

# Effect of Slag Composition on the Solubility of Rhodium in Molten Silicate Slags

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**Abstract:** Rhodium (Rh) is a key material in catalysts and electronics industries. The rarity of Rh resources makes recycling of Rh a significant issue. Aiming to optimize Rh recovery in an oxidizing atmosphere by controlling slag composition, the dissolution behavior of Rh and the effect of slag composition on Rh solubility was investigated. Rh solubility in slags was measured by equilibrating Na<sub>2</sub>O-SiO<sub>2</sub> and CaO-SiO<sub>2</sub> liquid slags with the pure solid Rh at 1473-1873 K in air and the pure O<sub>2</sub> atmosphere. For both slag systems, Rh solubility increased with basic oxide content, suggesting that Rh behaves as an acidic substance in slags. The influence of oxygen partial pressure ( $p_{O_2}$ ) on Rh solubility was found to be more significant than that of temperature. From the correlation of Rh solubility and sulfide capacity, it was proposed that Rh dissolves into slag as the rhodate ion, RhO<sub>2</sub><sup>-</sup>. The dependence of Rh solubility in the CaO-SiO<sub>2</sub> slag at 1873 K on slag composition was similar to those of Pt and Ru. In addition, the effects of Al<sub>2</sub>O<sub>3</sub> and Cu<sub>x</sub>O, addition to the Na<sub>2</sub>O-SiO<sub>2</sub> slag ( $X_{Na_2O} / X_{SiO_2} = 0.97$ ) on Rh solubility at 1473 K in air were examined. Al<sub>2</sub>O<sub>3</sub> was found to behave as an acidic oxide and decreased Rh solubility in the slag. In the presence of Cu<sub>x</sub>O, the dissolution of Cu from the slag into the solid Rh was observed. By using the normalized Rh solubility, it was suggested that Cu<sub>x</sub>O addition caused Rh to increasingly dissolve into the slag.

**Key words:** Platinum Group Metals, Rhodium, Molten Slag, Thermodynamics, Recycling

## 1. Introduction

Platinum group metals (PGMs) are extensively used as key materials in various specialized applications, such as catalysts and electronic devices. The worldwide scarcity of PGM mineral resources makes PGM recycling essential today.<sup>[1]</sup>

Rhodium, one of the major PGMs, is rare and commands very high prices. In order to sustainably use Rh resources, various recovery methods have been developed in recent years. Because Rh is chemically inert, separation of Rh from scrap using a liquid base metal (e.g., Cu and Fe)<sup>[2]-[4]</sup> as the collector metal has been a major recovery method. The conventional process using this approach is base metal matte smelting, in which Rh-containing scrap is mixed with sulfide minerals. While the process focuses on removing gangues, heavy metal impurities, and sulfur, it requires several steps and the recovered product has low Rh content.

As an alternative recovery process, direct Rh separation from scrap has been developed.<sup>[3]-[4]</sup> In this process, Rh is directly extracted from scrap into the collector metal after the melting of scrap. Then, a high Rh-content product is recovered by the partial removal of the collector metal by oxidation. Theoretically, Rh has lower affinity for oxygen at high temperature than most base metals, and it is possible to collect Rh in the metal phase during oxidation. Nevertheless, the process conditions must be carefully controlled in order to maximize Rh recovery. Hence, the effects

of process conditions on the dissolution behavior of Rh into molten slag must be clearly understood.

The dissolution behavior of Pt and Ru into molten slags in an oxidizing atmosphere and the effect of slag composition on Pt and Ru solubility in slags were investigated. Nakamura *et al.*<sup>[5]-[6]</sup> measured Pt solubility in air in various oxide melts, such as the Na<sub>2</sub>O-SiO<sub>2</sub>, the CaO-SiO<sub>2</sub>, and the CaO-Al<sub>2</sub>O<sub>3</sub> systems. It was suggested that Pt solubility depends on slag composition; and Pt exists as the Pt cation (Pt<sup>2+</sup>) in an acidic slag and as a platinate ion (PtO<sub>2</sub><sup>2-</sup>) in a basic slag. Shuto *et al.*<sup>[7]</sup> determined Ru solubility and the dissolution behavior of Ru in the Na<sub>2</sub>O-SiO<sub>2</sub>, the CaO-SiO<sub>2</sub>, and the Na<sub>2</sub>O-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> slag systems in an oxidizing atmosphere. It was reported that under the same experimental conditions, Ru solubility in the Na<sub>2</sub>O-SiO<sub>2</sub> slag was much larger than in the CaO-SiO<sub>2</sub> slag, and Ru dissolved into the slags as a ruthenate ion (RuO<sub>2</sub><sup>-</sup>).

Since the solubility of PGMs is apparently influenced by slag composition, the recovery of PGMs in an oxidizing atmosphere can be optimized by controlling this composition. In order to clearly understand the effect of slag composition on the dissolution behavior of Rh into molten slags, Rh solubility in the Na<sub>2</sub>O-SiO<sub>2</sub> and the CaO-SiO<sub>2</sub> binary slag systems was determined in this study. From the relationship between Rh solubility and sulfide capacity, the dissolution reaction of Rh in ionic form was proposed. In addition, considering that the major source of Rh is spent automobile catalysts (composed of Al<sub>2</sub>O<sub>3</sub>) and that Cu is used as the collector metal for Rh, the effects of Al<sub>2</sub>O<sub>3</sub> and Cu<sub>x</sub>O addition on Rh solubility in the Na<sub>2</sub>O-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> and the Na<sub>2</sub>O-SiO<sub>2</sub>-Cu<sub>x</sub>O slags was examined.

## 2. Experimental

### 2.1 Sample preparation

Slag samples were prepared by melting mixtures of reagent grade SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, Cu<sub>2</sub>O, Na<sub>2</sub>CO<sub>3</sub>, and calcined CaO from reagent grade CaCO<sub>3</sub> in a pure Pt crucible in air, at 1573 K for the Na<sub>2</sub>O-based slag system and at 1893 K for the CaO-based slag system.

Rh thin pellets, which were used in experiments for determining the effect of Cu<sub>x</sub>O, were prepared by compacting the pure Rh powder (about 0.05 g) at a pressing pressure of 50 tons/in<sup>2</sup>, and sintering the pressed Rh pellets at 1623 K under an Ar atmosphere for at least 6 h.

### 2.2 Experimental procedure

Rh solubility in the Na<sub>2</sub>O-SiO<sub>2</sub> and the CaO-SiO<sub>2</sub> binary slags was measured by varying slag composition at various temperature and  $p_{O_2}$ . The measurements were carried out by equilibrating the premelted slag (about 4 g) in a pure Rh crucible (18 mm I.D., 20 mm O.D., 20 mm in depth) in an electric resistance furnace. The schematic diagram of the experimental setup is shown in Figure 1.

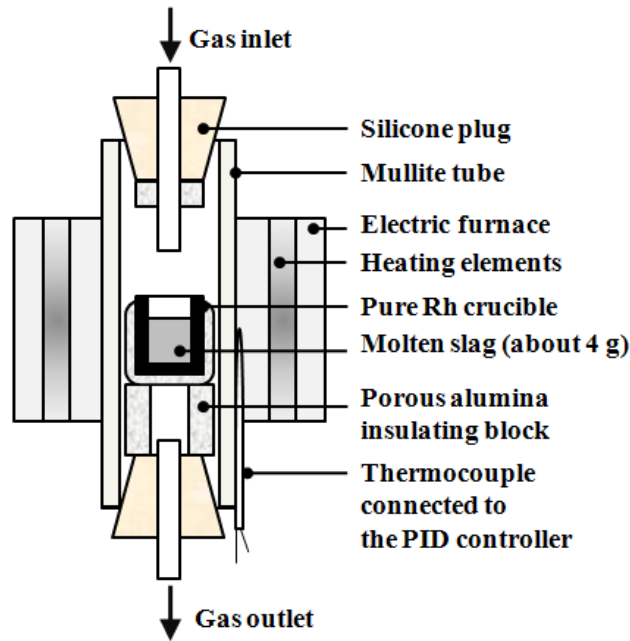


Fig. 1 Schematic diagram of the experimental apparatus.

Oxygen partial pressure,  $p_{O_2}$ , in the system was controlled by streaming dried air or pure  $O_2$  at a flow rate of 150 mL/min.  $CO_2$  was removed from all gases by passage through soda-lime. Moisture was removed by passage through silica gel and magnesium perchlorate, respectively. The temperature in the furnace was controlled within  $\pm 1$  K using a proportional-integral-derivative (PID) controller with a Pt/6%Rh-Pt/30%Rh thermocouple.

The equilibrium time was preliminarily determined as 18 h for both slag systems. After equilibration, samples were removed from the furnace and quenched at room temperature by flushing with Ar gas.

The slag composition in the quenched samples after equilibration was determined by wet chemical analysis. The Rh, Na, Ca, Al, and Cu contents were determined by inductively coupled plasma-atomic emission spectrometry (ICP-AES). The Si content in the slag was determined by the gravimetric method. For the experiments using the  $Cu_xO$ -bearing slags, the Cu content in the solid Rh was determined by ICP-AES.

### 3. Results and discussion

#### 3.1 Dependence of Rh solubility on slag composition

In the  $Na_2O-SiO_2$  slag, at a constant temperature and  $p_{O_2}$ , Rh solubility increased with increasing  $Na_2O$  content (Figure 2). At  $p_{O_2} = 0.21$  atm, Rh solubility in the  $Na_2O-SiO_2$  slag at the similar range of slag composition slightly increased with increasing temperature. Whereas the influence of the temperature change from 1473 to 1573 K on Rh solubility was very small, Rh solubility increases dramatically when  $p_{O_2}$  increases from 0.21 to 1 atm.

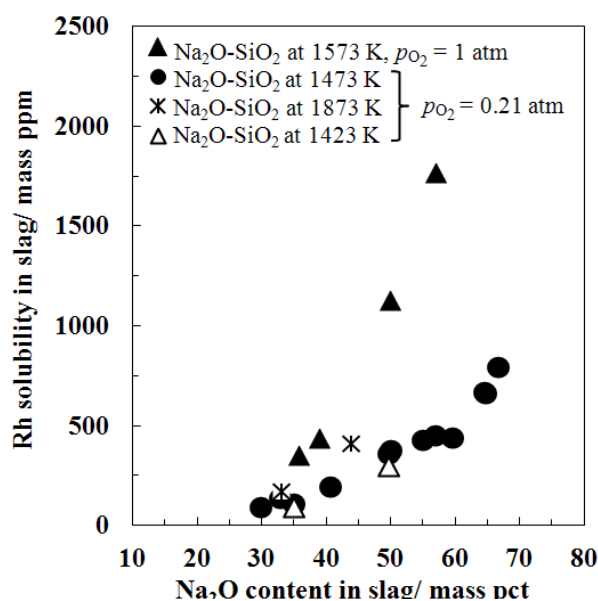


Fig. 2 Dependence of Rh solubility on slag composition in the Na<sub>2</sub>O-SiO<sub>2</sub> binary slag system.

It was proposed that Rh dissolves into the slags by Eq. (1), as stated in the following section. The relationship between Rh content in slags and  $p_{O_2}$  is written in Eq. (3). Consequently, Rh solubility measured at  $p_{O_2} = 0.21$  atm can be estimated to be  $(0.21)^{3/4}$  time of that measured at  $p_{O_2} = 1$  atm, at the same slag composition and temperature. According to the experimental results in Figure 2, the Rh solubility measured at  $p_{O_2} = 0.21$  atm was about  $(0.21)^{3/4}$  time of that measured at  $p_{O_2} = 1$  atm at the same slag composition, provided that the effect of temperature on Rh solubility was very small. Thus, the experimental results were considered to be reasonable.

Rh solubility in the Na<sub>2</sub>O-SiO<sub>2</sub> slag was compared to those of Pt and Ru determined in previous studies.<sup>[5],[7]</sup> The solubilities of the three PGMs increased with increasing Na<sub>2</sub>O content (Figure 3). Since Ru is more likely to be oxidized than Pt and Rh at high temperature, Ru solubility was measured at much lower  $p_{O_2}$ . Ru solubility in the slag was much higher than those of Rh and Pt, while Rh solubility was slightly higher than that of Pt.

In the CaO-SiO<sub>2</sub> slag at 1873 K (Figure 4), the solubilities of the three PGMs increased with increasing CaO content; Ru solubility again was higher than those of Rh and Pt. The PGMs solubilities in the Na<sub>2</sub>O-SiO<sub>2</sub> slag were much higher than in the CaO-SiO<sub>2</sub> slag.

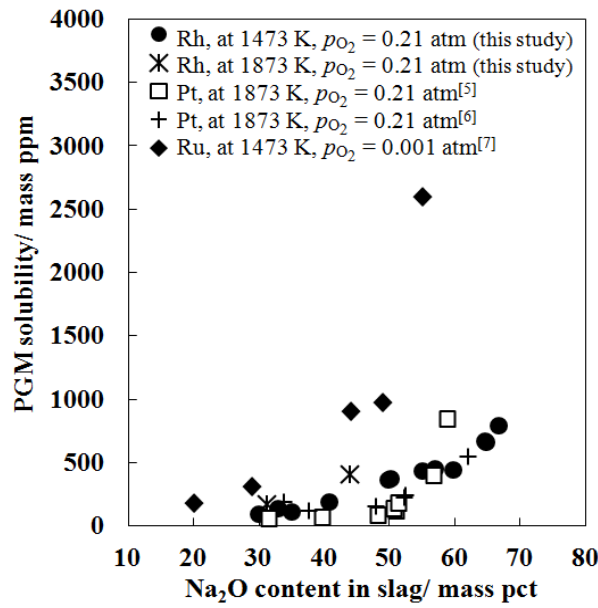


Fig. 3 Comparison of Rh solubility in the Na<sub>2</sub>O-SiO<sub>2</sub> binary slag at various slag compositions to those of Pt and Ru.

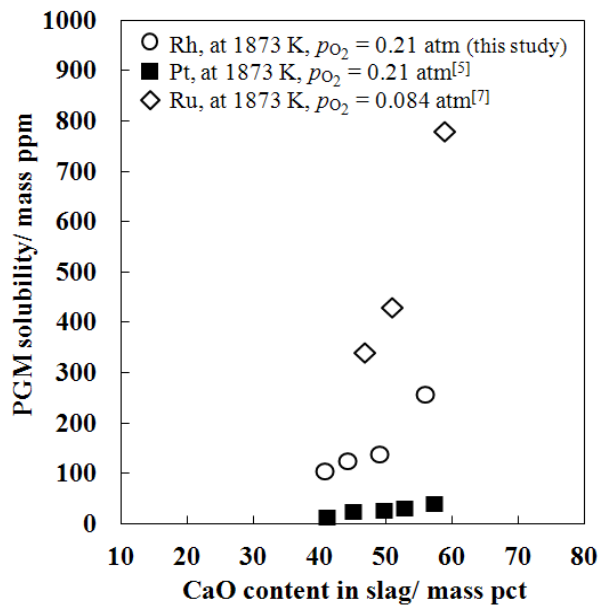
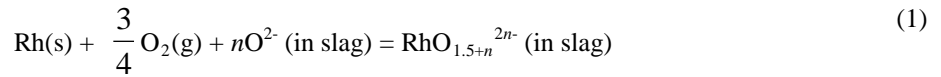


Fig. 4 Comparison of Rh solubility in the CaO-SiO<sub>2</sub> binary slag at various slag compositions to those of Pt and Ru.

### 3.2 Correlation of Rh solubility and sulfide capacity, and the dissolution mechanism of Rh into slags

The previous study reported that Rh dissolved into slag as Rh oxide, RhO<sub>1.5</sub>.<sup>[8]</sup> Since Rh solubility increased with increasing basic oxide content in slags, the dissolution reaction of Rh into slags was written alternatively as follows:



The equilibrium constant of the dissolution reaction (1),  $K_{(1)}$ , is written as:

$$K_{(1)} = \frac{f_{\text{RhO}_{1.5+n}{}^{2n-}} \cdot (\text{mass pct RhO}_{1.5+n}{}^{2n-})}{a_{\text{Rh}} \cdot (p_{\text{O}_2})^{3/4} \cdot (a_{\text{O}^{2-}})^n} \quad (2)$$

where  $a_{\text{Rh}}$  is the activity of the solid Rh,  $f_{\text{RhO}_{1.5+n}{}^{2n-}}$  is the activity coefficient in one mass pct standard state of  $\text{RhO}_{1.5+n}{}^{2n-}$  in slags, and  $a_{\text{O}^{2-}}$  is the activity of the free oxide ion ( $\text{O}^{2-}$ ) in slags, respectively. Accordingly, Eq. (2) can be rewritten as follows:

$$\log (\text{mass pct RhO}_{1.5+n}{}^{2n-}) = n \log a_{\text{O}^{2-}} + \frac{3}{4} \log p_{\text{O}_2} + \log K_{(1)} - \log f_{\text{RhO}_{1.5+n}{}^{2n-}} \quad (3)$$

The term  $\log a_{\text{O}^{2-}}$  is defined for slag basicity. The  $a_{\text{O}^{2-}}$  in slags cannot be directly measured. Instead, sulfide capacity was used to correlate Rh solubility to the slag basicity.

Sulfide capacity,  $C_{\text{S}^{2-}}$ , is the capacity of a melt to hold sulfur as sulfide.<sup>[9]</sup> The sulfide capacities of the CaO-SiO<sub>2</sub> and the Na<sub>2</sub>O-SiO<sub>2</sub> binary slag systems at 1873 K and 1523-1623 K, respectively, were previously reported.<sup>[9]-[10]</sup> The correlation of Rh solubility and sulfide capacity in the Na<sub>2</sub>O-SiO<sub>2</sub> and the CaO-SiO<sub>2</sub> binary slags is shown in Figure 5.

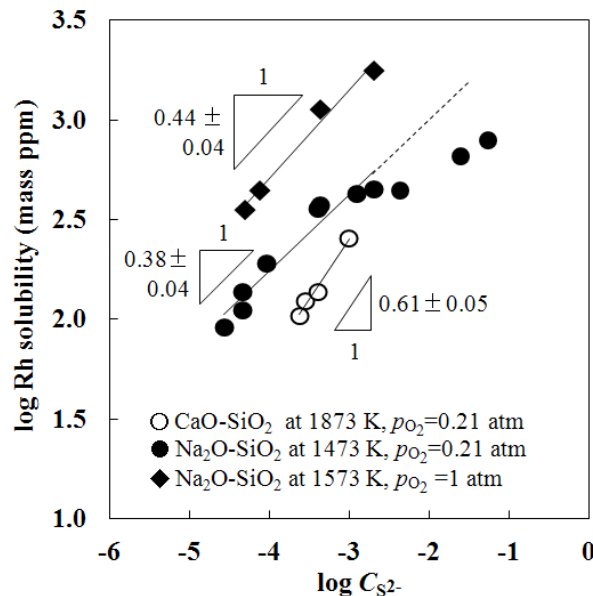
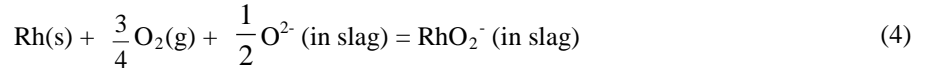


Fig. 5 The correlation of Rh solubility and sulfide capacity in the Na<sub>2</sub>O-SiO<sub>2</sub> and the CaO-SiO<sub>2</sub> binary slags.

Rh solubility increased with increasing sulfide capacity. In Eq. (3), when  $p_{O_2}$ , temperature, and  $f_{RhO_{1.5+n}}^{2n-}$  were assumed to be constant over the range of slag compositions applied in this study, the slope of the linear correlation between Rh solubility and sulfide capacity indicates the value of  $n$ . In Figure 5, the slope of the best-fit linear line was near 0.5. As a result,  $n$  was determined as 0.5 for the  $Na_2O-SiO_2$  and the  $CaO-SiO_2$  binary slags. Thus, the dissolution of Rh into slags can be written in terms of an ionic reaction as follows.



### 3.3 Effect of $Al_2O_3$ and $Cu_xO$ addition on Rh solubility in slag

Rh solubility in the  $Na_2O-SiO_2-Al_2O_3$  and  $Na_2O-SiO_2-Cu_xO$  slags at 1473 K and  $p_{O_2} = 0.21$  atm was measured by varying the content of  $Al_2O_3$  and  $Cu_xO$  at a fixed  $Na_2O/SiO_2$  mol ratio ( $X_{Na_2O}/X_{SiO_2} = 0.97$ ). Rh solubility drastically decreased with increasing  $Al_2O_3$  content in the slag (Figure 6). However, Rh solubility was fairly constant when the Cu content in the slag increased.

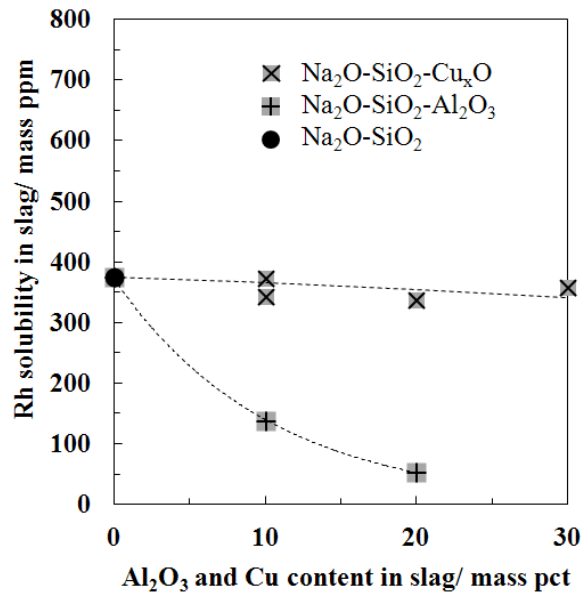


Fig. 6 Dependence of Rh solubility on  $Al_2O_3$  and Cu content in the  $Na_2O-SiO_2-Al_2O_3$  and the  $Na_2O-SiO_2-Cu_xO$  slags ( $X_{Na_2O}/X_{SiO_2} = 0.97$ ) at 1473 K and  $p_{O_2} = 0.21$  atm.

In the  $Cu_xO$  bearing slags, it was found that Cu in the slags dissolves into the solid Rh. This causes the activity of solid Rh to decrease from unity. Thus, the effect of  $Cu_xO$  addition on the dissolution of Rh into slags cannot be determined solely by the dependence of Rh solubility in slag on the Cu content. Considering that Rh dissolves into the slags according to Eq. (4), the relationship between the Rh content in the slags and that in solid alloy can be described by Eq. (4).

$$\Delta G^\circ_{(4)} = -RT \ln \quad (5)$$

$$\frac{f_{\text{RhO}_2^-} \text{ in slag} \cdot (\text{mass pct RhO}_2^- \text{ in slag})}{\gamma_{\text{Rh}} \text{ in solid alloy} \cdot X_{\text{Rh}} \text{ in solid alloy} \cdot p_{\text{O}_2}^{3/4} \cdot a_{\text{O}^{2-}}^{1/2}}$$

Tentatively, by assuming that Rh in the Rh-Cu solid alloy obeys Raoult's law, the normalized Rh solubility, defined as the Rh solubility in the slag divided by Rh content in the solid alloy, can describe the trend of Rh solubility due to  $\text{Cu}_x\text{O}$  addition into the slag. The dependence of the normalized Rh solubility on the Cu content of the slag was derived in Figure 7. The present study suggests that Rh solubility slightly increases with Cu content in the slag.

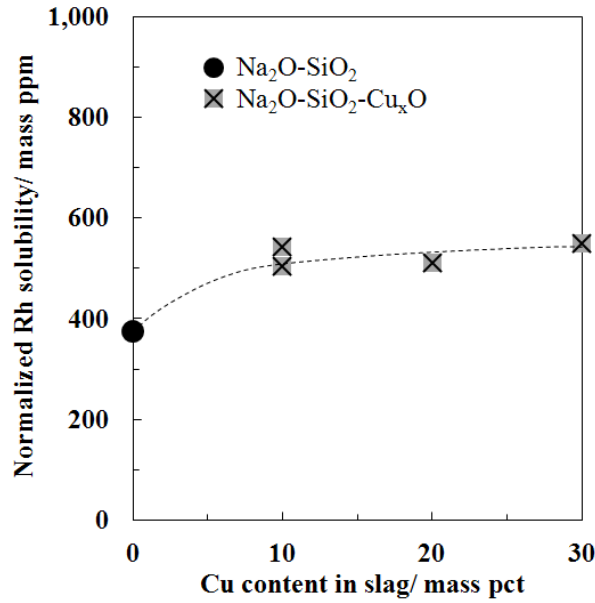


Fig. 7 Dependence of normalized Rh solubility on the content of Cu in the  $\text{Na}_2\text{O-SiO}_2\text{-Cu}_x\text{O}$  systems

( $X_{\text{Na}_2\text{O}} / X_{\text{SiO}_2} = 0.97$ ) at 1473 K and  $p_{\text{O}_2} = 0.21$  atm.

### 3.4 Rhodate capacity of slags

The rhodate capacity of slags is defined as the capacity of slags to absorb the rhodate ion. Following the ionic dissolution reaction of Rh into slags as in Eq. (4), rhodate capacity can be expressed as follows.

$$C_{\text{RhO}_2^-} = \frac{(\text{mass pct RhO}_2^-)}{a_{\text{Rh}} \cdot p_{\text{O}_2}^{3/4}} = K_{(4)} \frac{a_{\text{O}^{2-}}^{1/2}}{f_{\text{RhO}_2^-}} \quad (6)$$

Rhodate capacity depends on the temperature and the slag system. In order to correlate the rhodate capacities measured in this study to various slag systems, the theoretical optical basicity,  $A_{\text{th}}$ , was applied in the replacement of slag composition of the  $\text{Na}_2\text{O-SiO}_2$  and the  $\text{CaO-SiO}_2$  slags. Theoretical optical basicity is an index of oxide basicity, expressed in terms of the ability of an oxide to donate electrons, as proposed by Duffy and Ingram.<sup>[11]</sup> The relationship between rhodate capacity and theoretical optical basicity, plotted using the experimental results from this study, is shown in Figure 8. The rhodate capacities of the binary slag systems at the different temperature were fitted on the same



line. Accordingly, the rhodate capacity of a particular composition of the binary silicate slag at a given temperature is predictable from the correlation of rhodate capacity and theoretical optical basicity. However,  $\text{Al}_2\text{O}_3$  addition revealed the different trend, presumably due to the acidic behavior of  $\text{Al}_2\text{O}_3$  in the slags.

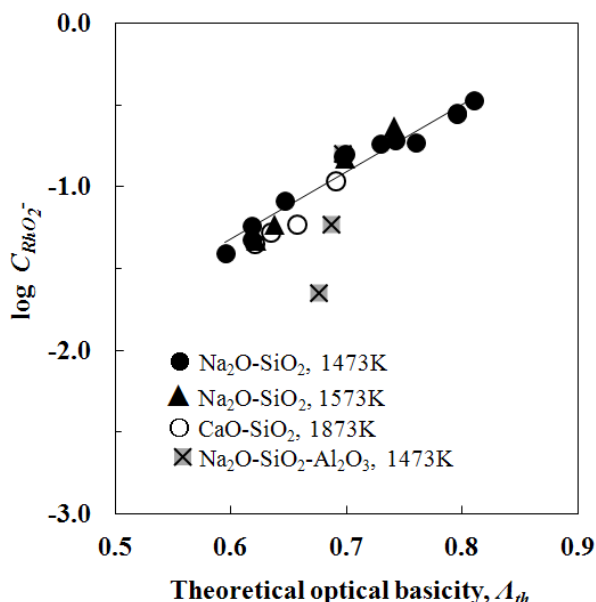


Fig 8. The correlation between rhodate capacity and optical basicity.

#### 4. Conclusions

The effect of slag composition on Rh solubility in molten slags was investigated. In binary slags, Rh solubility increased with increasing basic oxide content, suggesting that Rh behaves as an acidic substance in slag. At similar slag composition in the  $\text{Na}_2\text{O-SiO}_2$  slag, the influence of temperature on Rh solubility was smaller than that of  $p_{\text{O}_2}$ . In the  $\text{Na}_2\text{O-SiO}_2\text{-Al}_2\text{O}_3$  slag ( $X_{\text{Na}_2\text{O}} / X_{\text{SiO}_2} = 0.97$ ), Rh solubility dramatically decreased with increasing  $\text{Al}_2\text{O}_3$  content. With  $\text{Cu}_x\text{O}$  addition, the normalized Rh solubility, defined as the ratio of Rh solubility in the slag to Rh content in the solid alloy, increased with increasing Cu content in the slag, suggesting that the addition of  $\text{Cu}_x\text{O}$  causes Rh to increasingly dissolve into the slag. Among Rh, Pt, and Ru, Ru solubility in the  $\text{Na}_2\text{O-SiO}_2$  slag at the same temperature was much higher than those of Rh and Pt. These differences are considered to be resulted from the different affinity for oxygen of each PGM. By correlating the Rh solubility to the sulfide capacity of the  $\text{Na}_2\text{O-SiO}_2$  and the  $\text{CaO-SiO}_2$  binary slag systems, the dissolution reaction of Rh into slags was proposed. It was suggested that Rh dissolves into slag as the rhodate ion,  $\text{RhO}_2^-$ . Based on the dissolution reaction, the concept and application of the rhodate capacity of slags for estimating the possible Rh content in various slag systems using theoretical optical basicity was proposed.

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