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TECHNICAL NOTE

Recovery of Silver from Thiourea Solution by Ion Flotation

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ABSTRACT

A laboratory investigation was undertaken on the silver–thiourea system for the recovery of silver by ion flotation. An anionic surfactant, sodium dodecylbenzenesulfonate, reacted readily with the silver–thiourea complex cation to form a colloidal precipitate (sublate), and the sublate was then floated by tiny bubbles. The influences of several factors on the flotation efficiency were studied. The recovery rate reached 96% under optimum conditions. Pure metallic silver was easily obtained from the floated sublate by thermal decomposition at 900°C. The proposed process is fast, simple, and economical, and it may be useful for both laboratory and industrial recovery of silver.

Key Words. Recovery; Silver; Thiourea; Sodium dodecylbenzenesulfonate; Flotation

INTRODUCTION

Cyanide has been used for the leaching of gold and silver from crushed ores in hydrometallurgical processes for most of this century. Many successful hydrometallurgical plants have demonstrated that the cyanide-leaching technique is very practical. However, cyanide is a extremely dangerous chemical, and it is poisonous to all life forms. Growing public sensitivity to environmental and waste disposal issues has moved noncyanide-technique research into a priority position. Among the proposed noncyanide techniques, the thiourea-leaching technique is perhaps the most practical method. The metal-replacement process is a conventional method for the recovery of gold and silver from thiourea media. Metallic zinc and ferrum are used to replace the precious metals from leaching solutions. However, there are some disadvantages in the method: for example, the conditions for complete replacement are difficult to control, and the refinement procedures of gold and silver are usually complex and time-consuming. Therefore, there is great interest in developing other methods.

Among separation processes, flotation has the advantages of rapidity and simplicity, and it is suitable for the separation and preconcentration of ions from dilute solutions (1–5). In recent years, flotation has found use in the industrial recovery of gold and silver. Ion flotation processes for the recovery of silver from photographic bleach-fix solutions have been reported by two group of researchers (6, 7). Zouboulis et al. developed two flotation methods for the recovery of gold from thiourea leaching solutions (8, 9), but no flotation studies on the silver–thiourea system have been found in the literature.

Inspired by the previous successes of other researchers, we carried out a flotation investigation on the silver–thiourea system. The process presented here involves the flotation of the silver–thiourea complex cation with sodium dodecylbenzenesulfonate (SDBS). Pure metallic silver was recovered from the precipitate phase by thermal decomposition at 900°C. The influences of several factors on the recovery were studied, and the optimum conditions are presented.

EXPERIMENTAL

Apparatus and Reagents

The flotation apparatus used was similar to that described in an earlier paper (10). The flotation cell was made by joining a G4 (3–4 μm nominal pore size) funnel to a glass tube. A hole was drilled in the funnel 1 cm above the sintered-glass disk and fitted with a stopper for sample removal by a syringe. A non-oil compressor was used for bubbling. The flotation system is illustrated in Fig. 1 A Model WYX-401 Atomic Absorption Spectrometer (Shenyan Analytical Instrument Factory, China) was used for the determination of silver.

All chemicals used in this study were of analytical-reagent grade. A 0.02 mol·dm^{-3} $AgNO_3$ solution was prepared by dissolving 0.8494 g silver nitrate in distilled water and making the solution up to 250 cm^3. A 0.1 mol·dm^{-3} thiourea solution and a 0.01 mol·dm^{-3} SDBS solution were prepared in water.

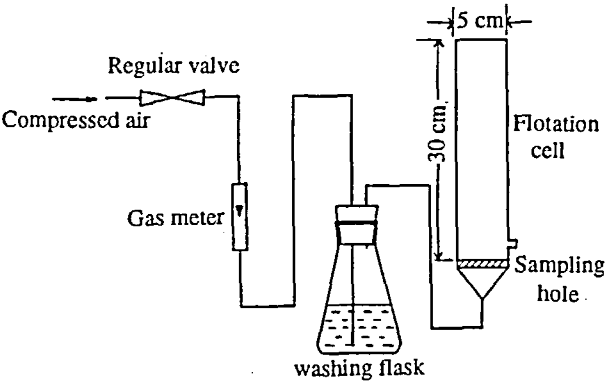

FIG. 1 Diagram of flotation system.

Procedures

A solution was prepared for flotation by pipeting a appropriate amount of silver solution into a 100-mL volumetric flask, followed by addition of 0.5 mL ethanol and appropriate amounts of thiourea solution and SDBS solution, and then diluting to volume. The solution was stirred for 10 minutes and then transferred to the dry flotation cell. Compressed air saturated with water was passed through the sintered-glass disk for 25 minutes. The flow rate was controlled by a regulator valve to be 30 $\mathrm{mL \cdot min^{-1}}$. The flotation rates were monitored by measurements on samples removed from the cell by a syringe. Silver in the thiourea medium was determined by a AAS method proposed by Zha (11), and the flotation rate (F) was then calculated as follows:

$$F(\%) = (1 - C_r/C_0) \times 100$$

where C_0 is the initial silver concentration in solution and C_r is the residual silver contentration in solution after precipitation and flotation.

After maximum flotation was achieved, the sublates were collected and decomposed by thermal treatment at 900°C for the recovery of metallic silver.

RESULTS AND DISCUSSION

Choice of Collector

In an ion flotation process, a collector with a charge opposite to that of the ion to be floated is desirable. It is known that silver exists as the complex cation $Ag(TU)_3^+$ in a thiourea medium, where TU represents thiourea. Therefore, anionic surfactants must be used as collectors. In our earlier study (10), SDBS was confirmed to be an efficient collector for the flotation of cationic ions. As a cheap anionic surfactant, SDBS is advantageous for industrial use. Therefore SDBS was chosen as a collector in the present investigation. Upon introduction of the collector into the solution containing $Ag(TU)_3^+$, a white colloidal precipitate appeared immediately. Because the filtration process for the recovery of the colloidal precipitate turned out to be tedious and time-consuming, a flotation procedure seemed to be a reasonable alternative for the recovery of silver.

Effect of Thiourea Concentration

At low thiourea concentration, silver forms a precipitate with thiourea. As the thiourea/silver ratio increases above 1:1, the precipitate begins to dissolve. To convert 100% silver into the complex cation of $Ag(TU)_3^+$, thiourea must be present in at least a 3:1 molar ratio to silver. Because the existing species of silver depend on the thiourea/silver ratio, it is important to know the effects of the ratio on flotation efficiency. Investigations for this purpose have been carried out, and the results are summarized in Table 1. It is observed that flotation of silver takes place at any thiourea/silver ratio. The reason for this phenomenon may be that all three species, Ag(TU), $Ag(TU)_2^+$, and $Ag(T)_3^+$, can be floated with SDBS. However, maximum flotation efficiency is achieved only when the molar ratio is above 3.5:1. From the experimental results, we came to the conclusion that careful control of thiourea concentration is not necessary for achieving complete flotation as long as there is an excess of thiourea.

Effect of Collector Concentration

As the sublate salt has a stoichiometric ratio of colligend to collector, in order to obtain complete flotation of monovalent ion the collector must

TABLE 1
Effect of TU/Ag Molar Ratio on Flotation Rates[a]

TU/Ag molar ratio	*F* (%)	TU/Ag molar ratio	*F* (%)
0.5	28.7	3.0	96.5
1.0	71.2	3.5	98.1
1.5	86.3	4.0	97.6
2.0	89.2	50.0	98.5
2.5	93.8	100.0	98.9

[a] $C_{Ag} = 2 \times 10^{-4}$ mol·dm^{-3}; $C_{SDBS} = 5 \times 10^{-4}$ mol·dm^{-3}.

be present in at least a 1:1 molar ratio to the ion. An excess of SDBS is required to produce the stable foam layer necessary to support the sublate. A large excess of SDBS, which produces a large volume of foam, should be avoided. A suitable free concentration of SDBS in the initial solution was found to be 2–5 × 10^{-4} mol·dm^{-3}.

Effect of Silver Concentration

Concentrations of silver vary considerably in leaching solutions or other samples. It is important to know whether variations in the initial concentration of silver result in significant differences in flotation efficiencies. In studies designed to determine this, the thiourea/silver molar ratio and the excess SDBS concentration were fixed at 4 and 3 × 10^{-4} mol·dm^{-3}, respectively, and the silver concentrations was varied from 10^{-3} to 10^{-5} mol·dm^{-3}. The experimental results indicated that flotation rates are not significantly affected by a variation in silver concentration. The flotation rates were up to 95% in all cases.

Effect of Sulfuric Acid

In practical thiourea-leaching processes, sulfuric acid is employed to adjust the acidity of the leaching solutions. The influence of sulfuric acid concentration on flotation was studied. The results showed that varying the sulfuric acid concentration from 0.5 to 10% had little influence on flotation efficiency. Since thiourea-leaching solutions usually contain a small amount of sulfuric acid, it is not necessary to adjust the acidity in leaching solutions for flotation.

Effect of Ethanol

It is known that bubbles with diameters below 0. 5 mm are easily captured by precipitates (14). In other words, tiny bubbles are more efficient than big ones for carrying a sublate salt into the foam layer. However, tiny bubbles produced by passing air through a sintered-glass disk tend to coalesce into bigger ones, so measures must be taken to prevent such coalescences. The addition of a small amount of ethanol is a valid way to prevent the coalescence of tiny bubbles. The addition of a suitable amount of ethanol increased flotation efficiency greatly, as expected. On the other hand, ethanol destroys the stability of the foam layer and causes partial redispersion of the sublate into the bulk solution. A decrease in flotation rates was observed in the presence of a large amount of ethanol. It was therefore important to control the amount of ethanol added. A suitable concentration of added ethanol was found to be 0.1–1% in the initial solution.

Optimization of Gas Flow-Rate

The gas flow-rate should be carefully optimized. If the flow rate is too low, a long time is required to achieve complete flotation. If it is too high, the stability of the foam layer will decrease, and some bulk solution will be carried into the foam layer. From the results of our earlier studies, an eclectic flow-rate of 30 mL·min^{-1} was chosen. Under this flow-rate condition, a quantitative recovery of silver was achieved after 20 minutes of bubbling.

Flotation Tests

When silver is leached from crushed ores with acidic thiourea solution in hydrometallurgical processess, other metals (Cu, Zn, Fe, etc.) also dissolve into the leaching solutions to some extent. It is important to know whether these coexisting ions interfere with the flotation of silver. For this purpose, two flotation tests were undertaken. The first involved the flotation of silver from a synthetic sample, and the second was for the flotation of silver from an actual thiourea-leaching solution of silver ore. The results presented in Table 2 indicate that the coexisting ions had little influence on the flotation of silver.

Silver Recovery from Sublate

After maximum flotation was achieved, the sublates were collected for the recovery of metallic silver. The thermal decomposition method was adopted to recover silver from the precipitate phase. After the precipitate was heated in a furnace at a set temperature for 2 hours, the residues

TABLE 2
Results of Flotation Tests

Sample	Composition (mg/100 mL)	Ag floated (mg)	Flotation rates (%)
Synthetic sample	Ag 5. 00, Cu 100, Fe 200, Zn 500, TU 3000, H_2SO_4 1000	4.90	98.0
Leaching solution	Ag 8.62, other ions, TU 3000, H_2SO_4 1000	8.31	96.4

TABLE 3
Effects of Decomposition Temperature on Silver Purity

Temperature (°C)	Purity (%)	Temperature (°C)	Purity (°C)
400	72.43	850	98.65
600	81.06	900	98.43
800	93.21	1000	98.07

were dissolved in hot HNO_3 (1:4), and the silver content in the residues was determined by the classic Volhard method. The relation between temperature and purity of silver is presented in Table 3. It is clear from the results in Table 3 that pure metallic silver is easily obtained from the sublates by thermal decomposition.

CONCLUSIONS

As an efficient and nonpolluting method, the thiourea-leaching technique is quite acceptable for hydrometallurgical processes of silver. However, it has not been used as extensively as might be expected. The lack of satisfactory methods to recover silver and the high cost of thiourea are mainly responsible for this situation.

For the recovery of silver from thiourea solution, the flotation method described in this paper has advantages over the conventional method. The flotation procedure is simple, fast, and economical. Furthermore, a leaching solution containing excess thiourea may be reused after silver and SDBS are removed by flotation. This recycling step lowers the cost of the thiourea-leaching technique. It is clear from the study presented in this paper that ion flotation is a potential technique for the recovery of silver from thiourea solution.

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