Activity of Iron Oxide in Steelmaking Slag

SOMNATH BASU, ASHOK KUMAR LAHIRI, and SESHADRI SEETHARAMAN

Most refining reactions in steelmaking involve oxidation of impurity element(s). The product(s) of oxidation either dissolve in the slag or escape as gaseous phase. The activities of oxygen in the metal (h_O), and that of "FeO" in slag (a_{FeO}), are major factors controlling these chemical reactions. The activities of oxygen and "FeO" are thermodynamically related, provided equilibrium distribution of oxygen between the slag and the metal is attained. This enables direct estimation of one parameter from the other. A thorough knowledge of the variation in activity of FeO, and factors affecting the same, is therefore of great importance in the process metallurgy of steelmaking. The present work experimentally measures the activity of FeO in steelmaking slags and attempts to develop a correlation for estimation of $\gamma(FeO)$ as a function of temperature and chemical composition of the slag.

I. FREE ENERGY OF FORMATION, AND ACTIVITY, OF FeO

SEVERAL workers have attempted to measure the free energy of formation of ferrous oxide and its activity in molten slag.[1–24] Equilibration of liquid iron and molten slag with H_2/H_2O or CO/CO_2 gas mixtures was the most common technique employed by these workers.[1–6,10,12–15] A summary of the investigations reported by the different authors is listed in Table I.

Most of the earlier workers[1,3–9,13–17] followed the assumption that oxygen in liquid steel remained dissolved in the form of ferrous oxide (FeO), and hence, under equilibrium, the activity of FeO was identical in slag and steel. Further, oxygen was assumed to behave as an ideal Henrian solute in liquid iron. Thus, the activity of FeO could be defined as

$$a_{FeO} = [\text{mass pct O}]/[\text{mass pct O}]_{satd.}$$

where

[mass pct O] = oxygen content of liquid steel in equilibrium with the slag, and
[mass pct O]$_{satd.}$ = oxygen content of liquid steel in equilibrium with pure liquid FeO.

These assumptions were probably necessitated by the nonavailability of published values of the interaction parameters between oxygen and other solutes in liquid iron. However, some workers[18,19] persisted with these assumptions even after Sigworth and Elliott,[20] in 1974, published a compilation of the interaction parameters between most solutes of importance in steelmaking.

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II. STOICHIOMETRY OF FERROUS OXIDE

It has been reported that solid FeO is not stoichiometric and is more appropriately described as Fe_xO, where $x = 0.95$ to 0.98.[10] Fetters and Chimpan observed that pure ferrous oxide melt, in equilibrium with oxygen saturated iron, contained approximately 94 mass pct FeO and 6 mass pct Fe_2O_3, corresponding to $FeO_{1.03}$.[5] They adopted the notation FeO_x, where x depended upon temperature and composition. However, Deo and Boom observed that this nonstoichiometry is of negligible significance in steelmaking operations.[25] They suggested that the free energy of formation of "FeO" and that of Fe_xO may be considered as the same. This convention has been followed up on in the present work.

III. EXPERIMENTATION

Simultaneous distribution of phosphorus and oxygen between liquid steel and slag was recently measured by the present authors.[26,27] The experimental conditions differed from those of earlier investigators,[1,2,5,6,13,15,17,23] because the liquid steel contained both oxygen and phosphorus while P_2O_5 and MgO were simultaneously present along with CaO, SiO_2, and FeO_x in the molten slag. Liquid steel and synthetic slag of previously determined quantity and composition were equilibrated in sintered dense magnesia crucibles under a gentle stream (0.15 to 0.20 mNm^3 min^{-1}) of Ar, using the MoS_2-heated horizontal tube furnace. The experimentation duration at the desired temperature was maintained at 8 hours, which had been found adequate for attainment of equilibrium.[26] The desired temperature was maintained within $\pm 1K$ in the furnace tube through the use of two B-type thermocouples, one located inside the furnace tube and the other just outside the same, together with a PID controller. The samples, after completion of an experiment, were withdrawn through one end of the horizontal tube. The details of

Table I. Summary of Earlier Investigations on Activity of FeO

Worker(s)	System Studied	Observations/Findings
Chipman[1]	vacuum decarburized liquid electrolytic iron in equilibrium with H_2/H_2O gas mixture; Fe (l) + H_2O (g) = FeO (l) + H_2 (g)	Fe (l) + ½O_2 (g) = (FeO); $\Delta G° = -31{,}200 - 1.0T$ (cal mol^{-1})
Vacher and Hamilton[2]	liquid Fe containing carbon and oxygen in equilibrium with CO/CO_2 gas mixture	free energy of formation of FeO similar to that reported by Chipman[1]
Chipman and Marshall[4]	solid wüstite, and liquid "FeO" (separately), in equilibrium with solid Fe and H_2/H_2O gas mixture	FeO (l) + H_2 (g) = Fe (s) + H_2O (g); $\Delta G° = -7240 + 4.67T$ (cal mol^{-1})
Fetters and Chipman[5,6]	nearly pure liquid iron in equilibrium with CaO-SiO_2-FeO-MgO slag rich in iron oxide	$\log[\text{mass pct O}]_{saturation} = -\dfrac{4860}{T} + 1.935$ local maximum of [O] solubility at mass pct ratio (CaO + MgO)/SiO_2 = 1.8–2.0, for all FeO levels
Darken and Gurry[10]	iron and wüstite equilibrated with CO/CO_2 mixture	effect of $p(O_2)$ on iron-wüstite equilibrium
Richardson and Jeffes[11]	2 Fe (l) + O_2 (g) = 2 FeO (l)	$\Delta G°(1808\text{–}2000\text{ K}) = -111{,}250 + 21.67\,T$ (cal mol^{-1})
Bodsworth[13]	liquid FeO-Fe_2O_3-SiO_2 slag in equilibrium with CO/CO_2 and H_2/H_2O gas mixtures	FeO (l) + H_2 (g) = γ-Fe (s) + H_2O (g); $\Delta G° = -23842 + 15.26\,T$ (cal mol^{-1})
Bishop et al.[17,18]	experimentally determined γ(FeO) in CaO-MgO-SiO_2-FeO_x slag	estimation of γ(FeO) and γ(MnO) in basic open hearth slag
Morales and Fruehan[15]	Fe (l) + [O] = Fe_tO (l)	$\Delta G° = -27{,}740 + 11.66T$ (cal mol^{-1})
Suito and Inoue[14]	equilibrium of CaO-SiO_2-Fe_tO-$MgO_{satd.}$-P_2O_5-MnO slag and liquid iron over 1823 to 1923 K	γ(Fe_tO) increases with increase in $X(SiO_2)$ and $X(P_2O_5)$ as well as increase in temperature
Lee and Suito[21]	experimentally determined γ(Fe_tO) in CaO-Al_2O_3-Fe_tO and CaO-Al_2O_3-SiO_2-Fe_tO slag at 1873 K	γ(Fe_tO) independent of $X(Fe_tO)$ for $X(Fe_tO)$ < 0.1 strong negative deviation of $a(SiO_2)$ upto $X(SiO_2)$ = 0.4
Liu et al.[32]	Measurement of a(FeO) in CaO-SiO_2-Al_2O_3-$MgO_{satd.}$-FeO slag using EMF technique at 1823 K	γ(FeO) ranges from 2.2 to 4.7 for X(FeO) upto 0.08 γ(FeO) decreases marginally with increase in FeO concentration within 0 to 5 mole pct marginal increase in γ(FeO) when basicity increases from 1.6 to 2.2 positive deviation of a(FeO)
Ogura et al.[23]	electrochemical measurement of a(FeO) in CaO-SiO_2-FeO slag at 1673 K using zirconia electrolyte	γ(FeO) decreases with increasing X(CaO)/X(SiO_2) for X(CaO)/X(SiO_2) > 1
Haneo and Itagaki[24]	equilibration of FeO-Fe_2O_3-CaO-SiO_2 slag with CO/CO_2 gas mixture at 1573 and 1673 K	γ(FeO) increases with increasing basicity but no appreciable effect of temperature within 1573 to 1673 K

the apparatus and the experimental procedure have been described elsewhere.[26]

Figure 1 shows the influence of soaking time on the oxygen content in liquid metal, MgO concentration in slag, and the phosphorus partition ratio. It can be seen that none of these three parameters show any perceptible change beyond 8 hours of soaking. All the experiments were started with MgO-free slags, and the saturation concentration was attained by dissolution of MgO from magnesia crucibles into the slag. Therefore, the possibility of the presence of solid/undissolved MgO in the slag was neglected.

Figure 2 provides a schematic illustration of the slag compositions, at the end of respective experiments, normalized to a (CaO + MgO) – FeO_x – (SiO_2 + P_2O_5) pseudo-ternary system. The liquidus curve of 1873 K has been indicated in the figure.[28] It is seen that some of the slag samples probably contained solid fractions at 1873 K. Similar results were obtained from the com-

mercial thermodynamic packages THERMOCALC*

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already confirmed the presence of two-phase slag in some of the samples, particularly those with higher basicity.[26,27] Microscopic examination of some selected slag samples, quenched from the equilibration temperature, confirmed the presence of solid fractions. Examination using a scanning electron microscope with
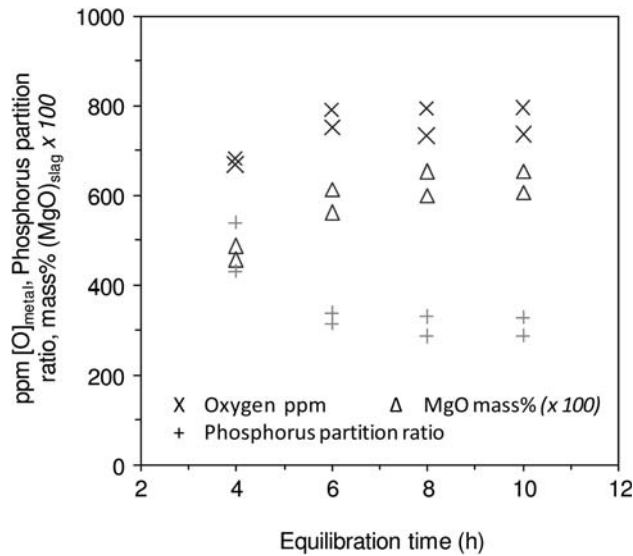
Fig. 1—Variation of (a) oxygen content in steel, (b) MgO content in slag, and (c) phosphorus partition ratio, with equilibration time.

energy dispersive X-ray spectroscopy and an electron probe microanalyzer revealed the solid phases to consist primarily of silicates of calcium, with traces of phosphorus and magnesium. Thus, the constituents in the slag were present partly in the silicate phase and partly in the liquid fraction of the slag. However, because the samples were at thermodynamic equilibrium, the activity of any species in both the phases would still be the same.

The activity of oxygen, $h_{[O]}$, was calculated from the chemical composition, using interaction parameters from standard sources.[29] The activity of FeO, $a(FeO)$, was calculated using the activity of oxygen and free energy of formation of FeO.[25]

$$Fe(l) + [O] = FeO(l) \qquad [1]$$
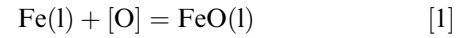
$$\Delta G^{\circ} = -121,983.61 + 52.26T \; (J \; mol^{-1})$$
$$= -RT \ln a(FeO)/h_{[O]}$$
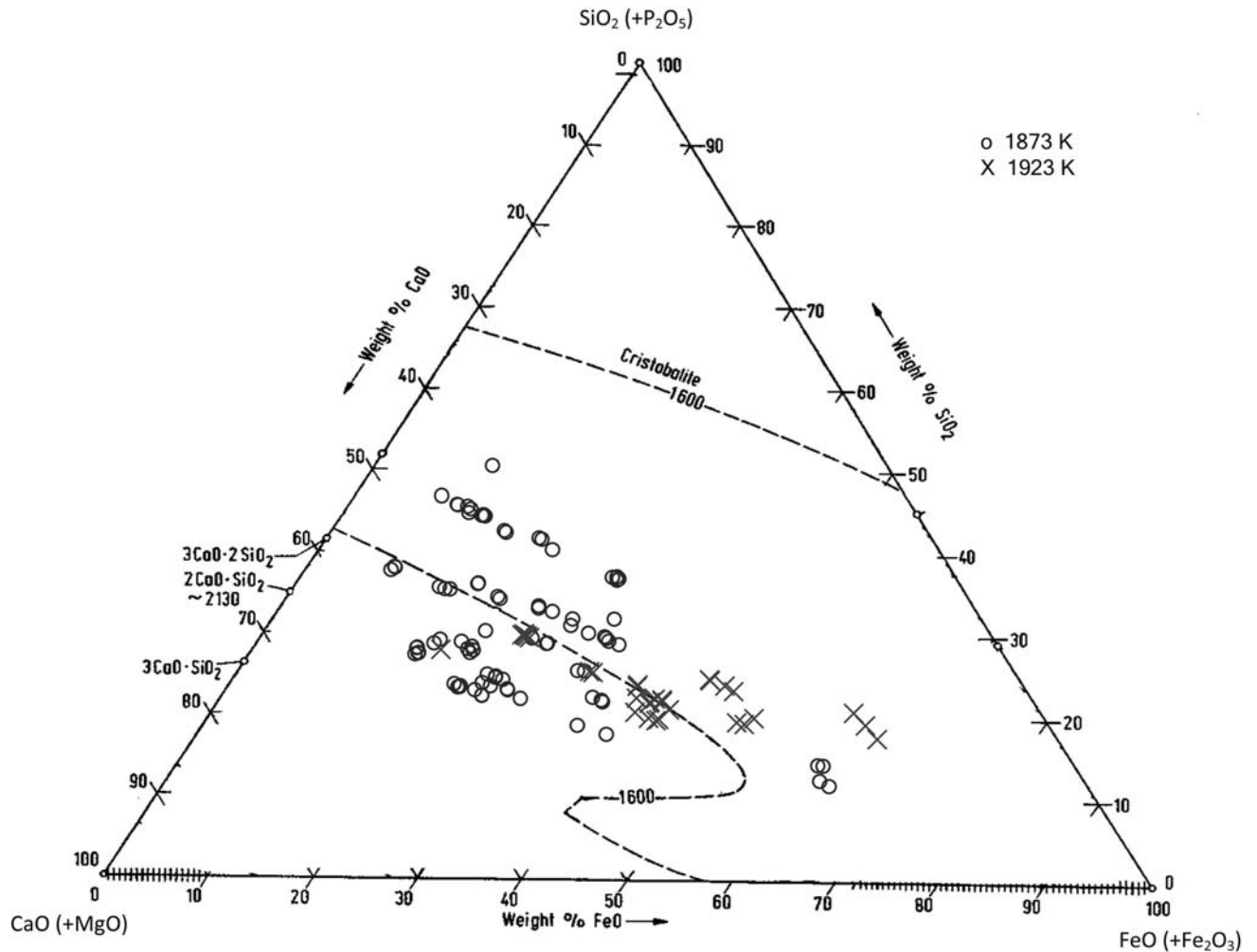$$h_{[O]} = [mass \; pct \; O] \times f_O$$

Fig. 2—Schematic representation of slag compositions on (CaO + MgO) − (FeO + Fe$_2$O$_3$) − (SiO$_2$ + P$_2$O$_5$) pseudo-ternary. Liquidus curves for 1873 K have been included for comparison.[28]

where

$$\log_{10} f_O = \sum e_O^i \text{ [mass pct } i\text{]} \text{ (neglecting higher order interactions).}$$

The standard states of iron, oxygen, and FeO were taken as pure liquid iron, unit activity coefficient at infinite dilution ($\lim_{[\text{pct O}] \to 0} f_O = 1$), and pure liquid FeO, respectively.

IV. RESULTS AND DISCUSSION

The slag samples in the present investigation were intended to resemble the evolving slag composition in the basic oxygen furnace (BOF).[30] Accordingly, the FeO concentration and the basicity (CaO/SiO$_2$, mass pct ratio) were varied within the ranges of 10 to 30 mass pct, and 1.2 to 3.5, respectively. Table II shows the chemical composition and the activities of FeO (a_{FeO}) and oxygen (h_O) for the samples equilibrated at 1873 K. The concentrations of CaO, SiO$_2$, FeO, P$_2$O$_5$, and MgO are considered in mass percent, and the oxygen concentration in steel is expressed in parts per million (by mass). Table III shows similar results for a temperature of 1923 K.

Figure 3 shows the variation in the activity of FeO with its concentration. It is clearly seen that FeO exhibits positive deviation from ideality for most chemical compositions investigated, except at high FeO concentrations, i.e., exceeding 0.4 mole fraction. Similar behavior of FeO activity was observed by several others as well.[18,22,31–34] Figure 4 shows the effect of iron oxide concentration on its activity, reported earlier by some workers.[1,18,22,31–35] The results of the present authors have been superimposed with filled circles for ease of comparison. It can be seen clearly that positive deviation of the activity of FeO was observed by these workers, with the exception of Chipman.[1] Turkdogan and Pearson had reported negative deviation of a(FeO) in CaO-MgO-MnO-FeO-SiO$_2$ slags at all FeO concentrations, but only when SiO$_2$ concentration was less than 0.8 molar pct (X(SiO$_2$) < 0.008).[9] At higher concentrations of SiO$_2$, the activity of FeO exhibited positive deviation. The results of Ichise and Iwase[32] show negative deviation in a few cases at low iron oxide concentrations (X(FeO) < 0.1), whereas Wrampelmeyer et al.[35] observed some incidences of negative deviation of FeO at intermediate concentrations (X(FeO) = 0.25 to 0.4). In contrast, the results of Chipman[1] exhibit no positive deviation at all, but a small negative deviation of a(FeO) at X(FeO) exceeding 0.4 is seen in Figure 4.

A. Effect of Basicity on γ(FeO)

Figure 5 shows the variation of the activity coefficient of FeO with basicity, defined as mass pct ratio CaO/SiO$_2$, for different ranges of FeO concentration and temperature. It is seen that the change in basicity as well as temperature has only a negligible influence on the activity coefficient of FeO, for any given range of FeO concentration. A marginal decrease of γ(FeO) with the increase of basicity can be noticed upon careful analysis of Figure 5. A similar trend was reported by Kishimoto and co-workers, who concluded that the increase in basicity over the range X(CaO)/X(SiO$_2$) = 2.0 to 6.0, at any level of FeO concentration, caused only a marginal decrease in the activity coefficient of FeO.[22] Bishop et al. reported a gentle decrease in a(FeO) when the basicity, defined as the ratio mole pct (CaO + MgO + MnO)/mole pct (SiO$_2$ + PO$_{2.5}$ + Al$_2$O$_3$), increased beyond 2, for Fe$_t$O concentration within the range of 10 to 60 mole pct.[16] On the other hand, Fetters and Chipman,[5] and also Turkdogan and Pearson,[9] reported that the activity of FeO reached a distinct local maximum corresponding to a basicity of approximately 2. It should be noted that Fetters and Chipman defined basicity as mass pct (CaO + MgO)/mass pct (SiO$_2$), while Turkdogan and Pearson followed the definition basicity = X(CaO + MgO + MnO)/X(SiO$_2$ + P$_2$O$_5$). However, no such local maximum was observed by the present authors. Also, no definite correlation could be obtained between γ(FeO) and optical basicity of the slags. The changes in γ(FeO), seen in Figure 5, are due primarily to changes in FeO concentration.

B. Effect of FeO Concentration on γ(FeO)

The activity coefficient of FeO depends very strongly on its concentration, irrespective of basicity and temperature, within the range investigated. Figure 6 shows the variation of $\log_{10}$ γ(FeO) with respect to $\log_{10}$ X(FeO). The figure shows a nearly linear decrease of the activity coefficient with increasing FeO concentration, and clearly illustrates that the activity of FeO exhibits positive deviation at lower FeO concentrations but moves closer to ideality as the FeO concentration increases. The activity coefficient of FeO appears to be independent of temperature, at least over the interval investigated. In fact, negative deviation is exhibited when the concentration of FeO exceeds 40 molar pct (X(FeO) > 0.4). A similar trend was reported by Bodsworth,[13] Kishimoto et al.,[22] and by Fetters and Chipman[5] as well as Turkdogan and Pearson,[9] whose findings are shown in Figure 7. The results of the present authors, already shown in Figure 6, have been indicated with filled circles. The results of Chipman[1] are an exception and show negative deviation over the entire range of FeO concentration.

C. Effect of SiO$_2$ and CaO Concentrations on γ(FeO)

It has already been mentioned that basicity has a negligible effect on the activity coefficient of FeO. Change in CaO concentration has a likewise minimal influence, but γ(FeO) is affected more significantly by the concentration of SiO$_2$. The variation of γ(FeO) with changes in the SiO$_2$ and CaO concentration is shown in Figures 8 and 9, respectively. It is seen that γ(FeO) increases with the increase in the molar concentration of SiO$_2$. However, no definite correlation of γ(FeO) with CaO concentration can be observed; the results appear segregated into different ranges based on FeO

Table II. Chemical Composition of Samples at 1873 K

Solution	Pct CaO	Pct SiO$_2$	Pct FeO	Pct MgO	Pct P$_2$O$_5$	a(FeO)	h_O
1	51.63	16.88	17.53	4.49	3.65	0.306	0.064
2	39.82	29.5	10.03	13.9	6.33	0.245	0.051
3	35.8	19.95	23.15	11.57	4.32	0.34	0.071
4	51.91	17.6	17.76	3.55	3.74	0.301	0.063
5	53.14	17.96	18.19	3.58	3.73	0.301	0.063
6	51.67	16.75	17.94	4.82	3.66	0.312	0.066
7	49.22	20.39	18.05	3.71	5.09	0.301	0.063
8	50.71	16.8	18.83	6.19	4.53	0.303	0.064
9	53.42	17.69	19.0	4.65	4.03	0.303	0.063
10	35.84	20.07	23.03	11.8	4.31	0.326	0.068
11	38.22	17.83	22.92	7.25	7.75	0.348	0.073
12	50.67	26.73	10.37	5.05	6.88	0.257	0.054
13	37.12	17.41	22.74	7.92	7.37	0.348	0.073
14	41.71	19.8	22.56	8.22	4.93	0.342	0.072
15	50.16	16.67	19.6	6.05	4.38	0.325	0.068
16	51.24	26.84	10.27	4.81	6.68	0.257	0.054
17	39.49	29.42	8.93	15.45	6.31	0.241	0.05
18	51.57	23.14	12.28	4.08	3.32	0.258	0.054
19	27.56	12.53	34.99	7.88	4.26	0.386	0.081
20	41.83	19.82	22.09	8.06	4.94	0.342	0.072
21	40.83	19.42	23.91	7.63	3.2	0.352	0.074
22	28.99	15.43	31.08	13.19	4.36	0.389	0.082
23	43.01	20.31	20.04	7.87	5.07	0.331	0.069
24	39.37	29.2	9.19	15.58	6.27	0.245	0.051
25	53.35	18.09	18.15	3.45	3.61	0.294	0.062
26	37.22	14.71	31.96	8.25	4.37	0.359	0.075
27	42.8	20.19	21.14	7.91	5.14	0.342	0.072
28	30.85	22.75	21.57	15.16	6.09	0.342	0.072
29	36.2	14.35	32.21	8.45	4.27	0.359	0.075
30	35.06	19.75	23.11	12.15	4.16	0.353	0.074
31	35.77	20.21	22.97	11.78	4.16	0.353	0.074
32	30.65	22.57	21.12	15.09	6.04	0.342	0.072
33	40.19	19.37	24.48	7.75	3.18	0.363	0.076
34	27.54	14.64	31.44	12.43	4.18	0.402	0.084
35	48.81	16.13	19.45	7.16	4.25	0.335	0.07
36	49.65	20.64	18.06	3.7	5.01	0.288	0.06
37	27.98	14.98	30.87	12.41	4.36	0.402	0.084
38	30.37	22.56	20.93	16.66	5.87	0.342	0.072
39	53.0	17.83	19.66	3.77	3.86	0.294	0.062
40	28.99	15.33	28.0	13.74	3.51	0.389	0.082
41	36.39	14.06	34.46	8.34	4.44	0.359	0.075
42	46.68	24.23	11.96	3.39	3.37	0.29	0.061
43	54.63	20.26	12.43	3.42	4.99	0.29	0.061
44	24.89	11.22	44.92	7.89	1.14	0.402	0.084
45	34.95	13.64	34.26	8.0	4.27	0.359	0.075
46	30.4	22.56	19.85	16.77	5.99	0.342	0.072
47	54.56	20.16	12.39	3.18	5.17	0.294	0.062
48	48.23	15.98	22.61	6.49	3.71	0.363	0.076
49	49.71	20.17	19.55	3.3	5.12	0.288	0.06
50	24.42	10.93	46.89	8.42	1.28	0.4	0.084
51	54.99	20.31	11.65	3.15	4.93	0.291	0.061
52	48.77	16.23	20.92	7.05	4.28	0.356	0.075
53	54.31	21.49	13.12	3.12	4.59	0.302	0.063
54	54.4	21.59	13.39	2.69	4.58	0.308	0.065
55	34.98	24.38	16.79	13.93	7.53	0.262	0.055
56	34.82	24.92	16.94	13.86	7.08	0.262	0.055
57	40.35	29.71	6.65	15.41	6.06	0.239	0.05
58	34.55	24.94	17.23	13.41	6.5	0.262	0.055
59	41.22	30.52	6.44	15.54	6.22	0.239	0.05
60	50.68	26.83	10.04	5.32	6.79	0.286	0.06
61	49.71	22.61	14.58	7.33	3.31	0.333	0.07
62	40.3	29.74	6.94	15.41	6.21	0.255	0.054
63	49.07	22.06	16.52	7.25	3.33	0.358	0.075

Table II. Continued

Solution	Pct CaO	Pct SiO$_2$	Pct FeO	Pct MgO	Pct P$_2$O$_5$	a(FeO)	h_O
64	29.49	12.42	40.97	8.76	3.83	0.524	0.11
65	52.41	21.2	14.76	5.05	4.76	0.358	0.075

All compositions are expressed in mass percent.
Standard state for calculation of a(FeO) is pure liquid "FeO".
Standard state for calculation of h_O is the unit activity coefficient of [O] at infinite dilution.

Table III. Chemical Composition of Samples at 1923 K

Solution	Pct CaO	Pct SiO$_2$	Pct FeO	Pct MgO	Pct P$_2$O$_5$	a(FeO)	h_O
1	38.99	24.42	17.33	11.68	3.35	0.299	0.077
2	47.91	22.69	12.8	8.59	7.34	0.268	0.069
3	43.11	20.15	18.67	8.57	4.83	0.307	0.079
4	33.68	18.26	24.64	7.19	7.99	0.346	0.088
5	44.74	13.72	25.07	6.03	3.17	0.352	0.09
6	39.88	24.81	18.52	10.78	3.73	0.299	0.076
7	48.54	18.01	19.54	6.15	3.54	0.322	0.083
8	38.52	28.48	10.62	16.0	6.14	0.241	0.062
9	40.04	24.69	18.84	10.89	3.61	0.299	0.076
10	35.52	14.26	29.44	8.11	4.5	0.359	0.092
11	48.95	18.29	19.15	6.16	3.62	0.322	0.083
12	49.08	18.35	21.09	6.47	3.69	0.333	0.085
13	38.79	28.83	9.98	15.08	6.22	0.233	0.06
14	36.97	12.9	33.87	7.89	3.93	0.403	0.103
15	39.49	17.34	24.17	10.81	3.49	0.354	0.091
16	42.64	13.05	27.87	5.68	2.94	0.346	0.089
17	38.58	28.89	10.17	15.04	6.23	0.233	0.06
18	36.3	15.99	26.62	10.64	3.54	0.372	0.095
19	47.51	22.4	13.09	8.26	7.51	0.286	0.073
20	37.6	18.84	24.37	9.24	7.08	0.36	0.092
21	36.13	15.93	26.29	11.25	3.59	0.372	0.095
22	49.61	18.48	20.03	6.42	3.88	0.333	0.085
23	47.06	22.4	12.53	8.53	7.4	0.286	0.073
24	39.74	17.39	22.2	10.48	3.6	0.354	0.091
25	36.63	12.84	30.95	8.4	4.0	0.403	0.103
26	34.91	13.95	30.8	7.97	4.74	0.347	0.089
27	43.95	23.25	13.72	11.98	6.32	0.297	0.076
28	35.0	13.98	31.21	8.03	4.55	0.347	0.089
29	38.36	13.45	29.81	7.83	4.22	0.403	0.103
30	41.3	15.36	29.68	7.59	4.01	0.336	0.086
31	37.5	13.16	29.0	8.38	3.85	0.403	0.103
32	40.69	15.0	29.65	7.21	4.0	0.331	0.085
33	44.04	23.16	13.45	12.18	6.29	0.303	0.078
34	40.68	15.14	32.25	7.16	4.02	0.336	0.086
35	25.82	8.55	48.6	10.08	1.74	0.394	0.101
36	43.25	20.17	17.77	8.84	4.8	0.27	0.069
37	43.52	20.54	17.81	8.85	4.55	0.266	0.068
38	43.23	20.27	18.73	8.94	4.82	0.27	0.069
39	52.25	20.86	14.59	3.53	4.75	0.334	0.086
40	25.28	8.34	48.91	10.15	1.41	0.357	0.091
41	17.74	12.46	35.75	21.48	2.47	0.289	0.074
42	17.52	11.62	36.27	21.29	2.37	0.289	0.074
43	17.39	12.0	36.85	20.46	1.08	0.289	0.074

All compositions are expressed in mass percent.
Standard state for calculation of a(FeO) is pure liquid "FeO".
Standard state for calculation of h_O is the unit activity coefficient of [O] at infinite dilution.

concentration only. At low concentrations of FeO, *i.e.*, X(FeO) < 0.1, γ(FeO) tends to decrease gradually with increasing CaO concentration. However, no such trend is visible at X(FeO) exceeding 0.1. Further, a change of temperature within the range investigated appears to cause insignificant change in the activity coefficient of
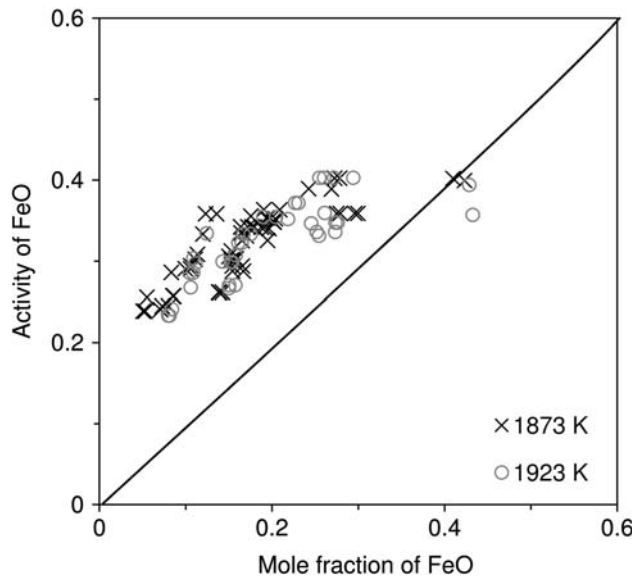
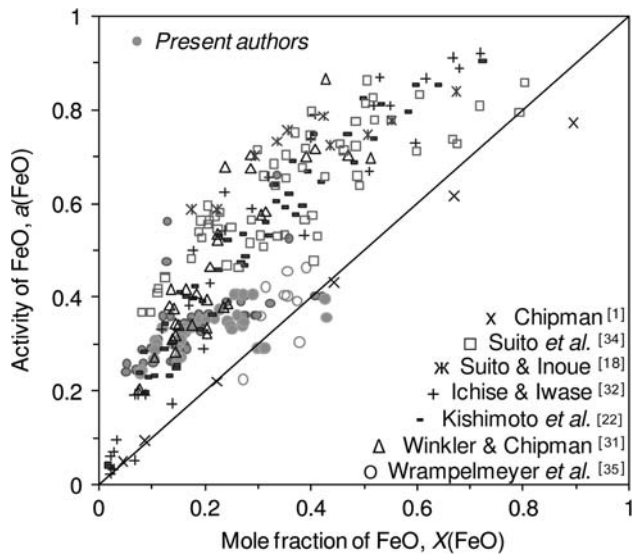Fig. 3—Variation of the activity of FeO with concentration.

Fig. 5—Effect of basicity on the activity coefficient of FeO.

Fig. 4—Effect of FeO concentration on its activity, as reported by others.

Fig. 6—Effect of FeO concentration on γ(FeO).

FeO, as is illustrated in Figures 3, 5, 6, 8, and 9. The scatter in the value of γ(FeO), for any particular level of SiO$_2$ (or CaO) concentration, may have resulted from variations in iron oxide concentration. Also, the nature of the plot remains the same if the concentration of SiO$_2$ (and CaO) is expressed in terms of mass percent instead of molar fraction. Turkdogan and Pearson observed that the activity of FeO showed a marginally negative deviation in silica-free steelmaking slags, which changed to positive deviation as the SiO$_2$ content was increased.[9] A similar trend has been reported by others as well. Figure 10 shows the variation of γ(FeO) with SiO$_2$ concentration, as has been reported by Fetters and Chipman,[5] Turkdogan and Pearson,[9] and Bodsworth,[13] and also by Kishimoto and co-workers.[22]

The results of the present authors have been superimposed on the figure for ease of comparison. It is interesting to note that all the workers, except Bodsworth,[13] reported an increase in the activity coefficient of FeO with increasing SiO$_2$ concentration. However, very little description of the effect of CaO concentration on γ(FeO) has been reported. It can be assumed that the earlier findings were probably similar to the absence of definite correlation with CaO concentration, as has been observed by the present authors.

It should be noted that the concentrations of SiO$_2$ and FeO were not strictly independent variables in the samples investigated in the present work. Increase in FeO concentration, at any given level of basicity, caused a proportionate decrease in the concentrations of both
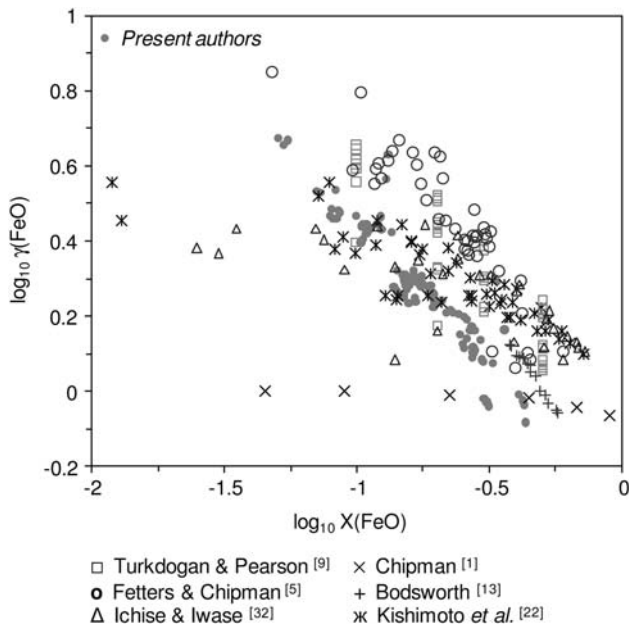
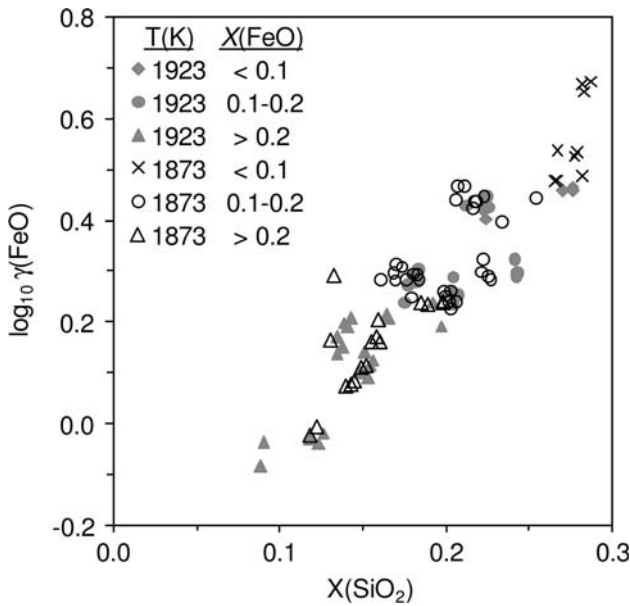Fig. 7—Variation of γ(FeO) with concentration, reported by others.[1,5,9,13,22,32]

Fig. 9—Variation of the activity coefficient of FeO with CaO concentration.
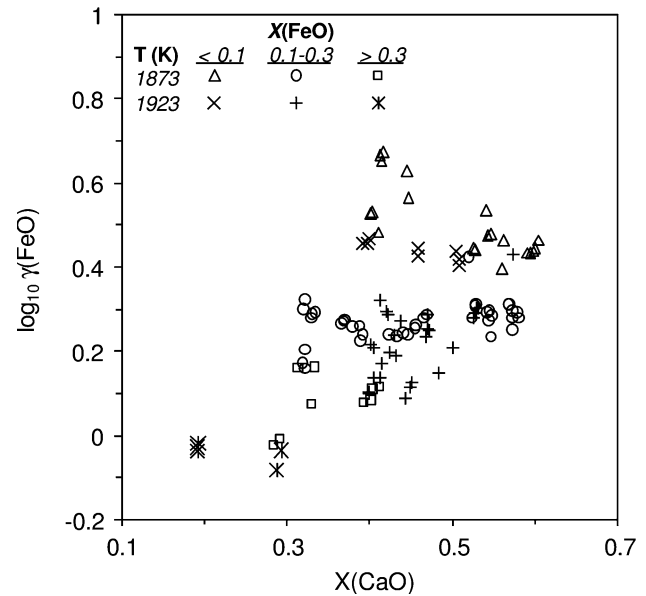

Fig. 8—Variation of the activity coefficient of FeO with SiO$_2$ concentration.
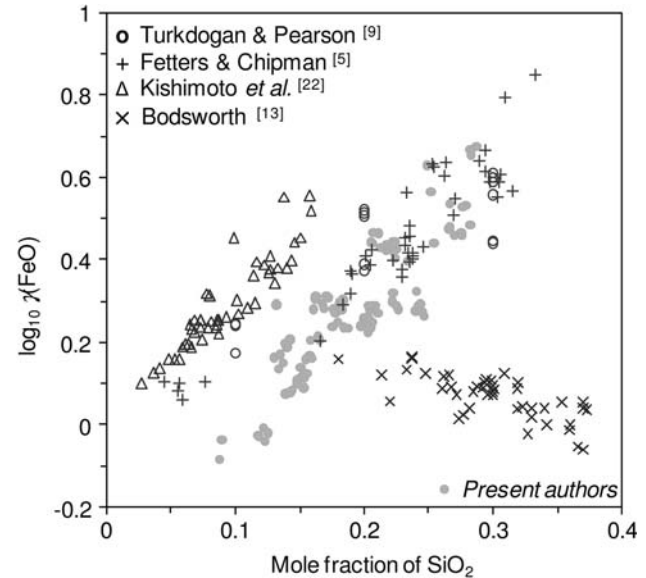
Fig. 10—Effect of SiO$_2$ concentration on the activity coefficient of FeO, as reported by others.[5,9,13,22]

CaO and SiO$_2$. This resulted in a negative correlation between X(FeO) and X(SiO$_2$), as is illustrated in Figure 11. Therefore, the trend shown in Figure 8 should be treated with caution. It is likely that a similar situation might have existed with some of the results shown in Figure 10, but that could not be verified due to the nonavailability of complete information for many of the sources.

D. Estimation of γ(FeO)

Figure 6 illustrates that the activity coefficient of FeO is practically a function of FeO concentration only, with

a negligible influence of temperature. The relatively small temperature interval of only 50 K could have been partly responsible for this. A mathematical correlation for estimation of the activity coefficient of FeO was attempted, neglecting the effect of temperature:

$$\log_{10}\gamma(FeO) = -0.7335\log_{10}X(FeO) - 0.2889 \;\; (r^2 = 0.93)$$

[2]

Correlation [2] is simple in form and easy to use for estimation of the activity coefficient of FeO. Basicity of the slag was found to be statistically insignificant as an
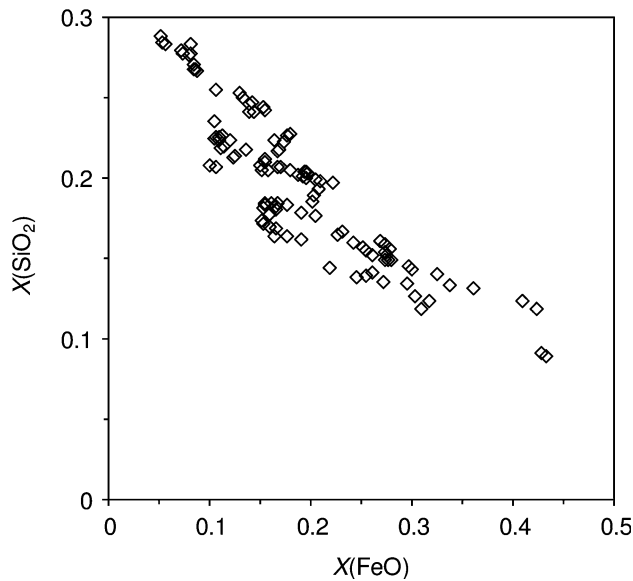
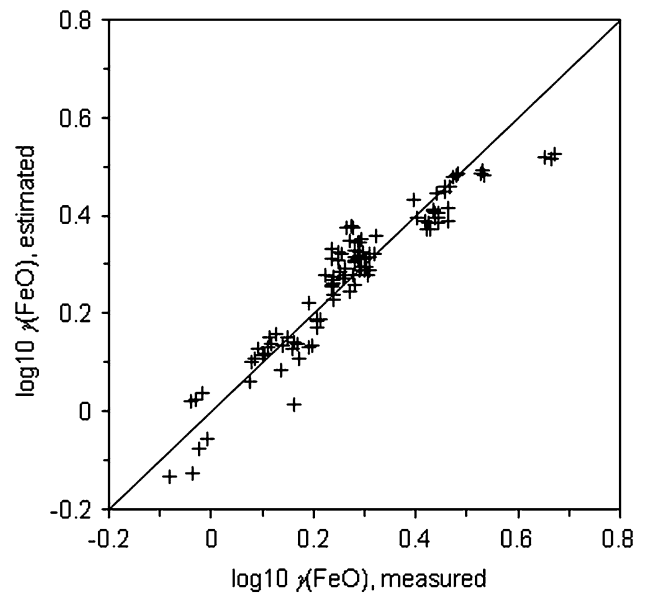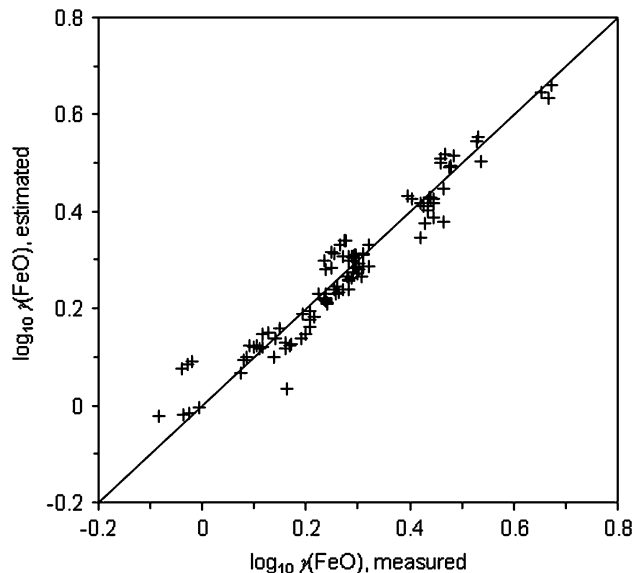Fig. 11—Interdependence of the concentrations of FeO and SiO₂.

Fig. 12—Comparison of γ(FeO), measured *vs* calculated using Eq. [2].

independent variable and, hence, was excluded from the correlation. This conforms to the trend seen in Figure 5, which shows no definitive influence of basicity on γ(FeO). The comparison between the measured and calculated values of γ(FeO), using correlation [2], is illustrated in Figure 12.

It can be seen in Figures 8 and 9 that the concentration of SiO₂ has an effect on the activity coefficient of FeO, while CaO concentration has a much weaker influence. Therefore, a correlation was also attempted considering CaO and SiO₂ concentrations separately, instead of considering basicity as a single variable. This led to the correlation

Fig. 13—Comparison of γ(FeO), measured *vs* calculated using Eq. [3].

$$\log_{10} \gamma(\text{FeO}) = \frac{1262}{T} - 1.1302 X(\text{FeO}) + 0.96 X(\text{SiO}_2)$$
$$+ 0.123 X(\text{CaO}) - 0.4198 \quad (r^2 = 89\,\text{pct})$$
$$[3]$$

The goodness of fit of this correlation is illustrated in Figure 13. Equation [3] shows that the activity coefficient of FeO is influenced by the concentrations of both CaO and SiO₂, even though it is unaffected by basicity. In fact, the coefficients of X(CaO) and X(SiO₂) have the same sign, which may explain why no perceptible dependence of γ(FeO) on basicity could be observed. The correlation coefficients of Eqs. [2] and [3] are practically the same (92 and 93 pct). Therefore, it can be concluded that γ(FeO) can be adequately estimated using Eq. [2], and incorporation of additional compositional variables does not yield any significant improvement.

V. CONCLUSIONS

1. The activity of FeO, measured by equilibration of liquid iron containing oxygen and phosphorus, with CaO-SiO₂-FeO$_x$-P₂O₅-MgO slag, shows pronounced positive deviation from ideality, at least up to X(FeO) = 0.4.
2. Change in basicity over the range (pct CaO)/(pct SiO₂) = 1 to 4 had a negligible effect on γ(FeO).
3. γ(FeO) shows a strong tendency to decrease with increasing mole fraction of FeO, irrespective of temperature and basicity.
4. Increase of SiO₂ mole fraction tends to have a positive effect on γ(FeO), but the trends cannot be confirmed, because X(SiO₂) was strongly dependent on X(FeO).

5. The proposed correlation is capable of fairly accurate estimation of the activity coefficient of FeO.

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