Selective Reduction of AuCl_4^- with CuCl_2^- in an Acidic Chloride Solution Containing Complex Ions of Precious Metals

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In order to obtain a fundamental information on the selective separation of Au from a non-oxidative acidic chloride solutions containing chloride complex ions of precious metals such as Au, Pt and Pd, the selective precipitation of Au by using a reduction method with CuCl_2^- ions was investigated from the electrochemical and kinetic points of view.

In the present study the electrochemical method was used to determine the anodic and cathodic polarization curves of Pt and Au electrodes in an acidic chloride solution containing AuCl_4^- and CuCl_2^- ions, the stoichiometry of reductive precipitation of Au with CuCl_2^- ions and the selective separation of Au from the solution containing chloride complex ions of precious metals such as Au, Pt and Pd.

From the experimental results, it has been concluded that Au can be selectively precipitated with CuCl_2^- ions from the non-oxidative acidic chloride solution containing chloride complex ions of Au and Pd.

However, the selective separation of Au from the solution containing complex ions of Au and Pt is difficult. On the other hand, the electrochemical measurement of the anodic and cathodic polarization curves of Pt and Au electrodes is useful in predicting the reductive precipitation behavior of Au with CuCl_2^- from the solution containing chloride complex ions of precious metals.

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I. Introduction

The recovery and refining of precious metals such as Au, Pt and Pd have been fascinated by metallurgists for a long time. The refining of these metals is treated by using either a traditional pyrometallurgical methods or a hydrometallurgical method such as cyanide leaching from various materials.

However, anode slime and complex sulfide ores containing these precious metals are less soluble in aqueous solutions, and thus in the hydrometallurgical method it is necessary to treat them by an oxidative leaching technique in an acidic solution containing complex forming reagents.

A few studies on the use of complex forming leachants such as thiosulfate, thiocyanate, acidic thiourea, chlorine gas and chloride have been reported for the treatments of various materials, including a few kinetic measurements⁽¹⁾⁻⁽⁷⁾.

On the other hand, the selective separation of various components from the leach solution is one of the most important steps in a series of hydrometallurgical treatments, and thus various separation methods were reported⁽⁸⁾⁻⁽¹²⁾. However, there is no detailed study for the

selective separation of Au by using the reduction method with CuCl_2^- ions from the non-oxidative acidic chloride solution containing chloride complex ions of precious metals.

The present experimental study was carried out to obtain the fundamental data on the selective separation of Au from the acidic chloride solution containing chloride complex ions of precious metals, and the results are discussed from the electrochemical and kinetic points of view.

II. Electrochemical Consideration of Selective Precipitation of Au with CuCl_2^- Ions from an Acidic Chloride Solution Containing Chloride Complex Ions of Precious Metals

In estimating the selective precipitation of Au with CuCl_2^- ions from the non-oxidative acidic chloride solution containing chloride complex ions of precious metals components, it is important to understand the necessary conditions for the required reductive precipitation reaction of Au and the soluble species in acidic chloride solution.

For this purpose, the important reactions were thermodynamically assessed as a function of the reduction potentials at 298 K based on thermodynamic data⁽¹³⁾.

The calculated reduction potentials for the chloride complex ions of precious metals and the reductant in the acidic chloride solution are summarized as follows:

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$$E_{\text{h(v)}} = 1.00 - 0.078 \log a_{\text{Cl}^{-}} + 0.0197 \log a_{\text{AuCl}_{4}^{-}} \quad (1')$$

$$E_{\text{h(v)}} = 0.959 - 0.0887 \log a_{\text{Cl}^{-}} + 0.0148 \log a_{\text{PdCl}_{6}^{2-}} \quad (2')$$

$$E_{\text{h(v)}} = 0.726 - 0.1182 \log a_{\text{Cl}^{-}} + 0.0295 \log a_{\text{PtCl}_{4}^{2-}} \quad (3')$$

$$E_{\text{h(v)}} = 0.702 - 0.0887 \log a_{\text{Cl}^{-}} + 0.0148 \log a_{\text{PtCl}_{6}^{2-}} \quad (4')$$

$$E_{\text{h(v)}} = 0.622 - 0.1182 \log a_{\text{Cl}^{-}} + 0.0295 \log a_{\text{PdCl}_{4}^{2-}} \quad (5')$$

$$E_{\text{h(v)}} = 0.495 - 0.0591 \log a_{\text{CuCl}_{2}^{-}} + 0.0591 \log a_{\text{Cu}^{2+}} + 0.1182 \log a_{\text{Cl}^{-}} \quad (6')$$

As mentioned above, the driving force of reductive precipitation of Au with CuCl_{2}^{-} ions from the solution containing AuCl_{4}^{-} is large. Furthermore, the reduction potential of AuCl_{4}^{-} ions is higher by about 0.3 V than that of PtCl_{6}^{2-} , PtCl_{4}^{2-} and PdCl_{4}^{2-} ions. Therefore, the selective precipitation of Au with CuCl_{2}^{-} ions is expected. However, the potential difference between AuCl_{4}^{-} and PdCl_{6}^{2-} ions is rather small, and thus the selective precipitation of Au from the solution containing AuCl_{4}^{-} and PdCl_{6}^{2-} ions seems to be difficult.

On the other hand, the difference in reduction potentials among PtCl_{4}^{2-} , PtCl_{6}^{2-} and PdCl_{4}^{2-} is small, and the selective precipitation of Pt and Pd with CuCl_{2}^{-} ions is also difficult.

From the electrochemical consideration mentioned above, it appears that Au is selectively separated by using the reduction method with CuCl_{2}^{-} ions from the non-oxidative acidic chloride solution containing chloride complex ions of precious metals. The overall reductive reaction of Au with CuCl_{2}^{-} ions may be expressed by eq. (7).

III. Experimental

1. Materials

The selective precipitation of Au with CuCl_{2}^{-} ions was investigated by using the prepared solution containing chloride complex ions of precious metals.

2. Reagents

All the reagents used in this study were of guaranteed reagent grade. Deionized water with specific resistivity of more than $5 \times 10^4 \Omega \cdot \text{m}$ was used for preparation of the solutions.

3. Analytical method

The concentrations of various ions in the aqueous solutions were analyzed by means of atomic absorption spectrometry. The percentage of precipitation of Au

and other precious metals was calculated by using the analytical data.

4. Experimental procedures

(1) Electrochemical measurements

The rest potentials of various electrodes in an acidic chloride solution containing chloride complex ions of precious metals and the cathodic polarization curves of Au electrode were measured by using a potentiostat and a recorder. A $1.5 \times 10^{-4} \text{ m}^3$ H-shape electrolytic cell fitted up with a rubber lid was used for these measurements. Four necks of the lid were used for inserting a working electrode, a salt bridge and glass tubes as an inlet and an outlet of purging gas, respectively. Prior to the electrochemical measurements, the electrolyte was deoxygenated by bubbling of high purity Ar gas. All of the measurements were carried out at a temperature of 303 K by using a water bath, unless otherwise stated.

A 3.3 M-KCl AgCl-Ag electrode was employed as a reference electrode. On the other hand, the cathodic polarization curves of Au electrode in the electrolyte containing AuCl_{4}^{-} ions were measured by the potential sweeping method at the speed of 0.56 mV/s. The values of potentials were shown by the normal hydrogen scale.

(2) Determination of reductive precipitation behaviors of Au with CuCl_{2}^{-} ions from the acidic chloride solutions containing chloride complex ions of precious methods

A $1 \times 10^{-4} \text{ m}^3$ cylindrical flask was used as a reactor for the reductive precipitation of Au with CuCl_{2}^{-} ions. The solution was agitated by using a magnetic stirrer at a constant speed of 5.3 rev/s. The temperature of solution was kept constant by keeping the reactor in a thermostatic water bath. A $1 \times 10^{-4} \text{ m}^3$ of prepared solution containing various concentrations of AuCl_{4}^{-} ions was introduced into the reactor. When the solution reached at the required temperature, a certain weight of cuprous chloride was added to the solution, and thus the reductive experiments were initiated. The aliquates of the sample solution were sucked up at regular time intervals, and the remaining concentrations of species were analyzed by means of atomic absorption spectrometry. The reductive precipitation degrees of various components were calculated from the analytical data.

IV. Experimental Results and Discussion

1. Rest potentials of various electrodes in an acidic chloride solution containing chloride complex ions of precious metals

In estimating the chloride complex ion form of precious metals in an acidic chloride solution, the rest potential measurements were carried out and the results are shown in Fig. 1. The figure shows that the observed rest potentials of the Au electrode in the acidic chloride solution containing chloride complex ions of Au increase with an increase in the concentration of Au species, and

Fig. 1 Rest potentials of various electrodes in acidic chloride solution containing complex ions of MCl_x^{y-} .

the potential is close to the reduction potential of eq. (1). On the other hand, the observed rest potential of the Pd electrode in the solution containing chloride complex ions of Pd is about 0.35 V lower than the reduction potential of eq. (2), and the potentials and slope are close to the reduction potential of eq. (5). Furthermore, the observed rest potentials of the Pt electrode in the solution containing complex ions of the Pt species increase with an increase in the concentration of the Pt species. The slope of the observed rest potentials is about 0.0145 mV/ $\log a_{\text{complex}}$, and thus the slope corresponds to the reduction potential of eq. (4).

From the rest potential measurements, it appears that the predominant chloride complex ions of precious metals in the non-oxidative acidic chloride solutions are AuCl_4^- , PtCl_6^{2-} and PdCl_4^{2-} .

On the other hand, the time variation of the rest potential of Au electrode in an acidic chloride solution containing complex ions of precious metals is shown in Fig. 2. A sharp drop of the rest potential of Au electrode in the solution containing AuCl_4^- ions is observed by addition of CuCl_2^- ions. However, no substantial difference of the rest potential is observed with or without the coexistence of the species of Pt and Pd, and its potentials after the addition of CuCl_2^- ions are close to the reduction potential of eq. (6). This indicates that the reductive precipitation of Au with CuCl_2^- ions is under cathodic control.

Fig. 2 Effect of CuCl_2^- ions on the rest potential of Au electrode in an acidic chloride solution containing complex ions of MCl_x^{y-} .

2. Anodic and cathodic polarization curves of the Pt and Au electrodes in an acidic chloride solution containing AuCl_4^- and CuCl_2^- ions

In order to obtain a better understanding of the selective precipitation behavior of Au with CuCl_2^- ions, the anodic and cathodic polarization measurements were carried out and the results are shown in Fig. 3.

The cathodic polarization curves of the Au electrode in the non-oxidative acidic chloride solution containing AuCl_4^- ions are divided into three stages. The cathodic current density increases with an increase in the cathodic potentials at the first stage. However, the cathodic current density is almost independent of the change in cathodic potential at the second stage, and the cathodic limiting current is observed. The cathodic limiting current density increases with an increase in the concentration of AuCl_4^- ions. In these stages Au deposition on the cathode occurs. The cathodic current density increases again with an increase in the cathodic potentials at the third stage. Furthermore, the evolution of hydrogen gas occurs on the cathode, and thus the reductions of AuCl_4^- ions and hydrogen ions proceed simultaneously on the cathode.

Fig. 3 Anodic and cathodic polarization behaviors of Au and Pt electrodes in acidic chloride solutions containing complex ions of AuCl_4^- or CuCl_2^- .

On the other hand, the anodic polarization curves of the Pt electrode in the acidic chloride solution containing CuCl_2^- ions are roughly divided into two stages. The anodic current density increases with an increase in the anodic potentials at the first stage. However, the anodic current density of Pt electrode is almost independent of the change in anodic potentials at the second stage, and the anodic limiting current density increases with an increase in the concentration of CuCl_2^- ions. The oxidation of CuCl_2^- ions proceeds in this stage.

From the polarization measurements, it is concluded that the reductive precipitation of Au with CuCl_2^- ions is under cathodic control at higher concentrations of CuCl_2^- ions as compared with that of AuCl_4^- ions.

Although the effects of pH and the concentration of NaCl on the cathodic limiting current density of the Au electrode are not shown in the figure, the values of the cathodic limiting current density are independent of the changes in pH and NaCl concentration at the concentrations below 2 kmol/m^3 .

The effect of the AuCl_4^- concentration on the cathodic limiting current density is shown in Fig. 4. The limiting

Fig. 4 Effect of the concentration of AuCl_4^- ions on the cathodic limiting current density for Au electrode in an acidic chloride solution.

Fig. 5 Effect of temperature on the cathodic limiting current density for Au electrode in an acidic chloride solution containing complex ions of AuCl_4^- .

current density increases with an increase in the concentration of AuCl_4^- ions, and its dependence is of first order with respect to the concentration of AuCl_4^- ions.

The effect of temperature on the cathodic limiting current density is given in Fig. 5. The apparent activation energy is found to be 24.7 kJ/mol for the reductive precipitation of Au. These effects support that cathodic limiting current is controlled by mass transport of AuCl_4^- ions.

3. Reductive precipitation behaviors of Au with CuCl_2^- ions in an acidic chloride solution containing AuCl_4^- ions

In order to understand the selective precipitation of Au with CuCl_2^- ions in an acidic chloride solution containing chloride complex ions of precious metals, a series of experiments were carried out.

The typical reductive precipitation curve of Au with CuCl_2^- ions in an acidic chloride solution containing AuCl_4^- ions is shown in Fig. 6. The change in the precipitation degrees of Au with the retention time at the initial stage is large, and then the degrees increase slightly with an increase in the retention time. The precipitation degree obtained is about 98% at 3.6 ks of the retention time.

The effects of various factors on the reductive precipitation behaviors of Au with CuCl_2^- ions in an acidic chloride solution containing AuCl_4^- ions were estimated by using the precipitation degrees at 3.6 ks of the retention time.

The effect of molar ratio of $\text{AuCl}_4^-/\text{CuCl}_2^-$ on the precipitation degree of Au in an acidic chloride solution is shown in Fig. 7. The precipitation degree of Au increases with an increase in the molar ratios of $\text{AuCl}_4^-/\text{CuCl}_2^-$ at the values below 5.25. In contrast, the precipitation degrees of Au are almost constant at the molar ratios above 5.25. However, the consumption of CuCl_2^- ions is larger than that expected theoretically. This indicates that the reduction of dissolved O_2 in the solution proceeds simultaneously.

The effect of the concentration of AuCl_4^- ions on the precipitation degree of Au is given in Fig. 8. The precipitation degree of Au increases with an increase in

Fig. 6 Typical precipitation curve for Au with CuCl_2^- ions from an acidic chloride solution containing AuCl_4^- ions.

Fig. 7 Effect of the molar ratio of $\text{AuCl}_4^-/\text{CuCl}_2^-$ on the precipitation of Au in an acidic chloride solution containing complex ions of AuCl_4^- .

Fig. 8 Effect of the concentration of AuCl_4^- ions on the precipitation of Au in an acidic chloride solution containing complex ions of AuCl_4^- .

the concentration of AuCl_4^- ions. However, the precipitation degrees of Au decrease with a decrease in the concentration of AuCl_4^- ions at the concentrations below $2 \times 10^{-4} \text{ kmol} \cdot \text{m}^{-3}$. This indicates that the recovery efficiency of metallic Au increases with an increase in the concentration of AuCl_4^- ions in the solution.

Although the effects of other factors on the precipitation behaviors of Au with CuCl_2^- ions were not shown in the figures, no effects of pH and concentration of NaCl on the precipitation of Au are observed. These coincide with the results of cathodic polarization measurements. Thus, the electrochemical measurements such as polarization curves are useful in predicting the selective precipitation behavior of Au with CuCl_2^- ions in the acidic chloride solution containing AuCl_4^- ions.

4. Reductive precipitation behavior of precious metals in the acidic chloride solution containing chloride complex ions of precious metals

In estimating the feasibility of selective precipitation of Au with CuCl_2^- ions from the acidic chloride solution containing chloride complex ions of precious metals, a series of experiments were carried out.

The effect of the coexistence of cupric ions on the precipitation degrees of Au in an acidic chloride solution

is given in Fig. 9. As shown in the figure, no effect of cupric ions on the precipitation degree of Au is observed, and the values of precipitation degrees are about 98% under various conditions.

The effect of coexistence of the complex ions of precious metals on the precipitation behaviors of Au is shown in Fig. 10. The precipitation degrees of Au are almost constant with or without coexistence of PdCl_4^{2-} ions, and its values are about 98% at the various concentration ratios of $\text{PdCl}_4^{2-}/\text{AuCl}_4^-$. Furthermore, no precipitation of Pd is observed. In contrast, the precipitation of Pt is observed at the various concentration ratios of $\text{PtCl}_6^{2-}/\text{AuCl}_4^-$, its values of the precipitation degrees being about 20%.

The effect of the molar ratios for chloride complex ions of precious metals on the precipitation behavior of Au is listed in Table 1. The precipitation of Au is more than 93% at various molar ratios of chloride complex ions of precious metals. Furthermore, the precipitation degrees of Pt are about 20% at any molar ratios. On the other hand, the precipitation of Pd is also observed at higher concentrations of PdCl_4^{2-} ions. However, the precipitation of Pd is less than 1.5%.

From the reductive precipitation experiments mentioned above, it is concluded that Au is selectively

Fig. 9 Effect of cupric ions on the precipitation of Au in an acidic chloride solution containing Complex ions of AuCl_4^- .

Fig. 10 Effect of the concentration ratio of $\text{MCl}_x^-/\text{AuCl}_4^-$ on the precipitation behaviors of precious metals in the binary solution of AuCl_4^- - PdCl_4^{2-} and AuCl_4^- - PtCl_6^{2-} .

Table 1 Effect of the molar ratio of complex ions of precious metals components on the precipitation behavior of Au from the prepared leach solution.

$\left[\begin{array}{l} \text{Solution: } 3.9 \times 10^{-4} \text{ kmol} \cdot \text{m}^{-3} \text{ AuCl}_4^- + \text{PtCl}_6^{2-} + \text{PdCl}_4^{2-} + 1.6 \\ \text{kmol} \cdot \text{m}^{-3} \text{ HCl, Temp: } 298 \text{ K, Rotating speed: } 5.3 \text{ rev/s,} \\ \text{Retention time: } 3.6 \text{ ks, Molar ratio of AuCl}_4^- / \text{CuCl}_2^- : 1/6 \end{array} \right]$			
Molar ratio of $\text{AuCl}_4^- : \text{PtCl}_6^{2-} : \text{PdCl}_4^{2-}$	Precipitation degree (%)		
	Au	Pt	Pd
1:0.5:5	97.5	21.0	1.15
1:0.5:1	92.7	16.8	0
1:0.1:5	98.0	24.3	0.69
1:0.1:1	97.6	17.2	0

precipitated with CuCl_2^- ions from the solution containing complex ions of Au and Pd. However, the selective precipitation of Au from the solution containing complex ions of Au and Pt is difficult. These results coincide with the thermodynamic considerations to the selective precipitation of Au with CuCl_2^- ions from the solution containing chloride complex ions of precious metals.

V. Conclusion

The experimental study was carried out to obtain the fundamental data for the selective separation of Au from the non-oxidative acidic chloride solution containing chloride complex ions of precious metals, and the results are discussed from the electrochemical and kinetic points of view.

The experimental results are summarized as follows:

(1) The predominant species of chloride complex ions of precious metals in the non-oxidative acidic chloride solutions are AuCl_4^- , PtCl_6^{2-} and PdCl_4^{2-} .

(2) The cathodic limiting current density for Au electrode in the acidic chloride solution containing AuCl_4^- ions increases with an increase in the concentration of

AuCl_4^- ions, and its dependence is of first order with respect to the concentrations of AuCl_4^- ions. Furthermore, the apparent activation energy is found to be 24.7 kJ/mol, and thus the reductive precipitation of Au is controlled by the mass transport of AuCl_4^- ions.

(3) The electrochemical measurement such as polarization curves of Pt and Au electrodes in the solution containing AuCl_4^- and CuCl_2^- ions are useful to expect the reductive precipitation behavior of Au with CuCl_2^- ions from the solution containing AuCl_4^- ions.

(4) Au is selectively separated by using the reduction method with CuCl_2^- ions from the non-oxidative acidic chloride solution containing complex ions of Au and Pd, and its values of recovery are more than 93% at the various concentration ratios of $\text{PdCl}_4^{2-} / \text{AuCl}_4^-$. However, the selective precipitation of Au from the solution containing complex ions of Au and Pt is difficult at any concentration ratios of $\text{PtCl}_6^{2-} / \text{AuCl}_4^-$.

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