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# On the Viscosities of Molten Slags. I

## Viscosities of CaO-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> Slags\*

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### Synopsis

Viscosities of synthetic CaO-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> slags were measured by rotating inner-cylinder viscosimeter, and iso-viscosity lines at 1,500 and 1,600°C are drawn on the diagram. Viscosity of CaO-SiO<sub>2</sub> slags at 1,600°C decreased with the increase of CaO content and anomaly was not found at the composition corresponding to CaO·SiO<sub>2</sub>.

By the addition of a small amount of Al<sub>2</sub>O<sub>3</sub> to CaO-SiO<sub>2</sub> slag, viscosity was almost unchanged as in the case of the previous investigator, but at more than 20% Al<sub>2</sub>O<sub>3</sub> the increase of viscosity became remarkable. In CaO-Al<sub>2</sub>O<sub>3</sub> slags, a minimum of viscosity was found on the isothermal line at low temperatures at about 50% Al<sub>2</sub>O<sub>3</sub>. Viscosities of CaO-Al<sub>2</sub>O<sub>3</sub> side slags which had hitherto never been determined were low and comparable to those of the low viscosity region in CaO-SiO<sub>2</sub> side slags.

And some considerations on structures of these molten slags were given from the experimental results.

### I. Introduction

Because of the theoretical interest with regard to structures of molten slags as well as the practical importance with regard to smelting reactions, many investigations have hitherto been carried out on the viscosity of molten slags.

Feild and Royster<sup>(1)</sup>, and McCaffery and coworkers<sup>(2)</sup> studied the viscosity of synthetic CaO-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> slags and Hasegawa, Taniguchi and Ueda<sup>(3)</sup>, Hartman<sup>(4)</sup> and Endell<sup>(5)</sup> measured viscosities of blast furnace slags and their changes with compositions. But results of these studies have not always agreed with one another

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\* The 28th report of the Research Institute of Mineral Dressing and Metallurgy.

- (1) A. L. Feild and P. H. Royster, U. S. Bur. Mines, Tech. Paper, 187 (1918), 189 (1918).
- (2) R. S. McCaffery and coworkers, A.I.M.E. Tech. Pub., No. 383 (1931).
- (3) K. Hasegawa, K. Taniguchi and T. Ueda, Seitetsu Kenkyu (in Japanese), No. 97 (1927).
- (4) F. Hartman, Stahl u. Eisen, **54** (1934), 564; **58** (1938), 1033.
- (5) K. Endell and R. Kley, Stahl u. Eisen, **58** (1939), 677; K. Endell and G. Brinkmann, Stahl u. Eisen, **59** (1939), 1319.

owing to the inaccuracy of measurements produced by high temperature.

## II. Experimental apparatus and method

At first, measurement of viscosity of molten slags was tried by a method of lifting up a ball dipped in molten slags using thermo-balance, but the results were inaccurate owing to sticking of slags to the suspension wire.

Therefore, this method was abandoned and the rotating inner-cylinder viscosimeter shown in Fig. 1 was used. Synthetic  $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3$  slag was melted in

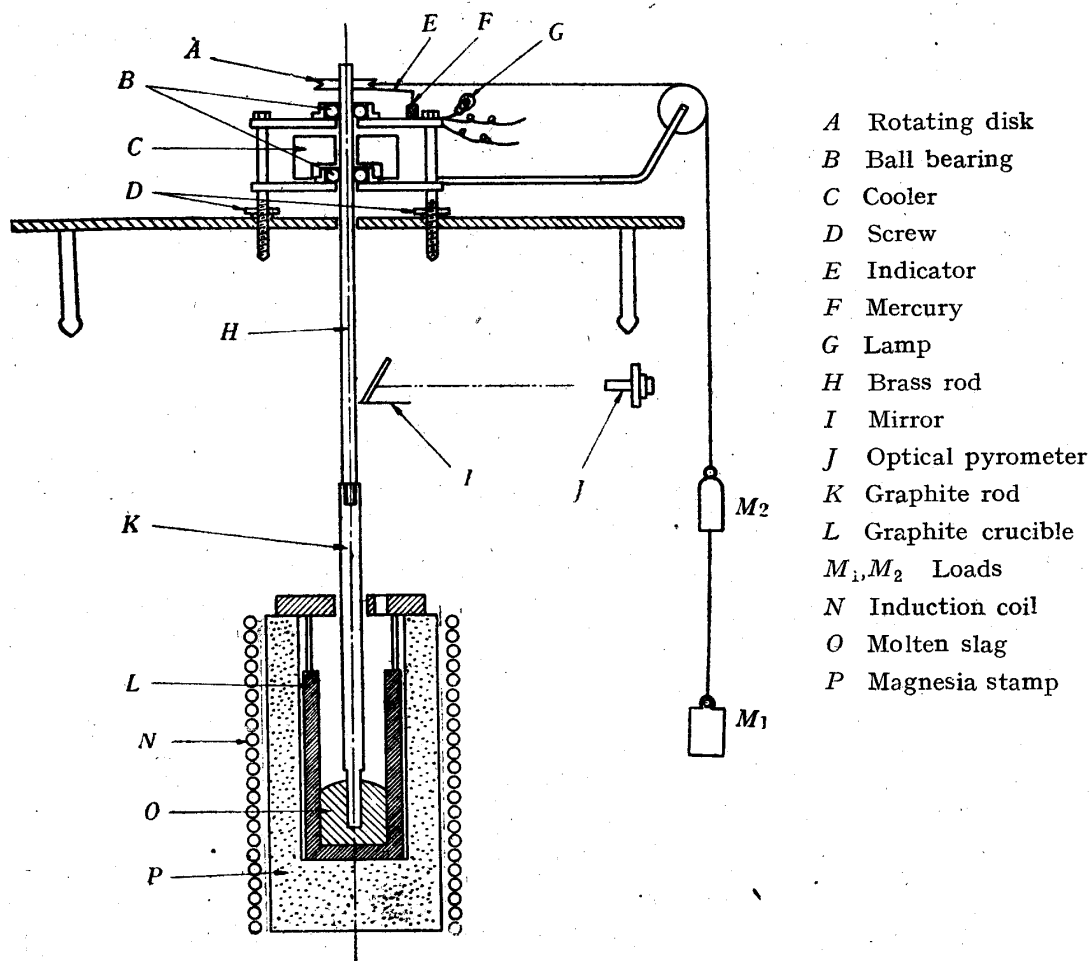


Fig. 1 Experimental apparatus.

a graphite crucible (L) in a high frequency induction furnace (35 kVA) and a graphite rod (K) dipped in molten slag (O) to a definite depth was rotated by a constant couple. From the measurement of the rotating speed, viscosity of molten slag was determined. The graphite crucible was 40 mm in inner diameter and 100 mm in depth and usually contained about 150 g of melt which filled it to a depth of about 45 mm. The rotating graphite rod, 12 mm in diameter and about 210 mm in length, was connected to a brass rod (H) which was supported by two ball

bearings (*B*). On the upper end of this brass rod a rotating disk (*A*) was set and silk-thread was wound around it. This disk was rotated by the difference of two loads ( $M_1, M_2$ ) which were hung with silk-thread. The adjustment in depth of dip and verticality of the graphite rod was made by four screws (*D*). The rotating speed was measured by sighting a lamp (*G*) which would glisten whenever an indicator (*E*) cut the surface of mercury pool (*F*). The temperature of molten slag was measured by an optical pyrometer which was calibrated by Pt-Pt-Rh thermocouple.

Considering an ideal case in which (i) a steady flow of molten slag in an infinitely large crucible is being caused by the revolution of graphite rod of infinite length, (ii) there is no slip between molten slag and graphite rod and (iii) there are no frictions in the apparatus, there should exist a relation among viscosity of molten slag ( $\eta$ ), angular velocity ( $\omega$ ) and couple ( $M$ ) as follows:

$$M = -2\pi r L \eta \cdot r \frac{d\omega}{dr} \cdot r,$$

where  $r$  is the distance from the centre of graphite rod to any cylindrical surface in molten slag,  $L$  the partial length now under consideration.

Integrating the equation, it becomes

$$\frac{M}{r^2} = 4\pi L \eta \omega + \text{const.}$$

From the boundary conditions that  $\omega = \omega_0$  at  $r = R_1$  (radius of graphite rod) and  $\omega = 0$  at  $r = R_2$  (radius of crucible), the above equation becomes

$$M = 4\pi L \cdot \eta \cdot \omega_0 \frac{R_1^2 R_2^2}{R_2^2 - R_1^2}.$$

As  $4\pi L R_1^2 R_2^2 / (R_2^2 - R_1^2) (\equiv K)$  is constant depending upon the apparatus,

$$\eta = \frac{M}{K} \cdot \frac{1}{\omega_0}.$$

From this equation it is shown that when the couple for rotating the graphite rod is constant, viscosity is proportional to the reciprocal of angular velocity.

In the actual experiment, the rotating graphite rod is of definite length, and the friction in the apparatus is not zero, so the relation between viscosity and angular velocity may be complex. But the results of preliminary experiments described later showed that there was a linear relation between viscosities and reciprocals of angular velocity within the experimental accuracy.

### III. Preliminary experiments

#### (1) Weight of loads

In order to measure the rotating speed accurately, the difference of the weight

of two loads ( $M_1 \sim M_2$ ) should be small, but when small, the effect of friction in the apparatus becomes remarkable. On the other hand, when it is large, not only the measurement of rotating speed becomes difficult, but also it is very likely that slip may occur between rotating graphite rod and molten slag.

Hence, there must be an adequate quantity in the difference of weight of the two loads and in this experiments it was decided to employ the constant values of 8 g after various tests.

## (2) Relation between viscosity of liquid and rotating speed

Using castor oil, glycerin and mixed solution of zinc iodide and soluble starch as the standards, the relation between rotating speed and viscosity was examined. Specific gravities of castor oil and glycerin were respectively 0.96 and 1.23 at 17°C. The mixed solution of zinc iodide and soluble starch which was prepared in the laboratory had a specific gravity of 2.45 at 16°C.

After measuring the viscosities at various temperatures by Ostwald's viscosimeter, about 60 cc of these liquids were taken into a glass crucible, 40mm in diameter, and rotating graphite rod was dipped to the depth of 25mm. The rotating speed reached constant after about five initial revolutions in this apparatus, so the time required for ten revolutions from the 6th to 15th revolution was measured with a stop-watch at various temperatures. When the times

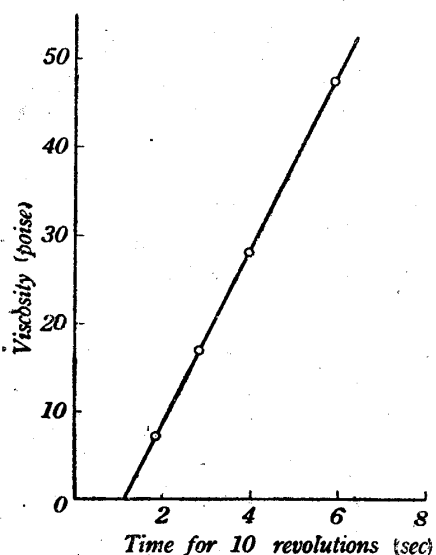


Fig. 2 Relation between viscosity and time for revolution.

required for ten revolutions were plotted against viscosities of liquids, a straight line relation was obtained within the experimental accuracy as shown in Fig. 2, and this relation was used for the determination of viscosity of molten slags.

## (3) Effects of depth of dip of graphite rod and inner diameter of crucible

The effect of depth of dip of graphite rod was examined in castor oil by varying the depth from 20, 25 to 30 mm. In each case, a straight line relation was obtained between the time required for ten revolutions and viscosities.

When the depth of dip was large, the rotating speed became slow and measurement of time became easy, but larger quantity of liquid was necessary. So in this

experiment, the depth of dip was kept constant at 25 mm.

The effect of size of crucible was examined with crucibles, 33, 40 and 50 mm in diameter, the depth of dip being kept constant at 25 mm, but the results were the same in each case.

## (4) Effect of surface condition of rotating rod

It was considered that slip might occur between rotating graphite rod and molten slag, because graphite surface was not kept wet by molten slags.

Whether there existed any slip or not was examined in the mixed solution of zinc iodide and soluble starch by comparing rotating speeds of the following two graphite rods: one was a graphite rod soaked in liquid paraffin and the other was that with no treatment. The former was not wet by the mixed solution and the latter was wet. In both cases the relations between the rotating speed and viscosity were the same in the rotating speed which was found in this experiment; therefore, it was presumed that a slip did not occur between the rotating graphite rod and liquid.

## IV. Experimental results

Powders of burnt  $\text{CaO}$ ,  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  were mixed thoroughly and melted in a graphite crucible. It was kept at about  $1,700^\circ\text{C}$  for a time to make the composition uniform and to exclude the bubbles contained.

About 150 g of these synthetic slags was taken for a sample and remelted in a graphite crucible, 40 mm in inner diameter, in a high frequency induction furnace. When the desired temperature was reached, a graphite rod, 12 mm in diameter, was

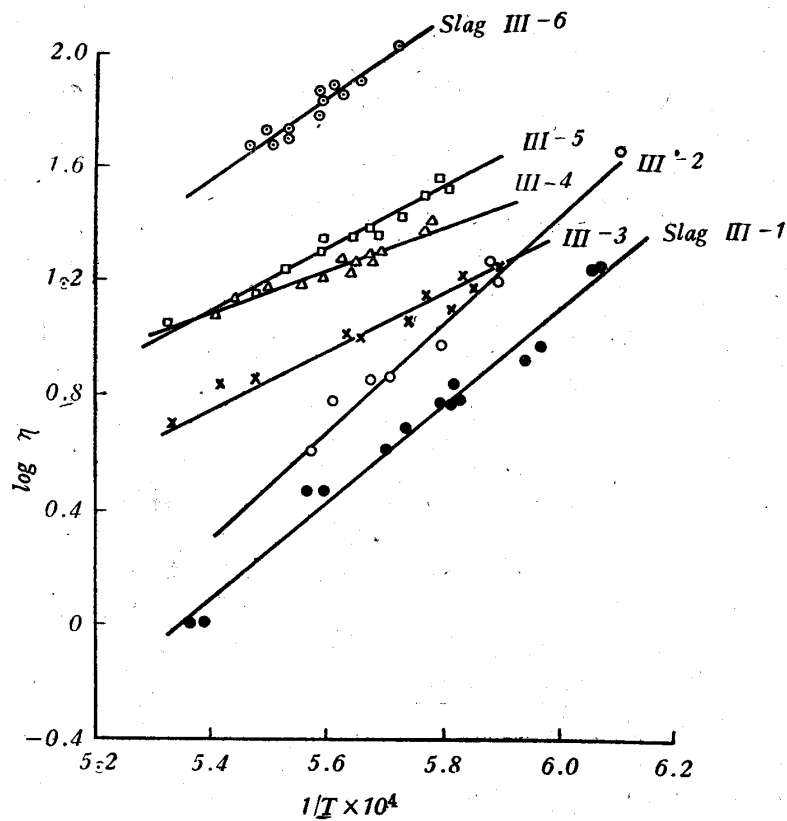


Fig. 3 Relations between  $\log \eta$  and  $1/T$ .

dipped in the slag to the depth of 25 mm and the time required for ten revolutions from the 6th to 15th revolution was measured, and, referring to Fig. 2, viscosity of the slag was determined. When logarithms of viscosities were plotted against reciprocals of absolute temperatures, straight line relations were obtained as shown in Fig. 3. Values of viscosity of slags at 1,400, 1,500 and 1,600°C calculated from these regression lines are given in Tables 1 and 2.

As the changes in slag compositions during melting for about three hours were found to be negligible, samples for chemical analyses were taken after measurements of viscosities. Owing to the melting in a high frequency induction furnace, it was considered that slag might be stirred, but there was no difference in the time required for ten revolutions in either case when current was applied to the coil or not. So it was believed that there was practically no effective movement of slag in the crucible.

Viscosities of CaO-SiO<sub>2</sub> system at 1,600°C are shown in Fig. 4 with the phase

Table 1. Experimental results on CaO-SiO<sub>2</sub> side slags in CaO-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> system.

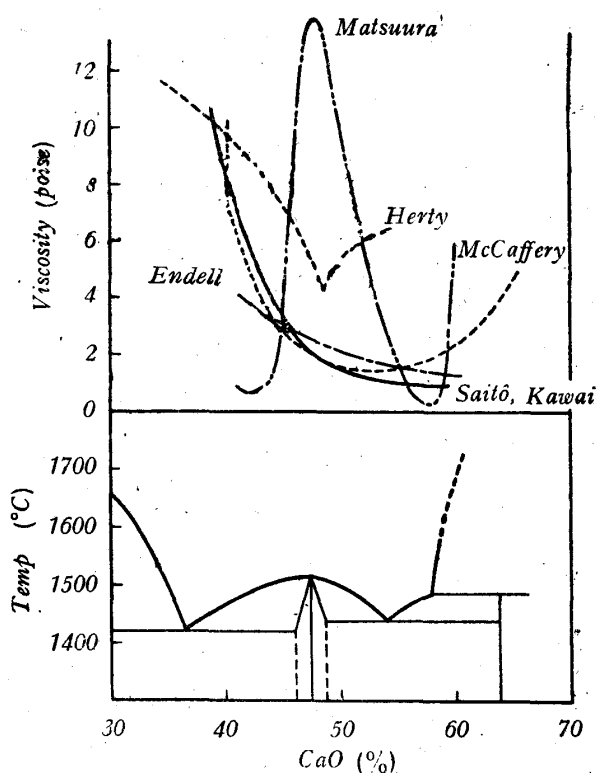
Slag No.	Composition (%)			Viscosity (poise)			A	U (kcal)
	CaO	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	1600°C	1500°C	1400°C		
I-1	55.6	44.4		1.1	8.1		1.04 · 10 <sup>-15</sup>	32.6
2	51.4	48.6		1.1	3.2		5.05 · 10 <sup>-9</sup>	18.1
3	45.3	54.7		4.5	(18)*		1.50 · 10 <sup>-10</sup>	22.8
4	41.8	58.2		4.2	(20)		4.68 · 10 <sup>-12</sup>	25.9
5	38.0	62.0		12	23		9.14 · 10 <sup>-5</sup>	11.1
II-1	44.1	52.1	3.8	2.4	12		2.37 · 10 <sup>-12</sup>	26.1
III-1	50.4	39.3	10.3	1.0	3.1	11	1.19 · 10 <sup>-9</sup>	19.4
2	48.1	41.1	10.8	1.5	5.5	23	1.77 · 10 <sup>-10</sup>	21.6
3	47.5	43.2	9.3	4.9	9.9	22	2.05 · 10 <sup>-5</sup>	11.7
4	42.4	47.9	9.7	11	19	33	9.31 · 10 <sup>-4</sup>	8.8
5	37.5	53.9	8.6	11	22	(50)	2.24 · 10 <sup>-5</sup>	12.3
6	30.8	58.2	11.0	29 about	76	(220)	8.89 · 10 <sup>-7</sup>	16.3
7	28.2	60.9	10.9	130				
IV-1	46.7	31.9	21.4	3.5	15	(71)	4.44 · 10 <sup>-11</sup>	23.7
2	45.5	34.9	19.6	1.7	5.1	18	4.71 · 10 <sup>-9</sup>	18.6
3	38.3	43.0	18.7	7.5	20	(61)	1.74 · 10 <sup>-7</sup>	16.6
4	29.5	52.0	18.5	28 about	90	(330)	2.97 · 10 <sup>-8</sup>	19.5
5	20.0	59.3	20.7	150				
V-1	39.9	29.7	30.4	9.3	29		1.71 · 10 <sup>-8</sup>	19.0
2	37.2	34.0	28.8	17	35		3.73 · 10 <sup>-5</sup>	12.3
3	29.3	42.7	28.0	24	71		6.90 · 10 <sup>-8</sup>	18.5

\* Values in parenthesis were obtained by extrapolation.

Table 2. Experimental results on CaO-Al<sub>2</sub>O<sub>3</sub> side slags in CaO-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> system.

Slag No.	Composition (%)			Viscosity (poise)		A	U (kcal)
	CaO	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	1600°C	1500°C		
VI-1	61.9		38.1	0.9	(42)	4.06 · 10 <sup>-30</sup>	63.7
2	55.3		44.7	1.4	9.3	3.57 · 10 <sup>-15</sup>	31.7
3	50.5		49.5	1.2	5.5	4.00 · 10 <sup>-12</sup>	24.9
4	45.9		54.1	1.2	7.8	2.93 · 10 <sup>-15</sup>	31.7
5	41.3		58.7	3.5	(117)	4.21 · 10 <sup>-27</sup>	58.4
VII-1	61.1	7.8	31.1	3.2	(29)	4.30 · 10 <sup>-17</sup>	36.6
2	59.6	8.0	32.4	1.9	12	1.36 · 10 <sup>-14</sup>	30.7
3	55.9	7.8	36.3	1.3	4.2	8.89 · 10 <sup>-10</sup>	19.9
4	49.3	8.0	42.7	1.5	3.9	2.28 · 10 <sup>-8</sup>	16.2
5	44.6	7.6	48.8	2.9	9.4	3.03 · 10 <sup>-9</sup>	19.5
6	39.0	8.0	53.0	2.6	16	6.27 · 10 <sup>-14</sup>	29.6
VIII-1	52.2	15.7	32.1	1.7	12	9.33 · 10 <sup>-16</sup>	33.1
2	48.9	15.7	35.4	1.0	9.0	2.26 · 10 <sup>-17</sup>	36.2
3	43.5	15.9	40.6	3.6	18	1.60 · 10 <sup>-12</sup>	26.8

diagram in which experimental results by Herty,<sup>(6)</sup> McCaffery<sup>(2)</sup>, Endell<sup>(7)</sup> and Matsuura<sup>(8)</sup> are also shown for comparison. In this experiment, viscosity of CaO-SiO<sub>2</sub> slags decreased with decrease of SiO<sub>2</sub> content, and any anomaly was not found at the composition corresponding to CaO·SiO<sub>2</sub> as similar to the result obtained by Endell. Isoviscosity lines of CaO-SiO<sub>2</sub> side slags at 1,500 and 1,600°C are shown in Fig. 5, in comparison with the data obtained by McCaffery. The positions of isoviscosity lines are nearly the same in both results at low Al<sub>2</sub>O<sub>3</sub> content. Though a minimum of viscosity was

Fig. 4 Viscosities of CaO-SiO<sub>2</sub> slags at 1600°C.

(6) C. H. Herty and coworkers, Mining Met. Invest. Bull., No. 47 (1930).

(7) K. Endell, G. Heidtkamp and L. Hax, Archiv Eisenhüttenw., **10** (1936/37), 85.(8) J. Matsuura, J. Iron Steel Inst. Japan (in Japanese), **29** (1943), 496.



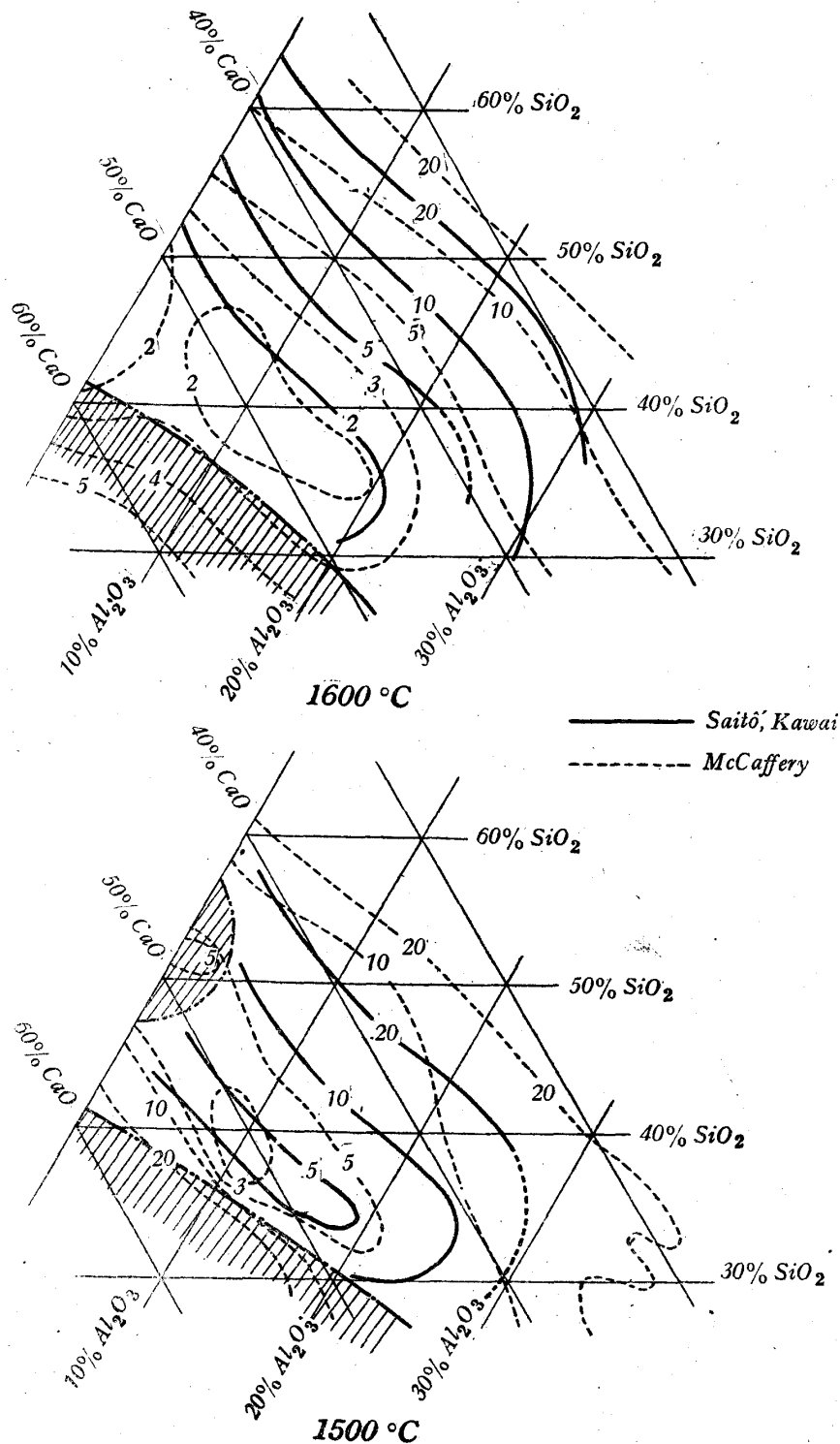


Fig. 5 Iso-viscosity lines of  $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3$  slags ( $\text{CaO-SiO}_2$  side).

reported by McCaffery, it could not be ascertained in this experiment owing to composition change of slag by the formation of calcium carbide.

Data by McCaffery in the region where solid and liquid coexist, that is, iso-viscosity lines in the regions hatched in Fig. 5, seem to be erroneous, because, in

general, viscosity of liquid increases suddenly when solid crystallizes out.

Viscosities of CaO-Al<sub>2</sub>O<sub>3</sub> system are shown in Fig. 6. In this system, there existed a minimum of viscosity on an isothermal line at 1,500°C near 50% CaO and it disappeared at 1,600°C. The results of viscosity measurements when SiO<sub>2</sub> was added to this system up to about 15% are shown in Fig. 7. With these slags viscosity measurements to be compared with had never been carried out. The results in this experiment showed that viscosities of these slags were low and comparable to those of the low viscosity region in CaO-SiO<sub>2</sub> side slags.

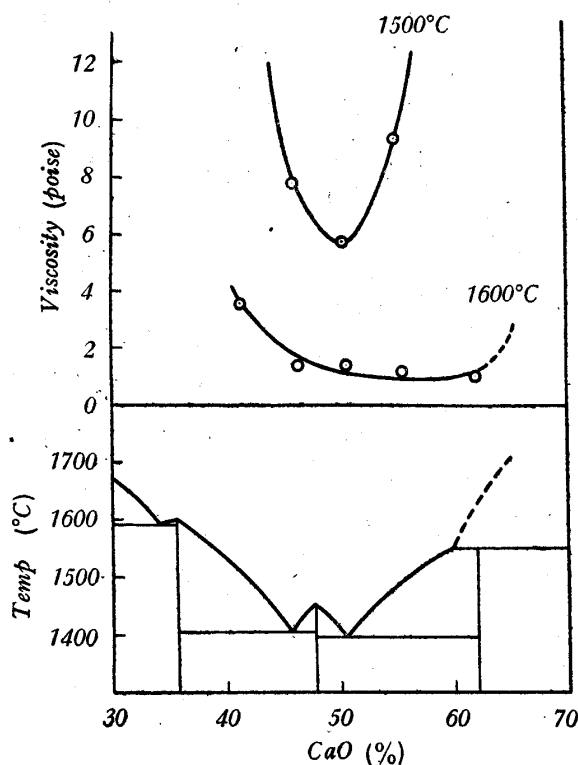


Fig. 6 Viscosities of CaO-Al<sub>2</sub>O<sub>3</sub> slags.

## V. Discussions of experimental results

Dependency of viscosity of liquid on temperature is generally shown as follows :

$$\eta = A \cdot \exp \frac{U}{RT},$$

where  $U$ , the activation energy of viscous flow, is the constant so far as the structure of liquid does not change, and  $A$  the constant characteristic of the liquid. Details of these constants were studied by Andrade<sup>(9)</sup>, Eyring<sup>(10)</sup> and others.

With slags examined in this experiment, logarithms of viscosities were in straight line relations against reciprocals of absolute temperatures, so  $U$  and  $A$  were calculated as shown in Tables 1 and 2. Values of  $U$  of CaO-SiO<sub>2</sub> system were 11.1~32.6 kcal and their changes with composition of slags were not simple. Values reported by Matsuura<sup>(8)</sup> were 25~96 kcal and their changes were also not simple.

From the studies with X-ray, electric conductivity and electrolysis of molten

(9) E. N. daC. Andrade, *Phil. Mag.*, **7** (1934), 17; 698.

(10) E. Eyring, *J. Chem. Phys.*, **4** (1936), 283.

silicates, molten slags are considered to be ionic solution and composed of various networks of  $\text{SiO}_4^{4-}$  tetrahedra. When metal oxides are added to the slags, networks are destroyed and finally become single  $\text{SiO}_4^{4-}$  tetrahedra.

If there is no compound in liquid  $\text{CaO-SiO}_2$  system, values of  $U$  must increase or decrease continuously with  $\text{SiO}_2$  content. The existence of maximum or minimum in viscosity-composition curve and  $U$ -composition curve at constant temperature suggests that compounds may exist in the liquid slag.

From this experiment in  $\text{CaO-SiO}_2$  system, the existence of compound in

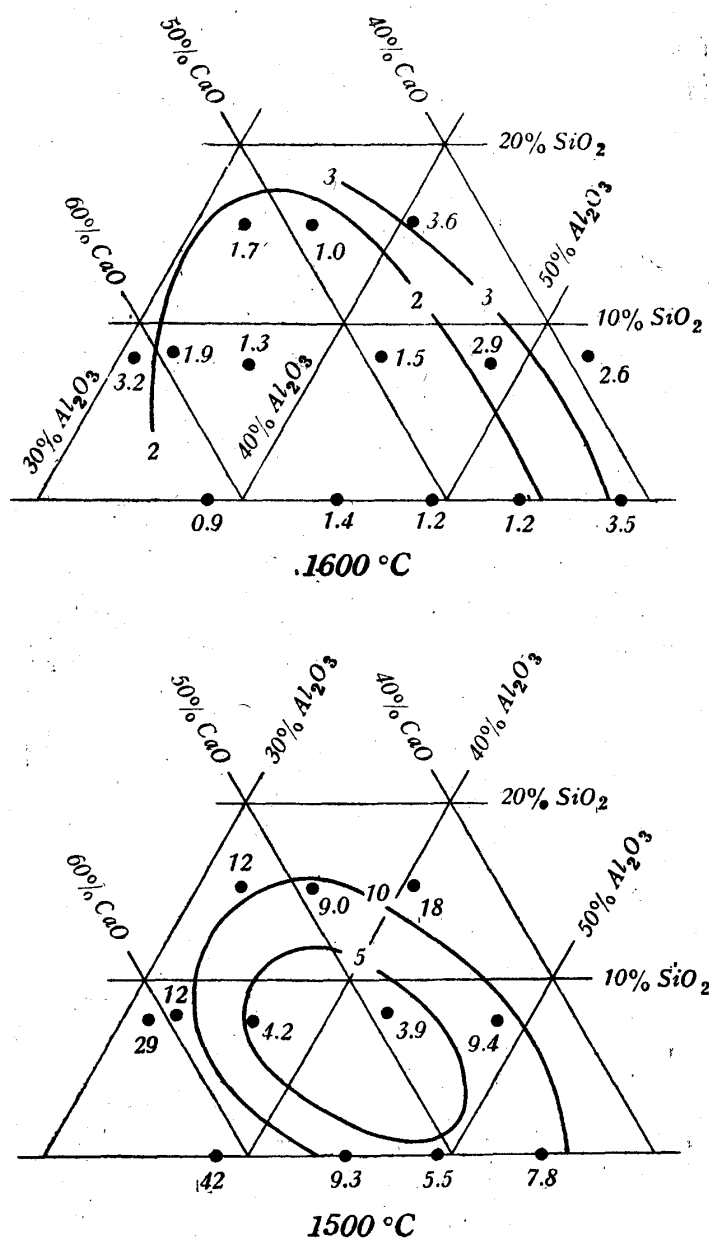


Fig. 7 Iso-viscosity lines of  $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3$  slags ( $\text{CaO-Al}_2\text{O}_3$  side).

liquid slag could not be confirmed. Bockris and coworkers<sup>(11)</sup> reported that the existence of compound in CaO-SiO<sub>2</sub> slag was not certain from the measurement of electric conductivity.

Though changes of viscosity were small with the addition of a small amount of Al<sub>2</sub>O<sub>3</sub> to CaO-SiO<sub>2</sub> slags, the viscosity increased remarkably with the addition of over 20% of Al<sub>2</sub>O<sub>3</sub>. Values of  $U$  were almost unchanged with the addition of Al<sub>2</sub>O<sub>3</sub>. Hence, it seemed that networks of SiO<sub>4</sub><sup>''''</sup> tetrahedra of molten slags were scarcely destroyed by the addition of a small amount of Al<sub>2</sub>O<sub>3</sub>, but when large amounts of Al<sub>2</sub>O<sub>3</sub> were added, cations such as AlO<sub>3</sub><sup>'''</sup> were formed in the slag.

In the case of CaO-Al<sub>2</sub>O<sub>3</sub> system a minimum of viscosity was found on an isothermal line at 1,500°C near 50% Al<sub>2</sub>O<sub>3</sub> and disappeared when the temperature was raised to 1,600°C. Also there was a minimum value of  $U$  at the corresponding composition. So it was considered that in CaO-Al<sub>2</sub>O<sub>3</sub> system there existed a compound such as CaO·Al<sub>2</sub>O<sub>3</sub> at 1,500°C, but it dissociated almost completely at 1,600°C.

When SiO<sub>2</sub> was added to CaO-Al<sub>2</sub>O<sub>3</sub> slag, viscosity was almost unchanged, that is, the increase of viscosity by the formation of SiO<sub>4</sub><sup>''''</sup> tetrahedra was not remarkable with the addition of SiO<sub>2</sub> below 10%.

### Summary

Synthetic CaO-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> slags were melted in a graphite crucible in a high frequency induction furnace and viscosities were determined by measuring the rotating speed of a graphite rod dipped in them.

The present data of CaO-SiO<sub>2</sub> side slags in CaO-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> system were nearly the same as those reported by McCaffery except those of high Al<sub>2</sub>O<sub>3</sub> slags in which remarkable increases of viscosity were observed in this experiment. Viscosities of CaO-Al<sub>2</sub>O<sub>3</sub> side slags which had never been studied were comparatively low and nearly equal to those of the low viscosity region in CaO-SiO<sub>2</sub> side slags.

From viscosity-composition and  $U$ -composition curves, it was considered that in CaO-SiO<sub>2</sub> system there existed no compound in liquid slags, but in CaO-Al<sub>2</sub>O<sub>3</sub> system there existed a compound at low temperatures.

In conclusion, the authors wish to express their cordial thanks to Prof. K. Ono, Director of the Research Institute of Mineral Dressing and Metallurgy, for his encouragement and to Mr. T. Gotô for his assistance.

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(11) J. O'M. Bockris and coworkers, *Discuss. Faraday Soc.*, No. 4 (1948), 265.