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

Activities of Fe$_x$O in Na$_2$O-Al$_2$O$_3$-SiO$_2$-Fe$_x$O
Homogeneous Liquid Slags at 1673 K

Abstract: Electrochemical measurements of the solid-oxide galvanic cell of the type Mo/Mo$^+$/ZrO$_2$(MgO)/Fe$^+$/[Na$_2$O-Al$_2$O$_3$-SiO$_2$-Fe$_x$O] slag/Ag/Fe were conducted at 1673 K in order to obtain the activities of Fe$_x$O in Na$_2$O-Al$_2$O$_3$-SiO$_2$-Fe$_x$O system. The iso-activity curves for Fe$_x$O at 1673 K were determined for Na$_2$O-(Al$_2$O$_3$+SiO$_2$)-Fe$_x$O pseudo-ternary slags with an Al$_2$O$_3$/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 Na$_2$O·Al$_2$O$_3$·2SiO$_2$ (= NaAlSiO$_4$) and K$_2$O·Al$_2$O$_3$·2SiO$_2$ (= KAlSiO$_4$), while the later is one of the natural resources which contain nepheline together with potash feldspar (K$_2$O·Al$_2$O$_3$·6SiO$_2$ = KAlSi$_3$O$_8$) and albite (Na$_2$O·Al$_2$O$_3$·6SiO$_2$ = NaAlSi$_2$O$_6$).

During a course of thermochemical studies on nepheline or nepheline syenite as an alternative fluidizer to replace fluorspar in steelmaking slags, it became necessary to determine the activities of Fe$_x$O within nepheline-containing slags. By employing electrochemical technique involving stabilized zirconia, the Fe$_x$O activities in CaO-nepheline-Fe$_x$O melts were determined in the previous study /1/. The experimental results concluded that substituting nepheline of a particular composition, i.e., (Na$_{3/4}$K$_{1/4}$)$_2$O·Al$_2$O$_3$·2SiO$_2$, for CaO raised the Fe$_x$O activities.

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

$$\text{Mo/Mo}^+\text{/ZrO}_2(\text{MgO})/\text{Fe}^+\{\text{Na}_2\text{O-Al}_2\text{O}_3\text{-SiO}_2\text{-Fe}_x\text{O}\} \text{ slag/Ag/Fe}$$

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, Mo/Mo$^+$/ZrO$_2$(MgO), consisted of a MgO-stabilized zirconia tube and a two-phase mixture of Mo + Mo$_2$O$_3$. 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$_x$O and Na$_2$O-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 Mo$_2$O$_3$ 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/.

**Note:** The full text includes references and additional details that are not shown in the snippet provided.
Starting materials used in this study were Na$_2$CO$_3$, Al$_2$O$_3$, 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 Na$_2$O-Al$_2$O$_3$-SiO$_2$-Fe$_x$O in Figure 2. All of the lines pass through the Fe$_x$O apex, and lie on the plane where the molar ratio of Al$_2$O$_3$/SiO$_2$ is 33/67 (= 1/2). During a single experimental run, the molar ratio of Na$_2$O to (Al$_2$O$_3$ + 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$_2$O, Al$_2$O$_3$, and SiO$_2$ were prepared by mixing requisite portions of Na$_2$CO$_3$, Al$_2$O$_3$, and SiO$_2$, and heating at 1273 K for 24 hours. The resultant mixtures were used for lowering the Fe$_x$O concentrations, while the Fe$_x$O 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 MΩ internal impedance with an accuracy of ±0.1 mV and were more accurately read with a digital voltmeter of 100 MΩ input resistance with an accuracy of ±0.01 mV. After the stable emfs (±0.1 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$_2$O to (Al$_2$O$_3$ + 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$_x$O concentration cycling. In order to avoid composition changes due to vaporization of Na$_2$O, 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 FeO$_{1.5}$ form Fe$_x$O in the slag as follows

\[ n_1\text{FeO} + n_2\text{FeO}_{1.5} = n\text{Fe}_x\text{O} \] (1)
From the stoichiometric relations for iron and oxygen, equations (2) and (3) can be obtained, respectively:

\[ n_1 + n_2 = nx \]  
(2)

\[ n_1 + 1.5n_2 = n \]  
(3)

where \( n_1, n_2 \), and \( n \) denote the numbers of moles of FeO, FeO\(_{1.5}\) and \( \text{Fe}_2\text{O}_3 \) per 100 g of oxide phases, and these values can be obtained through chemical analysis. The mole fractions of FeO in quaternary slags of Na\(_2\)O-Al\(_2\)O\(_3\)-SiO\(_2\)-Fe\(_2\)O were then defined by

\[ X_{\text{FeO}} = n/(n + n_{\text{Na}_2\text{O}} + n_{\text{Al}_2\text{O}_3} + n_{\text{SiO}_2}) \]  
(4)

where \( n_{\text{Na}_2\text{O}}, n_{\text{Al}_2\text{O}_3}, \) and \( n_{\text{SiO}_2} \) are the numbers of moles of \( \text{Na}_2\text{O}, \text{Al}_2\text{O}_3, \) and \( \text{SiO}_2 \) 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/;

\[ E = (RT/F) \ln[(P_{\text{O}_2\,(\text{ref.})}^{1/2} + P_{\theta}^{1/2})/(P_{\text{O}_2\,(\text{slag})}^{1/2} + P_{\theta}^{1/2})] + E_1 \]  
(5)

where \( R \) is the gas constant, \( T \) is temperature, \( F \) is the Faraday constant, \( E_1 \) is thermo-emf between Mo (+) and Fe (-) (23.6 mV at 1673 K) /4/ and \( P_{\theta} \) 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/;

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

The oxygen partial pressures at the reference electrode, \( P_{\text{O}_2\,(\text{ref.})} \), were calculated by the following equation /12/;

\[ RT \ln P_{\theta\,(\text{ref.})} /k \cdot \text{mol}^{-1} = -576.1 + 0.1692 \times (T/K) \]  
(7)

The activities of Fe\(_x\)O, \( a_{\text{Fe}_x\text{O}} \), were calculated by the following equation;

\[ a_{\text{Fe}_x\text{O}} = [P_{\text{O}_2\,(\text{slag})}/P_{\theta\,(\text{Fe}_x\text{O})}]^{1/2} \]  
(8)

where \( P_{\theta\,(\text{Fe}_x\text{O})} \) is the equilibrium oxygen partial pressure of the mixture, \( \text{Fe}(s) + \text{“pure” non-stoichiometric liquid Fe}_x\text{O} \), as given by the formula /7/;

\[ \log(P_{\theta\,(\text{Fe}_x\text{O})}/\text{Pa}) = 9.40 - 2.35 \times 10^4/(T/K) \]  
(9)

The standard state for Fe\(_2\)O was taken as pure non-stoichiometric liquid Fe\(_x\)O in equilibrium with pure solid iron at 1673 K.

The activities of Fe\(_x\)O obtained in this study are summarized in Table 1. The limits of accuracy of the Fe\(_x\)O activities given in this table were estimated from

\[ \frac{da_{\text{Fe}_x\text{O}}}{a_{\text{Fe}_x\text{O}}} = d \ln a_{\text{Fe}_x\text{O}} \leq |2F/RT| |dE| + |2EF/RT| |dT| + (1/2)d \ln P_{\theta\,(\text{Fe}_x\text{O})}/dT + (1/2)d \ln P_{\theta\,(\text{Fe}_x\text{O})}/dT |dT| \]  
(10)

By using the average standard deviation for \( E \), which was \( \pm 0.76 \text{ mV} \), the uncertainty of \( a_{\text{Fe}_x\text{O}} \) was estimated to be approximately \( \pm 1 \) 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 \( \pm 0.02 \) 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\(_x\)O activity increased drastically with an increase in the basicity of Na\(_2\)O. Al\(_2\)O\(_3\) ternary system at 1673 K together with the literature data for Na\(_2\)O-Fe\(_2\)O at 1673 K /13/ and Al\(_2\)O\(_3\)-SiO\(_2\)-Fe\(_2\)O ternary system at 1673 K /5/. It is seen that the systems exhibits positive deviations from Raoult’s law. For slags of X\(_{\text{Na}_2\text{O}}\)/(X\(_{\text{Al}_2\text{O}_3} + X_{\text{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\(_{\text{Na}_2\text{O}}\)/(X\(_{\text{Al}_2\text{O}_3} + X_{\text{SiO}_2}) > 33/67, the Fe\(_x\)O activity increased drastically with an increase in X\(_{\text{Na}_2\text{O}}\)/(X\(_{\text{Al}_2\text{O}_3} + X_{\text{SiO}_2})\) mole ratio. The further replacement of Al\(_2\)O\(_3\) \( + \) SiO\(_2\) by Na\(_2\)O, however, resulted in decreasing the activity.

The Fe\(_x\)O activities in nepheline-Fe\(_2\)O system /1/ could be compared directly with the present results for Na\(_2\)O-Al\(_2\)O\(_3\)-SiO\(_2\)-Fe\(_2\)O melts at X\(_{\text{Na}_2\text{O}}\)/(X\(_{\text{Al}_2\text{O}_3} + X_{\text{SiO}_2}) = 33/67 = 1/2. This was done in Figure 4. In this figure, the activity coefficients of Fe\(_2\)O at X\(_{\text{Fe}_2\text{O}}\) = 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., \( (\text{Na}_3/4\cdot\text{K}_{1/4})_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \) /1/, which was expressed by an arrow in Figure 4. As shown in this figure, the substitution of quarter amount of Na\(_2\)O within Na\(_2\)O-Al\(_2\)O\(_3\) : SiO\(_2\) for a more basic oxide of K\(_2\)O had an effect of raising the Fe\(_2\)O activities. This was not unacceptable because the present results indicated that the Fe\(_x\)O activity coefficient increased with an increase in the basicity of Na\(_2\)O-(Al\(_2\)O\(_3\) : SiO\(_2\))-Fe\(_2\)O melts in the composition range of X\(_{\text{Na}_2\text{O}}\)/(X\(_{\text{Na}_2\text{O}} + X_{\text{Al}_2\text{O}_3} + X_{\text{SiO}_2}) < 0.33. \)
From the smooth curves given in Figure 3, iso-activity curves for Fe\textsubscript{2}O within homogeneous liquid region at 1673 K could be drawn on Na\textsubscript{2}O-(Al\textsubscript{2}O\textsubscript{3} + SiO\textsubscript{2})-Fe\textsubscript{2}O pseudoternary field of $X_{\text{Al}_{2}O_{3}}/X_{\text{SiO}_{2}} = 33/67$, as shown in Figure 5. The Fe\textsubscript{2}O activities for Na\textsubscript{2}O-Al\textsubscript{2}O\textsubscript{3}SiO\textsubscript{2}-Fe\textsubscript{2}O melts would have maxima at $X_{\text{Na}_{2}O}(X_{\text{Al}_{2}O_{3}} + X_{\text{SiO}_{2}}) = 0.33$. Similar behavior could be observed for the other basic oxide-acidic oxide-Fe\textsubscript{2}O systems, e.g. (CaO + MgO)-SiO\textsubscript{2}-Fe\textsubscript{2}O /14/, (CaO + MnO + MgO)-(SiO\textsubscript{2} + P\textsubscript{2}O\textsubscript{5})-FeO /15/, Na\textsubscript{2}O-SiO\textsubscript{2}-Fe\textsubscript{2}O /16/ and CaO-SiO\textsubscript{2}-Fe\textsubscript{2}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,
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$_2$O-Al$_2$O$_3$-SiO$_2$-Fe$_x$O liquid slags by using the oxidation-reduction equilibria. Such reactions can be written by

\[
\text{Fe}^{2+} + (1/4) \text{O}_2 = \text{Fe}^{3+} + (1/2) \text{O}^{2-} \quad (11)
\]

or

\[
\text{Fe}^{2+} + (1/4) \text{O}_2 + (3/2) \text{O}^{2-} = (\text{FeO}_2)^- \quad (12)
\]

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

\[
(\text{FeO})_{\text{in} \text{Fe}_x\text{O}} = \text{Fe}^{2+} + \text{O}^{2-} \quad (13)
\]

\[
(\text{FeO}_{1.5})_{\text{in} \text{Fe}_x\text{O}} = \text{Fe}^{3+} + (3/2) \text{O}^{2-} \quad (14)
\]

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

\[
(\text{FeO})_{\text{in} \text{Fe}_x\text{O}} = \text{Fe}^{2+} + \text{O}^{2-} \quad (15)
\]

\[
(\text{FeO}_{1.5})_{\text{in} \text{Fe}_x\text{O}} + (1/2) \text{O}^{2-} = (\text{FeO}_2)^- \quad (16)
\]

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

\[
\log\left(\frac{\text{Fe}^{3+}}{\text{Fe}^{2+}} \right) P_{O_2}^{1/4} = -(1/2) \log a_{O^{2-}} + \log K(11) \quad (17)
\]

and

\[
\log\left(\frac{\text{Fe}^{3+}}{\text{Fe}^{2+}} \right) P_{O_2}^{1/4} = +(3/2) \log a_{O^{2-}} + \log K(12) \quad (18)
\]

For acidic melts, reaction (17) would be predominant; hence \(\log(\text{Fe}^{3+}/\text{Fe}^{2+}) P_{O_2}^{1/4}\) 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
reaction (18). Figure 6 shows the relation between \( \log\left(\frac{\text{Fe}^{3+}}{\text{Fe}^{2+}} P_{O_2}^{1/4}\right) \) and \( X_{\text{Fe}xO} \) for Na\(_2\)O-Al\(_2\)O\(_3\)-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 \( \log\left(\frac{\text{Fe}^{3+}}{\text{Fe}^{2+}} P_{O_2}^{1/4}\right) \) increased with an increase in \( X_{\text{Na}_2O}/(X_{\text{SiO}_2} + X_{\text{Al}_2O_3}) \) molar ratio, i.e., an increase in slag basicity. This result indicated that the oxidation-reduction equilibrium for the Fe\(^{3+}/\text{Fe}^{2+}\) couple could be given by reaction (12) for the Na\(_2\)O-Al\(_2\)O\(_3\)-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\(_2\)O-Al\(_2\)O\(_3\)-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 \( X_{\text{Na}_2O} \) (\( X_{\text{Al}_2O_3} + X_{\text{SiO}_2} = 33/67 \)). The results were discussed on the basis of the amphoteric nature of Fe\(_xO\).

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

### References