

Reevaluation and Measurements of Fe_xO Activities in Fe_xO – CaO – SiO_2 Pseudo-ternary System at 1 573 K

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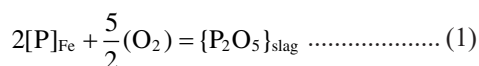
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The knowledge of Fe_xO activities in molten slags at lower temperatures is necessary for effective dephosphorization in hot metal pretreatments. However, there have been still differences among the reference data in the Fe_xO – CaO – SiO_2 pseudo-ternary system at 1 573 K. In the present study, the Fe_xO activities were measured with an electrochemical technique in order to reevaluate the iso-activity curves of Fe_xO . Subsequently, the CaO and SiO_2 activities along liquidus lines were calculated by the Gibbs-Duhem equation, and the equilibrium phosphorus contents in molten iron coexisted with dephosphorization slags were estimated by using the present results.

KEY WORDS: steelmaking; dephosphorization; activity; Fe_xO ; CaO ; SiO_2 .

1. Introduction

In steelmaking processes, phosphorus removal from hot metal is an exothermal reaction and can be expressed as



, where $[\text{P}]_{\text{Fe}}$ represents phosphorus in molten iron, (O_2) is gaseous oxygen, and $\{\text{P}_2\text{O}_5\}_{\text{slag}}$ indicates P_2O_5 in slag. It is well known that P_2O_5 in slag reacts with CaO to form solid solutions between tri-calcium phosphate, $\text{Ca}_3\text{P}_2\text{O}_8$, and di-calcium silicate, Ca_2SiO_4 .¹⁾ According to Le Chatelier's principle, the thermochemical conditions for effective dephosphorization are low temperature, high oxygen potential (high Fe_xO activity), and low P_2O_5 activity (high basicity). **Figure 1** shows the iso-thermal section of the Fe_xO – CaO – SiO_2 ternary system at 1 573 K,²⁾ which is one of the basic steelmaking slags. Figure 1 illustrates that liquid phase can be obtained in the region of high Fe_xO content and low slag basicity. As already mentioned above, the former is advantageous while the latter is disadvantageous to phosphorus removal.

A number of studies have been carried out to investigate thermochemical properties in Fe_xO – SiO_2 ,^{3–7)} Fe_xO – CaO ,^{5–11)} and Fe_xO – CaO – SiO_2 ^{12–19)} systems at higher temperature than 1 673 K. Ban-ya *et al.* applied a regular solution model to molten slags and suggested the following formula to calculate the activity of component i .^{5,20–25)}

$$RT \ln a_i = \sum_j \alpha_{ij} N_j^2 + \sum_j \sum_k (\alpha_{ij} + \alpha_{ik} - \alpha_{jk}) N_j N_k \quad \dots\dots (2)$$

$$+ RT \ln N_i + \Delta G_{\text{conv.}}$$

, where N_i is the cation fraction of component i , α_{ij} is the interaction energy between cation i –O–cation j , and $\Delta G_{\text{conv.}}$ is the conversion factor of activities between hypothetical regular solution and real solution. It was reported that the values of the parameters, α_{ij} , were optimized based on the experimental data,^{5,12,13,16,26,27)} and the calculated results

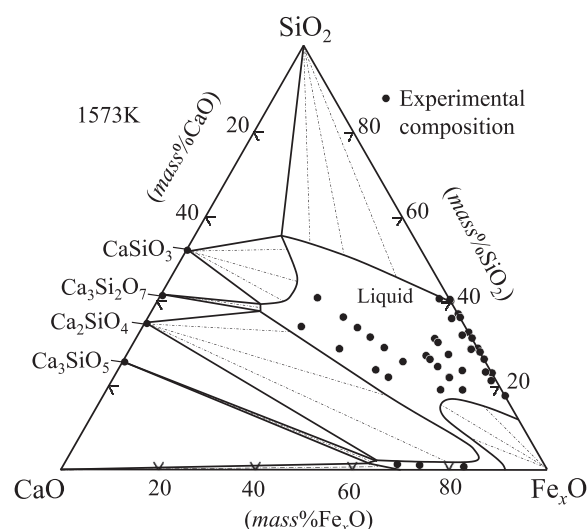


Fig. 1. Iso-thermal section of the Fe_xO – CaO – SiO_2 ternary system in contact with metallic iron at 1 573 K.²⁾

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were in good agreement with the measured values. Furthermore, it was shown that the phosphorus distribution ratios between the Fe_xO – CaO – SiO_2 – P_2O_5 quaternary slag and the molten iron could be accurately predicted with this model at 1 823 K–1 923 K.²⁴⁾

In order to discuss dephosphorization in hot metal pre-treatments, the attention is now focused on the thermochemical data in the Fe_xO – CaO – SiO_2 ternary system at lower temperature. The preceding studies to determine the Fe_xO activities around 1 573 K are summarized below.^{26–32)} Schuhmann and Ensio measured the Fe_xO activities in the Fe_xO – SiO_2 binary slags in the temperature range of 1 531 K–1 680 K by bubbling $\text{CO}+\text{CO}_2$ gas mixtures through the slags in iron crucibles.²⁶⁾ They showed that the Fe_xO activities in this system scarcely depended on temperature. Bodsworth equilibrated the Fe_xO – SiO_2 and Fe_xO – CaO – SiO_2 slags with $\text{H}_2+\text{H}_2\text{O}$ gas mixtures at 1 530 K–1 643 K.²⁷⁾ Takeda *et al.* determined the relationship between the oxygen partial pressure and the composition for the iron-saturated calcium ferrite slags at 1 473 K and 1 573 K by using $\text{CO}+\text{CO}_2$ gas mixtures.²⁸⁾ Wanibe used oxygen concentration cells involving zirconia solid electrolyte to measure the Fe_xO activities in the Fe_xO – SiO_2 binary system at 1 502 K–1 615 K and in the Fe_xO – CaO – SiO_2 ternary system at 1 560 K.²⁹⁾ The similar measurements with the electrochemical technique were conducted by Bygdén *et al.*,³⁰⁾ Kudo *et al.*,³¹⁾ and Enaka *et al.*³²⁾ Bygdén *et al.* investigated the temperature dependences of the FeO activities in the FeO – CaO – SiO_2 ternary system at 1 473 K–1 623 K.³⁰⁾ Kudo *et al.* carried out the thermodynamic study of the Fe_xO – CaO – SiO_2 ternary slags equilibrating with lead metal in iron crucibles at 1 473 K, 1 523 K, and 1 573 K from the viewpoint of lead smelting processes.³¹⁾ Enaka *et al.* determined the chemical potentials of oxygen within the three-phase assemblies of the Fe_xO – CaO – SiO_2 ternary system and confirmed that their results were consistent with the phase diagram of the CaO – SiO_2 binary system.³²⁾

Figure 2(a) shows the Fe_xO activities in the Fe_xO – CaO – SiO_2 ternary system at 1 573 K by Bodsworth,²⁷⁾ Kudo *et al.*,³¹⁾ and Enaka *et al.*³²⁾ As shown in this figure, the results by Kudo *et al.* are consistent with those by Enaka *et al.* Let us now consider a relation between the iso-activity and liquidus curves. The Gibbs-Duhem equation for the Fe_xO – CaO – SiO_2 pseudo-ternary system under constant temperature and pressure is given by

$$X_{\text{Fe}_x\text{O}}d(\log a_{\text{Fe}_x\text{O}}) + X_{\text{CaO}}d(\log a_{\text{CaO}}) + X_{\text{SiO}_2}d(\log a_{\text{SiO}_2}) = 0 \quad (3)$$

, where X_i is the mole fraction, and a_i is the activity of component i . Along the liquidus line coexisted with CaSiO_3 (line b – c of Fig. 2(b)), the activity of CaSiO_3 is unity. Hence, we have

$$d(\log a_{\text{CaO}}) + d(\log a_{\text{SiO}_2}) = 0 \quad (4)$$

Substitution of Eq. (4) into Eq. (3) leads to Eq. (5).

$$X_{\text{Fe}_x\text{O}}d(\log a_{\text{Fe}_x\text{O}}) + (X_{\text{CaO}} - X_{\text{SiO}_2}) \cdot d(\log a_{\text{CaO}}) = 0 \quad (5)$$

When the CaO/SiO_2 mole ratio is equal to 1, the second term of Eq. (5) can be eliminated.

$$d(\log a_{\text{Fe}_x\text{O}}) = 0 \quad (6)$$

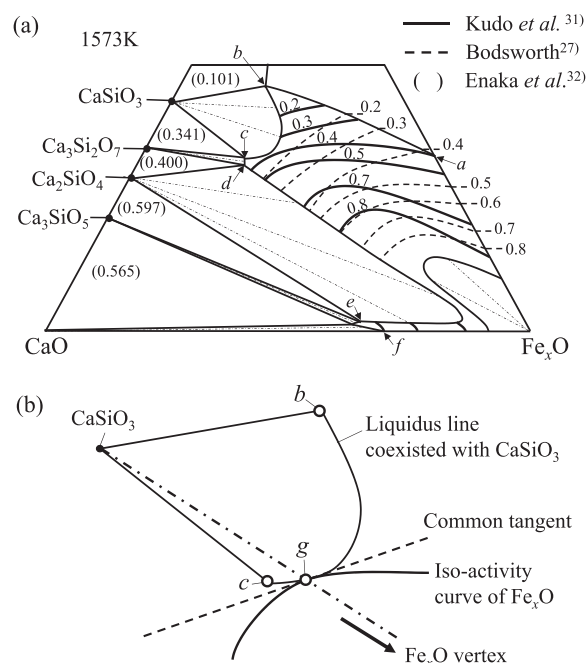


Fig. 2. (a) Fe_xO activities in the Fe_xO – CaO – SiO_2 ternary system at 1 573 K in preceding studies. (Standard state is taken as pure liquid Fe_xO) (b) Schematic relation between iso-activity curve and liquidus line.

Equation (6) indicates that the iso-activity curve of Fe_xO and the liquidus line coexisted with CaSiO_3 would have a common tangent at the intersection point of the liquidus line and the straight line connecting CaSiO_3 and Fe_xO (point g of Fig. 2(b)). As seen in Fig. 2(a) the iso-activity curves illustrated by Kudo *et al.* are considered to be more consistent with Eq. (6) than those by Bodsworth. However, it should be noted here that Kudo *et al.* simultaneously measured the lead solubilities in liquid slags, and the slags used in their study inevitably contained PbO .

Based on the considerations above, it is necessary to remeasure the Fe_xO activities for the accurate understanding of the thermochemical properties in the Fe_xO – CaO – SiO_2 ternary liquid at lower temperature. The purpose of the present study was to reevaluate the iso-activity curves of Fe_xO in the Fe_xO – CaO – SiO_2 ternary system equilibrated with solid iron at 1 573 K. An electrochemical technique was applied to measure the Fe_xO activities in the homogeneous liquid region. Subsequently, the activities of CaO and SiO_2 along liquidus lines were derived by the Gibbs-Duhem equation, and the phosphorus contents in molten iron coexisted with the dephosphorization slags were estimated by using the present results.

2. Experiments

The starting materials for slag samples were Fe , Fe_3O_4 , CaCO_3 , and SiO_2 obtained from Nacalai Tesque, Inc., Kyoto, Japan. Fe and Fe_3O_4 were mixed at a mole ratio of 1:1 and heated in an iron crucible at 1 223 K for 24 hours to obtain Fe_xO ; the resulting sample was submitted for X-ray diffraction analysis to confirm the expected oxide phase only. CaO was prepared by heating CaCO_3 at 1 373 K for 4 hours. SiO_2 was used after dried at 413 K. Then, the slag samples used for this study were prepared by mixing oxides

of Fe_xO , CaO , and SiO_2 . The initial bulk compositions of slag samples are shown in **Table 1**.

The experimental apparatus is schematically shown in **Fig. 3**. An iron crucible of 35 mm o.d., 25 mm i.d. and 100 mm height was charged with 10 g of the slag sample and 25 g of pure silver. Then, the crucible was put into a SiC resistance furnace and heated under a stream of argon purified by silica gel, phosphorus pentoxide, and Mg chips heated at 823 K. Temperature was measured with a Pt-PtRh13 thermocouple and controlled within ± 1 K of the target value with a PID-type temperature regulator.

After the temperature reached 1 573 K, an oxygen sensor was immersed in the liquid silver. The oxygen sensor con-

sisted of a zirconia tube as the solid electrolyte and a two-phase mixture of Mo and MoO_2 as the reference electrode. The zirconia tube of 6 mm o.d., 4 mm i.d. and 50 mm length was closed at one end and stabilized by 9 mol% of magnesia. A molybdenum rod of 3 mm diameter was used as an electrical conductor to the reference electrode. A steel rod of 3 mm diameter soldered to the iron crucible and the liquid silver made electrical contact to the outer electrode of the cell.

The equilibrium oxygen partial pressures between solid Fe and Fe_xO in slag, p_{O_2} , can be determined by using stable values for the open-circuit electromotive forces (*emf*) of the oxygen sensors, E . The relation between p_{O_2} and E is expressed by.³³⁾

$$E = \frac{RT}{F} \ln \frac{p_{\text{O}_2(\text{ref})}^{1/4} + p_e^{1/4}}{p_{\text{O}_2}^{1/4} + p_e^{1/4}} + E_t \dots\dots\dots (7)$$

, where R is the gas constant, F is the Faraday constant, T is temperature, $p_{\text{O}_2(\text{ref})}$ is the oxygen partial pressure at the reference electrode, p_e is the oxygen partial pressure at which the ionic and the n -type conductivities are equal, and E_t is thermo-*emf* between Mo(positive) and Fe(negative). Values for these parameters in this study have been reported as

$$\log[p_{\text{O}_2(\text{ref})} / \text{atm}] = 8.84 - 30\,100 / (T / \text{K})^{34)} \dots\dots\dots (8)$$

$$\log[p_e / \text{atm}] = 20.40 - 64\,500 / (T / \text{K})^{35)} \dots\dots\dots (9)$$

$$E_t / \text{mV} = -14.69 + 0.0227(T / \text{K})^{36)} \dots\dots\dots (10)$$

When the standard state for Fe_xO is taken as pure non-stoichiometric solid Fe_xO in equilibrium with pure solid Fe, the activity of Fe_xO in slag coexisted with pure solid Fe can be calculated as follows.

$$a_{\text{Fe}_x\text{O}(\text{s})} = \left(\frac{p_{\text{O}_2}}{p^{\circ}_{\text{O}_2(\text{s})}} \right)^{1/2} \dots\dots\dots (11)$$

, where $p^{\circ}_{\text{O}_2(\text{s})}$ represents the equilibrium oxygen partial pressure between pure solid Fe and pure solid Fe_xO , which is given by

$$\log[p^{\circ}_{\text{O}_2(\text{s})} / \text{atm}] = 6.71 - 27\,400 / (T / \text{K})^{36)} \dots\dots\dots (12)$$

Similarly, when the standard state for Fe_xO is taken as pure non-stoichiometric liquid Fe_xO in equilibrium with pure solid Fe, the activity of Fe_xO can be obtained as follows.

$$a_{\text{Fe}_x\text{O}(\text{l})} = \left(\frac{p_{\text{O}_2}}{p^{\circ}_{\text{O}_2(\text{l})}} \right)^{1/2} \dots\dots\dots (13)$$

, where $p^{\circ}_{\text{O}_2(\text{l})}$ is the equilibrium oxygen partial pressure between pure solid Fe and pure liquid Fe_xO , which is reported by

$$\log[p^{\circ}_{\text{O}_2(\text{l})} / \text{atm}] = 4.39 - 23\,500 / (T / \text{K})^{37)} \dots\dots\dots (14)$$

After the stable value for *emf* was measured, the slag sample was collected by immersing a Fe rod into the crucible. The rod with the molten slag was pulled out of the furnace and cooled rapidly in air. Then, about 1 g of Fe_xO was added into slag. During an experimental run, the *emf* measurements, collecting samples, and adding pure Fe_xO were repeated at a fixed CaO/SiO_2 ratio.

Table 1. Initial bulk compositions of slag samples.

No.	(mass% Fe_xO)	(mass% CaO)	(mass% SiO_2)	(mass% CaO) / (mass% SiO_2)
1	22.0	39.0	39.0	50/50
2	45.0	11.0	44.0	20/80
3	60.0	0.0	40.0	0/100
4	30.0	21.0	49.0	30/70
5	60.0	0.0	40.0	0/100
6	26.0	29.6	44.4	40/60
7	65.0	33.6	1.4	96/4
8	30.0	28.0	42.0	40/60
9	55.0	2.3	42.8	5/95

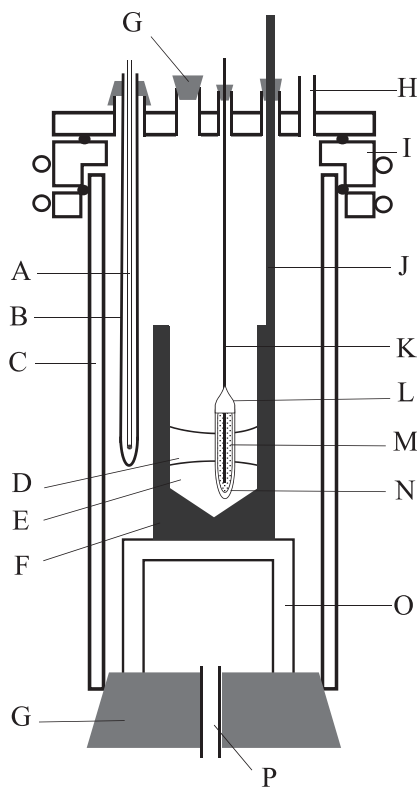


Fig. 3. Experimental apparatus. (A) Pt-PtRh13 thermocouple, (B) Alumina sheath, (C) Mullite reaction tube, (D) Slag, (E) Liquid Ag, (F) Iron crucible, (G) Rubber stopper, (H) Gas outlet, (I) Water-cooled brass flange, (J) Steel rod, (K) Mo rod, (L) Zirconia cement, (M) Mo+ MoO_2 reference electrode, (N) ZrO_2 (9 mol% MgO) solid electrolyte tube, (O) Alumina pedestal, (P) Gas inlet.

The collected samples were removed from the Fe rod and submitted for chemical analyses. The concentrations of total Fe in slags, ($\text{mass}\%\text{Fe}^{2+}$) + ($\text{mass}\%\text{Fe}^{3+}$), were determined by the inductively coupled plasma (ICP) spectrometer, and those of divalent Fe, ($\text{mass}\%\text{Fe}^{2+}$), were determined by the oxidation titrations with $\text{K}_2\text{Cr}_2\text{O}_7$. The concentrations of Fe_xO in slags can be obtained by

$$\begin{aligned} (\text{mass}\%\text{Fe}_x\text{O}) &= (\text{mass}\%\text{FeO}) + (\text{mass}\%\text{FeO}_{1.5}) \\ &= \frac{M_{\text{FeO}}}{M_{\text{Fe}}}(\text{mass}\%\text{Fe}^{2+}) + \frac{M_{\text{FeO}_{1.5}}}{M_{\text{Fe}}}(\text{mass}\%\text{Fe}^{3+}) \quad \dots (15) \end{aligned}$$

, where M_i denotes the molar mass of component i . The concentrations of CaO and SiO_2 are calculated from the CaO/

Table 2. Experimental results at 1 573 K.

No.	$\frac{(\text{mass}\%\text{CaO})}{(\text{mass}\%\text{SiO}_2)}$	mass%				E/mV	$\log(p_{\text{O}_2} / \text{atm})$	$a_{\text{Fe}_x\text{O}}(\text{s})^*$	$a_{\text{Fe}_x\text{O}}(\text{l})^{**}$
		FeO	$\text{FeO}_{1.5}$	CaO	SiO_2				
1-1	50/50	29.0	3.3	33.9	33.9	73.75 ± 1.25	-10.97	0.727	0.616
1-2		37.5	5.2	28.6	28.6	68.40 ± 0.05	-10.90	0.787	0.666
1-3		46.4	6.4	23.6	23.6	58.55 ± 0.25	-10.77	0.911	0.772
1-4		48.8	7.4	21.9	21.9	57.40 ± 0.20	-10.76	0.926	0.785
2-1	20/80	57.0	4.2	7.8	31.0	66.02 ± 0.10	-10.87	0.816	0.692
2-2		58.5	3.9	7.5	30.1	64.20 ± 0.20	-10.85	0.838	0.709
2-3		59.8	6.2	6.8	27.3	54.41 ± 0.05	-10.72	0.968	0.821
2-4		63.6	7.1	5.9	23.5	54.27 ± 0.03	-10.72	0.970	0.823
3-1	0/100	59.3	0.8	0.0	39.9	103.40 ± 0.05	-11.35	0.469	0.397
3-2		61.9	1.3	0.0	36.8	88.15 ± 0.05	-11.16	0.588	0.498
3-3		64.1	3.4	0.0	32.5	74.52 ± 0.04	-10.98	0.719	0.609
3-4		64.4	6.9	0.0	28.7	63.50 ± 0.05	-10.84	0.847	0.717
4-1	30/70	54.7	6.7	11.6	27.0	64.03 ± 0.05	-10.85	0.840	0.711
4-2		56.7	6.0	11.2	26.1	62.25 ± 0.05	-10.82	0.862	0.730
4-3		57.5	7.6	10.5	24.4	57.96 ± 0.06	-10.77	0.919	0.778
4-4		60.5	8.3	9.4	21.9	56.38 ± 0.05	-10.75	0.941	0.797
4-5		60.2	8.6	9.3	21.8	56.00 ± 0.05	-10.74	0.946	0.801
4-6		63.4	9.6	8.1	18.9	53.30 ± 0.06	-10.71	0.984	0.834
5-1	0/100	56.7	3.0	0.0	40.2	102.87 ± 0.03	-11.34	0.473	0.400
5-2		58.8	5.2	0.0	36.0	86.84 ± 0.10	-11.14	0.599	0.507
5-3		62.6	6.3	0.0	31.1	72.12 ± 0.05	-10.95	0.745	0.631
5-4		64.8	7.3	0.0	27.8	65.91 ± 0.05	-10.87	0.817	0.692
5-5		66.4	7.5	0.0	26.2	60.72 ± 0.05	-10.80	0.882	0.747
5-6		65.3	11.8	0.0	22.9	54.56 ± 0.15	-10.72	0.966	0.818
5-7		71.3	11.2	0.0	17.5	52.72 ± 0.03	-10.70	0.993	0.841
6-1	40/60	29.7	2.5	27.1	40.7	110.67 ± 0.05	-11.45	0.421	0.357
6-2		39.5	4.4	22.4	33.6	72.05 ± 0.05	-10.95	0.746	0.632
6-3		46.0	5.9	19.3	28.9	65.26 ± 0.10	-10.86	0.825	0.698
6-4		48.4	9.0	17.0	25.6	56.15 ± 0.10	-10.74	0.944	0.799
6-5		56.4	12.0	12.6	18.9	54.23 ± 0.05	-10.72	0.971	0.822
7-1	96/4	46.5	21.9	30.4	1.3	85.72 ± 0.05	-11.12	0.609	0.516
7-2		51.9	21.2	25.8	1.1	66.99 ± 0.10	-10.88	0.804	0.681
7-3		61.1	21.3	16.9	0.7	57.26 ± 0.05	-10.76	0.928	0.786
8-1	40/60	33.4	6.4	24.1	36.1	90.45 ± 0.05	-11.19	0.566	0.479
8-2		41.8	6.0	20.9	31.4	74.57 ± 0.05	-10.98	0.716	0.606
9-1	5/95	51.3	6.2	2.1	40.4	107.28 ± 0.05	-11.41	0.441	0.373
9-2		57.5	4.9	1.9	35.8	90.76 ± 0.05	-11.19	0.563	0.477
9-3		59.8	6.7	1.7	31.8	76.60 ± 0.05	-11.01	0.695	0.589
9-4		60.4	9.6	1.5	28.6	68.44 ± 0.05	-10.91	0.784	0.664
9-5		61.6	8.4	1.5	28.5	64.09 ± 0.05	-10.85	0.836	0.708
9-6		63.6	12.1	1.2	23.1	58.29 ± 0.05	-10.77	0.911	0.772
9-7		64.7	13.1	1.1	21.1	54.20 ± 0.05	-10.72	0.968	0.820

* The standard state is taken as pure non-stoichiometric solid Fe_xO in equilibrium with pure solid Fe.

** The standard state is taken as pure non-stoichiometric liquid Fe_xO in equilibrium with pure solid Fe.

SiO₂ mass ratio of the initial bulk compositions in Table 1.

Supposing Fe_xO consists of stoichiometric FeO and FeO_{1.5}, we have

$$n_{\text{Fe}_x\text{O}}\text{Fe}_x\text{O} = n_{\text{FeO}}\text{FeO} + n_{\text{FeO}_{1.5}}\text{FeO}_{1.5} \quad (16)$$

, where n_i is the number of moles of component i . The material balances of iron and oxygen are expressed as follows.

$$\text{Fe} : xn_{\text{Fe}_x\text{O}} = n_{\text{FeO}} + n_{\text{FeO}_{1.5}} \quad (17)$$

$$\text{O} : n_{\text{Fe}_x\text{O}} = n_{\text{FeO}} + 1.5n_{\text{FeO}_{1.5}} \quad (18)$$

Therefore, the mole fractions of Fe_xO in the Fe_xO–CaO–SiO₂ ternary system can be calculated by

$$X_{\text{Fe}_x\text{O}} = \frac{n_{\text{FeO}} + 1.5n_{\text{FeO}_{1.5}}}{n_{\text{FeO}} + 1.5n_{\text{FeO}_{1.5}} + n_{\text{CaO}} + n_{\text{SiO}_2}} \quad (19)$$

3. Experimental Results and Discussion

3.1. Electrochemical Measurements

Table 2 summarizes the experimental results in this study, and the measured compositions are plotted on the iso-thermal section of the Fe_xO–CaO–SiO₂ ternary system at 1 573 K in Fig. 1. As seen in this figure, all the compositions used in this study were in the homogeneous liquid region. Figure 4 shows the Fe_xO activities at 1 573 K in the present study plotted against the mole fractions of Fe_xO. At a given CaO/SiO₂ ratio, the Fe_xO activities increased as the mole fractions of Fe_xO increased, and the values for $a_{\text{Fe}_x\text{O}}(\text{s})$ approached unity toward the liquidus compositions saturated with solid Fe_xO.

For comparison, the present results of (mass%CaO)/(mass%SiO₂)=50/50 and the literature data at 1 573 K^{27,31,32)}

are shown in Fig. 5. The oxygen potential in the three-phase region of CaSiO₃ + Ca₃Si₂O₇ + Liquid measured by Enaka *et al.*³²⁾ was converted to the activity of Fe_xO by using Eqs. (11) to (14). The present results were compatible with the results by Kudo *et al.*³¹⁾ and Enaka *et al.*³²⁾ rather than those by Bodsworth.²⁷⁾

Figure 6(a) shows the iso-activity curves of Fe_xO at 1 573 K derived from the present results and the literature data^{26,28,31,32)} excluding those by Bodsworth.²⁷⁾ The Fe_xO activities had maxima when the CaO/SiO₂ ratio was close to 1. Similar behavior could be observed at other temperatures.^{9,17,18,25)} Figure 6(b) shows the enlarged view around the liquidus line coexisted with CaSiO₃. As seen in this figure, it was possible to illustrate the iso-activity curve of Fe_xO that satisfied Eq. (6); the iso-activity curve and the liquidus line coexisted with CaSiO₃ had a common tangent at point g. This indicated that the present measurements and the results reported by Kudo *et al.*³¹⁾ and Enaka *et al.*³²⁾ were considered to be more reliable than those by Bodsworth.²⁷⁾

3.2. Activities of CaO and SiO₂ by Gibbs-Duhem Equation

Figure 7(b) shows the Fe_xO activities along liquidus lines a – f as a function of $X_{\text{CaO}}/(X_{\text{CaO}} + X_{\text{SiO}_2})$, and the activities of CaO and SiO₂ along these liquidus lines can be derived by using the Gibbs-Duhem equation. On the liquidus line coexisted with Ca₂SiO₄, the activity of Ca₂SiO₄ is unity. Hence, the formation reaction of Ca₂SiO₄ from CaO and SiO₂ is expressed as follows.

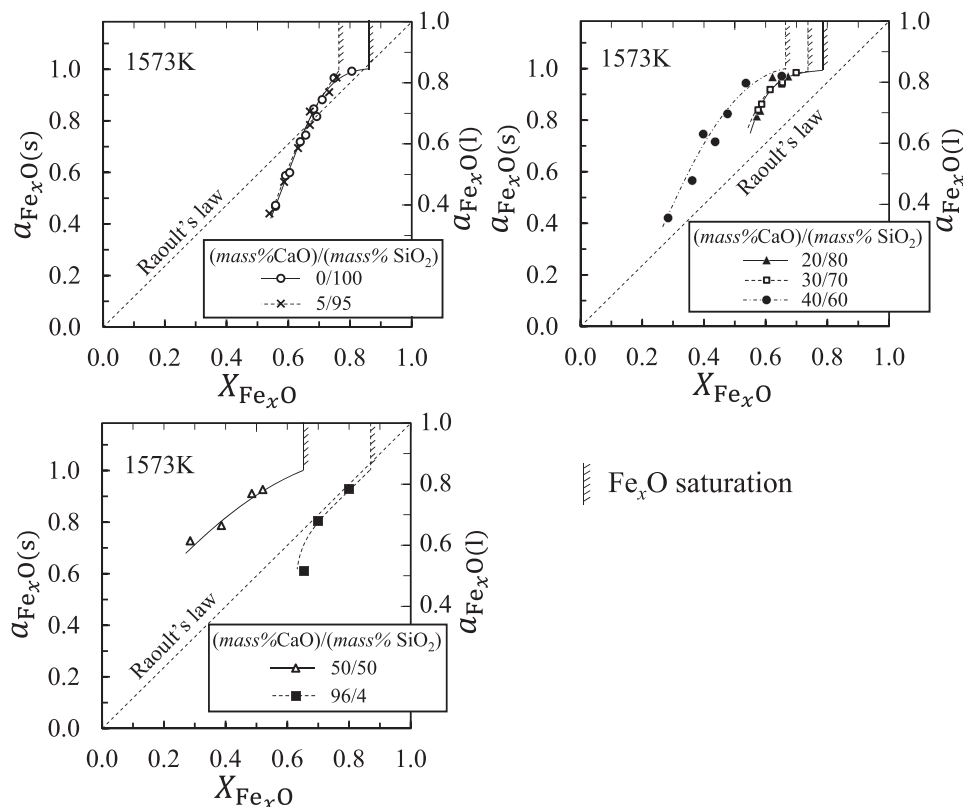
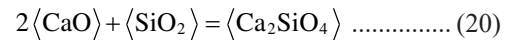


Fig. 4. Fe_xO activities plotted against mole fractions of Fe_xO at 1 573 K in the present study.

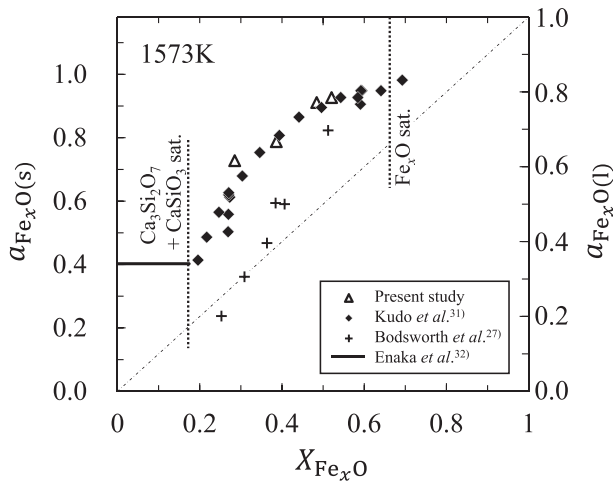


Fig. 5. Comparison of the present results with the literature data of $(\text{mass}\%\text{CaO})/(\text{mass}\%\text{SiO}_2) \approx 50/50$.

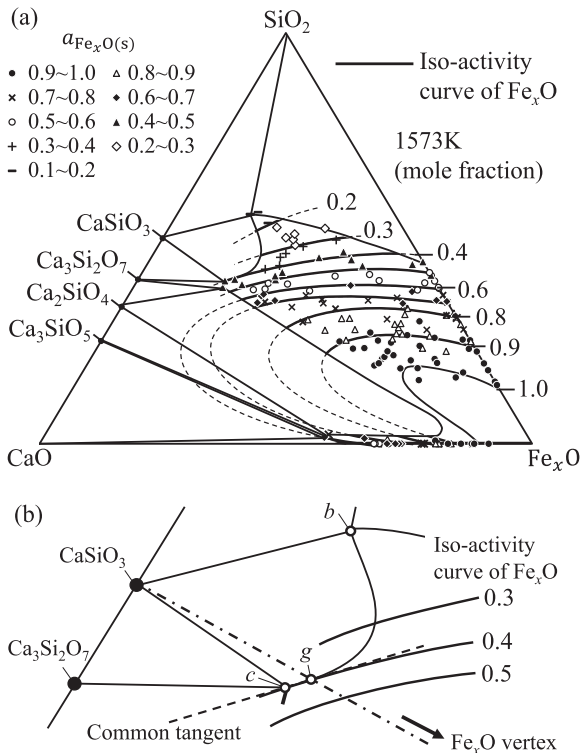


Fig. 6. (a) Iso-activity curve of Fe_xO in the Fe_xO - CaO - SiO_2 ternary system at 1573 K. (b) Enlarged view of the iso-activity curve of Fe_xO around the liquidus line coexisted with CaSiO_3 (Standard state is taken as pure solid Fe_xO).

$$\log K(20) = -2\log a_{\text{CaO}} - \log a_{\text{SiO}_2} = 4.79 \quad (\text{at } 1573 \text{ K})^{38,39} \quad (21)$$

, where the standard states for CaO and SiO_2 are taken as pure solid CaO and SiO_2 , respectively. By differentiating Eq. (21), we have

$$2d(\log a_{\text{CaO}}) + d(\log a_{\text{SiO}_2}) = 0 \quad (22)$$

Using Eq. (22), Eq. (3) can be rewritten as

$$d(\log a_{\text{CaO}}) = \frac{X_{\text{Fe}_x\text{O}}}{2X_{\text{SiO}_2} - X_{\text{CaO}}} d(\log a_{\text{Fe}_x\text{O}}) \quad (23)$$

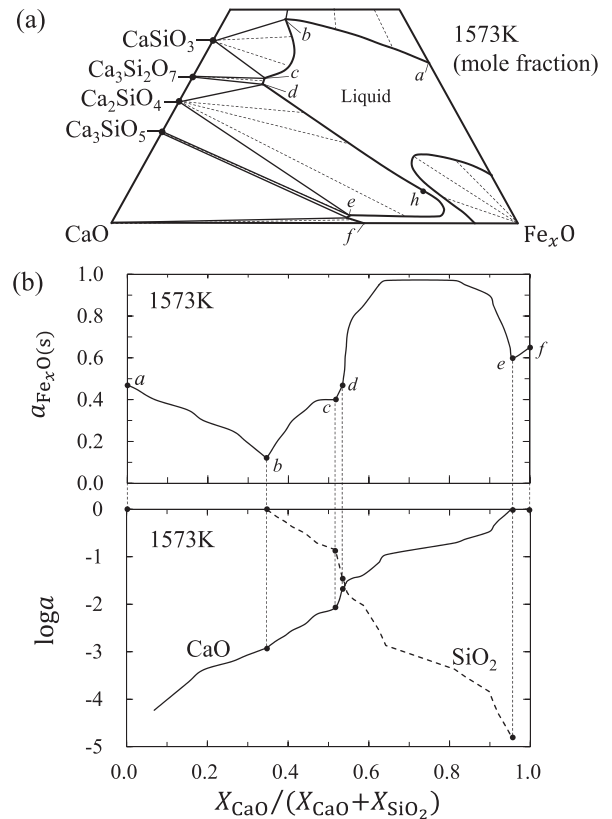


Fig. 7. (a) Phase diagram of the Fe_xO - CaO - SiO_2 ternary system at 1573 K. (b) Fe_xO , CaO , and SiO_2 activities along the liquidus lines plotted against $X_{\text{CaO}} / (X_{\text{CaO}} + X_{\text{SiO}_2})$.

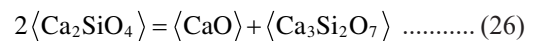
Figure 8 shows $X_{\text{Fe}_x\text{O}} / (2X_{\text{SiO}_2} - X_{\text{CaO}})$ plotted against $\log a_{\text{Fe}_x\text{O}}$ along liquidus line $d-e$. As shown in Fig. 8, $X_{\text{Fe}_x\text{O}} / (2X_{\text{SiO}_2} - X_{\text{CaO}})$ diverges when the CaO/SiO_2 mole ratio equals 2 (point h of Fig. 7(a)). Therefore, the CaO activities are calculated by integrating Eq. (23) from both ends of liquidus line $d-e$ for point h .

$$\log a_{\text{CaO}} = \log a_{\text{CaO}}(d) + \int_d^h \frac{X_{\text{Fe}_x\text{O}}}{2X_{\text{SiO}_2} - X_{\text{CaO}}} d(\log a_{\text{Fe}_x\text{O}}) \quad (\text{line } d-h) \quad (24)$$

$$\log a_{\text{CaO}} = \log a_{\text{CaO}}(e) + \int_e^h \frac{X_{\text{Fe}_x\text{O}}}{2X_{\text{SiO}_2} - X_{\text{CaO}}} d(\log a_{\text{Fe}_x\text{O}}) \quad (\text{line } e-h) \quad (25)$$

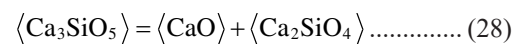
, where $a_{\text{CaO}}(d)$ and $a_{\text{CaO}}(e)$ correspond to the CaO activities in the three-phase regions of $\text{Ca}_2\text{SiO}_4 + \text{Ca}_3\text{Si}_2\text{O}_7 + \text{Liquid}$ and $\text{Ca}_2\text{SiO}_4 + \text{Ca}_3\text{SiO}_5 + \text{Liquid}$, respectively. The values for them can be obtained by the following reactions.

region of $\text{Ca}_2\text{SiO}_4 + \text{Ca}_3\text{Si}_2\text{O}_7 + \text{Liquid}$



$$\log K(26) = \log a_{\text{CaO}}(d) = -1.66 \quad (\text{at } 1573 \text{ K})^{38,39} \quad (27)$$

region of $\text{Ca}_2\text{SiO}_4 + \text{Ca}_3\text{SiO}_5 + \text{Liquid}$



$$\log K(28) = \log a_{\text{CaO}}(e) = -0.02 \quad (\text{at } 1573 \text{ K})^{38,39} \quad (29)$$

The SiO_2 activities can be calculated by Eq. (21), and the same calculations are conducted along the liquidus lines

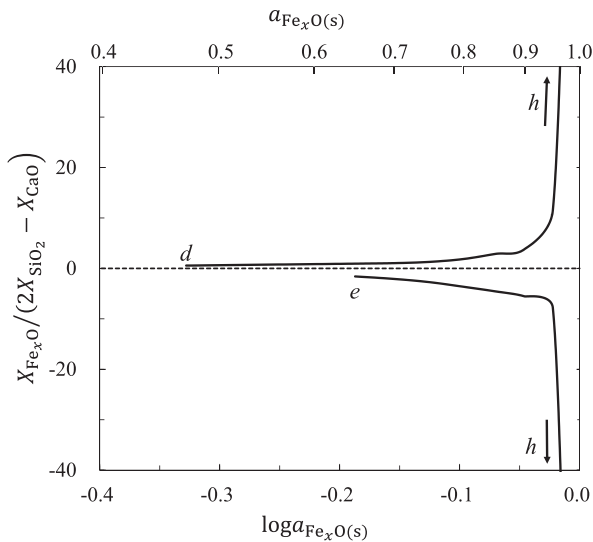


Fig. 8. Relation between $X_{\text{FeO}} / (2X_{\text{SiO}_2} - X_{\text{CaO}})$ and $\log a_{\text{FeO(s)}}$.

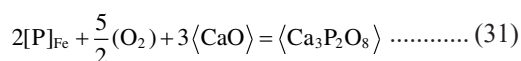
coexisted with CaSiO_3 and SiO_2 . Figure 7(b) shows $\log a_{\text{CaO}}$ and $\log a_{\text{SiO}_2}$ plotted against $X_{\text{CaO}} / (X_{\text{CaO}} + X_{\text{SiO}_2})$. The CaO activity increased and the SiO_2 activity decreased monotonically as $X_{\text{CaO}} / (X_{\text{CaO}} + X_{\text{SiO}_2})$ increased, and they changed drastically on the liquidus line coexisting with Ca_2SiO_4 .

3.3. Estimation of Phosphorus Concentration in Molten Iron

Phosphorus contents in molten iron could be estimated by using the present results. It has been reported that the phosphorus in the slag was condensed into the $\text{Ca}_2\text{SiO}_4\text{--Ca}_3\text{P}_2\text{O}_8$ solid solution, and the phosphorus distribution ratio between the $\text{Ca}_2\text{SiO}_4\text{--Ca}_3\text{P}_2\text{O}_8$ solid solution and the liquid slag, $L_P^{\text{SS/L}}$, increased with an increase in the Fe_xO concentration in liquid slag, $\{\text{mass}\%\text{Fe}_x\text{O}\}_L$.^{40–43)}

$$\log L_P^{\text{SS/L}} \equiv \log \frac{(\text{mass}\%\text{P}_2\text{O}_5)_{\text{SS}}}{\{\text{mass}\%\text{P}_2\text{O}_5\}_L} \\ = 0.023 \times \{\text{mass}\%\text{Fe}_x\text{O}\}_L - 0.09^{43)} \quad \dots (30) \\ (15 < \{\text{mass}\%\text{Fe}_x\text{O}\}_L < 80)$$

In Eq. (30), $(\text{mass}\%\text{P}_2\text{O}_5)_{\text{SS}}$ and $\{\text{mass}\%\text{P}_2\text{O}_5\}_L$ denote the P_2O_5 concentrations in the solid solution and the liquid slag, respectively. The value of $L_P^{\text{SS/L}}$ was greater than 10 at the composition of $\{\text{mass}\%\text{Fe}_x\text{O}\}_L > 50$, and then the concentrations of P_2O_5 in the liquid slag were so low that they were ignored. Namely, it could be assumed that the $\text{Ca}_2\text{SiO}_4\text{--Ca}_3\text{P}_2\text{O}_8$ solid solution coexisted with the $\text{Fe}_x\text{O}\text{--CaO--SiO}_2$ ternary liquid slag. As described later, the compositions of the solid solutions were fixed in this discussion, and the Ca_2SiO_4 activities were assumed to be constant along the liquidus line coexisting with the $\text{Ca}_2\text{SiO}_4\text{--Ca}_3\text{P}_2\text{O}_8$ solid solution. Therefore, the CaO and Fe_xO activities in the slags were equal to those in the $\text{Fe}_x\text{O}\text{--CaO--SiO}_2$ ternary liquid. In this case, the dephosphorization reaction can be expressed by



$$\log K(31) = \log \frac{a_{\text{Ca}_3\text{P}_2\text{O}_8}}{h_{\text{P}}^2 \cdot p_{\text{O}_2}^{5/2} \cdot a_{\text{CaO}}^3} = 35.59 \quad (\text{at } 1573 \text{ K})^{44,45)} \quad \dots (32)$$

, where a_i is the activity of component i , and h_i is the Henrian activity of component i . The Gibbs energy change in the formation reaction of $\text{Ca}_3\text{P}_2\text{O}_8$ has been reported by several researchers.^{45–49)} However, there was a maximum difference of $150 \text{ kJ}\cdot\text{mol}^{-1}$ among their reported values, and this was equivalent to about two digits difference in the phosphorus concentration in molten iron calculated later. In this discussion, the latest value reported by Nagai *et al.*⁴⁵⁾ was used.

For the $\text{Ca}_2\text{SiO}_4\text{--Ca}_3\text{P}_2\text{O}_8$ solid solution, a sub-regular solution model has been suggested on the assumption that $(1/2)\text{Ca}_3\text{P}_2\text{O}_8$ would replace with Ca_2SiO_4 .⁵⁰⁾ The substitution ratio of $(1/2)\text{Ca}_3\text{P}_2\text{O}_8$ and Ca_2SiO_4 in the solid solution was defined by

$$Y \equiv \frac{2n_{\text{Ca}_3\text{P}_2\text{O}_8}}{n_{\text{Ca}_2\text{SiO}_4} + 2n_{\text{Ca}_3\text{P}_2\text{O}_8}} \quad \dots (33)$$

In order to compare with the preceding studies in which the P_2O_5 contents in the solid solutions were between 6 mass% and 15 mass%, hereafter, the value for Y was set to be 0.3 corresponding to $(\text{mass}\%\text{P}_2\text{O}_5)_{\text{SS}} = 13$. The activity of $\text{Ca}_3\text{P}_2\text{O}_8$ in the solid solution was given as

$$\log a_{\text{Ca}_3\text{P}_2\text{O}_8} = 2 \log Y - 9.96(1-Y)^3 + 4.52(1-Y)^2 \quad (\text{at } 1573 \text{ K}) \\ = -2.25 \quad (Y=0.3) \quad \dots (34)$$

The Henrian activity of phosphorus in carbon-saturated Fe–C–P liquid alloy is given by⁵¹⁾

$$\log h_{\text{P}} = \log [\text{mass}\%\text{P}]_{\text{Fe}} + e_{\text{P}}^{\text{C}} [\text{mass}\%\text{C}_{\text{sat}}]_{\text{Fe}} \\ = \log [\text{mass}\%\text{P}]_{\text{Fe}} - 386 / (T / \text{K}) + 0.891 \quad \dots (35)$$

, where $[\text{mass}\%\text{P}]_{\text{Fe}}$ and $[\text{mass}\%\text{C}_{\text{sat}}]_{\text{Fe}}$ represent the mass concentrations of phosphorus and carbon, respectively, in molten iron saturated with the solid carbon, and e_{P}^{C} is the first order interaction coefficient in liquid iron. From Eqs. (32) through (35), $[\text{mass}\%\text{P}]_{\text{Fe}}$ is given by

$$\log [\text{mass}\%\text{P}]_{\text{Fe}} = 16.03 - \frac{5}{4} \log (p_{\text{O}_2} / \text{atm}) - \frac{3}{2} \log a_{\text{CaO}} \quad \dots (36)$$

Equation (36) indicates that $[\text{mass}\%\text{P}]_{\text{Fe}}$ can be calculated by using the CaO activity in Fig. 7(b) and the oxygen partial pressure. Figure 9 shows $\log [\text{mass}\%\text{P}]_{\text{Fe}}$ calculated by Eq. (36) plotted against $X_{\text{CaO}} / (X_{\text{CaO}} + X_{\text{SiO}_2})$. The solid line represents $\log [\text{mass}\%\text{P}]_{\text{Fe}}$ calculated when the oxygen partial pressure is determined by the equilibrium between Fe_xO in slag and metallic iron. The equilibrium phosphorus concentrations measured in the laboratory investigations^{52–54)} are also plotted in Fig. 9. Although, as already mentioned above, the calculated phosphorus contents had about two digits errors due to the uncertainty in the thermochemical data, the calculated values were agreed well with the measured ones.

Moreover, in Fig. 9, square plots indicate the phosphorus contents attainable with actual operating slags.^{55–57)} The discrepancies between square plots and the solid line are attributed to the presence of carbon. In the actual operations, the

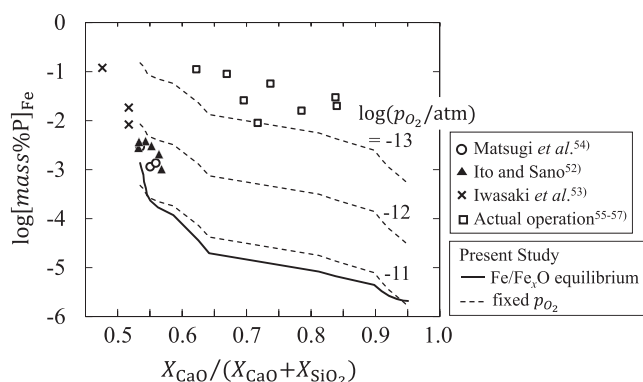


Fig. 9. $\log[\text{mass}\%P]_{\text{Fe}}$ plotted against $X_{\text{CaO}} / (X_{\text{CaO}} + X_{\text{SiO}_2})$.

oxygen partial pressure is considered to take values between the Fe/Fe_xO equilibrium of $\log(p_{\text{O}_2}/\text{atm}) \approx -11$ and the C/CO equilibrium of $\log(p_{\text{O}_2}/\text{atm}) \approx -17$. The broken lines in Fig. 9 are the calculated results at $\log(p_{\text{O}_2}/\text{atm}) = -11$, -12 , and -13 , respectively. The reached phosphorus contents in actual operations could be explained by assuming $\log(p_{\text{O}_2}/\text{atm}) \approx -13$.

It became possible to evaluate the dephosphorization abilities of the heterogeneous slags since the Fe_xO and CaO activities were determined in this study. The determination of the P₂O₅ activity along the liquidus lines would be our future work for more accurate understanding.

4. Conclusion

This study was aimed at reevaluating the Fe_xO activities in the Fe_xO–CaO–SiO₂ ternary system equilibrated with solid iron at 1 573 K. The electrochemical technique involving the stabilized zirconia solid electrolyte was conducted to measure the Fe_xO activities in the homogeneous liquid region. The present results were compatible with the literature data reported by Kudo *et al.*³¹⁾ and Enaka *et al.*,³²⁾ and the iso-activity curves of Fe_xO derived were consistent with the phase diagram. Subsequently, the CaO and SiO₂ activities along the liquidus lines were calculated by the Gibbs-Duhem equation. By using the Fe_xO and CaO activities, the phosphorus contents in molten iron in equilibrium with two-phase coexisting slags of the Ca₂SiO₄–Ca₃P₂O₈ solid solution and the Fe_xO–CaO–SiO₂ liquid were estimated. The present results made it possible to evaluate the dephosphorization abilities of the heterogeneous slags.

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