

# Research on the Activity of Components in Fundamental System of Iron Blast Furnace Slag. II

## Measurement of the Activity of Alumina in the System CaO-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>\*

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### Synopsis

The e.m.f. of the following cell



was measured at 1630°C with the reference slags CaO 45.2, SiO<sub>2</sub> 2.2 and Al<sub>2</sub>O<sub>3</sub> 53.7 wt % respectively. It was found that the e.m.f. sharply increased with increasing concentration of lime, and then decreased gradually. On the other hand, with constant alumina series, a marked increase of the e.m.f. was observed in the range near the liquidus of 2CaO·SiO<sub>2</sub>. Now choosing the standard state as the solid alumina at 1630°C, the activity of alumina in a given slag was calculated from the e.m.f. by the following equation:  $E = RT/6F \ln a_{\text{Al}_2\text{O}_3}$ .

From the authors' data, the isoactivity lines were drawn on the ternary coordinates of CaO-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>. And symmetrical isoactivity lines were obtained about the straight line connecting between 2CaO·SiO<sub>2</sub> at CaO-SiO<sub>2</sub> system and Al<sub>2</sub>O<sub>3</sub> coordinate, which may be explained by the change of existing anion species of aluminum in the slag. Finally the most probable anion species and their stabilities were discussed.

### I. Introduction

Since the slag plays an important role in iron making process, many investigations have been performed on the properties of slag and the equilibrium between the slag and the molten iron from the view point of physical chemistry. On the other hand, with the confirmation of the ionic nature of slag obtained through the physicochemical studies and the electrochemical studies, measurements of its activity using reversible cells offers a powerful weapon for the fundamental knowledge of the properties and behaviours of slags. Authors have continued the research on the activity of components in fundamental system of iron blast furnace slag and already finished measurements of the activity of silica in the system CaO-SiO<sub>2</sub> and CaO-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> using the double cell.<sup>(1)</sup>

The present investigation was performed in order to investigate the activity of alumina in the system CaO-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>, since no systematic measurements have been done except the measurement of activity of alumina in the system CaO-MgO-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> reported by Esin and Lepinskii.<sup>(2)</sup>

\* The 111th Report of the Research Institute of Mineral Dressing and Metallurgy.

(1) K. Sanbongi and Y. Omori, Sci. Rep. RITU, A 11 (1959), 244.

(2) O. A. Esin and B. M. Lepinski, Doklady Akad. Nauk, SSSR, 91 (1953), 1187.

## II. Experimental procedure

The apparatus for the e.m.f. measurement is shown in Fig. 1. When graphite was used to prepare the cell container, the two slag chambers of 20 mm in depth and 40 mm in diameter were partitioned by a wall of 3 mm in thickness. Under

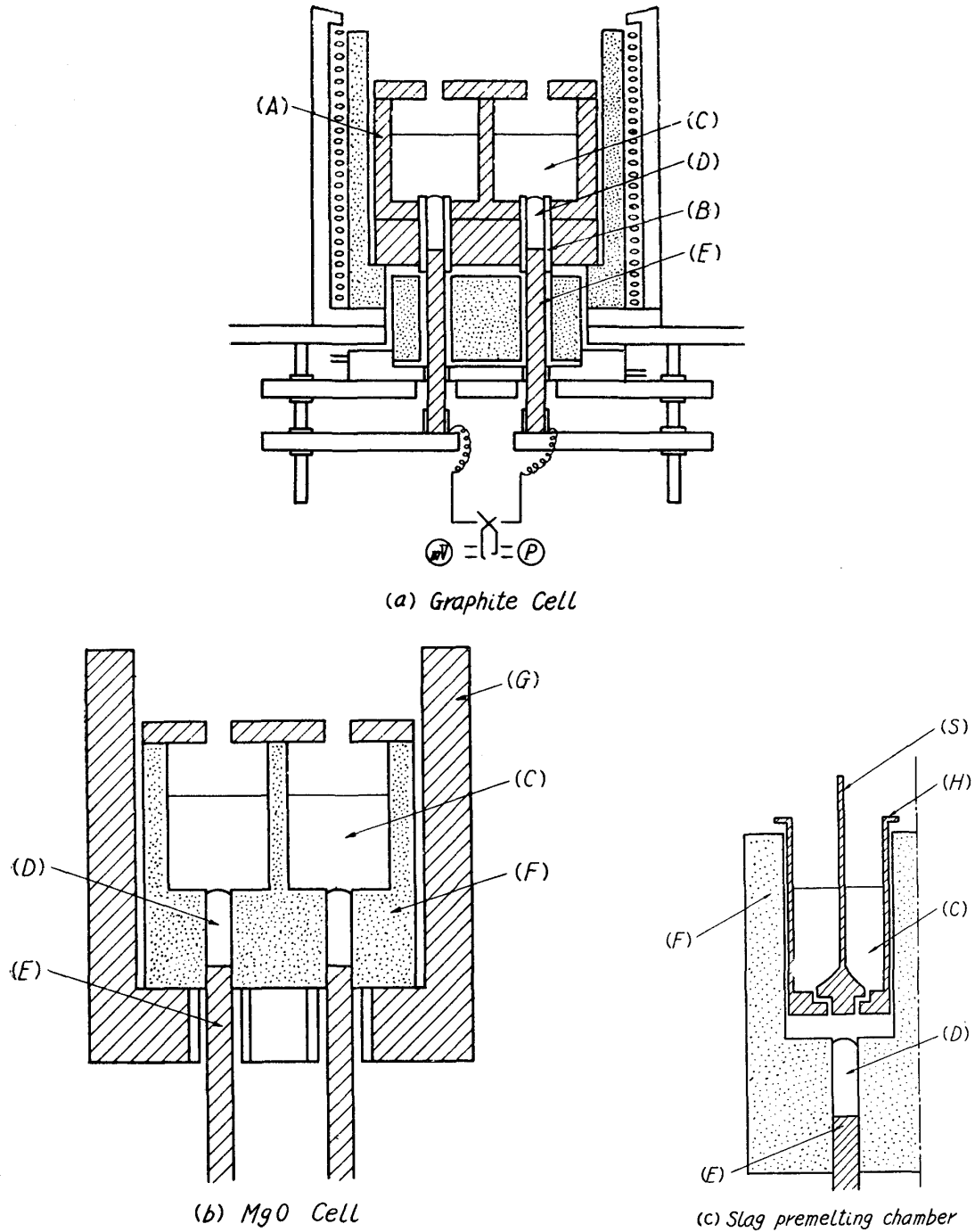


Fig. 1. Experimental apparatus.

- |   |                        |
|---|------------------------|
| A : Graphite cell                           | F : Magnesia cell      |
| B : Arandum tube                            | G : Graphite crucible  |
| C : Slag electrolyte                        | H : Premelting chamber |
| D : Fe-Al-C <sub>sat.</sub> alloy electrode | S : Stopper            |
| E : Graphite lead                           |                        |

each slag chamber was provided an electrode chamber 10 mm in diameter and 35 mm in depth in which an arandum tube containing the iron-aluminum alloy saturated with carbon was inserted.

To prevent the oxidation of graphite lead, it was inserted in a magnesia tube sealed with a silicon rubber gasket at the bottom and protected by a copper water-cooling tube.

When a cell container of magnesia was used, a wall of 3 mm in thickness partitioned off the two slag chambers of 15 mm in diameter and 30 mm in depth and iron-aluminum alloy saturated with carbon was directly inserted in the electrode chambers and connected with the graphite lead. Other details of this cell were the same as those in the graphite container.

To prevent any error caused by electrode condition, two pieces cut out from the adjacent parts of the same rod specimens 6 mm in diameter and 150~180 mm long were used as these electrodes.

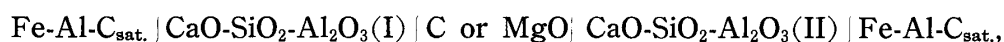
To preparing synthetic slag, used as specimen chemically pure silica, calcium carbonate and aluminum oxide were mixed in the weight rate of the slag composition, melted in graphite crucibles and powdered after solidification.

The experimental procedure was generally the same as that in the previous study<sup>1)</sup>: The iron aluminum alloy saturated with carbon was first inserted in the electrode chamber, the graphite container was heated in a high-frequency furnace to 1630°C and kept constant for 25 minutes. The graphite premelting chambers shown in Fig. 1 (c), filled with slag, were then inserted into the slag chambers.

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 thermocouple calibrated at the melting point of iron, nickel and silver, and inserted through the hole beside the slag chamber. Its reading showed a difference of  $\pm 5^\circ\text{C}$  at 1630°C from that of a thermocouple directly dipped in the slag 6 mm deep.

### III. Experimental results

In the following double cell:



there is to be no danger of thermal e.m.f. being generated, but before the electrodes come into contact with the molten slags, a blank e.m.f. of about 10 mV is generated. Thus, it is impossible to measure accurate cell e.m.f without making corrections for it when the slag specimens charged in the two slag chambers are not much different in composition. To ensure high accuracy in measurement of CaO-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> system slags within the composition range of blast furnace slags, it is preferable to choose a concentrated solution of alumina as reference slag, and in this study CaO 45.2 %, SiO<sub>2</sub> 2.2 % Al<sub>2</sub>O<sub>3</sub> 53.6 % similar to the previous report, was used. To investigate the reversibility of double cell, first of all, a comparison of the experimental results from graphite and magnesia container for

the double cell with the same slag and metal electrode are shown in Table 1. As shown in Table 1, the e.m.f. was considered to be the same in the experimental error of  $\pm 7$  mV, whether graphite or magnesia was used in preparing the con-

Table 1. Comparison of e.m.f. of the cell using graphite and magnesia container.

Slag composition (wt%)			Intermediate electrode	E.M.F. - V	Al content of Fe-Al-C <sub>sat.</sub> electrode wt%
Al <sub>2</sub> O <sub>3</sub>	CaO	SiO <sub>2</sub>			
38.7	56.2	5.6	MgO	0.38	40.6
			C	0.40	
35.8	26.0	39.7	MgO	0.53	40.6
			C	0.54	
24.3	50.8	25.2	MgO	0.171	33.5
			C	0.157	
11.3	47.2	41.1	MgO	0.237	40.6
			C	0.252	
4.8	36.6	58.1	MgO	0.122	33.5
			C	0.130	

tainer of the double cell. On the other hand, the comparison of the experimental results obtained by using the various content of aluminum in iron-aluminum alloy saturated with carbon for the metal electrode in the double cell with the same slag and intermediate electrode are shown in Table 2. As indicated with above table, iron-aluminum alloy saturated with carbon acts as aluminum electrode regardless of aluminum content.

Table 2. Comparison of e.m.f. of the cell at various contents of aluminum in iron-aluminum alloy saturated with carbon at 1630°.

Slag composition (wt%)			Al content of Fe-Al-C <sub>sat.</sub> electrode wt%	E.M.F. - V	Intermediate electrode
Al <sub>2</sub> O <sub>3</sub>	CaO	SiO <sub>2</sub>			
44.3	45.8	9.3	11.4	0.022	MgO
			40.6	0.018	
20.7	10.7	69.4	18.7	0.065	"
			40.6	0.065	
14.3	23.1	63.9	18.7	0.112	"
			40.6	0.108	
11.3	47.2	41.1	11.4	0.260	C
			40.6	0.252	
4.8	36.6	58.1	11.4	0.130	"
			40.6	0.130	

First, results of slags of CaO-Al<sub>2</sub>O<sub>3</sub> system in which graphite container, the above mentioned reference slag and 18.7% aluminum electrode, are used, are shown in Table 3. The values of e.m.f. in the fifth column are corrected for the blank e.m.f. with the electrode on the reference slag side as anode. As detailed later, the activity of alumina,  $a_{\text{Al}_2\text{O}_3}$  in the sixth column, is determined by  $E = -\frac{RT}{6F} \ln a_{\text{Al}_2\text{O}_3}$  with corundum at 1,630°C as the standard state. In Fig. 2.

it is shown from the composition-e.m.f. curve, shown in correlation with the phase diagram of CaO-Al<sub>2</sub>O<sub>3</sub> system reported by Rankin and Wright<sup>(3)</sup>, Greig<sup>(4)</sup> and Osborn and Shairer<sup>(5)</sup>, that the e.m.f. increased with the decrease of alumina

Table 3. Results of e.m.f. measurement on the system CaO-Al<sub>2</sub>O<sub>3</sub>.

No. of test	Slag composition				$N_{CaO}/N_{Al_2O_3}$	E.M.F. - V	$a_{Al_2O_3}$	$\gamma_{Al_2O_3}$
	wt%		mol%					
	CaO	Al <sub>2</sub> O <sub>3</sub>	CaO	Al <sub>2</sub> O <sub>3</sub>				
C A-1	61.2	38.5	74.1	25.9	2.86	0.075	0.05	0.193
C A-2	59.3	40.2	72.6	27.4	2.64	0.061	0.08	0.292
C A-3	56.1	43.8	69.9	30.1	2.32	0.043	0.16	0.532
C A-4	50.1	49.5	64.6	35.4	1.82	0.025	0.30	0.847
C A-5	45.0	54.8	59.8	40.2	1.49	0.010	0.52	1.293
C A-6	42.8	56.9	57.6	42.4	1.36	0.0056	0.61	1.439
C A-7	38.6	61.4	53.3	46.7	1.14	0	0.75	1.606
C A-8	35.5	64.5	50.0	50.0	1.00	0	0.75	1.50

concentration.

With CaO-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> system slags, measurements were carried out on the four series with 55, 45, 35 and 25 wt% of lime and on the two series with 10 and 20 wt% alumina. The results are shown in Table 4.

In the four series on the given lime content, relation between silica content and e.m.f. of the cell are shown in Fig. 3. The e.m.f. of the cell first increases with the silica content, then decreases with the increase of silica content. The value of e.m.f. at the quick point increases with the lime content and its composition turns to poor silica content. For instance, the compositions which would give rise to maximum e.m.f. were 42%, 48%, 59% of silica at 45, 35, 25% of lime respectively, which correspond to the maximum points to be presented in 12~15% of alumina as in the case of measurement for the activity of silica<sup>1)</sup>.

On the other hand, the relation between e.m.f. and lime content in the

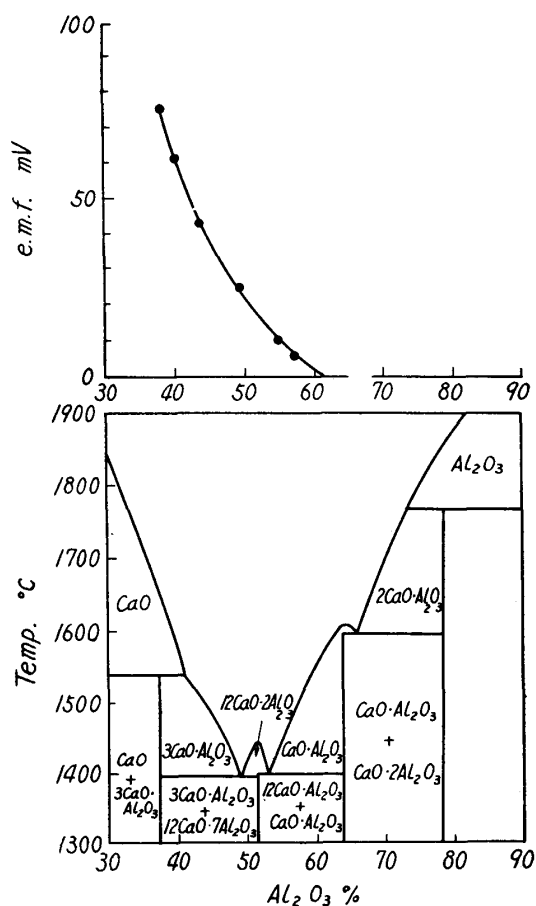


Fig. 2. Relation between slag composition and e.m.f. of the cell in the system CaO-Al<sub>2</sub>O<sub>3</sub>.

(3) G. A. Rankin and F. E. Wright, Am. J. Sci., **39** (1915), 1.

(4) J. W. Greig, Am. J. Sci., **13** (1927), 133.

(5) E. F. Osborn and J. F. Schairer, Am. J. Sci., **48** (1919), 8.

Table 4. Results of e.m.f. measurement on the system CaO-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>.

No. of test	Slag composition			Slag composition			$N_{CaO}N_{SiO_2}$	e.m.f. - V	$a_{Al_2O_3}$	$\gamma_{Al_2O_3}$
	wt%			mol%						
	CaO	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	CaO	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>				
T C 25-1	25	70	5	26.9	70.2	2.9	0.38	0.123	0.0060	0.207
T C 25-2	25	65	10	27.5	66.5	6.0	0.41	0.110	0.0092	0.153
T C 25-3	25	60	15	28.0	62.7	9.3	0.46	0.122	0.0062	0.067
T C 25-4	25	55	20	28.6	58.8	12.6	0.49	0.104	0.012	0.095
T C 25-5	25	50	25	29.3	54.6	16.1	0.54	0.090	0.020	0.124
T C 25-6	25	45	30	29.9	50.3	19.8	0.59	0.085	0.025	0.126
T C 25-7	25	40	35	30.6	45.8	23.6	0.67	0.054	0.073	0.309
T C 25-8	25	35	40	31.4	41.0	27.7	0.77	0.026	0.203	0.722
T C 25-9	25	30	45	32.1	36.0	31.9	0.89	0.004	0.45	1.411
T C 35-1	35	60	5	37.4	59.7	2.9	0.63	0.130	0.0046	0.159
T C 35-2	35	55	10	38.1	55.9	6.0	0.68	0.144	0.0028	0.047
T C 35-3	35	50	15	38.9	51.9	9.2	0.75	0.132	0.0043	0.047
T C 35-4	35	45	20	39.8	47.7	12.5	0.83	0.142	0.0030	0.024
T C 35-5	35	40	25	40.6	43.4	16.0	0.94	0.120	0.0067	0.034
T C 35-6	35	35	30	41.6	38.8	19.6	1.07	0.098	0.015	0.052
T C 35-7	35	30	35	42.6	34.0	23.4	1.25	0.078	0.031	0.132
T C 35-8	35	25	40	43.6	29.0	27.4	1.50	0.050	0.085	0.310
T C 35-9	35	20	45	44.6	23.8	31.6	1.87	0.016	0.29	0.918
T C 35-10	35	15	50	45.7	18.3	36.0	2.50	0.002	0.48	1.33
T C 45-1	45	50	5	47.7	49.4	2.9	0.97	0.184	0.00065	0.022
T C 45-2	45	45	10	48.6	45.4	5.9	1.07	0.200	0.00030	0.0051
T C 45-3	45	40	15	49.7	41.2	9.1	1.20	0.200	0.00030	0.0033
T C 45-4	45	35	20	50.8	36.8	12.4	1.38	0.168	0.0012	0.0097
T C 45-5	45	30	25	51.9	32.3	15.8	1.61	0.145	0.0027	0.0171
T C 45-6	45	25	30	53.0	27.5	19.5	1.93	0.110	0.0096	0.049
T C 45-7	45	20	35	54.3	22.5	23.2	2.41	0.089	0.021	0.091
T C 45-8	45	15	40	55.5	17.3	27.2	3.21	0.048	0.096	0.353
T C 45-9	45	10	45	56.9	11.8	31.3	4.82	0.022	0.023	0.735
T C 55-1	55	35	10	59.0	35.1	5.9	1.68	0.203	0.00033	0.0056
T C 55-2	55	25	20	61.6	26.1	12.3	2.36	0.173	0.00097	0.0079
T C 55-3	55	15	30	64.3	16.4	19.3	3.92	0.115	0.0080	0.0415
T C 55-4	55	10	35	65.8	11.2	23.0	5.88	0.082	0.027	0.117
T C 55-5	55	5	40	67.3	5.7	27.0	11.81	0.038	0.13	0.481
T A 05-1	15	75	10	16.6	77.4	6.0	0.21	0.062	0.055	0.917
T A 05-3	20	70	10	22.1	71.9	6.0	0.31	0.084	0.025	0.417
T A 05-5	30	60	10	32.8	61.2	6.0	0.54	0.126	0.054	0.0900
T A 05-7	40	50	10	43.4	50.6	6.0	0.86	0.165	0.0013	0.0217
T A 05-9	50	40	10	53.8	40.2	5.9	1.33	0.234	0.00011	0.0019
T A 10-1	10	70	20	11.6	75.7	12.7	0.15	0.062	0.055	0.433
T A 10-3	20	60	20	23.0	64.4	12.6	0.36	0.079	0.030	0.238
T A 10-5	30	50	20	34.2	53.2	12.6	0.64	0.120	0.0067	0.0532
T A 10-7	40	40	20	45.3	42.3	12.4	1.07	0.160	0.0016	0.0129
T A 10-9	50	30	20	56.2	31.4	12.4	1.79	0.181	0.00073	0.0059

series on the given alumina content are shown in Fig. 4.

At 10% alumina series, the e.m.f. increases with lime content, especially an abrupt increase at more than 40% of lime, and quick points are observed at 50% of lime. While at 20% alumina series, the e.m.f. increases with lime content as in 10% alumina series, but the quick point did not appear so distinctly.

Determination of the activity of alumina

From the facts that the e.m.f. of double cells was equal whether graphite or magnesia was used in preparing their container, it may be concluded that the intermediate graphite electrode acts as an oxygen electrode and the iron-aluminum electrode saturated with carbon as aluminum electrode. Since the form of the aluminum ions in the molten slags changes with the composition of the slag, the cell reaction should be expressed by the form involving the aluminum ion in the respective slag composition. Although exact form of the ion species do not known yet thoroughly, we may have some knowledge about it from the results of physico-chemical studies and the phase diagrams of slag systems. For example, we may assume that highly basic slag of  $\text{CaO}/\text{SiO}_2 > 2.0$  contains simple aluminate and silicate ions of  $\text{AlO}_2^{2-}$  and  $\text{SiO}_4^{4-}$  respectively besides  $\text{O}^{2-}$  in excess. In this case, in the single cell

$\text{Fe-Al-C}_{\text{sat.}} | \text{CaO-SiO}_2\text{-Al}_2\text{O}_3 | \text{C or MgO}$ , it is



at the intermediate magnesia or graphite electrode

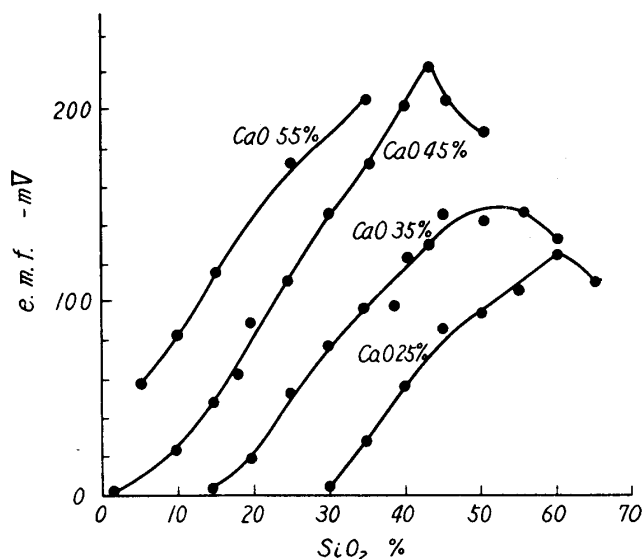


Fig. 3. Relation between slag composition and e.m.f. of the cell at constant lime series.

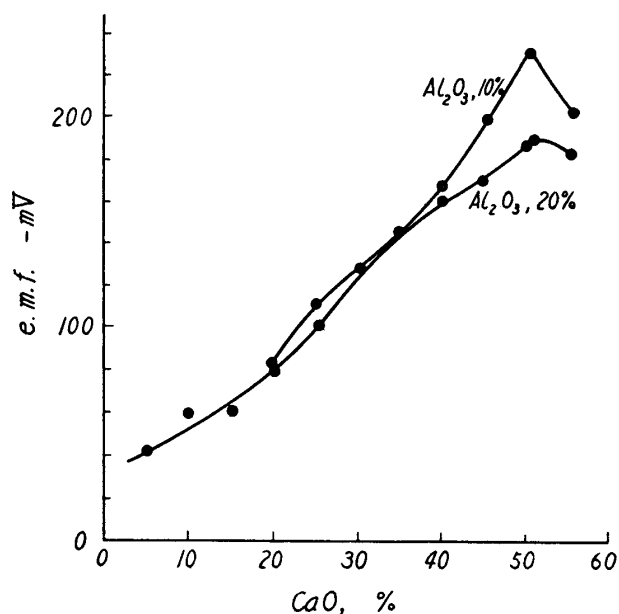


Fig. 4. Relation between slag composition and e.m.f. of the cell at constant alumina series.

$$\varepsilon_0 = \varepsilon_0^0 - \frac{RT}{2F} \ln a_{O^{2-}}/a_O \quad (1)'$$

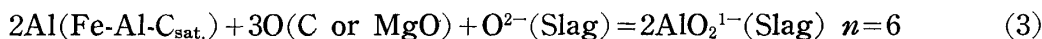
and at the Fe-Al-C<sub>sat.</sub> electrode, it is



$$\varepsilon_{Al} = \varepsilon_{Al}^0 + RT/3F \ln a_{AlO_2^{1-}}/a'^{3}_{O^{2-}} \quad (2)'$$

where  $\varepsilon_0^0$  and  $\varepsilon_{Al}^0$  stand for the standard electrode potentials at the respective electrode,  $a_{AlO_2^{1-}}$ ,  $a_{O^{2-}}$  for the activity of  $AlO_2^{1-}$  and  $O^{2-}$ ,  $a_{Al}$  for that of aluminum in the iron-aluminum alloy saturated with carbon and  $a_O$  for that of oxygen in the gas phase at the graphite or magnesia electrode.

The cell reaction of the single cell is expressed by the difference between (1) and (2) and its e.m.f. by (3)'

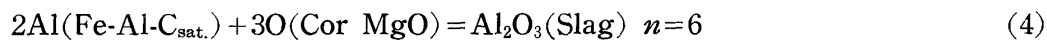


$$E_{Al_2O_3} = E^0_{Al_2O_3} + RT/6F \ln a^2_{AlO_2^{1-}}/a_{O^{2-}} \cdot a^2_{Al} \cdot a^3_O \quad (3)'$$

where  $E^0_{Al_2O_3}$  corresponds to the standard e.m.f. of the single cell.

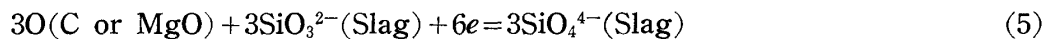
As the slag used in the present study may be considered to the strong electrolyte,  $a^2_{AlO_2^{1-}}/a_{O^{2-}}$  is equal to  $a_{Al_2O_3}$ .

Thus the equation (3) becomes identical with the formula of reaction of alumina formation (4) and the e.m.f. is expressed by (4)' as follows:



$$E_{Al_2O_3} = E^0_{Al_2O_3} + RT/6F \ln a_{Al_2O_3}/a^2_{Al} \cdot a^3_O \quad (4)'$$

In neutral slags of  $CaO/SiO_2 = 2.0 \sim 1.0$ , oxygen atoms are all combined in aluminate ions, silicate ions or aluminosilicate ions. Referring to the ternary phase diagram of lime-silica-alumina, these compounds of  $2CaO \cdot SiO_2$ ,  $CaO \cdot SiO_2$ ,  $2CaO \cdot Al_2O_3 \cdot SiO_2$  (Gehlenite),  $CaO \cdot Al_2O_3 \cdot 2SiO_2$  (Anorthite) are found in solid state, which indicate the existence of  $SiO_4^{4-}$ ,  $SiO_3^{2-}$  as stable silicate ions, and aluminum forms complex ion with silicate anion. For instance, in the range of Gehlenite,  $Al_2SiO_7^{4-}$  exist as complex anion. On the other hand in the range of Anorthite,  $AlSiO_4^{1-}$  is considered to be stable. Now the cell reaction in the former case is expressed as follows:



$$\varepsilon_0 = \varepsilon_0^0 - RT/6F \ln a^3_{SiO_4^{4-}}/a^3_{SiO_3^{2-}} \cdot a^3_O \quad (5)'$$

and at the aluminum electrode,



$$\varepsilon_{Al} = \varepsilon_{Al}^0 + RT/6F \ln a_{Al_2SiO_7^{4-}} \cdot a^3_{SiO_3^{2-}}/a^4_{SiO_4^{4-}} \cdot a^2_{Al} \quad (6)'$$

Thus, its cell reaction and its e.m.f. are given by following (7) and (7)';

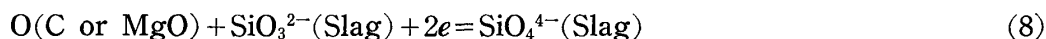


$$E_{Al_2O_3} = E^0_{Al_2O_3} + RT/6F \ln a_{Al_2SiO_7^{4-}}/a_{SiO_4^{4-}} \cdot a^2_{Al} \cdot a^3_O \quad (7)'$$

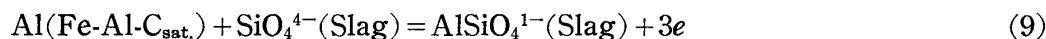
Since  $a_{Al_2SiO_7^{4-}}/a_{SiO_4^{4-}}$  is equal to  $a_{Al_2O_3}$  in ionic solution, and (7) like (4), stands for a reaction of alumina formation, the relation between e.m.f. of the cell and



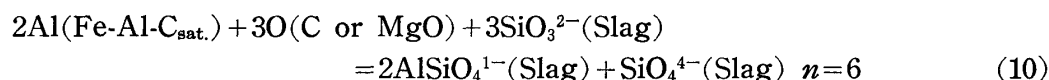
the activity of alumina is expressed by (4). On the other hand, in the range of anorthite, the cell reaction at the oxygen electrode expressed as follows:



and at the aluminum electrode,



Thus its cell reaction and its e.m.f. are given in (10) and (10)' respectively.



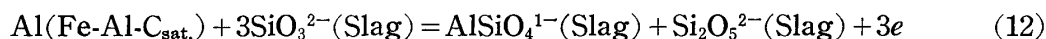
$$E_{\text{Al}_2\text{O}_3} = E_{\text{Al}_2\text{O}_3}^0 + RT/6F \ln a_{\text{AlSiO}_4^{1-}}^2 \cdot a_{\text{SiO}_4^{4-}} / a_{\text{SiO}_3^{2-}}^3 \cdot a_{\text{Al}}^2 \cdot a_{\text{O}}^3 \quad (10)'$$

In the above equation,  $a_{\text{AlSiO}_4^{1-}}^2 \cdot a_{\text{SiO}_4^{4-}} / a_{\text{SiO}_3^{2-}}^3$  should be accord with the activity of alumina. This relation is valid in the ionic solution, though it is difficult to understand that three species of anion participate in the activity of alumina. Now we may consider that silicate ion  $\text{SiO}_4^{4-}$  no longer exists in this range but more polimerized form  $\text{SiO}_3^{2-}$ ,  $\text{Si}_2\text{O}_5^{2-}$ .

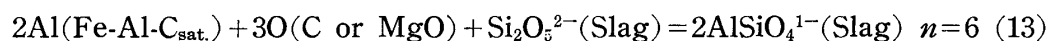
At the oxygen electrode,



and at the aluminum electrode,



Thus its cell reaction and e.m.f. are given by (13) and (13)' as follows;



$$E = E_1^0 + RT/6F \ln a_{\text{AlSiO}_4^{1-}}^2 / a_{\text{Si}_2\text{O}_5^{2-}} \cdot a_{\text{Al}}^2 \cdot a_{\text{O}}^3 \quad (13)'$$

In this case,  $a_{\text{Al}_2\text{O}_3}$  may be expressed by  $a_{\text{AlSiO}_4^{1-}}^2 / a_{\text{Si}_2\text{O}_5^{2-}}$ . The equation (13) may be preferable to (10). However, the stability of  $\text{Si}_2\text{O}_5^{2-}$  is not determined from the e.m.f.- composition curve.

According to the above-mentioned results, the cell reaction in various composition range of slag becomes identical with the formula of the reaction of alumina formation.

Therefore, in the double cell



when the electrodes are made of Fe-Al-C<sub>sat.</sub> alloy of the same composition and one of the slag is taken as reference slag, the activity of alumina in the tested slag can be determined from the difference in the e.m.f. of the two single cells as follows:

$$E = E_{\text{Al}_2\text{O}_3(\text{I})}^0 - E_{\text{Al}_2\text{O}_3(\text{II})}^0 + RT/6F \ln a_{\text{Al}_2\text{O}_3} / a_{\text{Al}_2\text{O}_3}^0 \quad (14)$$

As the iron-aluminum alloys saturated with carbon are of the same composition and the intermediate electrode is common to both the single cells,  $E_{\text{Al}_2\text{O}_3(\text{I})}^0 - E_{\text{Al}_2\text{O}_3(\text{II})}^0$  is equal to zero and (14) becomes

$$-E = RT/6F \ln a_{\text{Al}_2\text{O}_3} / a^0_{\text{Al}_2\text{O}_3} \quad (15)$$

If corundum at 1630°C was chosen as standard for  $a_{\text{Al}_2\text{O}_3}$ , (15) would be rewritten as follows:

$$E = -RT/6F \ln a_{\text{Al}_2\text{O}_3} \quad (16)$$

and at 1630°C,

$$-E = 0.0634 \log a_{\text{Al}_2\text{O}_3} \quad (17)$$

The activity of  $\text{Al}_2\text{O}_3$  in  $\text{CaO-Al}_2\text{O}_3$  melts could be obtained if slag was in equilibrium with solid alumina at 1630°C. According to the phase diagram, no such slag exists but the melt is in equilibrium with  $\text{CaO} \cdot 2\text{Al}_2\text{O}_3$  at high concentration of alumina. The liquidus of  $\text{CaO} \cdot 2\text{Al}_2\text{O}_3$ , indicates that the composition of the melt saturated in  $\text{CaO} \cdot 2\text{Al}_2\text{O}_3$  is 33.5 % of CaO 35.5 and 64.5 % of  $\text{Al}_2\text{O}_3$ . Such a slag, however, did not form homogeneous melt at 1630°C, and we failed in the measurement of the e.m.f. of the cell between that slag and the slag saturated with  $\text{Al}_2\text{O}_3$ . Then authors were obliged to choose a reference slag in CaO 38.6,  $\text{Al}_2\text{O}_3$  61.4 %. The e.m.f. of the cell against the standard slag in which CaO 20.8,  $\text{Al}_2\text{O}_3$  47.0,  $\text{SiO}_2$  31.1 % were taken arbitrarily as standard slag and which is in equilibrium with solid  $\text{Al}_2\text{O}_3$  is shown in Table 5. The values of e.m.f. in the

Table 5. The activity of alumina at the reference slag in  $\text{CaO-Al}_2\text{O}_3$ .

No. of test	Standard slag wt%			Reference slag wt%		$E$ - V	Blank e.m.f. mv	$a_{\text{Al}_2\text{O}_3}$
	CaO	$\text{SiO}_2$	$\text{Al}_2\text{O}_3$	CaO	$\text{Al}_2\text{O}_3$			
A-1	20.8	31.1	47.1	38.6	61.4	0.0087	+ 6.3	0.73
A-2	"	"	"	"	"	0.0080	- 10.2	0.75
A-3	"	"	"	"	"	0.0130	- 3.2	0.62

fourth column are given as the slag saturated with alumina to be in the standard state, which are corrected for the blank e.m.f. given in the fifth column. As shown in Table 5, order of the blank e.m.f. correspond to the e.m.f. of the cell, and we could not define  $a_{\text{Al}_2\text{O}_3}$  exactly.

Therefore,  $a_{\text{Al}_2\text{O}_3}$  shown in Table 3 represents  $a_{\text{Al}_2\text{O}_3} = 0.75$  at 38.6 % CaO. The e.m.f. of  $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3$  slag equivalent to that of the standard state in the other chamber was computed from the measured e.m.f. obtained by using the reference slag, and  $a_{\text{Al}_2\text{O}_3}$  values were calculated by (17) given above, as shown on the *iso*-activity line plotted on the ternary  $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3$  coordinates in Fig. 5. The course of the *iso*-activity lines of  $\text{Al}_2\text{O}_3$  shows a symmetry around the straight line through the points of  $\text{Al}_2\text{O}_3$  and of  $2\text{CaO} \cdot \text{SiO}_2$  saturation in  $\text{CaO-SiO}_2$  system,  $a_{\text{Al}_2\text{O}_3}$  under constant  $\text{Al}_2\text{O}_3$  being the smallest on this line and increasing when the basicity changes, either to the increase or to the decrease side. This effect is particularly notable in the range of low concentration of alumina and weakens with the rise in concentration.

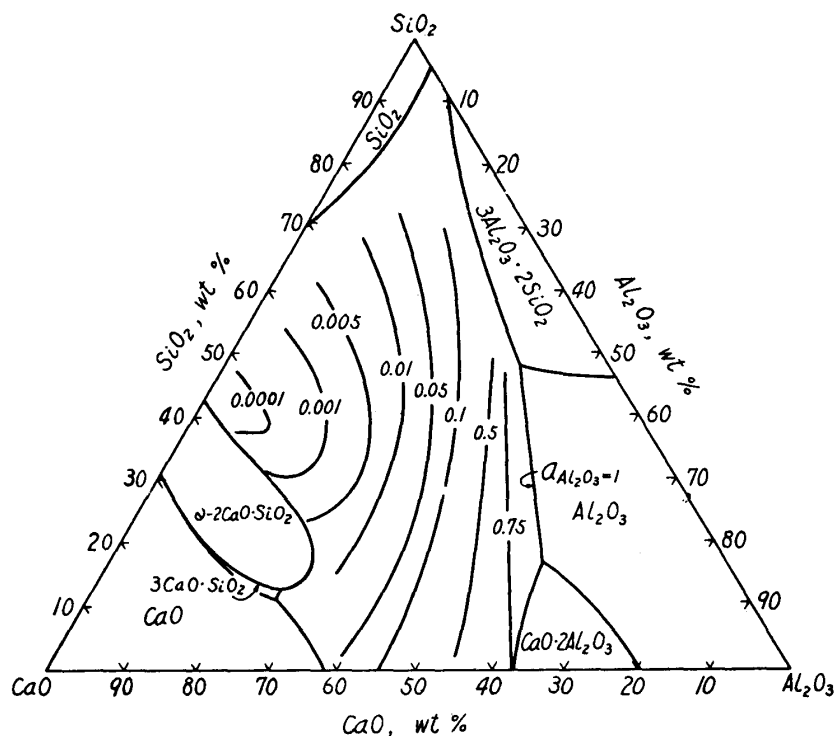


Fig. 5. Isoactivity lines of alumina in the system  $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3$ ,  $1630^\circ\text{C}$ .

#### IV. Discussion

There has been no report made experimentally on the  $a_{\text{Al}_2\text{O}_3}$  in  $\text{CaO-Al}_2\text{O}_3$  melts. Carter and Macfarlane<sup>(6)</sup> estimated  $a_{\text{Al}_2\text{O}_3} \approx 0.2$  for the slag saturated with  $\text{CaO-Al}_2\text{O}_3$  ( $\text{CaO} = 42.5\%$ ). Using  $35\%$   $\text{CaO}$  as the most probable value of  $\text{Al}_2\text{O}_3$  saturation which was obtained from tentative extrapolation of  $1500^\circ\text{C}$  isotherm in  $\text{Al}_2\text{O}_3$  field of the  $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$  system to the  $\text{CaO-Al}_2\text{O}_3$  binary system. A reliable value of  $a_{\text{Al}_2\text{O}_3}$  could not be obtained by extrapolation method, because our knowledge of the thermodynamic properties of  $\text{CaO-Al}_2\text{O}_3$  system is so meagre. Carter and Macfarlane also admitted that if the free energy curve would be only lowered or raised respectively by  $0.5\sim 0.75$  kcal, the  $a_{\text{Al}_2\text{O}_3}$  would undergo a change between  $0.1$  and  $0.4$  at  $42.5\%$   $\text{CaO}$ .

A comparison of the phase diagram  $\text{CaO-Al}_2\text{O}_3$  system with that of  $\text{CaO-SiO}_2$  system indicates in the latter that two liquids exist in extremely high silica content, while in the former, a compound formation occurs. Therefore,  $a_{\text{Al}_2\text{O}_3}$  near  $\text{Al}_2\text{O}_3$  saturation abruptly decreases, a negative deviation contrary to a positive deviation from Raoult's law in the case of activity of silica  $a_{\text{SiO}_2} = 0.75$  at  $\text{CaO} 38.6\%$  derived from the present study was not in agreement with the above information because of the difficulty of experiment in this composition range due to the high blank e.m.f. compared with the actual e.m.f. of the cell.

In the  $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3$  ternary system the course of the iso-activity lines of  $\text{Al}_2\text{O}_3$  shows a symmetry around the straight line through the points of  $\text{Al}_2\text{O}_3$

(6) P. T. Carter and T. G. Macfarlane, *J. Iron and Steel Inst.*, **185** (1957), 54.

and of  $2\text{CaO}\cdot\text{SiO}_2$  saturation in  $\text{CaO}\text{-SiO}_2$  system. This course of  $iso\text{-}a_{\text{Al}_2\text{O}_3}$  lines are in marked contrast to that of  $\text{FeO}$  in  $\text{CaO}\text{-FeO}\text{-SiO}_2$  system. Taylor and Chipman<sup>(7)</sup> derived the activity of iron oxide in the study of the distribution of oxygen between liquid iron and slags approaching the simple lime-silica-iron oxide. The course of  $iso\text{-}a_{\text{FeO}}$  line was in symmetry about the orthosilicate composition and the positive deviation from Raoult's law is greatest in slags of orthosilicate composition. The authors developed some concept of slag constitution which was based on the particular concept of molecular association containing  $\text{Ca}_2\text{SiO}_4$ ,  $\text{Ca}_4\text{Si}_2\text{O}_8$ .

At any rate, their consideration was based on the rigid combination between strong base (lime) and strong acid (silica) at neutral point of basicity  $N_{\text{CaO}}/N_{\text{SiO}_2} = 2.0$  which would enhance the activity coefficient of the iron oxide which is considered to be a neutral oxide.

From this point of view, alumina in  $\text{CaO}\text{-SiO}_2\text{-Al}_2\text{O}_3$  system can also regard as neutral and the activity coefficient of alumina,  $\gamma_{\text{Al}_2\text{O}_3}$  must increased in the orthosilicate range. Taylor and Chipmans' explanation about the slag constitution may be tentative and unreasonable, according to the present knowledge of slag constitution. It must be explained on the basis of the interaction energy among the ion species existing in slag. For instance, until the composition of orthosilicate  $\text{Ca}_2\text{SiO}_4$ , it is reasonable to consider  $\text{Fe}^{2+}$  and  $\text{Ca}^{2+}$  as stable cation and  $\text{O}^{2-}$ ,  $\text{SiO}_4^{4-}$  as stable anion respectively. On account of this, no such compound of metasilicate as  $\text{CaO}\cdot\text{SiO}_2$  in  $\text{CaO}\text{-SiO}_2$  exists in  $\text{FeO}\text{-SiO}_2$  system and the melting point of orthosilicate of  $2\text{FeO}\cdot\text{SiO}_2$  is considerably lower than that of  $2\text{CaO}\cdot\text{SiO}_2$ . In such a system the interaction force between  $\text{Fe}^{2+}$  and  $\text{O}^{2-}$  was by far stronger than that between  $\text{Fe}^{2+}$  and  $\text{SiO}_4^{4-}$  because of the difference of the ionic radius of anions. When weak cation  $\text{Ca}^{2+}$  added to the melts,  $\text{Fe}^{2+}$  and  $\text{O}^{2-}$  preferentially forms cationic group and  $\text{Ca}^{2+}$  is surrounded by weak anion  $\text{SiO}_4^{4-}$  and microheterogeneity prevails in slag. The activity of  $\text{FeO}$  is defined by  $a_{\text{Fe}^{2+}} \times a_{\text{O}^{2-}}$ , so the positive deviation from Raoult's law could be explained only by the entropy of mixture of each ion in the microheterogeneous distribution.

On the other hand, interaction energy between  $\text{Al}^{3+}$  and  $\text{O}^{2-}$  are almost the same as that between  $\text{Si}^{4+}$  and  $\text{O}^{2-}$ , and aluminum atom forms anion species, sharing the oxygen atom or substituting isomorphically the silicon atom which occupies in the center of silica tetrahedra. The most probable complex ion would be  $\text{Al}_2\text{SiO}_7^{4-}$  due to the facts that the minimum of the  $a_{\text{Al}_2\text{O}_3}$  exists near  $2\text{CaO}\cdot\text{SiO}_2$  saturation. The activity coefficient of aluminum atom existing in such a complex ion would sharply decrease. Therefore the activity of  $\text{Al}_2\text{O}_3$  defined by  $a_{\text{Al}_2\text{SiO}_7^{4-}}/a_{\text{SiO}_4^{4-}}$  decrease with reference to the increase of  $a_{\text{SiO}_4^{4-}}$ .

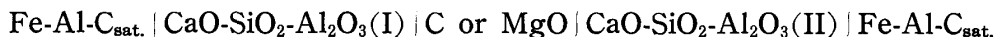
When the slag composition shifts to the acid range from the orthosilicate composition in given alumina, increase of  $a_{\text{Al}_2\text{O}_3}$  was obtained by the transition of aluminum ion from anion to cation  $\text{Al}^{3+}$ . In this case, the activity coefficient

(7) C. R. Taylor and J. Chipman, Trans. Am. Inst. Mining. Met. Engrs., 154 (1943), 228.

adruptly enhanced. On the other hand, in increase of  $a_{\text{Al}_2\text{O}_3}$ , when shifted to the basic range from the orthosilicate composition could be recognized by the dissociation of aluminosilicate ion into simple anion  $\text{SiO}_4^{4-}$  and  $\text{AlO}_2^{1-}$ .

### Conclusion

Constructing the following cell, the authors measured e.m.f. at 1630°C with the reference slag CaO 45.2, SiO<sub>2</sub> 2.2 and Al<sub>2</sub>O<sub>3</sub> 53.7 wt% respectively. The reversibility



of the double cell examined by using graphite and magnesia as intermediate electrode and the various content of aluminum in iron-aluminum alloy saturated with carbon as the metal electrode.

Choosing the standard state as the solid Al<sub>2</sub>O<sub>3</sub> at 1630°C, the activity of Al<sub>2</sub>O<sub>3</sub> in a given slag was calculated from the e.m.f. by the following equation:  $E = -RT/6F \ln a_{\text{Al}_2\text{O}_3}$ , from which the isoactivity lines were drawn on the ternary coordinates of CaO-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>. And symmetrical isoactivity lines were obtained about the straight line connecting between 2CaO·SiO<sub>2</sub> system and Al<sub>2</sub>O<sub>3</sub> coordinate.

In concluding this report, we wish to express their hearty thanks to Messors M. Ohtani and S. Watanabe.