Leaching of the Mixture of Metallic Gold and Silver

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Abstract

In order to exclude the effect of uneven distribution of gold in anode slime, the dissolution of gold and silver from the metal mixture was investigated in different systems, such as the mixture of hydrochloric acid and oxidizing reagents (H₂O₂, NaClO and HNO₃), thiosulfate and thiourea. In the mixture of HCl and either HNO₃ or H₂O₂, Au was completely dissolved but the leaching percentage of Ag was around 1%. In both thiosulfate and thiourea solution, gold was not dissolved at all. The presence of ferric ion in acidic thiourea solution showed a favorable effect on the leaching of silver but further study is necessary to elucidate the combined effect of ferric ion and sulfuric acid.

Key words: gold, silver, hydrochloric acid, thiosulfate, thiourea

1. INTRODUCTION

Gold and silver have excellent chemical and physical properties and thus lots of work have been performed to recover these two metals together with other precious metals from diverse resources, such as natural minerals, waste industry slags, spent catalysts, and waste printed circuit boards (WPCBs)¹-⁶. In recovering the precious
metals from the above resources, the first step in the process is to dissolve the valuable metals present in the resources. Recently some researchers have reported that the presence of copper could improve the dissolution of gold and silver in either thiosulfate or thiourea system\textsuperscript{7-9).} However, the higher concentration of Cu would result in high consumption of the leaching agents owing to the decomposition of leaching agents\textsuperscript{10,11).} On the basis of the effect on the consumption of the leaching agents, the presence of Ni seems to be more favorable than that of copper\textsuperscript{9).} Furthermore, some additives, such as sodium humic acid (HA), sodium carboxymethyl cellulose (CMC), sodium carboxymethyl starch (CMS) and EDTA could facilitate the leaching of gold and decrease the consumption of thiosulfate. However, Na\textsubscript{2}SO\textsubscript{3} has an adverse effect on the dissolution of gold\textsuperscript{12-14).} In addition, Pb also has a seriously detrimental impact on the dissolution of Au and Ag and thus it is advantageous to remove lead before the leaching step\textsuperscript{15).}

In our previous works on the leaching of gold and silver from anode slime resulted from the recovery of copper, various inorganic reagents and the mixture of HCl and some oxidizing agents were employed to find an efficient leaching system to dissolve both gold and silver from the anode slime\textsuperscript{20,21).} Since the weight percentage of gold and silver was about 1.5 and 4.6 wt\% in the anode slime, gold was not evenly distributed in the anode slime. Hence, there was some uncertainty in the absolute values of the leaching percentage of gold in the various conditions employed in those works. In order to exclude the effect of distribution of gold in the anode slime on the leaching, the mixture of pure gold and silver was employed in the leaching experiments of this work. For thiosulfate system, the effect of adding oxidizing agents and reaction temperature was investigated, while the effect of sulfuric acid concentration on the dissolution of silver and gold was also studied in the thiourea system.

2. EXPERIMENTAL

2.1. Materials

Pure silver (99.9%, 0.5-1 µm, spherical, Alfa Aesar) and gold (99.96%, 0.5-0.8 µm, spherical, Alfa Aesar) were employed for the leaching experiments. In each experiment, the mass of gold and silver in the mixture was maintained at 0.1 and 0.46 g, which resembles the mass ratio of the two metals in the anode slime employed in previous studies. All leaching solutions were prepared with deionized water. The leaching reagents, such as thiourea, thiosulfate, sodium hydroxide, sulfuric acid, hydrochloric acid and nitric acid were of analytical grade.

2.2. Procedures

The leaching experiments were performed in a 500 ml flat-bottom glass reactor fitted with a heating plate with magnetic stirrer. The stirring speed was fixed at 200 rpm in all experiments. During the leaching experiments, the teflon tape and plastic cover were utilized to avoid the solution loss due to evaporation. Once the solution temperature was arrived to the desired temperature, the mixture of gold and silver was put to the leaching solution and then the oxidizing agents were added to the resulting solution. When the leaching experiments were terminated, the solution was separated.
from the residue by using vacuum filtration. The concentration of the metals in the solution was measured by ICP-AES (Perkin Elmer, OPTIMA 8300) after dilution with the corresponding reagents.

3. RESULTS AND DISCUSSION

3.1. Leaching with the mixture of HCl and oxidizing reagents

According to our previous studies\textsuperscript{20}, silver can be completely dissolved in strong HNO\textsubscript{3} solution, while the presence of oxidizing agents is necessary to dissolve gold at the same conditions. Therefore, the effect of the nature of oxidizing agents on the leaching of gold and silver was investigated by using the mixture of HCl and these oxidizing agents. For this purpose, HNO\textsubscript{3}, H\textsubscript{2}O\textsubscript{2} and NaClO were added to the HCl solution and the leaching percentage of the two metals at several experimental conditions was obtained.

Fig. 1 shows the effect of reaction time on the leaching of Au and Ag in aqua regia solution at reaction temperature of 90°C. In these experiments, the volume ratio of HCl to HNO\textsubscript{3} in the leaching solution was controlled to 3:1. Gold was completely dissolved into the aqua regia, while only 1.4% of silver was dissolved in these leaching conditions. In the mixture of nitric and hydrochloric acid, combined effect of the oxidizing role and complex formation by the nitrate and chloride ion facilitates the dissolution of metallic gold into stable tetra-chloroauroinate species\textsuperscript{22}. After the completion of the leaching experiments, some solids were observed on the bottom of the reaction vessel. Since the oxidation potential of silver is much higher than that of gold, silver should be dissolved into aqua regia considering the complete dissolution of gold. The low leaching percentage of silver in Fig. 1 indicates that the silver ion forms solid precipitates AgCl with chloride ion in the leaching solution. Therefore, it can be concluded that the leaching of silver is very difficult in the presence of chloride ion in the leaching solution. Compared to the previous data on the leaching of silver from the anode slime, the leaching percentage of silver from the mixture of metallic gold and silver was much lower than that from the anode slime. This might be ascribed to the existence of copper ions in the leaching solution of anode slime.

The leaching experiments with the aqua regia indicated that the presence of chloride ion had adverse effect on the leaching of silver. Since the leaching percentage of silver by the aqua regia was only 1.4%, it would be easier to recover pure gold from the solution, while silver would be recovered as AgCl. In acidic solution, hydrogen peroxide is one of the most powerful oxidizing agents and can be converted into hydroxyl radicals (•OH),

![Fig. 1. Effect of reaction time on leaching of metals in the aqua regia solution. (Reaction temperature, 90°C; aqua regia, (HCl 75 mL + HNO\textsubscript{3} 25 mL))](image)

![Fig. 2. Effect of reaction time on leaching of metals in the mixture of HCl and H\textsubscript{2}O\textsubscript{2}. (reaction temperature, 90°C; HCl concentration, 3 M; H\textsubscript{2}O\textsubscript{2} concentration: 0.2 M)](image)
which are highly reactive\textsuperscript{23}. The effect of reaction time on the leaching of gold and silver was investigated in the mixture of 3 M HCl and 0.2 M H\textsubscript{2}O\textsubscript{2}. In these experiments, the reaction temperature was maintained at 90\textdegree C. Fig. 2 shows the leaching percentage of gold and silver at several reaction times. Complete dissolution of gold was obtained, while only 0.77\% of silver was dissolved in these experiments.

Owning to strong oxidation of NaClO, it can produce chlorine gas in HCl solution. Therefore, in this work, NaClO was employed as an oxidizing reagent to investigate the leaching behavior of gold and silver in the mixture of 3 M HCl and 0.054 M NaClO at reaction temperature of 90\textdegree C. Fig. 3 shows the effect of reaction time on the leaching of gold and silver by this mixture. As reaction time increased to 4 hours, the leaching percentage of Au decreased slightly from 100 to 96.2\%. In these experiments, the leaching percentage of Ag was about 0.75\%. The slight decrease in the leaching percentage of gold in the prolonged reaction time indicates that the oxidizing power of NaClO would be lessened with reaction time.

Although the absolute concentration of oxidizing agents was different in the above leaching experiments, complete dissolution of gold was possible with the mixture of HCl and either HNO\textsubscript{3} or H\textsubscript{2}O\textsubscript{2}. During the leaching with aqua regia, some toxic gases are evolved from the solution, which would be harmful for the worker and corrosive for the apparatus. Considering that the leaching percentage of silver was lower in the presence of H\textsubscript{2}O\textsubscript{2} than that in HNO\textsubscript{3}, hydrogen peroxide is recommended as an oxidizing agent for the dissolution of metallic gold.

3.2. Leaching with thiosulfate

Thiosulfate is a metastable reagent and a good ligand to gold and silver in alkaline or neutral solution. Therefore, thiosulfate was employed in this work as a leaching agent and the effect of reaction temperature on the leaching of metals is presented studied in Fig. 4. The leaching solution consisted of 40 g/L thiosulfate and 0.3 M H\textsubscript{2}O\textsubscript{2} in 0.5 M NaOH solution. H\textsubscript{2}O\textsubscript{2} was added to the solution as an oxidizing agent and alkaline solution was employed to facilitate the complex formation between the metal ions with thiosulfate. Fig. 4 shows that gold was not dissolved at all even at the reaction temperature of 75\textdegree C with 2 hours reaction time. It has been reported that the leaching kinetics of gold in thiosulfate solution is very slow\textsuperscript{24,25}. In the case of silver, its leaching percentage decreased from 16.4\% to zero as reaction temperature increased from 25 to 75\textdegree C. The decrease

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{fig3.png}
\caption{Effect of reaction time on leaching of metals in the mixture of HCl and NaClO (Reaction temperature, 90\textdegree C; HCl concentration, 3 M; NaClO concentration: 0.054 M)}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{fig4.png}
\caption{Effect of reaction temperature on the leaching of metals in the NaOH solution containing thiosulfate and H\textsubscript{2}O\textsubscript{2} (reaction time, 2 h; reaction temperature, (25, 50, 75\textdegree C); thiosulfate concentration, 40 g/L; H\textsubscript{2}O\textsubscript{2} concentration, 0.3 M, NaOH concentration, 0.5 M)}
\end{figure}
in the leaching percentage of silver with temperature is related to the decomposition of the thiosulfate, resulting in the formation of surface film containing sulfur on the surface of gold and thus in the prevention of the dissolution of silver\(^\text{26}\).

Ferric ion is a strong oxidizing reagent and is often used in the industry. Therefore, the effect of adding ferric ion into thiosulfate solution was investigated. Table 1 shows that the addition of 5 g/L of Fe\(_2\)(SO\(_4\))\(_3\) to 40 g/L thiosulfate solution had negligible effect on the leaching of gold and silver at the reaction temperature of 90°C. No gold was dissolved at all in this mixture. The reason why ferric ion had little effect was ascribed to solution pH. In these experiments, the solution pH was not adjusted and thus colloidal iron hydroxide coatings were observed to form on the surface of the metals due to the hydrolysis of ferric ion, which hindered the dissolution of silver and gold.

### 3.3. Leaching with thiourea

Thiourea is a strong complexing reagent to gold and silver. In acidic solution, thiourea can be transformed into formamidine disulfide in the presence of an oxidizing agent like H\(_2\)O\(_2\) and ferric ion. Since thiourea is unstable in alkaline solution, the leaching experiments with thiourea were performed in the acidic solution\(^\text{27-29}\).

Fig. 5 shows the effect of sulfuric acid concentration in 40 g/L thiourea solution on the leaching of metals at the reaction temperature of 90°C. No gold was dissolved at all and the leaching percentage of silver decreased rapidly from 11.4 to 0.4% as the concentration of H\(_2\)SO\(_4\) increased from zero to 4 M. Sulfuric acid has a strong tendency to protonate thiourea and thus the effective concentration of thiourea would be decreased as sulfuric acid concentration increases. Therefore, the rapid decrease in the leaching percentage of silver might be related to the protonation of thiourea by sulfuric acid\(^\text{30}\).

In the mixture of 40 g/L thiourea and 4 M sulfuric acid solution, the effect of adding ferric ion on the leaching of metallic Au and Ag was represented in Table 2 at the reaction temperature of 25°C. Table 2 shows that addition of ferric ion had favorable effect on the dissolution of silver but the leaching of gold was not affected. The presence of 5 g/L Fe\(_2\)(SO\(_4\))\(_3\) in the mixture of thiourea and sulfuric acid improved the dissolution of silver 7.9 to 49.0%. This is ascribed to the slower formation kinetics of formanidine disulphide, which will hinder the dissolution of silver and gold, with ferric ions than hydrogen peroxide\(^\text{31}\). Furthermore, some of thiourea can be oxidized by ferric ion to form either

### Table 1. Effect of ferric ion on the leaching of metals in the thiosulfate solution. (Reaction time, 2 h; reaction temperature, 90°C; thiosulfate concentration, 40 g/L; Fe\(_2\)(SO\(_4\))\(_3\) concentration 0; 5 g/L)

| Oxidants | Leaching percentage, % |
|----------|------------------------|
|          | Au        | Ag       |
| 0        | 0         | 0.87     |
| Fe\(^{3+}\) | 0        | 0.42     |

### Table 2. Effect of ferric ion on the leaching of metals in the mixture of thiourea and sulfuric acid. (H\(_2\)SO\(_4\) concentration, 4 M; reaction time, 2 h; reaction temperature, 25°C; thiourea concentration, 40 g/L; Fe\(_2\)(SO\(_4\))\(_3\) concentration 0; 5 g/L)

| Oxidants | Leaching percentage, % |
|----------|------------------------|
|          | Au        | Ag       |
| 0        | 0         | 7.94     |
| Fe\(^{3+}\) | 0        | 48.99    |
sulfur or ferric sulfate complex ([FeSO$_4$·CS(NH$_2$)$_2$]$_n$), which passivates the surface of the metals and thus prevents the leaching of gold$^{29,31}$. Therefore, extensive works are needed to correlate the effect of the constituents in this mixture with the leaching behavior of the metallic gold and silver.

4. CONCLUSION

Leaching of metallic gold and silver was investigated in three kinds of leaching solutions such as the mixture of HCl and oxidizing reagents (HNO$_3$, H$_2$O$_2$ and NaClO), thiosulfate and thiourea solutions. Gold was completely dissolved into the mixture of HCl and HNO$_3$ or H$_2$O$_2$, while less than 1.5% of silver was dissolved in the HCl mixture.

Gold was not dissolved at all in the NaOH solution containing thiosulfate and H$_2$O$_2$. The leaching percentage of silver was rapidly decreased from 16.4% to zero as reaction temperature increased from 25 to 75°C. The mixture of thiourea and sulfuric could not dissolve gold at all and the leaching percentage of silver was decreased from 11.4 to 0.4% as sulfuric acid concentration increased to 4 M. The addition of ferric ion to this mixture improved the leaching percentage of silver.

Acknowledgement

This work was supported by the Global Excellent Technology Innovation of the Korea Institute of Energy Technology Evaluation and Planning (KETEP), granted financial resource from the Ministry of Trade, Industry &Energy, Republic of Korea (No. 20165010100810). We express sincere thanks the Korea Basic Science Institute (KBSI), Gwangju branch for providing ICP-OES data.

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