Research on the Activity of Components in Fundamental System in Iron Blast Furnace Slag. III : Measurement of the Activity of Silica and Alumina in CaO-MgO-SiO_2-Al_2O_3 System

Research on the Activity of Components in Fundamental System in Iron Blast Furnace Slag. III Measurement of the Activity of Silica and Alumina in CaO-MgO-SiO$_2$-Al$_2$O$_3$ System*

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Synopsis

Our previous reports described the determination of activity of SiO$_2$ and Al$_2$O$_3$ in the slag of CaO-SiO$_2$-Al$_2$O$_3$ system by using the e.m.f. method of double cell. The present study investigated the effect of MgO on the activity of SiO$_2$ and Al$_2$O$_3$. From the experimental results it was found that at a constant concentration of Al$_2$O$_3$, activity coefficient of SiO$_2$, γ SiO$_2$ increased as substitution of MgO for CaO increased. With the addition of MgO, the activity of silica approached Raoult's law. At a constant MgO concentration, the amphoteric nature of Al$_2$O$_3$ was clarified as in CaO-SiO$_2$Al$_2$O$_3$ system.

Concerning the effect of MgO on the activity of Al$_2$O$_3$, an intimate relation exists between $a_{Al_2O_3}$ and basicity, that is, by chosing the basicity as $N_{CaO+MgO}/N_{SiO_2}$, a relationship could be found between log $a_{Al_2O_3}$ and basicity which corresponded to the results obtained in the slag of CaO-SiO$_2$-Al$_2$O$_3$ system. The above facts show the behaviour of MgO which acts as a base.

I. Introduction

Since the slag plays an important role in iron making process, many investigations have been made from the viewpoint of physical chemistry on the properties of the slag and the equilibrium measurement between the slag and the molten iron.
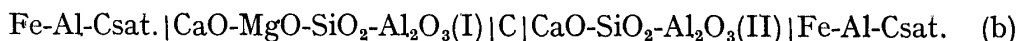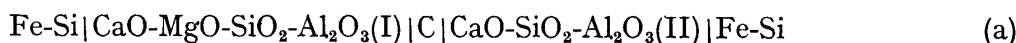
On the other hand, with the confirmation of the ionic nature of the slag obtained through physicochemical studies and electrochemical studies, measurements of its activity by using reversible cells offer a powerful weapon for obtaining fundamental knowledge of the properties and behaviours of slags. The authors have continued researches on the activity of components in the fundamental system of iron blast furnace slag and already reported on measurements of the activity of silca and alumina in the system CaO-SiO$_2$-Al$_2$O$_3$ by using the double cell[1][2].

The present study was performed to investigate the activity of silica and alumina in the CaO-MgO-SiO$_2$-Al$_2$O$_3$ system, with a view to studying the effect of magnesia on the activity of silica and alumina by using the following double cell :

(1) K. Sanbongi and Y. Omori, Sci. Rep. RITU, A11 (1959), 244.
(2) K. Sanbongi and Y. Omori, Sci. Rep. RITU, A11 (1959), 339.

$$\text{Fe-Si} \mid \text{CaO-MgO-SiO}_2\text{-Al}_2\text{O}_3(\text{I}) \mid \text{C} \mid \text{CaO-SiO}_2\text{-Al}_2\text{O}_3(\text{II}) \mid \text{Fe-Si} \qquad (a)$$

$$\text{Fe-Al-Csat.} \mid \text{CaO-MgO-SiO}_2\text{-Al}_2\text{O}_3(\text{I}) \mid \text{C} \mid \text{CaO-SiO}_2\text{-Al}_2\text{O}_3(\text{II}) \mid \text{Fe-Al-Csat.} \quad (b)$$

II. Experimental procedure

The apparatus for the e.m.f. measurement is shown in Fig. 1. Graphite was employed as a cell container and the two chambers 18 mm in diameter and 44 mm in depth containing the slags, are separated by a wall 3 mm thick.

Beneath each slag chamber is an electrode chamber 10 mm in diameter and 35 mm in depth, in which an alundum tube is firmly embedded. Both tubes contain electrodes of the same composition, which are in contact with high-purity graphite lead.

In the cell of type (a), molten sliver was inserted between iron-silicon alloy electrode of Si 42.1 wt% and the graphite lead, but in (b) the Fe-Al-Cast. alloy electrodes of Al 33.5 of 18.7 wt% were in direct contact with the lead.

Regardless of whether the double cell was of type (a), or (b), one of the

Fig. 1. Experimental apparatus.
A : Graphite cell   D : Metal electrode
B : Silver   E : Graphite lead
C : Slag electrolyte

slag chambers was always filled with the reference slag of composition SiO_2 2.2; CaO 45.2; Al_2O_3 53.7 wt%. The composition of the slag in the other chamber was then arranged to suit the test conditions.

The experimental procedure was generally the same as that in the previous studies.[1][2] The metal electrodes were first inserted in the electrode chamber, and the graphite container was heated in a high frequency furnace to 1630°C at which it was kept for 25 minutes. Then the graphite premelting chamber filled with slag was inserted in the slag chamber.

After melting the slag specimens, the attached stoppers were pulled up and the premelting chambers were simultaneously taken out and the e.m.f. was measured with K-2 potentiometer. Temperature was measured by Pt- Pt·Rh thermocoulpe inserted through the hole on the side of the slag chamber.

One hour keeping at a given temperature after pulling up the premelting chamber showed that the variation of e.m.f. was in the range of 10 mv.

Experimental range of slag composition in the $CaO\text{-}MgO\text{-}SiO_2\text{-}Al_2O_3$ system was selected in conformity with the phase diagram determined by Osborn *et al.*[3]. In Fig. 2 are shown liquidus lines of alumina 10, 20, 30% respectively in the quaternary slag.
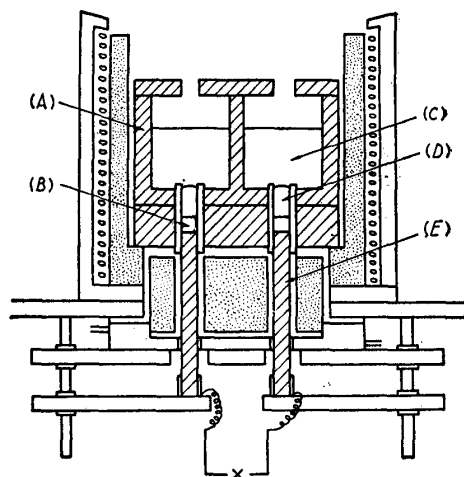
(3)   E.F. Osborn, R.C. DeVries, K.H. Gee and H.M. Kraner, J. Metals, 6 (1954), 33.
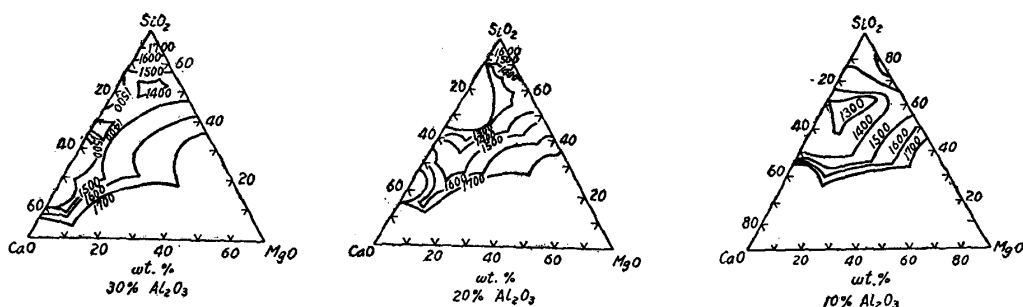
Fig. 2.   Liquidus lines of the system $CaO\text{-}MgO\text{-}SiO_2\text{-}Al_2O_3$

III. Experimental results

(a) Activity of silica

From the fact that the e.m.f. of the double cell was equal regardless of whether graphite or magnesia was used in preparing the container as described in the previous report[1], it may be concluded that the intermediate graphite electrode acts as an oxygen electrode and the Fe–Si electrode as silicon electrodes.
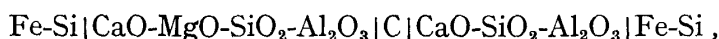
In this case, in the single cell ;

$$Fe\text{-}Si\,|\,CaO\text{-}SiO_2\text{-}Al_2O_3\,|\,C$$
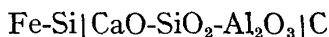
without specifying the form of the silicate ion in the molten slag, the cell reaction is expressed by the equation (1) as follows :

$$Si(Fe\text{-}Si) + 2O(C) = SiO_2(slag), \quad n=4 \tag{1}$$
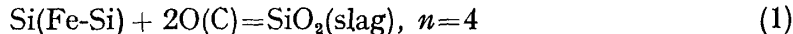
$$E = E_1{}^\circ + \frac{RT}{4F} \ln a_{SiO_2}/a_{Si} \cdot a_O{}^2 \tag{1'}$$

Thus in the double cell;

$$Fe\text{-}Si\,|\,CaO\text{-}MgO\text{-}SiO_2\text{-}Al_2O_3\,|\,C\,|\,CaO\text{-}SiO_2\text{-}Al_2O_3\,|\,Fe\text{-}Si\ ,$$

when the electrodes are made of Fe–Si alloy of the same composition and one of the slag is taken as the standard state which is chosen as β-cristobarite at 1630°C, the activity of silica in the tested slag can be determined from the difference in the e.m.f. of the two single cells as follows :

$$E = -RT/4F \ln a_{SiO_2} \tag{2}$$

As the e.m.f. obtained between the reference slag and standard state was 197±3mv, e.m.f. of tested slag against the reference slag were converted to e.m.f.'s against the standard state, then the activity of silica was determined by equation (2).

Measurements of the activity of silica were performed in two series with 10 and 20 wt% alumina in which magnesia was substituted for lime at 30 wt%.

The experimental results are shown in Table 1. The relation between silica content and e.m.f. of the cell from Table 1, is shown in Fig. 3. The e.m.f. of the cell increased with an increase in magnesia content in both series of Al_2O_3 10 and 20%. On the other hand, with a given content of magnesia, the e.m.f. curves of

Table 1. Experimental results of cell (a) on the system
CaO–MgO–SiO$_2$–Al$_2$O$_3$.

Slag composition								$\dfrac{N_{CaO+MgO}}{N_{SiO_2}}$	e.m.f. V	a_{SiO_2}	γ_{SiO_2}
wt. %				mol. %							
CaO	MgO	SiO$_2$	Al$_2$O$_3$	CaO	MgO	SiO$_2$	Al$_2$O$_3$				
40	10	40	10	41.3	14.4	38.7	5.7	1.44	0.095	0.085	0.220
30	10	40	20	32.5	15.5	40.5	11.9	1.18	0.110	0.10	0.247
35	10	45	10	36.3	14.4	43.6	5.7	1.16	0.116	0.12	0.275
25	10	45	20	27.2	15.1	45.7	12.0	0.93	0.130	0.20	0.438
30	10	50	10	31.2	14.5	48.6	5.7	0.94	0.155	0.35	0.720
20	10	50	20	21.9	15.2	51.0	12.0	0.70	0.139	0.23	0.451
25	10	55	10	26.1	14.5	53.6	5.7	0.76	0.164	0.45	0.840
15	10	55	20	16.4	15.3	56.3	12.1	0.56	0.166	0.46	0.817
20	10	60	10	17.9	14.6	61.7	5.8	0.53	0.192	0.93	1.51
10	10	60	20	10.9	15.4	61.6	12.1	0.43	0.185	0.70	1.14
30	20	40	10	29.8	27.6	37.1	5.5	1.55	0.098	0.091	0.255
20	20	40	20	20.8	28.9	38.8	11.5	1.28	0.116	0.14	0.363
25	20	45	10	24.9	27.7	41.9	5.5	1.26	0.125	0.17	0.406
15	20	45	20	15.6	29.0	43.9	11.5	1.03	0.131	0.20	0.358
20	20	50	10	20.0	27.8	46.7	5.5	1.03	0.156	0.37	0.792
10	20	50	20	10.5	29.1	48.9	11.5	0.81	0.148	0.32	0.656
15	20	55	10	15.0	28.0	51.5	5.5	0.83	0.170	0.52	1.010
5	20	55	20	5.2	29.2	54.0	11.6	0.63	0.162	0.43	0.796
20	30	40	10	19.1	39.9	35.7	5.3	1.65	0.098	0.091	0.255
10	30	40	20	10.0	41.7	37.3	11.0	1.38	0.118	0.12	0.322
15	30	45	10	14.4	40.0	40.3	5.3	1.34	0.118	0.12	0.298
5	30	45	10	5.0	41.8	42.1	11.0	1.11	0.137	0.22	0.523
10	30	50	10	9.6	40.2	44.9	5.3	1.11	0.152	0.34	0.757
	30	50	20		42.0	46.9	11.1	0.90	0.147	0.30	0.714
25	10	65		25.1	14.0	60.9		0.64	0.182	0.69	1.13
30	10	60		30.0	13.9	56.1		0.78	0.175	0.57	1.02
35	10	55		34.9	13.9	51.2		0.95	0.150	0.30	0.586
45	10	45		44.6	13.8	41.6		1.40	0.091	0.075	0.180
50	10	40		49.4	13.7	36.9		1.52	0.072	0.038	0.103
50	10	35	5	50.3	14.0	32.9	2.8	1.96	0.034	0.019	0.058
50	10	15	25	54.5	15.2	15.3	15.0	4.56	− 0.005	0.0070	0.046
50	10	10	30	55.7	15.5	10.4	18.4	6.80	− 0.031	0.0040	0.039
51	9	2	38	60.4	13.0	2.2	24.4	33.36	− 0.071	0.0009	0.041

Al$_2$O$_3$ 10% and 20% crossed each other, and the curve of Al$_2$O$_3$ 10% occupied the upper part when the content of silica increased, on the contrary, the curve of Al$_2$O$_3$ 20% occupied the upper part when the content of silica decreased.

Within the experimental range of slag composition, mol fraction of alumina varied within 0.053~0.057 and 0.11~0.12 in 10 and 20% Al$_2$O$_3$ respectively, so alumina content was considered to be constant, and the effect of the substitution of magnesia
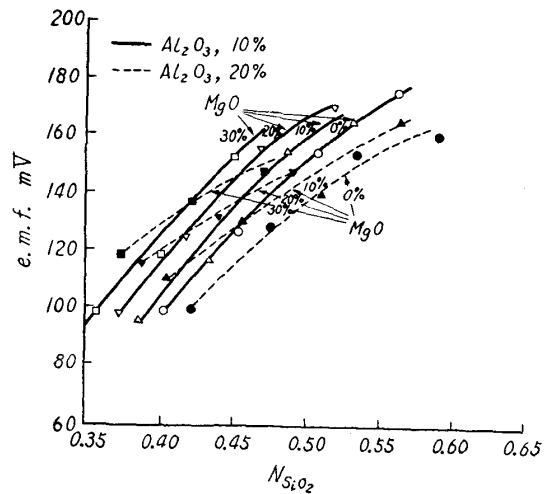

Fig. 3. Relation between slag composition and e.m.f. on the system CaO-MgO-SiO$_2$-Al$_2$O$_3$, at 1630°C
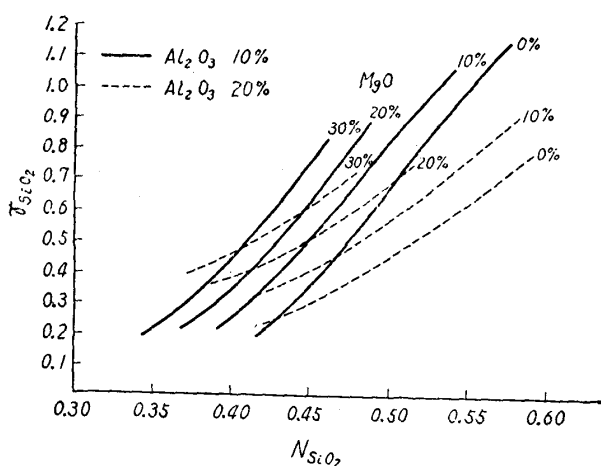
Fig. 4. Activity coefficient of silica at $CaO\text{-}MgO\text{-}SiO_2\text{-}Al_2O_3$ system.

for lime on the activity coefficient of silica, γ_{SiO_2} could be determined. The relation between γ_{SiO_2} and N_{SiO_2} is shown in Fig. 4. It is clear from Fig. 4 that the activity coefficient of silica considerably increased with increases in the amount of substitution of magnesia for lime. These fact clarified that the activity of SiO_2 would approach Raoult's law with the increase of magnesia.

When mol fraction of magnesia varied within 0.14~0.16 and 0.40~0.42 at 10 and 30 wt% of MgO respectively and the content of magnesia was considered to be constant, then the effect of the substitution of alumina for lime on the activity coefficient of SiO_2, γ_{SiO_2} could be determined. γ_{SiO_2} decreased with an increase in the amount of substitution of alumina for lime with higher content of silica but increased with lower content of silica. The above fact indicates the amphoteric nature of alumina prevailing even in the quaternary system containing magnesia as in $CaO\text{-}SiO_2\text{-}Al_2O_3$ system.

(b) Activity of alumina

As described in the previous report[2], in the single cell;

$$Fe\text{-}Al\text{-}Csat. \mid CaO\text{-}MgO\text{-}SiO_2\text{-}Al_2O_3 \mid C ,$$
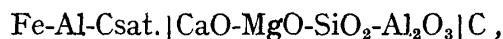
without specifying the form of the ion in the molten slag, the cell reaction is expressed by

$$2\,Al\,(Fe\text{-}Al\text{-}Csat.) + 3\,O(C) = Al_2O_3(slag),\ n=6 \qquad (3)$$

$$E_1 = E_1{}^0 + \frac{RT}{6F}\ln a_{Al_2O_3}/a^2{}_{Al}\cdot a_0{}^3 \qquad (3')$$

When the electrodes are made of Fe-Al-Csat. alloy of the same composition and one of the slag is taken as the standard state for which corundum is chosen at 1630°C, the activity of alumina in tested slag can be determined from the difference in the e.m.f. of the two single cells as follows :

$$E = -RT/6F \ln a_{Al_2O_3} \qquad (4)$$

E.m.f. obtained against the reference slag was converted to e.m.f. against the standard state by using the same procedure as in the case of investigation of $CaO\text{-}SiO_2\text{-}Al_2O_3$ system, and the activity of alumina was determined by equation (4).

Measurements of the activity of alumina were carried out on the two series with 10 and 20 wt% of alumina in which magnesia was substituted for lime at 20 wt%.

Table 2. Experimental results of cell (b) on the system
$CaO-MgO-SiO_2-Al_2O_3$.

| Slag composition | | | | | | | | $\dfrac{N_{CaO+MgO}}{N_{SiO_2}}$ | e.m.f. $-V$ | $a_{Al_2O_3}$ | $\gamma_{Al_2O_3}$ |
| wt. % | | | | mol. % | | | | | | | |
CaO	MgO	SiO$_2$	Al$_2$O$_3$	CaO	MgO	SiO$_2$	Al$_2$O$_3$				
35	10	45	10	36.3	14.4	43.6	5.7	1.16	0.200	0.00037	0.0065
25	10	55	10	26.1	14.5	53.6	5.7	0.76	0.142	0.0030	0.055
30	10	50	10	31.2	14.5	48.6	5.7	1.03	0.160	0.0016	0.028
25	20	45	10	24.9	27.7	41.9	5.5	1.26	0.189	0.00054	0.0098
15	20	55	10	15.0	27.9	51.5	5.5	0.76	0.145	0.0027	0.049
20	20	50	10	20.0	27.8	46.7	5.5	1.03	0.157	0.0017	0.031
25	10	45	20	27.2	15.1	45.7	12.0	0.93	0.148	0.0024	0.020
15	10	55	20	16.4	15.3	56.3	12.1	0.56	0.107	0.010	0.083
20	10	50	20	21.9	15.2	50.9	12.0	0.70	0.120	0.0067	0.056
15	20	45	20	15.6	29.0	43.9	11.5	1.03	0.150	0.0022	0.019
5	20	55	20	5.2	29.2	54.0	11.6	0.63	0.115	0.0080	0.069
10	20	50	20	10.5	29.1	48.9	11.5	0.81	0.126	0.0062	0.054
45	10	35	10	46.5	14.3	33.6	5.7	1.80	0.210	0.00025	0.0044
35	20	35	10	34.7	27.6	32.3	5.4	1.92	0.185	0.00063	0.012
35	10	35	20	37.8	15.0	35.3	11.9	1.50	0.160	0.0016	0.013
25	20	35	20	25.9	28.8	33.8	11.4	1.77	0.153	0.0020	0.013
40	10	40	10	41.3	14.4	38.7	5.7	1.44	0.222	0.0016	0.0028
30	10	40	20	32.5	15.1	40.5	11.9	1.16	0.160	0.0016	0.013
40	10	35	15	42.2	14.7	34.4	8.7	1.65	0.185	0.00063	0.0073

The results are shown in Table 2. The relation between log $a_{Al_2O_3}$ and content of alumina from that table is given in Fig. 5 in collation with that obtained from the $CaO-SiO_2-Al_2O_3$ system. In the $CaO-Al_2O_3-SiO_2$ system, the activity coeffecient of alumina increases with an increase in SiO$_2$ content in the range above $N_{SiO_2}=0.40$, and at a given SiO$_2$ content, the relation between log $a_{Al_2O_3}$ and $N_{Al_2O_3}$ is approximately

Fig. 5. Relation between activity of alumina and mol fraction of alumina.

represented by a straight line. The results obtained in the quaternary system containing magnesia are congruent with the straight line at a given content above $N_{SiO_2}=0.40$. On the contrary, the activity coefficient of alumina increases with a decrease in silica content to less than $N_{SiO_2}=0.40$, though the linear relationship between log $a_{Al_2O_3}$ and $N_{Al_2O_3}$ is considered to be still valid. The fact that the activity of alumina at a given alumina content is the smallest at $N_{SiO_2}=0.40$ and increases when silica content either increases or decreases indicates the existence of close connection between Al_2O_3 and basicity already shown in the source of the iso-activity line of alumina.
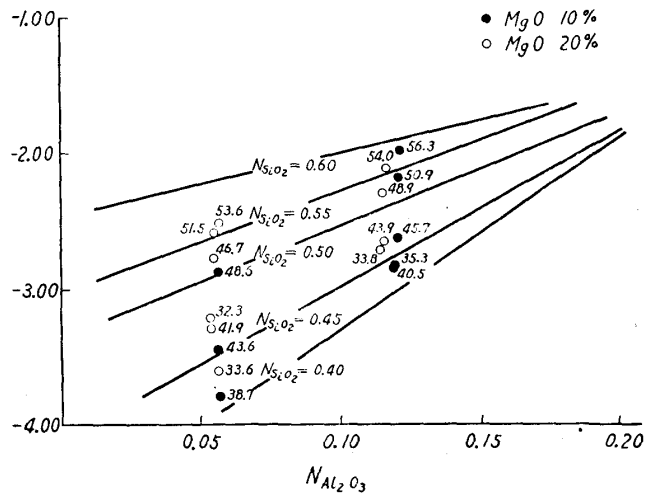
Now assuming magnesia to be equivalent to lime in strength of base, the
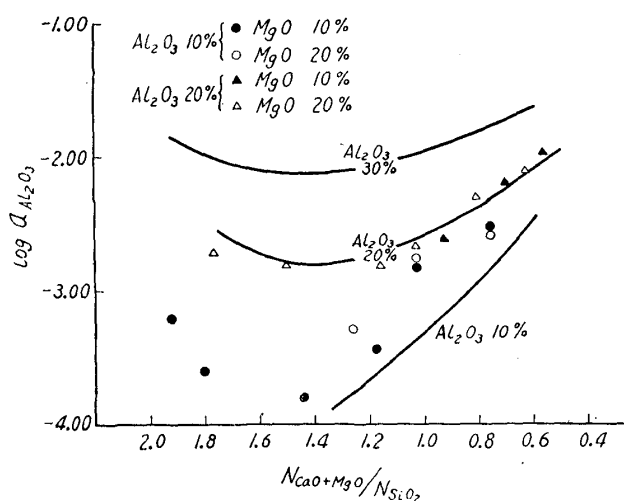
Fig. 6. Relation between activity of alumina and basicity $N_{CaO+MgO}/N_{SiO_2}$.

relation between $\log a_{Al_2O_3}$ and basicity expressed by $N_{CaO+MgO}/N_{SiO_2}$ is shown is Fig. 6. Full lines in Fig. 6 show the relation between $\log a_{Al_2O_3}$ and basicity expressed by N_{CaO}/N_{SiO_2} in the system $CaO-SiO_2-Al_2O_3$. In 20% alumina series of quaternary system the results consist of full lines obtained in the ternary system either 10 or 20 % of magnesia; but in 10 % alumina series, the activity of alumina increases with an increase in magnesia content from 10% to 20%. It is seen from the above facts that magnesia acts as a slightly weak base, compared with lime, in the range of slag composition studied.

IV. Discussion of the results

In our previous report[1], iso-activity line of silica was determined for the $CaO-SiO_2-Al_2O_3$ ternary diagram. In the $CaO-MgO-SiO_2-Al_2O_3$ system with constant Al_2O_3, the activity coefficient of SiO_2, γ_{SiO_2} increased as the amount of substitution of magnesia for CaO increased, and the activity of SiO_2 approached Raoult's law.

No report has been made experimentally on the activity of SiO_2 in $MgO-SiO_2$ melts, Richardson[4] estimated a_{SiO_2} at 1600°C for the system by using the phase diagram and thermodynamic data of compounds existing in melts.

Comparing the activity-composition diagram with $ZnO-SiO_2$ and $CaO-SiO_2$ system, the negative deviation from Raoult's law was remarkable in $ZnO-SiO_2$, $MgO-SiO_2$ and $CaO-SiO_2$ in the order named.

On the contrary, the valency of cation M^+, its radius, etc. were considered to be factors which would decide the strength of the oxide MO as acid or base. The greater the attraction of the M^+ ion for the oxygen ion, the greater the intensity as acid, and the smaller the attraction, the greater the intensity as base. As an indication of this attraction, the $2Z/r^2$ value is adopted generally ($Z=$ the valency of the M^+ ion).[5]

For the same valency, the smaller the ion radius, the larger the intensity as acid. As ion radius of Ca^{2+}, Zn^{2+} and Mg^{2+} decrease 1.06, 0.83, 0.78 in order respectively, and Mg^{2+} is considered to be the strongest acid.

(4) F.D. Richardson, "The Physical Chemistry of Melts" Institution of Mining and Metallurgy, London. (1953), 75.

(5) J.W. Tomlinson, "The Physical Chemistry of Melts" Institution of Mining and Metallurgy, London. (1953), 22.

The result estimated by Richardson[4] does not agree with this observation and activity of SiO_2 in MgO-SiO_2 shows more negative deviation, compared with ZnO-SiO_2. This fact is due to special character of Mg^{2+} as base.

At constant magnesia, γ_{SiO_2} decreased with an increase in alumina substitution for lime at higher concentration of silica, but increased with at lower concentration of silica. It can be seen only in the range higher in SiO_2 concentration where SiO_4 tetrahedron forms the network of three dimensions that the Al^{3+} ion is known to take four, five and six coordination number and that it coordinates four oxygens and substitutes for the Si^{4+} ion. Therefore, the intensity of Al_2O_2 as base increases with an increase in SiO_2 concentration. When the slag composition shift to lower SiO_2 content, the coordination number of Al^{3+} ion changes gradually from four to six and aluminate or silico-aluminate ion becomes predominant. Experimental results indicate that amphoteric nature of alumina mentioned above prevailed even in the quaternary system containing magnesia as in CaO-SiO_2-Al_2O_3 system.

Concerning the activity of silica in the system CaO-MgO-SiO_2-Al_2O_3, Esin and Lepinskiï[6] also determined it by the e.m.f. method similar to the authors' investigation.

Comparison of the present authors' results with those of Esin and Lepinskiï[6] is given in detail in Table 3. The reference slag chosen by Esin and Lepinskiï was the composition of 2% SiO_2, 50% CaO, 38% Al_2O_3, 10% MgO and the e.m.f. between the reference slag and the slag of N_{CaO} 0.251, N_{MgO} 0.140, N_{SiO_2} 0.609 was given as 278 mv.

Table 3. Comparison of a_{SiO_2} at CaO-MgO-SiO_2-Al_2O_3 system

Slag Composition				Present work, 1630°C		Esin, Lepinskiï, 1470°C	
N_{CaO}	N_{MgO}	N_{SiO_2}	$N_{Al_2O_3}$	E, mv	a_{SiO_2}	E, mv	a_{SiO_2}
0.251	0.140	0.609		182	0.69	0	1.00
0.300	0.139	0.561		175	0.57		
0.320	0.140	0.540				15	0.67
0.349	0.139	0.512		150	0.30		
0.368	0.139	0.492				22	0.56
0.381	0.141	0.471				48	0.28
0.446	0.138	0.416		91	0.075	78	0.13
0.494	0.137	0.369		72	0.038	106	0.061
0.503	0.140	0.329	0.028	34	0.019	149	0.020
0.521	0.160	0.138	0.081			160	0.015
0.545	0.152	0.153	0.150	− 5	0.007	188	0.0070
0.557	0.155	0.104	0.184	−31	0.004		
0.592	0.088	0.060	0.260			235	0.0020
0.605	0.132	0.021	0.242	−71	0.0009	278	0.00065

The latter slag was near the saturation of silica at 1470°C, and its value must be recalculated from this basis. In Table 3, the authors' result deviates from that of Esin and Lepinskiï near the saturation of silica because of the difference in silica

(6) O.A. Esin, L.K. Gavrilov and B.M. Lepinskiï, Doklady Akad. Nauk, SSSR **88** (1953), 713.
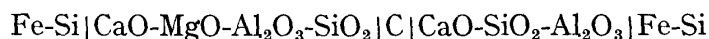
concentration taken as standard state due to the difference of experimental temperature, while fairly consistent results were obtained with a decrease in silica concentration.

In our previous reports[2], iso-activity line of alumina was determined on the CaO-SiO$_2$-Al$_2$O$_3$ ternary diagram. The course of the iso-activity lines of Al$_2$O$_3$ shows a symmetry around the straight line through the points of Al$_2$O$_3$ and of 2CaO·SiO$_2$ saturation in CaO-SiO$_2$ system.
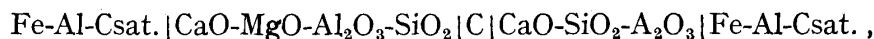
Activity coefficient of alumina increases with SiO$_2$ concentration in the range of N_{SiO_2}=0.40, and at a given SiO$_2$ concentration, the relation between log $a_{Al_2O_3}$ and $N_{Al_2O_3}$ is approximately represented by a linear curve. The results obtained in quaternary system containing magnesia consist of the line at a given concerntration above N_{SiO_2}=0.40. Experimental results also clarified that the linear re-lationship was even valid in the slag composition of silica concentration less than N_{SiO_2}=0.40, though $\gamma_{Al_2O_3}$ increased with a decrease in silica concentration.

Conclusion

By constructing the following cell:

$$Fe-Si\,|\,CaO-MgO-Al_2O_3-SiO_2\,|\,C\,|\,CaO-SiO_2-Al_2O_3\,|\,Fe-Si$$

and

$$Fe-Al-Csat.\,|\,CaO-MgO-Al_2O_3-SiO_2\,|\,C\,|\,CaO-SiO_2-A_2O_3\,|\,Fe-Al-Csat.\,,$$

the authors measured e.m.f. at 1630°C with the reference slags CaO 45.2, SiO$_2$ 2.2 and Al$_2$O$_3$ 53.7 wt% respectively.

Choosing the standard state as β-cristobarite and corundum at 1630°C, the activity of SiO$_2$ and Al$_2$O$_3$ in a given slag was calculated from the e.m.f. by the following equation respectively:

$$E = -RT/4F \ln a_{SiO_2} \quad \text{and} \quad E = -RT/6F \ln a_{Al_2O_3}$$

At constant Al$_2$O$_3$, activity coeffcient of SiO$_2$, γ_{SiO_2} increased as substitu-tion of magnesia for CaO increased and activity of SiO$_2$ approached Raoult's law. On the other hand, at constant magnesia, γ_{SiO_2} decreased with an increase in Al$_2$O$_3$ substitution of lime at higher concentration of SiO$_2$ but increased with lower concentration of silica. This phenomena was explained as being the amphoteric nature of Al$_2$O$_3$.

Concerning the effect of MgO on the activity of Al$_2$O$_3$, an intimate relation exists between $a_{Al_2O_3}$ and basicity. Choosing the basicity as $N_{CaO+MgO}/N_{SiO_2}$, the relationship between log $a_{Al_2O_3}$ and basicity corresponds to the results obtained in the slag of CaO-SiO$_2$-Al$_2$O$_3$ system. They represent the behaviour of MgO for acting as base.