A Thermodynamic Study of Dephosphorization Using BaO-BaF_2, CaO-CaF_2, and BaO-CaO-CaF_2 Systems

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Phosphorus partition ratios between BaO-BaF_2 fluxes and copper-phosphorus alloys have been measured as a function of slag composition at 1400 °C. A molybdenum sleeve has been used to avoid contact between the slag and the crucible in order to prevent the absorption of slag by the graphite crucible. The effects of additions of BaO to the CaO-CaF_2 system have been investigated by measuring the phosphorus partition ratios between these fluxes and Fe-C_{sat}-P alloy as a function of slag composition at 1400 °C. Also, the activity of BaO as a function of slag composition at 1400 °C has been determined by equilibrating a silver-barium alloy with the BaO-CaO-CaF_2 fluxes and CO in a graphite crucible. The results indicate that phosphorus partition ratios with carbon-saturated iron, L_P, for the BaO-BaF_2 system are relatively high, going up to 400, even for oxygen partial pressure as low as 7.8×10^{-16} atm. The phosphate capacity and the activity coefficient of $PO_{2.5}$ for this system were calculated from the experimental results using the available thermodynamic data. No effects of barium oxide addition in lime-based fluxes were observed for BaO contents less than 40 pct. One of the reasons for this phenomenon is that BaO activity in a lime-based flux is very small for BaO content less than 46 pct. However, for high BaO contents, $C_{PO_4^{3-}}$ increases significantly, as does the activity of BaO.

I. INTRODUCTION

HIGH-CARBON alloyed metal can be produced from stainless scrap or from carbon steel and high-carbon ferrochromium in an electric arc furnace. The phosphorus in stainless steel tends to increase through recycling scrap and by the addition of raw materials, such as chromium ore and coke. It is known that the presence of phosphorus is detrimental to the mechanical properties[1] and corrosion resistance[2] of stainless steel. However, it is difficult to reduce the phosphorus levels in a stainless steelmaking operation or subsequent refining processes, because chromium will oxidize in preference to phosphorus when using conventional slags. It is, therefore, necessary to investigate alternative processes for removing the phosphorus in stainless steel without chromium loss.

It is theoretically possible to remove phosphorus from carbon-saturated stainless steel if the phosphate capacity is sufficiently high. Generally, highly basic slags have high phosphate capacities. Numerous practical experiments have been done; however, few of them have dealt with the basic thermodynamic properties of slags used for dephosphorization under oxidizing conditions. Tabuchi and Sano[3,4] studied the thermodynamics of phosphate and phosphide in CaO-CaF_2 and BaO-BaF_2 melts by equilibrating these melts with silver in a graphite boat. They reported that BaO-BaF_2 fluxes have a larger phosphate capacity than CaO-CaF_2 fluxes. However, this study was only done for a small composition range for BaO

in BaO-BaF_2 melts. Hara and Sano[5] extended this work for higher BaO contents in the melts for 1200 °C and 1300 °C by equilibration with Fe-C_{sat} alloys.

Fluxes such as BaO-BaF_2 are very expensive and, in most cases, not feasible for use on an industrial scale. Therefore, there is a need for establishing an economical dephosphorization technique for chromium-containing iron. Lime-based slags are normally used in steelmaking but are ineffective for stainless steel. It may be possible that the addition of highly basic oxides to lime fluxes will increase the abilities of the flux to absorb phosphorus without being too expensive. This work examines the ability of the removal of phosphorus for CaO-CaF_2 and BaO-BaF_2 fluxes at 1400 °C and the effect of the addition of BaO to lime systems by measuring their phosphorus distribution ratio between the slag and metal and determining the phosphate capacity and activity coefficient of $PO_{2.5}$. Also, the activity of BaO in a lime system was measured and used to explain the behavior of these fluxes in the phosphorus removal.

II. THERMODYNAMIC CONSIDERATIONS

There are several ways to compare the ability of the fluxes to remove phosphorus. The phosphorus distribution ratio between the slag and metal at equilibrium is one of them, and it is used for comparison with the actual distribution ratio obtained in steel plants. It can only be experimentally determined, and it is defined as

$$L_P = \frac{(\text{pct P})}{[\text{pct P}]} \quad [1]$$

where (pct P) is the weight percent of phosphorus in slag and [pct P] is the weight percent of phosphorus in liquid iron alloys. Very often L_P is measured for carbon-saturated iron.

Another way to measure the ability of a slag to absorb

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phosphorus is phosphate capacity. It was first introduced by Wagner,[6] and is defined as

$$\frac{1}{2} P_2 \,(g) + \frac{5}{4} O_2 \,(g) + \frac{3}{2} O^{2-} \,(slag) = PO_4^{3-} \,(slag) \qquad [2]$$
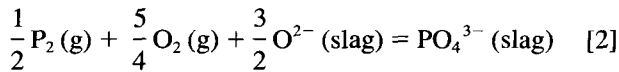
$$C_{PO_4^{3-}} = \frac{(pct\ PO_4^{3-})}{P_{P_2}^{1/2} P_{O_2}^{5/4}} = \frac{k_{(2)}(a_{O^{2-}})^{3/2}}{\gamma_{PO_4^{3-}}^0} \qquad [3]$$

where $(pct\ PO_4^{3-})$ is the weight percent of PO_4^{3-} dissolved in slag, P_{O_2} is the oxygen partial pressure at the slag-metal interface, and P_{P_2} is the phosphorus partial pressure in equilibrium with phosphorus in liquid iron. For a low concentration of PO_4^{3-}, the activity may be replaced by the respective concentrations of $(pct\ PO_4^{3-})$ and the limiting value $\gamma_{PO_4^{3-}}^0$, which is the activity coefficient at infinite dilution concentration.

The phosphate capacity can be related to L_P considering Reaction [4] and the equilibrium oxygen pressure.

$$\frac{1}{2} P_2 \,(g) = \underline{P}_{(1\ wt\ pct\ in\ liquid\ iron)} \qquad [4]$$
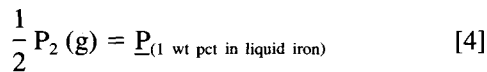
$$\Delta G^\circ = -37,547.6 + 1.29T \quad cal/mol^{[7]}$$

$$K_{(4)} = \frac{f_P[pct\ P]}{P_{P_2}^{1/2}} \qquad [5]$$

where f_P is the activity coefficient of phosphorus in 1 wt pct standard state. This value at 1400 °C was estimated as 6.73 and is obtained by extrapolating from 6.05[8] at 1600 °C, assuming the logarithm of f_P is inversely proportional to the temperature. Combining Eqs. [3] and [5] yields

$$C_{PO_4^{3-}} = \frac{L_P K_{(4)} M_P}{f_P P_{O_2}^{5/4} M_{PO_4^{3-}}} \qquad [6]$$

where $K_{(4)}$ is the equilibrium constant for Reaction [4] and M_P and $M_{PO_4^{3-}}$ are the molecular weight of P and PO_4^{3-}, respectively.

For the case in which L_P is measured for carbon-saturated iron, the P_{O_2}, partial pressure of oxygen, in equilibrium with carbon and 1 atm of CO can be obtained from Reaction [7] and is 7.8×10^{-16} atm at 1400 °C.

$$C \,(s) + \frac{1}{2} O_2 \,(g) = CO \,(g) \qquad [7]$$
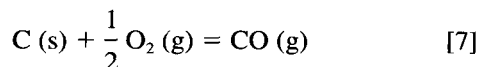
$$\Delta G^\circ = -27,340 - 20.5T \quad cal/mol^{[9]}$$

The metal used in some of the experiments in this study was a Cu-P alloy instead of a Fe-C_{sat}-P alloy. It is possible to calculate the equivalent amount of phosphorus in iron in equilibrium with the flux by knowing the amount of phosphorus in the copper using Reactions [8] and [4].

$$\frac{1}{2} P_2 \,(g) = \underline{P}_{(1\ wt\ pct\ in\ liquid\ copper)} \qquad [8]$$
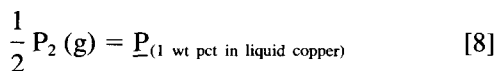
$$\Delta G^\circ = -29,875.7 + 0.129T \quad cal/mol^{[10]}$$

The activity coefficient of $PO_{2.5}$ can also be used to

evaluate the dephosphorization ability of a flux. It is defined as

$$\underline{P}_{(1\ wt\ pct\ liquid\ iron)} + \frac{5}{4} O_2 \,(g) = (PO_{2.5}) \,(slag) \qquad [9]$$
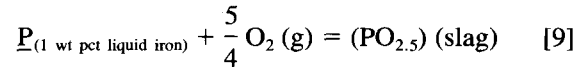
$$\Delta G^\circ = -154,313 + 64.75T \quad cal/mol^{[9]}$$

$$\gamma_{PO_{2.5}} = \frac{K_{(9)} f_P[pct\ P] M_{PO_{2.5}}}{(pct\ P) M_P}$$

As shown in Eq. [3], phosphate capacity is a function of the oxygen ion concentration in the slag, which is related to the activity of a basic oxide. The activity of BaO in a CaO-containing flux was measured by equilibrating the slag with a Ba-Ag alloy and CO in a graphite crucible. This activity is calculated from the following equilibrium:

$$BaO \,(slag) + C \,(s) = Ba_{(in\ Ag)} + CO \,(g) \qquad [10]$$
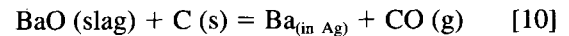
$$\Delta G^\circ = 105,831.74 - 45.03T \quad cal/mol^{[9]}$$

$$K_{(10)} = \frac{a_{Ba} P_{CO}}{a_{BaO}} = \frac{X_{Ba} \gamma_{Ba} P_{CO}}{a_{BaO}}$$

where a_{BaO} is the activity of BaO, γ_{Ba} is the activity coefficient of barium in silver, and X_{Ba} is the molar fraction of barium in silver alloy. The activity coefficient of barium can be estimated from the following relationship:[11]

$$\frac{\log \gamma_{Ba}}{(1 - X_{Ba})^2} = 2.3 - \frac{7700}{T}$$

III. EXPERIMENTAL

A. BaO-BaF₂ System

A schematic diagram of the experimental arrangement is shown in Figure 1. It consists of a molybdenum sleeve in a graphite crucible to avoid contact between the slag and the crucible in order to prevent the absorption of slag by the graphite crucible. The master alloys were prepared from electrolytic copper and reagent grade Cu_3P and were melted in a graphite crucible. The fluxes were prepared from mixtures of analytical grade BaO, BaF_2, and $Ba_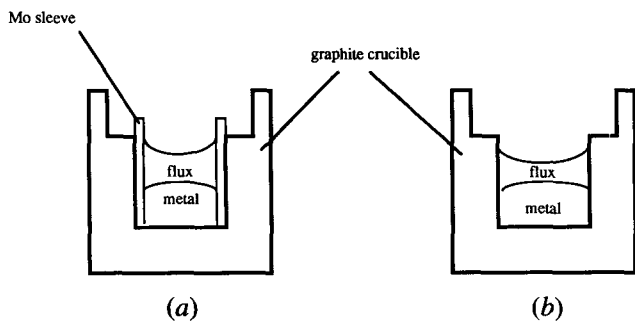3(PO_4)_2$ premelted in a graphite crucible. The experiments consisted of equilibrating 2 grams of BaO-BaF_2 with 5 grams of carbon-saturated copper, because the dissolution of molybdenum in liquid copper is negligible.[12] The samples were equilibrated under 1 atm of CO at 1400 °C in a SiC resistance furnace equipped with a mullite reaction tube. Preliminary experiments indicated that equilibrium was reached in less than 24 hours, which was used as equilibration time.

B. CaO-Containing Systems

The experimental apparatus is essentially the one described above. In measuring the phosphorus distribution ratio, the master alloys were prepared from electrolytic iron and reagent grade Fe-P and were premelted in a graphite crucible. The fluxes were prepared from a mixture of analytical grade $CaCO_3$, CaF_2, BaO, and $Ca_3(PO_4)_2$ and premelted in a graphite crucible. The experiments

Fig. 1 — (a) and (b) Schematic diagram of experimental arrangement.

Fig. 2—Phosphorus distribution ratio vs mole fraction of BaO in a BaO-BaF₂ system at 1400 °C.

consisted of equilibrating 2 grams of carbon-saturated iron alloy with 2 grams of CaO-CaF₂ or CaO-CaF₂-BaO in a graphite crucible at 1400 °C under 1 atm of CO. High-purity CO was used, and the analysis of the samples for CaF₂, before and after the experiments, indicated no significant loss. The equilibration time was 24 hours, and equilibrium was approached from both sides, i.e., transfer of phosphorus from slag to metal and vice versa. After each experiment, the slag and metal were chemically analyzed.

In measuring the activity of BaO, the experiments consisted of equilibrating 5 grams of CaO-CaF₂-BaO with 5 grams of silver in a graphite crucible at 1400 °C under 1 atm of CO. The equilibration time was 24 hours, and after each experiment, the slag and metal were chemically analyzed. Phosphorus in the iron and slag samples were analyzed by the molybdenum colorimetry method in copper by the molybivanadophosphoric acid method. In the slag, total barium was determined by the gravimetric method, total calcium and CaO via permanganate titration method, and calcium fluoride was estimated by the Ca mass balance. The BaF₂ content was determined by using a fluorine ion-selective electrode. Barium in the silver was determined by the atomic absorption method.

IV. RESULTS AND DISCUSSION

A. BaO-BaF₂ System

It is known that high basicity is required in the dephosphorization of stainless steel; barium oxide has received attention for this reason. The BaO decreases the activity coefficient of PO₂.₅, i.e., the slag has the ability of holding an appreciable amount of phosphorus under relatively low oxygen potentials. Thus, barium oxide can be used in the dephosphorization of high-carbon chromium metals without an excessive chromium loss.

The experimentally determined phosphorus distribution ratio in copper as a function of BaO in BaO-BaF₂ systems at 1400 °C under 1 atm of CO is shown in Figure 2. The value of L_P increases drastically with the low contents of BaO; however, this increase is less accentuated for high BaO contents. The equivalent phosphorus content in a carbon-saturated iron alloy was calculated by using Eqs. [4] and [7]. The phosphate capacities were calculated using Eq. [5], assuming the C-CO reaction ($P_{CO} = 1$ atm) sets the oxygen pressure ($P_{O_2} = 7.8 \times 10^{-16}$ atm). Both $C_{PO_4^{3-}}$ and L_P for Fe-C$_{sat}$ are plotted
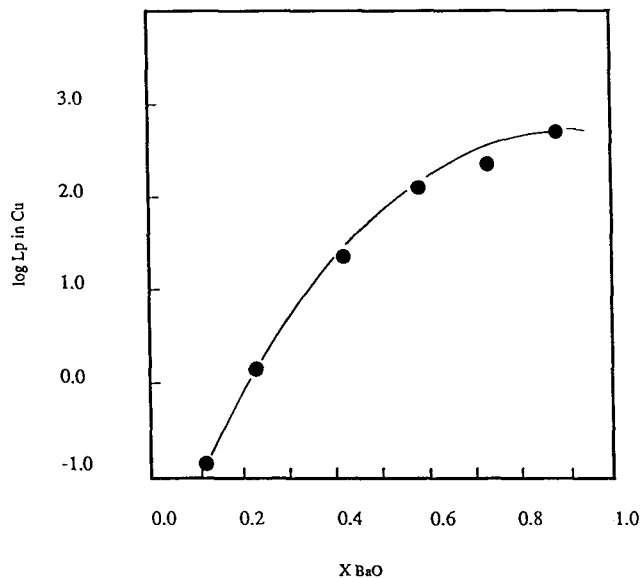
in Figure 3 as a function of the mole fraction of barium oxide. As can be seen, the phosphorus distribution ratio goes up to 400 even for low oxygen partial pressure. Also, the logarithm of $C_{PO_4^{3-}}$ ranges from 24 to 27, which means that it increases by 3 orders of magnitude with flux composition. For normal steelmaking slags (CaO-SiO₂-FeO), the logarithm of the phosphate capacity is 19.5 to 20; therefore, for a given oxygen potential, the BaO-BaF₂ is significantly better for phosphorus removal.

The comparison between this work and the one determined by Tabuchi and Sano[4] is shown in Figure 4. The data obtained is in good agreement with Tabuchi and Sano's results for low BaO concentration. Also, it shows the change of the phosphate capacity with temperature, and as expected, the phosphorus removal is more effective at low temperatures. However, in the real process, the temperature is around 1400 °C. Figure 5 shows the dependency of composition on the activity
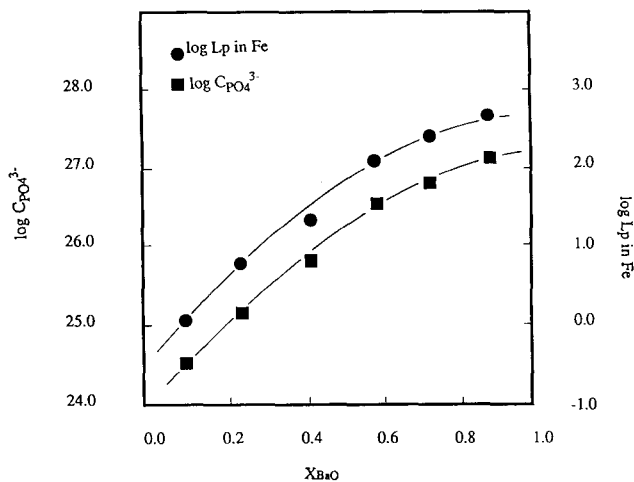

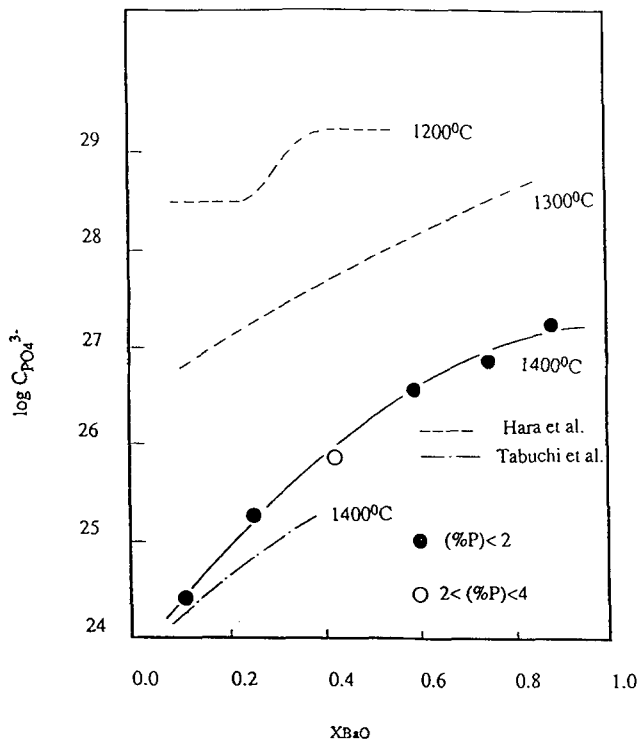Fig. 3—Phosphorus distribution ratio and phosphate capacity for BaO systems at 1400 °C.

Fig. 4—Phosphate capacities for BaO systems at 1200 °C, 1300 °C, and 1400 °C.

coefficient of $PO_{2.5}$ at 1400 °C. The $PO_{2.5}$ activity coefficient decreases with the increasing of the BaO content, which means that the presence of BaO increases the flux ability to hold phosphorus.

B. BaO-CaO-CaF₂ System

To understand the effect of the addition of BaO in a lime-based flux, the binary system of $CaO-CaF_2$ was first investigated. Figure 6 shows the change in the phosphate
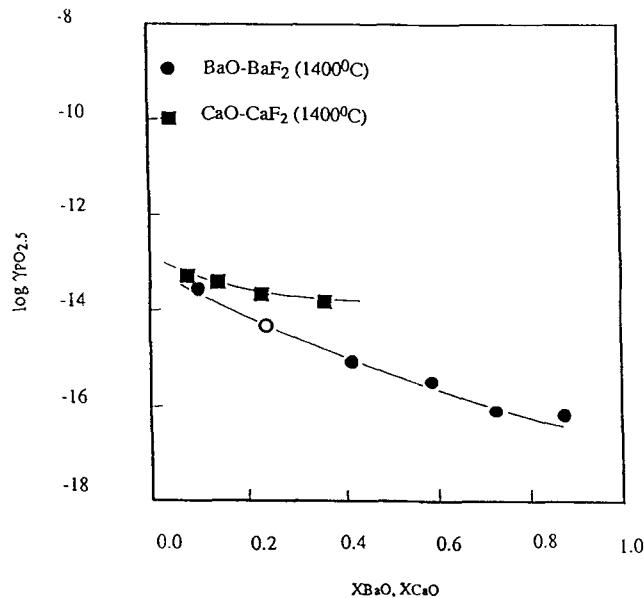

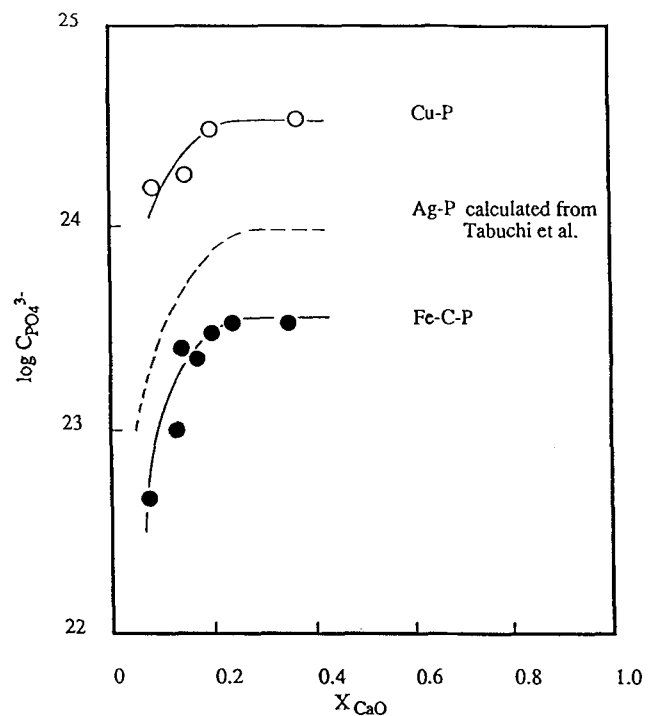Fig. 5—Activity coefficient of $PO_{2.5}$ for the BaO and CaO systems at 1400 °C.

Fig. 6—Phosphate capacities for $CaO-CaF_2$ melts at 1400 °C.

capacity as a function of the mole fraction of CaO at 1400 °C calculated from the distribution ratios between the slag and three different alloys, copper-phosphorus, silver-phosphorus,[3] and $Fe-C_{sat}-P$. From the definition, it is known that the phosphate capacity is only a function of flux composition and temperature; i.e., it is independent of the alloy used for equilibration. However, as shown in Figure 6, there is a relative change of a half order of magnitude between the values of $C_{PO_4^{3-}}$ with the three different types of equilibration. This discrepancy may be due to thermodynamic uncertainties in the free energy and activity coefficients of phosphorus in Cu, Ag, and Fe alloys. The free energy of dissolution of phosphorus in copper alloy has an error of 1.3 kcal, which corresponds to an uncertainty of 32 pct in the equilibrium constant. For iron alloy, the error in $\Delta G°$ is about 0.5 kcal, which corresponds to the uncertainty of 14 pct. The Henry's law was used to obtain the activity coefficient of phosphorus in Ag and Cu alloys because the phosphorus concentration in these alloys was small. The regular solution approach was used to obtain the activity coefficient of phosphorus in the iron alloy, as explained in Section II. Therefore, considering these uncertainties, the discrepancy is understandable. The lime saturation in this flux had been reported[13] to be at $X_{CaO} = 0.2$, and a break in the phosphate capacity may be expected at this composition because the oxygen ion activity becomes constant. In this work, the break appeared at $X_{CaO} = 0.24$; however, within the experimental error, this is reasonably close.

In any case, the phosphate capacity of a $CaO-CaF_2$ system is less than for a $BaO-BaF_2$; also, the activity coefficient of $PO_{2.5}$ is higher in the $CaO-CaF_2$ systems, as shown in Figure 5, which means that the phosphate

is more stable in a BaO than in a CaO-based system. In spite of this, BaO-BaF$_2$ fluxes are better at dephosphorizing than a CaO-CaF$_2$ system; it is interesting to study the effect of the addition of BaO in a lime-based flux from an economic point of view. Also, there is evidence that the addition of high basic oxides increases the $C_{PO_4^{3-}}$ of the flux. For example, Pak and Fruehan showed that adding a small amount of Na$_2$O to CaO-based slags greatly increased the phosphate capacity. The effect of the addition of BaO in a lime-based flux with a constant ratio of CaO/CaF$_2$ around 0.19 to 0.21 at 1400 °C is shown in Figure 7. For small BaO additions, no effect on the phosphate capacity can be observed for BaO < 40 pct; at higher BaO contents, large increase in $C_{PO_4^{3-}}$ is observed. This result is in agreement with that reported by Inoue et al.,[14] where chromium-containing iron and flux were reacted with an induction furnace in a magnesia crucible under argon atmosphere. Their results show that for BaO < 55 pct, there is a large decrease in the phosphorus removal. However, fluxes with high contents of BaO may not be economical in a commercial process due to the high cost of BaO.

In Figure 8, the activity coefficient of BaO in a lime-based flux as a function of the mole fraction of BaO at 1400 °C is shown. The activity of BaO is very small for low BaO contents; however, for $X_{BaO} > 0.29$, the BaO activity coefficient increases significantly. This result is consistent for the constant value of the phosphate capacity with low contents of barium oxide since $C_{PO_4^{3-}}$ increases with oxygen ion activity, as shown in Eq. [3]. The oxygen activity increases with the increasing of the activity of basic oxide, i.e., BaO.

C. Industrial Significance

In Figure 9, the calculated lines of the phosphorus distribution ratio for BaO-BaF$_2$ and CaO-CaF$_2$ systems in equilibrium with Fe-C$_{sat}$-18 pct Cr at 1400 °C are shown. The dashed lines are for partial pressure of oxygen controlled by C-CO equilibrium ($P_{O_2} = 7.8 \times 10^{-16}$ atm) and the solid lines are for Cr-Cr$_2$O$_3$ equilibrium ($P_{O_2} = 4.4 \times 10^{-15}$ atm); in the real processes, the partial pressure of oxygen is close to a Cr-Cr$_2$O$_3$ equilibrium. The phosphorus distribution ratio for a reasonable economical process is at least 50, which is represented by the horizontal line. As shown in Figure 10, a BaO-BaF$_2$ flux
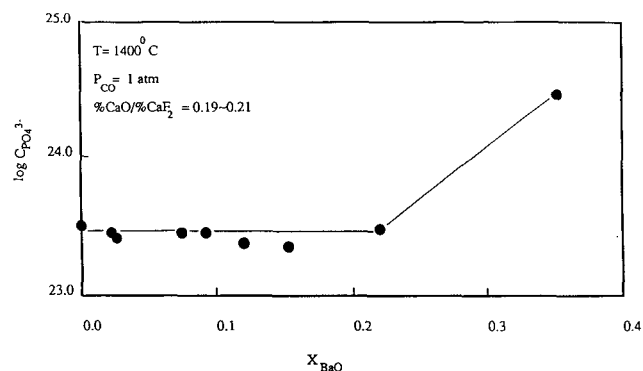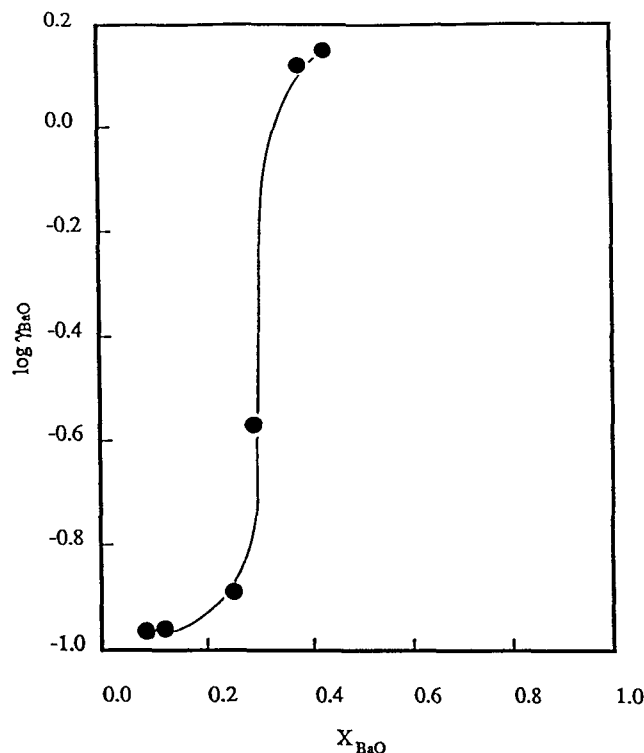
Fig. 8 — Activity of BaO in a lime-based flux for CaO/CaF$_2$ ~ 0.21 at 1400 °C.

can be used to dephosphorize stainless steel; however, a CaO-CaF$_2$ flux is not as efficient. The comparison of the phosphate capacity results of a BaO-BaF$_2$, CaO-CaF$_2$, BaO-CaO-CaF$_2$, and CaO-FeO-SiO$_2$ is shown in Figure 10. The ability of a BaO-BaF$_2$ flux to remove phosphorus is at least 10^7 greater than of CaO-FeO-SiO$_2$.

Fig. 7 — Effect of the addition of BaO in lime-based slags at 1400 °C under 1 CO atm.
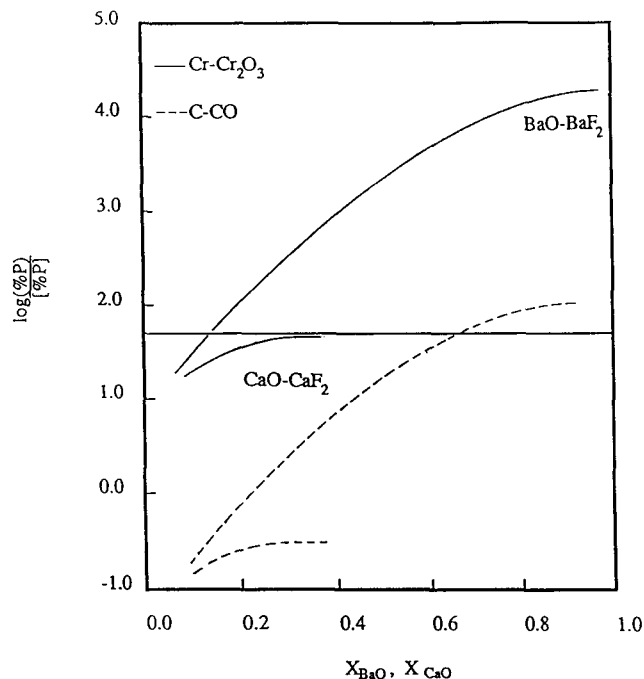
Fig. 9 — Calculated lines of L_P for BaO-BaF$_2$ and CaO-CaF$_2$ systems in equilibrium with Fe-C$_{sat}$-18 pct Cr at 1400 °C.
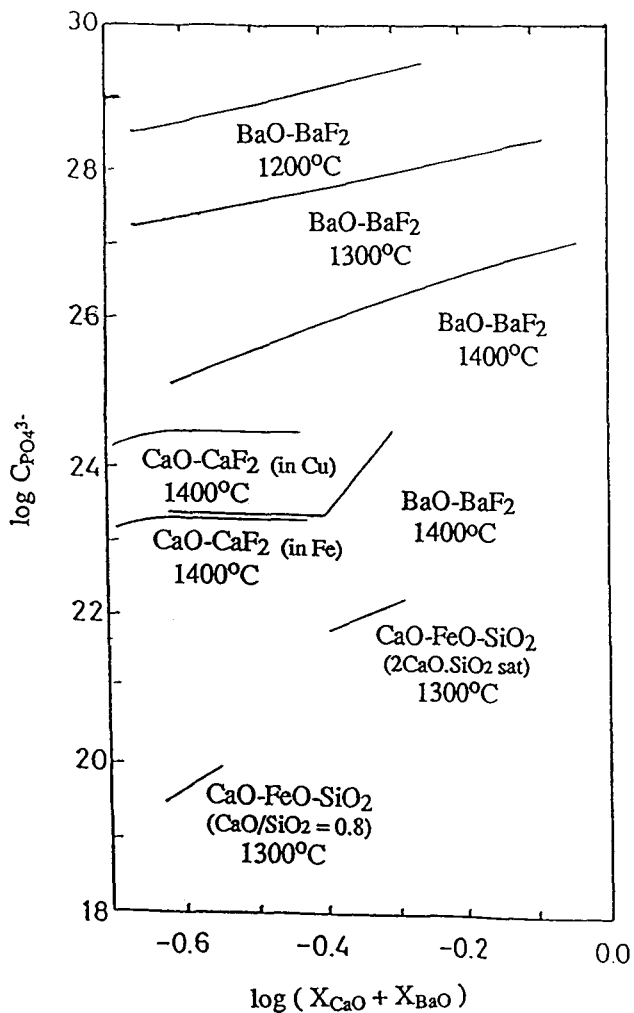
Fig. 10 — Phosphate capacities for various flux systems.

V. CONCLUSION

Phosphorus distribution ratios of $BaO-BaF_2$, $CaO-CaF_2$, and $BaO-CaO-CaF_2$ systems in equilibrium with copper or iron alloys and CO were measured. From this data, the phosphate capacity and $PO_{2.5}$ activity coefficient were determined. Also, the BaO activity coefficient in a $BaO-CaO-CaF_2$ system in equilibrium with silver alloy and CO was measured. By using this data, the following conclusions can be made:

1. $BaO-BaF_2$ fluxes are excellent dephosphorizers; *i.e.*, log $C_{PO_4^{3-}}$ ranges from 24 to 27 compared to 23 to 24 and 19 to 20 for a $CaO-CaF_2$ and $CaO-SiO_2$-FeO slag, respectively. It is possible to use this system to dephosphorize $Fe-C_{sat}$-Cr alloys.
2. The addition of BaO in a lime-based system was investigated, and no effect on the phosphate capacity was observed for small additions of BaO. However, for BaO > 40 pct, the phosphate capacity showed a significant increase.
3. The BaO activity in a $BaO-CaO-CaF_2$ system shows a negative derivation and very small value until $X_{BaO} \sim 0.3$. This is consistent with the constant value of $C_{PO_4^{3-}}$ for BaO < 40 pct.

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