

# Phase diagram for the CaO-SiO<sub>2</sub>-FeO<sub>x</sub> system at low oxygen partial pressure

Fumitaka Tsukihashi<sup>1)</sup> and Hisao Kimura<sup>2)</sup>

1) Professor, The University of Tokyo

2) Research Assistant, The University of Tokyo

**Abstract :** Phase diagrams for the CaO-SiO<sub>2</sub>-FeO<sub>x</sub> system at low oxygen partial pressure are necessary for the analysis of smelting reaction and ore sintering process. In this study, phase diagrams for the CaO-SiO<sub>2</sub>-FeO<sub>x</sub> systems at low oxygen partial pressure were observed at 1573K. The effect of addition of small amount of Al<sub>2</sub>O<sub>3</sub> on the liquidus lines of the CaO-SiO<sub>2</sub>-FeO<sub>x</sub> system was also investigated.

## 1. Introduction

Phase diagrams for the CaO-SiO<sub>2</sub>-FeO<sub>x</sub> system are important thermodynamic data for the analysis of melting mechanism of sinter in sintering process and smelting reaction. The phase diagram for the CaO-SiO<sub>2</sub>-Fe<sub>2</sub>O<sub>3</sub> system in air and that for the CaO-SiO<sub>2</sub>-FeO system equilibrated with iron were measured as shown in Figs. 1 and 2<sup>1)</sup>. The CaO-FeO-Fe<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub>-FeO-Fe<sub>2</sub>O<sub>3</sub> systems with changing partial pressure of oxygen are also reported.<sup>2)</sup> However, the phase diagrams for the CaO-SiO<sub>2</sub>-FeO<sub>x</sub> system at the oxygen partial pressure between air and the oxygen partial pressure determined by Fe-FeO equilibrium are not available. Characteristics of sinter ore in ironmaking process depend on the formation of melts during sintering. It is necessary to control melting behavior for the development of pre-treatment technique of iron ore. Therefore, knowledge of phase relationship for the CaO-SiO<sub>2</sub>-FeO<sub>x</sub> system at low oxygen partial pressure is required.

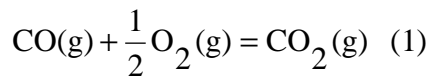
Recently, the alumina content of iron ore is increasing because of the shortage of high quality iron ore. The effect of Al<sub>2</sub>O<sub>3</sub> on liquidus for the CaO-SiO<sub>2</sub>-Fe<sub>2</sub>O<sub>3</sub> system is observed only in air and that at low oxygen partial pressure is not available.

Therefore, the phase diagrams for the CaO-SiO<sub>2</sub>-FeO<sub>x</sub> system at various low oxygen partial pressures and the effect of Al<sub>2</sub>O<sub>3</sub> addition on liquidus of phase diagram are observed in the present study.

## 2. Experimental

A chemical equilibration technique was employed to measure the phase relationships for the CaO-SiO<sub>2</sub>-FeO-Fe<sub>2</sub>O<sub>3</sub> and CaO-SiO<sub>2</sub>-FeO-Fe<sub>2</sub>O<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub> system. Eight grams of mixture of reagent grade of CaO, SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub> powders melted in a platinum crucible are equilibrated with a pellet of saturating oxide ( 2CaO·Fe<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, 2CaO·SiO<sub>2</sub>, 3CaO·2SiO<sub>2</sub>, CaO·SiO<sub>2</sub> and SiO<sub>2</sub>) in CO-CO<sub>2</sub> atmosphere. The oxygen partial pressure was controlled by the CO/CO<sub>2</sub> ratio according to reaction (1). A sample melt was held for 20 hours at 1573K in an electric furnace and after equilibration, melts in a platinum crucible were quenched in an argon flow. The content of CaO, Fe<sup>2+</sup>, Fe<sup>3+</sup>, SiO<sub>2</sub>, and Al<sub>2</sub>O<sub>3</sub> were analyzed by titration, gravimetry, and ICP spectrometry, respectively.

Pellets of 2CaO·Fe<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, 2CaO·SiO<sub>2</sub>, 3CaO·2SiO<sub>2</sub>, and CaO·SiO<sub>2</sub> were prepared by pressing and sintering a mixture of powder of reagent grade of oxides. Oxide melts were separated from a pellet of saturating oxide by platinum plate as shown in Fig. 3 to prevent the contamination of a pellet oxide into melts when the sample was quenched.



### 3. Results and discussion

#### 3.1. The CaO-SiO<sub>2</sub>-FeO-Fe<sub>2</sub>O<sub>3</sub> system

The isothermal phase relationships for the CaO-SiO<sub>2</sub>-FeO-Fe<sub>2</sub>O<sub>3</sub> system at 1573K with the oxygen partial pressure from  $1.8 \times 10^{-6}$  to  $9.7 \times 10^{-9}$  atm are shown in Figs. 4 and 5. The phase diagram is shown as CaO-SiO<sub>2</sub>-(FeO+Fe<sub>2</sub>O<sub>3</sub>) ternary system. In comparison with the phase diagrams shown in Figs. 1 and 2, liquid phase area is enlarged at high iron oxide region with decreasing oxygen partial pressure. The effects of the decrease of oxygen partial pressure on the liquidus of 2CaO·SiO<sub>2</sub>, 3CaO·2SiO<sub>2</sub>, and CaO·SiO<sub>2</sub> were small. The liquidus line of SiO<sub>2</sub> at high SiO<sub>2</sub> region is influenced by the oxygen partial pressure.

The relationship between the (Fe<sup>3+</sup>)/(Fe<sup>2+</sup>) ratio and basicity ((mass% CaO)/(mass% SiO<sub>2</sub>)) on 2CaO·SiO<sub>2</sub> liquidus with P<sub>O<sub>2</sub></sub>= $1.8 \times 10^{-8}$  atm at 1573K is shown in Fig. 6. The (Fe<sup>3+</sup>)/(Fe<sup>2+</sup>) ratio increases with increasing ((mass% CaO)/(mass% SiO<sub>2</sub>)).

#### 3.2. The CaO-SiO<sub>2</sub>-FeO-Fe<sub>2</sub>O<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub> system

The isothermal phase relationship for the CaO-SiO<sub>2</sub>-FeO-Fe<sub>2</sub>O<sub>3</sub>-5mass% Al<sub>2</sub>O<sub>3</sub> system at 1573K with the oxygen partial pressure of  $1.8 \times 10^{-8}$  atm is shown in Figs. 7 as CaO-SiO<sub>2</sub>-(FeO+Fe<sub>2</sub>O<sub>3</sub>) ternary system. The liquid area for the CaO-SiO<sub>2</sub>-FeO-Fe<sub>2</sub>O<sub>3</sub>-5mass% Al<sub>2</sub>O<sub>3</sub> system is almost same as that for the CaO-SiO<sub>2</sub>-FeO-Fe<sub>2</sub>O<sub>3</sub> system observed at the same oxygen partial pressure. Therefore, the effect of the addition of Al<sub>2</sub>O<sub>3</sub> on the liquid area is small. Comparing Fig. 7 with the phase diagram for the CaO-SiO<sub>2</sub>-Fe<sub>2</sub>O<sub>3</sub>-2mass% Al<sub>2</sub>O<sub>3</sub> system in air<sup>3)</sup>, the decrease of oxygen partial pressure enlarges the liquid area at high iron oxide region.

The relationship between the (Fe<sup>3+</sup>)/(Fe<sup>2+</sup>) ratio and basicity ((mass% CaO)/(mass% SiO<sub>2</sub>)) on 2CaO·SiO<sub>2</sub> liquidus with P<sub>O<sub>2</sub></sub>= $1.8 \times 10^{-8}$  atm at 1573K is shown in Fig. 8. The (Fe<sup>3+</sup>)/(Fe<sup>2+</sup>) ratio increases from 0.4 to 1.6 with increasing ((mass% CaO)/(mass% SiO<sub>2</sub>)) from 1 to 10.

### 4. Conclusions

Isothermal phase relationships for the CaO-SiO<sub>2</sub>-FeO<sub>x</sub>-Al<sub>2</sub>O<sub>3</sub> systems at 1573K with low oxygen partial pressure were investigated by a chemical equilibration technique. The effects of oxygen partial pressure and the addition of Al<sub>2</sub>O<sub>3</sub> on the liquid area of the system were observed. For the CaO-SiO<sub>2</sub>-FeO<sub>x</sub>-Al<sub>2</sub>O<sub>3</sub> system, liquid phase range is enlarged at high iron oxide region with decreasing oxygen partial pressure.

### References

- 1) Ernst M. Levin, Carl R. Robbins, and Howard F. McMurdie : Phase Diagrams for Ceramists vol. 1, American Ceramic Society, Inc., (1964), 204(Fig.656), 228(Fig.586).
- 2) Y.Takeda, S.Nakazawa and A.Yazawa : J. Mining Metall. Inst. Japan, **97** (1981), p.473.
- 3) C.K.Yang, T.Shoji and S.Takenouchi : J. Mining Metall. Inst. Japan, **94** (1978), p.575.

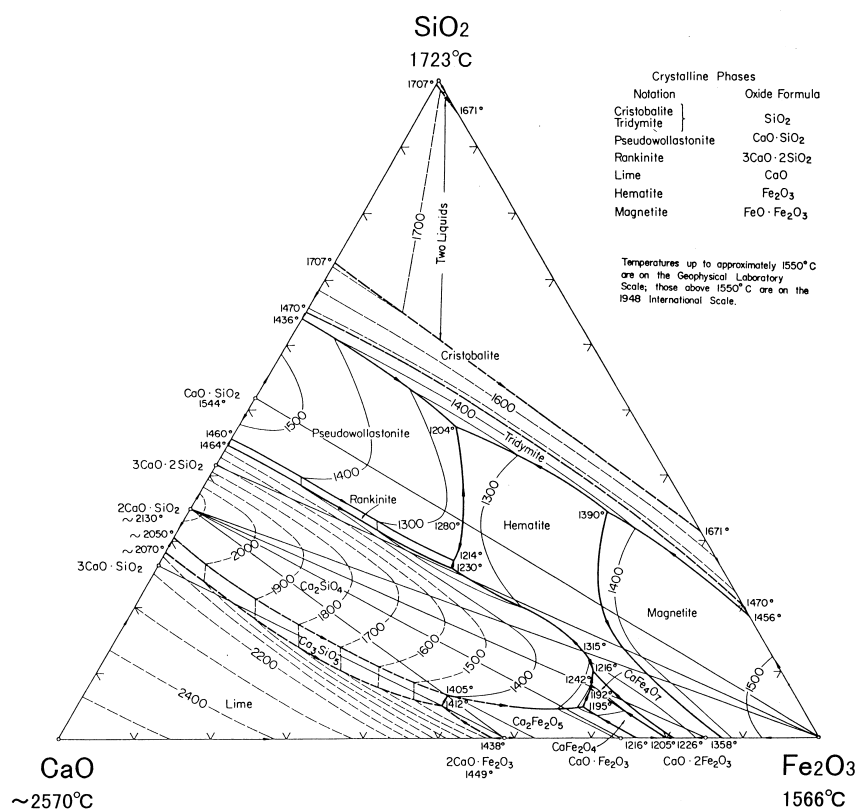


Fig. 1. Phase diagram for the CaO-SiO<sub>2</sub>-Fe<sub>2</sub>O<sub>3</sub> system in air.

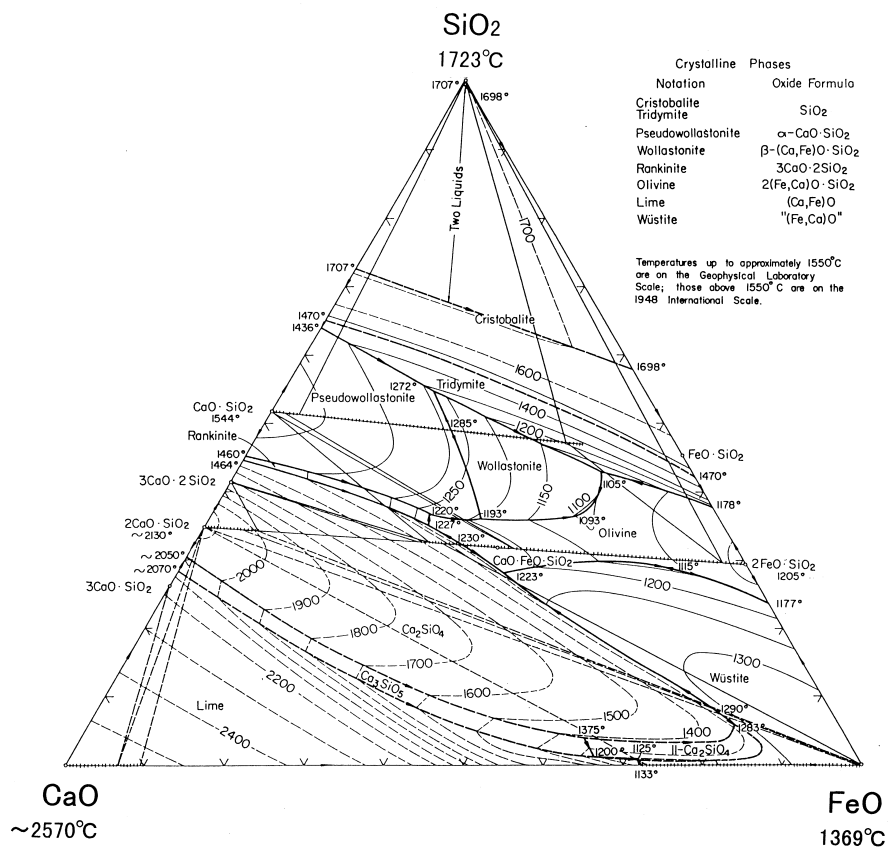


Fig. 2. Phase diagram for the CaO-SiO<sub>2</sub>-FeO system equilibrated with iron.

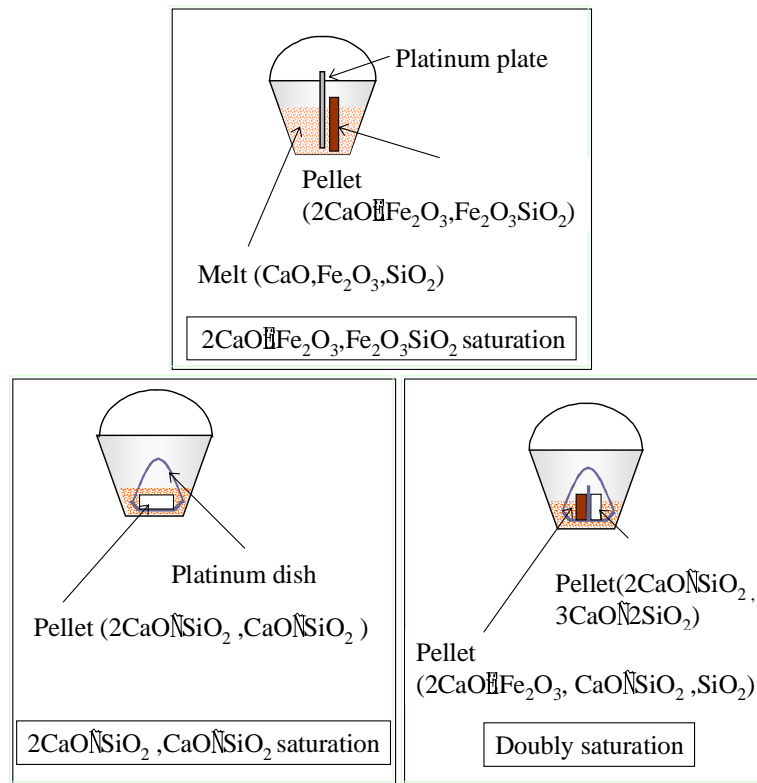


Fig. 3. Cross section of platinum crucibles.

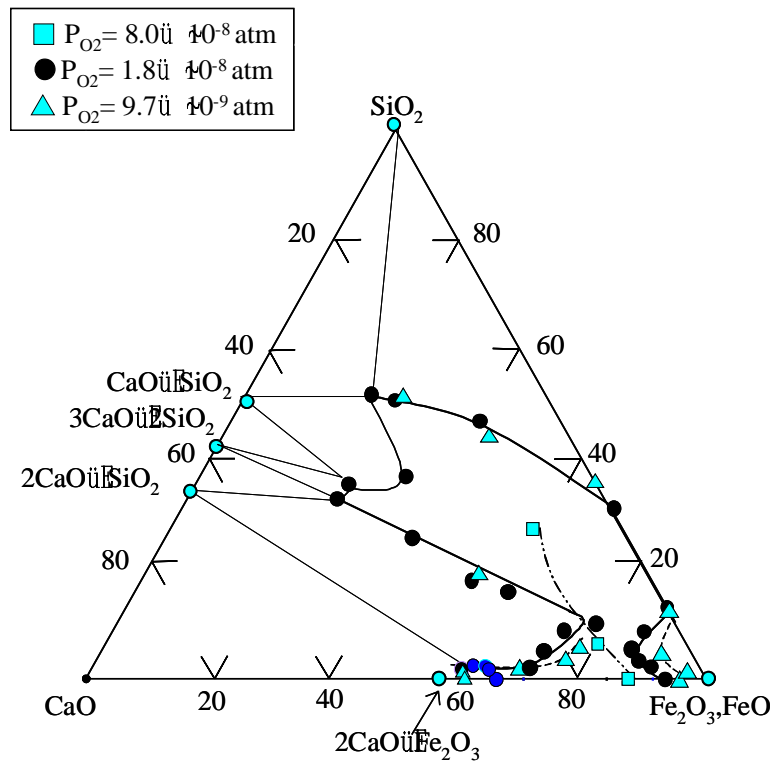


Fig. 4. Liquidus line for the  $\text{CaO}-\text{SiO}_2-(\text{FeO}+\text{Fe}_2\text{O}_3)$  system with  $P_{\text{O}_2}=9.7 \times 10^{-9}$  to  $8.0 \times 10^{-8}$  atm at 1573K,

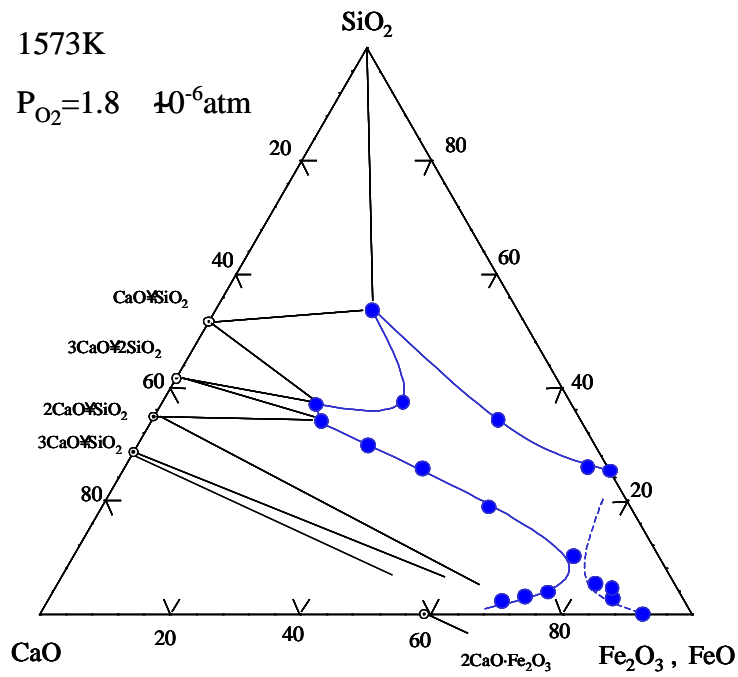


Fig. 5. Liquidus line for the CaO-SiO<sub>2</sub>-(Fe<sub>2</sub>O<sub>3</sub>,+FeO) system with  $P_{O_2} = 1.8 \times 10^{-6} \text{ atm}$  at 1573K.

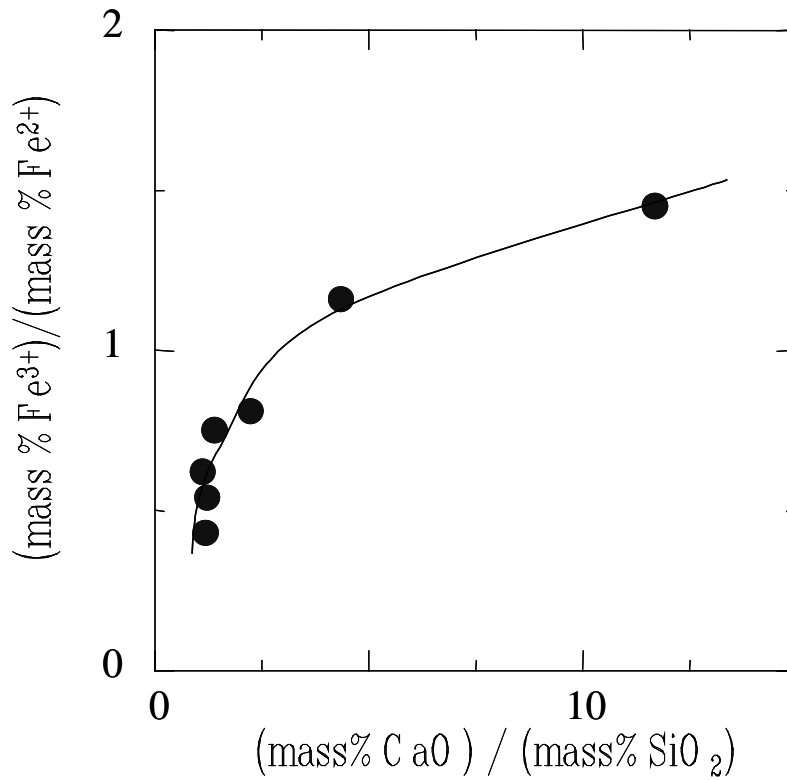


Fig. 6. Relationship between the  $(Fe^{3+})/(Fe^{2+})$  ratio and  $(\text{mass}\% \text{CaO})/(\text{mass}\% \text{SiO}_2)$  on 2CaO-SiO<sub>2</sub> liquidus with  $P_{O_2} = 1.8 \times 10^{-8} \text{ atm}$  at 1573K for the CaO-SiO<sub>2</sub> - (Fe<sub>2</sub>O<sub>3</sub>,+FeO) system.

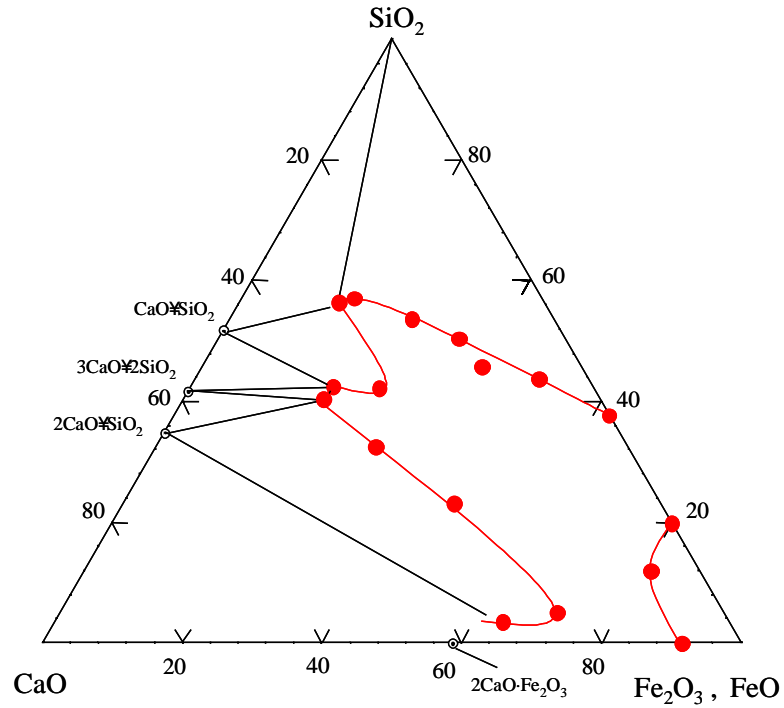


Fig. 7. Liquidus line for the CaO-SiO<sub>2</sub>-Fe<sub>2</sub>O<sub>3</sub>-FeO-5mass% Al<sub>2</sub>O<sub>3</sub> system with P<sub>O<sub>2</sub></sub> = 1.8x10<sup>-8</sup> atm at 1573K.

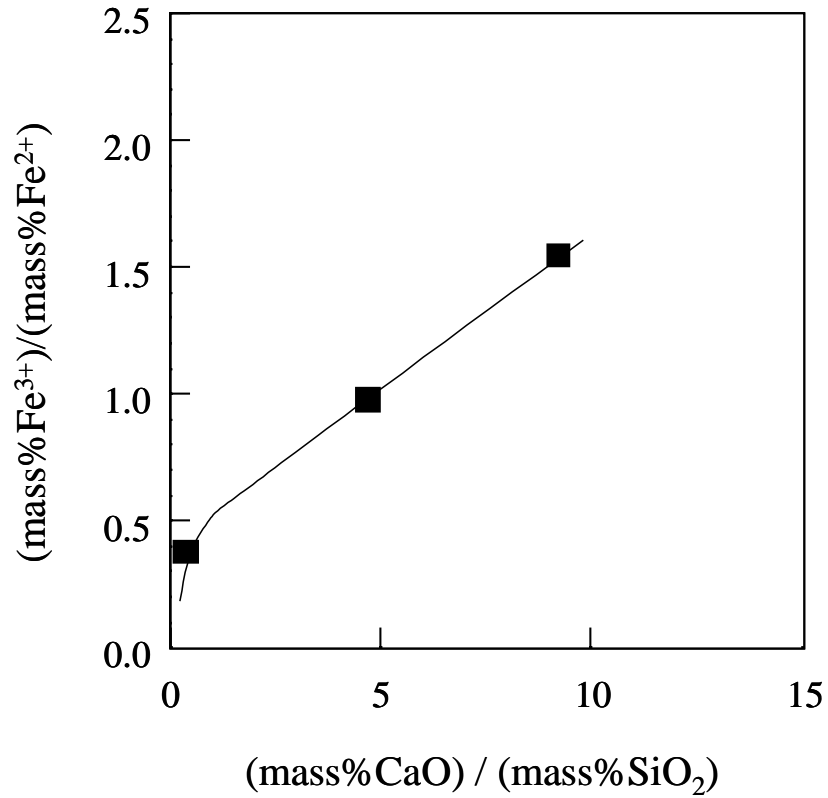


Fig. 8. Relationship between the (Fe<sup>3+</sup>)/(Fe<sup>2+</sup>) ratio and (mass%CaO)/(mass% SiO<sub>2</sub>) on 2CaO·SiO<sub>2</sub> liquidus with P<sub>O<sub>2</sub></sub>=1.8x10<sup>-8</sup> atm at 1573K for the CaO-SiO<sub>2</sub>-(Fe<sub>2</sub>O<sub>3</sub>,+FeO)-5mass% Al<sub>2</sub>O<sub>3</sub> system.

