

## Removal of Pb from Molten Copper by $\text{Fe}_1\text{O-SiO}_2$ (-CaO, $\text{Al}_2\text{O}_3$ ) Slag Treatment in Mitsubishi Process

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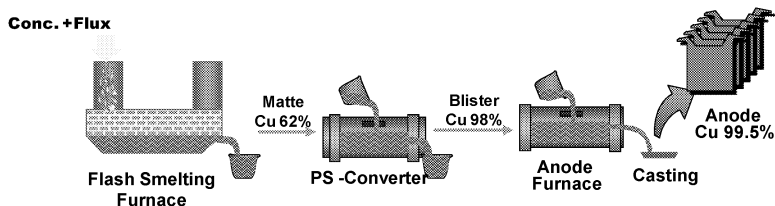
### Abstract

The distribution behavior of Pb between molten copper and  $\text{Fe}_1\text{O-SiO}_2$  (-CaO,  $\text{Al}_2\text{O}_3$ ) slags was investigated at 1473 K (1200 °C) and  $p(\text{O}_2)=10^{-10}$  atm in view of the reaction mechanism of Pb dissolution into the slag. The distribution ratio of Pb ( $L_{\text{Pb}}$ ) decreases with increasing CaO content (~6 mass pct) irrespective of Fe/SiO<sub>2</sub> ratio (1.4~1.7). However, the addition of alumina into a slag with Fe/SiO<sub>2</sub>=1.5 linearly decreases the  $L_{\text{Pb}}$ , whereas a minimum value is observed at about 4 mass pct  $\text{Al}_2\text{O}_3$  at Fe/SiO<sub>2</sub>=1.3. The log  $L_{\text{Pb}}$  continuously decreases with increasing Fe/SiO<sub>2</sub> ratio, and the addition of  $\text{Al}_2\text{O}_3$  (5 to 15 mass pct) into the silica-saturated iron silicate slag (Fe/SiO<sub>2</sub> < 1.0) yields the highest Pb distribution ratio. The log  $L_{\text{Pb}}$  linearly decreases by increasing the log ( $\text{Fe}^{3+}/\text{Fe}^{2+}$ ) value. The Pb distribution ratio increases and the excess free energy of PbO decreases with increasing  $\text{Cu}_2\text{O}$  content in the slag. However, from the viewpoint of copper loss into the slag, the silica-saturated system containing small amounts of alumina is strongly recommended to stabilize PbO in the slag phase at a low  $\text{Cu}_2\text{O}$  content.

### Introduction

It is very important in copper smelting and refining processes to remove several minor elements such as Pb, Bi, Sb, As, and Te [1-2]. Specifically, Pb is a troublesome impurity which increases the amount of slime in the electro-refining process. Also, from the viewpoint of copper smelting and refining processes, Pb is a detrimental element that is always present in sulfide concentrates and must be eliminated. Therefore, the content of Pb in molten copper should be lowered within an appropriate concentration range during plant operation.

Comparing Outokumpu flash smelting process and Mitsubishi continuous smelting process (Figure 1), there is a difference in the content of Pb in anode Cu as shown in Figure 2, which probably originates from a difference in slag chemistry in between both processes (The concentrate was nominally the same in each case).



(a)

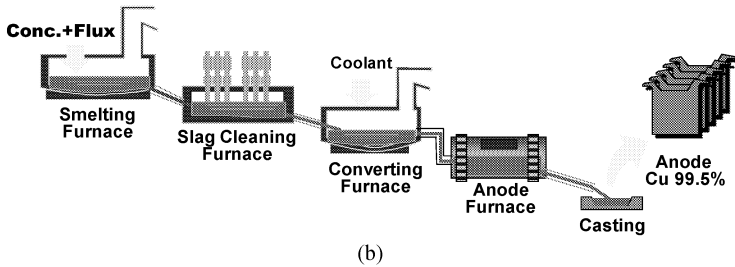


Figure 1. (a) Outokumpu flash smelting process and (b) Mitsubishi continuous smelting process.

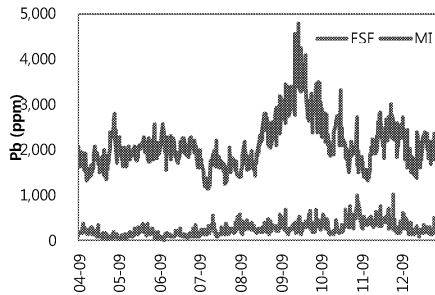


Figure 2. Residual Pb content in Cu anode in Outokumpu flash smelting process (FSF) and Mitsubishi continuous smelting process (MI).

Therefore, we need to increase the Pb removal ratio in the Mitsubishi continuous smelting process based on the fundamental knowledge for the slag chemistry of Pb removal.

Kim and Sohn examined the effects of CaO, Al<sub>2</sub>O<sub>3</sub>, and MgO additions on the distribution behavior of Pb between an iron silicate slag and liquid copper under a CO-CO<sub>2</sub> atmosphere  $p(\text{O}_2)=10^{-12} \sim 10^{-6}$  atm at 1523 K (1250 °C) and found that the distribution ratio of Pb and the activity coefficient of PbO were not significantly affected by the additives [3]. The governing factors affecting Pb solubility in iron silicate slag were proposed as the oxygen potential and the ratio of Fe<sub>2</sub>O/SiO<sub>2</sub> (or SiO<sub>2</sub> content).

Matsuzaki *et al.* [4] calculated the activity coefficient of PbO ( $\gamma_{\text{PbO}}$ ) with the regular solution model and plotted the iso- $\gamma_{\text{PbO}}$  contours for the CaO-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> ternary slag at 1623 K (1350 °C). The value of  $\gamma_{\text{PbO}}$  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. A similar tendency of the effect of CaO/SiO<sub>2</sub> ratio on the  $\gamma_{\text{PbO}}$  was also reported by Kudo *et al.* [5] using the Fe<sub>2</sub>O-CaO-SiO<sub>2</sub> system in equilibrium with metallic iron at 1573 K (1300 °C). In that study [5], the changes in temperature from 1473 to 1573 K (1200 to 1300 °C) did not have a significant effect on  $\gamma_{\text{PbO}}$  in the slag. Decterov and Pelton computed the distribution behavior of Pb among matte, slag, and liquid copper at 1523 K (1250 °C) and  $p(\text{O}_2)=10^{-12} \sim 10^{-5}$  atm under conditions from silica saturation to magnetite saturation [6]. The distribution ratio of Pb decreased with increasing Fe/SiO<sub>2</sub> ratio from silica to magnetite saturation. The small addition of CaO (3 mass pct) also decreased the Pb distribution ratio.

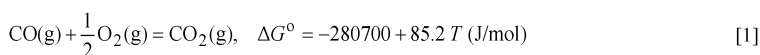
Even though the effectiveness of slag treatment for the removal of Pb from the Cu melt has been investigated as mentioned above, many studies focused on the equilibrium distribution

behavior of Pb in the Cu/matte/slag system during the smelting and converting processes. Therefore, in the present study, the distribution behavior of Pb between molten copper and Fe<sub>1</sub>O-SiO<sub>2</sub> (-CaO, Al<sub>2</sub>O<sub>3</sub>) slags was investigated from the view of the reaction mechanism of Pb dissolution into the slag.

### Experimental

The experiments were carried out using a super-kanthal electric furnace with a MoSi<sub>2</sub> heating element. An alloy sample with the composition of Cu-1 mass pct Pb was preliminarily prepared from pure (99.99 pct purity) Cu and Pb. The slag samples 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 (1000 °C) for 10 hours. The equilibration time was predetermined to be 6 hours at 1473 K (1200 °C) [7].

The metal (8 g) and slag (5 g) were loaded in a fused magnesia (99.9 pct purity) crucible (OD: 18 mm, ID: 14 mm, HT: 50 mm) placed in an alumina holder (OD: 50 mm, ID: 45 mm, HT: 70 mm) and attached to a molybdenum wire. The oxygen partial pressure of the system, p(O<sub>2</sub>)=10<sup>-10</sup> atm, was controlled by the following reaction [8],



Under the same experimental conditions as mentioned above, additional experiments were carried out for the equilibration between the silica-saturated Fe<sub>1</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.

The composition of metal and slag samples was determined using inductively coupled plasma spectrometry. Furthermore, the ferric (Fe<sup>3+</sup>) to ferrous (Fe<sup>2+</sup>) ratio in the slags was determined by titration using a potassium dichromate.

### Results and Discussion

#### 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 Pb ( $L_{\text{Pb}}$ ) between molten copper and Fe<sub>1</sub>O-SiO<sub>2</sub> (-CaO, Al<sub>2</sub>O<sub>3</sub>) slags at 1473 K (1200 °C) and p(O<sub>2</sub>)=10<sup>-10</sup> atm is shown in Figure 3 as a function of the CaO and Al<sub>2</sub>O<sub>3</sub> content, respectively, at different Fe/SiO<sub>2</sub> ratios. The distribution ratio of Pb between metal and slag phases in this study is defined as follows:

$$L_{\text{Pb}} = \frac{(\text{mass pct Pb})_{\text{slag}}}{[\text{mass pct Pb}]_{\text{metal}}} \quad [2]$$

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

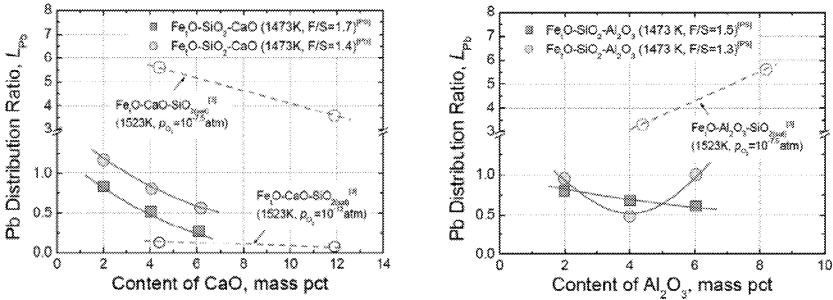
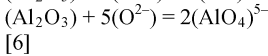


Figure 3. Influence of CaO and Al<sub>2</sub>O<sub>3</sub> on the distribution ratio of lead between molten copper and Fe<sub>1.0</sub>-SiO<sub>2</sub>-CaO slag at 1473 K (1200 °C) and  $p(\text{O}_2)=10^{-10}$  atm. [PS]: present study.



The addition of alumina in the iron silicate melts with the Fe/SiO<sub>2</sub>=1.5 linearly decreases the Pb distribution ratio, whereas a minimum value is observed at about 4 mass pct Al<sub>2</sub>O<sub>3</sub> with Fe/SiO<sub>2</sub>=1.3. Therefore, alumina is considered as a basic component in the former system (Fe/SiO<sub>2</sub>=1.5) and in the composition of Al<sub>2</sub>O<sub>3</sub> content less than 4 mass pct in the latter system (Fe/SiO<sub>2</sub>=1.3) based on Eq. [5]. However, the alumina behaves as an acidic component when Al<sub>2</sub>O<sub>3</sub> content greater than 4 mass pct in the latter system (Fe/SiO<sub>2</sub>=1.3) based on Eq. [6].<sup>[9]</sup>



The value of  $L_{\text{Pb}}$  between molten copper and Fe<sub>1.0</sub>-SiO<sub>2</sub> (-CaO, Al<sub>2</sub>O<sub>3</sub>) slags is shown in Figure 4 as a function of Fe/SiO<sub>2</sub> ratio. The log  $L_{\text{Pb}}$  continuously decreases with increasing Fe/SiO<sub>2</sub> ratio and this tendency is in good accordance with the literature data [1,6]. Furthermore, the addition of Al<sub>2</sub>O<sub>3</sub> (5 to 15 mass pct) into the silica saturated iron silicate slag (Fe/SiO<sub>2</sub> < 1.0) shows the highest Pb distribution ratio.

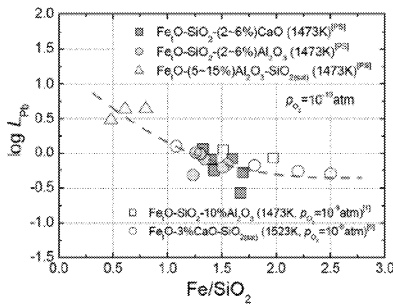


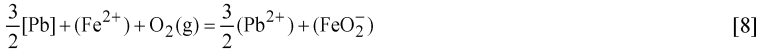
Figure 4. Influence of Fe/SiO<sub>2</sub> ratio on log L<sub>Pb</sub> in the Fe<sub>1</sub>O-SiO<sub>2</sub> (-CaO, Al<sub>2</sub>O<sub>3</sub>) slags at 1473 K (1200 °C) and p(O<sub>2</sub>)= 10<sup>-10</sup> atm. [PS]: present study.

Influence of Fe<sup>3+</sup>/Fe<sup>2+</sup> Ratio on the Distribution Ratio of Lead

Generally, the ferric ion, Fe<sup>3+</sup> is suggested to be predominant rather than ferrous ion, Fe<sup>2+</sup> by addition of basic oxide such as CaO, which produces the free O<sup>2-</sup> ions. Therefore, the equilibrium between Fe<sup>2+</sup> and Fe<sup>3+</sup> ions is expressed as follows [9].



By combining Eqs. [3] and [7], the Pb↔Fe exchange reaction can be deduced as follows.



From the equilibrium constant of Eq. [8] (K<sub>[8]</sub>), the relationship between Fe<sup>3+</sup>/Fe<sup>2+</sup> ratio and Pb distribution ratio is deduced as follows.

$$\log L_{\text{Pb}} = -\frac{2}{3}\log\left(\frac{\text{pct Fe}^{3+}}{\text{pct Fe}^{2+}}\right) - \frac{2}{3}\log\left(\frac{f_{\text{Pb}^{2+}}^{1.5} \cdot f_{\text{FeO}_2^-}}{f_{\text{Fe}^{2+}}}\right) + \log f_{\text{Pb}} + \frac{2}{3}\log p_{\text{O}_2} + \log K_{[8]} \quad [9]$$

Where, f<sub>i</sub> and p<sub>O<sub>2</sub></sub> are the activity coefficient of species i and the oxygen partial pressure, respectively. Thus, log L<sub>Pb</sub> is expected to be inversely proportional to log (Fe<sup>3+</sup>/Fe<sup>2+</sup>) 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. [9] would not be significantly affected by slag composition. Figure 5 shows a relationship between the log L<sub>Pb</sub> 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.

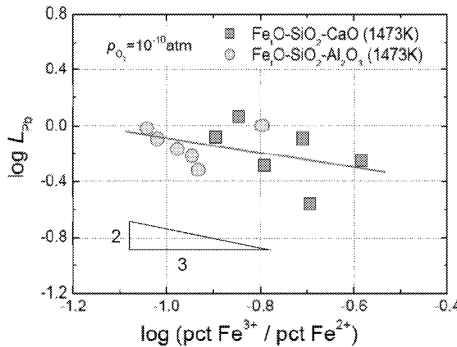


Figure 5. Relationship between log L<sub>Pb</sub> and log (Fe<sup>3+</sup>/Fe<sup>2+</sup>) in the Fe<sub>1</sub>O-SiO<sub>2</sub> (-CaO, Al<sub>2</sub>O<sub>3</sub>) slags at 1473 K (1200 °C) and p(O<sub>2</sub>)= 10<sup>-10</sup> atm.

The slope of the line is slightly lower than the expected value (-0.67) in Eq. [9], which probably originates from the attraction between  $Pb^{2+}$  and ferric complex ions with increasing  $Fe^{3+}/Fe^{2+}$  ratio. This is thermodynamically consistent to the fact that there are several stable lead ferrite compounds such as  $Pb_2Fe_2O_5$  (2:1,  $\delta$ -phase),  $PbFe_4O_7$  (1:2,  $\gamma$ -phase), and  $PbFe_{12}O_{19}$  (1:6,  $\beta$ -phase) [10].

#### Influence of $Cu_2O$ on the Distribution Ratio of Lead 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 (1200 °C) is shown in Figure 6.

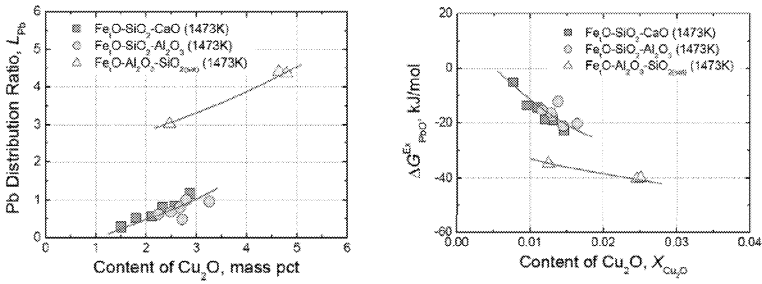


Figure 6. Influence of  $Cu_2O$  content on the distribution of lead between molten copper and  $Fe_1O-SiO_2$  (-CaO,  $Al_2O_3$ ) slags at 1473 K (1200 °C) and  $p(O_2)= 10^{-10}$  atm (Left) and Excess free energy of PbO in the  $Fe_1O-SiO_2$  (-CaO,  $Al_2O_3$ ) slags at 1473 K (1200 °C). (Right).

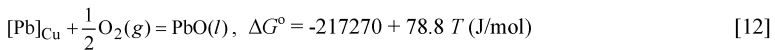
The Pb distribution ratio increases with increasing content of  $Cu_2O$  in the slag. It was known from the previous studies that Pb and Cu are present in the slag as PbO and  $Cu_2O$  in molecular form, respectively [4], and thus the following equilibrium reaction is given at slag/metal interface.



$$K_{[10]} = \frac{a_{PbO}}{a_{Pb} \cdot a_{Cu_2O}} = \frac{\gamma_{PbO} \cdot X_{PbO}}{\gamma_{Pb} \cdot X_{Pb} \cdot \gamma_{Cu_2O} \cdot X_{Cu_2O}} \quad [11]$$

Where,  $K_{[10]}$ ,  $a_i$ ,  $\gamma_i$  and  $X_i$  are the equilibrium constant of Eq. [10], 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 [11].



$$\gamma_{PbO} = \frac{K_{[12]} \cdot \gamma_{Pb}^0 \cdot X_{Pb} \cdot \sqrt{p_{O_2}}}{X_{PbO}} \quad [13]$$

$$\Delta G_{\text{PbO}}^{\text{Ex}} = -RT \ln \gamma_{\text{PbO}} \quad [14]$$

where  $\gamma_{\text{Pb}}^{\circ}$  is the Henrian activity coefficient of Pb in molten copper, which is  $\gamma_{\text{Pb}}^{\circ} = 5.27$  at 1473 K (1200 °C) [11]. The excess free energy of PbO calculated from Eqs. [13] and [14] is plotted against the mole fraction of Cu<sub>2</sub>O in Fig. 4. The excess free energy of PbO decreases with increasing Cu<sub>2</sub>O content, indicating that Cu<sub>2</sub>O is more acidic than PbO in the copper smelting iron silicate slags. However, from the viewpoint of copper loss into the slag, the silica-saturated system containing small amounts of alumina is strongly recommended to stabilize PbO in the slag phase at low Cu<sub>2</sub>O content.

### Conclusions

The distribution behavior of Pb between molten copper and Fe<sub>1</sub>O-SiO<sub>2</sub> (-CaO, Al<sub>2</sub>O<sub>3</sub>) slags was investigated at 1473 K (1200 °C) and p(O<sub>2</sub>)=10<sup>-10</sup> atm to observe the reaction mechanism of Pb dissolution into the slag. The experimental results are summarized below.

- 1) The value of  $L_{\text{Pb}}$  decreases with increasing CaO content (~6 mass pct) 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  $L_{\text{Pb}}$ , and there is a minimum value observed at about 4 mass pct Al<sub>2</sub>O<sub>3</sub> at Fe/SiO<sub>2</sub>=1.3.
- 2) The log  $L_{\text{Pb}}$  continuously decreases with increasing Fe/SiO<sub>2</sub> ratio, and the addition of Al<sub>2</sub>O<sub>3</sub> (5 to 15 mass pct) into the silica-saturated iron silicate slag (Fe/SiO<sub>2</sub> < 1.0) shows the highest Pb distribution ratio.
- 3) The log  $L_{\text{Pb}}$  and log (Fe<sup>3+</sup>/Fe<sup>2+</sup>) values show a linear relationship with a 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<sup>3+</sup>/Fe<sup>2+</sup> ratio.
- 4) The Pb distribution ratio increases and the excess free energy of PbO decreases with increasing Cu<sub>2</sub>O content in the slag, indicating that Cu<sub>2</sub>O is relatively more acidic than PbO in the copper smelting iron silicate slags.

### References

1. M. Nagamori, P.J. Mackey and P. Tarassoff, "Copper Solubility in FeO-Fe<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> Slag and Distribution Equilibria of Pb, Bi, Sb and As Between Slag and Metallic Copper", *Metall. Trans. B* 6B (1975) 295-301.
2. A.K. Kyllö and G.G. Richards, "Kinetic Modeling of Minor Element Behavior on copper converting", *Metall. Mater. Trans. B* 29B (1998) 261-68.
3. H. G. Kim and H.Y. Sohn, "Effects of CaO, Al<sub>2</sub>O<sub>3</sub>, and MgO Additions on the Copper Solubility, Ferric/Ferrous Ratio, and Minor-Element Behavior of Iron-Silicate Slags", *Metall. Mater. Trans. B* 29B (1998) 583-90.
4. K. Matsuzaki, T. Ishikawa, T. Tsukada and K. Ito, "Distribution Equilibria of Pb and Cu between CaO-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> Melts and Liquid Copper", *Metall. Mater. Trans. B* 31B (2000) 1261-66.
5. M. Kudo, E. Jak, P. Hayes, K. Yamaguchi and Y. Takeda, "Lead Solubility in FeO<sub>x</sub>-CaO-SiO<sub>2</sub> Slags at Iron Saturation", *Metall. Mater. Trans. B* 31B (2000) 15-24.

6. S.A. Decterov and A.D. Pelton, "Thermodynamic modeling of Lead distribution among Matte, Slag, and Liquid Copper", *Metall. Mater. Trans. B* 30B (1999) 1033-44.
7. J.H. Heo, S.S. Park and J.H. Park, "Effect of Slag Composition on the Distribution Behavior of Pb between  $\text{Fe}_1\text{O-SiO}_2$  (-CaO,  $\text{Al}_2\text{O}_3$ ) Slag and Molten Copper", *Metall. Mater. Trans. B* 43B (2012) 1098-1105.
8. E.T. Turkdogan, *Physical Chemistry of High Temperature Technology*, Academic Press, New York, NY, (1980) 1-24.
9. N. Sano, Thermodynamics of Slags (Chapter 2), in *Advanced Physical Chemistry for Process Metallurgy*, ed. by N. Sano, W.K. Lu, P.V. Riboud and M. Maeda, Academic Press, San Diego, CA, (1997) 46-51.
10. A.J. Mountvala and S.F. Ravitz, "Phase Relations and Structures in the System  $\text{PbO-Fe}_2\text{O}_3$ ", *J. Am. Ceram. Soc.* 45 (1962) 285-88.
11. G.K. Sigworth and J.F. Elliot, "The thermodynamics of dilute liquid copper alloys", *Can. Metall. Q.* 13 (1974) 455-61.
12. S. Ban-ya, "Mathematical Expression of Slag-Metal Reactions in Steelmaking Process by Quadratic Formalism Based on the Regular Solution Model", *ISIJ Int.* 33(1993) 2-11.