# Effect of Slag Composition on the Distribution Behavior of Pb between Fe<sub>t</sub>O-SiO<sub>2</sub> (-CaO, Al<sub>2</sub>O<sub>3</sub>) Slag and Molten Copper

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**Abstract:** The distribution behavior of lead between molten copper and Fe<sub>t</sub>O-SiO<sub>2</sub> (-CaO, Al<sub>2</sub>O<sub>3</sub>) slags was investigated at 1473 K and p(O<sub>2</sub>)= $10^{-10}$  atm in view of the reaction mechanism of lead dissolution into the slag. Furthermore, the lead capacity of the slag was estimated from the experimental results. The distribution ratio of lead ( $L_{Pb}$ ) decreases with increasing amount of CaO (~6wt%) irrespective of Fe/SiO<sub>2</sub> ratio ( $1.4\sim1.7$ ). However, the addition of alumina in the slag with Fe/SiO<sub>2</sub>=1.5 linearly decreases the  $L_{Pb}$ , whereas there is a minimum value at about 4wt%Al<sub>2</sub>O<sub>3</sub> at Fe/SiO<sub>2</sub>=1.3. The log  $L_{Pb}$  continuously decreases with increasing Fe/SiO<sub>2</sub> ratio and furthermore, the addition of Al<sub>2</sub>O<sub>3</sub> ( $5\sim15$ wt%) into the silica saturated iron silicate slag (Fe/SiO<sub>2</sub> < 1.0) shows the highest Pb distribution ratio. This is mainly due to a decrease in the activity of FeO even at silica saturation condition. The log  $L_{Pb}$  linearly decreases by increasing the log (Fe<sup>3+</sup>/Fe<sup>2+</sup>) values. The Pb distribution ratio increases with increasing content of Cu<sub>2</sub>O in the slag and the excess free energy of PbO decreases with increasing content of Cu<sub>2</sub>O. However, in viewpoint of copper loss into the slag, the silica saturated system containing small amounts of alumina is strongly recommended to stabilize PbO in slag phase at low content of Cu<sub>2</sub>O. The 'lead capacity' was defined in the present study and it shows a linear correlation with the activity of FeO in a logarithmic scale, indicating that the concept of lead capacity is a good measure of absorption ability of lead of iron silicate slags and the activity of FeO can be a good basicity index in the iron silicate slag.

**Key words:** Copper smelting and refining, Lead distribution ratio, Fe<sub>t</sub>O-SiO<sub>2</sub>(-CaO, Al<sub>2</sub>O<sub>3</sub>) slag, Refining, Fe<sup>3+</sup> to Fe<sup>2+</sup> ratio, Excess free energy of PbO

#### 1. Introduction

It is very important in copper smelting and refining processes to remove several minor elements such as lead, bismuth, antimony, arsenic and tellurium.<sup>[1,2]</sup> Specifically, lead is troublesome impurity which increases the amount of slime in the electro-refining process. Also, from the viewpoint of copper smelting and refining processes, lead is detrimental element that is always present in sulfide concentrates that must be eliminated. Therefore, the content of lead in molten copper should be lowered within appropriate concentration range in a plant operation and thus we need specific knowledge of the effect of slag composition on the thermodynamic behavior of lead in molten slag.

Kim and Sohn examined the effects of CaO, Al<sub>2</sub>O<sub>3</sub>, and MgO additions on the distribution behavior of lead between an iron silicate slag and liquid copper under a CO-CO<sub>2</sub> atmosphere ( $p(O_2)=10^{-12}\sim10^{-6}$  atm) at 1523 K and found that the distribution ratio of Pb and the activity coefficient of PbO was not significantly affected by the additives.<sup>[3]</sup> The governing factors affecting the Pb solubility in iron silicate slag were proposed as the oxygen potential ( $p(O_2)$ ) and the ratio of Fe<sub>1</sub>O/SiO<sub>2</sub> (or SiO<sub>2</sub> content) in the slag. Matsuzaki *et al.*<sup>[4]</sup> calculated the activity coefficient of

PbO ( $\gamma_{PbO}$ ) with the regular solution model and plotted the iso- $\gamma_{PbO}$  contours in the CaO-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> ternary slag at 1623 K. The value of  $\gamma_{PbO}$  decreased as CaO was replaced with SiO<sub>2</sub> at any fixed concentration of Al<sub>2</sub>O<sub>3</sub>, indicating the basic character of PbO in the slag. The similar tendency of the effect of CaO/SiO<sub>2</sub> ratio on the  $\gamma_{PbO}$  was also reported by Kudo et al.<sup>[5]</sup> in the Fe<sub>1</sub>O-CaO-SiO<sub>2</sub> system in equilibrium with metallic iron at 1573 K. In this study,<sup>[5]</sup> it is interesting that the changes in temperature from 1473 to 1573 K did not have a significant effect on  $\gamma_{PbO}$  in the slag. Degterov and Pelton computed the distribution behavior of lead among matte, slag, and liquid copper at 1523 K and p(O<sub>2</sub>)=10<sup>-12</sup>~10<sup>-5</sup> atm under condition from silica saturation to magnetite saturation.<sup>[6]</sup> The distribution ratio of Pb decreased with increasing Fe/SiO<sub>2</sub> ratio from silica to magnetite saturation. The small addition of CaO (3wt%) also decreased the Pb distribution ratio. Kashima *et al.*<sup>[7]</sup> observed that Pb was distributed among crude copper, white metal, and silica saturated iron silicate slag in rather similar concentrations at 1573 K under controlled SO<sub>2</sub> partial pressure. Also, Acuna and Yazawa found that the lead distribution ratio was in the order of iron silicate > barium ferrite ≥ calcium ferrite slag at copper content in matte phase was greater than about 50wt%.<sup>[8]</sup>

Even though the effectiveness of slag treatment for the removal of Pb from the Cu melt have been investigated as mentioned above, many of studies focused on the equilibrium distribution behavior of Pb among the Cu/matte/slag system in smelting and converting processes. Therefore, in the present study, the distribution behavior of lead between molten copper and Fe<sub>t</sub>O-SiO<sub>2</sub> (-CaO, Al<sub>2</sub>O<sub>3</sub>) slags was investigated in view of the reaction mechanism of lead dissolution into the slag. Furthermore, the lead capacity of the slag was estimated from the experimental results.

# 2. Experimental

## 2.1 Sample preparation

An alloy sample with the composition of Cu-1wt%Pb was preliminarily prepared from pure (99.99% purity) copper and lead. This alloy sample was melted in an alumina crucible (OD; 50 mm, ID; 45 mm, HT; 70 mm) in a highly purified Ar atmosphere using Mg turnings at 773 K for 2 hours at 1473 K. The slag samples divide into two classes that first sample type were prepared by mixing reagent-grade FeO, SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, and CaO calcined from CaCO<sub>3</sub> at 1273 K for 10 hours and second sample type were prepared silica-saturated Fe<sub>t</sub>O-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> slags under the same condition as mentioned above.

### 2.2 Measurement

The experiments were carried out using super-kanthal electric furnace with MoSi<sub>2</sub> heating element. A schematic diagram of the experimental apparatus is shown in Figure 1.

The temperature was controlled within ±2 K using a B-type (Pt-30wt%Rh / Pt-6wt%Rh) thermocouple and a proportional integral differential controller. The equilibration time was predetermined to be 6 hours at 1473 K. The metal (8 g) and slag (5 g) were loaded in a fused magnesia (99.9% purity) crucible (OD; 18 mm, ID; 14 mm, HT; 50 mm). This was placed in an alumina holder (OD; 50 mm, ID; 45 mm, HT; 70 mm) and then hooked with a molybdenum wire. The oxygen partial pressure of the system was controlled by the following reaction, [9]

$$CO(g) + \frac{1}{2}O_2(g) = CO_2(g), \quad \Delta G^0 = -280700 + 85.2 T \text{ (J/mol)}$$
 [1]

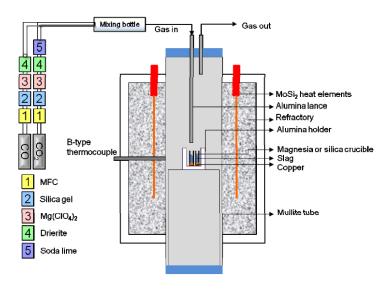


Fig. 1 Schematic diagram of the experimental apparatus.

The gas flow rate was controlled by a mass flow controller. The impurities in the CO<sub>2</sub> and CO gases were removed by passing the gases through the Drierite (W.A. Hammond Drierite Co. Ltd., Xenis, OH), Mg(ClO<sub>4</sub>)<sub>2</sub>, silica gel and soda lime.

Under the same experimental conditions as mentioned above, additional experiments were carried out for the equilibration between the silica-saturated Fe<sub>t</sub>O-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> slags (5 g) and copper melt (8 g) in a fused quartz crucible (OD; 20 mm, ID; 16 mm, HT; 40 mm) in order to investigate the effect of Al<sub>2</sub>O<sub>3</sub> addition on Pb distribution ratio between molten copper and silica saturated slag.

After equilibration was attained, the samples were quickly withdrawn from the hot zone of the furnace and rapidly quenched by flushing Ar gas, followed by dipping it into brine. The slag and metal samples were carefully separated from the crucible, and the metal-slag, metal-crucible and crucible-slag interfaces were removed. The sample was finely ground to powder, and the metal sample was cut into small pieces for chemical analysis. The composition of metal and slag samples was determined using ICP-AES (Optima 5300DV, PerkinElmer). Furthermore, the ferric (Fe<sup>3+</sup>) to ferrous (Fe<sup>2+</sup>) ratio in the slags was determined by the titration method using a potassium dichromate.

## 3. Results and Discussion

## 3.1 Influence of additives (CaO, Al<sub>2</sub>O<sub>3</sub>) and Fe/SiO<sub>2</sub> ratio on the distribution ratio of Pb

The distribution ratio of lead ( $L_{Pb}$ ) between molten copper and Fe<sub>t</sub>O-SiO<sub>2</sub> (-CaO, Al<sub>2</sub>O<sub>3</sub>) slags at 1473 K and p(O<sub>2</sub>)=10<sup>-10</sup> atm is shown in Figure 2 and Figure 3 as a function of the content of CaO and Al<sub>2</sub>O<sub>3</sub>, respectively, at different Fe/SiO<sub>2</sub> ratio.

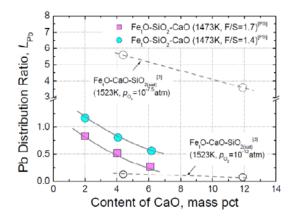


Fig. 2 Influence of CaO on the distribution ratio of lead between molten copper and  $Fe_tO-SiO_2-CaO$  slag at 1473 K and  $log p(O_2)=-10$ . [PS]; present study.

Fig. 3 Influence of  $Al_2O_3$  on the distribution ratio of lead between molten copper and  $Fe_tO-SiO_2-Al_2O_3$  slag at 1473 K and  $log p(O_2)=-10$ . [PS]; present study.

The distribution ratio of Pb between metal and slag phase in this study is defined as follows:

$$L_{\text{Pb}} = \frac{(\text{wt\%Pb})}{[\text{wt\%Pb}]}$$
[2]

The value of  $L_{Pb}$  decreases with increasing amount of CaO irrespective of Fe/SiO<sub>2</sub> ratio. This tendency is qualitatively similar to the results in the literature even at different temperature and oxygen potential, <sup>[3-6]</sup> indicating that CaO unambiguously behaves as a basic component (Eq. [4]) in the iron silicate slag based on the following ionic dissolution mechanism.

$$[Pb] + \frac{1}{2}O_2(g) = (Pb^{2+}) + (O^{2-})$$
 [3]

$$(CaO) = (Ca^{2+}) + (O^{2-})$$
 [4]

The addition of alumina in the iron silicate melts with the  $Fe/SiO_2=1.5$  linearly decreases the Pb distribution ratio, whereas there is a minimum value at about 4wt%  $Al_2O_3$  at  $Fe/SiO_2=1.3$ . Therefore, it is suggested that the alumina is considered as a basic component in the former system and in the composition of  $Al_2O_3$  content less than 4wt% in the latter system based on Eq. [5]. However, the alumina behaves as an acidic component in the composition of  $Al_2O_3$  content greater than 4wt% in the latter system based on Eq. [6]. [10]

$$(Al_2O_3) = 2(Al^{3+}) + 3(O^{2-})$$
 [5]

$$(Al_2O_3) + 5(O^{2-}) = 2(AlO_4)^{5-}$$
 [6]

Actually, the Pb distribution ratio increases with increasing content of alumina in the silica-saturated acidic system from the experimental data measured by Kim and Sohn.<sup>[3]</sup> They, however, originally concluded that the addition of Al<sub>2</sub>O<sub>3</sub> up to about 8wt% in the silica-saturated slag did not show a significant change in Pb distribution ratio in a logarithmic scale at a given oxygen potential. Reassessment of their experimental data provided the result shown in Figure 3. The amphoteric behavior of alumina in silicate melts (Eqs. [5] and [6]) have been reported in the previous studies.<sup>[10]</sup>

The value of  $L_{Pb}$  between molten copper and  $Fe_tO-SiO_2$  (-CaO,  $Al_2O_3$ ) slags is shown in Figure 4 as a function of  $Fe/SiO_2$  ratio.

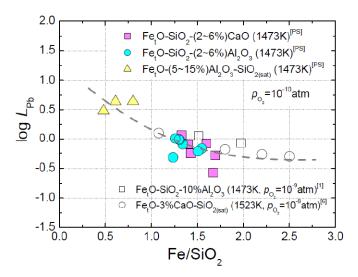


Fig. 4 Influence of Fe/SiO<sub>2</sub> ratio on log  $L_{Pb}$  in the Fe<sub>t</sub>O-SiO<sub>2</sub> (-CaO, Al<sub>2</sub>O<sub>3</sub>) slags at 1473 K and log p(O<sub>2</sub>)=-10. [PS]; present study.

The log  $L_{Pb}$  continuously decreases with increasing Fe/SiO<sub>2</sub> ratio and this tendency is in good accordance to the literature data. [1,6] Furthermore, the addition of Al<sub>2</sub>O<sub>3</sub> (5~15wt%) into the silical saturated iron silicate slag (Fe/SiO<sub>2</sub> < 1.0) shows the highest Pb distribution ratio. This can be understood by taking the variation of the activity of each component into account as follows.

Figure 5 shows the iso-activity contours of each component in the Fe<sub>t</sub>O-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> slag at 1473 K and p(O<sub>2</sub>)=10<sup>-10</sup>

atm, which was calculated using a commercial thermochemical computing package, FactSage<sup>TM</sup>6.2.<sup>[11]</sup> This software has been successfully applied in predicting the thermodynamic properties of multi-component metallurgical slags.<sup>[12]</sup>

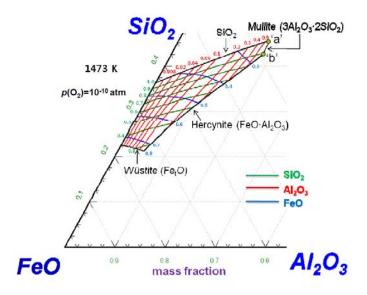


Fig. 5 Iso-activity contours for FeO, SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> in the Fe<sub>t</sub>O-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> ternary system at 1473 K and log p(O<sub>2</sub>)=-10.

The activity of  $Al_2O_3$  increases up to about 0.6 as the alumina content increases from  $FeO-SiO_2$  side to silica-mullite double saturation point 'a', which is in very good accordance to the following thermodynamic assessment at 1473 K.<sup>[9]</sup>

$$3Al_2O_3 \cdot 2SiO_2(s) = 3Al_2O_3(s) + 2SiO_2(s), \quad \Delta G^o = -8500 + 17.4 \ T (J/mol)$$
 [7]

$$a_{\text{Al}_2\text{O}_3} = \left[ \frac{K_{[7]} \cdot a_{3\text{Al}_2\text{O}_3} \cdot 2\text{SiO}_2}{a_{\text{SiO}_2}^2} \right]^{\frac{1}{3}} = K_{[7]}^{1/3} = 0.63$$
 [8]

Alternatively, the activity of FeO decreases from about 0.45 to 0.25 with increasing content of alumina at a fixed silica activity, i.e.  $a_{SiO_2} = 1.0$ . The activity of FeO at hercynite-mullite double saturation point is in good agreement to the following thermodynamic assessment.<sup>[9]</sup>

$$FeO \cdot Al_2O_3(s) = FeO(s) + Al_2O_3(s), \quad \Delta G^0 = 1800 + 12.9 \ T (J/mol)$$
 [9]

$$K_{[9]} = \frac{a_{\text{FeO}} \cdot a_{\text{Al}_2\text{O}_3}}{a_{\text{FeO-Al}_2\text{O}_3}}$$
[10]

Combining Eqs. [8] and [10], the activity of FeO at hercynite-mullite double saturation point 'b' ( $a_{SiO_2} = 0.9$ ) at 1473 K can be given as follows.

$$a_{\text{FeO}} = \frac{K_{[9]}}{K_{[7]}^{1/3}} \times a_{\text{SiO}_2}^2 = 0.27$$
 [11]

A decrease in the activity of FeO significantly increases the Pb distribution ratio, which originates from the basic character of FeO in the iron silicate melts, i.e. production of free O<sup>2-</sup> ions based on Eq. [12].

$$(FeO) = (Fe^{2+}) + (O^{2-})$$
 [12]

$$a_{O^{2-}} = \frac{K_{[12]} \cdot a_{FeO}}{a_{Fe^{2+}}}$$
 [13]

Consequently, a decrease in the activity of FeO, i.e. a decrease in the activity of free  $O^{2-}$  ions in the silicate melts assuming the proportionality between them from Eq. [13], the dissolution of Pb into the slag phase was promoted based on the ionic dissolution mechanism given in Eq. [3]. In Figure 5, the activity of FeO is not unity but 0.8 at wüstite saturation line, which is due to the coexistence of Fe<sub>2</sub>O<sub>3</sub>, i.e. Fe<sup>3+</sup> ions under the present conditions. This will be discussed in the following section.

# 3.2 Influence of Fe<sup>3+</sup>/Fe<sup>2+</sup> ratio on the distribution ratio of Pb

The ferric-to-ferrous ratio,  $Fe^{3+}/Fe^{2+}$  in the slag at a fixed temperature is dependent upon slag composition. Larson and Chipman reported that the  $Fe^{3+}/Fe^{2+}$  ratio increases as CaO content increases at constant oxygen potential in the CaO-FeO-Fe<sub>2</sub>O<sub>3</sub> and the CaO-SiO<sub>2</sub>-FeO-Fe<sub>2</sub>O<sub>3</sub> systems at 1823 K.<sup>[13]</sup> Generally, the ferric ion,  $Fe^{3+}$  is suggested to be predominant rather than ferrous ion,  $Fe^{2+}$  by addition of basic oxide such as CaO, which produces the free  $O^{2-}$  ions. Therefore, the equilibrium between  $Fe^{2+}$  and  $Fe^{3+}$  ions is expressed as follows.<sup>[10]</sup>

$$(Fe^{2+}) + \frac{1}{4}O_2(g) + \frac{3}{2}(O^{2-}) = (FeO_2^-)$$
 [14]

By combining Eqs. [3] and [14], the Pb \rightarrow Fe exchange reaction can be deduced as follows.

$$\frac{3}{2}[Pb] + (Fe^{2+}) + O_2(g) = \frac{3}{2}(Pb^{2+}) + (FeO_2^-)$$
 [15]

From the equilibrium constant of Eq. [15], the relationship between  $Fe^{3+}/Fe^{2+}$  ratio and Pb distribution ratio is deduced as follows.

$$\log L_{\text{Pb}} = -\frac{2}{3} \log \left( \frac{\text{wt\% Fe}^{3+}}{\text{wt\% Fe}^{2+}} \right) - \frac{2}{3} \log \left( \frac{f_{\text{Pb}}^{1.5} \cdot f_{\text{FeO}_{2}^{-}}}{f_{\text{Fe}^{2+}}} \right) + \log f_{\text{Pb}} + \frac{2}{3} \log p_{\text{O}_{2}} + \log K_{[15]}$$
[16]

Thus,  $\log L_{\rm Pb}$  is expected to be inversely proportional to  $\log ({\rm Fe}^{3+}/{\rm Fe}^{2+})$  with the slope of -2/3 at a given temperature and oxygen potential assuming that the second activity coefficient term on the right hand side in Eq. [16] would not be significantly affected by slag composition.

Figure 6 shows a relationship between the log  $L_{Pb}$  and log (Fe<sup>3+</sup>/Fe<sup>2+</sup>), wherein the linear relationship between them with the slope of about -0.44 is obtained from a linear regression analysis. The slope of the line is slightly lower than the expected value (-0.67) in Eq. [16], which probably originates from the attraction between Pb<sup>2+</sup> and ferric complex ions with increasing Fe<sup>3+</sup>/Fe<sup>2+</sup> ratio. This is thermodynamically consistent to the fact that there are several stable lead ferrite compounds such as Pb<sub>2</sub>Fe<sub>2</sub>O<sub>5</sub> (2:1, δ-phase), PbFe<sub>4</sub>O<sub>7</sub> (1:2, γ-phase), and PbFe<sub>12</sub>O<sub>19</sub> (1:6, β-phase). [14,15]

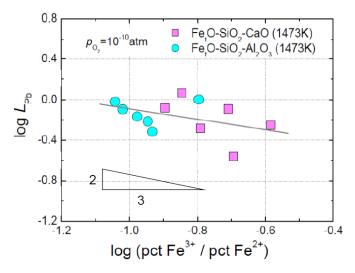


Fig. 6 Relationship between log  $L_{Pb}$  and log (Fe<sup>3+</sup>/Fe<sup>2+</sup>) in the Fe<sub>t</sub>O-SiO<sub>2</sub> (-CaO, Al<sub>2</sub>O<sub>3</sub>) slags at 1473 K and log p(O<sub>2</sub>)=-10.

## 3.3 Influence of Cu<sub>2</sub>O on the distribution ratio of Pb and stability of PbO in slag phase

The effect of  $Cu_2O$  on the Pb distribution ratio between molten copper and iron silicate slags at 1473 K is shown in Figure 7.

The Pb distribution ratio increases with increasing content of  $Cu_2O$  in the slag. It was known from the previous studies that Pb and Cu are present in the slag as PbO and  $Cu_2O$  in molecular form, respectively, [4,16-19] and thus the

following equilibrium reaction is given at slag/metal interface.

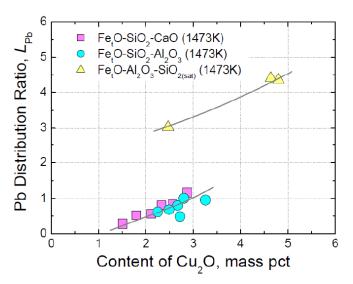


Fig. 7 Influence of  $Cu_2O$  content on the distribution of lead between molten copper and  $Fe_tO$ - $SiO_2$  (-CaO,  $Al_2O_3$ ) slags at 1473 K and  $log p(O_2)$ =-10.

$$[Pb] + (Cu2O) = (PbO) + 2Cu(I)$$
 [17]

$$K_{[17]} = \frac{a_{\text{PbO}}}{a_{\text{Pb}} \cdot a_{\text{Cu}_2\text{O}}} = \frac{\gamma_{\text{PbO}} \cdot X_{\text{PbO}}}{\gamma_{\text{Pb}} \cdot X_{\text{Pb}} \cdot \gamma_{\text{Cu}_2\text{O}} \cdot X_{\text{Cu}_2\text{O}}}$$
[18]

where  $K_{[17]}$ ,  $a_i$ ,  $\gamma_i$  and  $X_i$  are the equilibrium constant of Eq. [17], the activity, the activity coefficient and the mole fraction of component i, respectively.

On the other hand, the activity coefficient ( $\gamma_{PbO}$ ) and thus an excess free energy of PbO ( $\Delta G_{PbO}^{Ex}$ ) can be estimated from the following equations.<sup>[9,20]</sup>

$$[Pb]_{Cu} + \frac{1}{2}O_2(g) = PbO(l), \quad \Delta G^\circ = -217270 + 78.8 \ T (J/mol)$$
 [19]

$$\gamma_{\text{PbO}} = \frac{K_{[19]} \cdot \gamma_{\text{Pb}}^{0} \cdot X_{\text{Pb}} \cdot \sqrt{p_{\text{O}_{2}}}}{X_{\text{PbO}}}$$
[20]

$$\Delta G_{\rm PbO}^{\rm Ex} = -RT \ln \gamma_{\rm PbO} \tag{21}$$

where  $\gamma_{Pb}^{o}$  is the Henrian activity coefficient of Pb in molten copper, which is known as  $\gamma_{Pb}^{o} = 5.27$  at 1473 K. [20] The excess free energy of PbO calculated from Eqs. [20] and [21] is plotted against the mole fraction of Cu<sub>2</sub>O in Figure 8. The excess free energy of PbO decreases with increasing content of Cu<sub>2</sub>O, indicating that Cu<sub>2</sub>O is relatively more

acidic than PbO in the copper smelting iron silicate slags. However, in viewpoint of copper loss into the slag, the silica saturated system containing small amounts of alumina is strongly recommended to stabilize PbO in slag phase at low content of  $Cu_2O$ .

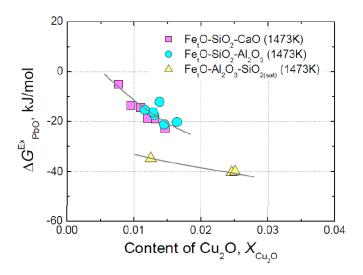


Fig. 8 Excess free energy of PbO in the  $Fe_tO-SiO_2$  (-CaO,  $Al_2O_3$ ) slags at 1473 K.

# 3.4 Correlation between the activity of FeO and the Pb Capacity

From an ionic dissolution mechanism of lead which is given in Eq. [3], the 'lead capacity' of the slag can be defined using an equilibrium constant of Eq. [3] as follows.

$$C_{\text{Pb}^{2+}} = \frac{K_{[3]}}{f_{\text{Pb}^{2+}} \cdot a_{\text{O}^{2-}}} = \frac{(\text{wt\% Pb}^{2+})}{f_{\text{Pb}} \cdot [\text{wt\% Pb}] \cdot \sqrt{p_{\text{O}_2}}} = \frac{L_{\text{Pb}}}{f_{\text{Pb}} \cdot \sqrt{p_{\text{O}_2}}}$$
[22]

Therefore, the lead capacity is a function of the basicity ( $a_{\rm O^{2-}}$ ) and the stability of Pb<sup>2+</sup> ion ( $f_{\rm Pb^{2+}}$ ) at a fixed temperature and it can be calculated from  $L_{\rm Pb}$ ,  $p_{\rm O_2}$  and  $f_{\rm Pb}$  in molten copper. The activity coefficient of Pb in molten copper at 1473 K is calculated using Eq. [23], resulting in  $f_{\rm Pb} \sim 1.0$ .<sup>[20]</sup>

$$\log f_{\rm Pb} = e_{\rm Pb}^{\rm Pb} \cdot [\text{wt\% Pb}] = -0.0006 \cdot [\text{wt\% Pb}] \cong 0$$
 [23]

By combining Eqs. [13] and [22], the lead capacity can be expressed as a function of FeO activity as follows.

$$\log C_{\rm Pb^{2+}} = -\log a_{\rm FeO} + \log a_{\rm Fe^{2+}} - \log f_{\rm Pb^{2+}} + \log \frac{K_{[3]}}{K_{[12]}}$$
 [24]

From Eq. [24], the lead capacity and FeO activity are expected to show a linear relationship with a slope of -1.0 in a logarithmic scale assuming that the composition dependency of  $a_{\rm Fe^{2+}}$  and  $f_{\rm Pb^{2+}}$  is not so critical at a given temperature. In the present study, the activity of FeO in the slag was calculated based on the Regular solution model provided by Banya and Shim. [21]

Figure 9 shows a relationship between the lead capacity,  $\log C_{\mathrm{Pb}^{2+}}$  and the activity of FeO,  $\log a_{\mathrm{FeO}}$ , wherein a good linearity is observed with the slope of about -1.5 from least square regression method. This is slightly larger than the expected value of -1.0, indicating a change in the  $a_{\mathrm{Fe}^{2+}}$  and/or  $f_{\mathrm{Pb}^{2+}}$  terms with increasing FeO activity. Hence, it is suggested that an increasing rate of  $f_{\mathrm{Pb}^{2+}}$  is relatively larger than that of  $a_{\mathrm{Fe}^{2+}}$  by increasing the activity of FeO because of a repulsive force between Fe<sup>2+</sup> and Pb<sup>2+</sup> ions. From a linear correlation between lead capacity and FeO activity in Figure 9, the concept of 'lead capacity' is a good measure of absorption ability of lead of iron silicate slags and the activity of FeO can be a qualitative basicity index in the slag.

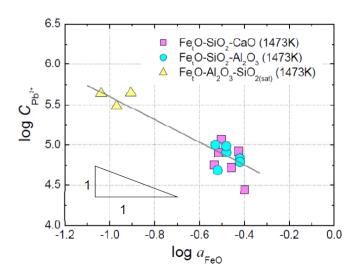


Fig. 9 Correlation between the activity of FeO and the lead capacity in the Fe<sub>t</sub>O-SiO<sub>2</sub> (-CaO, Al<sub>2</sub>O<sub>3</sub>) slags at 1473 K.

#### 4. Conclusions

- 1) The value of  $L_{Pb}$  decreases with increasing amount of CaO (~6wt%) irrespective of Fe/SiO<sub>2</sub> ratio (1.4~1.7). However, the addition of alumina in the slag with Fe/SiO<sub>2</sub>=1.5 linearly decreases the  $L_{Pb}$ , whereas there is a minimum value at about 4wt% Al<sub>2</sub>O<sub>3</sub> at Fe/SiO<sub>2</sub>=1.3.
- 2) The log  $L_{Pb}$  continuously decreases with increasing Fe/SiO<sub>2</sub> ratio and furthermore, the addition of Al<sub>2</sub>O<sub>3</sub> (5~15wt%) into the silica saturated iron silicate slag (Fe/SiO<sub>2</sub> < 1.0) shows the highest Pb distribution ratio. This is mainly due to a decrease in the activity of FeO even at silica saturation condition.
- 3) The log  $L_{Pb}$  and log  $(Fe^{3+}/Fe^{2+})$  shows a linear relationship with the slope of about -0.44, which was slightly lower than the expected value of -2/3. This probably originates from the attraction between Pb<sup>2+</sup> and ferric complex ions with increasing  $Fe^{3+}/Fe^{2+}$  ratio.
- 4) The Pb distribution ratio increases with increasing content of Cu<sub>2</sub>O in the slag and the excess free energy of PbO decreases with increasing content of Cu<sub>2</sub>O, indicating that Cu<sub>2</sub>O is relatively more acidic than PbO in the copper smelting iron silicate slags. However, in viewpoint of copper loss into the slag, the silica saturated system containing small amounts of alumina is strongly recommended to stabilize PbO in slag phase at low content of Cu<sub>2</sub>O.

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