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Separation of Gold from Other Metals in Thiosulfate Solutions by Solvent Extraction

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ABSTRACT

The extraction of gold, silver, copper, zinc, and nickel present in thiosulfate solutions with or without the presence of ammonia was studied. Results show that neither a primary amine nor the mixed extractants of a primary amine with tributyl phosphate or trialkyl amine oxide can separate gold from other metals in the absence of ammonia in aqueous solutions. In the case of ammonium thiosulfate solutions, the percent extraction of gold is increased tremendously in comparison with other metals, and thus gold can be separated from them. The pH_{50} of gold extraction for a mixed solvent of primary amine with amine oxide is about 9.0, which is very close to the pH of the actual leaching solutions. By using the mixed solvent to extract gold in the solutions from leaching of gold-containing sulfide concentrate, the separation factors of Au to Ag and Au to Cu could reach as high as 15 and 1695, respectively, for a pH less than 8.

INTRODUCTION

The process of leaching with thiosulfate solutions, as one of several noncyanide leaching processes of gold, has been studied and developed in recent years (1, 2). But there is not much work reported on the recovery of gold from thiosulfate solutions. Work has been started on this topic by cementation with zinc dust (3, 4) or iron powder, and adsorption on carbon, with a number of problems still to be solved (5, 6).

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Solvent extraction used in gold recovery offers higher capacity, better selectivity, and faster kinetics. With the increasing popularity of heap leaching of low-grade gold ores, there is scope for the development of solvents to treat these relatively clean, clarified liquors. Recovering extractants without using high pressure and high temperature shows a low cost, and extraction avoids the problems of fouling of medium and the losses of gold with attendant losses of fine grains which plague many activated carbon or resin systems.

The extraction of gold from cyanide solutions with neutral organophosphorus esters, primary amines, and their mixture as a solvent was studied by Miller and Caravaca, respectively (7–9). They found that with the addition of tributyl phosphate (TBP) the pH_{50} of gold increases significantly, but the other cyanoanions result in much smaller increases, indicating that the selective extraction of gold from alkaline cyanide solution would be possible. The order of extraction of cyanoanions by the modified amine was found to be controlled by the ratio of electric charge to their diameter:

$$\mathrm{Fe(CN)_6^{4-}} < \mathrm{Fe(CN)_6^{3-}} < \mathrm{Cu(CN)_4^{3-}} \\ < \mathrm{Ni(CN)_4^{2-}} < \mathrm{Zn(CN)_4^{2-}} < \mathrm{Ag(CN)_2^{-}} < \mathrm{Au(CN)_2^{-}}$$

In our laboratory, primary, secondary, and tertiary amines have been studied for the extraction of gold from thiosulfate solutions. Organophosphorus esters and their mixtures with amines have also been tested. The experimental results show that only in alkaline solutions could gold be extracted with alkyl phosphorus esters (10). The extent of gold extraction using amines or their mixtures with alkyl phosphorus esters from thiosulfate solutions both show the order as primary > secondary > tertiary (11, 12). The effect of the amine oxide on the enhancement of gold extraction is stronger than that of phosphorus oxide (13).

In order to investigate the possibility of separating gold from leaching solutions, the extraction of silver, copper, zinc, and nickel was studied. The present paper reports our experimental results on the separation of gold from other metals present in ammoniacal thiosulfate solutions.

EXPERIMENTAL

The primary amine N_{1923} with the formula $RR'CHNH_2$ (with a total of 19–23 carbon atoms) was supplied by the Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai. Trialky amine oxide (TRAO) was prepared by oxidizing the tertiary amine. TBP and *n*-octane were chemical pure. The other reagents, $AgNO_3$, $CuSO_4 \cdot 5H_2O$, $ZnSO_4 \cdot 7H_2O$, $NiSO_4 \cdot 6H_2O$, were of analytical grade.

Metallic gold was dissolved in aqua regia, and the other four metal solutions were prepared. The equilibrium distribution of metals between the aqueous and organic phases was determined by mixing the two phases using a magnetic stirrer. The pH was adjusted by addition of a very small volume of dilute H_2SO_4 or NaOH solution under agitation to prevent precipitation of elemental sulfur. An equal amount of the organic phase was added to maintain a fixed phase ratio of 1:1. When equilibrium was reached, stirring was stopped. The metal content in the aqueous phase was determined using a Perkin-Elmer 4000 Atomic Absorption Spectrophotometer.

RESULTS AND DISCUSSION

Extraction of Au, Ag, Cu, Zn, and Ni with N_{1923}

Figure 1 shows the extraction of Au, Ag, Cu, Zn, and Ni with 0.5 M N_{1923} in *n*-octane from 0.8 M $Na_2S_2O_3$ solutions when these metals exist simultaneously in the thiosulfate solutions. It can be seen that the extraction is very intricate and the separation of gold from other metals is difficult.

During the process of leaching gold with the thiosulfate solutions, aqueous ammonia solution is always added to catalyze the leaching process and to keep the solutions alkaline in order to stabilize the thiosulfate ions. So the separation of gold by solvent extraction from the thiosulfate solutions should be car-

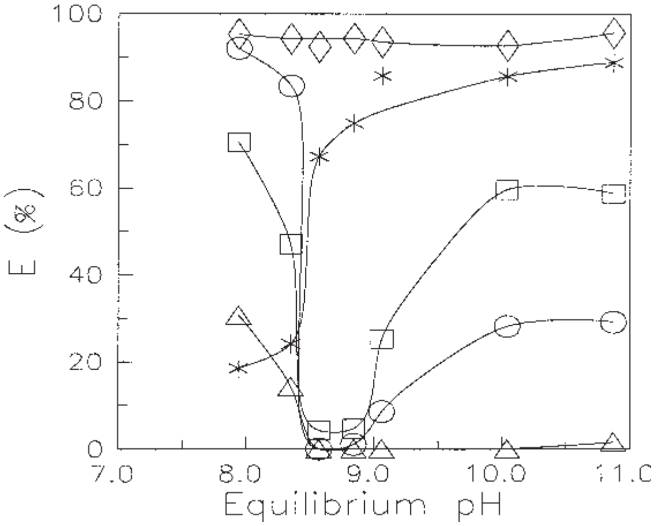

FIG. 1 Extraction of Au, Ag, Cu, Zn, and Ni with 0.5 M N_{1923} in *n*-octane from 0.8 M $Na_2S_2O_3$ solution versus equilibrium pH. Ratio of organic to aqueous phase (O/A) = 1, 20°C, 10 minutes. (○) 0.20 mM Au, (□) 0.24 mM Ag, (△) 14.98 mM Cu, (◊) 0.20 mM Zn, (*) 0.21 mM Ni.

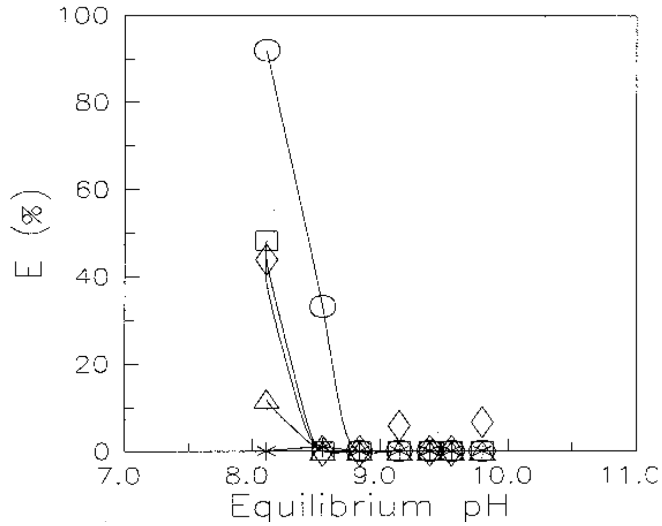

FIG. 2 Extraction of Au, Ag, Cu, Zn, and Ni with 0.5 M N_{1923} in *n*-octane from 0.8 M $(NH_4)_2S_2O_3$ solution versus equilibrium pH. O/A = 1, 20°C, 10 minutes. (○) 0.20 mM Au, (□) 0.24 mM Ag, (△) 14.98 mM Cu, (◊) 0.20 mM Zn, (*) 0.21 mM Ni.

ried out in the presence of ammonia. The extraction of gold, silver, copper, zinc, and nickel from 0.8 M $(NH_4)_2S_2O_3$ solution with 0.5 M N_{1923} in *n*-octane was carried out, and the results are shown in Fig. 2. It can be seen that the extraction is very different from the results of extraction in the absence of ammonia. The percent extraction of gold is much higher than the extraction of the other metals, and the order is Au $>$ Ag ~ Zn $>$ Cu $>$ Ni.

Extraction of Au, Ag, Cu, Zn, and Ni with Mixed Solvent

In our previous work it was found that the addition of neutral phosphorus reagents to the primary amine increases the extraction of gold, and in the case of ammonium thiosulfate solutions the mixed solvent gives even better extraction results in comparison with solutions containing sodium instead. It has also been indicated that amine oxide has a stronger synergistic effect on the extraction of gold than do neutral phosphorus reagents.

The results of the extraction with the mixture of 0.5 M N_{1923} and 0.6 M TBP in *n*-octane from 0.8 M $(NH_4)_2S_2O_3$ solution are shown in Fig. 3. It can be seen that the extraction of gold increases with the addition of TBP, as seen from the slight shift of the extraction curve to a higher pH value, while the extraction of other metals is slightly depressed.

The extraction was carried out using an organic phase of 0.5 M N_{1923} and 0.15 M TRAO in *n*-octane and an aqueous phase of 0.8 M $(NH_4)_2S_2O_3$ solu-

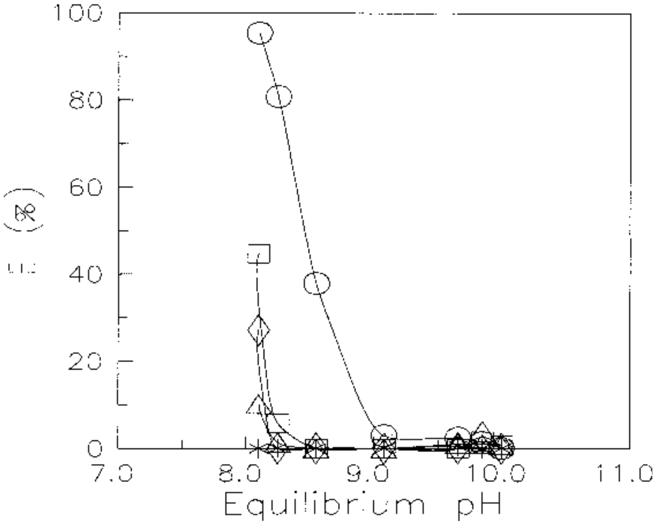

FIG. 3 Extraction of Au, Ag, Cu, Zn, and Ni with 0.5 M N_{1923} and 0.6 M TBP in *n*-octane from 0.8 M $(NH_4)_2S_2O_3$ solution versus equilibrium pH. O/A = 1, 20°C, 10 minutes. (○) 0.20 mM Au, (□) 0.24 mM Ag, (△) 14.97 mM Cu, (◊) 0.20 mM Zn, (*) 0.21 mM Ni.

tion. The results obtained are shown in Fig. 4. It can be seen that the extraction curves shift to the right, especially for gold, which indicates the gold can be separated from the coexisting other metals in thiosulfate solutions by the addition of TRAO to N_{1923}.

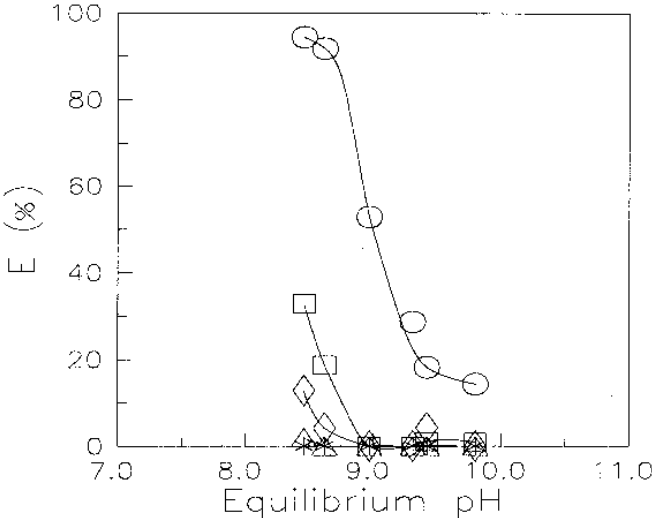

FIG. 4 Extraction of Au, Ag, Cu, Zn, and Ni with 0.5 M N_{1923} and 0.15 M TRAO in *n*-octane from 0.8 M $(NH_4)_2S_2O_3$ solution versus equilibrium pH. O/A = 1, 20°C, 10 minutes. (○) 0.20 mM Au, (□) 0.24 mM Ag, (△) 14.98 mM Cu, (◊) 0.20 mM Zn, (*) 0.21 mM Ni.

TABLE 1
pH_{50} for Gold Extraction from 0.8 M $(NH_4)_2S_2O_3$ Solutions

0.5 M N_{1923}	0.5 M N_{1923} and 0.6 M TBP	0.5 M N_{1923} and 0.15 M TRAO
8.42	8.47	9.01

Table 1 illustrates the pH_{50} values of the gold extraction studied above. For the mixed solvent of primary amine with amine oxide, the pH_{50} is about 9.0, which is very close to the pH of the actual leaching solutions.

Extraction with the Real Leaching Solutions

Aqueous ammonia solution is always added when leaching gold-containing ores with thiosulfate solutions to form a copper–ammonia complex as the catalyst for the process. The extractions of Au, Ag, and Cu from the real leaching solutions with 0.5 M N_{1923} in kerosene and with the mixed solvent of 0.5 M N_{1923} and 0.15 M TRAO in kerosene were carried out, and the results are shown in Fig. 5. The concentrations of metals in the leaching solution were Au 10.66 mg/L, Ag 5.59 mg/L, and Cu 0.11%. The solution was obtained by leaching gold-containing sulfide concentrate ores from Zhaoyuan, Guang-

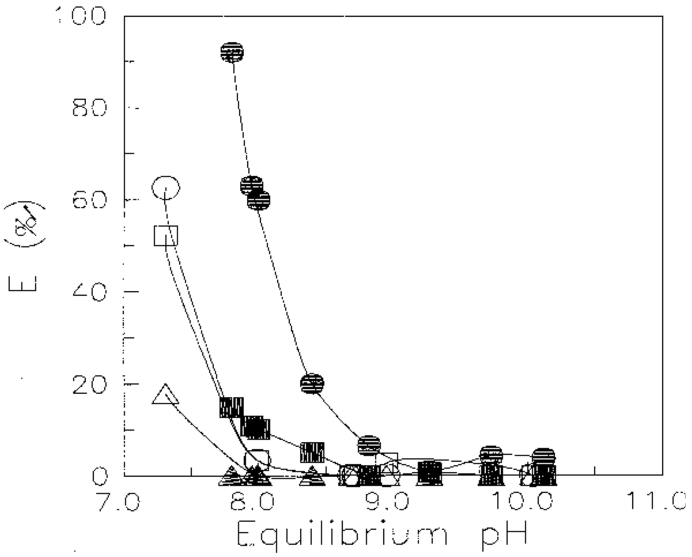

FIG. 5 Extraction of Au, Ag, and Cu from the thiosulfate solutions obtained by leaching gold-containing sulfide concentrate versus equilibrium pH. O/A = 1, 20°C, 10 minutes. (○ ●) Au, (□ ■) Ag, (△ ▲) Cu. Open symbols: 0.5 M N_{1923} in kerosene. Filled symbols: 0.5 M N_{1923} and 0.15 M TRAO in kerosene.

TABLE 2

Separation Factors of Au to Ag and Au to Cu for Extraction from the Solutions by Leaching of Gold-Containing Concentrate

Extractant	pH	$\alpha_{Au/Ag}$	$\alpha_{Au/Cu}$
0.5 M N_{1923}	7.8	1.21	4.61
In kerosene	8.0	1.03	35
0.5 M N_{1923} and 0.15 M TRAO	7.8	65	11,500
In kerosene	8.0	15	1,695

dong Province, and the metals contents in the ores were Au 54.6 g/t, Ag 28.0 g/t, and Cu 4.41%. The leaching process with 0.8 M $Na_2S_2O_3$ and 2.0 M $NH_3 \cdot H_2O$ was carried out at 50°C for 3 hours with no added copper.

The separation factors of Au to Ag and Au to Cu for pH 7.8 and 8.0 have been calculated and are listed in Table 2. It can be seen that when this mixed extractant is used for the extraction of gold from leaching solutions of gold-containing sulfide ores, the separation factors of Au to Ag and Au to Cu can reach as high as 15 and 1695 for a pH less than 8, respectively. Gold can be separated from other metals in thiosulfate solutions by the adjustment of the aqueous pH.

Although the results of extraction using the primary amine mixed with TBP are not as good as those with TRAO, it is possible that TBP will be favored for the separation of gold in the real leaching solution because TBP is in industrial production, is cheap, and convenient to use. TRAO is made from the oxidation of a tertiary amine. If its production cost were low, it might be feasible for a mixture of amine–amine oxide to be used to separate gold from thiosulfate solutions by leaching the gold-containing sulfide ores. This new mixed solvent extraction system is worthy of further research and development work.

CONCLUSIONS

The percent extraction of gold is increased tremendously in ammoniacal thiosulfate solutions in comparison with other metals by the addition of TBP or amine oxide in primary amine N_{1923}. The pH_{50} of gold extraction for the mixed solvent of N_{1923} with TRAO is about 9.0. When this mixed extractant is used for extraction from the leaching of a gold-containing sulfide concentrate, the separation factors of Au to Ag and Au to Cu could reach as high as 15 and 1695 for a pH lower than 8, respectively. Thus gold can be separated from other metals.

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