

Thermodynamic Behavior of Phosphorus in CaO-CaF₂-SiO₂ and CaO-Na₂O-SiO₂ Systems

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In order to understand the thermodynamic behavior of phosphorus, such as the polymerization of phosphate ions in slag melts, the influence of phosphorus content of slag melts on the partition of phosphorus between slags and carbon-saturated iron or silver was investigated for the CaO-CaF₂-SiO₂ and CaO-Na₂O-SiO₂ systems at 1573 and 1473 K, respectively. The predominant species changes from PO₄³⁻ to P₂O₇⁴⁻ approximately at 2 mass pct of phosphorus in slag melts, which is defined as the critical phosphorus content, for the CaO-CaF₂-SiO₂ system which is doubly saturated with CaO and 3CaO · SiO₂. The critical phosphorus content was found to be about 1 mass pct for the CaO-CaF₂-SiO₂ melts saturated with 2CaO · SiO₂. On the other hand, in the case of the 20CaO-35Na₂O-45SiO₂ system, PO₄³⁻ is the predominant species until the slag becomes saturated with Ca₃(PO₄)₂. No effect of sulfur on the phosphorus partition ratio was observed for the CaO-CaF₂-SiO₂ system.

I. INTRODUCTION

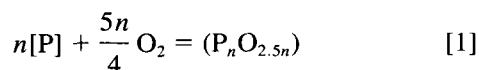
THE hot metal pretreatment process has been developed in order to remove phosphorus and sulfur simultaneously, and many fundamental studies on this process have been conducted. A variety of slags are used for this process, with CaO-based fluxes in especially wide use. The composition of slags after hot metal pretreatment is nearly saturated with CaO and 3CaO · SiO₂ in the CaO-CaF₂-SiO₂ ternary system. It is important to know the thermodynamic behavior of phosphorus in slags, particularly whether or not the phosphorus is polymerized in slags, because it leads to a different expression of the phosphorus partition between slag and metal, namely, (mass pct P)/[mass pct P] or (mass pct P)/[mass pct P]², depending on the species of phosphorus in slags.

In the present work, the effect of phosphorus content of CaO-based slags on the partition ratio of phosphorus, together with that of sulfur content, has been investigated using a chemical equilibrium technique.

II. EXPERIMENTAL

A. Principle of Measurement

The molecular formula for dephosphorization of metal is given by Eq. [1], in which n in (P_{*n*}O_{2.5*n*}) denotes the degree of polymerization and K_n is the equilibrium constant for Eq. [1].



$$K_n = \frac{a_{\text{P}_n\text{O}_{2.5n}}}{a_{\text{P}}^n \cdot \text{P}_{\text{O}_2}^{5n/4}} = \frac{f_{\text{P}_n\text{O}_{2.5n}} \cdot (\text{pct P}_n\text{O}_{2.5n})}{f_{\text{P}}^n \cdot [\text{pct P}]^n \cdot \text{P}_{\text{O}_2}^{5n/4}} \quad [2]$$

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where a_i and f_i are the activity and activity coefficient of component i relative to 1 mass pct, respectively, pct i is the mass pct of i , and P_i is the partial pressure of i .

Equation [2] can be rewritten in a logarithmic form as Eq. [3], where M_i is the molecular weight of i .

$$\log \frac{(\text{mass pct P})}{[\text{mass pct P}]} = \frac{n-1}{n} \log (\text{mass pct P}) + \frac{1}{n} \log \frac{f_{\text{P}}^n}{f_{\text{P}_n\text{O}_{2.5n}}} + \frac{1}{n} \log \left[K_n \cdot \text{P}_{\text{O}_2}^{5n/4} \cdot \frac{n \cdot M_{\text{P}}}{M_{\text{P}_n\text{O}_{2.5n}}} \right] \quad [3]$$

When n is equal to 1, Eq. [3] becomes Eq. [4], since the remaining terms of the right-hand side of Eq. [3] are constant at a fixed slag composition and temperature assuming Henrian behavior of the phosphorus both in metal and slag melts. It is reasonable to presume the dilute solution of P_{*n*}O_{2.5*n*} even when the phosphorus content of slags is relatively high, because the molar concentration of a species having a large molecular weight is rather small. Similarly, when n is equal to 2, Eq. [3] can be expressed by Eq. [5]:

$$\log \frac{(\text{mass pct P})}{[\text{mass pct P}]} = \text{constant} \quad [4]$$

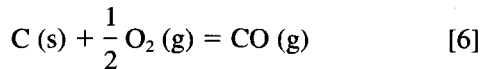
$$\log \frac{(\text{mass pct P})}{[\text{mass pct P}]} = \frac{1}{2} \log (\text{mass pct P}) + \text{constant} \quad [5]$$

In accordance with Eqs. [4] and [5], a plot of the partition ratio of phosphorus against the phosphorus content in a slag is to be linear on logarithmic scales.

B. Procedure

Two grams of slag and 2 g of Fe-P-C_{satd} alloy (or 4 g of Ag-P alloy) were equilibrated in a graphite crucible (ID: 8 mm; OD: 12 mm; height: 60 mm) under a flow of CO or CO-Ar mixture at temperatures from 1473 to

1623 K using a SiC electric resistance furnace. The composition of the CO-Ar mixture was controlled by calibrated constant-head capillary flow meters. The activity of carbon was fixed at unity by using a graphite crucible as a container. Since the partial pressure of CO varied from 5.1×10^4 Pa to 1.0×10^5 Pa, the partial pressure of oxygen ranged from 7.0×10^{-13} Pa to 2.8×10^{-12} Pa at 1573 K according to Eq. [6]:



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

After equilibrium was established, the crucible was quickly taken out and was cooled in a flushing argon. The samples were supplied for chemical analyses.

The holding time for the CaO-CaF₂-SiO₂ system was 18 hours, which had been determined to be enough for equilibration. For the CaO-Na₂O-SiO₂ system, Na₂O was lost due to continuous reduction by carbon so that an experiment was conducted for 1 or 2 hours, and in order to maintain a constant sodium potential in the system, a molten lead-sodium alloy was used as a sodium reservoir. In this case, the initial partition of phosphorus was chosen to be as close as possible to the expected equilibrium value. For most cases, the equilibrium was approached from both sides; namely, in more than two separate experiments, the initial partition ratio was chosen to be above and below the anticipated equilibrium value. The initial phosphorus contents of the slag and metal were adjusted to be nearly equal to their final content of the previous run for reaching equilibrium in a short time considering the slow establishment of the C-CO equilibrium.

The ratio of CaO, CaF₂, and SiO₂ was kept constant at CaO:CaF₂:SiO₂ = 64:23:13 for CaO and 3CaO·SiO₂ doubly saturated, at CaO:CaF₂:SiO₂ = 41:24:35 for 2CaO·SiO₂ saturation for the CaO-CaF₂-SiO₂ system, and at CaO:Na₂O:SiO₂ = 20:35:45 for the CaO-Na₂O-SiO₂ system. A small piece of CaO single crystal was dipped in the slag when the CaO saturation was required. Electrolytic iron was melted in a graphite crucible at the experimental temperature and P₂O₅ was added to prepare a Fe-P-C_{satd} alloy. Similarly, a silver-phosphorus alloy was made using metallic silver (99.9 mass pct) and P₂O₅. The slag samples were prepared by melting reagent grade Ca₃(PO₄)₂, SiO₂, CaF₂, or Na₂CO₃ and CaO which was obtained by calcination of CaCO₃. When the slag contained sulfur, reagent grade CaS was added. Lead and sodium were used for the lead-sodium alloy preparation.

Phosphorus in both slag and carbon-saturated iron was analyzed by molybdenum blue colorimetry and phosphorus in silver was determined by vanadium molybdate colorimetry. Sodium in slag and lead was determined by atomic absorption and sulfur by a LECO analyzer.

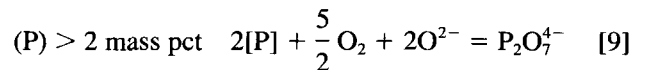
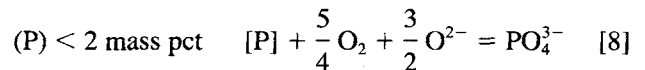
III. RESULTS AND DISCUSSION

A. The Effect of Phosphorus on Its Partition

The equilibrium partition ratios (L_P) of phosphorus in CaO-CaF₂-SiO₂ melts doubly saturated with CaO and 3CaO·SiO₂ to that in carbon-saturated iron are plotted against the phosphorus content of the slag at 1573 K in

Figure 1. The partition ratio is constant up to 2 mass pct of phosphorus in the slag, and it increases linearly beyond 2 mass pct. When the slag becomes saturated with Ca₃(PO₄)₂, the pellet of which was placed on the slag melt, the content of phosphorus in the slag reaches 12.8 mass pct, as marked by an open circle in Figure 1. The slope of the straight line representing the plots in Figure 1 is 0.57, which is in good agreement with 0.5, the expectation from Eq. [5]. Namely, the predominant species of phosphorus in the slag is likely to be a monomer, PO₄³⁻, up to 2 mass pct, and beyond 2 mass pct, it is to be a dimer, P₂O₇⁴⁻, for this slag composition. The phosphorus content in this slag is defined as the critical phosphorus content. This indicates that the phosphorus content does not influence the phosphorus partition at low phosphorus concentration in the slags, which is encountered in the normal operation of hot metal treatment.

In other words, the expression for the partition of phosphorus between the slag and metal should be (mass pct P)/[mass pct P] if the phosphorus content is below 2 mass pct, while (mass pct P)/[mass pct P]² is the more appropriate expression if it exceeds 2 mass pct in this slag, as described by Eqs. [8] and [9]:



According to these equations, (mass pct P)/[mass pct P] and (mass pct P)/[mass pct P]² are expected to be proportional to P_{O₂}^{5/4} and P_{O₂}^{5/2}, respectively. Figure 2 shows the relationships between the partitions of phosphorus and partial pressure of oxygen on logarithmic scales at 1573 K at two different levels of phosphorus content of the slag. The slopes of the lines in Figure 2 are 1.20 and 2.34 and are close to 1.25 and 2.5, as expected from Eqs. [8] and [9], respectively.

This critical phosphorus content depends on the slag

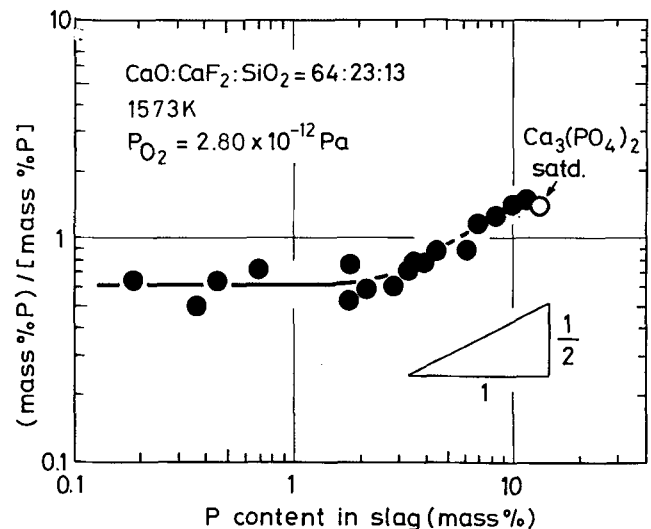


Fig. 1—Effect of the phosphorus content on the partition ratio of phosphorus between CaO-CaF₂-SiO₂ melts doubly saturated with CaO and 3CaO·SiO₂ and carbon-saturated iron at 1573 K.

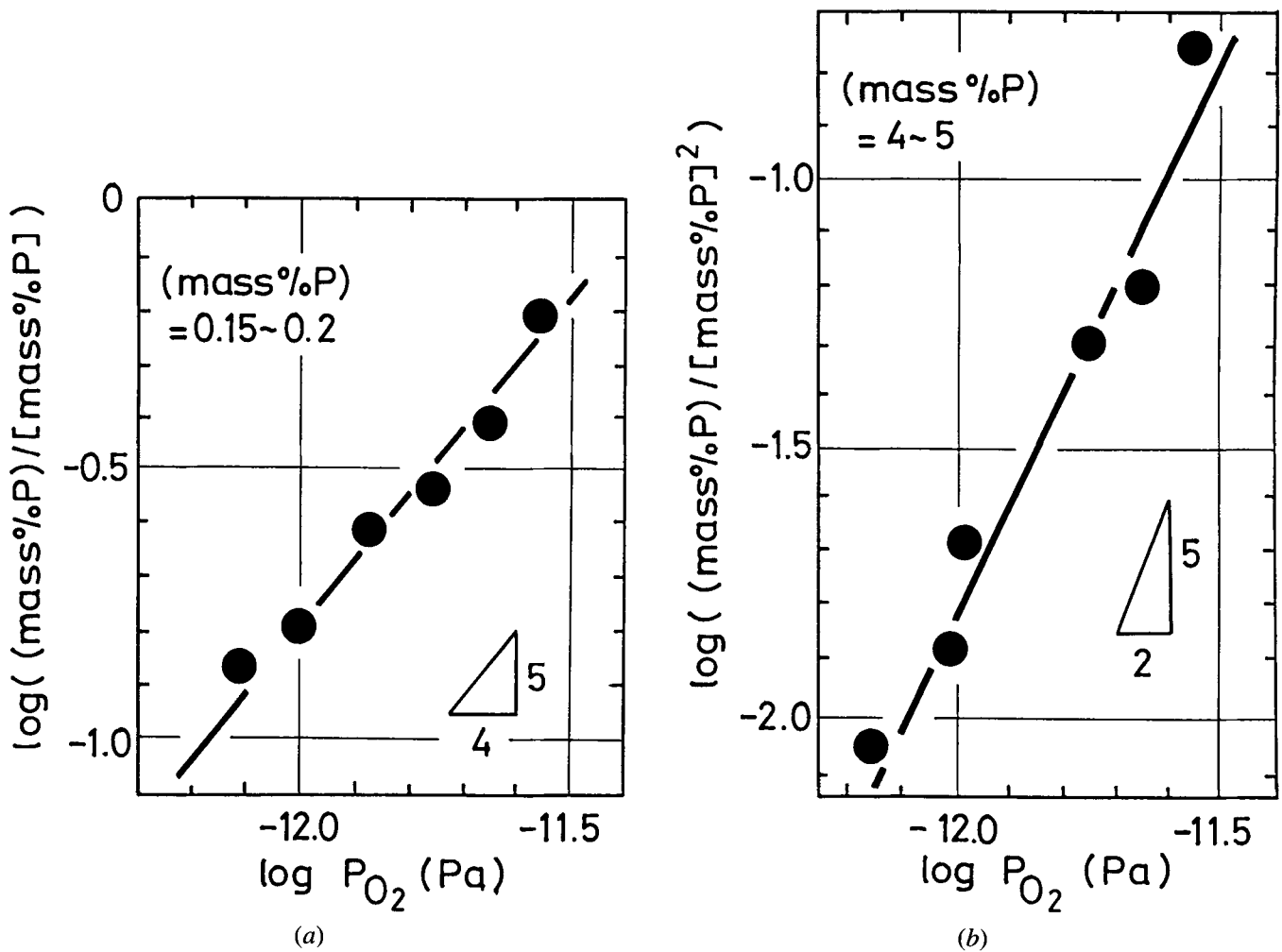
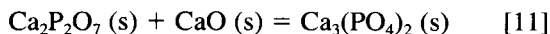


Fig. 2—(a) and (b) Dependence of the phosphorus partition ratio on oxygen partial pressure at different levels of phosphorus content for the same system as that in Fig. 1.

composition and temperature. The equilibrium partition ratio of phosphorus was measured for the doubly saturated slags between 1473 and 1623 K. As seen in Figure 3, the critical phosphorus content scarcely varies with increasing temperature.

The temperature dependence of the critical phosphorus content between the monomer and dimer may be discussed qualitatively by Eq. [11] as a simulation to Eq. [10].



$$\Delta G^\circ = -9000 - 82T \text{ J/mol}^{[1,2]} \quad [12]$$

Since Eq. [11] is slightly exothermic, it is expected that the critical phosphorus content decreases as temperature is raised, the $P_2O_7^{4-}$ becoming more predominant. However, this trend is not clearly observed in Figure 3, because the heat of reaction for Eq. [11] is very small.

Selin^[3] investigated the phosphorus species by a similar approach for the MgO-saturated CaO-SiO₂-Fe_xO system at 1873 K and found that PO_4^{3-} is predominant up to 2.5 mass pct phosphorus in slag. According to his findings, the content of $P_2O_7^{4-}$ continuously increases with increasing phosphorus content and approximately 35 pct of the total phosphorus exists as $P_2O_7^{4-}$ at 2 mass pct

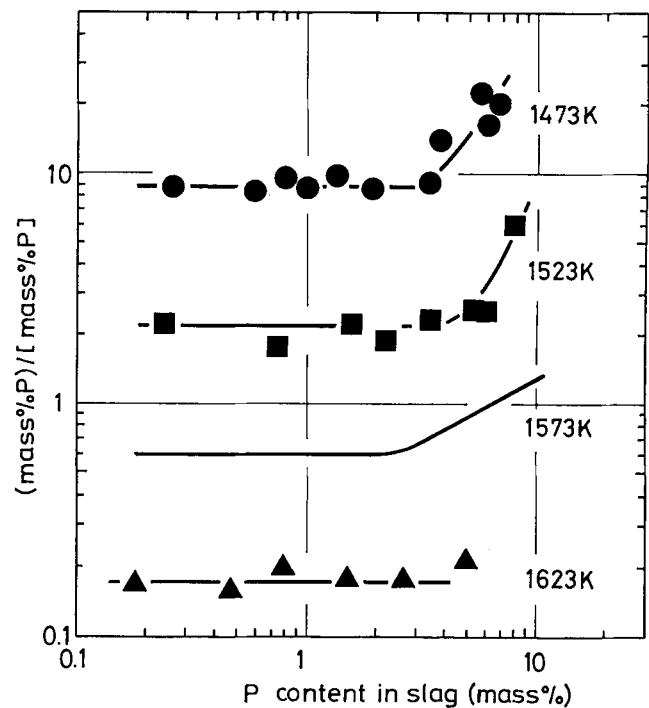


Fig. 3—Dependence of the partition ratio of phosphorus on temperature for the same system as that in Fig. 1.

phosphorus in slag. This agrees with the above prediction, in that the content of $P_2O_7^{4-}$ increases with rising temperature, considering that the temperature of Selin is higher than that in the present work. The experimental results for the $CaO-CaF_2-SiO_2$ melts saturated with $2CaO \cdot SiO_2$ and for the $CaO-Na_2O-SiO_2$ melts are shown in Figures 4 and 5.

For the slags saturated with $2CaO \cdot SiO_2$, which is more acidic than the former slag, a silver-phosphorus alloy was used because of the limitation of chemical analysis of phosphorus. The critical phosphorus content for this slag composition is 1 mass pct, which is lower than 2 mass pct for the slag with CaO and $3CaO \cdot SiO_2$ double saturation. This is obvious from Eq. [10], because $P_2O_7^{4-}$ is more predominant in a more acidic slag.

In the case of $CaO-Na_2O-SiO_2$ slags, the partition ratio of L_P was determined at 1473 K to minimize the loss of Na_2O . The constant L_P value was observed until the slag was saturated with $Ca_3(PO_4)_2$ at 4 mass pct.

Given the fact that L_P values for the $CaO-Na_2O-SiO_2$ system are higher than those for the $CaO-CaF_2-SiO_2$ sys-

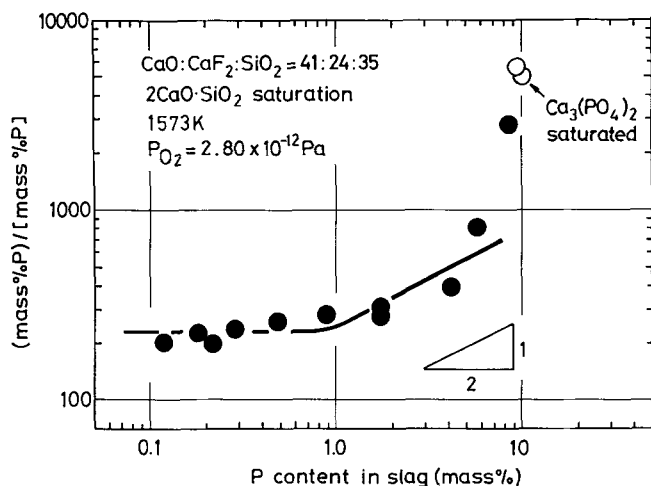


Fig. 4—Effect of the phosphorus content on the partition ratio of phosphorus between $CaO-CaF_2-SiO_2$ melts saturated with $2CaO \cdot SiO_2$ and silver at 1573 K.

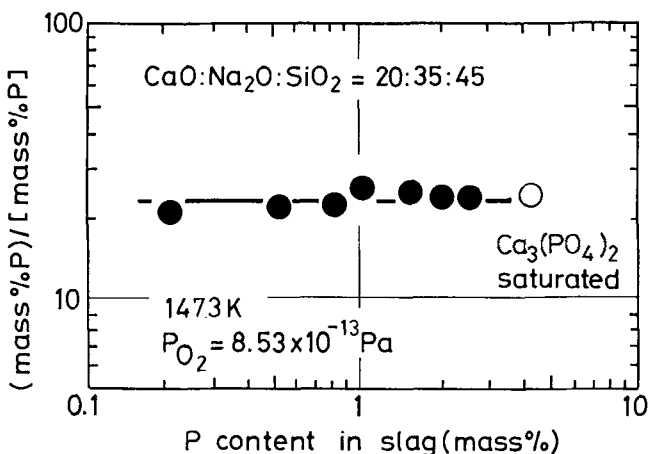


Fig. 5—Effect of the phosphorus content on the partition ratio of phosphorus between the $CaO-Na_2O-SiO_2$ melts and carbon-saturated iron at 1473 K.

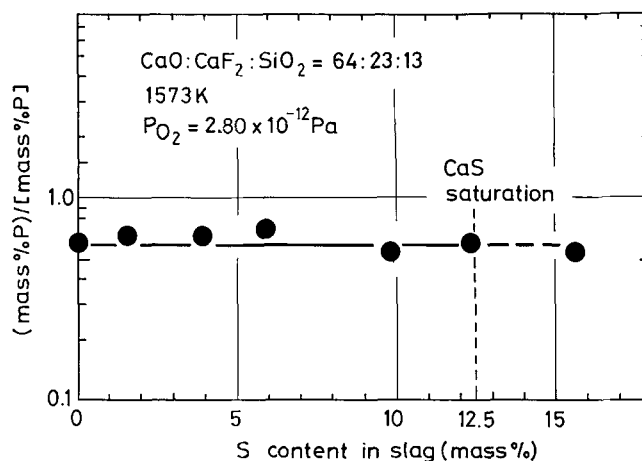


Fig. 6—Effect of the sulfur content on the partition ratio of phosphorus between $CaO-CaF_2-SiO_2$ melts doubly saturated with CaO and $3CaO \cdot SiO_2$ and carbon-saturated iron at 1573 K.

tem, the former is judged to be more basic than the latter. For this reason, a monomer is predominant for the $CaO-Na_2O-SiO_2$ system over the whole range of phosphorus content in the present study, according to Eq. [10].

B. The Effect of Sulfur on the Partition of Phosphorus

Since the slag systems studied in the present work are commonly used for simultaneous removal of phosphorus and sulfur from hot metal, the information on the effect of sulfur content on dephosphorization is valuable, particularly because the slag systems contain a large amount of sulfur if they are used for hot metal in a newly developed smelting reduction furnace.

Figure 6 shows (mass pct P)/[mass pct P] against (mass pct S) beyond 12.5 mass pct of a CaS solubility^[4] for $CaO-CaF_2-SiO_2$ melts with CaO and $3CaO \cdot SiO_2$ double saturation. Clearly, sulfur in the slag does not affect the phosphorus partition. This indicates that sulfur is not likely to take part in the polymerization of phosphorus in slag melts.

IV. CONCLUSIONS

The influence of the phosphorus content in CaO -based slags on phosphorus partition has been studied. It was found that a monomeric ion PO_4^{3-} is predominant up to 2 mass pct in a $CaO-CaF_2-SiO_2$ melt doubly saturated with CaO and $3CaO \cdot SiO_2$ at 1573 K. Consequently, (mass pct P)/[mass pct P] is preferred to (mass pct P)/[mass pct P]² for expressing the phosphorus partition in the hot metal pretreatment. It was also found that the sulfur in slags does not affect the phosphorus partition.

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