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Citation	Transactions of JWRI. 1982, 11(1), p. 135-136
Version Type	VoR
URL	<a href="https://doi.org/10.18910/11267">https://doi.org/10.18910/11267</a>
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# Clustering of $\text{Fe}^{3+}$ Ion in Calcium Fluorosilicate Slag<sup>†</sup>

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**KEY WORDS:** (Fluorosilicate) (State Analysis) ( $\text{Fe}^{3+}$ - $\text{F}^-$  Interaction) (Electron Spin Resonance)

Fluorosilicate slags are widely used for metallurgical refining in steelmaking and welding. The state of iron ions in these slags are important to understand the distribution of oxygen between slag and metal. It is indicated that the content of ferrous oxide in slag is closely related to oxygen content in iron and steels.<sup>1)</sup>

In this study, the state of  $\text{Fe}^{3+}$  ions in calcium fluorosilicate slags and the interaction between  $\text{Fe}^{3+}$  and  $\text{F}^-$  ions were investigated by electron spin resonance (ESR).

Glassy slags were prepared from reagent grade  $\text{CaF}_2$ ,  $\text{CaCO}_3$ ,  $\text{SiO}_2$  and  $\text{Fe}_2\text{O}_3$ . The reagents were accurately weighed, mixed in an agate mortar and pestle using acetone as the immersion liquid and then were well dried. The mixtures were melted in platinum crucibles at temperature  $100^\circ\text{C}$  higher than their liquidus temperatures for 30 min. After cooling, the glassy slags were crushed in an agate mortar and pestle. Those pulverized slags were weighed for 20 mg, and then sealed in evacuated silica tubes.

ESR measurements were made at room temperature using a Varian E-109 spectrometer, operating at X-band frequency ( $\nu=9.3$  GHz).

The ESR absorption derivative spectrum of  $0.2\text{CaF}_2 \cdot 0.8\text{CaO} \cdot \text{SiO}_2$  slag containing 1.5 mol %  $\text{Fe}_2\text{O}_3$  is shown in Fig. 1. Similar measurements were made on  $x\text{CaF}_2 \cdot (1-x)\text{CaO} \cdot \text{SiO}_2$  slags with various content of  $\text{Fe}_2\text{O}_3$ .

In generally, ESR absorptions due to  $\text{Fe}^{3+}$  ion in slag are observed at  $g=2.0$ ,  $g=4.3$  and  $g=6.0$ .<sup>2)-5)</sup>  $\text{Fe}^{3+}$  ions in the axial crystal field produce both  $g=2.0$  and  $g=6.0$  resonances. The  $g=4.3$  resonance arises from  $\text{Fe}^{3+}$  ions in the rhombically distorted environment.

According to the previous studies,<sup>3)-7)</sup> the  $g=2.0$  resonance has been attributed to both  $\text{Fe}^{3+}$  ions in an axial crystal field and clustering of  $\text{Fe}^{3+}$  ions coupled by exchange interaction.

If the  $g=2.0$  resonance observed in this study arises

from  $\text{Fe}^{3+}$  ions in an axial crystal field, the intensity of the  $g=6.0$  resonance should increase with increasing  $\text{Fe}_2\text{O}_3$ . However the increase of the  $g=6.0$  resonance was not observed irrespective of  $\text{Fe}_2\text{O}_3$  content. Therefore the  $g=2.0$  resonance can be assigned to clustered  $\text{Fe}^{3+}$  ions and it is indicated that  $\text{Fe}^{3+}$  ions do not distribute at random but form the clusters.

ESR absorption of  $g=4.3$  line,  $N_{g=4.3}$ , is shown as a function of  $\text{Fe}_2\text{O}_3$  concentration in Fig. 2. ESR absorption can approximately be estimated by the following equation<sup>7)</sup>

$$N=I \cdot (\Delta H)^2$$

where  $I$  is the relative peak to peak derivative intensity and  $\Delta H$  is the line width of resonance. ESR absorption of  $g=4.3$  line,  $N_{g=4.3}$ , is proportional to the number of isolated  $\text{Fe}^{3+}$  ion.

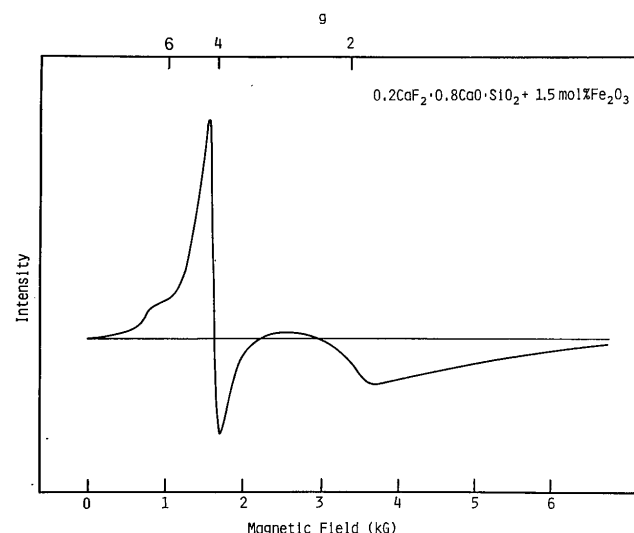


Fig. 1 ESR spectrum of  $0.2\text{CaF}_2 \cdot 0.8\text{CaO} \cdot \text{SiO}_2$  slag containing 1.5 mol %  $\text{Fe}_2\text{O}_3$ .

In Fig. 2 at about 1.5 mol %  $\text{Fe}_2\text{O}_3$ , the number of isolated  $\text{Fe}^{3+}$  ions reaches a maximum and decreases monotonically thereafter. Moon et al.<sup>7)</sup> calculated

<sup>†</sup> Received on March 31, 1982

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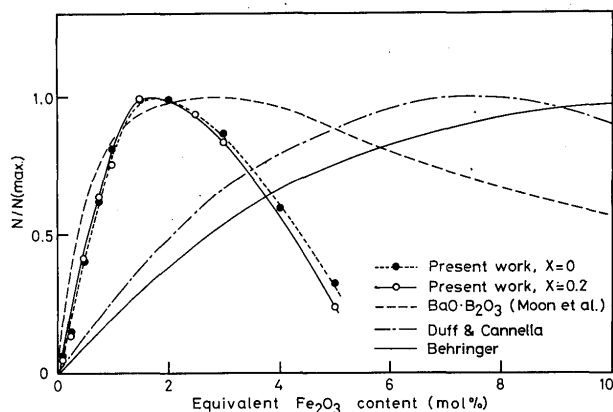


Fig. 2 Relative value of isolated  $\text{Fe}^{3+}$  ion concentration,  $N$  to maximum value of  $N$ ,  $N(\text{max.})$ , against  $\text{Fe}_2\text{O}_3$  content.

$N_{g=4.3}$  in  $\text{BaO-B}_2\text{O}_3$  glasses (Fig. 2). Theoretical curves by Duff and Cannella<sup>8)</sup> and by Behringer,<sup>9)</sup> which calculated in binary alloy under the assumption of random cluster formation, are also illustrated in Fig. 2.

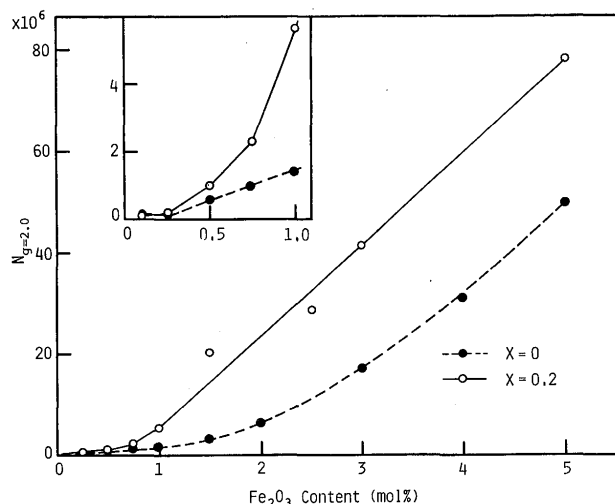


Fig. 3 Dependence of  $N_{g=2.0}$  in systems  $\text{CaO-SiO}_2$  and  $0.2\text{CaF}_2 \cdot 0.8\text{CaO-SiO}_2$  upon  $\text{Fe}_2\text{O}_3$  content.  $N_{g=2.0}$  in arbitrary units.

As shown in Fig. 2, a maximum is observed in the slags of the systems  $\text{CaO-SiO}_2$  and  $\text{CaF}_2\text{-CaO-SiO}_2$  at lower  $\text{Fe}_2\text{O}_3$  concentrations respectively. Thereafter,  $N_{g=4.3}/N_{g=4.3}(\text{max})$  falls off more rapidly than those in the previous results.

ESR absorption of  $g=2.0$  line ( $N_{g=2.0}$ ) is shown as a function of  $\text{Fe}_2\text{O}_3$  content in Fig. 3.  $N_{g=2.0}$  attributed to the cluster formations of  $\text{Fe}^{3+}$  ions increases rapidly with increasing  $\text{Fe}_2\text{O}_3$  content. The slag containing 10 mol%  $\text{CaF}_2$  ( $X=0.2$ ) forms cluster more easily than the slags containing no  $\text{CaF}_2$ , ( $X=0$ ).

It has been suggested that the  $\text{Fe}^{3+}$  ion tends to bind oxygen ion and not to fluorine ion,<sup>10)</sup> from the compensation effect of ionic potential ( $=Z_e/r$ ;  $Z$ : valency of cation,  $r$ : ionic radius of cation) between cation and anion. That is, fluorine ion has an inclination to repel  $\text{Fe}^{3+}$  ion by charge unbalance of ionic potential between these ions.

Thus, the easily clustering of  $\text{Fe}^{3+}$  ions in fluoro-silicate slags shows an excellent agreement with the explanation based on the compensation effect of ionic potential between anion and cation. Conclusively clustering of  $\text{Fe}^{3+}$  ions in slags can be enhanced by the repulsion between  $\text{Fe}^{3+}$  and  $\text{F}^-$  ions.

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