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# Structure of Slag (Review 1)<sup>†</sup>

## —Basicity of Slag—

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### Abstract

*Although the basicity of slag is the most important concept to understand various chemical reactions occurring in steel refinement and welding, no systematic review has been done until now. In this review, the relation between the solubility of gas such as oxygen, nitrogen and water vapor in slag and the concept of basicity is given.*

### 1. Definition of Basicity

#### 1.1 Definition by Arrhenius

Arrhenius defined acids as molecules which can produce protons in aqueous solution. On the contrary, bases have ability to deny the habits of acids, and they can produce hydroxyl ion (OH<sup>-</sup>).

#### 1.2 Definition by Brønsted and Lowry

Brønsted (1923) and Lowry (1923) have offered the extension of the Arrhenius concept at the same time.

An acid is defined as a substance which is capable of releasing protons. There is another molecule (base) available which can accept the proton. Therefore, acid-base reaction is treated as competitions for protons.

In the following example, water becomes a base with respect to molecule having tendency to release a proton:



Water can behave as an acid or as a base depending on the molecular species with which it interacts. Secondary, water is an acid with respect to molecules that can accept protons, e. g., NH<sub>3</sub>:



#### 1.3 Definition by Lewis

Lewis has given concept of acid-base reactions which involves the formation of a covalent coordinate bond between two atoms and this concept cannot be applied to systems which are ionic<sup>1)</sup>. He applied the thought described above to nonaqueous solvents and gases, and an example of reaction of gas is as,



and in the case of coordinated compound,



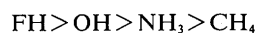
is given.

Either cases do not show the reaction of proton. From these equations, the one which can donate electron pairs is base such as NH<sub>3</sub> and it defines acids as molecules that contain atoms with incomplete electron shells such as HCl and BF<sub>3</sub>.

### 2. Essential Factor Governing the Acidity-Basicity

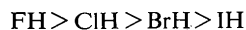
#### 2.1 Electronegativity<sup>2)</sup>

The factor which dominates the equilibrium of equation (1) is that either the stability of A-H bond or the stability of A<sup>-</sup> ion predominate. From other experiment, it is proved that the stability of A<sup>-</sup> ion is main factor to determine the equilibrium. Therefore, it will be anticipated that an acid composed of negative ion having high electronegativity is stronger.



#### 2.2 Size of ions

If the strength of acid depends on the electronegativity of anion, the following order



must be accepted. However, IH is the strongest while FH is the weakest practically. This means that the more charge disperses, the more it becomes stable. The fact that H<sub>2</sub>S is stronger than H<sub>2</sub>O comes from the same reason in opposition to the cause that sulphur has higher value of electronegativity than oxygen.

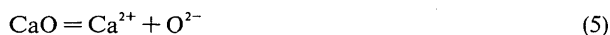
<sup>†</sup> Received on July 3, 1974

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The bigger base conjugated, the more basicity becomes weak in other words.

### 3. Problems of Molten Slag (Glass)

It is defined that a basic constituent can release a basic ion  $O^{2-}$ .



On the contrary, an acidic constituent is defined as the one that can catch the basic ion.



#### 3.1 Theory of Flood and Förland<sup>3)</sup>

Acidity-basicity was attributed to the difference of polarizability of  $O^{2-}$  ion. Accordingly, the basis of the acid-base reaction is discussed with the movement of  $O^{2-}$  ion from some polarizing state to the other.



According to this reaction, the formation of a pair of  $O^-$  ions, which is the more intense polarizing state, from the breakdown of oxygen bridge  $O^0$  having intense polarization is reduced to the polarizing action of cations to take stable form with the surrounding  $O^{2-}$  ion.

#### 3.2 Reaction between $SiO_2$ and other oxides

1) When  $SiO_2$  reacts with  $Cr_2O_3$ ,  $MgO$ ,  $FeO$  and  $CaO$  and  $SnO$  and  $PbO$  which have intermediate polarizing intensity, they form a limited liquid miscibility.

2) Alkali oxide consisted of cation having low ionic potential (charge/radius of cation) or  $Al_2O_3$ ,  $BeO$  and  $TiO_2$  whose cation has high ionic potential forms complete liquid miscibility.

3) There exists miscibility gap near melting point of  $SiO_2$  at the region between 60~98 mol% in the system  $MgO-SiO_2$  and between 80~98 mol% in the system  $SrO-SiO_2$  respectively.

These evidences show that there exist three different structures in liquid silicate. These differences are probably related to the polarizing intensity of cation in liquid silicate.

### 4. Development of Generalized Indices for Basicity

#### 4.1 Basicity of individual oxide

Free oxygen ion is unstable, so it becomes stable by neighbouring cation. The stability increases with increasing field strength. After all, the reacting ability show decrease with decreasing basicity.

Dietzel has examined the enthalpy change of all kinds of cation for the following equation<sup>4)</sup>.



$H_{298}^0$ , which is driving force of this reaction, decreases with increasing field strength,  $z/a^2$  ( $z$ : charge,  $a$ : sum of radius of cation and anion). These tendencies are shown in Fig. 1.

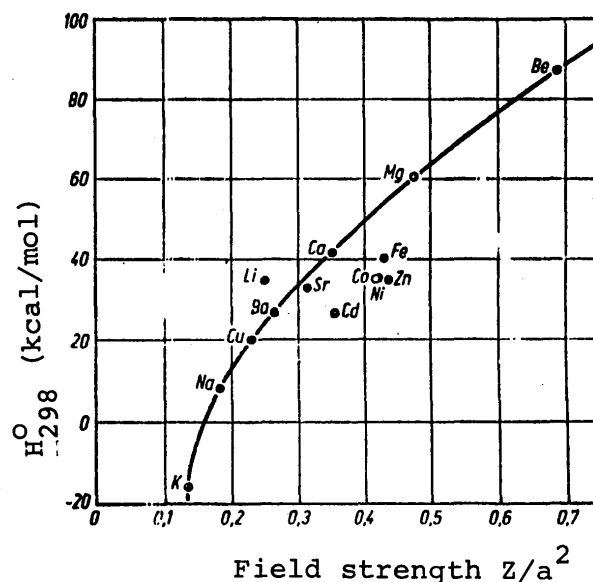


Fig. 1. Enthalpy change of the reaction,  $O^{2-} + S = 1/2\{O_2\} + S^{2-}$ , and field strength<sup>4)</sup>.

Sun and Silverman<sup>5)</sup> and Sun<sup>6)</sup> have drawn the relative intensity of metal-oxygen bond by using the energy that is necessary to decompose for metal and oxygen. That is difficult to decompose for each constituents was treated as strong acid. Their order proposed are shown in the left-hand side of Table 1<sup>7)</sup>.

There are another ways to compare the intensity of basicity of individual oxide from the easiness to decompose individual carbonate or sulphate. The one having intense basic property is difficult to evolve  $CO_2$  or  $SO_2$  gas.

Classified results by these means by Flood and Förland<sup>3)</sup> are shown in the right-hand side of Table 1. It will be seen that the values from two different compounds almost agree.

Stegmaier and Dietzel<sup>8)</sup> have considered that slags composed of oxide system having much  $O^{2-}$  ion have greater basicity and the concentration of  $O^{2-}$  ion is the dominating factor because the concentrations of  $F^-$  and  $S^{2-}$  ions are negligible small.

#### 4.2 Conventional basicity of slag

In the steel-making,  $CaO/SiO_2$ ,  $CaO-4P_2O_5/SiO_2$  (L-ratio) or  $CaO/SiO_2 + P_2O_5$  (V-ratio) ratios are used for conventional basicity of slag. Historically, the

Table 1. Oxides arranged in order of increasing basic strength<sup>7)</sup>.

From relative bond strength	From carbonate decomposition	From sulphate decomposition
B <sub>2</sub> O <sub>3</sub>	P <sub>2</sub> O <sub>5</sub>	
SiO <sub>2</sub>	B <sub>2</sub> O <sub>3</sub>	
P <sub>2</sub> O <sub>5</sub>	SiO <sub>2</sub>	
Al <sub>2</sub> O <sub>3</sub>	TiO <sub>2</sub>	
Sb <sub>2</sub> O <sub>5</sub>		
ZrO <sub>2</sub>		
TiO <sub>2</sub>		BeO
BeO		Fe <sub>2</sub> O <sub>3</sub>
SnO <sub>2</sub>		CuO
FeO	FeO	CoO
PbO	ZnO	NiO
MgO	CoO	ZnO
MnO	MnO	CdO
Li <sub>2</sub> O	PbO	MnO
PbO	CdO	PbO
CaO	MgO	MgO
SrO	CaO	CaO
BaO	Li <sub>2</sub> O	Li <sub>2</sub> O
Na <sub>2</sub> O	BaO	BaO

transition of suggestion of basicity of slag is given in Table 2<sup>9)</sup>.

Besides, estimation from aqueous extracts of powdered slags was given<sup>10)</sup>, but it seems qualitative.

#### 4.3 Basicity estimation from calculation

Matsushita has presented a method to obtain basicity of slag based on molar heat of formation of the compositions, from the comparison between lattice energy of ion in slag and the scratching hardness of slag<sup>11)</sup>.

It becomes possible to obtain total heat of formation of slag under the assumption that, in the acidic slag, Al<sub>2</sub>O<sub>3</sub> may ionize to AlO<sub>3</sub><sup>3-</sup> and PO<sub>4</sub><sup>3-</sup> from P<sub>2</sub>O<sub>5</sub> and FeO<sub>3</sub><sup>3-</sup> from Fe<sub>2</sub>O<sub>3</sub> appear from accepting O<sup>2-</sup> ion. The basicity of slag was defined with these values<sup>12)</sup>.

Further, this thought has been developed, and  $B_r = \frac{\sum_B}{\sum_A}$  was calculated from  $\sum_B$  of basic components and  $\sum_A$  of acidic components. Still, free O<sup>2-</sup> ion was calculated from the equation,  $(O^{2-}) = \sum_A O^{2-} - \sum_B O^{2-}$ , and the relationship between O<sup>2-</sup> content and  $B_r$  about the practical slags are well illustrated in Fig. 2. However, this thought is hardly accepted hence the calculation is complex.

#### 4.4 $B_L$ indication by Mori<sup>26)</sup>

The following equation is utilized as indicator for

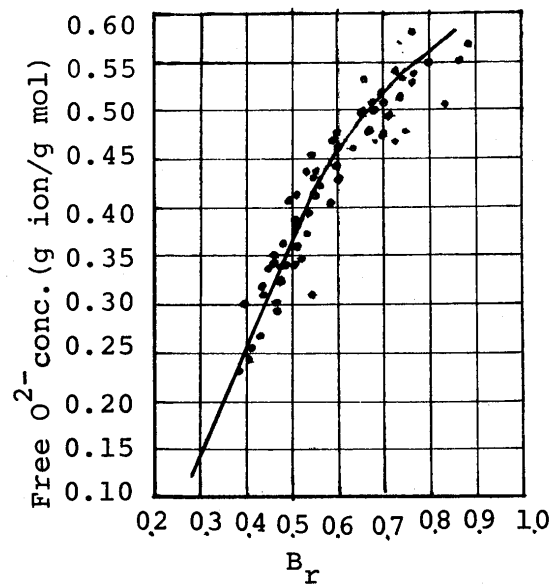
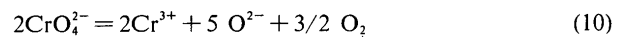


Fig. 2. Relation between free O<sup>2-</sup> concentration in the basic open hearth furnace's slags and the basicity  $B_r$ <sup>10)</sup>.

determining the acidity of glasses since old times.



However, it becomes a serious problem to bring a specimen as quench without structure change from molten state, because the judgement must be done with color change as a function of oxygen ion activity.

While, it is a well established fact that element which can take different states of oxidized number takes higher value when it acts as acid, but takes lower value when it is base conversary.

Mori has considered that the ratio ( $r = Fe^{3+}/Fe^{2+} + Fe^{2+}$ ) in slag determines the basicity of slag. It is necessary to hold the condition that the state in melt should be brought into room temperature without structure change in the same way.

Generally, only the ionic fractions of cations must be considered because oxygen ion belongs to each compositions.

As concentration of slag added to iron oxide to determine the basicity is

$$C = \frac{\sum M}{(\sum Fe + \sum M)} \quad (11)$$

where,  $\sum Fe = Fe^{2+} + Fe^{3+}$

$$\sum M = Ca^{2+} + Si^{4+} + Ti^{4+} + Al^{3+} + \dots$$

From the results obtained experimentally

$$B = \{(r - r_0)/C\} \times 10 \quad (12)$$

is given. where,

$$(dr/dC)_{C \rightarrow 0} = (r - r_0)/C \quad (13)$$

As conclusion, basicity of slag is experimentally

Table 2. Conventional basicity given by many investigators<sup>9)</sup>.

No.	Basicity	Year	Ref.
1	$\%O(\text{from MeO})/\%O(\text{from SiO}_2)$	1869	13
2	$\%(\text{MeO})/\%(\text{SiO}_2) + \%(\text{Al}_2\text{O}_3)$	1892	14
3	$\%(\text{CaO})/\%(\text{SiO}_2)$	1901	15
4	$\frac{(\text{MeO}) - 3(\text{P}_2\text{O}_5)}{(\text{SiO}_2)}$	1922/23	16
5	$\%(\text{CaO}) - 1.86\%(\text{SiO}_2) - 1.19\%\text{P}_2\text{O}_5$	1934	17
6	$\frac{(\text{CaO}) - 4(\text{P}_2\text{O}_5)}{(\text{SiO}_2)}$	1942	18
7	$(\text{MeO}) - 2(\text{SiO}_2) - 4(\text{P}_2\text{O}_5) - 2(\text{Al}_2\text{O}_3) - (\text{Fe}_2\text{O}_3)$	1946	19
8	$\frac{(\text{MeO})}{(\text{SiO}_2) + 2(\text{P}_2\text{O}_5) + 1/3(\text{Al}_2\text{O}_3) + 1/2(\text{Fe}_2\text{O}_3)}$	1946	20
9	$\frac{\%(\text{CaO})}{\%(\text{SiO}_2) + \%(\text{P}_2\text{O}_5)}$	1947	21
10	$(\text{CaO}) + 2/3(\text{MgO}) - (\text{SiO}_2) - (\text{Al}_2\text{O}_3)$	1949	22
11	$\frac{\%(\text{CaO}) + \%(\text{MgO})}{\%(\text{SiO}_2) + 0.6\%(\text{Al}_2\text{O}_3) \left[ \frac{\%(\text{CaO}) + \%(\text{MgO})}{\%(\text{SiO}_2)} \right]}$	1956	23
12	$\frac{\%(\text{CaO}) + 0.7\%(\text{MgO})}{0.94\%(\text{SiO}_2) + 0.18\%(\text{Al}_2\text{O}_3)}$	1960	24
13	$\frac{\%(\text{CaO}) + \alpha\%(\text{MgO}) + 2.0\%(\text{MnO})}{\%(\text{SiO}_2) + 0.6\%(\text{Al}_2\text{O}_3) \left[ \frac{\%(\text{CaO}) + \alpha\%(\text{MgO})}{\%(\text{SiO}_2)} - 1.19 \right]}$ where, $\alpha = \frac{1.84\%(\text{SiO}_2) - 0.9\%(\text{CaO})}{\%(\text{SiO}_2) + 0.9\%(\text{MgO})}$	1962	25
14	$\text{pO} = -\lg a_{\text{O}^{2-}}$	1971	9

obtained whether r value increases or decreases depending on base or acid when slag is added to ferrous oxide.

The indication is usually used for determining basicity of flux in Japan,  $B_L$  indication is as follows:

$$B_L = \sum a_i N_i = a_1 N_1 + a_2 N_2 + a_3 N_3 + \dots \quad (14)$$

where,

- $N_1, N_2, N_3, \dots$  ionic fractions of each components
- $a_1, a_2, a_3, \dots$  characteristic constants for each constituents

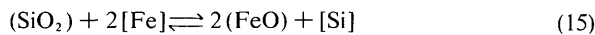
Constant,  $a_i$  is given in **Table 3**.

Table 3. Constants  $a_i$ <sup>26)</sup>

Oxide	$a_i$
CaO	6.05
SiO <sub>2</sub>	-6.31
TiO <sub>2</sub>	-4.97
Al <sub>2</sub> O <sub>3</sub>	-0.2
MnO	4.8
MgO	4.0
FeO	3.4

As an application to welding, silicon content reduced to weld metal with changing SiO<sub>2</sub> content in covered electrode of the types of ilumenite and rutile by Andou and Kugai<sup>27)</sup> was compared with the slag compositions formed.

If the equilibrium holds for slag formed and weld metal, the following relation



is obtained.

So, the equilibrium constant

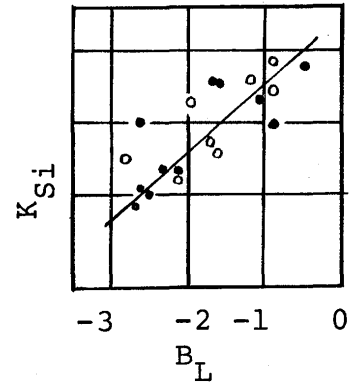


Fig. 3. Relation between  $K_{Si} = (\text{SiO}_2) / \{(\text{FeO})^2(\text{Si})\}$  and basicity  $B_L$ <sup>12)</sup>.

$$K_{Si} = (\text{SiO}_2) / \{(\text{FeO})^2 [\text{Si}]\} \quad (16)$$

is obtained.

In **Fig. 3**, the relation between  $B_L$  and  $K_{Si}$  are shown.

#### 4.5 Concept of excess base<sup>19)</sup>

Grant and Chipman advanced following assumption.

- 1) FeO and CaF<sub>2</sub> are neutral.
- 2) CaO, MnO and MgO are bases of equal value.
- 3) As correspondences of each acids and bases,
  - 2 Base: 1 SiO<sub>2</sub>
  - 4 Base: 1 P<sub>2</sub>O<sub>5</sub>
  - 2 Base: 1 Al<sub>2</sub>O<sub>3</sub>
  - 1 Base: 1 Fe<sub>2</sub>O<sub>3</sub>

are given.

In **Fig. 4**, excess base are compared with (S)/[S].<sup>19)</sup> It was shown that large variations in MnO, CaF<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> and FeO and temperature caused no significant variations from the standard curve.

#### 4.6 Suggestion of oxygen ion concentration pO

Frohberg and Kapoor presented the indication of pO similar to pH<sup>9)</sup>.

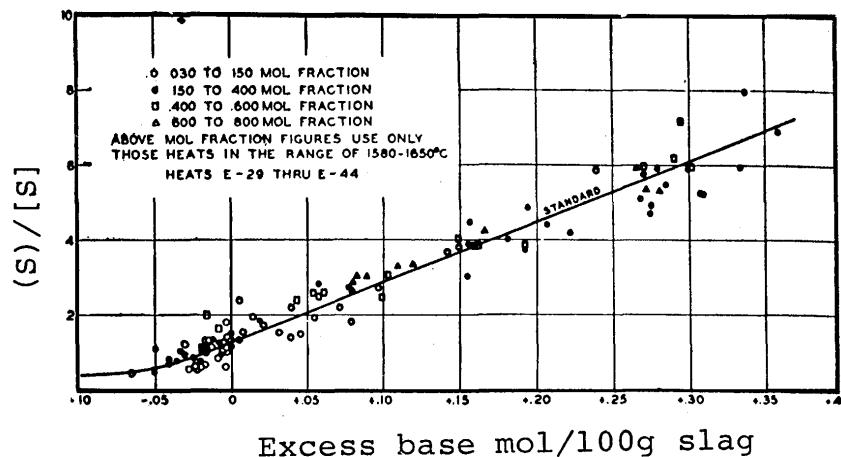
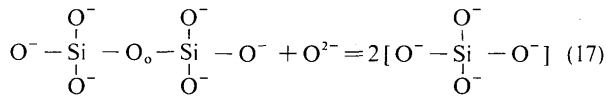


Fig. 4. Effect of excess base on the removal of sulphur at the temperature between 1580 and 1650°C.<sup>19)</sup>

Polymerization or dissociation of silicate will be considered as follows:



equals to

$$2 \text{O}^- = \text{O}^0 + \text{O}^{2-} \quad (18)$$

Therefore, the equilibrium constant is

$$K = a_{\text{O}^{2-}} \cdot a_{\text{O}^0} / a_{\text{O}^-} \quad (19)$$

When modified, it becomes

$$a_{\text{O}^{2-}} = \left[ \frac{N_{\text{MeO}}}{(1 + N_{\text{SiO}_2})} - \frac{1 - \sqrt{1 - 8N_{\text{MeO}}N_{\text{SiO}_2}(1 - 4k)}}{(1 + N_{\text{SiO}_2})^2} \right] \times e^{\alpha} \cdot N_{\text{MeO}}^2 \cdot N_{\text{SiO}_2} \quad (20)$$

where, K and  $\alpha$ , are given from the thermodynamical values by fitting to  $a_{\text{MeO}}$  curve of the system MeO-SiO<sub>2</sub>. The values are given in **Table 4**.

Extension of this concept for multi-components system, Förland and Grjotheim have given the following relations<sup>29)</sup>.

$$\ln K = \sum N_i \cdot \ln K_i \quad (21)$$

$$\alpha = \sum N_i \cdot \alpha_i \quad (22)$$

Frohberg and Kapoor have presented the following equation.

$$p\text{O} = -\ln a_{\text{O}^{2-}} \quad (23)$$

For example, the system CaO-FeO-SiO<sub>2</sub> (37:24:39) is taken.

$$N_{\text{CaO}} = 0.4, N_{\text{FeO}} = 0.2, N_{\text{SiO}_2} = 0.4$$

In binary systems the following values are given.

$$\text{CaO-SiO}_2: K = 5 \times 10^{-4}, \alpha = 6.4$$

$$\text{FeO-SiO}_2: K = 12, \alpha = 2.24$$

From the equation (21), the value of K is obtained.

$$\ln K = 0.67 \ln(5 \times 10^{-4}) + 0.33 \ln 12$$

$$K = 1.1 \times 10^{-2}$$

From the equation (22) the value of  $\alpha$  is obtained.

$$\alpha = 0.67 \times 6.4 + 0.33 \times 2.24 = 5.1$$

From **Fig. 5**, the value of pO is obtained as 1.2. Still, good coincidence was obtained for explaining on the removal of sulphur.

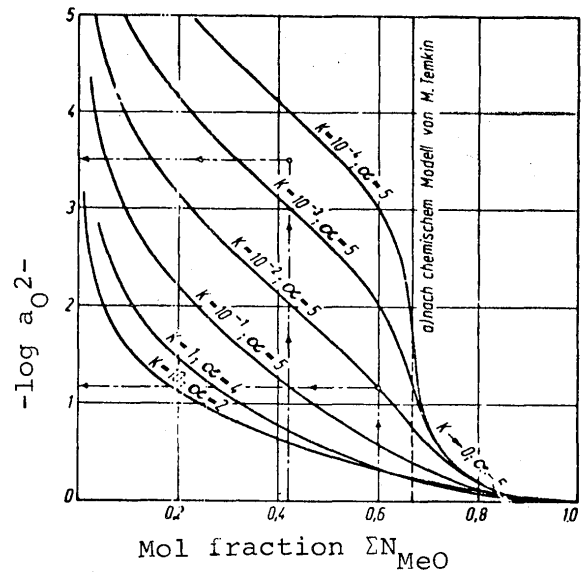


Fig. 5. pO value as a function of MeO content when different values of k and  $\alpha$  were used<sup>29)</sup>.

### 5. Relation Between Basicity of slag and Gas Content in Slag

#### 5.1 Oxygen

Activity of iron oxide as the indication of measure of the oxidizing ability of slag is being thought to be an essential factor in the refinement of steel.

FeO signifies that the total concentration of iron in slag is calculated as ferrous oxide.

Table 4. k and  $\alpha$  in the system MeO-SiO<sub>2</sub><sup>29)</sup>.

System	field strength (z/a <sup>2</sup> )	constants	
		k	$\alpha$
FeO-SiO <sub>2</sub>	0.429	12	2.24
PbO-SiO <sub>2</sub>	0.400	0.12	4.0
CaO-SiO <sub>2</sub>	0.350	$5 \times 10^{-4}$	6.4
MnO-SiO <sub>2</sub>	0.413	$5 \times 10^{-2}$	6.4
MgO-SiO <sub>2</sub>	0.476	$2 \times 10^{-2}$	0.8

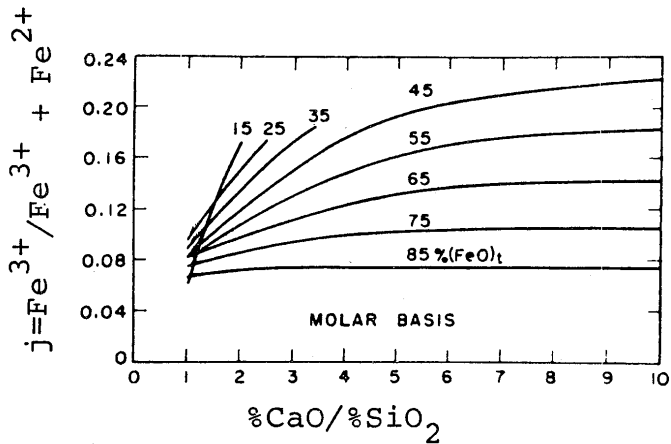


Fig. 6. Effects of iron oxide content and basicity on the  $j$  value<sup>30</sup>.

In Fig. 6, variation of ferric ions to total iron ions is plotted against the CaO/SiO<sub>2</sub> ratio for MgO-saturated slags<sup>30</sup>.

The activity of ferrous oxide,  $a_{FeO}$ , is introduced from the following relation,

$$a_{FeO} = [\%O]/[\%O]_{max} = K_{Fe}[\%O] \quad (24)$$

where

$$Fe + \dot{O} = (FeO) \quad (25)$$

$$K_{FeO} = a_{FeO}/a_{Fe} \cdot a_O \quad (26)$$

As for the activity of FeO, many investigators have studied for various systems because the relation between the activity value of FeO and slag composition is very complex.

As an example,  $a_{FeO}$  in the system FeO-SiO<sub>2</sub>-CaO is shown in Fig. 7<sup>31</sup>. From the diagram, it is anticipated that  $a_{FeO}$  increases when SiO<sub>2</sub> is substituted to CaO and reaches to maximum at  $N_{SiO_2}/N_{CaO} = 1/2$  and shows reduction at constant FeO.

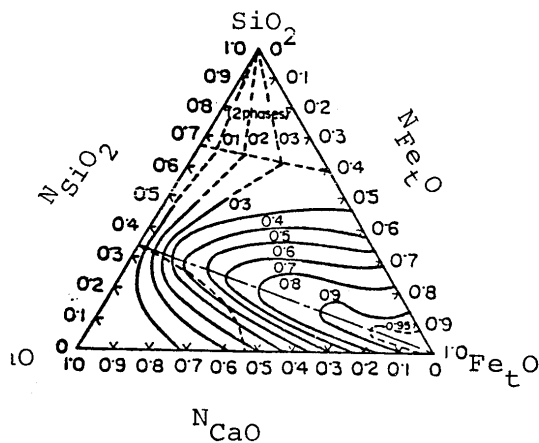


Fig. 7. The activities of ferrous oxide in the system Fe<sub>t</sub>O-CaO-SiO<sub>2</sub> at 1600°C<sup>31</sup>.

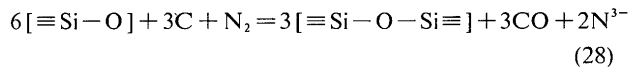
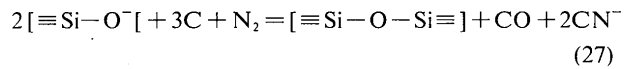
### 5.2 Nitrogen

Davis and Maherali have investigated the nitrogen solubility in the system CaO(MgO)-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub><sup>32</sup>. They said that the nitrogen absorption does scarcely occur when equilibrated with pure nitrogen for 24hr at 1550°C.

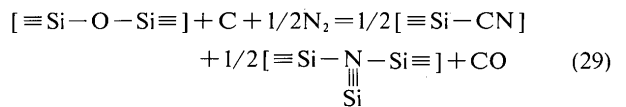
They have emphasized that the reducing operation by N<sub>2</sub>/CO atmosphere is necessitated for the absorption. Their result is different from those by other investigators.

They have shown that the solubility of nitrogen decreases with increasing basicity of slag.

The investigators in USSR have given the following mechanisms<sup>33, 34</sup>



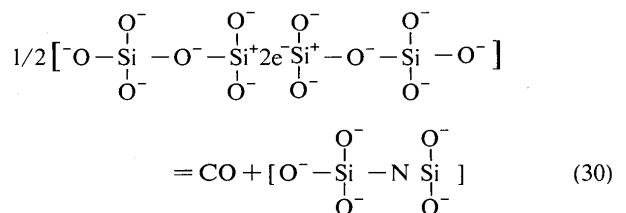
Davis and Maherali have combined the presentation of Mulfinger<sup>35</sup> with their opinion as follows.



The formation of cyanide was not proved experimentally and further it has a problem that this mechanism is independent on the slag composition.

Adopting other opinion that SiO<sub>2</sub> is apt to take defect structure under low oxygen partial pressure, Davis and Maherali presented the summarized mechanism that the degree of defect becomes greater with the increase of SiO<sub>2</sub> content.

This mechanism is as follows:

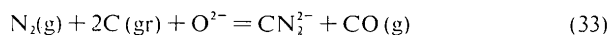
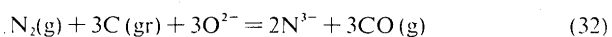
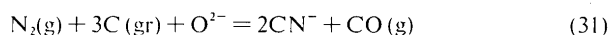


The following results were obtained.

- 1) The solubility of nitrogen in slag decreases with the increase of slag basicity. The substitution of MgO to CaO in slag does not give remarkable variation of solubility content.
- 2) The solubility is proportional to  $P_{N_2}^{1/2}/P_{CO}$  ratio.
- 3) The solubility of nitrogen in slag increases with the temperature rise.

Shimoo, Kimura and Kawai have given the following processes<sup>36</sup>.





As shown in Fig. 8, the variation of the solubility of nitrogen in slag with  $\text{Al}_2\text{O}_3$  content is interesting. According to their interpretation, the increase of the solubility of nitrogen is due to the increase of  $a_{\text{O}^{2-}}$  with the increment of basicity of slag because CaO

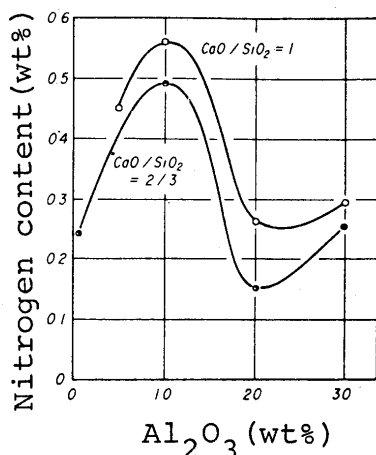


Fig. 8. Effect of  $\text{Al}_2\text{O}_3$  addition to the nitrogen content in the melt of CaO-SiO<sub>2</sub><sup>33)</sup>.

acts as network-modifier. The cause that the solubility of nitrogen decreases with the further increment of  $\text{Al}_2\text{O}_3$  content was reduced to the neutral action of  $\text{Al}_2\text{O}_3$ . In this case, it was thought that they behaved as network-former.

### 5.3 Absorption of water vapor

In the welding, it is an important subject to pursue the behaviour of hydrogen because they induce hydrogen embrittlement.

They are induced from various origins such as 1) moisture and water of crystallization in the coated electrode

2) organic compounds added to coated substance or water induced from contamination

3) absorption of water vapor in slag.

In Table 5, hydrogen content in the deposition arc welded are given. In Table 6, hydrogen limits allowed for electrode are shown<sup>37)</sup>.

Hydrogen content in the molten pool is determined from the content of water vapor dissolved in slag. Therefore, the elucidation of the dissolving behaviour of water vapor in molten glass or slag is wanted.

Walsh et al, have shown the relations between

Table 5. Hydrogen content of weld metal<sup>37)</sup>.

Electrode	Hydrogen content ( $\text{cm}^3 \text{H}_2 / 100\text{g}$ )		
	Diffusible	Residual	Total
High-cellulose	15.3	1.7	17.0
High-iron oxide	14.0	1.5	15.5
Low-hydrogen, CaO-coated	5.6	1.0	6.6
	6.6	0.9	7.5
	2.9	1.8	4.7

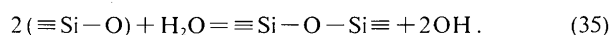
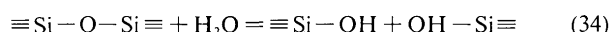
Table 6. Hydrogen limits allowed for each electrodes<sup>37)</sup>.

Electrode		Limit allowed ( $\text{Cm}^3 \text{H}_2 / 100\text{g}$ )
Classification	Type	
E 6010	cellulose	8 ~ 22
E 6012	titania	7 ~ 22
E 6013	titania	4 ~ 20
E 6015	low-hydrogen	0.9 ~ 4
E 6020 & E 6030	iron oxide	4 ~ 16
	uncovered-wire	2.4
18-8 Cr-Ni	good quality	8 ~ 15
18-8 Cr-Ni	usual	15 ~ 32

water dissolved in slag in the systems,  $40\text{CaO}-20\text{Al}_2\text{O}_3-40\text{SiO}_2$  and  $62\text{MnO}-38\text{SiO}_2$ , and the partial pressure of water vapor<sup>38)</sup>.

Tomlinson<sup>39)</sup> and Russel<sup>40)</sup> have studied the relation concerning the system  $30\text{Na}_2\text{O}-70\text{SiO}_2$  separately. Every studies have shown coincidence that the solubility of water vapor in slag is proportional to the square of the partial pressure. Moulson and Roberts<sup>41)</sup> have obtained the same tendency in silica glass.

Uye and King have studied the relation between the solubility of water vapor in the systems,  $\text{Li}_2\text{O}-\text{SiO}_2$ ,  $\text{Li}_2\text{O}-\text{CaO}-\text{SiO}_2$ ,  $\text{CaO}-\text{SiO}_2$  and  $\text{ZnO}-\text{SiO}_2$  and  $\text{CoO}-\text{SiO}_2$  and cation-oxygen interaction value  $I$ , whose cation is composed of compound added to  $\text{SiO}_2$ <sup>42)</sup>. From the relation, they certified that the solubility of water vapor in slag increases when the value  $I$  becomes smaller. They have presented the dissolving mechanism of water vapor in molten glass or slag as follows:



Actually, they said that the overlapping effect of both mechanisms must consider. Besides, they said that the latter predominates with the increase of the basicity in slag.

Kurkjian and Russel have advanced the mechanisms described and have noticed the absorptions at  $2.8\mu \sim 3.5\mu$  by infrared experiment<sup>43)</sup>.

Further, Uye and King have studied the variation of solubility of water vapor in slag in the system  $\text{FeO}-\text{Fe}_2\text{O}_3-\text{SiO}_2$  with the change of oxygen partial pressure<sup>44)</sup>. It was certified that the solubility of water vapor decreases with the increase of oxygen partial pressure, but the variation is negligible at constant  $\text{SiO}_2$  content. However, they said that the solubility of water vapor increases with the increase of  $\text{SiO}_2$  content at constant oxygen partial pressure. They have considered the reason from the change of  $\text{Fe}^{3+}/\text{Fe}^{2+}$  ratio and cation-oxygen interaction value.

Imai, Ooi and Emi have investigated the solubility of water vapor in the practical and synthetic slags<sup>45)</sup>.

From the results of infrared absorption, they concluded that the solution of water vapor in slag occurs mostly in the form of OH radical from the comparison with the absorption intensities at  $3200\sim 3500\text{ cm}^{-1}$ , which comes from OH bond, and at  $2800\sim 3000$  and  $2300\sim 2400\text{ cm}^{-1}$ , which comes from H bond.

Iguchi, Banya and Fuwa have studied the solubility of water vapor in slags in the system  $\text{CaO}-\text{SiO}_2$  when alkali metal oxide or alkali earth oxide are added<sup>46)</sup> and concluded that cation-oxygen interaction value  $I$  is the effective factor to the solubility in the former,

while ionic radii of cation is chief factor in the latter. These relations are shown in Fig. 9 and Fig. 10.

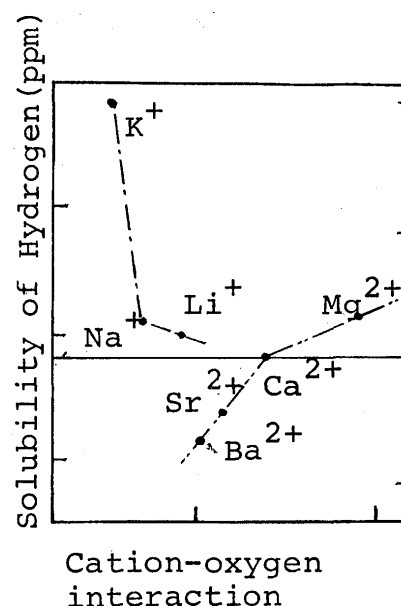


Fig. 9. Effect of cation-oxygen interaction  $I$  on the solubility of hydrogen<sup>46)</sup>.

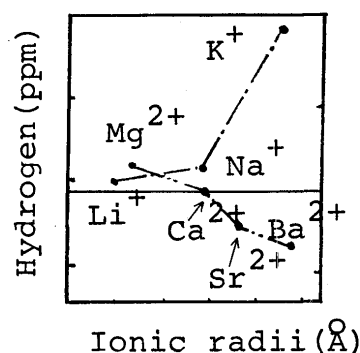


Fig. 10. Relation the solubility of hydrogen and ionic radii of cation added<sup>46)</sup>.

Sachdev, Majdic and Schenck have studied the solubility of water vapor in slag in the system  $\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ , and obtained the following conclusions<sup>47)</sup>.

- 1) The solubility of water vapor is proportional to the square of water vapor partial pressure.
- 2) The solubility shows increase with increasing the basicity of slag
- 3) As shown in Fig. 11, the decrease of the solubility occurs with the addition of  $\text{Al}_2\text{O}_3$  in silicate melt. The minimum solubility exists at  $\text{CaO}/\text{SiO}_2(\text{wt}\%) = 0.6$ , and the change of coordination of Al ion at there occurs.
- 4) When basicity of slag is unity, the addition of  $\text{Fe}_x\text{O}$  to  $\text{CaO}-\text{SiO}_2$  melt did not give the effect on the solubility and it has become clear that the absorption velocity of gas from the atmosphere was only accelerated.

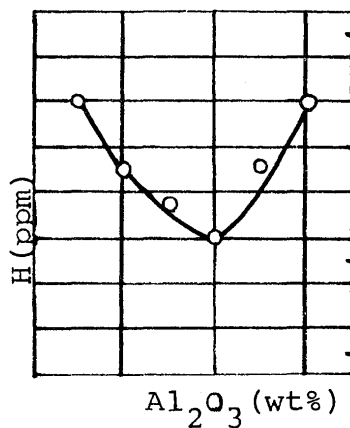


Fig. 11. Effect of  $\text{Al}_2\text{O}_3$  addition to the solubility of hydrogen in the slag in the system  $\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2$  having basicity of 0.6 at  $1550^\circ\text{C}$  under partial pressure of  $P_{\text{H}_2\text{O}}=190 \text{ torr}^m$ .

### Summary

In this review, the author summarized the concept of basicity of slag and the effect on the solubility of gases such as oxygen, nitrogen and water vapor.

In the following reviews, relation between physical properties of slag such as surface tension, viscosity and density so on and structure of slag, behaviour of fluorine ion in slag, and problem of coordination number of ions are referred.

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