Activities of \( \text{Fe}_x\text{O} \) in Molten Slags Coexisting with Solid \( \text{CaO} \) and \( \text{Ca}_2\text{SiO}_4-\text{Ca}_3\text{P}_2\text{O}_8 \) Solid Solution

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In steelmaking processes, there are incentives to reduce slag volume and \( \text{CaO} \) consumption. The key to meet these requirements is the better understanding of \( \text{CaO} \) dissolution mechanism into molten slag, which relies on the knowledge of the thermochemical properties of slags and fluxes used for dephosphorization. In this study, the liquidus compositions coexisted with solid \( \text{CaO} \) and \( \text{Ca}_2\text{SiO}_4-\text{Ca}_3\text{P}_2\text{O}_8 \) solid solution simultaneously were determined in the quaternary system \( \text{CaO}-\text{SiO}_2-\text{P}_2\text{O}_5-\text{Fe}_x\text{O} \) at 1573 K. Measurements were also conducted on the \( \text{Fe}_x\text{O} \) activities at temperatures between 1542 K and 1604 K by virtue of an electrochemical technique. By using the present experimental results, phosphorus distribution ratios were estimated.

KEY WORDS: dephosphorization; activity; di-calcium silicate; tri-calcium phosphate; solid solution.

1. Introduction

From the viewpoint of environmentally friendly steelmaking processes, there is a strong incentive to reduce slag volume. The key toward this end is a more effective utilization of \( \text{CaO} \) in removing phosphorus from hot metal, which can be expressed by

\[
[\text{P}]_{\text{Fe}} + 5(\text{FeO})_{\text{slag}} = (\text{P}_2\text{O}_5)_{\text{slag}} + 5(\text{Fe})
\]

\[
\log K = \log \left( a_{\text{FeO}} / h^5 a_{\text{Fe}} \right) = -15.48 + 5.026 / (T / K)^{1.4}
\]

where \( a_i \) is the activity of component \( i \), and \( h_i \) is the Henrian activity of component \( i \).

In Eq. (1), \( [\text{P}]_{\text{Fe}} \) is phosphorus in liquid iron, \( (\text{FeO})_{\text{slag}} \) and \( (\text{P}_2\text{O}_5)_{\text{slag}} \) represent \( \text{FeO} \) and \( \text{P}_2\text{O}_5 \) in slag, respectively, and \( [\text{Fe}] \) is molten iron. It has been reported that \( \text{P}_2\text{O}_5 \) in slag reacts with \( \text{CaO} \) to form solid solution between di-calcium silicate, \( \text{Ca}_2\text{SiO}_4 \), and tri-calcium phosphate, \( \text{Ca}_3\text{P}_2\text{O}_8 \). Matsushima et al. determined the dissolution rate of solid \( \text{CaO} \) into liquid slag by measuring the decreasing rate of a diameter of a \( \text{CaO} \) cylinder dipped in \( \text{CaO}-\text{SiO}_2-\text{Fe}_x\text{O} \) molten slag. They concluded that the driving force of \( \text{CaO} \) dissolution was the difference between initial and equilibrium contents of \( \text{CaO} \) in molten slag saturated with \( \text{Ca}_2\text{SiO}_4 \). It has been also pointed out that \( \text{Ca}_2\text{SiO}_4 \) prevents dissolution of solid \( \text{CaO} \) into molten slag, because it is often formed on the surfaces of \( \text{CaO} \) particles, although \( \text{Ca}_2\text{SiO}_4-\text{Ca}_3\text{P}_2\text{O}_8 \) solid solution is an important phase in which \( \text{P}_2\text{O}_5 \) is condensed.

The reaction mechanism between solid \( \text{CaO} \) and \( \text{CaO}-\text{SiO}_2-\text{P}_2\text{O}_5-\text{Fe}_x\text{O} \) molten slag has been reported by Hamano et al. and Fukagai et al. as follows.

(a) Solid \( \text{CaO} \) dissolves into molten slag. \( \text{CaO} \) and \( \text{SiO}_2 \) are consumed due to the formation of \( \text{Ca}_2\text{SiO}_4 \).

\[ (\text{a}) \quad \text{Solid CaO dissolves into molten slag. CaO and SiO}_2 \text{ are consumed due to the formation of Ca}_2\text{SiO}_4 \]  

(b) The \( \text{FeO} \) content in molten slag increases. According to the activity gradient of \( \text{FeO} \), \( \text{Fe}^{2+} \) diffuses from \( \text{FeO} \)-rich melt to both \( \text{CaO} \) and bulk slag. \( \text{CaO}-\text{FeO} \) layer is formed beside solid \( \text{CaO} \).

Based on these foregoing comments, the present study aimed at determining the liquidus compositions and the \( \text{Fe}_x\text{O} \) activities at temperatures between 1542 K and 1604 K by virtue of an electrochemical technique. By using the present experimental results, phosphorus distribution ratios were estimated.

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When iron oxide is added to the ternary system of CaO–SiO$_2$–P$_2$O$_5$, Fe$_x$O would form quaternary liquid phase. Figure 2(b) schematically shows phase relations in the CaO–SiO$_2$–P$_2$O$_5$–Fe$_x$O quaternary system at 1 573 K; the base CaO–SiO$_2$–P$_2$O$_5$ and the side CaO–SiO$_2$–Fe$_x$O of this tetrahedron represent the phase diagrams of the corresponding ternary systems at 1 573 K, $^{9,10}$ respectively.

As the P$_2$O$_5$ content increases, the 3-phase coexistences of CaO + C$_3$S + L$_3$ and C$_3$S + C$_2$S + L$_3$ would change to the 4-phase coexistences of CaO + C$_3$S + <C$_2$S–C$_3$P> ss + L$_4$ and C$_3$S + C$_2$S + <C$_2$S–C$_3$P> ss + L$_4$, respectively, $^{11}$ and then these two 4-phase regions would join to form the 3-phase region of CaO + <C$_2$S–C$_3$P> ss + L$_4$. In the present study, the compositions of L$_4$ coexisted with solid CaO and <C$_2$S–C$_3$P> ss simultaneously were determined by using electron probe micro analysis (EPMA), and, subsequently the activities of Fe$_x$O in the 3-phase region of CaO + <C$_2$S–C$_3$P> ss + L$_4$ were determined by employing an electrochemical technique incorporating magnesia stabilized zirconia.

2. Experimental Aspects

2.1. EPMA Studies

The experimental apparatus is schematically shown in Fig. 3, and starting materials used for phase equilibrium study are listed in Table 1. The compounds listed in this table were mixed with iron oxide, and pressed into a steel die. The bulk compositions of the oxide mixtures are given in Table 2. As shown in Fig. 3(b), oxide pellets were charged in an iron crucible with powdery oxide of the same bulk composition as pellets, in order to facilitate removing pellets from a crucible after heating. Oxide samples were held at 1 573 K over 48 hours under a stream of purified argon to yield the appropriate 3-phase region. The gas purification train consisted of silica-gel, phosphorus pentoxide and magnesium chips held at 823 K. By pushing down a magnesia crucible, a plastic plate was broken, and then samples were quenched in liquid nitrogen. The resulting samples were submitted, firstly, to X-ray diffraction analysis to confirm the expected solid compounds, and, subsequently, to EPMA to determine the compositions of quaternary liquid phase and <C$_2$S–C$_3$P> ss.

2.2. Electrochemical Measurements

The slags under considerations were prepared by mixing CaO, <C$_2$S–C$_3$P> ss and iron oxide; the bulk compositions...
was used as an electric conductor to the reference electrode, while the electrical contact to the outer electrode of the zirconia probe was made by the liquid silver and a steel rod soldered to the iron crucible. The zirconia tubes used in this study has a satisfactory resistance to the FeO-containing slags.

Values for the open-circuit electromotive forces \( (emf) \) of the oxygen probes were read with a digital voltmeter of 100 M\( \Omega \) input resistance with an accuracy of \( \pm 0.01 \) mV. \( Emf \) readings were continued until stable cell potentials were obtainable, and the reproducibilities of cell potentials were confirmed by temperature cycling. Temperatures were measured with a Pt-PtRh13 thermocouple and controlled to \( \pm 1 \) K by using a control thermocouple and PID-type temperature regulator.

The open-circuit electromotive force, \( E \), of the cell is given by
\[
E = \frac{RT}{F} \ln \left( \frac{P_{O_2} (ref.)^{1/4} + P_e^{1/4}}{P_{O_2}^{1/4} + P_e^{1/4}} \right) + E_r \quad \ldots (3)
\]
where \( R \) is the gas constant, \( T \) is temperature, \( F \) is the Faraday constant, \( E_r \) is thermo-emf between Mo (positive) and Fe (negative), and \( P_e \) is the oxygen partial pressure at which the ionic and the \( n \)-type electronic conductivities are equal. Values for \( E_r \) and \( P_e \) used in this study have been reported as follows, respectively.

\[
E_r / \text{mV} = -14.69 + 0.0227 \left( \frac{T}{K} \right)^{13} \quad \ldots (4)
\]

\[
\log \left( P_e / \text{atm} \right) = +20.40 - 6.45 \times 10^4 / \left( \frac{T}{K} \right)^{14} \quad \ldots (5)
\]

The oxygen partial pressure at the reference electrode, \( P_{O_2} (\text{ref.}) \), was given by
\[
\log \left[ P_{O_2} (\text{ref.}) / \text{atm} \right] = +8.84 - 30100 / \left( \frac{T}{K} \right)^{15} \ldots (6)
\]

When the standard state for \( Fe_2O \) was taken as pure non-stoichiometric liquid \( Fe_2O \) in equilibrium with pure solid Fe, the activities of \( Fe_2O \) could be calculated by
\[
a_{Fe_2O} = \left( \frac{P_{O_2}}{P_{O_2}^0} \right)^{12} \quad \ldots (7)
\]
where \( P_{O_2}^0 \) is the equilibrium oxygen partial pressure of the mixture of pure solid Fe + pure liquid \( Fe_2O \), as given by the following formula.

\[
\log \left[ P_{O_2}^0 / \text{atm} \right] = +4.39 - 2.35 \times 10^4 / \left( \frac{T}{K} \right)^2 \quad \ldots (8)
\]

Table 1. Starting materials used for phase equilibrium study.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Preparation</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaCO₃</td>
<td>Obtained from Nacalai Tesque, Inc., Kyoto, Japan, and dried at 413 K.</td>
</tr>
<tr>
<td>SiO₂</td>
<td>Obtained from Nacalai Tesque, Inc., Kyoto, Japan, and dried at 413 K.</td>
</tr>
<tr>
<td>C₃P</td>
<td>Obtained from Nacalai Tesque, Inc., Kyoto, Japan, and dried at 413 K.</td>
</tr>
<tr>
<td>CaO</td>
<td>CaCO₃ heated at 1 273 K for 2 hours.</td>
</tr>
<tr>
<td>C₃S</td>
<td>CaCO₃ mixed with SiO₂, and fired at 1 573 K for 24 hours.</td>
</tr>
<tr>
<td>&lt;C₃S–C₃P&gt;</td>
<td>C₃P mixed with C₃S, and fired at 1 573 K for 24 hours.</td>
</tr>
</tbody>
</table>
3. Experimental Results and Discussion

3.1. EPMA Studies

XRD and EPMA studies confirmed that all the slags investigated in this study occurred at the expected 3-phase region of $\text{CaO} + <\text{C}_2\text{S}–\text{C}_3\text{P}>_{\text{ss}} + \text{L}_4$, and the compositions are numerically given in Table 2.

Figure 5 shows the present values for the contents of $\text{Fe}_x\text{O}$, $\text{SiO}_2$, and $\text{P}_2\text{O}_5$ in the quaternary liquid slags plotted against the $\text{C}_3\text{P}$ content in $<\text{C}_2\text{S}–\text{C}_3\text{P}>_{\text{ss}}$, together with the literature data for the 3-phase regions of $\text{CaO} + \text{C}_3\text{S} + \text{L}_3$ and $\text{C}_3\text{S} + \text{C}_2\text{S} + \text{L}_3$ in the CaO–SiO$_2$–Fe$_x$O ternary system$^{10}$ and the 4-phase regions of $\text{CaO} + \text{C}_3\text{S} + <\text{C}_2\text{S}–\text{C}_3\text{P}>_{\text{ss}} + \text{L}_4$ and $\text{C}_3\text{S} + \text{C}_2\text{S} + <\text{C}_2\text{S}–\text{C}_3\text{P}>_{\text{ss}} + \text{L}_4$ in the CaO–SiO$_2$–P$_2$O$_5$–Fe$_x$O quaternary system. The $\text{Fe}_x\text{O}$ content decreased as the $\text{C}_3\text{P}$ content increased up to 12 mass%, and then it increased, but it was almost constant in the 3-phase region of $\text{CaO} + <\text{C}_2\text{S}–\text{C}_3\text{P}>_{\text{ss}} + \text{L}_4$.

The concentrations of $\text{SiO}_2$ and $\text{P}_2\text{O}_5$ were very low in the composition range investigated. Based on these results, the liquid phase coexisted with $\text{CaO}$ and $<\text{C}_2\text{S}–\text{C}_3\text{P}>_{\text{ss}}$ simultaneously could be considered to be $\text{CaO}–\text{Fe}_x\text{O}$ binary melt.

The compositions of molten slags equilibrated with $<\text{C}_2\text{S}–\text{C}_3\text{P}>_{\text{ss}}$, in which ($\text{mass}\%\text{C}_3\text{P})_{\text{SS}}$ were lower than 5, have been reported in the literature. In Fig. 6, the present results are projected onto the pseudo-ternary field of $\text{CaO}–(\text{SiO}_2 + \text{P}_2\text{O}_5)–\text{Fe}_x\text{O}$ at 1 573 K, together with the literature data. $^{16,17}$ The 3-phase region of $\text{CaO} + <\text{C}_2\text{S}–\text{C}_3\text{P}>_{\text{ss}} + \text{L}_4$ and the liquidus lines coexisted with $<\text{C}_2\text{S}–\text{C}_3\text{P}>_{\text{ss}}$ could be illustrated in this diagram. As mentioned above, the liquidus compositions in the 3-phase region investigated in this study were insensitive to the variation of ($\text{mass}\%\text{C}_3\text{P})_{\text{SS}}$. The liquidus line saturated with $<\text{C}_2\text{S}–\text{C}_3\text{P}>_{\text{ss}}$, however, should depend on ($\text{mass}\%\text{C}_3\text{P})_{\text{SS}}$. This would be future work.

Next, consider the phosphorus distribution ratio along the liquidus line saturated with $<\text{C}_2\text{S}–\text{C}_3\text{P}>_{\text{ss}}$ seen in Fig. 6. For effective dephosphorization, $\text{P}_2\text{O}_5$ in slag should be condensed in solid phases. The distribution ratio of $\text{P}_2\text{O}_5$ between solid and liquid phases was defined by

$$L_{\text{P}2\text{O}_5} = \frac{\text{mass}\%\text{P}_2\text{O}_5}_{\text{SS}}{\text{mass}\%\text{P}_2\text{O}_5}_{\text{L}} \quad \text{(9)}$$
Table 2 gives the values for $L_{SS}^{L}$ of the heterogeneous slags investigated in this study, and Fig. 7 shows $L_{SS}^{L}$ plotted against ($mass\%Fe_xO$). It has been reported that the relationship between logarithmic value for $L_{SS}^{L}$ and ($mass\%Fe_xO$) would be linear and scarcely dependent on temperature.\textsuperscript{17–19)} As seen in this figure, the present results were in very good agreement with the literature data.

3.2. Electrochemical Measurements

In this study, the $Fe_xO$ activities were determined in the $3$-phase region of $CaO + <C_3S-C_3P>_{SS} + L4$. Tables 4, 5 and 6 give the experimental results obtained when ($mass\%C_3P$)\textsubscript{SS} are $18$, $24$ and $31$, respectively, and the present values for $log a_{Fe_xO}$ are shown in Fig. 8 as functions of reciprocal temperature. By using the least squares method, the present values could be well expressed by the following formulae;

$$log K_{a T}^{mass CPFe O SSx} = -0.418 \times \frac{1075}{T/K} \pm 0.009 \times (mass\%C_3P)_{SS} = 18$$

\hspace{10cm} \text{(10)}
reaction between solid CaO and CaO–SiO₂–P₂O₅–FexO molten slag, CaO–FeₓO layer is formed beside solid CaO in the 3-phase region of CaO. noted that the FeₓO activities at 1573 K in FeₓO rich melt were 0.85 and 0.27, respectively, 7) by using the regular solution model. 21) Based on the present experimental results, CaO–FeₓO layer would correspond to the liquid phase coexisted with solid CaO and <CS₂–C₃P>ss simultaneously, in which the FeₓO activity at 1573 K was determined to be 0.53–0.54 in this study. Consequently, it could be concluded that the FeₓO activity for CaO–FeₓO liquid phase was lower than that for FeₓO rich melt saturated with C₂S; this was not inconsistent with the dissolution mechanism of solid CaO into molten slag. 23)

Table 5. Experimental results for activity measurements; (mass%C₃P)ss=24.

<table>
<thead>
<tr>
<th>No.</th>
<th>T/K</th>
<th>E/mV</th>
<th>log(α₁₋₁₀₀/atm)</th>
<th>log α₉₋₀₀</th>
</tr>
</thead>
<tbody>
<tr>
<td>5-1</td>
<td>1575</td>
<td>86.35 ± 0.08</td>
<td>−11.11</td>
<td>−0.288</td>
</tr>
<tr>
<td>5-3</td>
<td>1595</td>
<td>85.58 ± 0.12</td>
<td>−10.84</td>
<td>−0.249</td>
</tr>
<tr>
<td>5-4</td>
<td>1552</td>
<td>76.64 ± 0.12</td>
<td>−11.27</td>
<td>−0.259</td>
</tr>
<tr>
<td>5-5</td>
<td>1583</td>
<td>83.21 ± 0.09</td>
<td>−10.96</td>
<td>−0.254</td>
</tr>
<tr>
<td>5-9</td>
<td>1603</td>
<td>87.61 ± 0.08</td>
<td>−10.77</td>
<td>−0.249</td>
</tr>
<tr>
<td>6-1</td>
<td>1576</td>
<td>83.77 ± 0.11</td>
<td>−11.06</td>
<td>−0.270</td>
</tr>
<tr>
<td>6-2</td>
<td>1593</td>
<td>88.85 ± 0.12</td>
<td>−10.91</td>
<td>−0.273</td>
</tr>
<tr>
<td>6-3</td>
<td>1552</td>
<td>79.07 ± 0.06</td>
<td>−11.31</td>
<td>−0.281</td>
</tr>
<tr>
<td>6-4</td>
<td>1582</td>
<td>86.45 ± 0.06</td>
<td>−11.02</td>
<td>−0.277</td>
</tr>
<tr>
<td>6-7</td>
<td>1574</td>
<td>84.54 ± 0.13</td>
<td>−11.10</td>
<td>−0.278</td>
</tr>
<tr>
<td>6-8</td>
<td>1583</td>
<td>87.02 ± 0.12</td>
<td>−11.01</td>
<td>−0.279</td>
</tr>
<tr>
<td>6-9</td>
<td>1583</td>
<td>85.11 ± 0.12</td>
<td>−10.99</td>
<td>−0.267</td>
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<tr>
<td>6-10</td>
<td>1552</td>
<td>78.33 ± 0.11</td>
<td>−11.30</td>
<td>−0.276</td>
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<tr>
<td>6-11</td>
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<td>75.05 ± 0.06</td>
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<tr>
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<tr>
<td>6-15</td>
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<td>81.37 ± 0.09</td>
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<td>−0.261</td>
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<tr>
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<td>1603</td>
<td>93.46 ± 0.13</td>
<td>−10.84</td>
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<td>1562</td>
<td>79.80 ± 0.11</td>
<td>−11.19</td>
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<td>6-18</td>
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<td>76.15 ± 0.08</td>
<td>−11.29</td>
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<tr>
<td>6-20</td>
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<td>91.09 ± 0.08</td>
<td>−10.95</td>
<td>−0.289</td>
</tr>
<tr>
<td>6-21</td>
<td>1573</td>
<td>84.01 ± 0.08</td>
<td>−11.10</td>
<td>−0.277</td>
</tr>
<tr>
<td>6-22</td>
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<td>73.58 ± 0.08</td>
<td>−11.38</td>
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<tr>
<td>6-23</td>
<td>1542</td>
<td>73.42 ± 0.06</td>
<td>−11.37</td>
<td>−0.262</td>
</tr>
<tr>
<td>6-24</td>
<td>1553</td>
<td>75.47 ± 0.07</td>
<td>−11.25</td>
<td>−0.256</td>
</tr>
<tr>
<td>6-25</td>
<td>1573</td>
<td>83.63 ± 0.06</td>
<td>−11.10</td>
<td>−0.274</td>
</tr>
</tbody>
</table>

\[
\log \alpha_{\text{Fe}O} = -0.393 + \frac{195}{(T / K)} \pm 0.009 \quad (\text{mass\%C}_3\text{P})_{\text{ss}} = 24
\]

\[
\log \alpha_{\text{Fe}O} = 0.493 - \frac{1211}{(T / K)} \pm 0.022 \quad (\text{mass\%C}_3\text{P})_{\text{ss}} = 31
\]

Figure 9(a) shows the FeₓO activities at 1573 K plotted against (mass%C₃P)ss, in comparison with the literature data. 11,20) The FeₓO activity had a minimum in the 4-phase regions CaO + C₃S + <C₃S–C₃P>ss + L₄ or C₃S + C₃S + <C₃S–C₃P>ss + L₄, and was almost constant in the 3-phase region of CaO + <C₃S–C₃P>ss + L₄; such behaviors were consistent with those of FeₓO content in liquid phase, seen in Fig. 5(a).

As already mentioned, it has been reported that, in the reaction between solid CaO and CaO–SiO₂–P₂O₅–FeₓO molten slag, CaO–FeₓO layer is formed beside solid CaO due to the activity gradient of FeO. 7) (Fig. 1(b)) Hamano et al. noted that the FeₓO activities at 1573 K in FeₓO rich melt saturated with C₂S and bulk slag could be calculated to be 0.85 and 0.27, respectively, 7) by using the regular solution model. 21) Based on the present experimental results, CaO–FeₓO layer would correspond to the liquid phase coexisted with solid CaO and <C₃S–C₃P>ss simultaneously, in which the FeₓO activity at 1573 K was determined to be 0.53–0.54 in this study. Consequently, it could be concluded that the FeₓO activity for CaO–FeₓO liquid phase was lower than that for FeₓO rich melt saturated with C₂S; this was not inconsistent with the dissolution mechanism of solid CaO into molten slag. 23)
Fig. 8. Relation between logarithmic value for Fe$_x$O activity and reciprocal temperature.

Fig. 9. Relation between the activity and the C$_3$P content in C$_2$S–C$_3$P solid solution at 1573 K. (a) Fe$_x$O, (b) P$_2$O$_5$.

3.3. Phosphorus Distribution Ratio between Liquid Slag and Molten Iron

By the present authors, the C$_3$P activity in $\text{C}_2\text{S}$–C$_3$P ss at 1573 K has been formulated as\textsuperscript{22)

$$\log a_{\text{C}_3\text{P}} = 6.80 \times 10^{-3} + 2 \log Y + 3.81 \times 10^{-1} \times (1 - Y)^2 \ldots (13)$$

where $Y$ represents the substitution ratio and is defined by

$$Y = 2 n_{\text{C}_3\text{P}} / (n_{\text{C}_2\text{S}} + 2 n_{\text{C}_3\text{P}}) \ldots (14)$$

In Eq. (14), $n_i$ denotes the number of moles of component $i$ in solid solutions. As seen in Table 2, $(\text{mass}\% \text{Fe}_x\text{O})_{\text{SS}}$ was less than 2.5 in the 3-phase region of CaO + $\text{C}_2\text{S}$–C$_3$P ss + L4. Therefore, it was assumed that the C$_3$P activity in the 3-phase region under consideration was identical to that calculated by Eq. (13). Furthermore, based on the assumption that the CaO activity was unity in this 3-phase region, the P$_2$O$_5$ activity could be derived by the following reaction, which represented the formation of C$_3$P from CaO and P$_2$O$_5$.

$$3\text{CaO} + \text{P}_2\text{O}_5 = \text{C}_3\text{P} \ldots (15)$$

$$\log K_{(23)} = \log a_{\text{C}_3\text{P}} - 3 \log a_{\text{CaO}} - \log a_{\text{P}_2\text{O}_5} = 24.80$$

at 1573 K\textsuperscript{1,23,24)  
(16)

$$\log a_{\text{P}_2\text{O}_5} = \log a_{\text{C}_3\text{P}} - 24.80$$

$$\quad - 24.79 + 2 \log Y + 3.81 \times 10^{-1} \times (1 - Y)^2 \ldots (17)$$

Figure 9(b) shows the P$_2$O$_5$ activity at 1573 K calculated from Eq. (17). In the 3-phase region of CaO + $\text{C}_2\text{S}$–C$_3$P ss + L4, the P$_2$O$_5$ activity increased with an increase in $(\text{mass}\% \text{C}_3\text{P})_{\text{SS}}$.

Now, consider the distribution ratio of phosphorus between liquid slag and molten iron, defined by

$$L_{\text{P}/\text{Fe}} = \frac{\text{(mass}\% \text{P})_{\text{L}}}{\text{(mass}\% \text{P})_{\text{Fe}}} \ldots (18)$$

For carbon-saturated $\{\text{Fe–C–P}\}$ liquid alloys, the Henrian activity of phosphorus is expressed by

$$\log b_P = \log \left[\text{(mass}\% \text{P})_{\text{Fe}}\right] + e_P \left[\text{(mass}\% \text{C})_{\text{Fe}}\right] + e_P \left[\text{(mass}\% \text{P})_{\text{Fe}}\right] \ldots (19)$$

, where $e_P$ represents the first order interaction coefficient.
in liquid iron and \([\text{mass}\%C]_{Fe}\) is the carbon concentration in liquid iron saturated with solid carbon. Eqs. (2), (18) and (19) imply that \(L^{\text{LIQ}}_0\) for the 3-phase region of \(\text{CaO} + \text{FeO} + \text{C} \rightarrow \text{FeO} + \text{FeS} + \text{FeP} = \text{L4} + \text{P}_{2}\text{O}_5\) and \(L^{\text{LIQ}}_0\) for the 3-phase region of \(\text{CaO} + \text{SiO}_2 + \text{P}_2\text{O}_5 + \text{FeO} = \text{L4} + \text{P}_{2}\text{O}_5\) can be calculated by using the FeO activities (Eqs. (10), (11) and (12)), the \(P_{2}\text{O}_5\) activity (Eq. (17)) and the phosphorus content in liquid slag (Table 2). The calculation results are shown in Fig. 10, together with the literature data at 1 573 K.\(^9,25\) By applying Le Chatelier’s principle to Reaction (1), the thermochemical conditions to achieve high \(L^{\text{LIQ}}_0\) for high FeO activity and low \(P_{2}\text{O}_5\) activity (high basicity). The variations of \(L^{\text{LIQ}}_0\) along the liquidus lines coexisted with \(<C_2\text{S}–C_3\text{P}>_{\text{ss}}\) and \(\text{CS}\) illustrated in Fig. 10 were consistent with these conditions and the phase relations in Fig. 6. It should be noted here that the values for \(L^{\text{LIQ}}_0\) in Fig. 10 were estimated by assuming that the oxygen potential was fixed by the equilibrium between \(\text{FeO}\) in slag and metallic iron, in order to compare the present values with those reported in the literature at temperature below the melting point of pure iron.

### 4. Conclusion

In this study, attention was focused on the 3-phase assemblage of \(\text{CaO} + \text{Ca}_2\text{SiO}_3 + \text{Ca}_3\text{P}_2\text{O}_5\) solid solution + liquid slag in the quaternary system \(\text{CaO}–\text{SiO}_2–\text{P}_2\text{O}_5–\text{FeO}\). The liquidus compositions of this 3-phase region at 1 573 K were determined by employing EMPA. The contents of \(\text{SiO}_2\) and \(\text{P}_2\text{O}_5\) were very low in these quaternary liquid slags. The \(\text{FeO}\) activities were also measured by using an electrochemical technique involving stabilized zirconia electrolyte. The present results were consistent with the reaction mechanism between solid \(\text{CaO}\) and molten slag. Based on the present experimental data, phosphorus distribution ratios were estimated.

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