

Article

# **Distribution Behavior of Phosphorus in** 2CaO·SiO<sub>2</sub>-3CaO·P<sub>2</sub>O<sub>5</sub> Solid Solution Phase and Liquid Slag Phase

Bin Zhu<sup>1,2</sup>, Mingmei Zhu<sup>1,3,\*</sup>, Jie Luo<sup>1</sup>, Xiaofei Dou<sup>1</sup>, Yu Wang<sup>1,3</sup>, Haijun Jiang<sup>2</sup> and Bing Xie<sup>1,3</sup>

- 1 College of Materials Science and Engineering, Chongqing University, Chongqing 400044, China; zhubincq@foxmail.com (B.Z.); 201909131200@cqu.edu.cn (J.L.); dxf09381@126.com (X.D.); wangyu@cqu.edu.cn (Y.W.); bingxie@cqu.edu.cn (B.X.)
- 2 Chongqing Iron and Steel Research Institute Co. LTD, Chongqing 400084, China; 13627687756@139.com
- 3 Chongqing Key Laboratory of Vanadium-Titanium Metallurgy and New Materials, Chongqing University, Chongqing 400044, China
- Correspondence: zhumingmei@cqu.edu.cn; Tel.: +86-23-6512-7306

Received: 28 July 2020; Accepted: 14 August 2020; Published: 17 August 2020



Abstract: In this paper, the CaO-SiO<sub>2</sub>-Fe $_t$ O-P<sub>2</sub>O<sub>5</sub> dephosphorization slag system during the premier and middle stage of the converter process was studied, the effect of slag composition on the distribution ratio and activity coefficient of P in the  $n \cdot 2CaO \cdot SiO_2 - 3CaO \cdot P_2O_5$  (recorded as  $nC_2S - C_3P$ ) solid solution phase and liquid slag phase in the slag system was studied used by the high temperature experiment in laboratory, the theoretical calculation of thermodynamics, and the scanning electron microscope and the energy dispersive spectrometer (recorded as SEM/EDS). The research results show that when the FeO content in the liquid slag increases from 32.21% to 50.31%, the distribution ratio of phosphorus (recorded as  $L_P$ ) in the liquid slag phase increases by 3.34 times. When the binary basicity in the liquid slag increases from 1.08 to 1.64, the  $L_P$  in the liquid slag phase decreases by 94.21%. In the initial slag, when the binary basicity increases from 2.0 to 3.5, the  $L_P$  decreases by 70.07%. When FeO content increases from 38.00% to 51.92%, the  $L_P$  increases by 6.15 times. When P<sub>2</sub>O<sub>5</sub> content increases from 3.00% to 9.00%, the  $L_P$  increased by 10.67 times. When the FeO content in the liquid slag increases from 32.21% to 50.31%, the activity coefficient of  $P_2O_5$  in the liquid slag phase (recorded as  $\gamma_{P_2O_5(L)}$ ) increases by 54.33 times. When the binary basicity in the liquid slag increases from 1.08 to 1.64,  $\gamma_{P_2O_5(L)}$  decreases by 99.38%. When the binary basicity increases from 2.0 to 3.5, the activity coefficient of  $P_2O_5$  in the solid solution phase (recorded as  $\gamma_{P_2O_5(SS)}$ ) in the solid solution phase decreases by 98.85%. When P<sub>2</sub>O<sub>5</sub> content increases from 3.00% to 9.00%,  $\gamma_{P_2O_5(SS)}$ increases by 1.14 times. When the binary basicity decreases from 3.5 to 2.0, *n* decreases from 0.438 to 0.404. When the FeO content increases from 38.00% to 51.92%, *n* decreases from 0.477 to 0.319. When the  $P_2O_5$  content increases from 3.00% to 9.00%, *n* decreases from 0.432 to 0.164. The decrease of binary basicity and the increase of FeO and  $P_2O_5$  content in the initial slag can reduce the value of *n* and enrich more phosphorus in the solid solution phase. The results can not only provide a theoretical basis for industrial production, but also lay a theoretical foundation for finding more effective dephosphorization methods.

Keywords: CaO-SiO<sub>2</sub>-Fe<sub>t</sub>O-P<sub>2</sub>O<sub>5</sub> slag system; distribution ratio of phosphorus; dephosphorization; n·2CaO·SiO<sub>2</sub>-3CaO·P<sub>2</sub>O<sub>5</sub> solid solution



#### 1. Introduction

Dephosphorization is one of the main tasks in the steelmaking process, and it is also a significant problem for integrated steelmakers. Phosphorus removal is required because phosphorus has a deleterious effect on the mechanical properties of steel. With the gradual depletion of high grade and low phosphorus iron ores resources in the world, the proportion of high phosphorus iron ore is increasing. Therefore, the requirements for the dephosphorization capacity of steelmaking slag system will be more stringent. Many studies have studied the distribution behavior of phosphorus between molten slag and molten steel [1–8], but the research on the distribution behavior of phosphorus between the solid solution phase and the liquid slag phase is not thorough enough.

The dephosphorization slag system of the converter steelmaking process mainly consists of the CaO-SiO<sub>2</sub>-Fe<sub>t</sub>O-P<sub>2</sub>O<sub>5</sub> slag system, which usually exists in the state of a solid solution within the composition range of  $2CaO \cdot SiO_2$  (recorded as  $C_2S$ ) saturation in the slag system [9]. Fix et al. [10] plotted the pseudo binary phase diagram of the  $2CaO \cdot SiO_2 - 3CaO \cdot P_2O_5$  (recorded as  $C_2S - C_3P$ ) solid solution. The phase diagram shows that C<sub>2</sub>S and 3CaO·P<sub>2</sub>O<sub>5</sub> (recorded as C<sub>3</sub>P) can form a stable solid solution in any composition range during the temperature range of the steelmaking process. Some studies [11–15] showed that phosphorus in the CaO-SiO<sub>2</sub>-Fe<sub>t</sub>O-P<sub>2</sub>O<sub>5</sub> slag system mainly exists in the form of the  $nC_2S-C_3P$  solid solution, which is irregular granular or a long strip in slag, while almost no phosphorus or a small amount of phosphorus is in other phases. When the composition and temperature of the slag are in a certain range, phosphorus will exist in the independent form of  $C_{3}P$  [14]. The pseudo binary phase diagram of  $C_{2}S-C_{3}P$  plotted by Fix et al. [10] and the research results of Kitamura et al. [16] showed that phosphorus is very stable in the  $C_2S-C_3P$  solid solution in the steelmaking temperature range. All of the above results indicate that during the steelmaking process of the converter, phosphorus can be migrated as much as possible by changing the composition of slag and be stably present in the solid solution, which is beneficial to reduce the concentration of phosphorus in the liquid slag phase, improve the driving force of mass transfer of phosphorus from molten iron to the liquid slag phase, and improve the dephosphorization efficiency of converter steelmaking. Therefore, the  $C_2S-C_3P$  solid solution plays a key role in the dephosphorization process of converter steelmaking. It is necessary to study the influence of slag composition on the distribution ratio of phosphorus between the  $nC_2S-C_3P$  solid solution and liquid slag.

Some researchers have studied the effect of  $C_2S$  in the dephosphorization slag system on dephosphorization efficiency. Suito et al. [17] found that according to the experimental study, the dephosphorization rate would be greatly improved when the slag system contains more solid lime particles and dicalcium silicate particles. Shimauchi et al. [14] studied the effect of slag composition on the distribution ratio of phosphorus between the solid solution phase and the liquid slag. The results showed that the higher the content of T. Fe in slag, the higher the content of phosphorus in the solid solution. Son et al. [18] analyzed the effect of binary basicity and FeO content of slag on the precipitation of calcium silicate in situ by hot thermocouple technology (HTT). The results showed that the distribution ratio of phosphorus increased significantly when there was solid solution precipitation. In the current research work, there is little research on the distribution behavior of phosphorus in the solid and liquid phases of  $nC_2S-C_3P$  in the dephosphorization slag system of the converter. Therefore, it is necessary to systematically study the influence of slag composition on the distribution behavior of phosphorus in the solid and liquid phases.

In this paper, the dephosphorization slag system of CaO-SiO<sub>2</sub>-Fe<sub>t</sub>O-P<sub>2</sub>O<sub>5</sub> during the converter steelmaking process is taken as the research object. By means of a high temperature experiment and SEM/EDS detection, the distribution ratio of the slag composition to phosphorus in the  $nC_2S-C_3P$  solid solution phase and liquid slag phase is systematically studied. The influence of slag composition on the activity coefficient of phosphorus in the solid solution phase and liquid slag phase is studied by means of thermodynamics theory analysis. The research results can not only provide a theoretical basis for the establishment of the slagging system in the converter steelmaking process, but also lay a theoretical foundation for finding more effective dephosphorization methods.

#### 2. Experiment

The dephosphorization slag system in the premier and middle stages of converter steelmaking process has the characteristics of high basicity and strong oxidation. At this time, the temperature in the converter is relatively low, and the dephosphorization capacity of the slag system is also high under the condition that the slag has good fluidity. According to the characteristics of the slag system studied, the slag was prepared in the laboratory according to the composition shown in Table 1. The binary basicity of the slag system studied is in the range of 2.0–3.5, the content of FeO is 38.00–51.98%, and the content of  $P_2O_5$  is in the range of 3.00–9.00%. According to the position in the liquidus diagram of the CaO-FeO-SiO<sub>2</sub> ternary system, the slag compositions are all in the  $C_2S$  primary crystal zone to ensure that the calcium silicate precipitated from the slag during cooling process are all  $C_2S$ , and the compositions are basically between 1400 and 1500 °C liquidus, as shown in Figure 1. High temperature silicon molybdenum furnace was used in the experiment, and the temperature control precision was ±2 °C. In the experiment, the slag samples were placed in the MgO crucible, and the MgO crucible was covered with graphite crucible. During the experiment, argon gas was introduced as protective gas. The temperature control curve during the experiment is shown in Figure 2. When the temperature rises to 1500  $^{\circ}$ C, the slag is kept for 1–2 h to make the slag melt evenly; in order to precipitate more phosphorus rich phases, it is reduced to 1400 °C at a slow rate of 1.67 K/min and kept for 1 h; when the precipitates and liquid phase are uniform, take out the crucible immediately and quickly cool it with liquid nitrogen. The slag samples were taken out, ground, and polished with sandpaper after drying. Then, the samples were detected and analyzed by SEM/EDS (Carl Zeiss AG, Oberkochen, Germany) after spraying gold. When analyzing the content of each composition in each phase by EDS (Carl Zeiss AG, Oberkochen, Germany), the method of taking the average value for many times is adopted to reduce the error caused by EDS detection as far as possible. The experiment did not achieve the equilibrium state, and the experimental data obtained based on the high temperature experiment in this article are all the experimental results of the non-equilibrium state.



**Figure 1.** Position of the slag composition in the liquidus diagram of the CaO-FeO-SiO<sub>2</sub> ternary system at 1400 °C and 1500 °C.

No.	(%CaO)/(%SiO <sub>2</sub> )	CaO	SiO <sub>2</sub>	FeO	$P_2O_5$
1	2.0	31.67	15.83	47.50	5.00
2	2.5	33.93	13.57	47.50	5.00
3	3.0	35.63	11.88	47.50	5.00
4	3.5	36.94	10.56	47.50	5.00
5	2.0	38.00	19.00	38.00	5.00
6	2.0	34.83	17.42	42.75	5.00
7	2.0	28.68	14.34	51.98	5.00
8	2.0	33.00	16.50	47.50	3.00
9	2.0	30.33	15.17	47.50	7.00
10	2.0	29.00	14.50	47.50	9.00

Table 1. Composition of the slag samples/wt %.



Figure 2. Temperature control curve.

## 3. Results

## 3.1. Definition of the Phosphorus Distribution Ratio and Phosphorus Activity Coefficient

The distribution ratio of phosphorus between the solid solution phase and the liquid slag phase,  $L_P$ , can characterize the dephosphorization effect of the slag systems. The larger the  $L_P$ , the more phosphorus in the solid solution phase; conversely, the more phosphorus in the liquid slag phase. Since the phosphorus in the liquid slag phase may return to the molten steel in the middle and final stage of converter process, the less phosphorus in the liquid slag phase, that is to say, the greater  $L_P$ , the better dephosphorization effect of slag systems.

When the  $L_P$  of the slag sample is analyzed by SEM,  $L_P$  is defined as shown in Equation (1).

$$L_P = A_{SS}(\% P_2 O_5)_{SS} / A_L(\% P_2 O_5)_L \tag{1}$$

Among them, A represents the area fraction of solid solution phase or liquid slag phase, %, and the area fraction A is calculated by Image Pro Plus software; the subscripts SS and L represent the solid solution phase and liquid slag phase of  $nC_2S-C_3P$  respectively, the same below; (%P<sub>2</sub>O<sub>5</sub>) represents the mass percentage content of P<sub>2</sub>O<sub>5</sub>.

Metals 2020, 10, 1103

When  $L_P$  is defined by the thermodynamic analysis, based on the regular solution model [18], the activity of P<sub>2</sub>O<sub>5</sub> in the CaO-SiO<sub>2</sub>-Fe<sub>t</sub>O-P<sub>2</sub>O<sub>5</sub> slag system was calculated, as shown in Equations (2) and (3).

$$RT \ln a_{P_2O_5(l)} = RT \ln a_{P_2O_5(RS)} + 52720 - 230.706T = 2RT \ln \gamma_{PO_{2.5}(RS)} + RT \ln x_{P_2O_5(RS)} + 52720 - 230.706T(J)$$
(2)

$$RTln\gamma_{PO_{2.5}(RS)} = -251040x_{CaO}^{2} + 83680x_{SiO_{2}}^{2} - 37660x_{MgO}^{2} - 31380x_{FeO}^{2} - 33470x_{CaO}x_{SiO_{2}} - 188280x_{CaO}x_{MgO} - 243930 - 251040x_{CaO}x_{FeO} + 112960x_{SiO_{2}}x_{MgO} + 94140x_{SiO_{2}}x_{FeO} - 102510x_{MgO}x_{FeO}(J)$$
(3)

Among them, the subscript RS is the regular solution;  $\gamma$  is the activity coefficient; *a* is the activity; *x* is the molar percentage content, %; and *T* is the Kelvin temperature, *K*.

In the CaO-SiO<sub>2</sub>-Fe<sub>t</sub>O-P<sub>2</sub>O<sub>5</sub> slag system, when the liquid slag phase and  $nC_2$ S-C<sub>3</sub>P solid solution phase are in equilibrium, the activity of P<sub>2</sub>O<sub>5</sub> in these two phases should be equal, that is, as shown in Equation (4).

$$a_{P_2O_5(SS)} = a_{P_2O_5(L)} \tag{4}$$

Therefore, the phosphorus distribution ratio can be written as Equation (5).

$$L_P = \frac{(\%P_2O_5)_{SS}}{(\%P_2O_5)_L} = k \frac{a_{P_2O_5(SS)} \times \gamma_{P_2O_5(L)}}{a_{P_2O_5(L)} \times \gamma_{P_2O_5(SS)}} = k \frac{\gamma_{P_2O_5(L)}}{\gamma_{P_2O_5(SS)}}$$
(5)

According to this, the activity coefficient of  $P_2O_5$  in the  $nC_2S-C_3P$  solid solution phase can be obtained, as shown in Equation (6).

$$\gamma_{P_2O_5(SS)} = k \frac{\gamma_{P_2O_5(L)}}{L_P} \tag{6}$$

Among them, k is the conversion coefficient between the mole fraction and the mass fraction of  $P_2O_5$  in the solid solution phase and the liquid slag phase, as shown in Equation (7).

$$k = \frac{({}^{\%}P_2O_5)_{SS} \times (x_{P_2O_5})_L}{({}^{\%}P_2O_5)_L \times (x_{P_2O_5})_{SS}}$$
(7)

## 3.2. Test and Calculation Results

Taking samples No. 8 and No. 10 as examples, the SEM photographs of slag samples are shown in Figure 3. Taking samples No. 8 and No. 10 as examples, the SEM photographs of slag samples are shown in Figure 3. The irregular black particles or long strips are the  $nC_2S-C_3P$  solid solution phase, and the gray or light gray continuous distribution areas are the liquid slag phase, and the white area is the RO phase. RO phase is the general term of the solid solutions formed by the divalent metal oxides such as FeO, MgO and MnO in the slags. No MgO was added to the experimental slag. The MgO detected by EDS originated from the MgO crucible used in the experiment. The MgO crucible was eroded by the slag at high temperature and entered the slag. Therefore, there is little RO phase in the slag, which is different from the slag sample in the practical production. The EDS detection results of each phase in the 10 schemes were converted into oxides of each element, as shown in Table 2. It can be seen from the table that most of the phosphorus exists in the solid solution phase.



(a) Sample No. 8.

(**b**) Sample No. 10.

Table 2.	Composition	of the solid	solution	phase and	liquid	slag phase/wt %.
----------	-------------	--------------	----------	-----------	--------	------------------

No.	Phase	CaO	SiO <sub>2</sub>	FeO	MgO	$P_2O_5$	A/%	L <sub>P</sub>
1	Solid solution phase Liquid slag phase	58.12 28.64	23.75 20.5	5.08 47.2	0.56 2.46	12.50 1.20	46.97 53.03	9.22
2	Solid solution phase Liquid slag phase	58.88 31.21	25.57 24.36	1.82 40.93	1.00 1.24	12.73 2.26	49.98 50.02	5.63
3	Solid solution phase Liquid slag phase	61.06 34.08	23.04 24.51	3.27 35.16	1.08 1.91	11.55 4.34	56.39 43.61	3.44
4	Solid solution phase Liquid slag phase	64 36.42	21.11 24.98	4.22 32.21	0.85 1.36	9.82 5.03	58.55 41.45	2.76
5	Solid solution phase Liquid slag phase	62.87 36.24	26.39 22.15	2.39 34.23	1.06 2.53	7.29 4.85	- -	1.50
6	Solid solution phase Liquid slag phase	59.70 31.21	25.21 21.12	4.27 42.23	1.13 2.97	9.69 2.47	42.78 57.22	2.93
7	Solid solution phase Liquid slag phase	57.42 25.77	17.95 19.35	2.57 50.31	1.23 3.05	20.83 1.52	42.00 58.00	9.92
8	Solid solution phase Liquid slag phase RO phase	59.68 29.23 3.01	24.96 19.22 -	4.22 45.9 78.19	0.60 2.71 18.8	10.54 2.94 -	33.80 49.83 16.37	2.43
9	Solid solution phase Liquid slag phase	54.36 25.86	15.48 21.34	5.06 49.49	1.07 1.18	24.03 2.13	58.18 41.82	15.69
10	Solid solution phase Liquid slag phase	51.41 23.9	9.69 22.05	4.79 50.27	0.79 1.24	33.32 2.84	68.84 31.16	25.92

## 3.3. Composition Distribution Characteristics of the Solid Solution Phase and Liquid Slag Phase

According to the composition of CaO, SiO<sub>2</sub>, and P<sub>2</sub>O<sub>5</sub> in the solid solution phase and the liquid slag phase obtained in Table 2, the composition of the solid solution phase and the liquid slag phase of the ten slag samples were characterized in the phase diagram of the CaO-SiO<sub>2</sub>-P<sub>2</sub>O<sub>5</sub> ternary system. The positions of the solid solution phase and the liquid slag phase in the slag samples in the phase diagram are shown in Figures 4 and 5, respectively. It can be seen that the solid solution phase compositions were basically on the connection line of C<sub>2</sub>S and C<sub>3</sub>P. It indicates that the solid solution was formed by combining C<sub>2</sub>S and C<sub>3</sub>P in different proportions. The composition of the liquid slag phase was

basically near the liquidus at 1400 °C, which indicates that the slag sample could basically represent the state near 1400 °C.



**Figure 4.** Position of solid solution phase components in different slag samples in the phase diagram of the CaO-SiO<sub>2</sub>-P<sub>2</sub>O<sub>5</sub> ternary system.



**Figure 5.** Position of liquid slag phase components in different slag samples in the phase diagram of the CaO-SiO<sub>2</sub>-FeO ternary system.

## 4. Discussions

# 4.1. Effect of Slag Compositions on L<sub>P</sub>

Figure 6a,b shows the effects of FeO content and binary basicity in the liquid slag phase on  $L_P$ , respectively. When the FeO content in the liquid slag increased from 32.21% to 50.31%, the  $L_P$  increased from 2.76 to 9.22, and the  $L_P$  in the liquid slag phase increased by 3.34 times. When the binary basicity in the liquid slag increased from 1.08 to 1.64, the  $L_P$  decreased from 25.92 to 1.50, and the  $L_P$  in the liquid slag phase decreased by 94.21%. The effect of FeO and binary basicity in liquid slag on  $L_P$  was just the opposite. This is because the increase of FeO content in liquid slag can reduce the viscosity of the molten slag, and it is beneficial to help the phosphorus in liquid slag diffuse into the solid solution phase, thus increasing the distribution ratio of phosphorus in the solid solution phase and liquid slag

phase. The increase of binary basicity in liquid slag will increase the viscosity of molten slag, which ultimately leads to the decrease in the distribution ratio of phosphorus between the solid solution phase and the liquid slag phase. The influence trend of FeO content in the liquid slag phase on  $L_P$  was consistent with the research results of reference [9].



**Figure 6.** Effect of FeO content and binary basicity in the liquid slag phase on  $L_{\rm P}$ .

Figure 7a–c shows the effect of the compositions of the experimental primary slag on the  $L_P$ . Essentially, the effect of the compositions of the experimental primary slag on  $L_P$  is only apparent, but the essence is the influence of the compositions of the liquid slag and solid solution phase caused by the compositions of the initial slag on the  $L_P$ . It can be seen from Figure 7 that within the range of the initial slag composition, when the binary basicity increased from 2.0 to 3.5, the  $L_P$  decreased from 9.22 to 2.76, and the  $L_P$  decreased by 70.07%. When FeO content increased from 38.00% to 51.92%, the  $L_P$  increased from 1.50 to 9.22, and the  $L_P$  increased by 6.15 times. When  $P_2O_5$  content increased from 3.00% to 9.00%, the  $L_P$  increased from 2.43 to 25.92, and the  $L_P$  increased by 10.67 times. This is because when the binary basicity of the experimental initial slag is greater than 2.0, with the increase of basicity, the CaO content in the liquid slag phase will increase, which will lead to the decrease of  $L_P$ . The increase of FeO content in the experimental initial slag will cause the increase of FeO content in the liquid slag phase, which will cause the increase of  $L_P$ . The increase of  $P_2O_5$  content increased the concentration difference of phosphorus diffusion from the liquid slag phase to the solid solution phase, and increased the driving force of phosphorus migration from the liquid slag phase to the solid solution phase, thus promoting the increase of  $L_P$ .



Figure 7. Cont.



(c) Effect of P2O5 content on LP.

**Figure 7.** Effect of the components of the initial slag on  $L_P$ . Note: The subscript t represents the experimental initial slag, which is the same below.

The slag compositions of the 10 groups of schemes and their corresponding  $L_P$  values were plotted, and Figure 8 was obtained. Figure 8 shows the slag composition and its corresponding  $L_P$  values in the CaO-(SiO<sub>2</sub>+ P<sub>2</sub>O<sub>5</sub>)-FeO pseudo ternary system phase diagram. It can be seen from the figure that  $L_P$ increased in the direction toward FeO and P<sub>2</sub>O<sub>5</sub> content, which indicates that the increase of FeO and P<sub>2</sub>O<sub>5</sub> content in the slag was beneficial to the diffusion of phosphorus from the liquid slag phase to the solid solution phase.  $L_P$  decreased in the direction toward CaO content, which indicates that when the binary basicity of the initial slag was greater than 2.0, the increase of CaO content in the slag was not beneficial to the diffusion of phosphorus from the liquid slag phase.



**Figure 8.** Slag composition and its corresponding  $L_P$  value in the CaO-(SiO<sub>2</sub> + P<sub>2</sub>O<sub>5</sub>)-FeO pseudo ternary composition diagram.

#### 4.2. Effect of Slag Composition on the Activity Coefficient of Phosphorus

Figure 9 shows the effect of FeO content and binary basicity in the liquid slag phase on the activity coefficient of P<sub>2</sub>O<sub>5</sub> calculated by the regular solution model. It can be seen from the figure that within the range of the initial slag composition, when the FeO content in the liquid slag increased from 32.21% to 50.31%,  $\gamma_{P_2O_5(L)}$  increased from  $2.54 \times 10^{-15}$  to  $1.38 \times 10^{-13}$  and increased by 54.33 times. When the binary basicity in the liquid slag increased from 1.08 to 1.64,  $\gamma_{P_2O_5(L)}$  decreased from  $2.65 \times 10^{-13}$  to  $1.64 \times 10^{-15}$  and decreased by 99.38%. The results show that the increase of FeO content could reduce the stability of phosphorus in the liquid slag phase, which is helpful for phosphorus diffusion from the

liquid slag phase to the solid solution phase. While the increase of binary basicity could increase the stability of phosphorus in the liquid slag phase, which is not beneficial for the diffusion of phosphorus into the solid solution phase. According to the calculation results,  $\gamma_{P_2O_5(L)}$  was mainly affected by the content of FeO and binary basicity in the liquid slag, and other components had little influence on it. Comparing Figure 9 with Figure 6, it can be seen that the effect of the liquid slag composition on the phosphorus activity coefficient calculated by regular solution model was consistent with the experimental results.



(a) Effect of FeO content on  $\gamma_{P_2O_5(L)}$ . (b) Effect of binary basicity on  $\gamma_{P_2O_5(L)}$ .

**Figure 9.** Effect of FeO content and binary basicity in the liquid slag phase on  $\gamma_{P_2O_5(L)}$ .

Figures 10 and 11 show the effects of the binary basicity of the experimental initial slag and  $P_2O_5$  content in the solid solution phase on the activity coefficient of  $P_2O_5$  in the solid solution phase. It can be seen from the figure, when the binary basicity increased from 2.0 to 3.5,  $\gamma_{P_2O_5(SS)}$  in the solid solution phase decreased from  $8.34 \times 10^{-14}$  to  $9.56 \times 10^{-16}$  and decreased by 98.85%. When  $P_2O_5$  content increased from 3.00% to 9.00%,  $\gamma_{P_2O_5(SS)}$  increased from  $8.14 \times 10^{-15}$  to  $9.28 \times 10^{-15}$  and increased by 1.14 times. It shows that the increase of the basicity in the initial slag was beneficial to improve the stability of the phosphorus in the solid solution phase. This is because under the experimental conditions, the increase of the basicity in the initial slag was helpful to the formation of the solid solution phase will reduce its stability. This is because as the amount of phosphorus fixed in the solid solution phase increases, the phosphorus fixation capacity will decrease accordingly.



**Figure 10.** Effect of binary basicity in the initial slag on  $\gamma_{P_2O_5(SS)}$ .



**Figure 11.** Effect of P<sub>2</sub>O<sub>5</sub> content in the solid solution phase on  $\gamma_{P_2O_5(SS)}$ .

## 4.3. *n* in the $nC_2S$ - $C_3P$ Solid Solution

The ratio of  $C_2S$  and  $C_3P$  in the  $nC_2S-C_3P$  solid solution phase will change with different slag compositions, that is to say, the value of n will change. If the value of n in the  $nC_2S-C_3P$  solid solution molecular formula is smaller, the proportion of  $C_3P$  in the solid solution phase is larger. Therefore, the value of n can characterize the amount of phosphorus enriched in the solid solution phase. Figure 12 shows the influence of composition changes on the value of n in the solid solution phase within the range of the initial slag composition. It can be seen from the figure that within the range of the initial slag composition. It can be seen from the figure that within the range of the initial slag composition in the experiment, when the binary basicity decreased from 3.5 to 2.0, n decreased from 0.438 to 0.404 and decreased by 7.76%. When the FeO content increased from 38.00% to 51.92%, n decreased from 0.432 to 0.164 and decreased by 62.04%. The decrease of basicity and the increase of FeO and  $P_2O_5$  content in the initial slag can reduce the value of n, that is, more phosphorus is enriched in the solid solution phase.



(c) Effect of  $P_2O_5$  content on *n*.

Figure 12. Effect of the slag compositions on *n*.

# 5. Conclusions

In this paper, the CaO-SiO<sub>2</sub>-Fe<sub>t</sub>O-P<sub>2</sub>O<sub>5</sub> slag system was taken as the research object, and the combination method of high temperature experiments and thermodynamic calculations was used. The compositions of the  $nC_2S-C_3P$  solid solution phase and the liquid slag phase in the CaO-SiO<sub>2</sub>-Fe<sub>t</sub>O-P<sub>2</sub>O<sub>5</sub> slag system prepared in the laboratory were analyzed by means of SEM/EDS detection methods. The influence of the slag composition on the distribution ratio and activity coefficient of phosphorus between the  $nC_2S-C_3P$  solid solution phase and the liquid slag phase was studied. The main conclusions are as follows:

- (1) When the FeO content in the liquid slag increased from 32.21% to 50.31%, the  $L_P$  in the liquid slag phase increased by 3.34 times. When the binary basicity in the liquid slag increased from 1.08 to 1.64, the  $L_P$  in the liquid slag phase decreased by 94.21%.
- (2) When the binary basicity increased from 2.0 to 3.5, the  $L_P$  decreased by 70.07%. When FeO content increased from 38.00% to 51.92%, the  $L_P$  increased by 6.15 times. When P<sub>2</sub>O<sub>5</sub> content increased from 3.00% to 9.00%, the  $L_P$  increased by 10.67 times.
- (3) When the FeO content in the liquid slag increased from 32.21% to 50.31%,  $\gamma_{P_2O_5(L)}$  increased by 54.33 times. When the binary basicity in the liquid slag increased from 1.08 to 1.64,  $\gamma_{P_2O_5(L)}$  decreased by 99.38%.
- (4) When the binary basicity increased from 2.0 to 3.5,  $\gamma_{P_2O_5(SS)}$  in the solid solution phase decreased by 98.85%. When P<sub>2</sub>O<sub>5</sub> content increased from 3.00% to 9.00%,  $\gamma_{P_2O_5(SS)}$  increased by 1.14 times.
- (5) When the binary basicity decreased from 3.5 to 2.0, *n* decreased from 0.438 to 0.404. When the FeO content increased from 38.00% to 51.92%, *n* decreased from 0.477 to 0.319. When the  $P_2O_5$  content increased from 3.00% to 9.00%, *n* decreased from 0.432 to 0.164. The decrease of basicity and the increase of FeO and  $P_2O_5$  content in the initial slag can enrich more phosphorus in the solid solution phase.

**Author Contributions:** Methodology, Y.W.; formal analysis, J.L. and X.D.; investigation, X.D.; data curation, H.J. and X.D.; writing—original draft preparation, M.Z.; writing—review and editing, B.Z.; supervision, B.X. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Conflicts of Interest: The authors declare no conflict of interest.

# References

- Assis, N.A.; Tayeb, M.A.; Sridhar, S.; Fruehan, R.J. Phosphorus equilibrium between liquid iron and CaO-SiO<sub>2</sub>-MgO-Al<sub>2</sub>O<sub>3</sub>-FeO-P<sub>2</sub>O<sub>5</sub> Slags: EAF slags, the effect of alumina and new correlation. *J. Met.* 2019, *9*, 116.
- Du, C.M.; Lv, N.N.; Su, C.; Liu, W.M.; Yang, J.X.; Wang, H.C. Distribution of P2O5 between solid solution and liquid phase in dephosphorization slag of CaO–SiO2–FeO–P2O5–Na2O system. *J. Iron Steel Res. Int.* 2019, 26, 1162–1170. [CrossRef]
- 3. Li, B.; Li, L.; Guo, H.; Guo, J.; Duan, S.; Sun, W. A phosphorus distribution prediction model for CaO-SiO2-MgO-FeO-Fe2O3-Al2O3-P2O5 slags based on the IMCT. *Ironmak. Steelmak.* 2019, 1–10. [CrossRef]
- 4. Lin, L.; Bao, Y.P.; Gu, C.; Wu, W.; Zeng, J.Q. Distribution of P2O5 between P-rich phase and matrix phase in P-bearing steelmaking slag. *J. High Temp. Mater. Process.* **2018**, *37*, 655–663. [CrossRef]
- 5. Drain, P.B.; Monaghan, B.J.; Longbottom, R.J.; Chapman, M.W.; Zhang, G.; Chew, S.J. Phosphorus partition and phosphate capacity of basic oxygen steelmaking slags. *ISIJ Int.* **2018**, *58*, 1965–1971. [CrossRef]
- 6. Drain, P.B.; Monaghan, B.J.; Zhang, G.; Longbottom, R.J.; Chapman, M.W.; Chew, S.J. A review of phosphorus partition relations for use in basic oxygen steelmaking. *Ironmak. Steelmak.* **2017**, *44*, 721–731. [CrossRef]
- Han, X.; Li, J.; Zhou, C.G.; Shi, C.B.; Zheng, D.L.; Zhang, Z.M. Study on mineralogical structure of dephosphorisation slag at the first deslagging in BOF steelmaking process. *Ironmak. Steelmak.* 2017, 44, 262–268. [CrossRef]

- Assis, A.N.; Tayeb, M.A.; Sridhar, S.; Fruehan, R.J. Phosphorus equilibrium between liquid iron and CaO-SiO2-MgO-Al2O3-FeO-P2O5 slag part 1: Literature review, methodology, and BOF slags. *Met. Mater. Trans. B* 2015, 46, 2255–2263. [CrossRef]
- 9. Ito, K.; Yanagisawa, M.; Sano, N. Phosphorus distribution between solid 2CaO·SiO<sub>2</sub> and molten CaO-SiO<sub>2</sub>-FeO-Fe<sub>2</sub>O<sub>3</sub> Slags. *J. Tetsu Hagané* **1982**, *68*, 150–152.
- 10. Fix, W.; Heymann, H.; Heinke, R. Subsolidus relations in the system 2CaO·SiO<sub>2</sub>-3CaO·P<sub>2</sub>O<sub>5</sub>. *J. Am. Ceram. Soc.* **1969**, *52*, 342–346. [CrossRef]
- Inoue, R.; Suito, H. Phosphorous partition between 2CaO·SiO<sub>2</sub> particles and CaO-SiO<sub>2</sub>-Fe<sub>t</sub>O slags. *J. ISIJ Int.* 2006, 46, 174–179. [CrossRef]
- 12. Inoue, R.; Suito, H. Mechanism of dephosphorization with CaO-SiO<sub>2</sub>-Fe<sub>t</sub>O slags containing mesoscopic scale 2CaO-SiO<sub>2</sub> particles. *J. ISIJ Int.* **2006**, *46*, 188–194. [CrossRef]
- 13. Fukagai, S.; Hamano, T.; Tsukihashi, F. Formation reaction of phosphate compound on multiphase flux at 1573K. *J. ISIJ Int.* **2007**, 47, 187–189. [CrossRef]
- 14. Shimauchi, K.; Kitamura, S.; Shibata, H. Distribution of P<sub>2</sub>O<sub>5</sub> between solid dicalcium silicate and liquid phases in CaO-SiO<sub>2</sub>-Fe<sub>2</sub>O<sub>3</sub> system. *J. ISIJ Int.* **2009**, *49*, 505–511. [CrossRef]
- 15. Pahlevani, F.; Kitamura, S.Y.; Shibata, H.; Maruoka, N. Distribution of P<sub>2</sub>O<sub>5</sub> between solid solution of 2CaO·SiO<sub>2</sub> and 3CaO·P<sub>2</sub>O<sub>5</sub> and liquid phase. *J. ISIJ Int.* **2010**, *50*, 822–829. [CrossRef]
- 16. Kitamura, S.Y.; Saito, S.; Utagawa, K.; Shibata, H.; Robertson, D.G. Mass transfer of P<sub>2</sub>O<sub>5</sub> between liquid slag and solid solution of 2CaO·SiO<sub>2</sub> and 3CaO·P<sub>2</sub>O<sub>5</sub>. *J. ISIJ Int.* **2009**, *49*, 1838–1844. [CrossRef]
- 17. Inoue, R.; Suito, H. Behavior of phosphorus transfer from CaO-Fe<sub>t</sub>O-P<sub>2</sub>O<sub>5</sub> (-SiO<sub>2</sub>) slag to CaO particles. *J. ISIJ Int.* **2006**, *46*, 180–187.
- 18. Son, P.K.; Kashiwaya, Y. Phosphorus partition in dephosphorization slag occurring with crystallization at initial stage of solidification. *J. ISIJ Int.* **2008**, *48*, 1165–1174. [CrossRef]



© 2020 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/).