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A Model for Estimating the Viscosity of Molten Aluminosilicate Containing Calcium Fluoride

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A model to estimate the viscosity of aluminosilicate melts including alkali oxides, as derived in our previous study, was extended to molten slag systems containing CaF_2. The bonding state of oxygen in molten silicate and the flow mechanism of melts with a network microstructure were considered for this model. To evaluate the bonding states of oxygen for given chemical compositions, a model proposed by Susa *et al.* was applied. Their model is easily extended to any multi-component molten slag system without the need to consider thermodynamic parameters. In this work, the above-mentioned viscosity model was applied to evaluate the effect of CaF_2 on the viscosity of molten SiO_2–CaO–CaF_2, SiO_2–CaO–Al_2O_3–CaF_2 and SiO_2–Al_2O_3–CaO–CaF_2–Na_2O–MgO systems.

KEY WORDS: viscosity; silicate melts; structure; aluminosilicate melts; calcium fluoride.

1. Introduction

Demand has been increasing for the treatment of waste from smelting furnaces, in terms of detoxification, as well as the recycling of industrial waste such as asbestos, shredder residue and glass dust containing lead. The essential issue in smelting furnace operations is the determination of adequate conditions for stabilization of the process operation against the wide variety of chemical compositions in industrial wastes. For example, slag containing asbestos is a multi-component aluminosilicate composed of SiO_2, Al_2O_3, CaO, FeO, Fe_2O_3, MgO, K_2O and Na_2O *etc*. In addition, fluorides like CaF_2 are also occasionally present. To control the process operation we decided to use a specific property and monitored the change in its physical value during the operation. Miyabayashi *et al.*[1] pointed out that the fluidity of molten slag can be a crucial operating factor. The fluidity of molten slag is generally evaluated by measuring its viscosity, but the estimation of viscosity by physical models is also considered useful because of the difficulty in measuring the viscosity of molten slags containing a wide variety of chemical compositions. The authors thus derived a physical model to evaluate the viscosity of molten slags in multi-component systems.[2] For this model, the authors focused on the network structure of silicate slags and examined the number of non-bridging oxygens and free oxygen ions to evaluate the viscosity of silicate melts. Viscosity is expected to decrease when the amount of those oxygen ions increase, and this increase severs the network structure.

In a previous paper,[3] this viscosity model was modified for application to aluminosilicate melts containing alkali oxides in melting furnaces, *i.e.*, SiO_2–CaO–MgO–FeO–K_2O–Na_2O–Al_2O_3 systems. The bonding state of oxygen in molten silicate and the flow mechanism of melts composed of a network structure were considered for this model. In addition, the method used to evaluate bonding states of oxygen in the molten silicate as proposed by Susa *et al.* was incorporated into the above-mentioned viscosity model. Their model can be easily extended to any multi-component molten slag system without any consideration of thermodynamic parameters. The number of non-bridging oxygens and free oxygen ions for given chemical compositions may thus be evaluated.

In this work, the above-mentioned viscosity model was extended to evaluate the effect of CaF_2 on the viscosity of molten SiO_2–CaO–CaF_2, SiO_2–CaO–Al_2O_3–CaF_2 and SiO_2–Al_2O_3–CaO–CaF_2–Na_2O–MgO systems.

2. Aluminosilicate Melts Containing Calcium Fluoride

The authors have previously proposed a model for estimating the viscosity of silicate melts by considering the bonding state of oxygen and the flow mechanism of melts with a network structure in molten silicates.[2] The model is summarized as follows: silicate slag has a network structure that consists of bonded SiO_4^{4-} units (Si tetrahedral ions) as shown in **Fig. 1**(a). Si tetrahedral ions are connected through bridging oxygens O^0, which are convex oxygens within the structure of Si tetrahedral ions. The non-bridging oxygen ion O^- (NBO) and the free oxygen ion O^{2-} (FO) are generated by partially severing the network structure of the tetrahedral Si in SiO_2 upon addition of basic oxides such as CaO in the silicate slag as shown in **Fig. 1**(b). The NBO and the FO are more mobile than bridging oxygens within the network structure because there are "severance" points near NBO and FO ions. Assuming that movement of

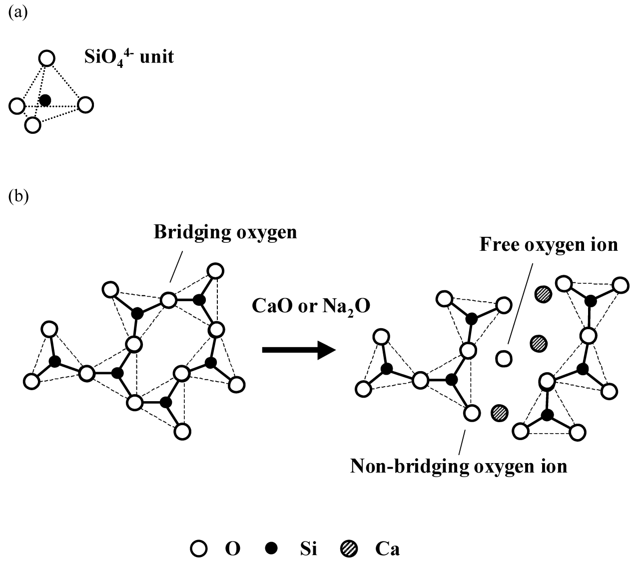


Fig. 1. Structure of silicate slag.

“severance” points causes viscous flow, an increase in the number of non-bridging oxygen ions and free oxygen ions lowers the activation energy of viscosity. The equation for viscosity η is given by:

$$\eta = A \cdot \exp\left(\frac{E_\mathrm{V}}{RT}\right) \quad \text{.............................(1)}$$

$$E_\mathrm{V} = \frac{E}{1 + \sqrt{\sum_i \alpha_i \cdot N_{(\mathrm{NBO+FO})_i} + \sum_j \alpha_{j\,\mathrm{in\,Al}} \cdot N_{(\mathrm{Al \pm BO})_j}}} \quad \text{...(2)}$$

where Arrhenius’s equation is applied to describe the viscosity in the same way in our previous work,[3)] A ($=4.80\times10^{-8}$) is a constant, E_V is the activation energy for viscosity, R is the gas constant and T is the temperature. E ($=5.21\times10^5$ (J)) is the activation energy for the viscosity of pure SiO_2. The activation energy E_V is a function of the sum of the fractions of NBO and FO $N_{(\mathrm{NBO+FO})}$ as well as the bridging oxygen (BO) fraction in the Al tetrahedral unit $N_{(\mathrm{Al\text{–}BO})}$. α_i and $\alpha_{j\,\mathrm{in\,Al}}$ are parameters that relate to the weakness of the bonding between the cation and the oxygen ion at the “severance” point. i is a component of the melt excluding SiO_2, *i.e.* CaO, MgO, FeO, K_2O, Na_2O and Al_2O_3. j is the charge-compensating ion of component i excluding Al_2O_3, *i.e.* Ca^{2+}, Mg^{2+}, Fe^{2+}, K^+ and Na^+.

To evaluate bonding states of oxygen in the molten silicate the model proposed by Susa *et al.* was incorporated into the above-mentioned model. Their model is easily extended to any multi-component molten slag system without the need to consider thermodynamic parameters and thus the number of NBO and FO for a given chemical composition may be evaluated. In the model proposed by Susa *et al.*, the ratio of the number of oxygen bonds except for bridging oxygen to Si to the total number of the oxygen bonds in silicate melts is treated as the sum of the fractions of non-bridging oxygen ions and free oxygen ions $N_{(\mathrm{NBO+FO})}$, where non-bridging oxygen ions and free oxygen ions are not distinguished each other. In addition, the ratio of the number of oxygen bonds in the Al tetrahedral to the total number of oxygen bonds in the melts is considered to be the content of the bridging oxygen in Al tetrahedral $N_{(\mathrm{Al\text{–}BO})}$.[3)] In the method of Susa *et al.*,[4)] F ions do not sever the network structure in aluminosilicate melts. In other words, F ions do not form Si–F and/or Al–F bonds but form O–Ca–F bonds when the network is severed by adding CaO. In addition, Susa *et al.*[4)] reported that their model supports the structural model proposed by Bills model,[5)] where O–Ca–F bonds formed by the addition of CaF_2 promoted a “severance” as shown in **Fig. 2**. As a result, it is likely that formation of O–Ca–F bonds lowers the viscosity.

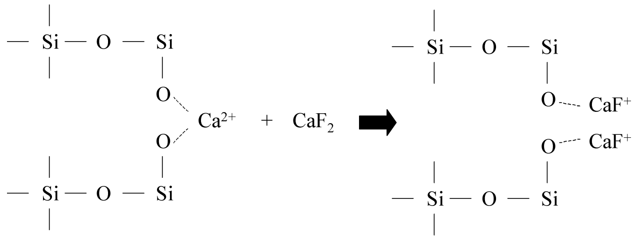


Fig. 2. Structural change by addition of CaF_2 into silicate.

The effect of the O–Ca–F bond on viscosity from Bills model can be applied to the present viscosity model by introducing a parameter $\alpha_{\mathrm{CaF_2}}$ and a variable $N_{(\mathrm{NBO+FO})_{\mathrm{CaF_2}}}$, corresponding to the O–Ca–F bond, to the term $\sum_i \alpha_i \cdot N_{(\mathrm{NBO+FO})_i}$ in Eq. (2). Here, the ratio of the number of O–Ca–F bond to the total number of the oxygen bonds in the system is as $N_{(\mathrm{NBO+FO})_{\mathrm{CaF_2}}}$. The number of charge-compensating Ca^{2+} ions and the number of NBOs and FOs produced by adding CaO decreased by an increment determined by the number of O–Ca–F bonds. The composition range where this model is applicable is limited to where the content of CaO is larger than the content of CaF_2. Therefore, $N_{(\mathrm{NBO+FO})_i}$ and $N_{(\mathrm{Al\text{–}BO})_j}$ in the multi-component $a\mathrm{SiO_2}$–$\sum b_i(\mathrm{M}_x\mathrm{O}_y)_i$–$c\mathrm{Al_2O_3}$–$d\mathrm{CaO}$–$e\mathrm{CaF}$ systems $\{a+\sum b_i+c+d+e=1\ (\mathrm{mol}),\ d\geq e\}$ ($(\mathrm{M}_x\mathrm{O}_y)_i$=MgO, FeO, K_2O, Na_2O) are given as follows:

$$N_{(\mathrm{NBO+FO})_{\mathrm{CaF_2}}} = e/(2a+\sum b_i+3c+d) \quad \text{................(3)}$$

$$N_{(\mathrm{Al\text{–}BO})_j} = 4c(b_i/(\sum b_i+d))/(2a+\sum b_i+3c+d)$$
$$(j=\mathrm{Mg^{2+}},\ \mathrm{Fe^{2+}},\ \mathrm{K^+},\ \mathrm{Na^+}) \quad \text{................(4)}$$

$$N_{(\mathrm{Al\text{–}BO})_{\mathrm{Ca^{2+}}}} = 4c(d-e)/(\sum b_i+d))/(2a+\sum b_i+3c+d) \text{....(5)}$$

$$N_{(\mathrm{NBO+FO})_i} = \{b_i - c(b_i/\sum b_i)\}/(2a+\sum b_i+3c+d)$$
$$(i=\mathrm{MgO},\ \mathrm{FeO},\ \mathrm{K_2O},\ \mathrm{Na_2O},\ \mathrm{Al_2O_3}) \text{....(6)}$$

$$N_{(\mathrm{NBO+FO})_{\mathrm{CaO}}} = \{(d-e) - c((d-e)/\sum b_i)\}/(2a+\sum b_i+3c+d)$$
$$\text{...(7)}$$

3. Determination of Parameters

There are two types of parameters, α_i and $\alpha_{j\,\mathrm{in\,Al}}$, in Eq. (2). The former parameter relates to the NBO and the FO while the latter is a parameter that relates to the bridging oxygen in tetrahedral Al.

In this study, α_i and $\alpha_{j\,\mathrm{in\,Al}}$ were determined from experimental data of the viscosity in binary silicate systems,[6–15)] ternary aluminosilicate systems[7,15–17,18–20)] and ternary SiO_2–CaO–CaF_2 systems.[21–23)] The parameters were determined as follows:

(i) The value of α_i for each oxide i was determined by applying the above equation to fit the experimental values of the viscosity for each binary SiO_2–$(M_xO_y)_i$ system where $(M_xO_y)_i$ is CaO, MgO, FeO, K_2O, Na_2O or Al_2O_3.

(ii) Subsequently the $\alpha_{j\,\mathrm{in\,Al}}$ value was assessed for each charge-compensating cation j by fitting the calculated viscosity with α_i for the binary system as determined in (i) to the experimental data for each ternary SiO_2–$(M_xO_y)_i$–Al_2O_3 system where $(M_xO_y)_i$ is CaO, MgO, FeO, K_2O or Na_2O.

(iii) Finally, assessment of the α_{CaF_2} value was done by fitting the calculated viscosity with parameter α_i as determined in (i) and (ii) above to the experimental data in ternary SiO_2–CaO–CaF_2. The assessed parameters are listed in **Table 1**.

4. Calculated Results of Molten Silicate Viscosity

To investigate the reliability of the viscosity obtained from the above procedures the calculated results were compared with literature values as quoted above to determine the parameters. **Figure 3** shows the viscosity of molten SiO_2–CaO–CaF_2 at 1 873 K. In this figure, the iso-viscosity curves obtained from the present model are shown in the area where the mole fraction of CaO is more than that of CaF_2. Plots of ■ and △ in this figure are experimental results reported in Refs. 21) and 22). The ratio of $\alpha_{CaF_2}/\alpha_{CaO}$ was 2.7, which showed that the influence of CaF_2 on the viscosity of molten SiO_2–CaO–CaF_2 was 2 or 3 times larger than that of CaO. This value is similar to that reported by Shiraishi *et al.*[22] for the addition of CaF_2 to molten SiO_2–CaO–CaF_2, which decreased the viscosity 2.2 times more than CaO did. The viscosity of the molten quaternary SiO_2–CaO–Al_2O_3–CaF_2 system is shown in **Figs. 4** and **5**. In these figures, solid lines are viscosities calculated by the present model and plots indicate experimental data[24,25] which show that the viscosity decreased as the concentration of CaF_2 decreased. The influence of CaF_2 on the viscosity is reproduced well although there is a small difference between the experimental values and the calculated values.

Table 1. Model parameters.

$(M_xO_y)_i$	α_i	j	$a_{j\ \mathrm{in\ Al}}$
CaO	**4.00**	**Ca^{2+}**	**1.46**
MgO	**3.43**	**Mg^{2+}**	**1.56**
FeO	**6.05**	**Fe^{2+}**	**3.15**
K_2O	**6.25**	**K^+**	**-0.69**
Na_2O	**7.35**	**Na^+**	**0.27**
Al_2O_3	**1.14**		
CaF_2	**10.8**		

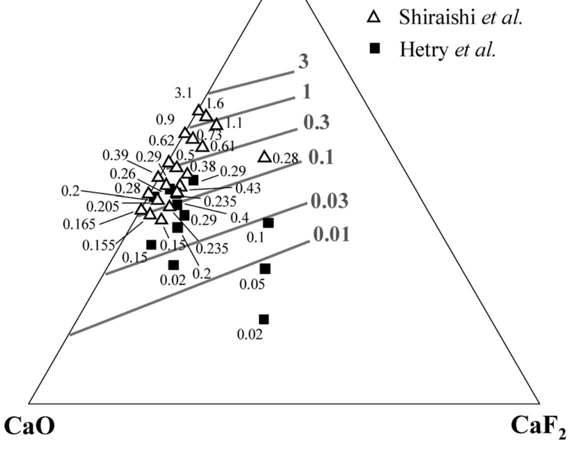
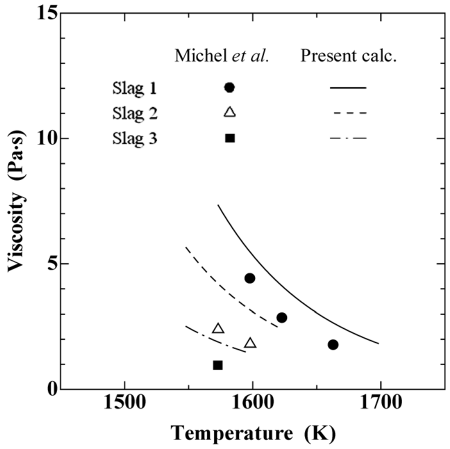


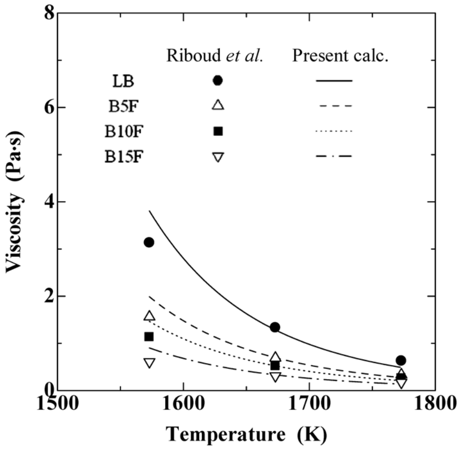
Fig. 3. Viscosity (Pa·s) of SiO_2–CaO–CaF_2 (mass%) at 1 873 K.[21,22]



	SiO_2	CaO	Al_2O_3	CaF_2
Slag 1	42	38	20	
Slag 2	40.3	36.5	19.2	4
Slag 3	37.8	34.2	18	10

(mass%)

Fig. 4. Viscosity of SiO_2–CaO–Al_2O_3–CaF_2.[24]



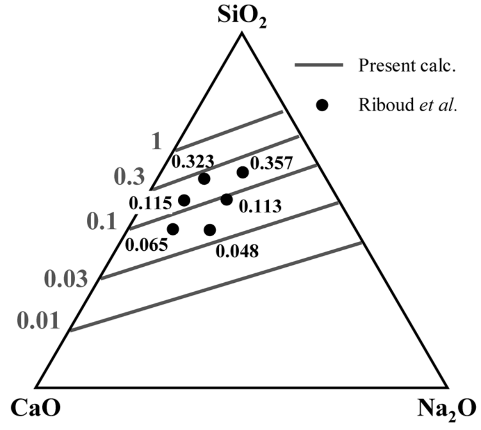
	SiO_2	**CaO**	**Al_2O_3**	**CaF_2**
LB	**42.1**	**45.9**	**11.9**	**0**
B5F	**39.6**	**44.7**	**11.3**	**4.3**
B10F	**38.6**	**43.3**	**11**	**7.1**
B15F	**37.2**	**40.5**	**10.5**	**11.7**

(mass%)

Fig. 5. Viscosity of molten SiO_2–CaO–Al_2O_3–CaF_2.[25]

The viscosity of the molten quaternary SiO_2–CaO–Na_2O–CaF_2 system is shown in **Fig. 6**. In this figure, the solid lines are iso-viscosities calculated by the present model and the plots represent experimental data[25] which

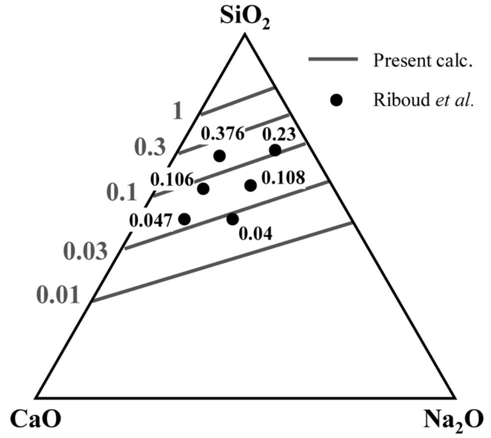
(a)



	SiO$_2$	CaO	Na$_2$O	CaF$_2$
A	40.6	32.7	18.4	8.3
C	48.3	25.2	18.3	8.2
E	56.2	18	18.6	7.1
G	40.5	40.8	10	8.7
I	47.9	34.3	9.1	8.7
K	53.3	27.2	10.7	9.1

(mass%)

(b)



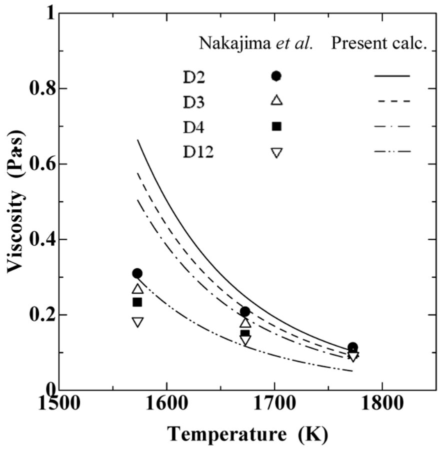
	SiO$_2$	CaO	Na$_2$O	CaF$_2$
B	40.8	23.8	18.4	17
D	49	16.6	18.2	16.2
F	56.1	7.6	18.8	17.5
H	40.6	32.8	8.9	17.7
J	48.1	26.4	9.1	16.4
L	56.2	19.4	8.8	15.7

(mass%)

Fig. 6. Viscosity (Pa·s) of the SiO_2–CaO–Na_2O–CaF_2 system (mass%) at 1 773 K.[25] The calculations were conducted at (a) 8mass%CaF_2 and (b) 17mass%CaF_2.

shows that the viscosity decreased as the concentration of CaF_2 decreased.

The viscosity of the molten SiO_2–Al_2O_3–CaO–CaF_2–Na_2O–MgO system is shown in **Fig. 7**.[26] For our calculation the effect of Li_2O was not considered although Li_2O was included in the system quoted in Ref. 26). Although the calculated viscosity is less than the experimental data in order of D2, D3, D4 and D12, the calculated results show a similar composition dependence of the viscosity.



	SiO$_2$	Al$_2$O$_3$	CaO	CaF$_2$	Na$_2$O	MgO	Li$_2$O
D2	41.76	7.67	24.07	14.63	9.23	2.65	0
D3	40.62	6.97	25.21	14.25	9.19	2.5	1.26
D4	39.04	7.65	24.53	15.29	8.8	2.83	1.85
D12	35.87	7.88	21.4	16.05	9.58	9.22	0

(mass%)

Fig. 7. Viscosity of SiO_2–Al_2O_3–CaO–CaF_2–Na_2O–MgO.[26]

5. Iso-viscosity Curves in a Molten SiO_2–CaO–CaF_2 Ternary System

The composition dependence of iso-viscosity curves in a molten SiO_2–CaO–CaF_2 ternary system has recently been discussed in detail by Sasaki *et al.*[27] and Park.[28] They focused on the influence of CaF_2 on the structure of the silicate melt.

As CaF_2 was assumed to act as a diluent for a given composition ratio of SiO_2/CaO in a molten SiO_2–CaO–CaF_2 ternary system Sasaki *et al.* presumed that the fraction of complex ion units such as SiO_4^{4-}, $Si_2O_7^{6-}$, $Si_2O_6^{4-}$, $Si_2O_5^{2-}$ and SiO_2 does not change although their absolute amounts decreased due to the addition of CaF_2. The viscosity was thus assumed constant along the straight composition line that connects the fixed composition in the SiO_2–CaO binary system and pure CaF_2. This is true if the viscosity is simply determined by polymerization of the silicate network structure in the molten SiO_2–CaO–CaF_2 ternary system. In actuality, the viscosity decreases gradually, although the absolute amounts of the above complexions decrease due to the addition of CaF_2. Park *et al.* also considered the influence of basicity on the amount and the size of the above-mentioned complex ion units and discussed composition dependence of the viscosity for the molten SiO_2–CaO–CaF_2 ternary system in detail. Nakamoto and Tanaka[29] also investigated composition dependence of the viscosity for the molten SiO_2–CaO–CaF_2 ternary system by producing an iso-viscosity map based on literature values. They concluded that the substitution of CaO by CaF_2 results in a decrease of the viscosity in an acid composition area where the SiO_2 concentration is high but shows little increase or is constant in the basic composition area with high CaO content. Mills *et al.*[30] proposed that iso-viscosity curves are convex from the SiO_2–CaO binary area to the pure CaF_2 area and they are symmetric from the $CaO\cdot SiO_2$ area composition to the pure CaF_2 area. The composition dependence of the viscosity for the molten SiO_2–CaO–CaF_2 system is currently unclear.

Recently, Hanao and Tanaka *et al.*[31] reported that the mold flux viscosity of multi-component systems can be evaluated with high accuracy by neural network computations. The composition dependency on the viscosity of the molten SiO_2–CaO–CaF_2 system was evaluated by a neural network computation for this work. The data used for the regression calculation was the same data used for the determination of the CaF_2 parameter in the viscosity model derived in this work. The total number of data points was 175. The temperature range was 1 607–1 925 K and the composition regions were SiO_2 17–65 mol%, CaO 20–61 mol% and CaF_2 0–34 mol%. The neural network computation software NEUROSIM/L produced by FUJITSU Ltd. was used to calculate the viscosity in this research. The input paragraph was temperature and concentrations of SiO_2, CaO and CaF_2. The output paragraph was viscosity. The number of interlayers selected was 4. The number of iterations for the procedure was 300 000. **Figure 8** shows a comparison between the neural network's calculated viscosities and experiment values. As shown by this figure they are in good agreement with each other. The error as evaluated by $\Sigma|(\eta_{calc}-\eta_{expe})/\eta_{calc}|\times 100$ (%) was 22.0%. Iso-viscosity curves of the molten SiO_2–CaO–CaF_2 system as determined by the neural network computation are shown in **Fig. 9**. The gray area in this figure indicates composition areas where viscosity data were quoted in the above computation. Iso-viscosity curves showed that the viscosity increased with SiO_2 content in the acid composition area where the SiO_2 concentration was high. Substitution of CaO by CaF_2 decreased the viscosity and this tendency weakened in the basic composition area where the CaO concentration was high. This composition dependence was similar to results obtained by Nakamoto and Tanaka.[29] Although the calculated result obtained by the present viscosity model shows the same composition dependence of the viscosity as the results of the neural network computation in the acid composition area, the difference between them increases in the basic composition area. The iso-viscosity curves obtained by Sasaki *et al.* and Park agreed well with the calculated results from the neural network computation in the basic composition area but the tendency in the acid composition area, with low CaF_2 concentration, was different.

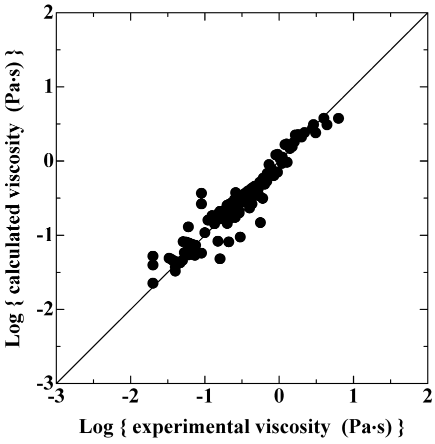


Fig. 8. Comparison between experimental viscosity and calculated viscosity by using a neural network computation in a molten SiO_2–CaO–CaF_2 ternary system.

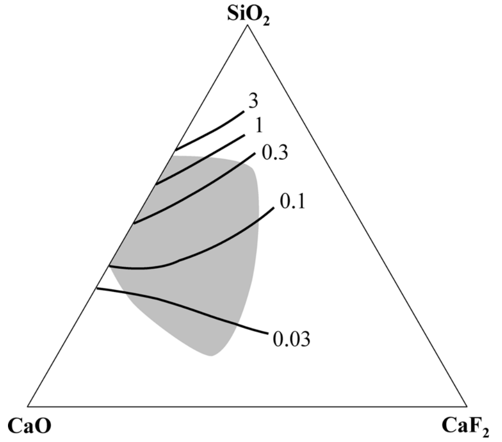


Fig. 9. Iso-viscosity curves (Pa·s) obtained by using neural network computations in a molten SiO_2–CaO–CaF_2 ternary system at 1 873 K.

The effect of CaF_2 on the silicate structure as proposed by Bills, to which we referred in this work, is different to the model given by Sasaki *et al.* In Bills' model, O–Ca–F is formed by the addition of CaF_2 when the network has been severed by CaO. On the other hand, in the model of Sasaki *et al.* CaF_2 is assumed to act as a diluent and is not integrated into the silicate network structure to produce a Ca–2F bond. **Figure 10** shows both these structural changes for molten SiO_2–CaO–CaF_2 systems obtained by

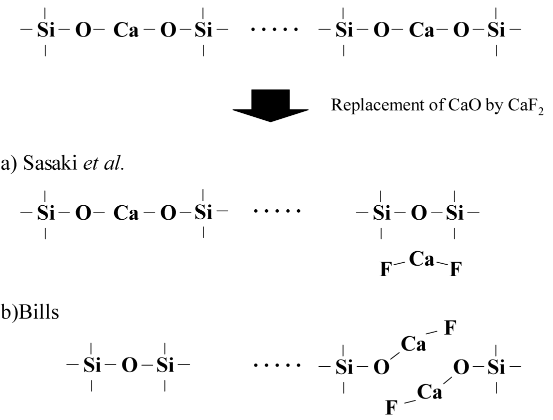


Fig. 10. Structural change of SiO_2–CaO–CaF_2 melts by the replacement of CaO by CaF_2.

replacing CaO with CaF_2. In this figure, one Si–O–Si bond is added to substitute a CaO by a CaF_2. This structural change agreed with some experimental results as the substitution of CaO by CaF_2 increased the degree of polymerization in the SiO_2–CaO–CaF_2 system. This data was obtained from experiments by Luth(32) on the effect of CaO substitution by CaF_2 on the polymerization by using Raman scattering spectroscopy and by Hayashi *et al.*(33) using X-ray photoelectron spectroscopy.

Consequently, as described above, we assume that the composition dependence of the viscosity for the molten SiO_2–CaO–CaF_2 system may be explained by considering that the silicate network structure changes with the composition of the silicate melt. Essentially the structural change proposed by Bills *et al.* occurs in the acidic composition region with high SiO_2 content and a different structural change, based on the model by Sasaki *et al.*, occurs in the basic composition region with high CaO content. This composition dependence of the change in the silicate structure enables us to produce the iso-viscosity curve, as obtained by the neural network computation. Experimental evidence which would clearly explain the composition dependence and the influence of CaF_2 on the structure of the SiO_2–CaO–CaF_2 system has, however, not been reported.

From a thermodynamic viewpoint, however, research on activities that support the composition dependency of the influence of CaF_2 on the structure of the SiO_2–CaO–CaF_2 system, as discussed in this work, have been reported by Nagata and Hayashi *et al.*(34) They studied the activities of CaF_2 at several regions, where two solid compounds and a liquid phase coexist, and found that the activity of CaF_2 was low in the composition area with low CaF_2 and high SiO_2 content, while at lower SiO_2 content the activity of CaF_2 was high. The activity of CaF_2 was based on the models of Bills and Sasaki *et al.* and it describes structural changes corresponding to iso-viscosity curves. A Neural Network Computation at high SiO_2 and at low SiO_2 was used to predict the activity. For a given composition, the activity of CaF_2 is low in the model by Bills because CaF_2 is integrated within the network. On the other hand, the activity of CaF_2 is high in the model by Sasaki *et al.* because CaF_2 exists as a Ca–2F unit. These estimations are consistent with results from the thermodynamic research by Hayashi *et al.* However, Zaitsev *et al.*(35) reported that the activity of CaF_2 gradually changes with CaF_2 content and did not show the change in activity with SiO_2 content, which is different from the composition dependence of activity as reported by Hayashi *et al.* Therefore, we cannot specifically discuss the composition dependence concerning the influence of CaF_2 on the silicate structure from a thermodynamic viewpoint at this stage.

6. Conclusion

A model to estimate the viscosity of molten aluminosilicate containing CaF_2 was derived by considering the bonding state of oxygen in molten silicate and the flow mechanism of melts with a network microstructure. A model proposed by Susa *et al.* was applied to evaluate the bonding states of oxygen for given chemical compositions. The composition dependence of the viscosity for molten SiO_2–CaO–CaF_2, SiO_2–CaO–Al_2O_3–CaF_2 and SiO_2–Al_2O_3–CaO–CaF_2–Na_2O–MgO systems was determined from the above model as well as a neural network computation to show the effect of CaF_2 on the viscosity of molten silicates.

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