# The Solubility of Platinum in Molten Slags

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## 1. INTRODUCTION

The basicity of a slag is theoretically to be defined as log $a_{O^{2-}}$, where $a_{O^{2-}}$ is the activity of oxide ion, analogous to PH for an aqueous solution. However, because $a_{O^{2-}}$ cannot be measured in principle, many alternative expressions have been proposed. We have measured carbonate solubility[1)], redox equilibria of $Mn^{3+}/Mn^{2+}$ [2)], $Cu^{2+}/Cu^{+}$ [3)] so far in a series of the attempts to improve the expression of slag basicity. In the measure of $Cu^{2+}/Cu^{+}$, as shown later, the $CaO-Al_2O_3$ systems showed an unexpected trend that as CaO content increases, the $Cu^{2+}/Cu^{+}$ ratio increased. The fluoride containing systems had similar problems, because of the probable formation of $Cu_2F_6^{4-}$ or so. Therefore there is definitely a limit to use the $Cu^{2+}/Cu^{+}$ ratio to express slag basicity. In this paper, we will report the correlation between the platinum solubility and composition for some highly basic slag systems.

Beforehand we had tried to measure the solubility of molten solver, using the reaction: $Ag + \frac{1}{4}O_2 = Ag^{+} + \frac{1}{2}O^{2-}$. Unfortunately, we could not receive reliable results because a large amount of silver was contained in a slag as suspended particles to form a colloidal solution. On the other hand, platinum is stable as solid at temperatures at which most slags are molten and is not likely to form a colloidal solution like molten silver. Classical text books on chemical analysis warn us not use a platinum crucible to fuse alkaline hydroxide or peroxide, because it ruins the crucible through its significant dissolution. This was a hint to start the present work, believing that a large Pt solubility in a highly basic slag may be used as a measure of basicity. Platinum has two stable oxides, PtO and $PtO_2$, and in an aqueous solution $PtO_2^{2-}$ is known as in ionic species. Accordingly, we assume that Pt dissolves in a slag as Eq.(1).

$$Pt + mO_2 + nO^{2-} = PtO^{2n-}_{(2m+n)} \qquad (1)$$

Since basic oxides have larger solubilities as shown later, m and n are positive and Pt is considered to exist as an anion, $PtO_{(2m+n)}^{2n-}$. In the present work, we will discuss the validity of Eq.(1).

## 2. EXPERIMENTAL

The details of the experimental procedures have been written in a separate paper[4)] so that a brief summary is described here. A slag sample prepared from constituent oxide chemicals was held in a platinum crucible for 5 to 15 hours for equilibration mostly in air and in some cases in a $P_{O_2}$ controlled $Ar-O_2$ gas flow. The platinum content of slag was determined by ICP spectrometry.

## 3. RESULTS AND DISCUSSION

In order to examine the dependence of Pt solubility on partial pressure of oxygen, the 65.5 mol pct $CaO-Al_2O_3$ melt was chosen for this purpose. As Figure 1 shows, the slope of the straight line is 0.4, when logarithms of Pt content is plotted against that of $P_{O_2}$. This suggests that m in Eq.(1) is approximately 0.5. In other words, the valence of platinum is +2. Similarly, the temperature dependence of the above system is shown in Figure2.
The solubility increases with raising temperature with heat of the reaction being 20.7 kJ/mol. Since this value is the sum of heat of oxidation of platinum and heat of solution of the oxide into the slag, it must be a small figure because the absolute value of the former is small although it is not exactly known.

Figure 3 shows that the platinum solubility of silicates increases with increasing the content of basic oxide, indicating that in Eq.(1) a complex anion is a stable form rather than a cation as $Pt^{2+}$. Barium oxide is likely to be more basic than $Na_2O$ and is much more so than CaO. This is in contrary to trend in the electro negativity or optical basicity for which BaO and $Na_2O$

have almost identical values.

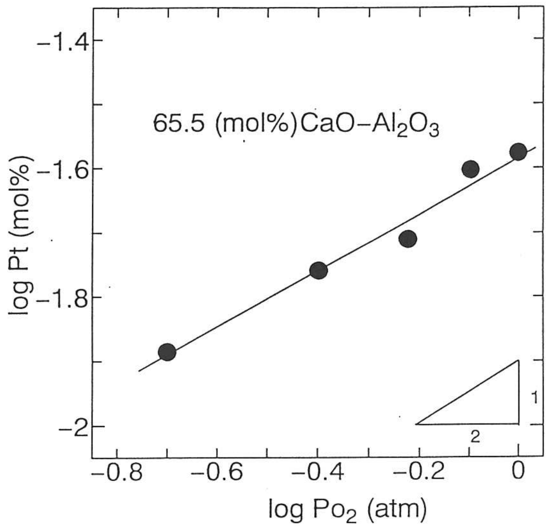

Fig.1. Dependence of Pt solubility on oxygen partial pressure for the 65.5(mol%) CaO-$Al_2O_3$ melt at 1873K.

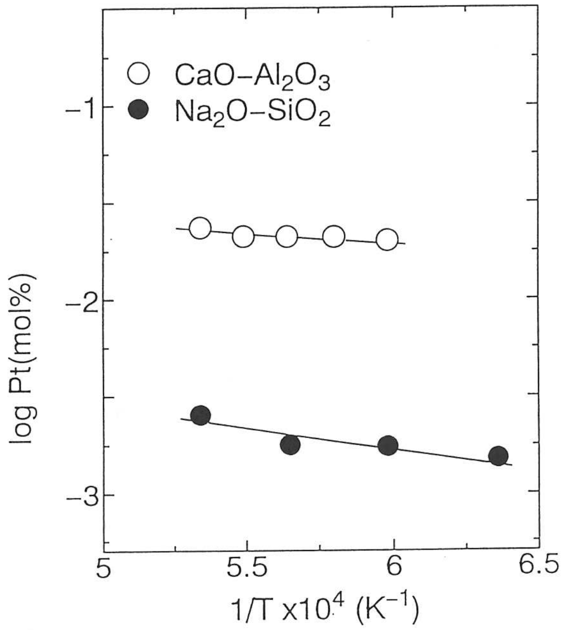

Fig. 2. Dependence of Pt solubility on temperature for the 65.5(mol%)CaO-$Al_2O_3$ and 47.5(mol%) $Na_2O$-$SiO_2$ melts.

As seen in Figure 3, the platinum solubility in the CaO-$SiO_2$ in air is close to the lower limit of chemical analysis, so that this may be a good measure of basicity only for highly basic slags. Sodium silicate are shown to have as much as 0.27mass% of solubility, proving the danger of its use as a flux in chemical analysis.

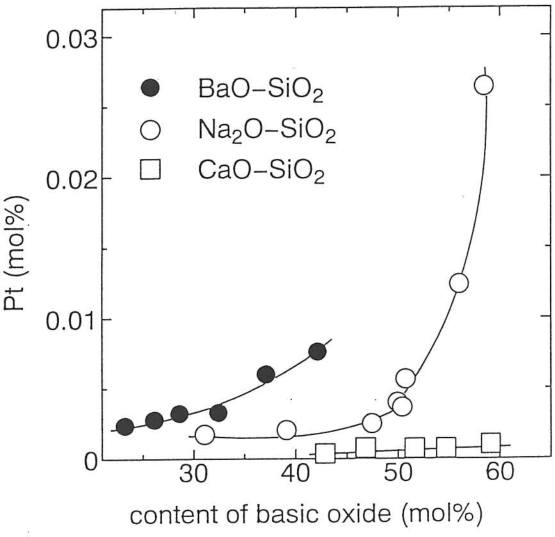

Fig.3. Dependence of Pt solubility on content of basic oxides for the BaO-$SiO_2$, $Na_2O$-$SiO_2$ and CaO-$SiO_2$ systems at 1873K.

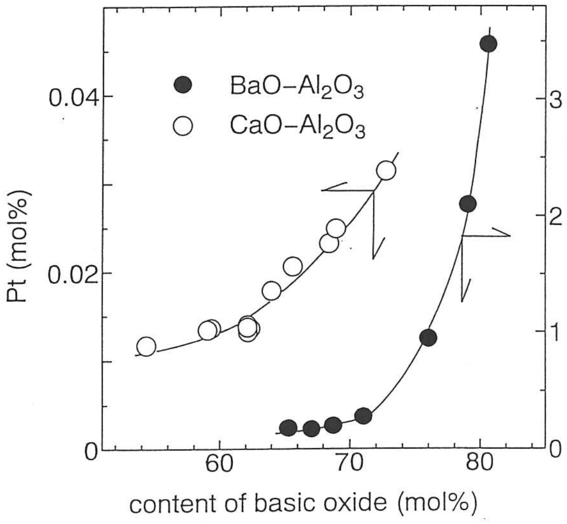

Fig.4. Dependence of Pt solubility on content of basic oxides for the BaO-$Al_2O_3$ and CaO-$Al_2O_3$ systems at 1873K.

Figure 4 compares the Pt solubilities of the BaO-$Al_2O_3$ and CaO-$Al_2O_3$ systems, showing that the Pt solubility increases with increasing the contents of basic oxide. This indicates that according to Eq.(1) $Al_2O_3$ behaves as an acidic component in these systems. In contrary, the behavior of the $Cu^{2+}/Cu^{+}$ in the CaO-$Al_2O_3$ system is not understable, because the relationship described by Eq.(2) is not followed as shown in Figure 5.

$$Cu^{+} + \frac{1}{4}O_2 = Cu^{2+} + \frac{1}{2}O^{2-} \qquad (2)$$

The BaO-$Al_2O_3$ system has an extraordinarily large solubility, suggesting that this can be a strong metal refining agent as a very basic slag.

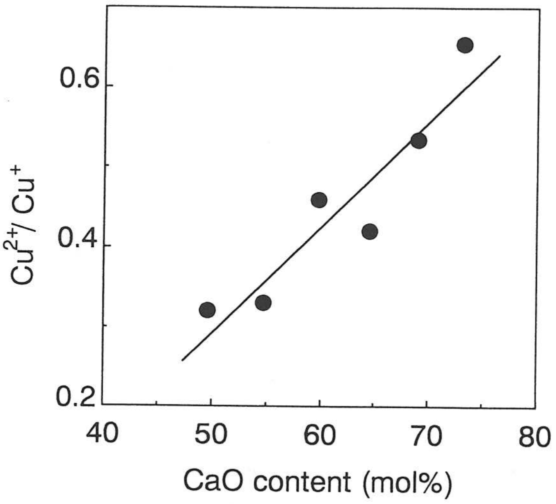

Fig.5. Effect of CaO content on the ratio of $Cu^{2+}/Cu^{+}$ in CaO-$Al_2O_3$ melts.

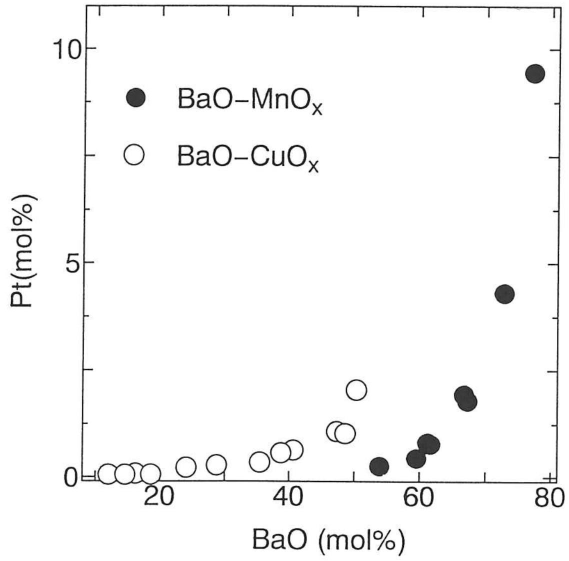

Fig.6. Dependence of Pt solubility on content for the BaO-$MnO_x$(at 1873K) and BaO-$CuO_x$(at 1673K) systems.

The Pt solubility of BaO-$MnO_x$ and BaO-$CuO_x$ systems are shown in Figure 6. Unfortunately, our conventional method to determine the valence of copper or manganese could not be used because platinum ion disturbs the reduction of $Fe^{3+}$ to $Fe^{2+}$ for quantitative oxidation of $Cu^{+}$ or $Mn^{2+}$ in an aqueous solution. Both systems have a very large Pt solubility. In particular, the BaO-MnO system has been found to have a very strong ability to remove phosphorus in carbon saturated Fe-Mn alloys containing a large manganese content, as shown in Figure 7 through its strongly basic property[5]. This is on the same line as the trend in Pt solubility.

The correlations between Pt solubility and carbonate capacity, phosphate capacity and sulfide capacity are shown in Figure 8 for this system, although the temperature for measurement except Pt solubility is 1573K. As seen in the figure, the slope is far smaller than the expected one for every case, because the composition dependences of the activity coefficients differ for different species.

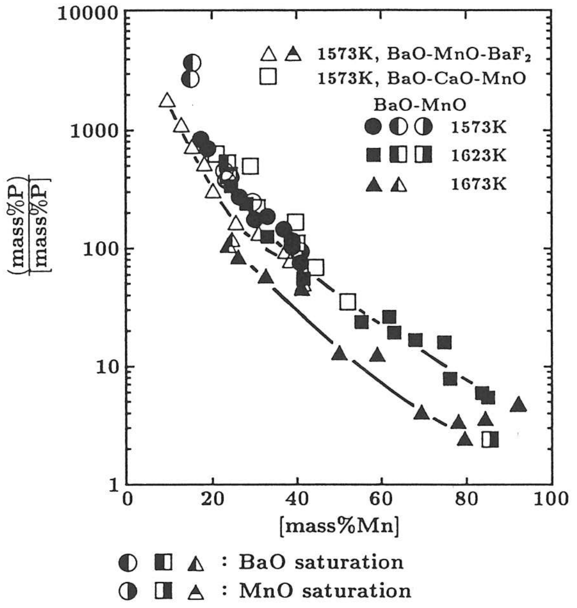

Fig.7. Phosphorus partition ratio between the BaO-MnO, BaO-MnO-$BaF_2$ and BaO-$CaO_{satd.}$-MnO fluxes and Fe-Mn-$C_{satd.}$ alloy at 1573, 1623 and 1673 K as a function of Mn content of Fe-Mn-$C_{satd.}$ alloy.

The $BaO-CuO_x$ system shows an even higher Pt solubility than the $BaO-MnO_x$ system considering the difference in temperature for measurement in Figure 6 and is likely to have a good refining ability of molten copper with a low melting temperature. Since there seems to be no literature in this area and we are planning to examine refining capacities of this slag system.

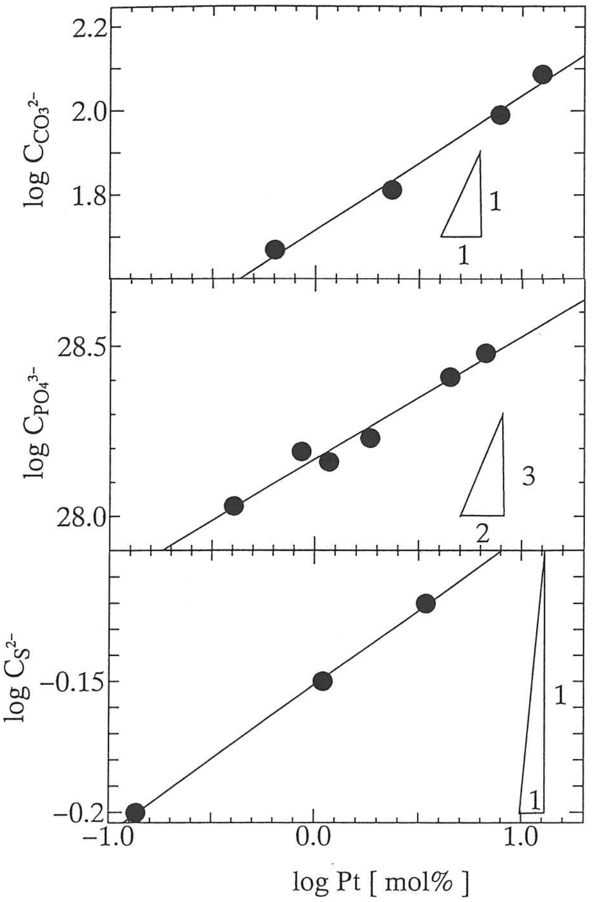

Fig.8. Correlations of $C_{CO_3^{2-}}$, $C_{PO_4^{3-}}$, $C_{S^{2-}}$ with the Pt solubility at 1573K for the $BaO-MnO_x$ system.

## 4. CONCLUTIONS

The platinum solubility in highly basic slags is likely to have a good correlation with other basicity affected parameters such as sulfide capacity. Therefore more data should be accumulated for its use as a measure of slag basicity, because the measurement is relatively easy.

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