

금과 은 금속혼합물의 침출

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Leaching of the Mixture of Metallic Gold and Silver

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요 약

양극홀에서 금의 불균일 분포에 따른 영향을 배제하기 위해 금과 은 금속혼합물을 사용하여 염산과 산화제(질산, 과산화수소, 차아염소산나트륨)의 혼합용액, thiourea 및 thiosulfate에 의한 침출실험을 수행했다. 염산에 산화제로 질산이나 과산화수소를 첨가한 용액에서 금은 모두 용해되었으나, 은의 침출율은 1% 정도이었다. Thiourea와 thiosulfate용액에서 금은 전혀 용해되지 않았다. 산성의 thiourea용액에 제 2철이온을 첨가하면 은의 침출율이 상승했으며 제 2철이온과 황산의 복합효과를 규명하기 위해서는 추가 연구가 필요하다.

주제어 : 금, 은, 염산, thiosulfate, thiourea,

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 (H_2O_2 , NaClO and HNO_3), thiosulfate and thiourea. In the mixture of HCl and either HNO_3 or H_2O_2 , 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

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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 system⁷⁻⁹). However, the higher concentration of Cu would result in high consumption of the leaching agents owing to the decomposition of leaching agents^{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 copper⁹). 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, Na₂SO₃ has an adverse effect on the dissolution of gold¹²⁻¹⁴). 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 step¹⁵).

In addition, the kinetic study on the leaching of gold and silver using different systems has been done to investigate the leaching mechanism in each system^{4,16-19}). According to these works, the leaching reaction of gold and silver in either thiosulfate or thiourea solution is mostly controlled by either the mass transfer of oxygen to the solid-liquid interface or the chemical reaction at the interface.

Compared with the traditional cyanide leaching, the mixtures of hydrochloric acid and oxidizing reagents are also effective in the leaching of gold from anode slime. However, some toxic gases were evolved during the leaching process and the reagents are seriously corrosive to the instruments. Nonetheless, thiosulfate and thiourea are less toxic to environment and have a greater selectivity to the gold and silver and faster kinetics of gold dissolution. The disadvantages of thiosulfate and thiourea are the high consumption of reagent and the high price of oxidants. Since the related problems have not been solved, thiosulfate and thiourea systems have not been applied to commercial operation²).

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^{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 studies²⁰⁾, silver can be completely dissolved in strong HNO₃ solution, while the presence of oxidizing agents are 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, HNO₃, H₂O₂ 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 HNO₃ 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-chloroaurate species²²⁾. 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

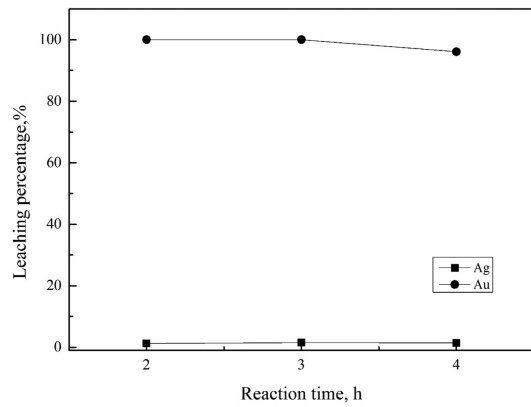


Fig. 1. Effect of reaction time on leaching of metals in the aqua regia solution. (Reaction temperature, 90°C; aqua regia, (HCl 75 mL + HNO₃ 25 mL))

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 ($\cdot\text{OH}$),

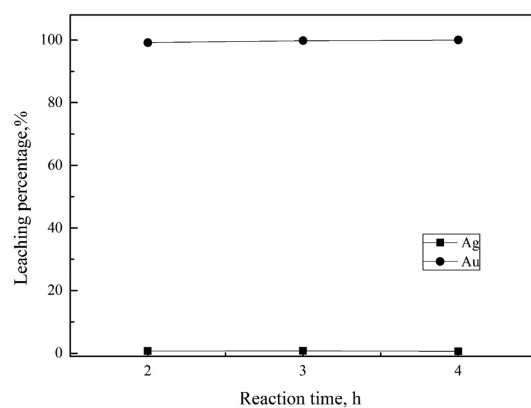


Fig. 2. Effect of reaction time on leaching of metals in the mixture of HCl and H₂O₂. (reaction temperature, 90°C; HCl concentration, 3 M; H₂O₂ concentration: 0.2 M)

which are highly reactive²³). 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 H₂O₂. In these experiments, the reaction temperature was maintained at 90°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.

Owing 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°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 HNO₃ or H₂O₂. During the leaching with aqua regia, some toxic gases are evolved

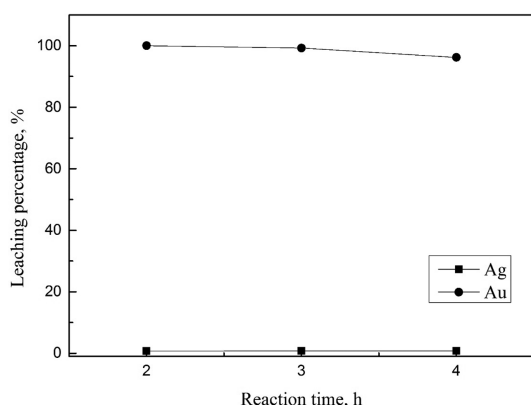


Fig. 3. Effect of reaction time on leaching of metals in the mixture of HCl and NaClO (Reaction temperature, 90°C; HCl concentration, 3 M; NaClO concentration: 0.054 M)

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 H₂O₂ than that in HNO₃, 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 H₂O₂ in 0.5 M NaOH solution. H₂O₂ 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°C with 2 hours reaction time. It has been reported that the leaching kinetics of gold in thiosulfate solution is very slow^{24,25}). In the case of silver, its leaching percentage decreased from 16.4% to zero as reaction temperature increased from 25 to 75°C. The decrease

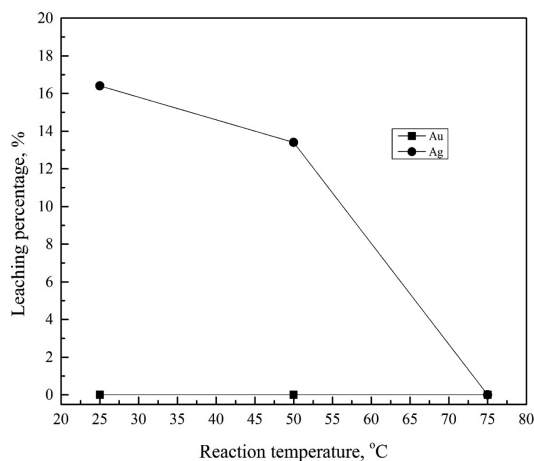


Fig. 4. Effect of reaction temperature on the leaching of metals in the NaOH solution containing thiosulfate and H₂O₂ (reaction time, 2 h; reaction temperature, (25, 50, 75°C); thiosulfate concentration, 40 g/L; H₂O₂ concentration, 0.3 M, NaOH concentration, 0.5 M)

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; Fe₂(SO₄)₃ concentration 0; 5 g/L)

Oxidants	Leaching percentage, %	
	Au	Ag
0	0	0.87
Fe ³⁺	0	0.42

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 silver²⁶).

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 Fe₂(SO₄)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 H₂O₂ and ferric ion. Since thiourea is unstable in alkaline solution, the leaching experiments with thiourea were performed in the acidic solution²⁷⁻²⁹).

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 H₂SO₄ 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

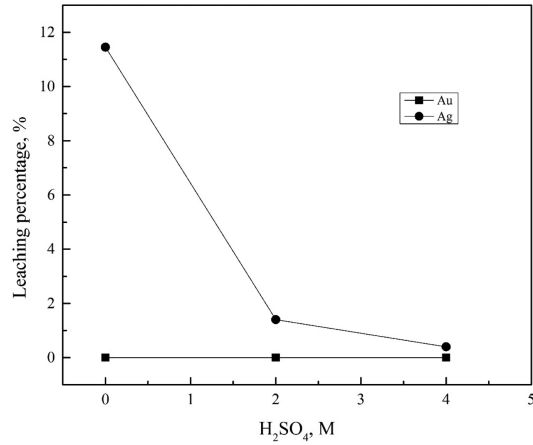


Fig. 5. Effect of H₂SO₄ concentration on leaching of metals in the mixture of thiourea and sulfuric acid solution (Reaction time, 2 h; reaction temperature, 25°C; thiourea concentration, 40 g/L)

acid concentration increases. Therefore, the rapid decrease in the leaching percentage of silver might be related to the protonation of thiourea by sulfuric acid³⁰).

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 Fe₂(SO₄)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 formamidine disulphide, which will hinder the dissolution of silver and gold, with ferric ions than hydrogen peroxide²). Furthermore, some of thiourea can be oxidized by ferric ion to form either

Table 2. Effect of ferric ion on the leaching of metals in the mixture of thiourea and sulfuric acid. (H₂SO₄ concentration, 4 M; reaction time, 2 h; reaction temperature, 25°C; thiourea concentration, 40 g/L; Fe₂(SO₄)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 ($[\text{FeSO}_4 \cdot \text{CS}(\text{NH}_2)_2]^+$), 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_2O_2 and NaClO), thiosulfate and thiourea solutions. Gold was completely dissolved into the mixture of HCl and HNO_3 or H_2O_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_2O_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.

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