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# Structure of Slag (Review 2)<sup>†</sup>

## — The Role of CaF<sub>2</sub> in Slag —

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### Abstract

*The role of CaF<sub>2</sub> in slag during the purification of steel ingot still uncertain up to the present time. In this review, the effect of CaF<sub>2</sub> on the various physical and chemical properties of slag are summarized. The effect of fluorine ions on Si-O-Si bond in slag is also described.*

Nowadays, the demand for getting materials having superior properties such as good workability to deep drawing, high creep strength and good corrosion resistance have been grown.

For these requirements, new refinements to exclude sulphur and phosphor contents and to minimize the amount of non-metallic inclusions in steels have been developed. The former is oxygen-blowing LD method, and the latter is atmospheric melting or ESR (electro-slag remelting) and ESW (electro-slag welding).

CaF<sub>2</sub> or fluorides are generally used not only for ESR and ESW, but also for regular refinements.

Several years ago, it has been mentioned that CaF<sub>2</sub> as raw material seems sparse in the world. Therefore, the investigations to seek for new additions which can replace CaF<sub>2</sub> have been done Japan. Recently, new deposits of CaF<sub>2</sub> were found out, so that the most of recent researches are made based on the new deposits.

On the other hand, the development of new slag without fluoride is becoming necessary not to produce harmful gas such as HF when fluoride and water vapor reacts. For the solution of these problems, the role of CaF<sub>2</sub> in slag should be understood.

In this review, the studies about slags containing CaF<sub>2</sub> are summarized and discussed from the structural viewpoints.

### 1. Fundamental knowledge on fluorine ion

Fluorine ion is preserved 0.078 % as the combined state in the crust. From the resemblance of ionic radii among fluorine, oxyhydride and oxygen ions, it is often apt to be inter-substituted in the natural silicates. Many times, substituted state containing 4.76—7.30 % is found. The typical example is Topaz [Al<sub>2</sub>(F·OH)<sub>2</sub>SiO<sub>4</sub>].<sup>1)</sup>

In **Table 1**, the value of electronegativity of anions are given.

Table 1. Electronegativity.

F	O	Cl	Br	I	S	Se	Te
4.0	3.5	3.0	2.8	2.4	2.5	2.4	2.1

From these values, the mutual resemblance of bond strength between F and O can be anticipated.

In **Table 2**, ionic radii of anions are given.

Table 2. Ionic radii.

F <sup>-</sup>	O <sup>2-</sup>	Cl <sup>-</sup>	Br <sup>-</sup>	I <sup>-</sup>	S <sup>2-</sup>	Se <sup>2-</sup>	Te <sup>2-</sup>
1.36	1.40	1.81	1.95	2.16	1.84	1.98	2.21

From these values, similar behaviour between O<sup>2-</sup> and F<sup>-</sup> ions is understood. Furthermore, it is surprising that oxide and fluoride consisted from the same kind of cation take the same crystal structure.

### 2. Typical fluorides

Fluorides such as LiF, NaF, KF, MgF<sub>2</sub> and LaF<sub>3</sub> excluding CaF<sub>2</sub> is sometimes used for refining non-ferrous metals.

#### 2.1 Physical properties

##### 2.1.1 Crystal structure

When fluoride was added to silicate or aluminate slags, crystal structure of the fluoride determines what kind of behaviour it takes.

The role of addition should be considered from the standpoints based on the formation of miscibility

<sup>†</sup> Received on Dec. 16, 1974

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gap and the difficulty of crystallization. These subjects are important in peeling of slag from weldment.

In **Table 3**, the isomorphous structure of each fluorides are given.

Table 3. Crystal structure.

Fluoride	Isomorphous to
NaF	CaO
LiF	MgO
MgF <sub>2</sub>	TiO <sub>2</sub>
CaF <sub>2</sub>	ThO <sub>2</sub>
BeF <sub>2</sub>	SiO <sub>2</sub>

### 2.1.2 Melting point

The published values of melting point of CaF<sub>2</sub> up to this time are compared.

Table 4. Melting point of CaF<sub>2</sub>.

m. p.	Publisher	Age
1386	Eitel	1938 <sup>2)</sup>
1418	Naylor	1945 <sup>3)</sup>
1390	Budnikov & Tresviatski	1953 <sup>4)</sup>
1404	Bååk & Ölander	1954 <sup>5)</sup>
1390	Porter & Brown	1962 <sup>6)</sup>
1418	Kelly	1963 <sup>7)</sup>
1418	Mukerji	1963 <sup>8)</sup>
1423	Kojima, Whiteway, Masson	1968 <sup>9)</sup>
1419±1	Winterhager, Kammel, Gad	1970 <sup>10)</sup>
1421	Iwamoto, Suito, Hamamatsu & Satoh	1973 <sup>11)</sup>

Mitchell and Cameron<sup>12)</sup> reported that the difference of melting point published by investigators is originated from impurities in the sample, especially, CaO which was introduced from the hydrolysis operation. It results in the decrement on the melting point.

### 2.1.3 Atomic refraction

Refractivity represents the packing state of anions which have greater ionic radii in crystal. Therefore, the refractivity would give beneficial information about the configuration of O<sup>2-</sup> and F<sup>-</sup> ions in slag. In **Table 5**, the values of atomic refractivity are given.

### 2.1.4 Electrical conductivity

Electrical property of slag is an important factor to choose appropriate slag for ESR or ESW.

Electrical conductivity of molten slag is governed

Table 5. Atomic refractivity of fluorine.

Investigator	R <sub>D</sub>	R <sub>∞</sub>
Young and Fimm <sup>13)</sup>	0.5 (F <sup>-</sup> )	
Haggins <sup>14)</sup>	0.8 (F)	
Vogel <sup>15)</sup>	0.81 (F <sup>-</sup> )	0.7
Eisenlohr <sup>16)</sup>	1.0~1.35 (F)	
Gas <sup>17)</sup>	1.60 (F)	1.60

by concentration of the existing ions and their mobility. The mobility is inversely proportional to the size of ion and viscosity<sup>18)</sup>.

Electrical conductivity of fluoride-containing slag is about 10~100 times greater than that of fluoride-free slag.

In the following, the electrical property of various kinds of slag is described.

### The system CaO-CaF<sub>2</sub>

There is only an investigation by Bååk<sup>19)</sup> on this system, and the mechanism of electrical conduction remains uncertain. He reports that the increase of electrical conduction with the addition of CaO until 7.35 mol% is due to the formation of vacant sites because the substitution of one oxygen ion to two fluorine ions occurs. However, it is inexplicable why the decrease of electrical conduction occurs when the addition of CaO exceeds 7.35 mol%.

### The system Al<sub>2</sub>O<sub>3</sub>-CaF<sub>2</sub>

The electrical conduction of CaF<sub>2</sub> decreases with the addition of Al<sub>2</sub>O<sub>3</sub>. This is attributed to the formation of anionic complex groups such as Al-O and Al-O-F<sup>20), 21)</sup>.

Generally, the decrease of electrical conduction of cryolite with Al<sub>2</sub>O<sub>3</sub> addition induces the formation of (Al-O-F<sub>2</sub>)<sup>-</sup> complex ion. The thought is supported by the fact that the increase of electrical conduction occurs with the addition of NaF to Al<sub>2</sub>O<sub>3</sub>. In this case, the mobility of Na<sup>+</sup> ion is thought to be nearly unity, so the formation of such a complex group can be acceptable.

Mitchel and Cameron<sup>12)</sup> say that the movement of Ca<sup>++</sup> ion passing through the network is necessary for interpreting the temperature dependance of the electrical conduction if the following reaction occurs.



This opinion can well explain the fact that viscosity increases when Al<sub>2</sub>O<sub>3</sub> above 10 wt.% is added and the formation of complex ions is accelerated when Al<sub>2</sub>O<sub>3</sub> above 25 wt.% is added.

### The system CaF<sub>2</sub>-FeO

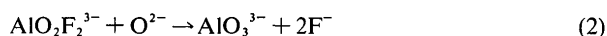
Electrical conductivity of CaF<sub>2</sub> increases with the addition of FeO.

### The systems, CaF<sub>2</sub>-SiO<sub>2</sub>, CaF<sub>2</sub>-TiO<sub>2</sub> and CaF<sub>2</sub>-ZrO<sub>2</sub>

Effect of addition of these components on the electrical conductivity of CaF<sub>2</sub> is almost negligible.

### The system CaF<sub>2</sub>Al<sub>2</sub>O<sub>3</sub>-CaO

When small quantity of CaO is added to the system CaF<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>, electrical conduction increases substantially. With further addition, oxide and aluminate contribute to conduction depending on the following reactions<sup>12)</sup>.



In other words, electrical conduction is based on the amount of oxide and the ratio CaO/Al<sub>2</sub>O<sub>3</sub> in slag.

Generally, low conductivity slags are used for ESR of pure iron, Fe-Cr alloys and some low-carbon steels. As an example of slag, (CaF<sub>2</sub>) + (20~30 wt.% Al<sub>2</sub>O<sub>3</sub>) is used.

On the other hand, high conduction slags are used for ESR of Ni- and Cu- base superalloys. They are for example, CaF<sub>2</sub>-30% LiF, pure CaF<sub>2</sub> and CaF<sub>2</sub>-15 wt.% Al<sub>2</sub>O<sub>3</sub>-15 wt.% CaO.

Although various combination of slags are possible to attain some conduction value, the following conditions that the primary phase appeared on cooling determines heat balance profile on liquid metal region should be considered<sup>12)</sup>. However, the problem of chemical reaction, especially water vapor absorption, should be taken into account to obtain well-balanced weldment.

In **Table 6**, the electrical conduction values of various slags at 1650°C usually used for ESR are compared.

In **Table 7**, typical compositions used for ESR are given.

#### 2.1.5 Surface tension

In the refinement, the following requirements are necessary:

- 1) Removal of slag from molten metal pool
  - 2) Ease of removing slag crust from the solidified metal.
- The latter is the most important problem in welding.

The value of surface tension of CaF<sub>2</sub> changes with temperature as

$$400/1400^\circ\text{C}^{22)} \rightarrow 280/1480 \sim 1500^\circ\text{C}^{23)} \rightarrow 255/1800^\circ\text{C}^{24)}$$

Table 6. Electrical conductivity values.

Component	ohm <sup>-1</sup> cm <sup>-1</sup>
CaF <sub>2</sub> alone	4.54
80CaF <sub>2</sub> -20Al <sub>2</sub> O <sub>3</sub>	4.54
60CaF <sub>2</sub> -40Al <sub>2</sub> O <sub>3</sub>	4.00
60CaF <sub>2</sub> -20CaO-20Al <sub>2</sub> O <sub>3</sub>	2.00
90CaF <sub>2</sub> -10Al <sub>2</sub> O <sub>3</sub>	3.85
70CaF <sub>2</sub> -30Al <sub>2</sub> O <sub>3</sub>	1.76

almost 1~6

Table 7. Slag compositions.

No	CaF <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	CaO	MgO	others
1	87	2	2	—	
2	60	25	10	—	
3	19	33	32	—	
4	63	32	11	—	
5	50	20	10	—	TiO <sub>2</sub> 20
6	70	30	—	—	
7	—	45	55	—	

Richardson<sup>25)</sup> says that an addition of fluoride, KF as an example, to CaO + SiO<sub>2</sub> melt gives  $d\gamma/dx_{\text{KF}} \times 100 = 36$  and shows the decrease of surface tension but it gives less surface activity than sulphur.

Yakobashvili and Frumin<sup>22)</sup> have calculated surface tension value of various slags containing fluoride by weighing droplet from the slag stick hanging in argon atmosphere. It was superior way although the measurement is alone limited at the melting point and it necessitates the value of density at the temperature.

Safonnikov and Nikitin<sup>23)</sup> have measured contact angle and gave the following conclusions that the contribution of SiO<sub>2</sub> to surface tension seems negligible but CaO had intense effect. On the other hand, Al<sub>2</sub>O<sub>3</sub> showed only weak surface activeness.

While, Yakobashvili and Frumin<sup>22)</sup> say that Al<sub>2</sub>O<sub>3</sub>, MgO and CaO as additive show increment of surface tension of CaF<sub>2</sub>, Whereas, ZrO<sub>2</sub>, TiO<sub>2</sub> and SiO<sub>2</sub> as additive show decrease of surface tension. In **Fig. 1**, the additive effect of various oxide on the surface tension value of CaF<sub>2</sub> is shown.

Sommerville<sup>18)</sup> mentions that an additive effect of oxide to CaF<sub>2</sub> is composed of mutual functions from the following factors, 1) dilution effect and 2) solution dynamics. However, it is impossible to speak about intrinsic interpretation of surface tension because the values of pure oxides are unknown with the present technical level.

Ejima and Shimoji<sup>26)</sup> have measured the surface tension of molten CaO + SiO<sub>2</sub> systems, containing 0~

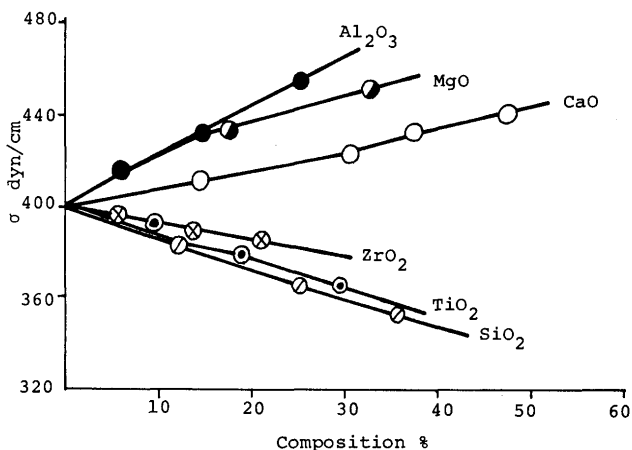


Fig. 1. Effects of oxides on  $\sigma$  for binary  $\text{CaF}_2$ -base mixture<sup>22</sup>.

20 mol.% fluoride of alkali metal and alkaline-earth metal as a function of composition and temperature. They found that the surface tensions of these systems decrease with increasing fluoride concentration although the trend of which depends on the basicity of silicates and the cation species of fluorides. In Fig. 2, the effect of fluoride content on the surface tension of the molten ( $\text{CaO} + \text{SiO}_2 + \text{fluoride}$ ) systems ( $\text{CaO}/\text{SiO}_2 = 1$ ) at  $1550^\circ\text{C}$  is shown.

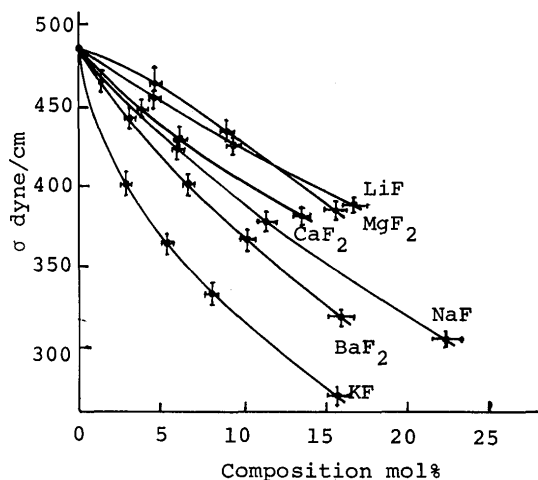


Fig. 2. Effects of fluorides on  $\sigma$  for  $\text{CaO-SiO}_2$ -base mixtures<sup>26</sup>.

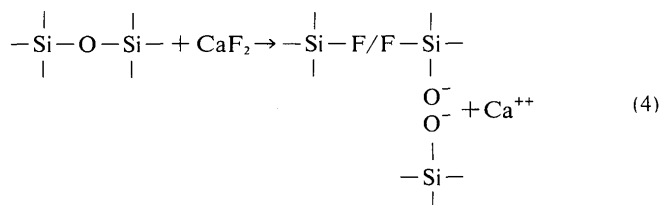
### 2.1.6 Density

As for the separation of slag from molten metal, it becomes easier when the difference of density between slag and molten metal is greater. With the addition of  $\text{CaF}_2$ , slag density increases, but decreases by increasing temperature. The addition of  $\text{Al}_2\text{O}_3$  or  $\text{CaO}$  to  $\text{CaF}_2$  increases density.

### 2.1.7 Viscosity

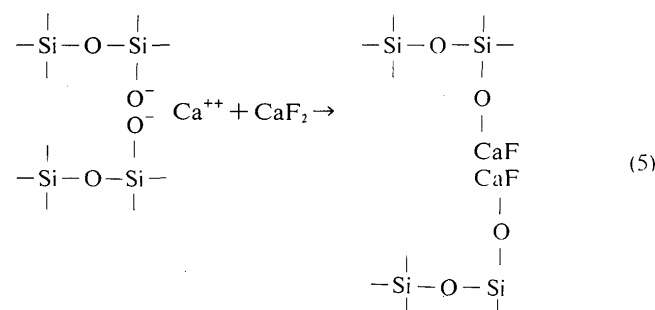
Kozakevitch<sup>27</sup> have measured viscosity of slags of the systems,  $\text{Al}_2\text{O}_3\text{-SiO}_2\text{-CaO}$  and  $\text{Al}_2\text{O}_3\text{-SiO}_2\text{-CaF}_2$ . Because of the reduction of viscosity by the addition

of  $\text{CaF}_2$ , the following structural change was suggested.



He thought that  $\text{CaF}_2$  broke the ( $\text{Si}-\text{O}-$ ) bond alike  $\text{CaO}$ . However, the experimental result did not show an equivalent reduction of viscosity between 2 mol.%  $\text{CaO}$  and 1 mol.%  $\text{CaF}_2$ .

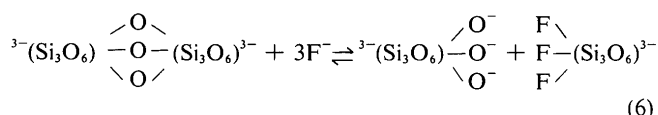
Bills<sup>28</sup> has carried out viscosity measurement about system 40  $\text{SiO}_2$ -20  $\text{Al}_2\text{O}_3$ -40  $\text{CaO}$  added 2 and 9.9%  $\text{CaF}_2$  and the system 50  $\text{SiO}_2$ -15  $\text{Al}_2\text{O}_3$ -35  $\text{CaO}$  added 5 and 15%  $\text{CaF}_2$ . He found that the greater the addition of  $\text{CaF}_2$ , the more the viscosity reduces and the decreasing tendency is remarkable at lower temperature. He could not find equivalent breaking action between 1 mol.%  $\text{CaF}_2$  and 2 mol.%  $\text{CaO}$ . Therefore, to interpret the viscosity change, he thought appropriate the following solvating effect of  $\text{CaF}_2$  on silicate melt which was suggested by Bååk<sup>19</sup>. The solvating effect of  $\text{CaF}_2$  reduces restraint of the electrostatical attraction induced from  $\text{Ca}^{++}$  cation to larger anionic ions and results in the decrease of viscosity.



Shiraishi and Saito<sup>29</sup> have measured viscosity of the system  $\text{CaO-SiO}_2$  when various fluorides are added. They recognized that viscosity of acidic region showed decrement notably, but basic slag did not show reduction. Furthermore, there was not any difference from the sort of fluoride added, and cation species. Also, they found that 1 mol.% fluoride is equivalent to 2.2 mol.%  $\text{CaO}$  and considered that the breaking of  $\text{Si-O}$  bond by  $\text{F}^-$  ion, accordingly, the formation of  $\text{Si-F}$  bond in the melt occurs because bond energy of 83.2 kcal/mole. The experiment showed a contradictory result to the breaking mechanism by Kumar, Ward and Williams<sup>30, 31</sup>. That is to say, random network theory<sup>32, 33</sup> gives that larger anionic species are formed in acidic melt, but it is difficult to assume the formation of flow units having similar size

by breaking action of  $F^-$  ion to interpret the decrement of viscosity.

Therefore, they applied discrete anion model which was presented by Bockris, Mackenzie and Kitchener<sup>34</sup>, and thought the oxygen bridges connecting each  $Si_3O_6^{6-}$  anions. From the comparison of bond angle between the oxygen bridge and Si-O-Si in ring, it is easy to break the oxygen bridge. Accordingly, the formation of flow units having similar size becomes possible.

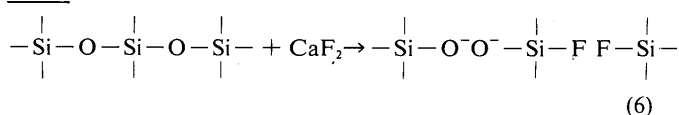


## 2.2 Chemical properties

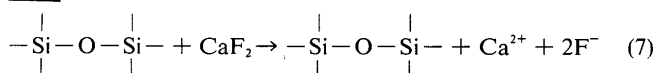
### 2.2.1 Infrared absorption

Kumar, Ward and Williams<sup>30, 31</sup> have reported the infrared absorption studies on the systems  $Na_2O-SiO_2-NaF$  and  $CaO-SiO_2-CaF_2$ . They found absorption band which can be considered as Si-F near  $765\text{ cm}^{-1}$  in the specimen of  $Na_2O/SiO_2=0.85/1$  ( $NaF=16.5\text{ wt.}\%$ ). Further, absorption band at  $857\text{ cm}^{-1}$  probably originated from Si-F was determined by the specimen containing  $CaO : CaF_2 : SiO_2 = 1 : 1.49 : 1$ . However, the following additive effects of  $CaF_2$  were suggested because another experimental results that no Si-F absorption was observed from the specimen in the system  $Na_2O-SiO_2-NaF$  which contains  $Na_2O$  above  $55\text{ mol.}\%$ , and that behaviour of  $F^-$  ion in acidic and basic metal is different in the measurements of weight-loss and viscosity.

acidic



basic



Ito, Yanagase, Suginozaki and Miyazaki<sup>35</sup> have studied infrared absorption of the systems,  $PbO-SiO_2$ ,  $Na_2O-SiO_2$  and  $CaO-SiO_2$  when  $10\text{ mol.}\%$  various fluoride (Li, Na, Mg, Ca, Be and Pb) was added. The absorption of  $\nu_3$ , stretching vibration, remained without shift by adding Li, Na, Mg and Ca fluoride. From these results, they concluded that fluoride acts as dilutant to silicate melt and remains just as it is. Then, they pointed out that Si-F band, which Kumar et al.<sup>30, 31</sup> indicated, is attributed to crystallized  $3CaO \cdot 2SiO_2$ , because the following reaction between  $CaF_2$  and  $SiO_2$  occurs.



Mitchell<sup>36</sup> has studied infrared absorption of specimens ranging from  $(0.1\text{ mol. } CaSi_2O_5) + (0.9\text{ mol. } CaF_2)$  to  $(0.1\text{ mol. } Ca_3SiO_5) + (0.9\text{ mol. } CaF_2)$ . From the considerations about absorption modes obtained experimentally and the calculation, he concluded that new absorption band does not appear and has no contribution to other adsorption mode even if there remains Si-F bond from the equilibrium,



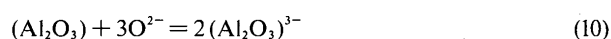
In addition to the thought described above, he thinks that  $CaF_2$  is very stable, and fluoro-silicate ions will be unstable on quenching.

### 2.2.2 Gas absorption

#### a) Oxygen absorption

##### 1) D. C. method

Free oxygen or  $(Al_2O_3)^{3-}$  ion is released and results in increment of oxygen content from the following reactions.



##### 2) A. C. method

Oxygen content is determined from various factors such as slag composition, basicity of slag, existence of unstable oxides and quality of remelting metal<sup>37</sup>.

Generally, oxygen content becomes higher when unstable oxide is contained. Accordingly, stable oxide such as  $CaO$ ,  $BaO$ ,  $ZrO_2$ ,  $Al_2O_3$  and  $MgO$  is used for ESR. Especially, Ti, V, Cr, Mn, Fe and Cu forms unstable oxide and it acts for transfer material of oxygen<sup>37</sup>.

Winterhager, Kammel and Gad<sup>10</sup> have studied physical properties such as electrical conductivity, surface tension and density, and oxygen content of the system  $CaO-Al_2O_3-CaF_2$  having various compositions at  $1500^\circ\text{C}$ . These relation between physical properties and the oxygen content is shown in Fig. 3<sup>10</sup>. They

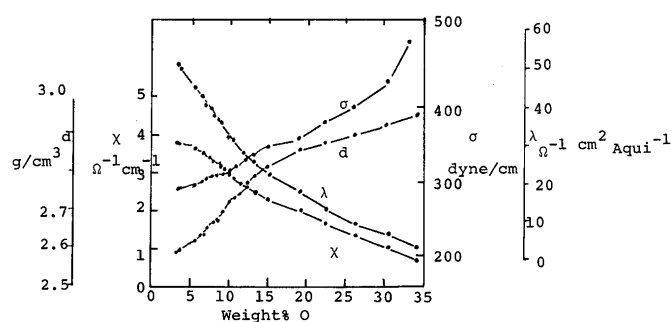
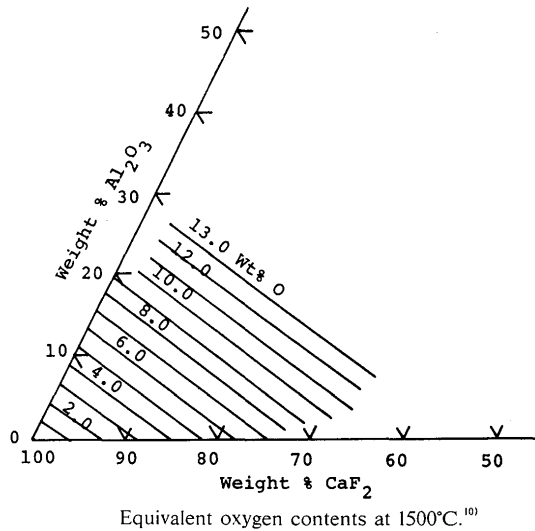


Fig. 3. Relationship between various physical properties and oxygen content at  $1500^\circ\text{C}$ .<sup>10</sup>



claim that a certain kind of relationship exists between electrical conductivity and the oxygen content. In Fig. 4<sup>10)</sup> equivalent oxygen content is shown. Higher oxygen content come from slags of the systems, CaO-Al<sub>2</sub>O<sub>3</sub> and CaF<sub>2</sub>-CaO.

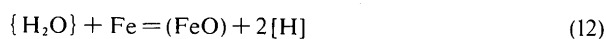
Kay, Mitchell and Ram<sup>38)</sup> studied thermodynamic properties of iron oxide in CaF<sub>2</sub>-CaO-Fe<sub>2</sub>O fluxes and indicated the importance of the effect of high oxygen potential due to iron oxide. They say that the relatively low oxygen potential of CaF<sub>2</sub>-based fluxes of high basicity contribute excellently towards the sulphur removal.

Hawkins and Davis<sup>39)</sup> studied in detail about thermodynamics of FeO-bearing CaF<sub>2</sub>-based slags. The activity coefficients of FeO decreased with increasing CaO content. Addition of Al<sub>2</sub>O<sub>3</sub> to the CaF<sub>2</sub>-CaO-FeO system increased  $\gamma_{\text{FeO}}$  due to its strong interaction with CaO.

#### b) Hydrogen absorption

It is generally accepted that the decrement of hydrogen absorption by ESR can not be expected, and there remains about 2.5~3.0 ppm as an average.

Pocklington<sup>40)</sup> studied the relationship between hydrogen content in molten steel and slag composition of the system CaF<sub>2</sub>-CaO having different FeO, and recognized that hydrogen content decreases with increasing FeO. Following equations were given by him.



$$[\text{H}] = 1/(x_{\text{FeO}} \gamma_{\text{FeO}}^0)^{1/2} \quad (13)$$

It can be imagined easily that hydrogen pick up is higher in the system 70CaF<sub>2</sub>-30CaO than 95CaF<sub>2</sub>-5CaO because activity coefficient of FeO in CaF<sub>2</sub> slag decreases with increasing CaO. However, Pocklington<sup>40)</sup> did not find this tendency.

Although small scale experiment shows that higher

FeO content in slag is better to provide for hydrogen pick up, it is not desirable for clean steel manufacture from the viewpoint of oxide inclusion.

Slag of the system CaF<sub>2</sub>-CaO is convenient for desulphurization, but it is apt to take up water vapor during storage.

Masui, Sasajima and Yamamura<sup>41)</sup> studied behaviour of hydrogen in ESR, and found that the hydrogen absorption is governed by the following factors such as partial pressure of water vapor, interfacial area between gas and slag, slag composition, hydrogen content of electrode, dissolving velocity, and the quantity of slag.

#### c) Nitrogen absorption

Usually, it is considered that there occurs decrease of 20~40 % nitrogen in ESR but the nitrogen absorption shows increase when Ti, Nb or Zr is contained.

However, we can not find any paper which treated the relation between nitrogen content and flux composition, because the variation of nitrogen content is little even if flux composition is changed.

#### d) Sulphur pick up

Higher sulphide capacity is obtained when adding CaO because substitution between sulphur and oxygen occurs.

In Fig. 5, sulphide capacities at 1500°C for (CaO + CaF<sub>2</sub> + Al<sub>2</sub>O<sub>3</sub> melts) is shown<sup>42)</sup> Richardson<sup>25)</sup> says that (CaO + CaF<sub>2</sub>) slag has higher sulphide capacity than (CaO + SiO<sub>2</sub>) slag having equal mole fraction of CaO content.

For the desulphurization, following reactions between slag and metal, gas and solid must be considered.

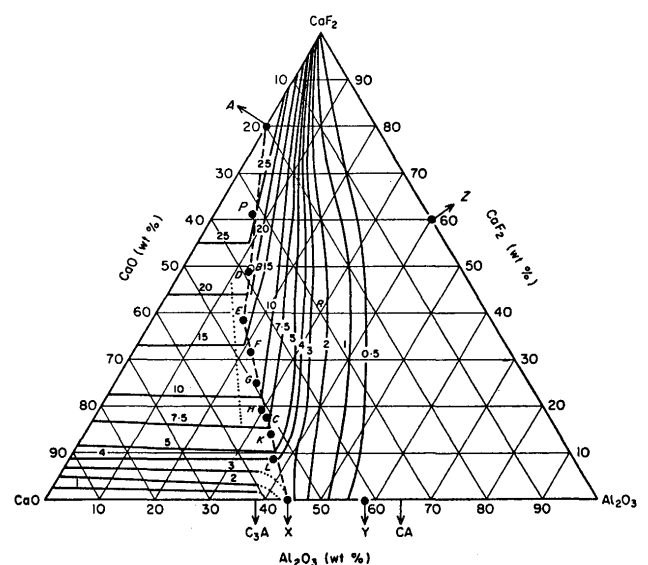
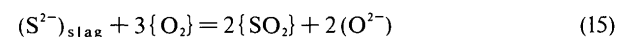
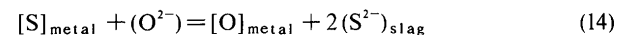


Fig. 5. Sulphide capacities at 1500°C for CaO + CaF<sub>2</sub> + Al<sub>2</sub>O<sub>3</sub>.<sup>40)</sup>

Equation (14) comes from the electrochemical reaction too.

Duckworth and Hoyle<sup>37)</sup> say that the following factors such as high CaO and MgO content in slag, minimum SiO<sub>2</sub> content, minimum iron oxide, air as atmosphere and AC conditions and small CaC<sub>2</sub> addition are necessitated for sulphur removal.

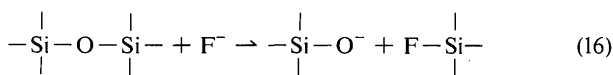
### 2.2.3 Depression of the freezing point

It is impossible to estimate size of anionic ion from viscosity measurement, especially, in acidic region of silicate slag.

Bååk and Ölander<sup>43)</sup> have determined the degree of polymerization of calcium metasilicate in fused calcium fluoride by cryoscopic measurement. They concluded that the silicate formed groups of three tetrahedra connected in a ring structure.

Föland<sup>44)</sup> carried out cryoscopic measurement and derived conclusion that larger groups would be transformed into cations containing several nonbridging oxygens if both alkali and alkaline-earth oxides are added to silica.

Further, Föland calculated structural units from the phase diagram of NaF-Na<sub>2</sub>SiO<sub>3</sub>, given by Booth and Starrs<sup>45)</sup> Using the values 8.23 kcal/mole for the heat of fusion of NaF, he could estimate that the complex containing four to six SiO<sub>3</sub><sup>2-</sup> groups, and derived an important conclusion that the presence of fluoride ions did not cause a depolymerization of the complex. Similar treatment was performed on the phase diagram of NaF-Na<sub>2</sub>Si<sub>2</sub>O<sub>5</sub>, given by Booth, Starrs and Bahnsen<sup>46)</sup>. He could estimate the number of Si<sub>2</sub>O<sub>5</sub><sup>2-</sup> groups in a complex silicate to be of the order of magnitude of six to eight. However, Föland suggested that the F<sup>-</sup> ions break up some of the oxygen bridges according to the equation to release some of the strain in the complex ion, and said that further study to solve this problem would be necessary.



Kojima and Masson<sup>47)</sup> have studied depression of the freezing point of calcium fluoride by alkaline-earth fluorides and oxides, and calcium silicates. As an example, the effect of MgO, CaO, SrO and BaO as solute on the depression of freezing point of CaF<sub>2</sub> is shown in Fig. 6<sup>45)</sup>. According to the following equation,  $v$  is obtained;

$$1/T = 1/T_0 - vR/\Delta H_f^0 \ln N_{\text{CaF}_2} \quad (17)$$

where  $T$  is the temperature at which pure solid component crystallizes from a solution on cooling,  $\Delta H_f^0$  is the molar heat of fusion of pure component at its melt-

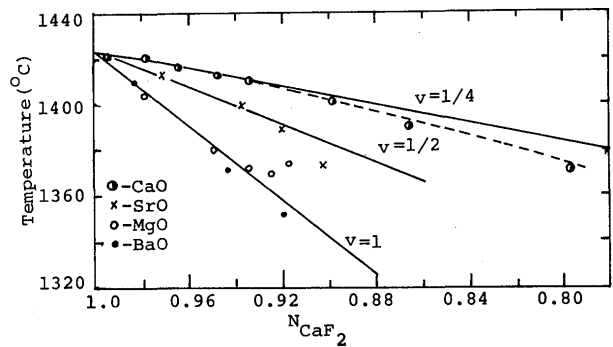


Fig. 6. Depression of the freezing point of CaF<sub>2</sub> by MgO, CaO, SrO and BaO.<sup>45)</sup>

ing point  $T_0$  and  $v$  are number of foreign ions per molecule from the dissociation of solute. At low concentrations,  $v=1$  in MgO and BaO, while SrO shows intermediate behaviour, with  $v=1/2$ . They concluded that the relatively small depression due to CaO should be attributed to the formation of solid solution of CaO-CaF<sub>2</sub> system according to Delbove's opinion<sup>48)</sup>. When distribution coefficient  $\rho$  (the ratio of the concentration of solute in the solid to that in the liquid solution) is high, it can be concluded that oxide ions readily substitute for fluoride ions in CaF<sub>2</sub>. While, MgO and BaO remain largely associated as ion pairs in the melt from the interpretation by Lumsden<sup>49)</sup>.

In our laboratory, depression of the melting points of alkali-fluoride/alkali-disilicate, alkaline-earth-fluoride/alkaline-earth-disilicate and lead-fluoride/lead-disilicate systems were studied<sup>50), 51)</sup>. Activities of each fluorides were calculated and the results are shown in Figs. 7, 8, 9 and 10 respectively. Shape of activity curve determines the form of anionic complex ion. In the case of upper convex shape from the activity curve, it is thought that fluorine ions simply act to dilute and give no change to anionic complex ions. On the other hand, downside convex shape is thought to mean that the breaking action of fluorine ion to Si-O-Si bond and therefore fluoro-silicate ion is formed. From these considerations, it was suggested that there chiefly remain ring ions of (SiO<sub>3</sub>)<sub>4</sub><sup>12-</sup> in the case of alkali-fluoride/alkali-metasilicate from the simple diluting action of fluorine ions.

In the systems, alkaline-earth fluoride/alkaline-earth-metasilicate and lead-fluoride/lead-metasilicate, it was shown that fluorine ions broke Si-O-Si bond and therefore the polymerization reaction to form (SiO<sub>3</sub>F)<sup>3-</sup> anions is accompanied. In the systems, alkali-fluoride/alkali-disilicate and alkaline-earth-fluoride/alkaline-earth-disilicate, the breaking action of fluorine ions on the Si-O-Si bond was certified. In these cases, polymerization reaction from a unit of (Si<sub>2</sub>O<sub>5</sub>F<sub>2</sub>)<sup>4-</sup> ion was considered appropriate. In the case of alkaline-earth fluoride/alkaline-earth ortho- or



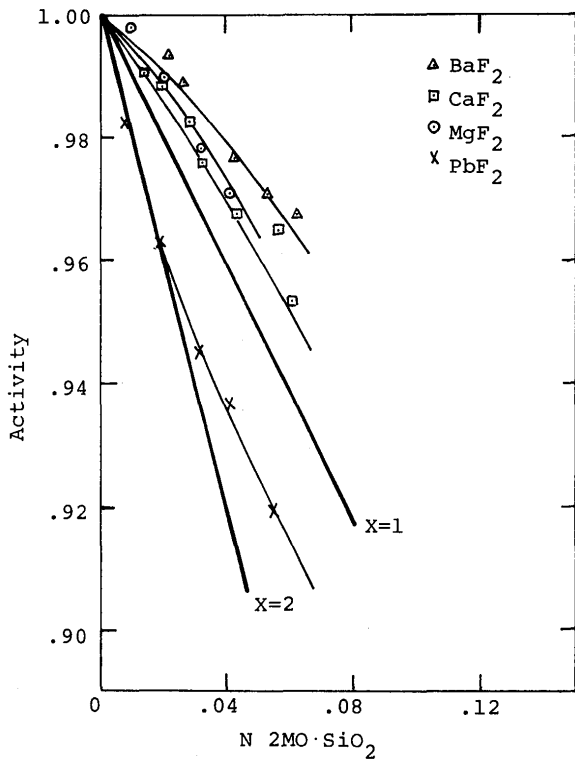


Fig. 7. Activities of alkaline-earth fluorides and lead fluoride as a function of mole fraction of orthosilicates.<sup>48)</sup>

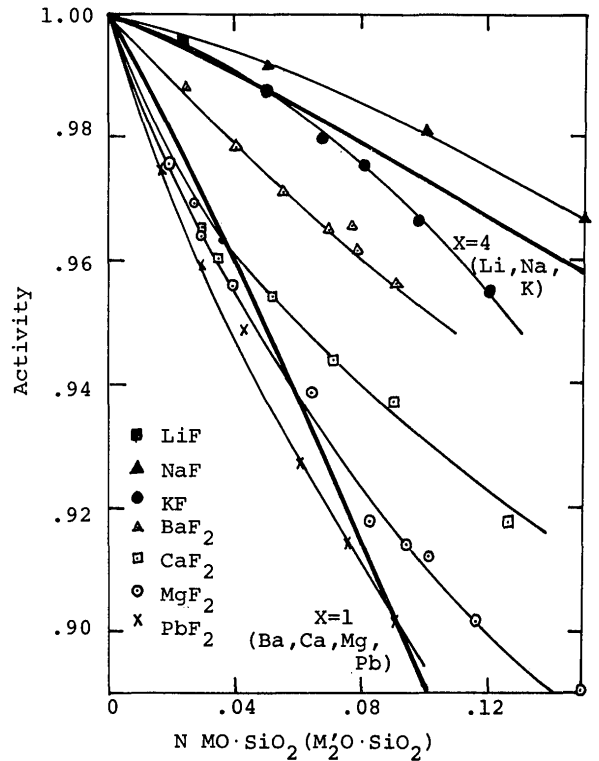


Fig. 9. Activities of alkali fluorides and alkaline-earth fluorides and lead fluoride as a function of mole fraction of metasilicates.<sup>48)</sup>

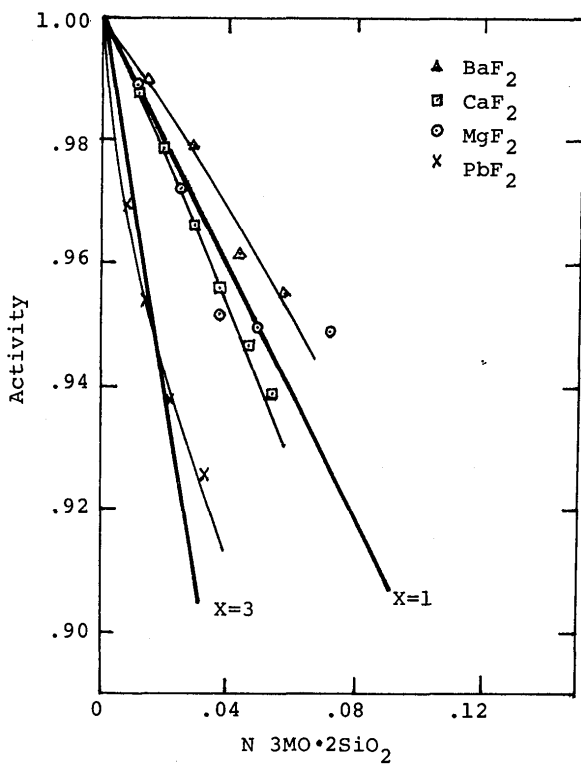


Fig. 8. Activities of alkaline-earth fluorides and lead fluoride as a function of mole fraction of pyrosilicate.<sup>48)</sup>

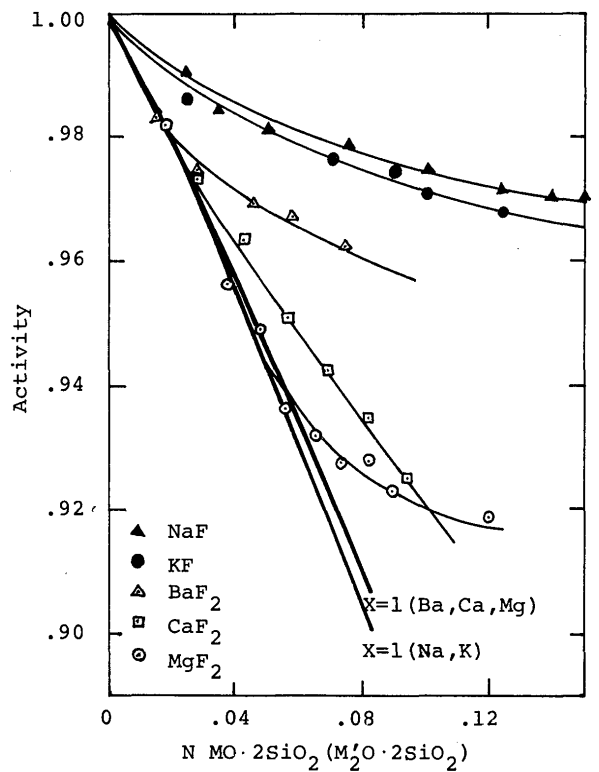


Fig. 10. Activities of alkali fluorides and alkaline-earth fluorides as a function of mole fraction of disilicates.<sup>48)</sup>

pyrosilicate system, proof of breaking action of fluorine ion on the Si-O-Si bond was not recognized, and the polymerization model of binary silicate system (MO-SiO<sub>2</sub>) given by Masson<sup>51</sup> is thought to be apposite. In the case of lead fluoride/lead ortho- or pyrosilicate system, it was determined that fluorine ions broke the Si-O-Si bond and (SiO<sub>3</sub>F)<sup>3-</sup> ion was considered as unit.

### Summary

In this review, the author summarized mainly the role of calcium fluoride in slag from physical and chemical viewpoints. Until now, it remains unclear whether fluorine ions break Si-O-Si bond in slag or not. Similarly, the role of fluorine ions on the physical properties of slag such as surface tension, electrical conductivity and viscosity is obscure.

The dynamical measurement of slag containing fluorine ions is now being studied in our laboratory, and such a problem will be clarified in near future.

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