# A Thermodynamic Study on the Dephosphorization of Chromium Containing Molten Iron

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## ABSTRACT

A thermodynamic study was carried out on the equilibrium distribution ratio of phosphorus, $L_P$ between molten CaO-$CaF_2$ and CaO-BaO-$CaF_2$ slags and Fe-16%Cr-$C_{sat}$-P melts at 1400 °C. In the CaO-$CaF_2$ slag system, the $L_P$ increases with CaO/$CaF_2$ ratio until the slag becomes saturated with CaO. The phosphate capacity of slag increases markedly when BaO is added to CaO-$CaF_2$ slag especially at low $CaF_2$ content. A small addition of BaO to CaO-$CaF_2$ binary slag decreases the melting temperature of slag significantly, and hence to improve the slag fluidity.

## 1. INTRODUCTION

Recently, there has been an increased demand for low phosphorus stainless steels. However, the average phosphorus content in stainless steel tends to increase every year through the recycling scrap[1)]. In addition, there is a trend of using the blast furnace hot metal to produce stainless steel in BOF or EAF, which increases the phosphorus input. This situation prompted studies on proper ways for the removal of phosphorus from high chromium containing iron melts.

Dephosphorization of chromium containing iron melts is possible either under reducing[2-4)] or oxidizing condition[1, 5-7)]. The reduction dephosphorization process, however, has not yet been implemented due to its high flux cost and environmental problems[8)]. The oxidation dephosphorization is also difficult, because the chromium lowers the activity of phosphorus and the chromium is oxidized preferentially at a high oxygen potential. In addition, the chromium oxide, $Cr_2O_3$, generated forms high melting point compounds in slag such as CaO · $Cr_2O_3$ or FeO · $Cr_2O_3$ lowering the slag fluidity[9)]. Several systems of strong basic fluxes such as BaO[8)] and $Li_2CO_3$[10)] based fluxes showed excellent efficiecies of dephosphorization for high chromium containing iron melts under a relatively low oxygen potentials. However, high cost and hazardousness of these fluxes limit their application in practice. It is desired to develop a cost effective and less hazardous dephosphorization process for chromium containing hot metal. One way of doing this is to add a small amount of strong basic oxides, such as BaO, to conventional CaO based slag to improve dephosphorization capability.

In this study, the equilibrium phosphorus distribution ratios between CaO-$CaF_2$ and CaO-BaO-$CaF_2$ slags and Fe-16%Cr-$C_{sat}$-P melts have been measured at 1400 °C under 1 atm CO pressure. The effect of small BaO addition to CaO-$CaF_2$ slags was examined for the dephosphorization capability and melting point of slag. The obtained phosphate capacity data can be utilized to determine the phosphorus distribution ratio in actual practice.

## 2. THERMODYNAMIC CONSIDERATIONS

The conditions for effective dephosphorization by oxidation are well defined[11)]. They are low temperature, high oxygen potential, high slag basicity and high slag fluidity to optimize the thermodynamics and kinetics. During the dephosphorization of chromium containing iron melts, the oxygen potential should be controlled in order not to oxidize the chromium in the melt. Therefore, the slag basicity must be kept as high as possible without deterioration of the slag fluidity at the refining temperature. BaO is known to be more basic than CaO and shows a higher refining capability for phosphorus[8].

The dephosphorizing power of a slag can be normalized for oxide systems by the phosphate capacity defined by Equation [2] for Reaction [1][12]:

$$1/2\ P_2(g) + 5/4\ O_2(g) + 3/2\ (O^{2-}) = (PO_4^{3-}) \qquad [1]$$

$$C_{PO_4^{3-}} = \frac{(\%PO_4^{3-})}{P_{P_2}^{1/2}\ P_{O_2}^{5/4}} = \frac{K_{(1)}\ a_{O^{2-}}^{3/2}}{f_{PO_4^{3-}}} \qquad [2]$$

where $(\%PO_4^{3-})$ is the phosphate ions dissolved in slag, $K_{(1)}$ is the equilibrium constant of Reaction [1], and $f_{PO_4^{3-}}$ and $a_{O^{2-}}$ are the activity coefficient of phosphate ion and the activity of oxygen ion in the slag, respectively.

The partial pressure of phosphorus can be evaluated from the phosphorus content in metal and the available thermodynamics[13].

$$1/2\ P_2(g) = [P]_{wt\%\ in\ Fe} \qquad [3]$$

$$\Delta G^o = -157{,}700 + 5.4\ T\ (J/mole)^{13)}$$

$$K_{(3)} = \frac{f_P\ [\%P]}{P_{P_2}^{1/2}} \qquad [4]$$

where [%P] and $f_P$ are the phosphorus content in iron melt and the activity coefficient of phosphorus in 1 wt% standard state, respectively. The $f_P$ value in Fe-16%Cr-$C_{sat}$-P melts can be obtained from the following equation:

$$\log f_P = \log f^c_P + \log f^{Cr}_P \qquad [5]$$

where $f^c_P$ is the activity coefficient of phosphorus in Fe-$C_{sat}$-P melts and Hadrys et al.[14] obtained this value as 6.05 at 1600 °C. Assuming the regular solution, this value can be extrapolated to 1400 °C to be 7.5. Hara et al.[7] determined $e_P^{Cr}$ and $r_P^{Cr}$ values in Fe-Cr-$C_{sat}$-P melts as -0.085 and 0.00233 at 1300 °C, respectively. This would give the $f^{Cr}_P$ value as 0.192 for Fe-16%Cr-$C_{sat}$-P melt at 1400 °C. Thus the $f_P$ value for can be estimated as 1.44 from equation [5].

For carbon-saturated chromium containing iron melt under 1 atm CO pressure, the oxygen potential, $P_{O_2}$ at the slag-metal interface is controlled by the C-CO equilibrium ($P_{O_2}$ = 7.86 x $10^{-17}$ atm at 1400 °C)

$$C\ (gr) + 1/2O_2\ (g) = CO\ (g) \qquad [6]$$

$$\Delta G^o = -144{,}400 - 85.77\ T\ (J/mole)^{15)}$$

Therefore, the phosphate capacity of a slag can be calculated from the experimentally measured phosphorus distribution ratio, $L_P$ = (%P)/[%P] and Equations [2], [3] and [6]. Conversely, the obtained phosphate capacity data of a given slag composition can be utilized to determine the $L_P$ as a function of oxygen potential.

$$\log L_P = \log C_{PO_4^{3-}} + \log f_P + 5/4 \log P_{O_2} - \log K_{(3)} - 0.486 \qquad [7]$$

In actual dephosphorization process, the oxygen potential at the slag-metal interface may be controlled by different reactions. For an example, if the oxygen potential is determined by the formation of $CaO \cdot Cr_2O_3$ as shown in Equation [8].[6, 9]

$$2Cr(l) + CaO(s) + 3/2O_2(g) = CaO \cdot Cr_2O_3 \qquad [8]$$

$$\Delta G^o = -1{,}383{,}800 + 359.9\ T\ (J/mole)^{6,\ 15)}$$

$$K_{(8)} = \frac{1}{X_{Cr}^2\ \gamma_{Cr}^2\ a_{CaO}\ P_{O_2}^{3/2}} \qquad [9]$$

where $\gamma_{Cr}$ is the activity coefficient of chromium in iron melt. Hadrys et al.[14] reported $\gamma_{Cr}$ and $\gamma_C$ values in Fe-Cr-$C_{sat}$ melts at 1600 °C as Equation [10] and [11], respectively.

$$\ln \gamma_{Cr} = -1.7 + 3.5X_{Cr}^2 \qquad [10]$$

$$\ln \gamma_C = 1.56 - 1.4X_{Cr} + 2.0X_{Cr}^2 \qquad [11]$$

Assuming the regular solution for the Fe-16%Cr-$C_{sat}$-P melts, $X_C$, $X_{Cr}$ and $\gamma_{Cr}$ can be estimated as 0.21, 0.14 and 0.16 at 1400 °C, respectively. Then the oxygen potential determined by the Reaction [8] would be 8.41 x $10^{-15}$ atm when the activity of CaO in slag is 1. Therefore, from Equation [7], the $L_P$ value is expected to be more than two orders of magnitude higher than the measured $L_P$ under the present experimental condition ($P_{CO}$ = 1 atm and $a_C$ =1).

## 3. EXPERIMENTAL METHOD

### 3.1 Equilibrium phosphorus distribution

The experiments consisted of equilibrating 10 g of carbon-saturated Fe-16%Cr-P alloy (0.2 - 0.6% P) with 5g of prefused $CaO-CaF_2-PO_{2.5}$ or $CaO-BaO-CaF_2-PO_{2.5}$ slags (0 - 0.2%P) in a graphite crucible at 1400 °C under 1 atm CO pressure. The experimental apparatus consisted of a $LaCrO_4$ resistance furnace and is shown in Figure 1. The holding time was determined by approaching the equilibrium from both metal and slag sides in separate experiments. The equilibration time ranged from 25 to 40 hours depending on the slag composition. After equilibration, the graphite crucible was withdrawn quickly using a Mo wire, and the bottom of the crucible was cooled by water and the slag surface by Ar gas. After each experiment, the slag and metal samples were chemically analyzed.

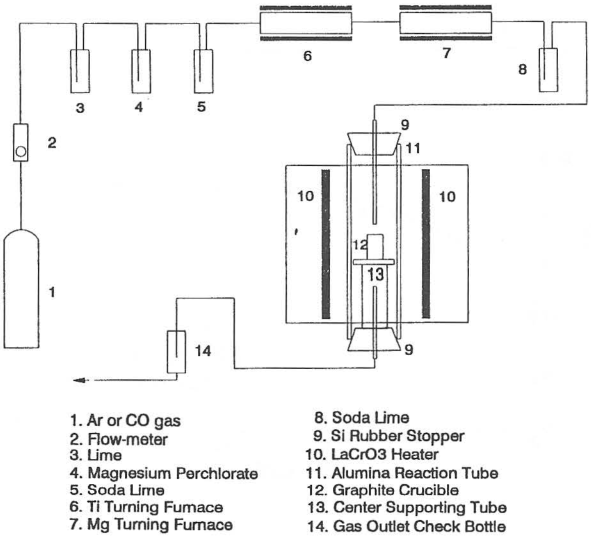

Figure 1. Schematic diagram of experimental system

### 3.2 Melting point measurement

The phase diagram of $CaO-BaO-CaF_2$ slag system is not available. Figure 2 shows the phase diagram of $CaO-CaF_2$ system[16)]. In this work, the change of melting point was measured when BaO was added to $CaO-CaF_2$ slag system by the heating microscope image analysis. The slag was pelletized by pressing into a cylindrical shape and heated at a constant rate. The height of slag sample was observed with the temperature reading. The calibration with standard samples of known melting points showed that the melting point of a slag could be defined when the slag height decreased to 2/3 of its original value.

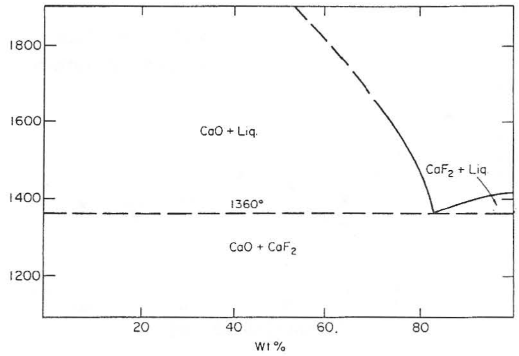

Figure 2. The phase diagam of $CaO-CaF_2$ system

## 4. RESULTS AND DISCUSSION

Figure 3 shows the change of phosphorus distribution ratios between $20\%CaO-80\%CaF_2$ slag and metal with experimental holding time. At 1400 °C, the slag composition is in the two phase region (liquid + solid CaO) and the reaction rate was expected to be very slow. The equilibrium was obtained within 30 hours whether it was approached from metal or slag sides. Figure 4 shows the change of chromium distribution ratios with time. The equilibrium was obtatined within 20 hours. Under the present experimental condition of $P_{CO}$ = 1 atm and $a_C$ =1, the oxidation of chromium in the melt was negligible. The activity of $Cr_2O_3$ in slag can be calculated to be about 3.5 x $10^{-6}$ for the Reaction [12].

$$2Cr\ (l) + 3/2O_2\ (g) = Cr_2O_3\ (l) \qquad [12]$$

$$\Delta G^{o} = -1{,}145{,}800 + 263.9\ T\ (J/mole)^{15)}$$

$$K_{(12)} = \frac{a_{Cr_2O_3}}{X_{Cr}^{2}\ \gamma_{Cr}^{2}\ P_{O_2}^{3/2}} \qquad [13]$$

Table 1 summarizes the experimental results of equilibrium phosphorus distribution between CaO-CaF$_2$ slags and Fe-16%Cr-C$_{sat}$-P melts at 1400 °C. Figure 5 shows the equilibrium L$_P$ ratios as a function of CaO content in CaO-CaF$_2$ slag. When the slag is not saturated with CaO, i.e. less than 20% CaO content, the L$_P$ ratio increases with CaO content. However, at higher CaO content, the ratio remained at a roughly constant value. This is probably due to the constant CaO activity ($a_{CaO(s)}$ = 1) in CaO saturated two phase region (Figure 2). The phosphate capacity of CaO saturated CaO-CaF$_2$ slags at 1400 °C is calculated to be about 8.91 x 10$^{24}$ from the Equations [2] and [3].

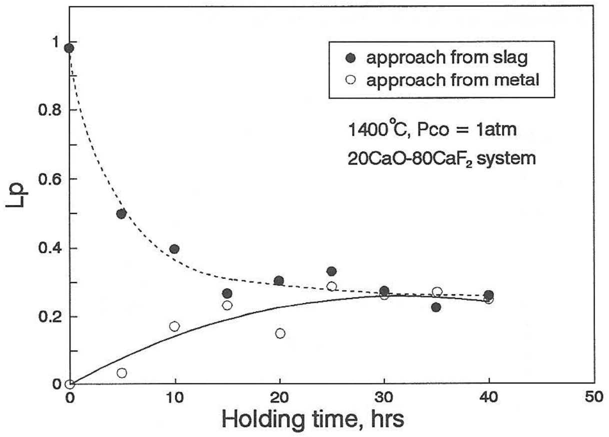

Figure 3. Change of phosphorus distribution ratio during experimental holding time

Table I. Experimental results for CaO-CaF$_2$ slag at 1400 °C

| No | Slag, wt% CaO | CaF$_2$ | PO$_{2.5}$ | Cr$_2$O$_3$ | Metal, wt% [P] | [Cr] |
|---|---|---|---|---|---|---|
| B1 | 0 | 99.79 | 0.13 | 0.011 | 0.542 | 15.76 |
| B2 | 10.19 | 89.64 | 0.22 | 0.019 | 0.504 | 15.66 |
| B3 | 13.22 | 86.60 | 0.23 | 0.039 | 0.50 | 15.67 |
| B4 | 16.20 | 83.62 | 0.23 | 0.025 | 0.50 | 15.64 |
| B5 | 20.23 | 79.57 | 0.26 | 0.030 | 0.488 | 15.73 |
| B6 | 23.22 | 76.59 | 0.25 | 0.020 | 0.491 | 15.37 |
| B7 | 30.22 | 69.59 | 0.25 | 0.024 | 0.488 | 14.80 |
| B8 | 40.23 | 59.57 | 0.26 | 0.034 | 0.489 | 15.71 |

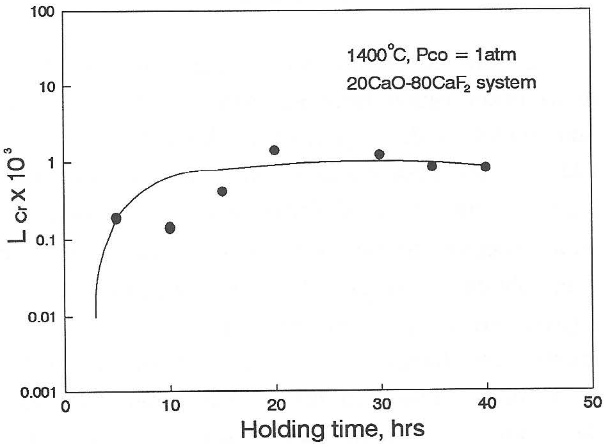

Figure 4. Change of chromium distribution ratio during experimental holding time

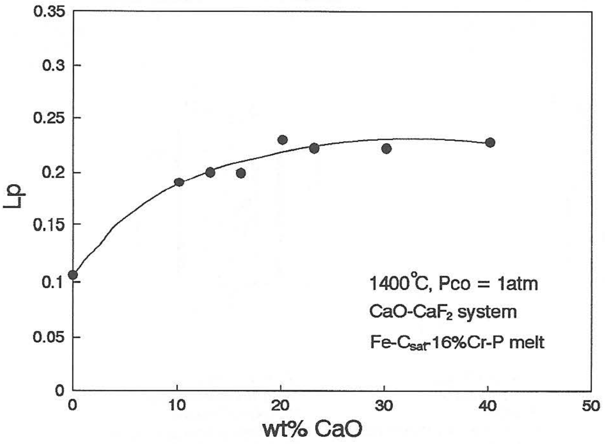

Figure 5. The equilibrium phosphorus distribution ratio for CaO-CaF$_2$ slags at 1400 °C

The experimental results for BaO-CaO-$CaF_2$ slags are summarized in Table 2. Figure 6 shows the changes of $L_P$ with the addition of BaO to CaO-$CaF_2$ slags, in which the $CaF_2$ content is varied from 40 to 80%. Up to about 10% of BaO additions, there is no significant change of $L_P$. However, further addition of BaO increases $L_P$, and the effect is more significant at lower $CaF_2$ content. It is of interest to see that the $L_P$ reaches the maximum values and decreases again as more BaO is replaced with CaO. The similar result was observed by Inoue et al.[1)] for the same slag system at 15% $CaF_2$ content in slag. There was an optimum BaO content in slag to achive the maximum dephosphorization degree. They attributed this phenomena to that the coexistence of calcium and barium as cations in slag is more effective in dephosphorization.

Table II. Experimental results for CaO-BaO-$CaF_2$ slag at 1400 °C

| No | Slag, wt% | | | | Metal, wt% | |
|---|---|---|---|---|---|---|
| | CaO | BaO | $CaF_2$ | $PO_{2.5}$ | [P] | [Cr] |
| T1 | 20.01 | 0 | 79.94 | 0.254 | 0.550 | 15.98 |
| T2 | 14.98 | 4.17 | 80.23 | 0.250 | 0.586 | 16.08 |
| T3 | 9.96 | 8.97 | 80.41 | 0.254 | 0.566 | 16.03 |
| T4 | 4.97 | 14.02 | 80.31 | 0.305 | 0.367 | 16.13 |
| T5 | 0 | 18.98 | 80.45 | 0.275 | 0.354 | 16.12 |
| T6 | 40.26 | 0 | 57.41 | 0.169 | 0.390 | 15.90 |
| T7 | 35.21 | 6.17 | 57.94 | 0.160 | 0.331 | 16.05 |
| T8 | 30.13 | 10.42 | 58.74 | 0.220 | 0.298 | 16.11 |
| T9 | 20.26 | 21.25 | 57.36 | 0.281 | 0.302 | 16.05 |
| T10 | 15.20 | 26.08 | 58.04 | 0.280 | 0.309 | 16.12 |
| T11 | 10.11 | 30.20 | 58.87 | 0.282 | 0.350 | 16.07 |
| T12 | 5.14 | 35.25 | 58.65 | 0.280 | 0.366 | 16.06 |
| T13 | 60.26 | 0 | 37.44 | 0.245 | 0.530 | 15.84 |
| T14 | 55.26 | 6.75 | 37.4 | 0.245 | 0.532 | 15.86 |
| T15 | 50.20 | 10.87 | 37.95 | 0.419 | 0.481 | 15.87 |
| T16 | 45.11 | 14.38 | 38.88 | 0.664 | 0.506 | 15.84 |
| T17 | 40.15 | 19.71 | 38.48 | 0.790 | 0.505 | 15.90 |
| T18 | 35.16 | 24.40 | 38.35 | 0.934 | 0.488 | 15.83 |
| T19 | 30.16 | 29.18 | 38.41 | 1.02 | 0.504 | 15.84 |
| T20 | 25.04 | 33.0 | 39.56 | 1.035 | 0.491 | 15.90 |

Figure 7 shows the logarithm of phosphate capacity calculated from the $L_P$ data. They are plotted against the molar ratio of $X_{BaO}/X_{CaO}$ in slag. The phosphate capacity increases drastically when a small amount of BaO is replaced with CaO in CaO-BaO-40%$CaF_2$ slag. The phosphate capacity data obtained in the present experiment can be utilized to determine the $L_P$ between slag and Fe-16%Cr-$C_{sat}$-P melt in actual practice. For an example, when the $X_{BaO}/X_{CaO}$ ratio is 1/4 in CaO-BaO-40%$CaF_2$ slag, the logarithm of phosphate capacity is about 25.6. Assuming that the oxygen potential at the slag-metal interface is controlled by the formation of $CaO \cdot Cr_2O_3$ as in Equation [8], the $L_P$ ratio is obtained as 300 from Equation [7].

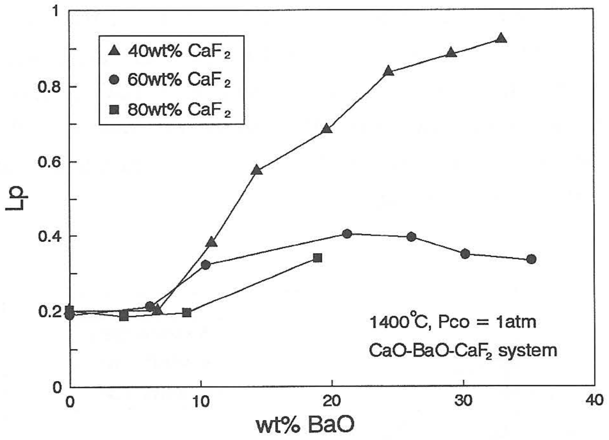

Figure 6. The effect of BaO addition to CaO-$CaF_2$ slags on phosphrous distribution ratio

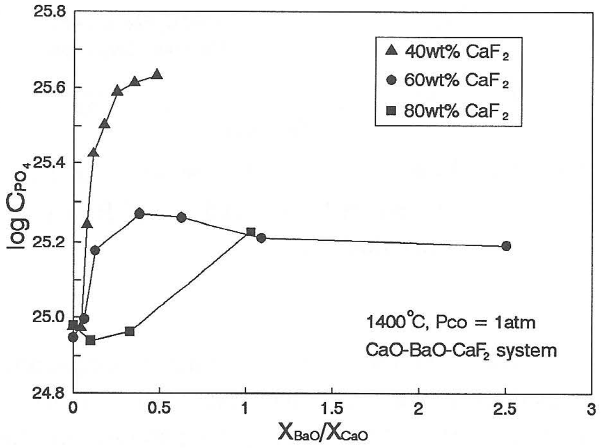

Figure 7. The phosphate capacity changes with the addtion of BaO to CaO-$CaF_2$ slags

The activity coefficient of $PO_{2.5}$ in the slag can be calculated from the $L_P$ data. The dephosphorization reaction can also be expressed in a molecular form as Equation [14].

$$[P]_{wt\%\ in\ Fe} + 5/4O_2\ (g) = PO_{2.5}\ (l) \qquad [14]$$

$$\Delta G^\circ = -609{,}300 + 247.6\ T\ (J/mole)^{13,\ 15)}$$

$$\gamma_{PO_{2.5}} = \frac{K_{(14)}\ f_P\ [\%P]\ P_{O_2}^{5/4}}{X_{PO_{2.5}}} \qquad [15]$$

The logarithm of activity coefficients of $PO_{2.5}$ is plotted against the $X_{BaO}/X_{CaO}$ ratio in slag as shown in Figure 8. When the $X_{BaO}/X_{CaO}$ ratio is 1/4 in CaO-BaO-40%$CaF_2$ slag, the activity coefficient of $PO_{2.5}$ is lower by a factor of 6 compared to the value for the CaO-40%$CaF_2$ slag. From this result, it can be said that BaO is more basic than CaO, and the effect of lowering the activity coefficient of $PO_{2.5}$ is more significant at lower $CaF_2$ content.

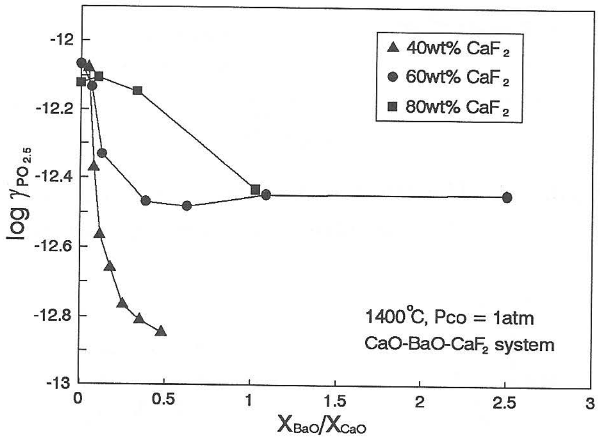

Figure 8. Changes in activity coefficient of $PO_{2.5}$ in slag with the addition of BaO to CaO-$CaF_2$ slags

The result of melting temperature measurement for CaO-BaO-$CaF_2$ slags is plotted in Figure 9. The melting temperature of slag decreases significantly with the addition of BaO. For an example, when the $X_{BaO}/X_{CaO}$ ratio is changed from 0 to 1/4 in CaO-BaO-40%$CaF_2$ slag, the melting temperature decreases from 1433 °C to below 1300 °C. Therefore, the addition of BaO to CaO-$CaF_2$ slag in a relatively small amount not only increases the phosphate capacity of slag, but also decreases the melting temperature of slag significantly and hence to improve the slag fluidity.

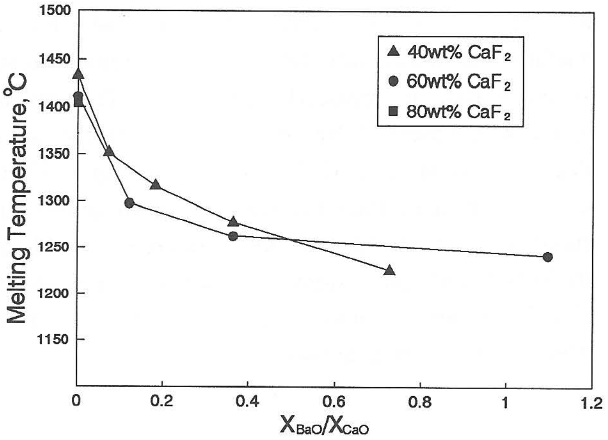

Figure 9. Changes in melting temperature of slag with the addition of BaO to CaO-$CaF_2$ slags

## 5. CONCLUSIONS

Phosphorus distribution ratio between CaO-$CaF_2$ and CaO-BaO-$CaF_2$ slags and Fe-16%Cr-$C_{sat}$-P melts has been measured at 1400 °C. In the CaO-$CaF_2$ slag system, the $L_P$ ratio increases with CaO content until the slag becomes saturated with CaO. A small addition of BaO to CaO-$CaF_2$ binary slag increases the phosphate capacity of slag markedly when the $CaF_2$ content is low. In addition, the addition of BaO decreases the melting temperature of slag significantly, and hence to improve the reaction kinetics. The $L_P$ ratio of 300 is possible for Fe-16%Cr-$C_{sat}$-P melt with 36%CaO-24%BaO-40%$CaF_2$ slag under an oxygen potential determined by the formation of $CaO \cdot Cr_2O_3$.

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