

# Phase Relationship of CaO-SiO<sub>2</sub>-FeO-5 mass pct P<sub>2</sub>O<sub>5</sub> System with Low Oxygen Partial Pressure at 1673 K (1400 °C)

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Dephosphorization by using multiphase flux could considerably decrease the consumption of CaO and prevent the addition of fluorite. However, the equilibrium phase relationship within this system, which is of significant importance for understanding the formation mechanism of multiphase flux, remains unclear. Thus, it is required to provide reliable phase diagrams of the basic slag system of multiphase flux. In this research, the phase relationship of the CaO-SiO<sub>2</sub>-FeO-5 mass pct P<sub>2</sub>O<sub>5</sub> system at 1673 K (1400 °C) with  $P_{O_2}$  of  $9.24 \times 10^{-11}$  atm has been studied by using the chemical equilibration method. It has been found that solid solution consists mainly of 2CaO·SiO<sub>2</sub>-3CaO·P<sub>2</sub>O<sub>5</sub>, but occasionally it contains 3CaO·SiO<sub>2</sub>. Liquidus saturated with solid solution shrinks toward the FeO corner compared with the isothermal at 1673 K (1400 °C) of the CaO-SiO<sub>2</sub>-FeO system equilibrated with metallic iron. Thermodynamically stable CaO-FeO phase is confirmed, which could promote the condensation of 3CaO·P<sub>2</sub>O<sub>5</sub> into the solid solution and increase the phosphorus partition ratio between the solid solution and molten slag. Based on the regular solution model, the effect of T.Fe and CaO content in the liquid phase on the phosphorus partition ratio between the solid solution and molten slag is discussed.

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## I. INTRODUCTION

IN the modern steel producing process, the dephosphorization process is often operated at the dicalcium silicate primary area for achieving a high basicity of molten flux. However, excessive CaO-CaF<sub>2</sub> injection for maintaining a high phosphate capability often leads to environmental issues and to difficulties in phosphorus recovery from the dephosphorization slag. Because of the forbiddance of adding a melting agent such as fluorite and the pursuit of an environment friendly producing idea, such multiphase flux must be considered innovatively.

Fix *et al.*<sup>[1]</sup> proved that the solid solution consisting of dicalcium silicate (2CaO·SiO<sub>2</sub>) and tricalcium phosphate (3CaO·P<sub>2</sub>O<sub>5</sub>) exists over a wide concentration range at hot metal pretreatment temperature. Ito *et al.*<sup>[2]</sup> discovered a strategy for less CaO consumption by using dicalcium silicate as a phosphorus fixtute instead of CaO is feasible, and a high phosphorus partition ratio between the 2CaO·SiO<sub>2</sub>-3CaO·P<sub>2</sub>O<sub>5</sub> solid solution and the liquid phase is achieved with increasing the T.Fe

content in the molten slag. All the preceding statements indicate that the dephosphorization process with less environment hamification and smaller slag generation could be realized by using multi phase flux.

For a more complete understanding of the multiphase flux system, Inoue and Suito<sup>[3-5]</sup> studied the transfer behavior and the partition of phosphorus between the solid solution and molten slag by adding dicalcium silicate and lime particles into a homogeneous CaO-SiO<sub>2</sub>-Fe<sub>1</sub>O molten slag at various temperatures. They explained the reaction mechanism of phosphorus in the CaO-SiO<sub>2</sub>-Fe<sub>1</sub>O system containing mesoscopic scale dicalcium silicate particles. Kitamura *et al.*<sup>[6]</sup> clarified the mass transfer of phosphorus between the 2CaO·SiO<sub>2</sub>-3CaO·P<sub>2</sub>O<sub>5</sub> solid solution and the 2CaO·SiO<sub>2</sub>-3CaO·P<sub>2</sub>O<sub>5</sub> saturated CaO-SiO<sub>2</sub>-Fe<sub>2</sub>O<sub>3</sub>-P<sub>2</sub>O<sub>5</sub> slag at 1673 K (1400 °C). At the same temperature, the phosphorus partition was studied by Shimauchi *et al.*<sup>[7]</sup> for the CaO-SiO<sub>2</sub>-Fe<sub>2</sub>O<sub>3</sub>-P<sub>2</sub>O<sub>5</sub> (6 to 18 mass pct) systems sometimes containing MgO or MnO. Also, the effects of MgO, MnO, and Al<sub>2</sub>O<sub>3</sub> on the phosphorus partition in various slag systems with FeO or Fe<sub>2</sub>O<sub>3</sub> as iron oxides have been discussed by Pahlevani *et al.*<sup>[8]</sup>

In contrast, to clarify the formation and reaction mechanism of phosphorus with the perspective of microscopic reactions in multiphase flux, first the dissolution and reaction mechanism of solid CaO with molten slag was clarified by Hamano *et al.*<sup>[9]</sup> and based on that, the reaction behavior of phosphorus in both the homogeneous and heterogeneous slag systems was explained by Yang *et al.*<sup>[10,11]</sup>

However, because the proper phase diagram such as the CaO-SiO<sub>2</sub>-FeO-P<sub>2</sub>O<sub>5</sub> system with various oxygen

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partial pressures under certain temperatures remains unclear, the equilibrium phase relationship between the solid solution and the liquid slag cannot be clarified. For this purpose, the isothermal of the CaO-SiO<sub>2</sub>-FeO-P<sub>2</sub>O<sub>5</sub> system with low oxygen partial pressure at hot metal pretreatment temperature, which could maintain high FeO activity, has been studied experimentally in the current work.

More specifically, the P<sub>2</sub>O<sub>5</sub> content was set to be constantly 5 mass pct before equilibration within all the experiments as considering the practical steelmaking operations, and the CO/CO<sub>2</sub> gas was introduced for achieving low oxygen partial pressure. The equilibrium slag phases were observed and analyzed by a scanning electron microscope (SEM) and energy disperse spectroscopy (EDS). For the sake of the discussion on the thermodynamic properties of each phase, a regular solution model was adopted for calculating the activity coefficients of the components in liquid phase.

## II. EXPERIMENTAL

### A. Sample Preparation

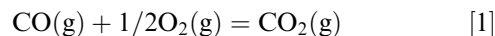
The CaO-SiO<sub>2</sub>-FeO-P<sub>2</sub>O<sub>5</sub> slag was made by mixing the reagent grade of SiO<sub>2</sub>, 3CaO·P<sub>2</sub>O<sub>5</sub>, and synthesized FeO, CaO according to Table I. Both the homogeneous and heterogeneous slags after premelting are concerned as the initial conditions before equilibrium referring to the phase diagram of the CaO-SiO<sub>2</sub>-FeO ternary system equilibrated with metallic iron,<sup>[12]</sup> as shown in Figure 1. The slag with a high CaO/SiO<sub>2</sub> ratio was paid special attention in this study. The method of making synthesized FeO and CaO are prepared as follows.

FeO: An equimolar mixture of reagent-grade Fe<sub>3</sub>O<sub>4</sub> and Fe powder was melted at 1723 K (1450 °C) for 1 hour with argon gas by using ferrous crucible, and then it was dumped on a steel plate with argon blowing for quenching. After that, the product was ground into fine particles (≤0.15 mm), and the unreacted Fe particles were separated magnetically.

CaO: The reagent grade of calcium carbonate was calcined in an alumina crucible for 24 hours at 1273 K (1000 °C) and then kept in a desiccator until it was cooled down slowly to room temperature.

### B. Procedure

A chemical equilibration technique was adopted in this research.<sup>[13–17]</sup> Approximately 0.1 g slag mixture was put into a platinum crucible (diameter: 5 mm × height: 5 mm) and hanged quickly into the hot zone of a vertical furnace with a recrystallized alumina tube. For premelting the slag, the crucible with the slag was kept for 1 to 3 hours at 1923 K (1650 °C) with an argon gas atmosphere. After melting, the temperature was decreased slowly by 10 K/min to 1673 K (1400 °C); during this period, the atmosphere inside the tube was switched from argon to CO/CO<sub>2</sub> gas to control the oxygen partial pressure. In this study, the oxygen partial pressure was chosen to be  $9.24 \times 10^{-11}$  atm for maintaining high FeO activities, and the volume ratio of the CO/CO<sub>2</sub> gas was set to be 5:1 according to Eq. [1].<sup>[18]</sup>



$$\Delta G^\circ = -281000 + 85.23T/\text{mol}$$

All the samples were preserved for 5 to 24 hours until equilibrium based on the slag compositions. For confirming the equilibration, the repetition by using the same slag preserved for different times was done as preexperiments, and then the preservation times for equilibrium were determined. Liquid nitrogen was adopted for achieving rapid quenching. After quenching, the samples were embedded in resin and polished for an analysis. SEM and EDS were used to observe the morphology and analyze the composition of each sample.

For obtaining more accurate phase compositions, the partition of elements in each phase was examined several times in different areas of the samples by a large scale

Table I. Original Slag Compositions (mass pct)

No.	FeO	SiO <sub>2</sub>	CaO	P <sub>2</sub> O <sub>5</sub>	CaO/SiO <sub>2</sub> (Mole Ratio)
1	31.36	26.51	37.13	5.00	1.50
2	45.60	17.23	32.17	5.00	2.00
3	52.25	11.40	31.35	5.00	2.95
4	51.54	8.63	34.83	5.00	4.32
5	45.83	9.86	39.31	5.00	4.27
6	38.58	9.74	46.68	5.00	5.13
7	37.81	7.97	49.22	5.00	6.62
8	45.60	3.80	45.60	5.00	12.9
9	55.10	0.00	39.90	5.00	—
10	19.00	35.15	40.85	5.00	1.25
11	47.50	17.81	29.69	5.00	1.79
12	28.50	20.48	46.02	5.00	2.41
13	38.00	19.00	38.00	5.00	2.14
14	33.25	16.03	45.72	5.00	3.06
15	54.33	2.67	38.00	5.00	15.3

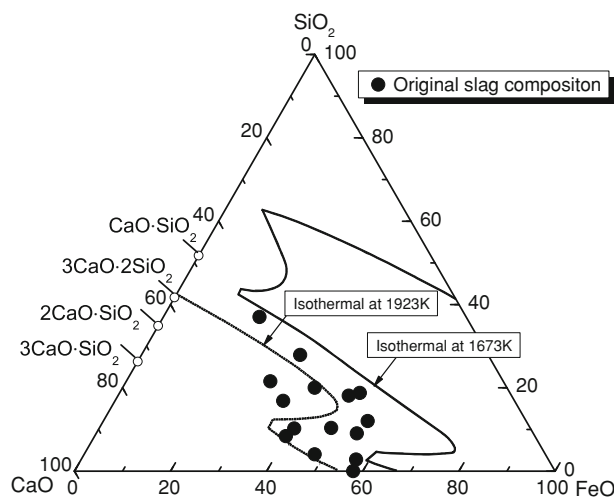


Fig. 1—Original slag compositions (mass pct).

**Table II. Compositions of Equilibrium Phases (mass pct)**

Equilibrium Status	No	Equilibrium Phases	SiO <sub>2</sub>	P <sub>2</sub> O <sub>5</sub>	CaO	FeO
Liquid phase and metallic iron equilibrated	1	liquid	32.2	5.0	45.1	17.7
	2	liquid	29.8	6.0	47.6	16.6
		metallic iron	4.2	0.4	7.7	87.7
	10	liquid	40.6	4.2	46.5	8.7
	11	liquid	32.1	4.8	40.9	22.2
Liquid phase, solid solution, and metallic iron equilibrated		metallic iron	10.7	0.4	11.5	77.4
	3	liquid	1.0	0.4	28.8	69.8
		solid	29.9	7.9	59.9	2.3
		metallic iron	0.2	0.3	9.2	90.3
	12	liquid	1.4	0.0	16.2	82.3
		solid	27.9	6.7	63.3	2.1
	13	liquid	9.3	0.2	18.5	72.0
		solid	27.7	7.9	60.3	4.1
		metallic iron	0.3	0.0	3.1	96.6
		CaO-FeO phase	1.5	0.0	43.2	55.4
CaO-FeO phase, solid solution, and liquid phase equilibrated		solid	22.5	12.0	63.9	1.6
		liquid	0.1	0.0	17.7	82.2
	5	CaO-FeO phase	2.5	0.0	44.4	53.0
		solid	23.5	12.3	63.0	1.2
		liquid	0.5	0.1	21.2	78.2
	6	CaO-FeO phase	2.6	0.6	44.2	52.6
		solid	23.2	9.5	64.4	2.9
		liquid	0.2	0.0	21.6	78.3
	7	CaO-FeO phase	2.4	1.7	43.9	51.9
		solid	21.1	10.6	64.0	4.3
		liquid	0.1	0.1	11.7	88.2
	8	CaO-FeO phase	2.7	2.3	44.3	50.7
		solid	17.8	15.9	62.2	4.2
		liquid	0.1	0.0	9.9	90.0
	14	CaO-FeO phase	2.4	0.9	45.8	50.9
	solid	26.0	6.7	64.3	2.9	
	liquid	0.2	0.0	9.0	90.7	
CaO-FeO phase, solid CaO, and liquid phase equilibrated	9	CaO-FeO phase	0.1	1.1	42.0	56.7
		CaO	0.2	29.6	58.6	11.7
		liquid	0.0	0.0	12.2	87.7
CaO-FeO phase, solid solution, and CaO equilibrated	15	CaO-FeO phase	0.7	0.7	46.0	52.7
		solid solution	17.4	20.3	59.7	2.7
		CaO	0.0	0.0	95.9	4.1

mapping analysis. The average concentration of each phase was determined through repeated analyses to conquer the roughness of EDS. Although electron probe microanalysis (EPMA) would be more accurate to measure the compositions of phases than EDS, EPMA was not applicable because of the smaller cross section of some solid phases than the EPMA spot size.

### III. RESULTS AND DISCUSSION

The average equilibrium compositions of each phase are shown in Table II, reordered by equilibrium status, and the typical morphology of each phase is shown in Figures 2(a) through (c). In Table II, the composition of the metallic iron of sample 12 has not been shown because the surface area of metallic iron is too small to analyze in this sample. Because the valence of ions cannot be detectable by EDS and also the Fe<sup>3+</sup>/Fe<sup>2+</sup> ratio could not be determined appropriately in current experimental conditions,<sup>[13]</sup> only the existence of Fe<sup>2+</sup> is

assumed for presentation purpose and discussion.<sup>[15,16]</sup> Because of the low P<sub>2</sub>O<sub>5</sub> (5 mass pct) concentration in the original slag, occasionally the P<sub>2</sub>O<sub>5</sub> content in the liquid phase was not detected. The decrease of FeO, which forms metallic iron, occurred, but sometimes the composition of this metallic iron phase is not easy to analyze because of its tiny superficial area, just as the morphology shown in Figure 2(c).

#### A. Condensation of 2CaO·SiO<sub>2</sub>-3CaO·P<sub>2</sub>O<sub>5</sub> Containing Solid Solution

The projection of the equilibrium concentration of the solid solution on the CaO-SiO<sub>2</sub>-P<sub>2</sub>O<sub>5</sub> system by using all raw data is shown in Figure 3. All the points are located close to the tie line between 2CaO·SiO<sub>2</sub> and 3CaO·P<sub>2</sub>O<sub>5</sub> with various 3CaO·P<sub>2</sub>O<sub>5</sub> content, but they switch a little toward the CaO corner. As neither pure 3CaO·SiO<sub>2</sub> nor 4CaO·P<sub>2</sub>O<sub>5</sub> was found, 3CaO·P<sub>2</sub>O<sub>5</sub> is the only stable form for phosphorus in solid solution under the current experimental conditions.

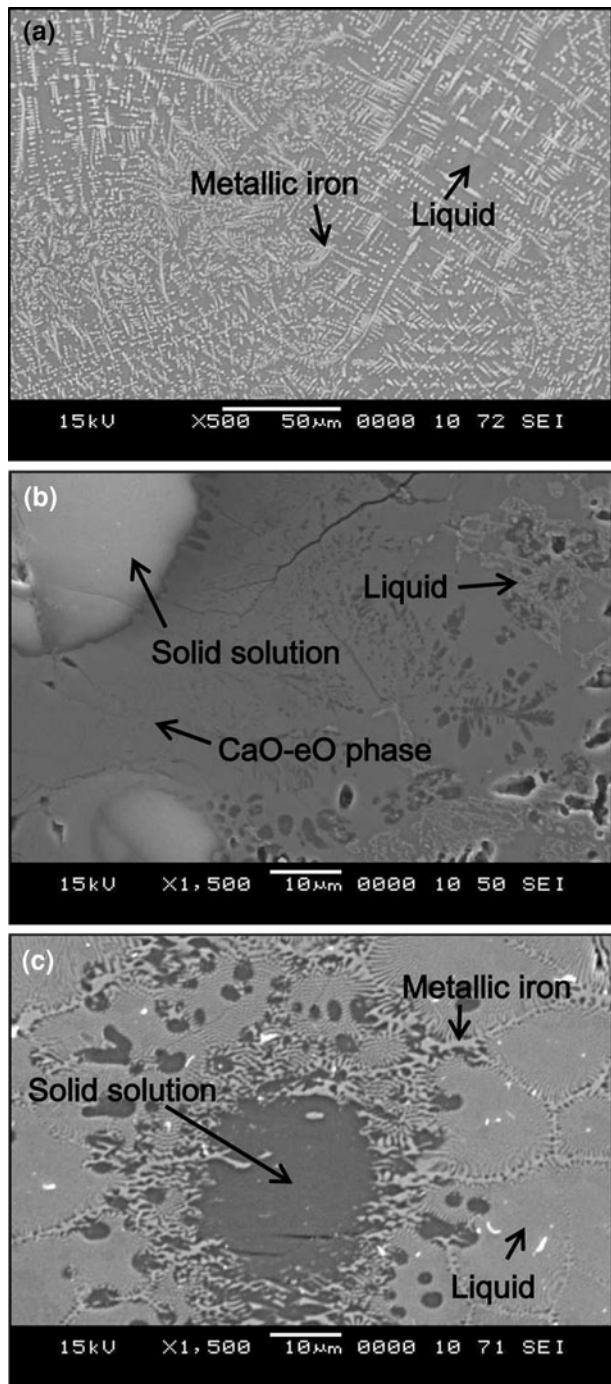


Fig. 2—Typical equilibrium morphologies: (a) liquid phase and reduced FeO equilibrated (No. 11), (b) liquid, solid solution and CaO-FeO phase equilibrated (No. 7), and (c) Liquid, metallic iron, and solid solution equilibrated (No. 13).

Figure 4 shows the relationship between the  $3\text{CaO}\cdot\text{P}_2\text{O}_5$  content and the  $\text{CaO}/\text{SiO}_2$  mole ratio (without  $3\text{CaO}\cdot\text{P}_2\text{O}_5$ ) in solid solution. It should be noticed that when solid CaO occurs in the solid phase, the  $\text{CaO}/\text{SiO}_2$  mole ratio in the solid solution should be much higher than the gray solid circle in Figure 3, but the amount of this individual solid CaO phase could not be converted together with the solid solution. According

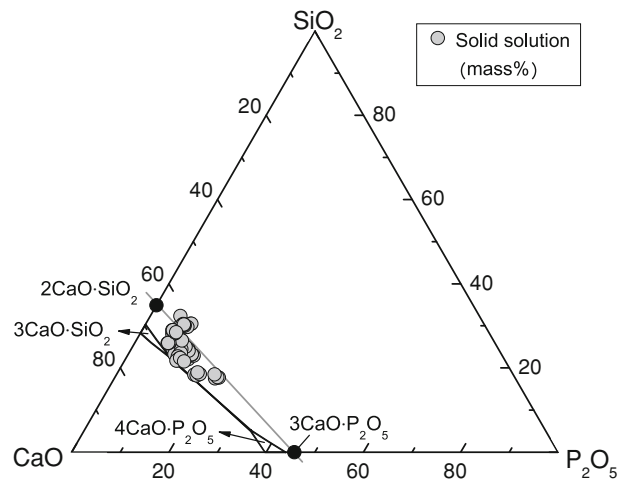


Fig. 3—Projection of equilibrium solid solution on the  $\text{CaO}\text{-SiO}_2\text{-P}_2\text{O}_5$  system (mass pct).

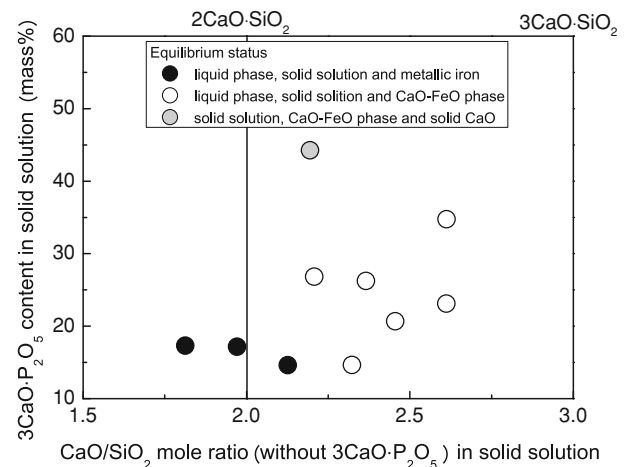


Fig. 4—Relationship among the  $\text{P}_2\text{O}_5$ , CaO, and  $\text{SiO}_2$  content in the solid solution.

to Figure 4, the content of  $3\text{CaO}\cdot\text{P}_2\text{O}_5$  increases with the  $\text{CaO}/\text{SiO}_2$  mole ratio (without  $3\text{CaO}\cdot\text{P}_2\text{O}_5$ ). Therefore, the points that are distributed between  $2\text{CaO}\cdot\text{SiO}_2$  and  $3\text{CaO}\cdot\text{SiO}_2$  prove that the solid solution responding to those parts is the mixture of  $2\text{CaO}\cdot\text{SiO}_2\text{-}3\text{CaO}\cdot\text{P}_2\text{O}_5$  and  $3\text{CaO}\cdot\text{SiO}_2$ . However, because the observed solid solution presents a homogeneous phase and an independent  $3\text{CaO}\cdot\text{SiO}_2$  phase could not be confirmed by Figure 3, the existence of  $3\text{CaO}\cdot\text{SiO}_2$  is ambiguous.

Concerned with the equilibrium status, the  $3\text{CaO}\cdot\text{P}_2\text{O}_5$  content in the solid solution remains at a lower level when the liquid phase, metallic iron, and solid solution coexist; then, it shifts to a moderate level when the CaO-FeO phase occurs, and the highest value appears in the case of the solid condensed CaO. It is also considered that the existence of the solid CaO could cut down the condensation amount of  $2\text{CaO}\cdot\text{SiO}_2$  in the  $2\text{CaO}\cdot\text{SiO}_2\text{-}3\text{CaO}\cdot\text{P}_2\text{O}_5$  based on the view of mass balance.

Because the T.Fe and CaO content in the liquid phase affect the partition ratio of phosphorus between the solid solution and liquid slag, somehow those two should have a certain relationship with the  $3\text{CaO}\cdot\text{P}_2\text{O}_5$  content in the solid solution. Figures 5 and 6 show the relationship between  $3\text{CaO}\cdot\text{P}_2\text{O}_5$  and CaO as well as the FeO content in the liquid phase. It is assumed that the liquid phase does not exist in the case of the CaO-FeO phase, solid solution, and solid CaO equilibration; therefore, the results of this equilibration have not been discussed in this article. The reason for this assumption will be discussed subsequently. The effects of the CaO and T.Fe contents in the liquid phase are not clear, but the appearance of the CaO-FeO phase promotes the condensation of  $3\text{CaO}\cdot\text{P}_2\text{O}_5$ .

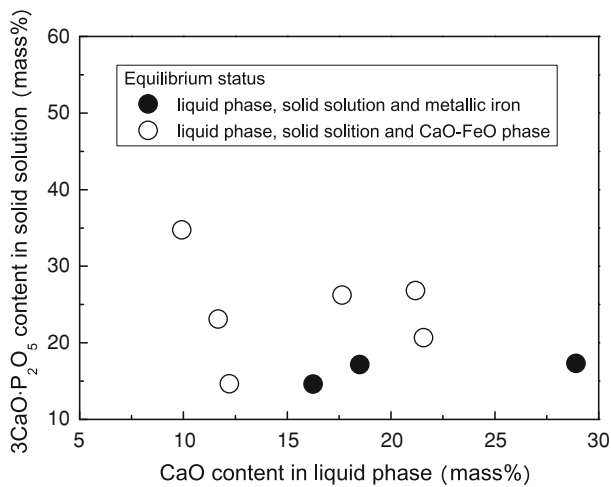


Fig. 5—Relationship between the CaO content in the liquid phase and the  $3\text{CaO}\cdot\text{P}_2\text{O}_5$  content in the solid solution.

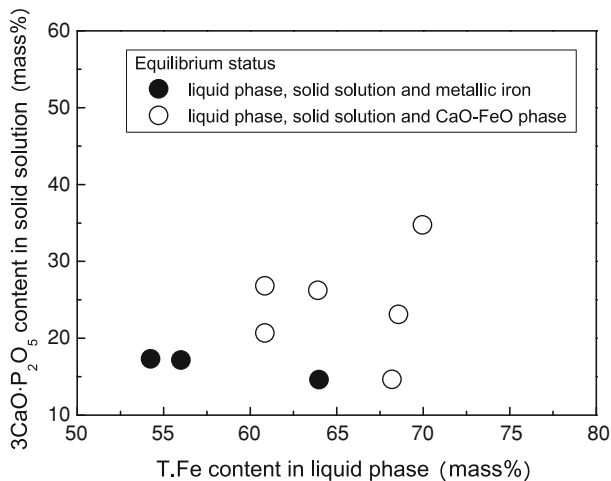
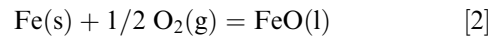


Fig. 6—Relationship between the T.Fe content in the liquid phase and the  $3\text{CaO}\cdot\text{P}_2\text{O}_5$  content in the solid solution.

### B. Phase Relationship of the CaO-SiO<sub>2</sub>-FeO-5 mass pct P<sub>2</sub>O<sub>5</sub> System at 1673 K (1400 °C) with P<sub>O<sub>2</sub></sub> of $9.24 \times 10^{-11}$ atm

By using the data obtained from the EDS analysis in Table II, the projections of each phase have been made by comparing with the 1673 K (1400 °C) isothermal of the CaO-SiO<sub>2</sub>-FeO system equilibrated with metallic iron as shown in Figure 7(a). The equilibrium phase sections are proposed in Figure 7(b), and a more distinct subregion of each phase can be observed in Figure 8. Even though the solid solution equilibrated with the liquid phase or other phases is marked as  $2\text{CaO}\cdot\text{SiO}_2$  because it has been projected on the ternary system as shown in Figure 8, this solid phase is still  $3\text{CaO}\cdot\text{P}_2\text{O}_5$ - $2\text{CaO}\cdot\text{SiO}_2$  containing a different P<sub>2</sub>O<sub>5</sub> content. Thus, the  $3\text{CaO}\cdot\text{P}_2\text{O}_5$ - $2\text{CaO}\cdot\text{SiO}_2$  is used in the legend of Figure 8.

In both Figures 7(a) and (b), the FeO-penetrated solid solution is located around the area between  $2\text{CaO}\cdot\text{SiO}_2$  and  $3\text{CaO}\cdot\text{SiO}_2$  because the CaO content in the solid solution is increased by the condensation of the  $3\text{CaO}\cdot\text{P}_2\text{O}_5$ - $2\text{CaO}\cdot\text{SiO}_2$  solid solution. An assumed liquid with a constant FeO activity, which is equilibrated with metallic iron only, is located at a moderated SiO<sub>2</sub> area plotted as a dotted line in Figures 7(b) and 8. In the preceding equilibrium status, the appearance of constant FeO activity is caused by the low oxygen partial pressure used in current experiments, and the reduction of FeO as mentioned is shown in Eq. [2].<sup>[18]</sup> The FeO activity of the liquid phase equilibrated with metallic iron at the current experimental conditions is calculated to be about 0.4.



$$\Delta G^\circ = -242300 + 46.07T \text{ J/mol}$$

The liquid surface moves toward the FeO corner compared with the isothermal at 1673 K (1400 °C) equilibrated with the metallic iron according to Figure 7(a). The formation of solid solution and the low oxygen partial pressure provide the driving force for this phenomenon.

Because Figures 7(b) and 8 are projections of the quaternary slag system on a ternary phase diagram, no liquidus could pass through the three-phase-equilibrated area. Thus, by the existence of the three phases in equilibrated zone 2 (liquid phase, metallic iron, and P<sub>2</sub>O<sub>5</sub> containing  $2\text{CaO}\cdot\text{SiO}_2$  solid solution coexist) in Figure 8, the liquidus is blocked. In addition, no liquid phase is saturated with the solid solution confirmed at a moderated SiO<sub>2</sub> content area. Similarly, zone 4 in Figure 8 becomes another blocker for the liquidus.

The CaO-FeO phase has been found thermodynamically stable with an assumed concentration range shown as a dashed line in Figures 7(b) and 8, which has been reported previously as a solid solution when solid CaO comes in contact with the molten slag.<sup>[4,19,20]</sup> However, because the existence of a low SiO<sub>2</sub> content inside the CaO-FeO phase cannot be ignored in the current work, it is uncertain whether this CaO-FeO phase is liquid or

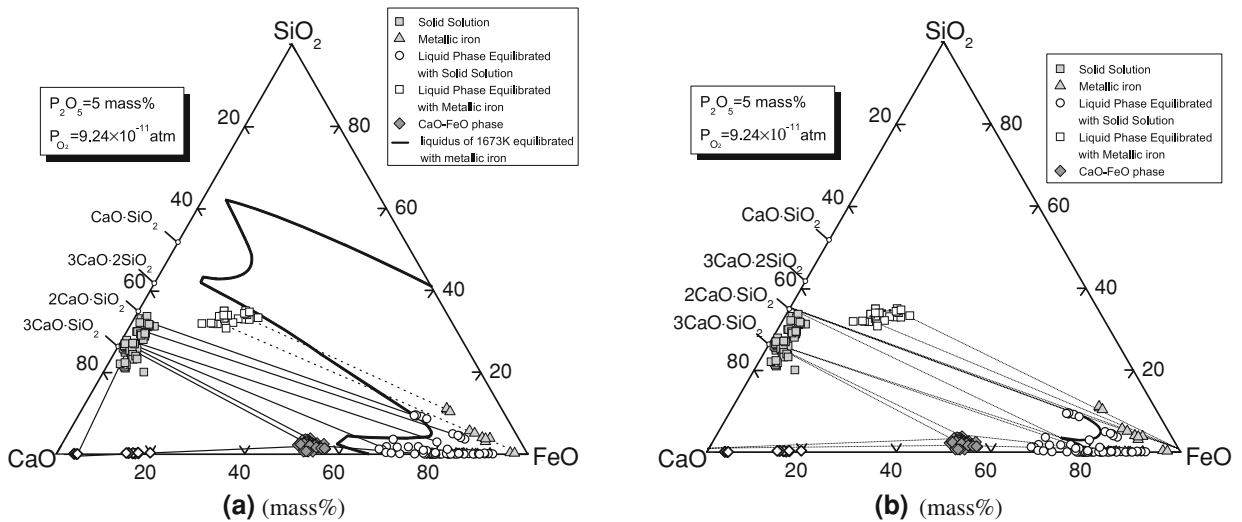


Fig. 7—Projections of the various phases observed in the CaO-SiO<sub>2</sub>-FeO-5 mass pct P<sub>2</sub>O<sub>5</sub> system on the CaO-SiO<sub>2</sub>-FeO ternary section at 1673 K (1400 °C) with P<sub>O<sub>2</sub></sub> of  $9.24 \times 10^{-11}$  atm: (a) direct comparison with 1673 K (1400 °C) isothermal equilibrated with metallic iron and (b) equilibrium phase sections.

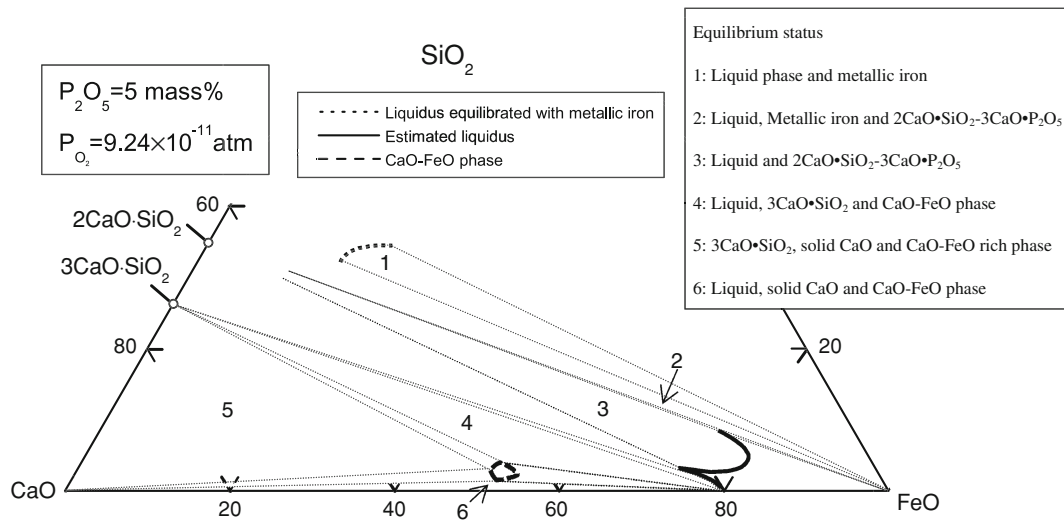


Fig. 8—Phase relationship of the CaO-SiO<sub>2</sub>-FeO-5 mass pct P<sub>2</sub>O<sub>5</sub> system at 1673 K (1400 °C) with P<sub>O<sub>2</sub></sub> of  $9.24 \times 10^{-11}$  atm (mass pct).

solid judged only by the EDS analysis, although the thermodynamic calculation by FactSage 6.2 (CRCT École Polytechnique, Montreal, Canada) and the isothermal section by Riboud<sup>[21]</sup> showed it could be a liquid phase with similar equilibrium conditions. Therefore, the CaO-FeO phase has to be regarded as an individual phase different from the liquid, which agrees with the assumption proposed in the last part of Section III-A. Anyway, the appearance of this phase could promote the 3CaO•P<sub>2</sub>O<sub>5</sub> condensation as discussed previously, and its effect on the phosphorus partition will be discussed in the next section.

### C. Partition Ratio of Phosphorus Between Solid Solution and Liquid Slag

The phosphorus partition ratio between the solid solution and liquid slag increases with the T.Fe content

in the liquid phase, as shown in Figure 9 by comparing these results with the work of Ito *et al.*<sup>[2]</sup> Although the linear relationship proposed by Ito *et al.* ends at the T.Fe content at approximately 60 mass pct, the current results fit its extension at a higher T.Fe content region. The highest value of the phosphorus partition ratio occurs when the CaO-FeO phase exists. Moreover, the CaO content in the liquid phase has the opposite effect with the T.Fe content as shown in Figure 10.

As is well known, the partition ratio of phosphorus between the solid solution and liquid phase is proportional to the activity coefficient of P<sub>2</sub>O<sub>5</sub> in the liquid phase but inverse to that in the solid solution. Consequently, the activity coefficients of P<sub>2</sub>O<sub>5</sub> in the liquid slag have been calculated by the regular solution model,<sup>[22]</sup> and the activity coefficient of phosphorus in the solid solution can be obtained. The calculated results are shown in Table III, in which only the results that

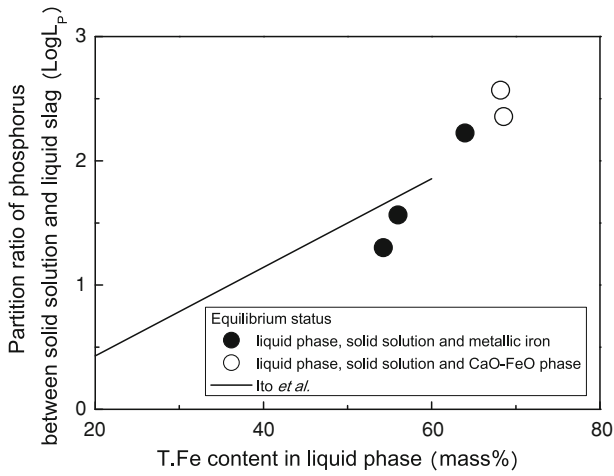


Fig. 9—Relationship between the phosphorus partition ratio and the T.Fe content in the liquid phase.

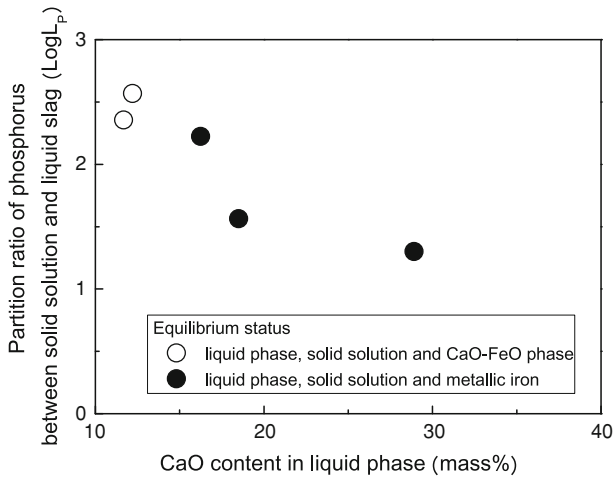


Fig. 10—Relationship between the phosphorus partition ratio and the CaO content in the liquid phase.

could be calculated by the partition ratio of phosphorus have been concerned.

It is believed that the larger T.Fe content, which means a larger FeO content in this work, could increase the solubility of CaO in the liquid phase. The liquid area occurs only at a high FeO content region according to the phase diagram for the CaO-FeO<sub>x</sub> system.<sup>[12]</sup> This will affect the activity coefficient of CaO in the liquid phase as shown in Figure 11. In the case of the liquid phase equilibrated with a solid solution only, the activity coefficient of CaO seems to decrease with the T.Fe content in the liquid phase, but the trend is obscure. With the increasing T.Fe content in the liquid phase, the depressed activity coefficient of CaO in the liquid phase leads to a higher dissolved amount of CaO because the molten slag is saturated with a CaO-containing solid solution in which the CaO activity is almost constant. Then, the liquid phase of a multiphase flux could have a high CaO/SiO<sub>2</sub> ratio, which is favorable not only for the condensation of solid solution but also for the

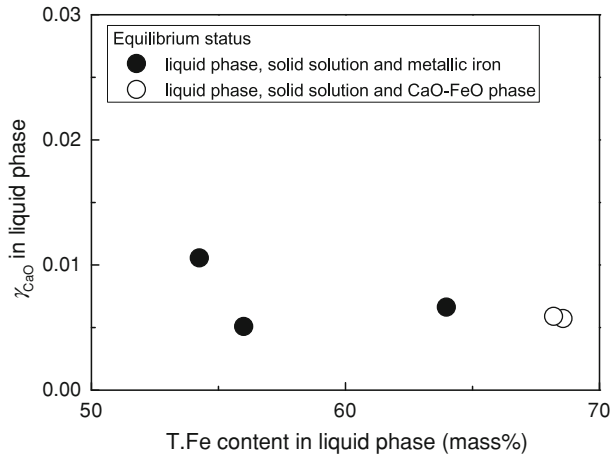


Fig. 11—Effect of the T.Fe content on the activity coefficient of CaO in liquid phase.

**Table III. Activity Coefficient of CaO in Liquid Phase, P<sub>2</sub>O<sub>5</sub>, in Both Solid and Liquid Phase Calculated by Regular Solution Model**

Equilibrium Status	No.	Equilibrium Phases	$\gamma_{CaO}$	$\gamma_{P_2O_5}$	
				In Liquid	In Solid Solution
Liquid phase, solid solution, and metallic iron	3	liquid	$1.1 \times 10^{-2}$	$3.5 \times 10^{-17}$	—
		solid	—	—	$14 \times 10^{-20}$
		metallic iron	—	—	—
CaO-FeO phase, solid solution, and liquid phase	12	liquid	$6.6 \times 10^{-3}$	$2.4 \times 10^{-15}$	—
		solid	—	—	$1.3 \times 10^{-20}$
	13	liquid	$5.1 \times 10^{-3}$	$1 \times 10^{-14}$	—
		solid	—	—	$1.2 \times 10^{-18}$
		metallic iron	—	—	—
	7	CaO-FeO phase	—	—	—
		solid	—	—	$2.7 \times 10^{-21}$
		liquid	$5.7 \times 10^{-3}$	$7.6 \times 10^{-15}$	—
	14	CaO-FeO phase	—	—	—
		solid	—	—	$5.4 \times 10^{-22}$
	liquid	$5.9 \times 10^{-3}$	$6.3 \times 10^{-15}$	—	

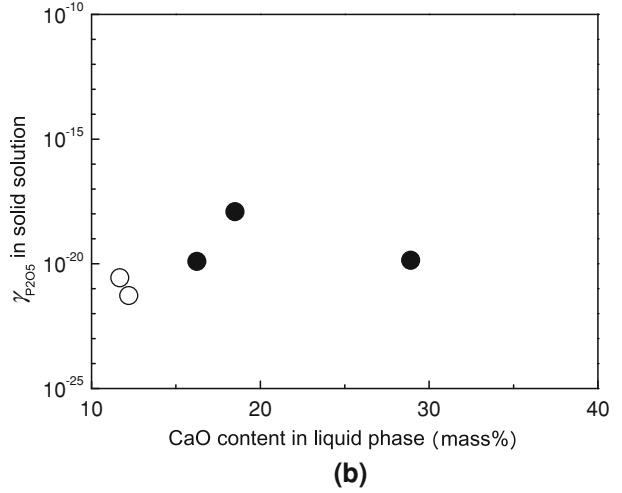
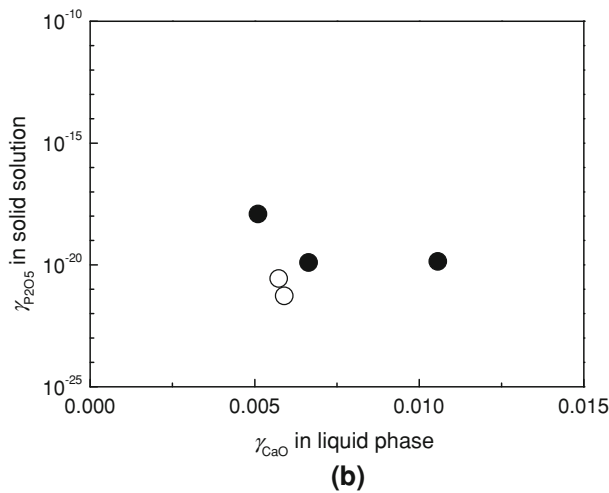
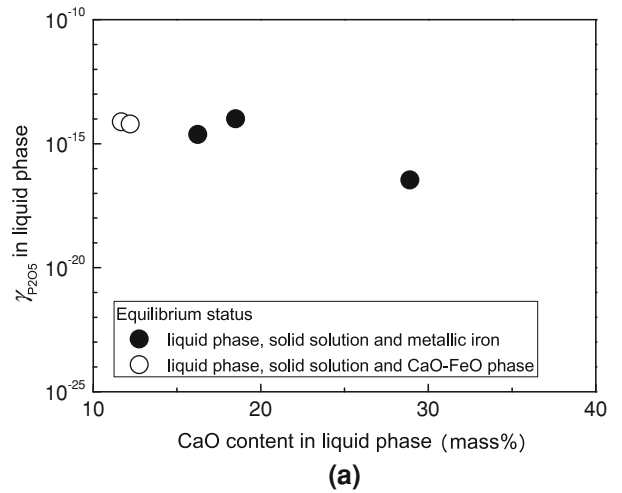
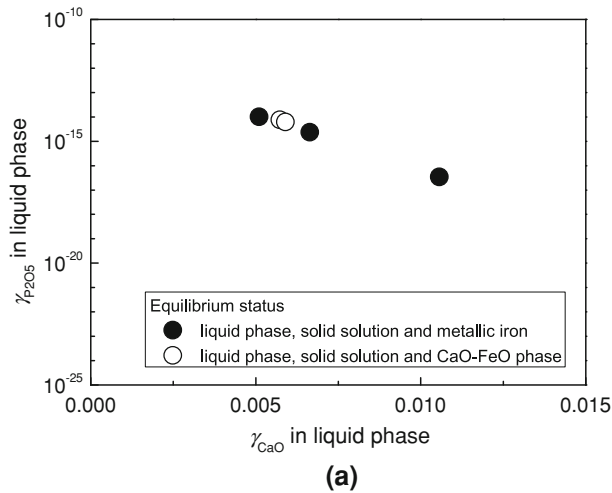


Fig. 12—Effect of activity coefficient of CaO on the activity coefficient of  $P_2O_5$ .

Fig. 13—Effect of the CaO content in the liquid phase on the activity coefficient of  $P_2O_5$ .

dephosphorization reaction that occurs at the slag-metal interface.

As shown in Figures 12(a) and 13(a), the activity coefficients of  $P_2O_5$  in the liquid phase decrease linearly with the increasing activity coefficient of CaO and CaO content in the liquid phase, whereas the alteration of the activity coefficient of  $P_2O_5$  in the solid solution reveals a similar result in Figures 12(b) and 13(b). Coupling of the preceding two tendencies leads to the decrease of the phosphorus partition ratio between the solid solution and the liquid phase. Considering the preceding discussion, the effect of the CaO content on the phosphorus partition ratio between the solid solution and the liquid phase as mentioned in Figure 10 could be explained.

In contrast, the activity coefficient of  $P_2O_5$  in the liquid phase increases with the increasing T.Fe content in the molten slag, whereas the activity coefficient of  $P_2O_5$  in the solid solution decreases as shown Figure 14. This finding indicates a clear tendency that the phosphorus partition ratio between the solid solution and liquid phase increases with the T.Fe content, as discussed in Figure 9.

The coexistence of the CaO-FeO phase and the solid solution would lead to a higher FeO content in the

liquid phase than the case of only the condensation of the solid solution. The precipitation of those phases would benefit the partition of phosphorus between the solid solution and the liquid, and thus, the reason for that the highest value of phosphorus partition ratio is observed when the CaO-FeO phase exists as mentioned could be explained.

#### IV. CONCLUSIONS

By using the chemical equilibration method, the phase relationship of the CaO-SiO<sub>2</sub>-FeO-5 mass pct  $P_2O_5$  system at 1673 K (1400 °C) with  $P_{O_2}$  of  $9.24 \times 10^{-11}$  atm has been studied. The following results were obtained:

1. The solid solution is confirmed to be  $2CaO \cdot SiO_2 - 3CaO \cdot P_2O_5$ , which occasionally contains  $3CaO \cdot SiO_2$ .
2. The liquid area shrinks toward the FeO corner compared with the isothermal at 1673 K (1400 °C) of the CaO-SiO<sub>2</sub>-FeO system equilibrated with metallic iron. The liquidus equilibrated with metallic iron is proposed, which has a constant FeO activity.



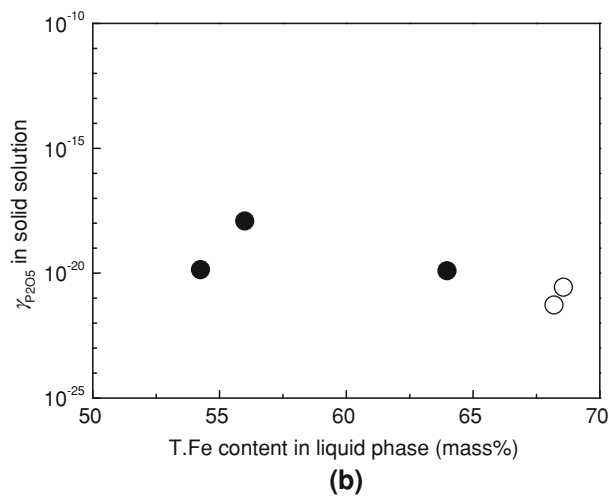
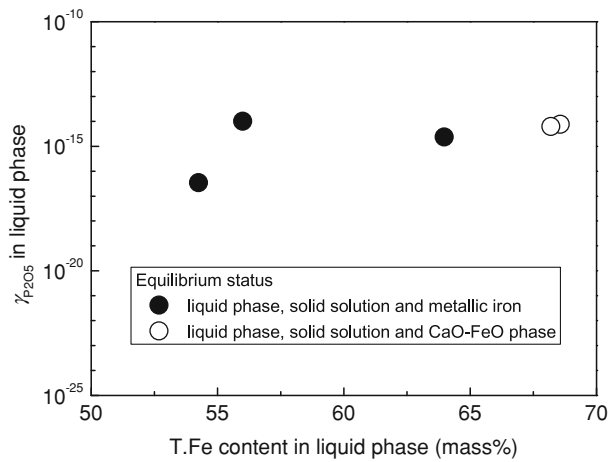


Fig. 14—Effect of the T.Fe content in the liquid phase on the activity coefficient of  $P_2O_5$ .

- The thermodynamically stable CaO-FeO phase is confirmed and the condensation of  $3CaO \cdot P_2O_5$  into the solid solution is promoted; in addition, the phosphorus partition ratio between the solid solution and the liquid phase increased.
- The phosphorus partition ratio between the solid solution and the liquid phase increases with the

increasing T.Fe content in the liquid phase; in contrast, the CaO content in the liquid phase shows the opposite effect.

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