The Role of Ca and Na Ions in the Effect of F Ion on Silicate Polymerization in Molten Silicate System

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For CaO–CaF₂–SiO₂ and CaO–CaF₂–Na₂O–SiO₂ systems, the effect of Na and Ca cation ions on the polymerization of silicate slags containing F ions and their structures are investigated by using molecular dynamics simulation. The substitution of F for O in the CaO–SiO₂ melts enhances the polymerization of the melt due to the formation of loosely bonded Ca–2F complexes. The substitution of Na ions for Ca ions without changing the total number of F, O and Si ions in the CaO–CaF₂–Na₂O–SiO₂ melts has a negligible effect on the distribution of silicate complex anions. For the CaO–CaF₂–Na₂O–SiO₂ system, the existence of the loosely bonded Ca–2F and Na–F complex are confirmed from the running coordination number variation. The relative amounts of the loosely bonded Ca–2F and Na–F complex in the CaO–CaF₂–Na₂O–SiO₂ system are depended on Na/Ca ratio. It is found that the loosely bonded Ca–2F and Na–F complexes in the CaO–CaF₂–Na₂O–SiO₂ melts are not randomly distributed but are clustered.

KEY WORDS: F ions; clustering; polymerization; molecular dynamics simulation; running coordination number.

1. Introduction

In our previous study,¹⁾ the effect of F on the structure of Na₂O–NaF–SiO₂ system was investigated. It has been known that F ions in molten fluxes and slags are preferentially bonded to higher field-strength modifier cations.^{2–5)} Thus, their coulombic environments certainly influence the behaviour of F ions in the melts. Industrial mould fluxes contain alkaline-earth metal cations of Ca²⁺ and alkali metal cations such as Na⁺. In the present study, to evaluate the details of the effect of cation ions on the polymerisation of silicate slags containing F ions, the structure of CaO–CaF₂–SiO₂ and CaO–CaF₂–Na₂O–SiO₂ systems are investigated by using molecular dynamics simulation.

2. Molecular Dynamics Simulation Method

Molecular dynamics simulation calculations were carried out by using the MXDORTHO program.⁶⁾ The pair potential used in the simulations was the Busing approximation of the Born–Mayer–Huggins form⁷⁾

$$U_{ij}(r) = Z_i Z_j e^2 / R_{ij} + f_0 (b_i + b_j) \exp((a_i + a_j - R_{ij}) / (b_i + b_j)) \quad (1)$$

where R_{ij} is the distance between ions i and j , Z_i is the charge of ion i and $f_0 = 6.9472 \times 10^{-11}$ N. The variables a_i and b_i are potential parameters that are related to the size and softness of the i th atom, respectively. The reliability of parameter sets for the Born–Mayer–Huggins potential was

well discussed by Sangster and Dixon.⁸⁾ The values of the parameters used in this calculation are listed in **Table 1**. Hirao and Kawamura⁹⁾ established these values after showing that they satisfied the reproduction of various stable crystal structures of 30 compounds. These parameters have been successfully used by many researchers to simulate molten oxides and fluorides.

For the calculation, three-dimensional periodic boundary conditions were applied to basic cells containing approximately 3000 atoms. The long-range coulombic forces were calculated by Ewald summation¹⁰⁾ within an uncertainty of 0.01 %. The equation of motion was integrated by the Verlet algorithm¹⁰⁾ with a time step of 2.0 fs. At the start of the calculation, the distribution of the constituent atoms in the basic cells was statistically random. The calculation was carried out at constant pressure (of 101 kPa) and temperature. The initial temperature was set to 3 273 K to agitate the atoms and eliminate the effect of the initial distribution on the final structure. The temperature was then decreased to 2 773 K, to 2 273 K, and finally to 1 873 K, and the calcu-

Table 1. Parameter set used in the molecular dynamics calculation.

	Z	a (10 nm)	b (10 nm)
Si	4	1.102	0.080
Na	1	1.260	0.080
Ca	2	1.414	0.080
F	–1	1.565	0.085
O	–2	1.626	0.085

lation was carried out at each temperature for 10 000 steps. The setting of the temperature decreasing rate was 1 K for every 10 steps. Structural data were collected at each temperature. Based on the calculated data, cumulative coordination numbers, average distance between atoms, pair correlation functions and anionic structural unit distributions were calculated.

3. Results and Discussion

3.1. CaO–CaF₂–SiO₂ System

Silicate melts consist of a mixture of five distinct types of structural units that have 4, 3, 2, 1 and 0 non-bridging oxygens per silicon, *i.e.*, SiO⁴⁻ (monomer), Si₂O₇⁶⁻ (dimer), Si₂O₆⁴⁻ (chain unit), Si₂O₅²⁻ (sheet unit) and SiO₂ (three-dimensional structure) units.¹¹⁾ In the terminology commonly employed in NMR spectroscopy, these structures are referred to as Q⁰, Q¹, Q², Q³ and Q⁴ where the superscript refers to the number of bridging oxygen in a given structural unit.

The molecular dynamics calculations were carried out for CaO·SiO₂ and 4CaO·CaF₂·5SiO₂ systems. In the latter system, the total number of Ca and Si ions is the same as that in the former system, and 1/15 of the total number of O ions (100 atoms) in the CaO·SiO₂ system is replaced by F ions (200 atoms).

The calculated distributions of Q^{*i*} (*i*=1 to 4) for the CaO·SiO₂ and 4CaO·CaF₂·5SiO₂ systems are listed in **Table 2**. The details of the calculation are presented elsewhere.¹⁾ As shown in Table 2, the substitution of F for O increases the fractions of Q³ and Q⁴, whereas those of Q¹ and Q² decrease. In other words, the degree of polymerisation is enhanced by the substitution of F ions. Luth¹²⁾ studied the structure of the CaO–CaF₂–SiO₂ system by Raman spectroscopic analysis and confirmed that the F ions in the CaO–CaF₂–SiO₂ system enhance silicate polymerisation. In other words, our calculated result agrees with the Raman spectroscopic measurement.¹¹⁾ From previous results^{1,12)} and the abovementioned molecular dynamics simulation, it can be said that the substitution of F with O in molten silicate melts enhances the polymerisation of the silicate melts.

Luth¹²⁾ discussed a mechanism to enhance polymerization by the substitution of F. The mechanism, which is consistent with polymerisation accompanying the substitution of F with O, involves the formation of loosely bonded Ca–2F complexes. The formation of such complexes prevents Ca ions from having a network-modifying role so that the degree of polymerisation can be enhanced.

Table 2. Distributions of Q^{*i*} for the melts of the 4CaO·CaF₂·SiO₂ and CaO·SiO₂ systems.

	CaO·SiO ₂	4CaO·CaF ₂ ·5SiO ₂
Q ⁰	2.6	1.0
Q ¹	20.20	11.90
Q ²	32.60	33.84
Q ³	33.40	38.46
Q ⁴	11.20	14.80

3.2. Effect of F on Viscosity

It is believed that the existence of F in the melts decreases the viscosities of molten silicate slags and that the viscosity decreases with a decrease in the degree of polymerisation. The present study, however, shows a contradictory result: the degree of polymerisation increases with an increase in F content.

The mechanism proposed by Luth¹²⁾ predicts that the melts along a join from CaF₂ to a point on a particular CaO–SiO₂ join in a CaO–CaF₂–SiO₂ phase diagram have the same distribution ratio of silicate network units except for the relative amount of Ca–2F complexes. In other words, the addition of CaF₂ to the melt produces loosely bonded Ca–2F complexes and therefore the relative distribution of the silicate network units is not influenced. If this is true, the Raman spectra of the silicate melts on this line can be expected to be identical and this was confirmed by Luth.¹²⁾ In other words, CaF₂ in the calcium silicate melts functions as a diluter when F is supplied as CaF₂ to a particular CaO–SiO₂ join. Under this condition, the amount of Ca and F ions in the CaO–CaF₂–SiO₂ melt increases as compared with that of the initial CaO–SiO₂ melt.

However, the calculated result in the present study has been obtained by replacing one O ion by two F ions without changing the total amount of Ca and Si ions. In this case, the substituted F ions tend to bond with the Ca ions and therefore the role of the latter is retarded. As a result, the polymerization of the melt is enhanced. Based on reported values,^{13–15)} the most plausible iso-viscosity line in the CaO–CaF₂–SiO₂ system at 1 873 K¹⁶⁾ is presented in **Fig. 1**. The viscosities measured by Herty *et al.*¹⁷⁾ are considerably different from those measured by other researchers^{13–15)}; therefore, their viscosities are omitted in the estimation of iso-viscosity lines. The viscosity along line A in Fig. 1 for a relatively low CaF₂ content increases with an increase in the F content; however, the viscosity along line B in Fig. 1 decreases with an increase in F. In other words, the effect of F on the viscosity depends on how F ions are supplied to the melts. The present result that F ions enhance the polymerization of silicate melts corresponds to the increase of viscosity along line A, and it does not oppose the general belief that F ions decrease the viscosity.

3.3. CaO–CaF₂–Na₂O–SiO₂ System

In the previous section, it was confirmed that Ca and F

Fig. 1. Viscosity distribution in the CaO–CaF₂–SiO₂ system at 1 873 K.

Table 3. Chemical compositions of the simulated CaO–Na₂O–CaF₂–SiO₂ system with various Na/Ca ratios.

	(mol%)			
	CaO	Na ₂ O	CaF ₂	SiO ₂
2CaO·3Na ₂ O·CaF ₂ ·5SiO ₂ , 18.2	27.3	9.0	45.5	
3CaO·2Na ₂ O·CaF ₂ ·5SiO ₂ , 27.3	18.2	9.0	45.5	
4CaO·Na ₂ O·CaF ₂ ·5SiO ₂	36.6	9.0	9.0	45.5

Fig. 2. Chemical compositions in the simulated CaO–CaF₂–Na₂O–SiO₂ system.

ions form the loosely bonded Ca–2F complexes and enhance the polymerisation of silicate melts. Since the electrical charge and F coordination numbers for Ca and Na ions are different, their relative effects of these ions on the polymerization of silicate melts are not evaluated. To understand the role of Ca and Na ions when they coexist with F ions in silicate melts, the distribution of the silicate network units and the running coordination numbers of F around the Ca and Na ions in the molten CaO–CaF₂–Na₂O–SiO₂ system were calculated by varying the Ca/Na ratio with a constant F/O ratio. To maintain electrical neutrality, a certain amount of Ca ions is replaced by twice the corresponding amount of Na ions. The studied compositions are presented in **Table 3** and **Fig. 2**.

Information regarding the coordination of O and F for Na and Ca ions in the CaO–CaF₂–Na₂O–SiO₂ melts can be obtained from the pair correlation function (PCF) between ions i and j , $g_{ij}(r)$, and the running coordination number (RCN) curve, $R(r)$, which are given¹⁸⁾ by

$$g_{ij}(r) = \frac{V}{N_i N_j} \sum_j \frac{\langle n_{ij}(r) \rangle}{4\pi r^2 \Delta r} \dots \dots \dots (2)$$

$$R(r) = 4\pi \delta_j \int_0^r r^2 g_{ij}(r) dr \dots \dots \dots (3)$$

where r is the distance between ions i and j , N is the number of ions in the box; V , the volume of the simulated melt; n_{ij} , the number of ions of j about ion i in the shell within the distance $r \pm \Delta r/2$; $\langle \rangle$, the time average; and δ , the particle density of the ion. RCN is a coordination number at the particular distance and the cumulative coordination number (CCN) is defined as the RCN value at the distance at which PCF has the minimum value. The details of the calculation are presented elsewhere.¹⁸⁾

The calculated distributions of Q^i ($i=1$ to 4) in the molten CaO–CaF₂–Na₂O–SiO₂ system with various Ca/Na

Table 4. Distributions of Q^i for the melts of the CaO–Na₂O–CaF₂–SiO₂ system with various Ca/Na ratios.

	Q^0	Q^1	Q^2	Q^3	Q^4
4CaO·CaF ₂ ·5SiO ₂	1.0	11.9	33.84	38.46	14.80
2CaO·3Na ₂ O·CaF ₂ ·5SiO ₂	1.40	10.20	36.46	38.04	13.90
3CaO·2Na ₂ O·CaF ₂ ·5SiO ₂	1.96	10.04	31.90	38.24	17.86
4CaO·Na ₂ O·CaF ₂ ·5SiO ₂	2.20	10.64	32.06	36.58	18.52

Fig. 3. Distribution of Q^i for the melts of the CaO–CaF₂–Na₂O–SiO₂ system with various Ca/Na ratios.**Table 5.** Calculated CCNs of the CaO–Na₂O–CaF₂–SiO₂ system with various Na/Ca ratios. NS: Na₂O·SiO₂, NFS: 4Na₂O·2NaF·5SiO₂, CN1: CaO·3Na₂O·CaF₂·5SiO₂, CN2: 2CaO·2Na₂O·CaF₂·5SiO₂, CN3: 3CaO·Na₂O·CaF₂·5SiO₂, CFS: 4CaO·CaF₂·5SiO₂ and CS: CaO·SiO₂.

	NS	NFS	CN1	CN2	CN3	CFS	CS
Ca/Na	-	-	1/3	3/4	2.0	-	-
Ca-F	-	-	1.0	1.8	2.4	3.5	-
Na-F	-	5.1	3.3	2.3	1.3	-	-
Ca-O	-	-	4.5	4.5	4.5	4.5	5.5
Na-O	4.3	3.5	3.4	3.8	4.0	-	-

ratios are presented in **Table 4** and **Fig. 3**. It shows that the distributions of Q^i ($i=1$ to 4) essentially do not change by varying the Ca/Na ratio. Thus, the substitution of Na for Ca in the CaO–CaF₂–Na₂O–SiO₂ melts has negligible effect on the distribution of Q^i ($i=1$ to 4).

The calculated CCN of O and F around Na and Ca, respectively, at 1 873 K in the CaO–CaF₂–Na₂O–SiO₂ melts for various Ca/Na ratios are shown in **Table 5**. The CCN of O around Na and Ca is almost independent of the variation in the Ca/Na ratio. The CCN of F around Na increases with the decrease in Ca/Na ratio and the CCN of F around Ca decreases with a decrease in Ca/Na ratio. In these calculations, the total numbers of F and O ions are constant. Thus, a change in the CCN simply indicates that some F ions that were initially coordinated around the Ca ions move to the vicinity of the Na ions due to the substitution of Na ions with Ca ions. Hayashi *et al.*⁵⁾ investigated cation ordering at fluoride sites in CaO–CaF₂–Na₂O–SiO₂ glasses by using ¹⁹F NMR and confirmed that F ions are fourfold-coordinated by Ca ions for the slags with Ca/Na ratio of more than 0.7. For the slags with Ca/Na ratio of less than 0.7, however, F ions are coordinated with both Na and Ca ions or Na ions.⁵⁾ The Ca/Na ratios of the present study are all

Fig. 4. PCF and running coordination number for Ca-F pairs in the $4\text{CaO} \cdot \text{CaF}_2 \cdot 5\text{SiO}_2$ system as a function of the distance between Ca and F ions.

less than 0.7. Thus, their results⁵⁾ of coordination of F with Ca and Na ions qualitatively agrees with the present study.

The PCF for Ca-F pairs and their running coordination number in the $4\text{CaO} \cdot \text{CaF}_2 \cdot 5\text{SiO}_2$ system as a function of the bond length between Ca and F are shown in Fig. 4. The equilibrated bond length is determined to be 0.234 nm from the position of the first peak of the PCF. The CCN is found to be 3.6 from the value at the minimum value of PCF. The RCN for the Ca-F pair at the equilibrated bond length is found to be about 0.9 from Fig. 4. The bond length at which the RCN reaches 2 is approximately 0.253 nm, which is only 8% greater than the equilibrated bond length. For the $4\text{CaO} \cdot \text{CaF}_2 \cdot 5\text{SiO}_2$ system, the existence of the loosely bonded Ca-2F complex is also confirmed from the CCN variation.

The bond lengths that correspond to RCN of 1 for the Na-F and 2 for Ca-F pairs are defined as the effective bond length. The effective bond lengths for the Na-F and Ca-F pairs, respectively, as a function of the Na/Ca ratio are shown in Fig. 5. For the Ca-F pair, the effective bond length of the Ca-2F complex approaches that of the $4\text{CaO} \cdot \text{CaF}_2 \cdot 5\text{SiO}_2$ system (0.251 nm) with an increase in the Ca/Na ratio; alternately, the bond between the Ca and F ions strengthen. On the other hand, the effective bond length of the Na-F complex approaches that of the $4\text{NaO} \cdot 2\text{NaF} \cdot 5\text{SiO}_2$ system (0.223 nm¹⁾) with a decrease in the Ca/Na ratio. Thus, the structure of the loosely bonded complexes is not fixed but changes according to the surrounding ions. In other words, the chemical ordering of F ions around Ca ion (Ca-2F complexes) in CaO-CaF₂-SiO₂ system will be gradually destroyed by the substitution of Na ions for Ca ions and finally F ions will be distributed randomly around Ca ions in the melt with very low Ca/Na ratio. The similar view can be drawn for the Na-F pairs in Na₂O-NaF-SiO₂ system concerning with Ca substitution for Na.

In the simulation of $3\text{CaO} \cdot \text{Na}_2\text{O} \cdot \text{CaF}_2 \cdot 5\text{SiO}_2$ system (Ca/Na=2), the numbers of Ca and F ions are 400 and 200 respectively. From the coordination number for Ca-F pair at the equilibrated bond length, all F ions must be used to construct Ca-2F complexes. If Ca ions are randomly distributed, however, F ions of 800 are required. It means that F ion of the Ca-2F complex in $3\text{CaO} \cdot \text{Na}_2\text{O} \cdot \text{CaF}_2 \cdot 5\text{SiO}_2$ system must be shared by another Ca-2F complexes. Based on the Similar discussion, F ions of Ca-2F complex in $4\text{CaO} \cdot \text{CaF}_2 \cdot 5\text{SiO}_2$ system and F ions of Na-F complex in

Fig. 5. Bond lengths that reach the running coordination number of 1 and 2 for Na-F and Ca-F pairs, respectively, as a function of the Na/Ca ratio. The open circles and closed circles represent Ca-F and Na-F pairs, respectively.

Fig. 6. (a) The simulated structure of $4\text{CaO} \cdot \text{CaF}_2 \cdot 5\text{SiO}_2$ melt. (b) The corresponding positions of Ca and F ions shown in Fig. 6(a).

$\text{CaO} \cdot 3\text{Na}_2\text{O} \cdot \text{CaF}_2 \cdot 5\text{SiO}_2$ system (Ca/Na=1/3) must be shared by another Ca-2F and Na-F complexes respectively. In other words, loosely bonded Ca-2F and Na-F complexes in $\text{CaO} \cdot \text{CaF}_2 \cdot \text{Na}_2\text{O} \cdot \text{SiO}_2$ melts are not randomly distributed but are clustered. The simulated structure of $4\text{CaO} \cdot \text{CaF}_2 \cdot 5\text{SiO}_2$ melt is shown in Fig. 6(a). The corresponding positions of Ca and F ions shown in Fig. 6(a) are shown in Fig. 6(b). The clustering of Ca and F ions is clearly shown in Fig. 6(b). The alkali atoms clustering in binary silicates was also reported.^{19,20)} Thus, the clustering of Na-F or Ca-2F complexes is quite possible.

4. Conclusions

The effect of cation ions on the polymerisation of silicate slags containing F ions and the structure of the CaO–CaF₂–SiO₂ and CaO–CaF₂–Na₂O–SiO₂ systems are investigated by using molecular dynamics simulation, and the following conclusions can be drawn.

(1) The substitution of F for O in the CaO–SiO₂ melts enhances the polymerisation of the melt due to the formation of loosely bonded Ca–2F complexes.

(2) The viscosity of the CaO–SiO₂ melts decreases when F is supplied to the melt as CaF₂; however, it increases when F is replaced by O under constant Ca and Si contents.

(3) The substitution of Na ions for Ca ions without changing the total number of F, O and Si ions in the CaO–CaF₂–Na₂O–SiO₂ melts has a negligible effect on the distributions of Q^i ($i=1$ to 4).

(4) The loosely bonded Ca–2F and Na–F complexes in the CaO–CaF₂–Na₂O–SiO₂ melts are not randomly distributed but are clustered.

REFERENCES

- 1) Y. Sasaki, H. Urata and K. Ishii: *ISIJ Int.*, **43** (2003), 1897.
- 2) J. F. Stebbins and Q. Zeng: *J. Non-Cryst. Solids*, **262** (2000), 1.
- 3) T. J. Kiczenski and J. F. Stebbins: *J. Non-Cryst. Solids*, **306** (2002), 160.
- 4) J. F. Stebbins: *Solid State Ionics*, **112** (1998), 137.
- 5) M. Hayashi, T. Watanabe, K. Nagata and S. Hayashi: *ISIJ Int.*, **44** (2004), 1527.
- 6) K. Kawamura: MXDORTHO. Japan Chemistry Program Exchange, No. 076, (1996).
- 7) W. R. Busing: *J. Chem. Phys.*, **57**, (1972), 3008.
- 8) M. J. L. Sangster and M. Dixon: *Adv. Phys.*, **25** (1976), 247.
- 9) K. Hirao and K. Kawamura: Material Design Using Personal Computer, Shokabo, Tokyo, (1994), 52.
- 10) D. Frenkel and B. Smit: Understanding Molecular Simulation, Academic Press, San Diego, (1996), 60–64, 347.
- 11) B. O. Mysen: Structure and Properties of Silicate Melts, Elsevier, New York, (1988), 247.
- 12) R. W. Luth: *Am. Mineral.*, **73** (1988), 297.
- 13) K. C. Mills: *NPL Report Che.*, **65** (1977), 1.
- 14) A. M. Muratov: *Russ. Metall. Metally*, **3** (1972), 51.
- 15) Y. Shiraishi and T. Saito: *J. Jpn. Inst. Met.*, **29** (1965), 614.
- 16) Y. Sasaki, M. Iguchi and M. Hino: *ISIJ Int.*, **47** (2007), 346.
- 17) C. H. Herty, F. A. Hartgen, G. L. Frear and M. B. Royer: Rep. Investigat. U. S. Bur. Mines, No. 3232, (1934), 31.
- 18) Y. Kawamoto, T. Horisaki, K. Hirao and N. Soga: *J. Chem. Phys.*, **83** (1985), 2398.
- 19) C. Huang and A. N. Cormack: *J. Chem. Phys.*, **93** (1990), 8180.
- 20) B. Vessal, G. N. Grieves, P. T. Marten, A. V. Chadwick, R. Mole and S. Houde-Walter: *Nature (London)*, **356** (1992), 504.