PbO Activity and Impurity Dissolution in $PbO\text{-}FeO_X\text{-}CaO\text{-}SiO_2$ Slag

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ABSTRACT

In order to clarify the behavior of the metallurgical phases in the oxidation zone of the QSL lead smelting process, the phase equilibrium between the metallic lead and the $PbO\text{-}FeO_X\text{-}CaO\text{-}SiO_2$ slag was investigated at 1423K. The EMF method using a solid electrolyte with calcia-stabilized zirconia was applied to measure the oxygen partial pressure in the system. The oxygen potential increases with increasing PbO content in the slag. The PbO activity and activity coefficient estimated from the oxygen potential increase with the addition of CaO in the slag. However, the PbO activity is slightly affected by the FeO_X content at constant PbO concentration in the experimental region. The distribution ratios $L_M^{s/m}$ = (mass% M in slag) / [mass% M in metal] of As, Sb, Cu, and Ag between the metallic lead and the $PbO\text{-}FeO_X\text{-}CaO\text{-}SiO_2$ slag at $\log p_{O_2} = -8$ corresponding to the oxygen potential in the oxidation zone of the QSL process are 3, 1, 0.1 and 2×10^{-3}, respectively. These values decrease with decreasing the oxygen potential. Based on these relationships $AsO_{1.5}$, $SbO_{1.5}$, $CuO_{0.5}$ and $AgO_{0.5}$ are estimated in the slag.

1.INTRODUCTION

The conventional lead smelting process using the blast furnace and the ISF for sulfide ore smelting consists of two steps, the sintering followed by the reduction stage. The sulfide concentrate is oxidized in a separate sintering machine. The calcine is discharged and cooled down prior to feeding in the furnaces. In this two step operation, the exothermic heat by the oxidation reactions of sulfides is not utilized for smelting. The new continuous smelting processes such as the QSL, Isasmelt and KLS processes for lead sulfide ores have been developed to take advantage of the sensible heat to reduce the energy requirement in the lead smelting.

The conventional two stage process corresponds to the oxidation and reduction zones in the QSL reactor. In the oxidation zone, the sulfides in the concentrate are converted under high oxygen potential, because even a small amount of sulfur remaining in the slag leads to an increase of the lead solubility in the discard slag[1]. This slag flows to the reduction zone, where the lead bullion is produced by reduction of the PbO in the slag. Both slags equilibrate with the bullion in the QSL reactor. To analyze the QSL smelting process, equilibrium studies between the slag and metallic lead phases is important, however there are very few papers reported.

In the present study, the oxygen potential and the distribution behavior of minor elements such as As, Sb, Cu and Ag between the metallic lead and the $PbO\text{-}FeO_X\text{-}CaO\text{-}SiO_2$ slag phases related to the oxidation zone in the QSL lead smelting process were investigated at 1423K.

2. EXPERIMENTAL PROCEDURE

The following oxygen concentration cell with solid electrolyte was adopted for measuring the emf in the $PbO\text{-}FeO_X\text{-}CaO\text{-}SiO_2$ slag equilibrated with the metallic lead.

$$Pt / Ni\cdot NiO / ZrO_2\cdot CaO / Sample / Ir / Pt$$

Ten grams of metallic lead and 6.5 grams of PbO, FeO, Fe_2O_3, SiO_2 and CaO were charged in a dense sintered magnesia crucible. In order to vary the oxygen partial pressure, the ratio between FeO and Fe_2O_3 in the charged materials was adjusted. To determine the distribution of minor element between the metallic lead and slag phases, 2 mass% copper and silver and 0.5 mass% arsenic and antimony were added to the total charge. Arsenic was charged in the form of a Pb-As alloy to prevent the vaporization loss of arsenic during the melting. After keeping the sample at the experimental temperature for 5 hours under argon atmosphere the cell was immersed into the sample. The emf measurements were conducted when the readings have become constant. A water-cooled copper tube was immersed in the slag after the emf measurement to take a sample for analysis. The components of the sample were analyzed mainly by ICP while the conventional titration method by $K_2Cr_2O_7$ was used for total iron and Fe^{2+}. The SiO_2 content in the slag was determined gravimetrically.

In this study, Q and R are defined as follows to represent the $PbO\text{-}FeO_X\text{-}CaO\text{-}SiO_2$ slag composition.

$$Q = \text{mass\%CaO}/(\text{mass\%CaO} + \text{mass\%SiO}_2)$$

$$R = N_{FeO_X}/(N_{FeO_X} + N_{CaO} + N_{SiO_2})$$

The series of experiments were conducted at Q=0.3 and 0.4 in the present investigation.

3. RESULTS AND DISCUSSIONS

3-1 Oxygen Potential

The fundamental slag of the conventional lead smelting is $FeO_X\text{-}CaO\text{-}SiO_2$ system. In the QSL process, the oxidation slag dissolves a significant amount of PbO, thus, this slag is better represented as the $PbO\text{-}FeO_X\text{-}(CaO\text{-}SiO_2\text{-}MgO)$ pseudo-ternary system in this study. The MgO solubility in the $PbO\text{-}FeO_X\text{-}CaO\text{-}SiO_2$ slag at 1423K is analyzed to be less than 2 mass%.

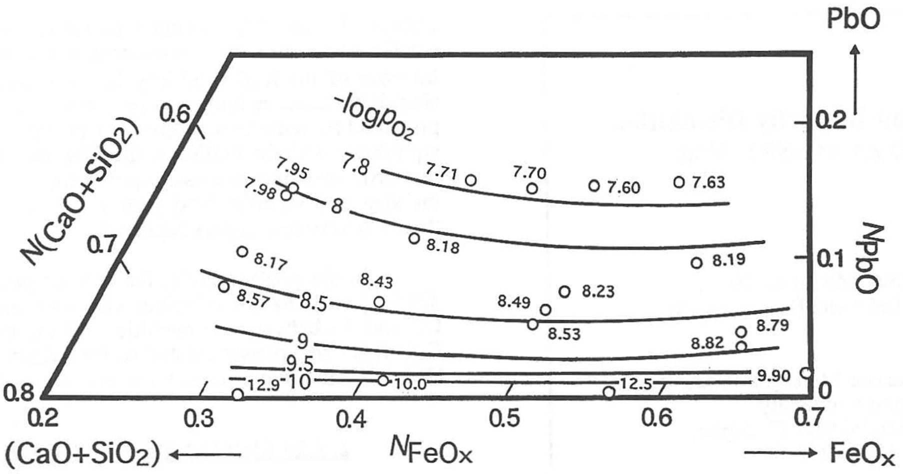

Fig.1. The measured logp_{O_2} and the isobars of oxygen pressue where Q is nearly equal to 0.3 in the PbO-FeOx-CaO-SiO2 pseudo-ternary system at 1423K.

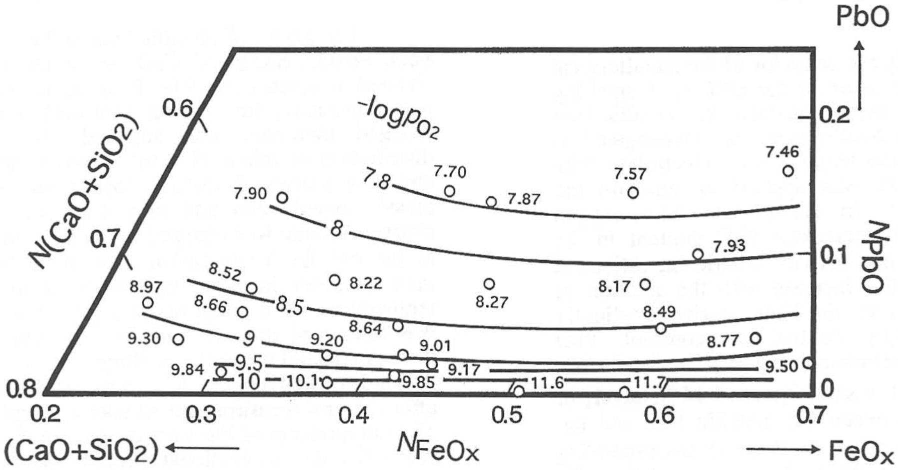

Fig.2. The measured logp_{O_2} and the isobars of oxygen pressue where Q is nearly equal to 0.4 in the PbO-FeOx-CaO-SiO2 pseudo-ternary system at 1423K.

The measured oxygen partial pressure is exhibited with -logp_{O_2} in Figs. 1 and 2 for Q=0.3 and 0.4 at 1423K, respectively. The circles show the slag composition corresponding to these emf measurements and the numerical values besides the points express the oxygen potential. The oxygen partial pressure increases with increasing PbO content but is kept approximately constant even though the ratio of $N_{FeO_X}/(N_{FeO_X}+N_{CaO}+N_{SiO_2})$ is changed at constant PbO content in the experimental region. Since oxygen potential in the PbO-CaO-SiO2 ternary system is lower than that in the present system at the same PbO content, the addition of FeOx to the PbO-CaO-SiO2 slag results in a rapid increase of the oxygen potential[2]. By comparing with Figs. 1 and 2, it is understood that the oxygen potential in the slag equilibrating with molten lead decreases with increasing CaO content.

The relationship between the lead solubility in the slag and the oxygen potential on a composition line near R=0.4 is illustrated in Fig. 3. The lead solubility in the slag which has almost the same Q values with the QSL process at 0.3 and 0.4 increases with increasing the oxygen potential and the slope is approximately 1/2. This experimental result suggests that lead dissolves in the form of PbO in the slag phase as describing with Eq. (4) in the distribution ratio subsequently. In the QSL lead smelting process, the slag produced in the oxidation zone contains almost 30 mass% Pb. This corresponds to composition approximately 10^{-3} Pa (10^{-8} atm) in oxygen pressure according to Fig. 3. Yazawa *et al*. have reported the lead solubility in the SiO2-saturated FeOx-SiO2 slag (Q=0) and in the FeOx-CaO calcium ferrite slag (Q=1) at 1473K[3]. The results are compared with the present experimental results in Fig. 3. The lead solubility in the CaO-free FeOx-SiO2 slag decreases by addition of CaO. The minimum lead solubility is observed in the SiO2-free FeOx-CaO calcium ferrite slag.

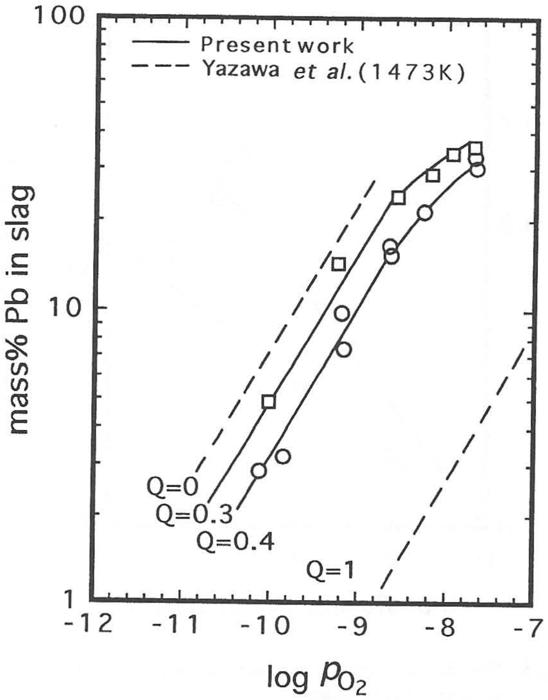

Fig.3. The relationship between the lead solubility in the slag and logP_{O_2} at Q=0.3 and 0.4. (----- Yazawa *et al*[3].)

3-2 PbO Activity in PbO-FeO_x-CaO-SiO_2 Slag

In the present investigation, the slag phase is equilibrium with the metallic lead phase. The PbO activity can be calculated from Reaction (1) and the measured oxygen pressure.

$$PbO(l) + 1/2\ O_2(g) = PbO(l) \qquad (1)$$

The iso-activity lines of PbO in the slag where Q is nearly equal to 0.4 are illustrated by the solid lines with the measured points in Fig. 4. The activity curves for Q=0.3 are also drawn by the dashed lines without measured point. The PbO activity increases with increasing PbO content but does not change with R in the composition region higher than R=0.5 in the experimental range.

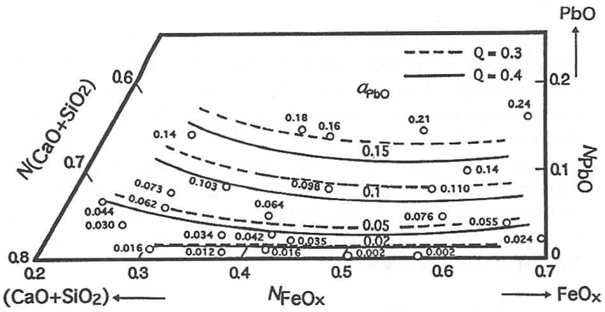

Fig.4. The experimental result and isoactivity curves of PbO in the PbO-FeO_x-(CaO-SiO_2) pseudo-ternary system at Q=0.4 and 1423K. The dashed line are the isoactivity curved at Q=0.3.

The PbO activities near the composition line of R =0.4 are plotted against the PbO content at 1423K in Fig. 5. The PbO activity shows a slightly positive deviation from ideal behavior in both Q values of 0.3 and 0.4 which simulate the oxidation slag of the QSL lead smelting process. An increase in the PbO activity in the slag is observed by the addition of CaO in this figure. The production of high PbO content slag is effective to reduce the volume of discard slag. However, since a rise of the PbO content in the oxidation slag accompanies the formation of a large quantity of dust by vaporization, the PbO concentration in the slag should be controlled in the furnace. For example, the PbO activity is approximately 0.17 at the composition of 35 mass% Pb, Q=0.4 and R=0.4. The equilibrium vapor pressure of PbO over this slag containing 35 mass% Pb is estimated 4×10^{-3} atm. Strong vaporization phenomena might be recognized from the slag phase. Therefore it is concluded that the production of the high PbO slag is disadvantage in the smelting process.

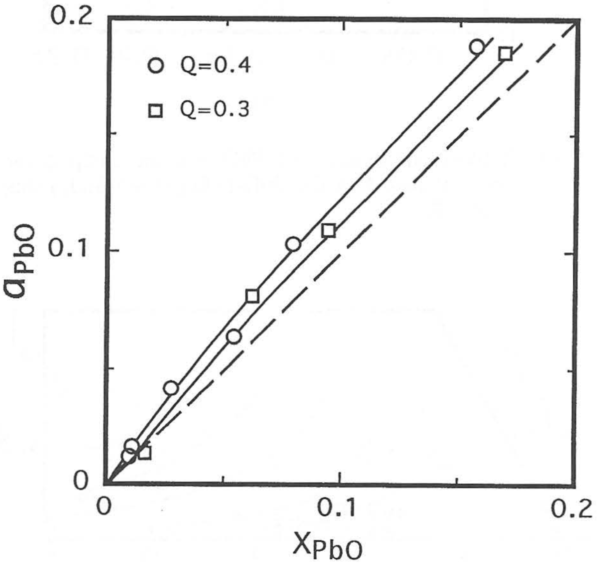

Fig.5. PbO activity near the composition line of R=0.4.

The activity coefficients of PbO along the composition line where R= 0.4 are calculated and shown in Fig. 6. These are compared with the values estimated from the data reported by Taskinen *et al.* at 1473K[4]. A slightly positive deviation from ideality in the present study is obtained while Taskinen *et al.* reported a negative deviation. Takeda investigated the lead loss into ISF slag at 1573K[5]. By interpolating the value of γ_{PbO} reported by Takeda, the activity coefficient of PbO at dilute solution in almost the same slag composition is estimated to be 1.3 at 1573K. This value agrees with the tendency of γ_{PbO} obtained in the present study.

The magnetite activity in the slag increases under strong oxidation atmosphere. To prevent the magnetite precipitation in the smelting process, the information on the (Fe^{3+}/Fe^{2+}) ratio in a slag is required. The isobars of the ratio are shown in Fig. 7. The (Fe^{3+}/Fe^{2+}) ratio increases with increasing FeO_x content even though the oxygen potential is kept constant.

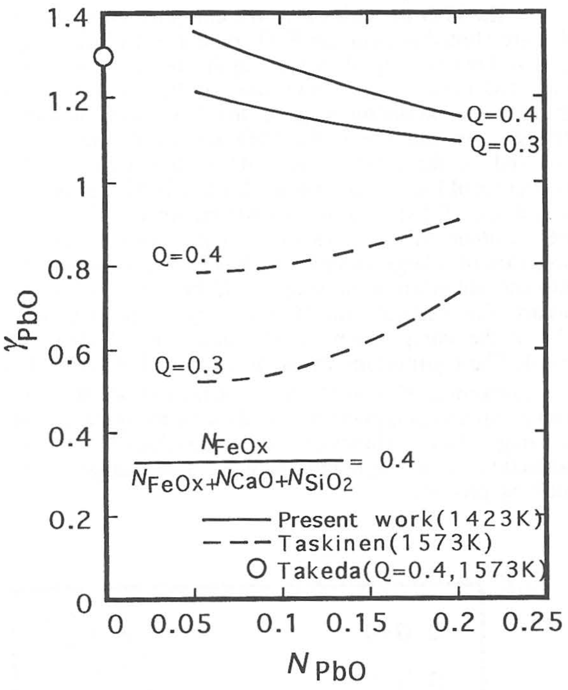

Fig.6. Activity coefficients of PbO near the composition line of R=0.4 in the PbO-FeOx-(CaO-SiO2) slag at 1423K.

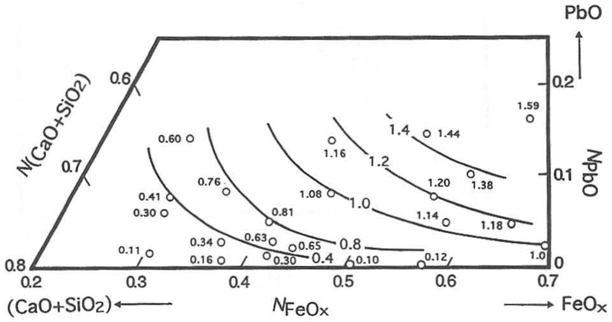

Fig.7. Fe^{3+}/Fe^{2+} ratio of Q=0.4 in the PbO-FeOx-(CaO-SiO2) slag at 1423K.

3-3 Distribution of Minor Element

The distribution ratio of a minor element between the metallic lead and slag phases is defined by Equation (2).

$$L_M^{s/m} = (\text{mass\% M in slag}) / [\text{mass\% M in alloy}] \quad (2)$$

where ( ) and [ ] denote the slag and metal phases, respectively. When the distribution ratio is larger then unity, the minor element condenses in the slag phase.

The concentration of the minor element should be limited within a range where the constant distribution ratio is obtained in the distribution experiment of a minor element. The concentration of the minor element in the metallic lead phase is plotted against the content in the slag phase for copper and silver at a constant slag composition in Fig. 8. A linear relationship passing through the origin is obtained for both cases. Similar behaviors are obtained for arsenic and antimony. Thus, the concentrations of the minor elements were kept within the range in this figure.

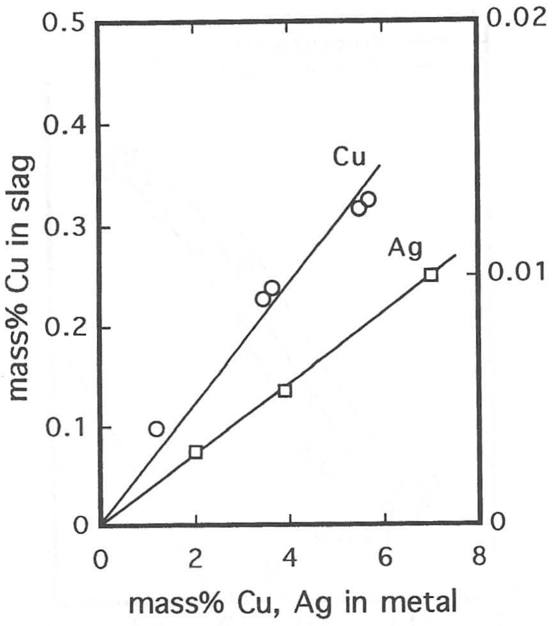

Fig.8. The distribution of copper and silver between the lead and slag phases.

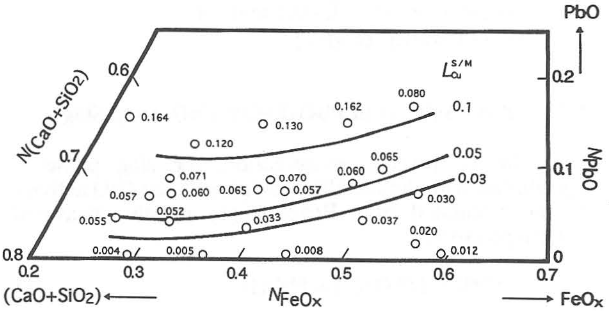

Fig.9. The experimental values and the iso-distribution ratio lines of copper between the lead and slag phases at Q=0.4.

The distribution ratio of copper and the iso-distribution ratio lines near Q=0.4 estimated from the experimental results are illustrated in Fig. 9. The distribution ratio of copper is around 0.05 and the value decreases with decreasing the PbO content. Thus, copper is mainly concentrated in the lead phase and is expected to remain there as the process progresses towards the reduction stage. A slight increase in the distribution ratio of copper however is obtained by dereasing the R value in the experimental region.

The experimental results on the silver distribution are summarized in Fig. 10. Since the value is approximately 1/1000, most of silver dissolves in the molten lead phase. The $L_{Ag}^{s/m}$ value is almost constant over the whole composition region. However, a slight increases is observed with increasing FeOx content in the slag phase. As the value of R in the slag is approximately 0.35 in the QSL slag, the distribution ratios of Cu, Ag, Sb and As between the two phases are plotted against the oxygen potential in the composition region between 0.3 and 0.4 of R in Fig 11. Almost linear relationship is obtained for these minor elements. The distribution ratios of these minor elements at $\log p_{O_2} = -8$ which is similar to the oxygen potential in the oxidation zone of the QSL reactor were determined. The distribution ratios of Ag, Cu, Sb, and As are approximately 2×10^{-3}, 0.1, 1 and 3 at $\log p_{O_2} = -8$, respectively. Judging by these values, silver and copper will dissolve in bullion on the QSL furnace while arsenic might remain in the slag phase. On the other hand, antimony will be distributed in both the bullion and slag phases.

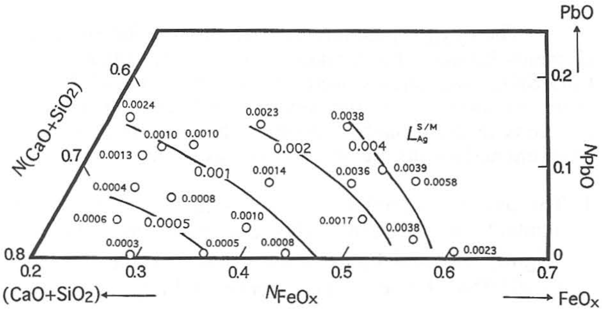

Fig.10. The experimental values and the iso-distribution ratio lines of silver between the lead and slag phases at Q=0.4.

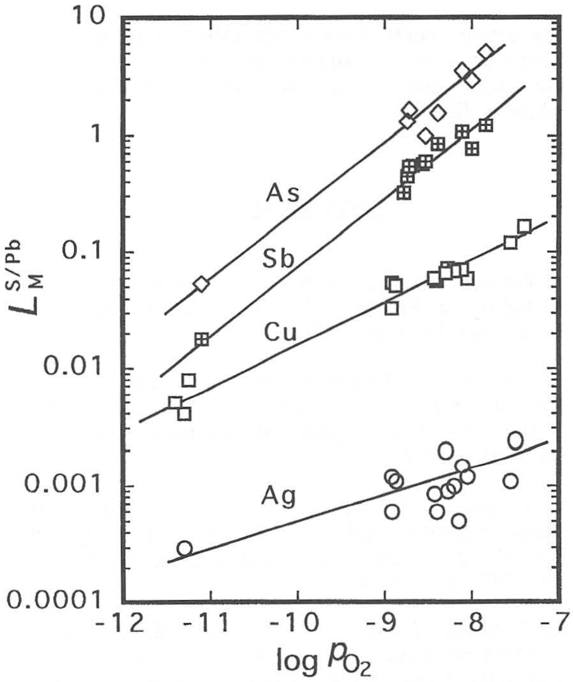

Fig.11. The relationship between $\log L_M^{s/m}$ and $\log p_{O_2}$ in the comosition region between R= 0.3 and 0.4.

The reaction of metal M between the metal and slag phases is expressed by (3).

$$M(l) + \nu/4\ O_2(g) = MO_{\nu/2}\ (l) \tag{3}$$

By rearranging the relationship on the equilibrium constant K_3, activity coefficients of components and the oxygen partial pressure, the distribution ratio is expressed by Equation (4).

$$\log L_M^{s/m} = \log\{(n_T)/[n_T]\} + \log\{[\gamma_M]/(\gamma_{MO\nu/2})\} + \log K_3 + \nu/4 \log p_{O_2} \tag{4}$$

n_T is the total mole numbers in 100g of each phase. If the ratios of activity coefficients and the total mole numbers are constant against the oxygen potential, the valence ν of the minor element in the slag may be evaluate by the slope of the $\log L_M^{s/m}$ agains $\log p_{O_2}$.

Since the distribution ratios of the minor elements increase with increasing the oxygen potential, oxidic dissolution in the slag is presumed for these minor elements as represented by Eq. (4). However, the total mole numbers in the slag phane is not kept at constant as shown in Fig. 12. Then $AgO_{0.5}$, $CuO_{0.5}$, $SbO_{1.5}$ and $AsO_{1.5}$ were estimated based on the slopes that are close to the corresponding oxide species in the present study.

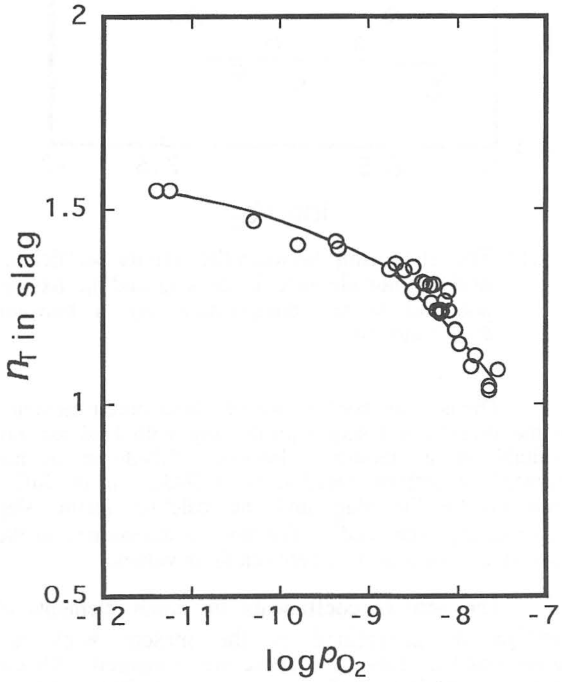

Fig.12. The relationship between (n_T) and $\log p_{O_2}$ in the PbO-FeOx-CaO-SiO2 slag

3.4 Activity Coefficient of Minor Element in Slag Phase.

By applying the experimentally determined distribution ratio of the minor element, the activity coefficient of the element in the slag phase can be estimated based on Eq. (4). The lead phase can be regarded as a Pb-M binary alloy where the minor element

M is dissolved in the metal phase. The activity coefficients of As[6], Sb[7], Ag[8] and Cu[9] at infinite dilute solution in molten lead are 0.96, 0.63, 2.2, and 3.88 at 1423K, respectively. The estimated activity coefficients of the minor elements in the slag phase are illustrated against the oxygen potential higher than $\log p_{O_2}$= -9 in Fig. 13, which corresponds to the oxidation zone of the QSL furnace. The activity coefficient of the $MO_{v/2}$ seems to change very slightly with changes the oxygen potential while the tendency for the arsenic oxide is not clear with wide scatterings.

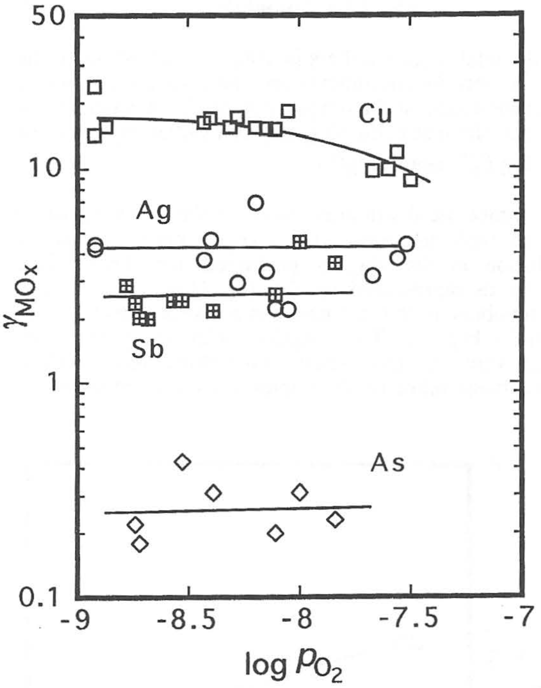

Fig.13. The relationship between the activity coefficients of the minor elements in the slag and the oxygen potential in the composition region between R=0.3 and 0.4.

The activity coefficients of these minor elements in the investigated slag equilibrating with lead are not available in a literature. However, Takeda *et al.* has reported the activity coefficients of $SbO_{1.5}$ in the SiO_2-saturated fayalite slag and the calcium ferrite slag equilibrating with lead[10]. The $SbO_{1.5}$ determined in the present investigation lies between these values.

The activity coefficients of minor elements at $\log p_{O_2}$= -8 determined in the present work are summarized in Table 1. These are compared with the activity coefficients of Cu and Ag in the FeO_x-CaO-SiO_2 slag equilibrating with copper at $\log p_{O_2}$= -8 and 1573K repoted by Takeda.[11,12] The activity coefficients of $SbO_{1.5}$ and $AsO_{1.5}$ were estimated in the FeO_x-CaO slag by Takeda[13]. Nearly identical activity coefficient values were obtained for copper and silver in a similar slag composition even if the equilibrated alloy phase is different. For antimony and arsenic, a discrepancy in the activity coefficient values is observed. The addition of SiO_2 to the FeO_x-CaO slag tends to increase the activity coefficient. Thus a similar behavior is expected for these minor elements in the same composition even though the slags are equilibrated with a different alloy phase.

Table I. The activity coefficients of minor elements in the present work and in the calcium ferrite slag equilibrated with the copper at constant log p_{O_2}.

Element	Present work (1423K)	Cu-slag (1573K)	Reference
$\gamma_{CuO_{0.5}}$	15	9	11
$\gamma_{AgO_{0.5}}$	4	2	12
$\gamma_{SbO_{1.5}}$	2	0.2	13
$\gamma_{AsO_{1.5}}$	0.3	0.02	13

4. CONCLUSIONS

The oxygen potential and the distribution of minor elements between the metallic lead and the PbO-FeO_x-CaO-SiO_2 slag phases were investigated at 1423K in order to obtain the fundamental information on the reactions in the oxidation zone of the QSL reactor. The experimental results are summarized as follows.

1. The oxygen potential increases with increasing PbO content in the PbO-FeO_x-CaO-SiO_2 slag but is slightly affected by changes of the $N_{FeO_x}/(N_{FeO_x}+N_{CaO}+N_{SiO_2})$ ratio in the experimental region.

2. The PbO activity in the slag shows slightly positive deviation from ideality and the activity coefficient of PbO increases with increasing CaO content.

3. The values of 2×10^{-3}, 0.1, 1 and 3 are obtained for the distribution ratio of Ag, Cu, Sb and As at $\log p_{O_2}$=-8 in the composition of %CaO/(%CaO+%SiO_2)=0.4

4. The activity coefficients of the minor elements in the slag with a similar composition are expected to have the same values even when the equilibrating metal phase is different.

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