

Title	Activities of FexO in Na ₂ O-Al ₂ O ₃ -SiO ₂ -FexO Homogeneous Liquid Slags at 1673 K
Author(s)	Hasegawa, M.; Hayashi, T.; Sasaki, T.; Iwase, M.
Citation	High Temperature Materials and Processes (2012), 31(4-5): 415-420
Issue Date	2012-01-30
URL	http://hdl.handle.net/2433/182960
Right	© 2012 by Walter de Gruyter
Type	Journal Article
Textversion	publisher

M. Hasegawa*, T. Hayashi, T. Sasaki and M. Iwase

Activities of Fe_xO in $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{Fe}_x\text{O}$ Homogeneous Liquid Slags at 1673 K

Abstract: Electrochemical measurements of the solid-oxide galvanic cell of the type $\text{Mo}/\text{Mo} + \text{MoO}_2/\text{ZrO}_2(\text{MgO})/\text{Fe} + \{\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{Fe}_x\text{O}\}$ slag/ Ag/Fe were conducted at 1673 K in order to obtain the activities of Fe_xO in $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{Fe}_x\text{O}$ system. The iso-activity curves for Fe_xO at 1673 K were determined for $\text{Na}_2\text{O}-(\text{Al}_2\text{O}_3 + \text{SiO}_2)-\text{Fe}_x\text{O}$ pseudo-ternary slags with an $\text{Al}_2\text{O}_3/\text{SiO}_2$ molar ratio of 33/67.

Keywords: activity, ferrous oxide, fluidizer

PACS® (2010). 82.60.-s

*Corresponding author: M. Hasegawa: Department of Energy Science and Technology, Kyoto University, Kyoto, 606-8501, Japan
E-mail: hasegawa@energy.kyoto-u.ac.jp

T. Hayashi: Department of Energy Science and Technology, Kyoto University, Kyoto, 606-8501, Japan

T. Sasaki: Department of Energy Science and Technology, Kyoto University, Kyoto, 606-8501, Japan

M. Iwase: Department of Energy Science and Technology, Kyoto University, Kyoto, 606-8501, Japan

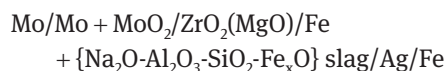
1 Introduction

In the steelmaking industries, fluorspar, CaF_2 , is one of fluxes most widely used to lower the melting temperature of slags, to decrease the slag viscosities, and to increase the rate of lime dissolution into slags. However, there is a strong incentive to explore suitable substitutes for fluorspar, which causes emission of hazardous fluoride species. As such alternative reagents to replace fluorspar, attention is focused on nepheline and/or nepheline syenite. The former corresponds to solid solutions between $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ ($= \text{NaAlSiO}_4$) and $\text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ ($= \text{KAlSiO}_4$), while the later is one of the natural resources which contain nepheline together with potash feldspar ($\text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2 = \text{KAlSi}_3\text{O}_8$) and albite ($\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2 = \text{NaAlSi}_3\text{O}_8$).

During a course of thermochemical studies on nepheline or nepheline syenite as an alternative fluidizer to replace fluorspar in steelmaking slags, it became neces-

sary to determine the activities of Fe_xO within nepheline-containing slags. By employing electrochemical technique involving stabilized zirconia, the Fe_xO activities in CaO -nepheline- Fe_xO melts were determined in the previous study /1/. The experimental results concluded that substituting nepheline of a particular composition, *i.e.*, $(\text{Na}_{3/4}\text{K}_{1/4})_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$, for CaO raised the Fe_xO activities.

In the present study, the activity measurements were extended to liquid $\{\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{Fe}_x\text{O}\}$ slags to aim at clarifying the influence of molar ratios of Na_2O to $(\text{Al}_2\text{O}_3 + \text{SiO}_2)$ upon Fe_xO activities. The electrochemical cell used in this study can be expressed as



2 Experimental aspects

The experimental apparatus is illustrated schematically in Figure 1. An iron crucible was charged with about 35-g of pure silver and 20- to 30-g of slags, and heated to 1673 K under a stream of purified argon inside a SiC resistance furnace. The argon gas was supplied by Daiwa-yozai Co., Osaka, Japan. The commercial argon gas was purified using a gas purification train, which consisted of silica-gel, phosphorus pentoxide and magnesium chips held at 823 K. The electrochemical oxygen probe, $\text{Mo}/\text{Mo} + \text{MoO}_2/\text{ZrO}_2(\text{MgO})$, consisted of a MgO -stabilized zirconia tube and a two-phase mixture of $\text{Mo} + \text{MoO}_2$. The zirconia tubes closed at one end used in the present study had an inner diameter of 4 mm, an outer diameter of 6 mm and a length of 50 mm supplied by Nikkato Co., Osaka, Japan. Earlier experiments have shown that the electrolyte tubes from this supplier had satisfactory resistance to even Fe_xO and Na_2O -containing liquid slags /1-7/. A molybdenum rod of 3-mm diameter was used as an electrical lead to the reference electrode, which consisted of four parts Mo and one part MoO_2 by weight. 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 use of dissimilar electrical connectors required a correction for the thermo-electromotive force of the steel-molybdenum couple /4/.

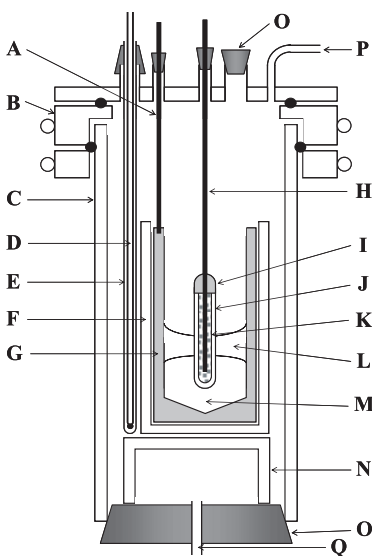


Fig. 1: Schematic diagram of the experimental apparatus. (A) iron rod, (B) water-cooled brass flange, (C) mullite reaction tube, (D) Pt-PtRh13 thermocouple, (E) alumina sheath, (F) alumina crucible, (G) iron crucible, (H) molybdenum rod, (I) zirconia cement, (J) $\text{ZrO}_2(\text{MgO})$ solid electrolyte tube, (K) $\text{Mo} + \text{MoO}_2$ reference electrode, (L) slag, (M) liquid silver, (N) alumina pedestal, (O) rubber stopper, (P) gas outlet, (Q) gas inlet.

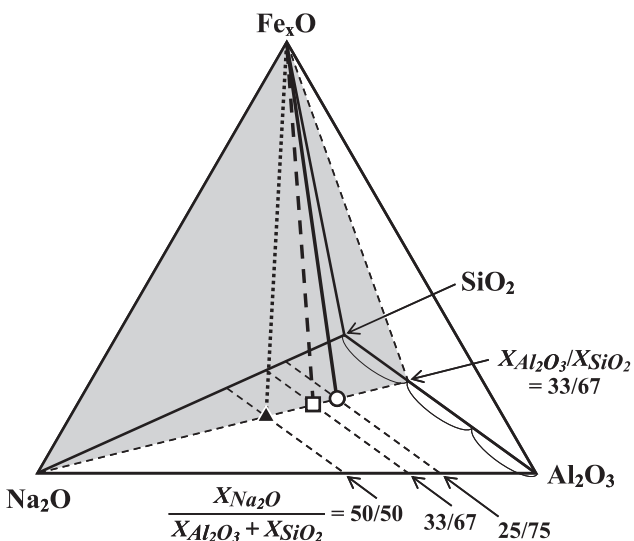


Fig. 2: Composition tetrahedron of the quaternary system $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{Fe}_x\text{O}$.

Starting materials used in this study were Na_2CO_3 , Al_2O_3 and SiO_2 obtained from Nakalai Tesuque. Inc., Kyoto, Japan. Iron oxide was obtained from Mitsuwa Chemicals Co., Osaka, Japan. The slag compositions investigated in this study are given by three straight lines drawn in the

quaternary field of $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{Fe}_x\text{O}$ in Figure 2. All of the lines pass through the Fe_xO apex, and lie on the plane where the molar ratio of $\text{Al}_2\text{O}_3/\text{SiO}_2$ is $33/67 (= 1/2)$. During a single experimental run, the molar ratio of Na_2O to $(\text{Al}_2\text{O}_3 + \text{SiO}_2)$ within the bulk of the slag was kept constant at 50/50, 33/67 or 25/75. Mixtures of appropriate triple oxides of Na_2O , Al_2O_3 and SiO_2 were prepared by mixing requisite portions of Na_2CO_3 , Al_2O_3 and SiO_2 , and heating at 1273 K for 24 hours. The resultant mixtures were used for lowering the Fe_xO concentrations, while the Fe_xO concentrations could be increased by the addition of iron oxide.

The experimental procedure consisted of measuring the open-circuit *emfs* of the oxygen probes and subsequently sampling the slag. The zirconia probe was gradually moved downward until the probe contacted both the slag and the molten silver. Cell potentials generated were monitored on a strip-chart recorder of $2 \text{ M}\Omega$ internal impedance with an accuracy of $\pm 0.1 \text{ mV}$ and were more accurately read with a digital voltmeter of $100 \text{ M}\Omega$ input resistance with an accuracy of $\pm 0.01 \text{ mV}$. After the stable *emfs* ($\pm 0.1 \text{ mV}$) were obtained, the zirconia probe was raised so that the lower end of the zirconia tube located about 30- to 50-mm above the surface of the slag. This procedure was repeated 3 to 4 times with a single probe until the reproducibilities of *emf* measurements were confirmed, and subsequently sample was withdrawn from the slag by dipping a steel rod in the molten slag for 2 to 3 seconds. The compositions of the samples were determined by wet chemical analysis. The zirconia probe was replaced whenever the slag composition was changed. A single experimental run with a fixed molar ratio of Na_2O to $(\text{Al}_2\text{O}_3 + \text{SiO}_2)$ was thus continued with *emf* readings, sampling, and addition procedures at a fixed temperature of 1673 K. The reproducibilities of *emf* measurements were also confirmed by Fe_xO concentration cycling. In order to avoid composition changes due to vaporization of Na_2O , all of slag was replaced several times during an experimental run by using the same methods as sampling and addition procedures.

Concentrations of ferrous iron and total iron in the slags were determined by wet chemical analysis. Ferrous iron was determined by dissolving the samples in HCl under a stream of purified argon, and titrating with standard potassium dichromate /8/. Total iron was determined by dissolving in HCl, reducing with stannous chloride and titrating with standard potassium dichromate /9/. It is considered that FeO and $\text{FeO}_{1.5}$ form Fe_xO in the slag as follows



From the stoichiometric relations for iron and oxygen, equations (2) and (3) can be obtained, respectively;

$$n_1 + n_2 = nx \quad (2)$$

$$n_1 + 1.5n_2 = n \quad (3)$$

where n_1 , n_2 and n denote the numbers of moles of FeO, FeO_{1.5} and Fe_xO per 100 g of oxide phases, and these values can be obtained through chemical analysis. The mole fractions of Fe_xO in quaternary slags of Na₂O-Al₂O₃-SiO₂-Fe_xO were then defined by

$$X_{Fe_xO} = n / (n + n_{Na_2O} + n_{Al_2O_3} + n_{SiO_2}) \quad (4)$$

where n_{Na_2O} , $n_{Al_2O_3}$ and n_{SiO_2} are the numbers of moles of Na₂O, Al₂O₃ and SiO₂ per 100-g of slag, respectively.

3 Experimental results and discussion

The open-circuit *emf*, E , of the cell used in this study is given by /10/;

$$E = (RT/F) \ln \left\{ \frac{P_{O_2}(ref.)^{1/4} + P_{\theta}^{1/4}}{P_{O_2}(slag)^{1/4} + P_{\theta}^{1/4}} \right\} + E_t \quad (5)$$

where R is the gas constant, T is temperature, F is the Faraday constant, E_t is thermo-*emf* between Mo (+) and Fe (-) (23.6 mV at 1673 K) /4/ and P_{θ} is the oxygen partial pressure at which the ionic and the n -type electronic conductivities are equal. Values for this parameter were taken from Iwase *et al.* /11/;

$$\log(P_{\theta}/Pa) = 25.41 - 6.45 \times 10^4/(T/K) \quad (6)$$

The oxygen partial pressures at the reference electrode, $P_{O_2}(ref.)$, were calculated by the following equation /12/;

$$RT \ln P_{O_2}(ref.) / kJ \cdot mol^{-1} = -576.1 + 0.1692 (T/K) \quad (7)$$

The activities of Fe_xO, a_{Fe_xO} , were calculated by the following equation;

$$a_{Fe_xO} = [P_{O_2}(slag)/P_{O_2}^{\circ}\{Fe_xO\}]^{1/2} \quad (8)$$

where $P_{O_2}^{\circ}\{Fe_xO\}$ is the equilibrium oxygen partial pressure of the mixture, Fe(s) + “pure” non-stoichiometric liquid Fe_xO, as given by the formula /7/;

$$\log(P_{O_2}^{\circ}\{Fe_xO\}/Pa) = 9.40 - 2.35 \times 10^4/(T/K) \quad (9)$$

The standard state for Fe_xO was taken as pure non-stoichiometric liquid Fe_xO in equilibrium with pure solid iron at 1673 K.

The activities of Fe_xO obtained in this study are summarized in Table 1. The limits of accuracy of the Fe_xO activities given in this table were estimated from

$$\begin{aligned} da_{Fe_xO}/a_{Fe_xO} = d \ln a_{Fe_xO} \leq & |2F/RT| |dE| + |2EF/RT^2| |dT| \\ & + (1/2) |d \ln P_{O_2}(ref.)| |dT| \\ & + (1/2) |d \ln P_{O_2}^{\circ}\{Fe_xO\}| |dT| \end{aligned} \quad (10)$$

By using the average standard deviation for E , which was ± 0.76 mV, the uncertainty of a_{Fe_xO} was estimated to be approximately ± 1 percent. In Table 1, the limits of the accuracy are given for the individual activity data. The uncertainty in the slag composition, which did not exceed ± 0.02 in mole fraction, arisen from mainly from errors in chemical analysis.

X-ray diffraction analysis confirmed that all the slag compositions investigated in this study were in the homogeneous liquid region. Figure 3 illustrates the Fe_xO activities as functions of X_{Fe_xO} in homogeneous liquid region at 1673 K together with the literature data for Na₂O-Fe_xO binary system /13/ and Al₂O₃-SiO₂-Fe_xO ternary system at $X_{Al_2O_3}/X_{SiO_2} = 33/67$ /5/. It is seen that the systems exhibit positive deviations from Raoult's law. For slags of $X_{Na_2O}/(X_{Al_2O_3} + X_{SiO_2}) = 50/50, 33/67$ and $25/75$, the activities could be well-expressed by smooth curves drawn through the data points. For slags with $X_{Na_2O}/(X_{Al_2O_3} + X_{SiO_2}) < 33/67$, the Fe_xO activity increased drastically with an increase in $X_{Na_2O}/(X_{Al_2O_3} + X_{SiO_2})$ mole ratio. The further replacement of Al₂O₃ + SiO₂ by Na₂O, however, resulted in decreasing the activity.

The Fe_xO activities in nepheline-Fe_xO system /1/ could be compared directly with the present results for Na₂O-Al₂O₃-SiO₂-Fe_xO melts at $X_{Al_2O_3}/X_{SiO_2} = 33/67 = 1/2$. This was done in Figure 4. In this figure, the activity coefficients of Fe_xO at $X_{Fe_xO} = 0.3$ are plotted against proportions of basic oxides. Nepheline investigated in the previous study as an alternative fluidizer to replace fluorspar had a particular composition, *i.e.*, (Na_{3/4}K_{1/4})₂O · Al₂O₃ · 2SiO₂ /1/, which was expressed by an arrow in Figure 4. As shown in this figure, the substitution of quarter amount of Na₂O within Na₂O · Al₂O₃ · 2SiO₂ for a more basic oxide of K₂O had an effect of raising the Fe_xO activities. This was not unacceptable because the present results indicated that the Fe_xO activity coefficient increased with an increase in the basicity of Na₂O-(Al₂O₃ · 2SiO₂)-Fe_xO melts in the composition range of $X_{Na_2O}/(X_{Na_2O} + X_{Al_2O_3} + X_{SiO_2}) < 0.33$.

Sample No.	Emf (mV)*	$a_{\text{Fe}_x\text{O}}$	$X_{\text{Fe}_x\text{O}}$	x	$(\text{Fe}^{3+})/(\text{Fe}^{2+})$
$X_{\text{Na}_2\text{O}}/(X_{\text{Al}_2\text{O}_3} + X_{\text{SiO}_2}) = 50/50$					
6-1	109.32 ± 1.82	0.537 ± 0.014	0.238 ± 0.007	0.859	0.488
6-2	114.33 ± 0.76	0.501 ± 0.006	0.231 ± 0.009	0.852	0.531
6-3	94.90 ± 0.86	0.659 ± 0.008	0.310 ± 0.003	0.874	0.407
6-4	106.90 ± 1.15	0.557 ± 0.009	0.277 ± 0.014	0.842	0.598
6-5	88.37 ± 0.45	0.721 ± 0.005	0.369 ± 0.003	0.882	0.364
6-6	102.63 ± 0.32	0.590 ± 0.003	0.290 ± 0.005	0.862	0.472
6-7	87.00 ± 1.21	0.736 ± 0.013	0.458 ± 0.006	0.867	0.442
6-8	80.60 ± 0.10	0.806 ± 0.002	0.542 ± 0.010	0.875	0.401
7-1	121.53 ± 1.29	0.454 ± 0.008	0.223 ± 0.002	0.872	0.414
7-2	103.37 ± 0.25	0.582 ± 0.002	0.319 ± 0.002	0.849	0.552
7-3	94.47 ± 0.15	0.661 ± 0.002	0.393 ± 0.006	0.860	0.484
7-4	98.63 ± 0.31	0.624 ± 0.003	0.376 ± 0.004	0.821	0.774
7-5	82.70 ± 0.26	0.780 ± 0.004	0.476 ± 0.004	0.870	0.425
7-6	85.00 ± 0.10	0.756 ± 0.002	0.457 ± 0.007	0.877	0.391
7-7	89.83 ± 0.12	0.706 ± 0.002	0.438 ± 0.004	0.848	0.558
7-8	122.73 ± 0.06	0.445 ± 0.001	0.296 ± 0.001	0.784	1.228
7-9	116.53 ± 0.90	0.486 ± 0.006	0.283 ± 0.002	0.826	0.731
7-10	77.07 ± 0.21	0.843 ± 0.003	0.679 ± 0.018	0.868	0.435
$X_{\text{Na}_2\text{O}}/(X_{\text{Al}_2\text{O}_3} + X_{\text{SiO}_2}) = 33/67$					
8-4	87.70 ± 1.73	0.732 ± 0.018	0.272 ± 0.003	0.956	0.101
8-5	91.53 ± 1.04	0.690 ± 0.010	0.245 ± 0.004	0.951	0.115
8-6	81.67 ± 1.00	0.796 ± 0.012	0.321 ± 0.010	0.975	0.055
8-7	79.17 ± 0.35	0.825 ± 0.005	0.499 ± 0.003	0.967	0.074
8-8	77.00 ± 0.79	0.850 ± 0.010	0.576 ± 0.007	0.961	0.089
9-3	94.47 ± 0.15	0.661 ± 0.002	0.223 ± 0.008	0.925	0.194
9-4	87.37 ± 0.23	0.730 ± 0.002	0.300 ± 0.012	0.930	0.178
9-5	88.57 ± 0.21	0.717 ± 0.002	0.284 ± 0.006	0.936	0.158
$X_{\text{Na}_2\text{O}}/(X_{\text{Al}_2\text{O}_3} + X_{\text{SiO}_2}) = 25/75$					
2-4	103.85 ± 0.12	0.581 ± 0.001	0.238 ± 0.007	0.967	0.073
2-5	92.60 ± 1.30	0.680 ± 0.013	0.329 ± 0.016	0.981	0.040
2-6	87.17 ± 0.81	0.732 ± 0.009	0.435 ± 0.007	0.953	0.109
2-7	83.83 ± 0.12	0.773 ± 0.002	0.489 ± 0.002	0.958	0.095
2-8	81.43 ± 0.06	0.795 ± 0.001	0.526 ± 0.004	0.961	0.087
4-4	103.87 ± 0.68	0.582 ± 0.006	0.248 ± 0.006	0.978	0.048
4-10	107.97 ± 1.01	0.549 ± 0.009	0.209 ± 0.001	0.973	0.059
5-2	114.80 ± 0.95	0.498 ± 0.007	0.205 ± 0.012	0.904	0.211
5-5	104.60 ± 1.85	0.576 ± 0.016	0.235 ± 0.003	0.959	0.084
5-6	90.30 ± 0.40	0.708 ± 0.005	0.401 ± 0.001	0.961	0.081
5-7	81.47 ± 0.21	0.796 ± 0.002	0.583 ± 0.004	0.944	0.119
5-8	79.67 ± 0.06	0.811 ± 0.001	0.615 ± 0.003	0.932	0.145
5-9	76.03 ± 0.06	0.857 ± 0.001	0.771 ± 0.003	0.935	0.139
5-10	72.03 ± 0.06	0.905 ± 0.001	0.858 ± 0.001	0.939	0.130

* Emf values are not corrected for thermo emf between Fe(-) and Mo(+). For correction, subtract 23.6 mV from those given in the table.

Table 1: Experimental results at 1673 K.

From the smooth curves given in Figure 3, iso-activity curves for Fe_xO within homogeneous liquid region at 1673 K could be drawn on $\text{Na}_2\text{O}-(\text{Al}_2\text{O}_3 + \text{SiO}_2)-\text{Fe}_x\text{O}$ pseudo-ternary field of $X_{\text{Al}_2\text{O}_3}/X_{\text{SiO}_2} = 33/67$, as shown in Figure 5. The Fe_xO activities for $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{Fe}_x\text{O}$ melts would have maxima at $X_{\text{Na}_2\text{O}}/(X_{\text{Na}_2\text{O}} + X_{\text{Al}_2\text{O}_3} + X_{\text{SiO}_2}) = 0.33$. Similar

behavior could be observed for the other basic oxide-acidic oxide- Fe_xO systems, e.g. $(\text{CaO} + \text{MgO})-\text{SiO}_2-\text{FeO}$ /14/, $(\text{CaO} + \text{MnO} + \text{MgO})-(\text{SiO}_2 + \text{P}_2\text{O}_5)-\text{FeO}$ /15/, $\text{Na}_2\text{O}-\text{SiO}_2-\text{Fe}_x\text{O}$ /16/ and $\text{CaO}-\text{SiO}_2-\text{Fe}_x\text{O}$ /17/. Such a phenomenon is often interpreted as an amphoteric property of iron oxide /15/. At very acidic solutions iron oxide forms iron silicate,

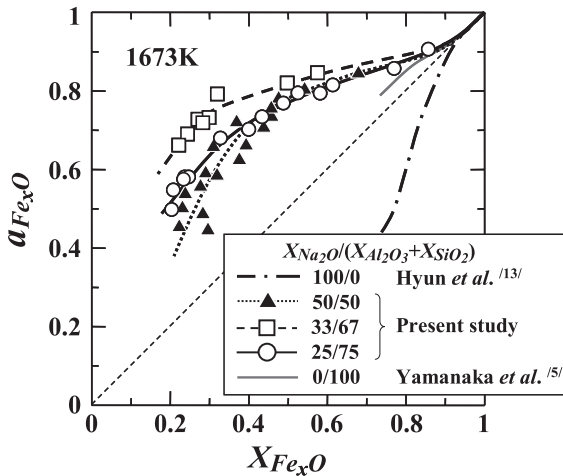


Fig. 3: Relation between a_{Fe_xO} and X_{Fe_xO} for Na_2O - SiO_2 - Al_2O_3 - Fe_xO slags with an Al_2O_3/SiO_2 mole ratio of 33/67 at 1673 K.

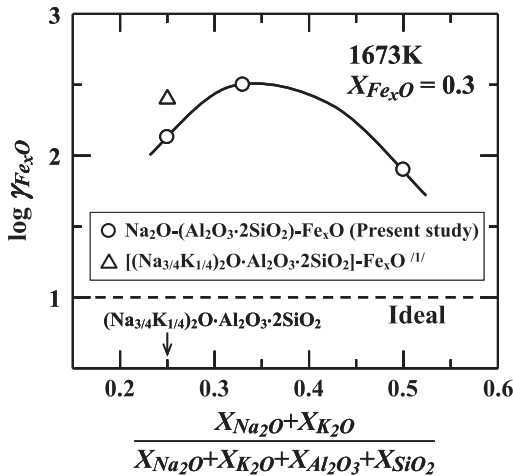
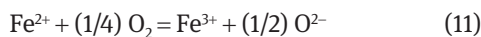


Fig. 4: Relation between activity coefficients of Fe_xO for $X_{Fe_xO} = 0.3$ and $(X_{Na_2O} + X_{K_2O}) / (X_{Na_2O} + X_{K_2O} + X_{Al_2O_3} + X_{SiO_2})$.

while at basic systems it forms ferrite; the activities are lowered in both cases. Hence there is a maximum at the intermediate region.

The consideration mentioned above would make it of interest to consider the behavior of ferrous and ferric ions within Na_2O - Al_2O_3 - SiO_2 - Fe_xO liquid slags by using the oxidation-reduction equilibria. Such reactions can be written by



or

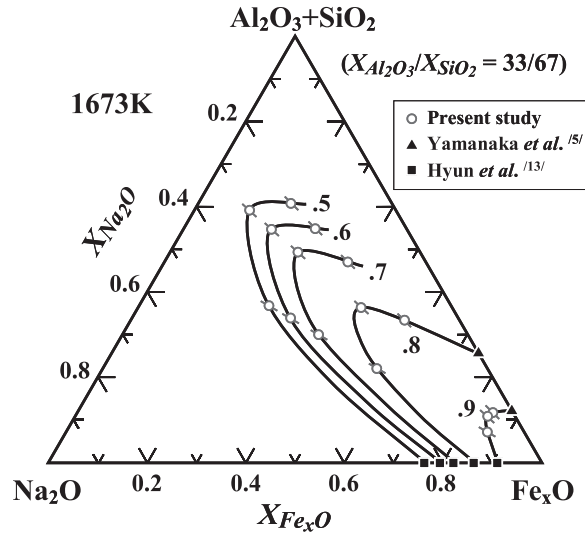
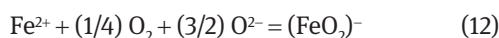
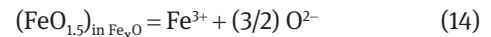
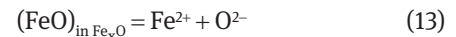
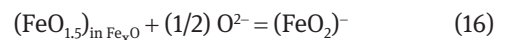
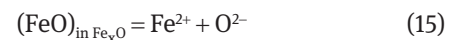


Fig. 5: Iso-activity curves for Fe_xO in the pseudo-ternary system Na_2O - $(Al_2O_3 + SiO_2)$ - Fe_xO with an Al_2O_3/SiO_2 mole ratio of 33/67 at 1673 K.

Equations (11) and (12) are predominant for acidic and basic melts, respectively /18/. Equation (11) implies that iron oxide in acidic melts would behave as a basic oxide expressed as



On the other hand, equation (12) indicates that iron oxide in basic or amphoteric melts would behave as an amphoteric oxide expressed as follows.



It should be noted here that conventional wet chemical analysis does not distinguish between Fe^{3+} and $(FeO_2)^-$. Namely, from equations (11) and (12), one obtains

$$\log\{(Fe^{3+}) / (Fe^{2+}) P_{O_2}^{1/4}\} = -(1/2) \log a_{O^{2-}} + \log K(11) \quad (17)$$

and

$$\log\{(Fe^{3+}) / (Fe^{2+}) P_{O_2}^{1/4}\} = +(3/2) \log a_{O^{2-}} + \log K(12) \quad (18)$$

For acidic melts, reaction (17) would be predominant; hence $\log\{(Fe^{3+}) / (Fe^{2+}) P_{O_2}^{1/4}\}$ should decrease with an increase in basicity or oxygen anion activity. For basic melts, the reverse should hold true, because the oxidation-reduction equilibrium would be prevailed by

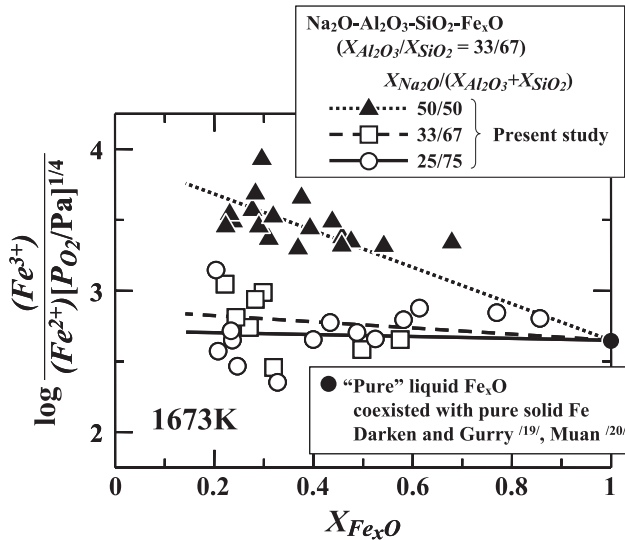


Fig. 6: Relation between $\log\{(Fe^{3+})/(Fe^{2+}) P_{O_2}^{1/4}\}$ and X_{Fe_xO} at 1673 K.

reaction (18). Figure 6 shows the relation between $\log\{(Fe^{3+})/(Fe^{2+}) P_{O_2}^{1/4}\}$ and X_{Fe_xO} for $Na_2O-Al_2O_3-SiO_2-Fe_xO$ slags. The value for pure non-stoichiometric liquid Fe_xO coexisted with pure solid iron is based upon the works by Darken and Gurry [19], and Muan [20]. As shown in this figure, the values for $\log\{(Fe^{3+})/(Fe^{2+}) P_{O_2}^{1/4}\}$ increased with an increase in $X_{Na_2O}/(X_{SiO_2} + X_{Al_2O_3})$ molar ratio, i.e. an increase in slag basicity. This result indicated that the oxidation-reduction equilibrium for the Fe^{3+}/Fe^{2+} couple could be given by reaction (12) for the $Na_2O-Al_2O_3-SiO_2-Fe_xO$ slags investigated in this study; ferric ion could be expressed by $(FeO_2)^-$. Thus, iron oxide, Fe_xO , in these melts would behave as an amphoteric oxide.

4 Conclusion

An electrochemical technique was applied for the determination of the activities of Fe_xO in $Na_2O-Al_2O_3-SiO_2-Fe_xO$ slags at 1673 K. For the homogeneous liquid slags investigated in this study, the Fe_xO activities showed positive deviations from Raoult's law, and had maxima at $X_{Na_2O}/$

$(X_{Al_2O_3} + X_{SiO_2}) = 33/67$. The results were discussed on the basis of the amphoteric nature of Fe_xO .

Received: March 1, 2012. Accepted: July 10, 2012.

References

- [1] H. Ozawa, M. Hasegawa, Y. Kashiwaya and M. Iwase; *Steel Res. Int.*, **81** (1), 25–30 (2010).
- [2] M. Iwase, E. Ichise, N. Yamada and K. Nishida; *Trans. Iron Steel Soc. AIME*, **4**, 47–53 (1984).
- [3] M. Iwase, N. Yamada, K. Nishida and E. Ichise; *Trans. Iron Steel Soc. AIME*, **4**, 69–75 (1984).
- [4] M. Iwase, N. Yamada, E. Ichise and H. Akizuki; *Trans. Iron Steel Soc. AIME*, **5**, 53–59 (1984).
- [5] R. Yamanaka, S. Koyama and M. Iwase; *Metall. Trans. B*, **22B**, 839–845 (1992).
- [6] S. Yamashita, H. Fujiwara, E. Ichise and M. Iwase; *Iron Steelmaker*, **19** (9), 57–63 (1992).
- [7] H. Hoshino and M. Iwase; *Metall. Mater. Trans. B*, **27B**, 375–378 (1996).
- [8] Japanese Standard Association, “Method for Determinations of Ferrous Oxide in Iron Ores”, JIS-M-8213, 1978, Japanese Standard Association, Tokyo.
- [9] Japanese Standard Association, “Method for Determinations of Total Iron in Iron Ores”, JIS-M-8221, 1979, Japanese Standard Association, Tokyo.
- [10] H. Schmalzried; *Z. Electrochem.*, **66** (7), 572–576 (1962).
- [11] M. Iwase, E. Ichise, T. Yamasaki and M. Takeuchi; *Trans. Jpn. Inst. Met.*, **25** (2), 43–52 (1984).
- [12] M. Iwase, M. Yasuda and T. Mori; *Electrochimica Acta*, **19** (3), 261–266 (1979).
- [13] D. B. Hyun, J. D. Shim, S. N. Kim and E. C. Lee; *J. Korean. Inst. Metals*, **23** (3), 19–27 (1985).
- [14] C. R. Taylor and J. Chipman; *Trans. TMS-AIME*, **154**, 228–245 (1943).
- [15] E. T. Turkdogan and J. Pearson; *J. Iron Steel Inst.*, **173** (3), 217–223 (1953).
- [16] S. Ban-ya, M. Hino and H. Takezoe; *Tetsu-to-Hagane* (in Japanese), **71**, 1765–1772 (1985).
- [17] T. Ogura, R. Fujiwara, R. Mochizuki, Y. Kawamoto, T. Oishi and M. Iwase; *Metall. Trans. B*, **23B**, 459–466 (1992).
- [18] M. Iwase, T. Okumura, K. Kawamura, Y. Miyamoto and H. Oh-uchi; *Glass Technology*, **39** (4), 142–146 (1998).
- [19] L. S. Darken and R. W. Gurry; *J. Am. Chem. Soc.*, **68** (5), 798–816 (1946).
- [20] A. Muan; *Am. Ceram. Soc. Bull.*, **37** (2), 81–84 (1958).