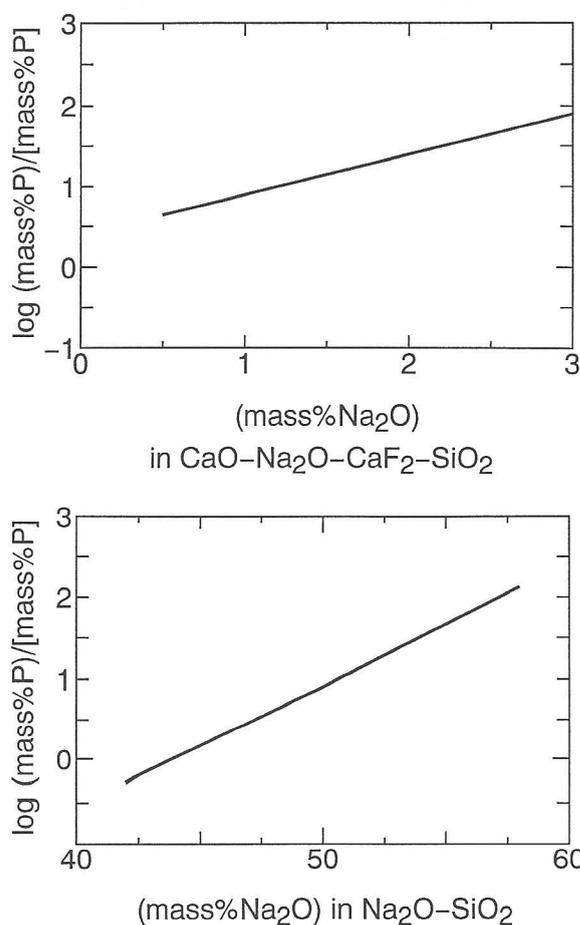


Fig.9. (a) Phosphorus partition ratio between CaO–Na<sub>2</sub>O–CaF<sub>2</sub>–SiO<sub>2</sub> fluxes doubly saturated with CaO and 3CaO·SiO<sub>2</sub> and carbon saturated iron and (b) estimated phosphorus partition ratio of Na<sub>2</sub>O–SiO<sub>2</sub> fluxes at 1573K with P<sub>O<sub>2</sub></sub> = 2.80 × 10<sup>-12</sup>Pa.

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