LEACHING OF PRECIOUS METALS FROM

COMPLEX SULPHIDE ORES[①]

2. DIRECT LEACHING OF Cu SULFIDE CONCENTRATE

BY ACIDIC THIOUREA SOLUTIONS

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ABSTRACT

Recovery of gold and silver from a sulphide concentrate by thiourea leaching was investigated. The effects of various parameters on the process, such as oxidants, the initial concentration of thiourea and acidity in solutions as well as reaction temperature, were systematically examined. From the results it was confirmed that (a) oxidants had no significant influence on the dissolution of gold and silver at a fixed initial concentration of thiourea; (b) the initial concentration of thiourea and acidity affected the dissolution rate only in the earliest period of leaching; (c) the rate of the process was controlled by reagent diffusion. The optimum operations were worked out for the thiourea leaching process of the concentrate.

Key words: sulphide concentrate thiourea leaching recovery of gold silver

1 INTRODUCTION

Thiourea is an effective and promising nonconventional leaching agent for the recovery of precious metals. Under acidic and oxidizing conditions, thiourea reacts rather selectively with gold and silver, thus resulting in the formation of the cationic complexes Au $[SC(NH_2)_2]_2^+$, $Ag[SC(NH_2)_3]^{+[1-1]}$. The kinetics of the leaching of precious metals by thiourea is much faster than those of alkaline cyanidation[1]. Several oxidants have been used in thiourea leaching. Molecular oxygen, ferric salt and hydrogen peroxide are the most common oxidants. Ferric ions are

considered an effective oxidant. However, excess ferric ions lead to excess consumption of the leaching agent with the formation of stable iron-thiourea complexes, for example $FeSO_4[SC(NH_2)_2]$ and $Fe_2SO_4[H_2)_2]_2^{3+}$.

High consumption of thiourea is a violate point for the development and optimization of the process. Most interest in thiourea leaching has therefore involved treating high-grade concentrates, which have proved sufficiently valuable to justify the use of thiourea. In this study our major objective is to examine the effects of process factors, including oxidants. leaching agent concentration, solution acidity and reaction tempera-

ture; and to determine the optimum conditions for the Cu- Au sulfide concentrate under study.

2　EXPERIMENTAL

The concentrate used had the chemical and mineral composition shown in Table 1. In this study only one mono- sized sample with particle size —120 mesh was used.

All the chemicals used were of A. R. grade. The experimental procedures were the same as those described previously. The acidities of the leach liquors was adjusted with sulfuric acid. The leaching was carried out under thermostatic conditions. The stirring speed was kept constant at an impeller speed of 700 r/min, and the ratio of liquor to solid was 5:1 in all the experiments. The analyses of the different metal ions in the leach liquors were carried out by using ICP (inductively coupled plasma-atomic emission spectroscopy(ARL 3502)).

3　RESULTS

3. 1　*Effects of the Oxidant Used*

Oxygen, hydrogen peroxide and ferric ions were studied as oxidizing agents during thiourea leaching. The results shown in Fig. 1 indicate that addition of ferric sulfate to the leaching liquors up to 10g/L has no favorable effect on dissolution of gold. On the other hand, the dissolution rate and extracted fraction of silver in a certain period are
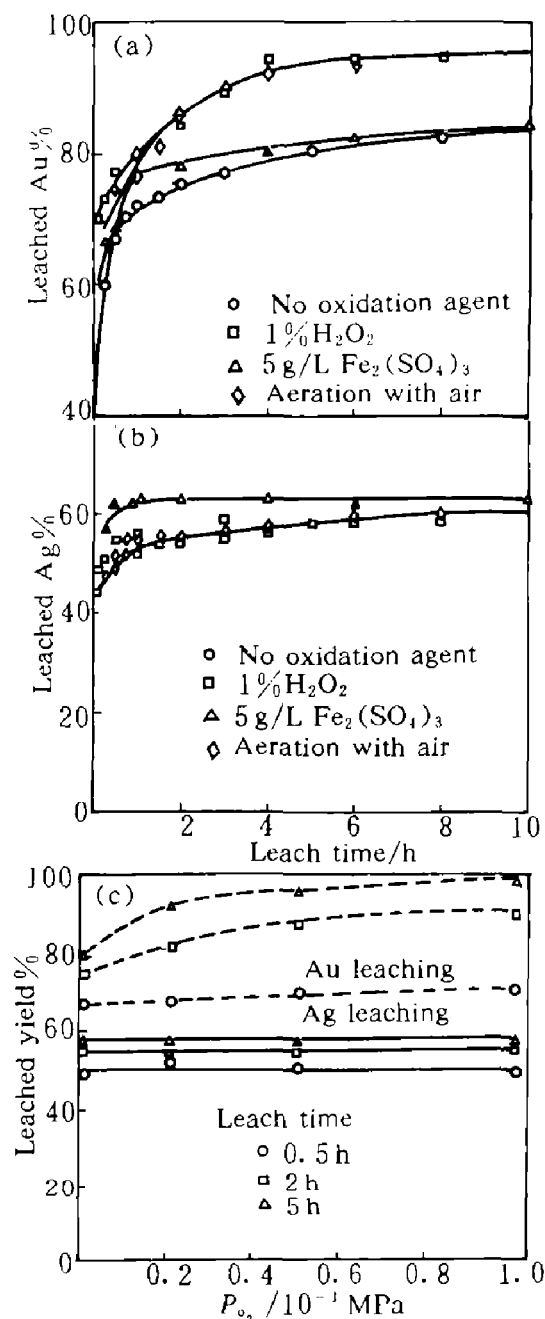
Fig. 1　Effects of oxidants in thourea leaching process

(a)—on gold dissolution; (b)—on silver dissolution; (c)—effects of different partial pressures of oxygen　$[Th]_0 = 50 g/L; [H_2SO_4]_0 = 0. 15 mol/L$

Table 1　Chemical and mineral analysis of the concentrate used

Element	Cu	Fe	Pb	Zn	S	As	Ni	Hg
wt. -%	9. 3	36. 4	1. 84	0. 77	30. 7	0. 024	0. 004	0. 0018 mg/kg

mineral	Au	Ag	$CuFeS_2$	ZnS	PbS	FeAsS	FeS_2	FeS	silicate
wt. -%	55. 0~56. 3	150	20. 7	1. 15	2. 12	0. 033	11. 9	1. 1	20. 9

increased by addition of ferric sulphate to the leach liquors. Ferric sulphate is the most effective oxidant for silver leaching, as seen from Fig. 1(b). The tests illustrate that the oxygen concentration in a liquor has no significant influence on the dissolution of gold and silver. It can, however, be seen that less gold is dissolved under conditions of no aeration in comparison to similar runs with aeration. The results demonstrate that hydrogen peroxide and oxygen have a similar influence on the dissolution of gold and silver.

3. 2　Effect of Solution pH

Fig. 2 gives the plots of pH values of leach liquors as a function of leaching time under different experimental conditions. In general, the pH value of leach liquors increases as the process proceeds. The elevation of the pH value depends on the initial acidity and the oxidant used.

The experiments confirm that the initial acidity probably is a sensitive parameter affecting the initial rate of gold extraction. It can be seen that in the acidity range from pH = 0. 2 to pH = 1. 8 the dissolution fraction of gold appears to have a maximum at pH = 0. 6 under conditions of 20 g/ L thiourea concentration and the ambient tem-
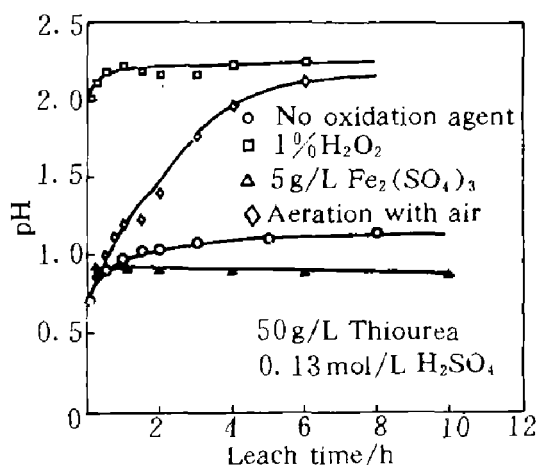
perature, as shown in Fig. 3(a). Also, the curves of dissolution in Fig. 3(a) are almost parallel each other, which indicates that initial pH is a significant factor affecting gold dissolution only in the earliest period.

Fig. 3(b) shows dissolution of silver in a thiourea solution with a different initial acidity. It is seen that the dissoution rate increases, almost linearly, with solution acidity. A majority of the silver is dissolved in the first two hours of leaching regardless of initial acidities. No significant effect of solution acidities on dissolution of copper was observed. However, as the initial pH increases up to pH = 1, the dissolved copper decreases slightly. The dissloution of iron greatly increases with the increase of the solution acidity.
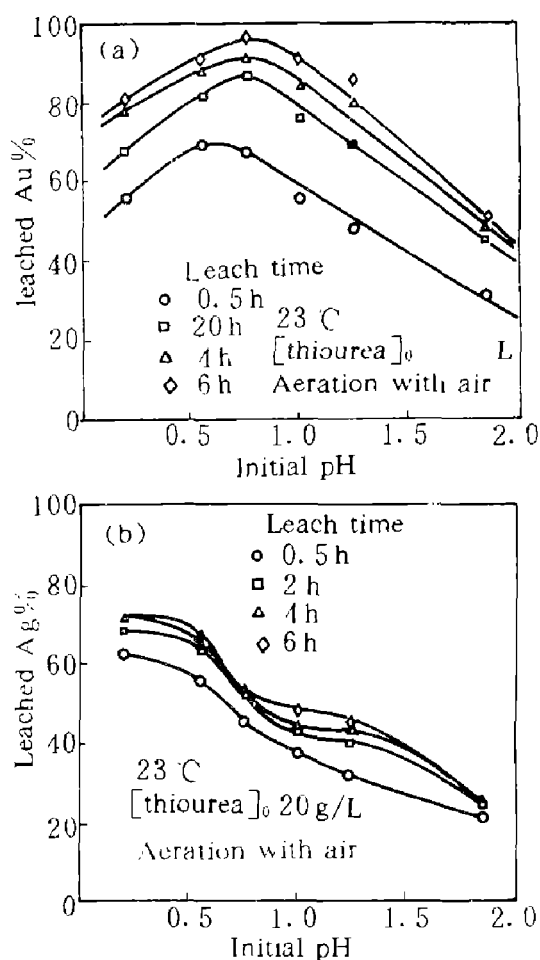

Fig. 3　Effects of initial pH
(a)—on gold dissolution;
(b)—on silver dissolution

Fig. 2　pH value in leach liquors as a function of leach time

3. 3   *Effect of Thiourea Concentrations*

The experiments on the effect of leaching agent concentrations were carried out at a given constant oxygen partial pressure (air bubbling) and ambient temperature. Fig. 4 is the plot of extracted gold and silver as a function of leaching time at different initial concentrations of thiourea. The initial rate of gold dissolution and cumulative recovery of gold increase with the elevation of thiourea concentration. The influence of thiourea concentration on gold and silver dissolution is not so efficient when the thiourea concentration is higher than 10 g/L under the experimental conditions, as seen from Fig. 4(b).

The consumption of thiourea is dependent on the redox potential in the slurry under controlled conditions. At a lower controlled potential the consumption of thiourea decreased. Meanwhile, the leached yield also decreased. The results confirm that the minimum consumption of thiourea is observed when the redox potential is controlled so the the fraction of thiourea converted to formamine disulphide is kept at 25% or so. In that case, 92% ～ 95% of the gold is leached in 4 h.

4   EFFECT OF LEACH TEMPERTURE

Fig. 5 shows dissolution curves for gold and silver at different temperatures. It appears that gold dissolution is not affected by leach temperature in the range from the ambient to 47 C, as seen from Fig. 5(a), and is depressed at high temperatures. For silver extraction, on the other hand, higher temperature results in more effective leaching extraction. The reaction rate can be estimated from the amount of silver dissolved during the first 30 min of leaching. The apparent activation energy, calculated from the Ar-

rhenius plot, is 30 kJ/mol. This indicates that process of silver dissolution by thiourea is controlled by ion diffusion.

The results demonstrate that more iron minerals are dissolved at higher leaching temperatures up to about 67 C. However, at temperatures higher than 67 C, the concentration of iron in leach liquor decreases. Similarly, the dissolution of chalcopyrite increases linearly with elevation of the leachingtemperature at the beginning.

5   DISCUSSION

The rate of dissolution of both gold and silver in acidic thiourea leaching is much higher than in alkaline cyanide leaching.
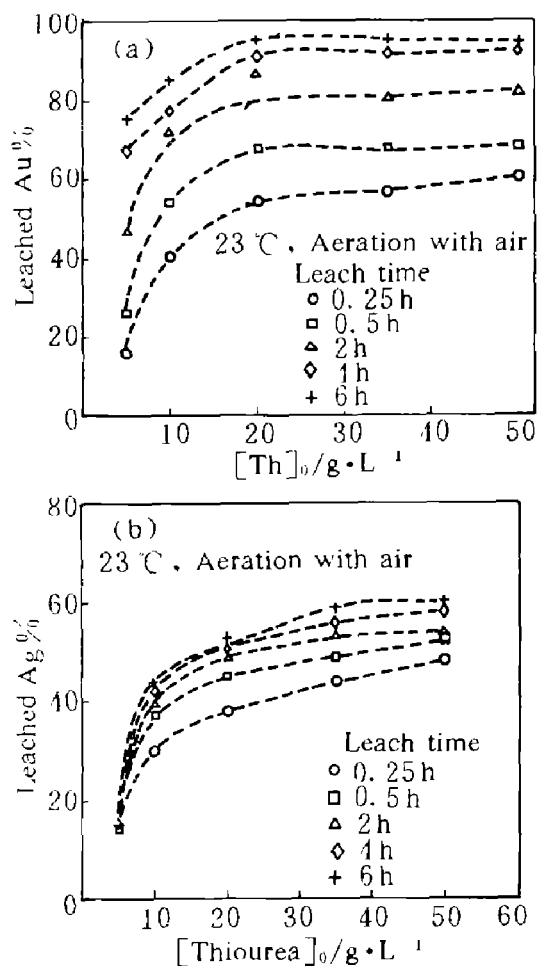

Fig. 4   Effects of initial concentration of thiourea
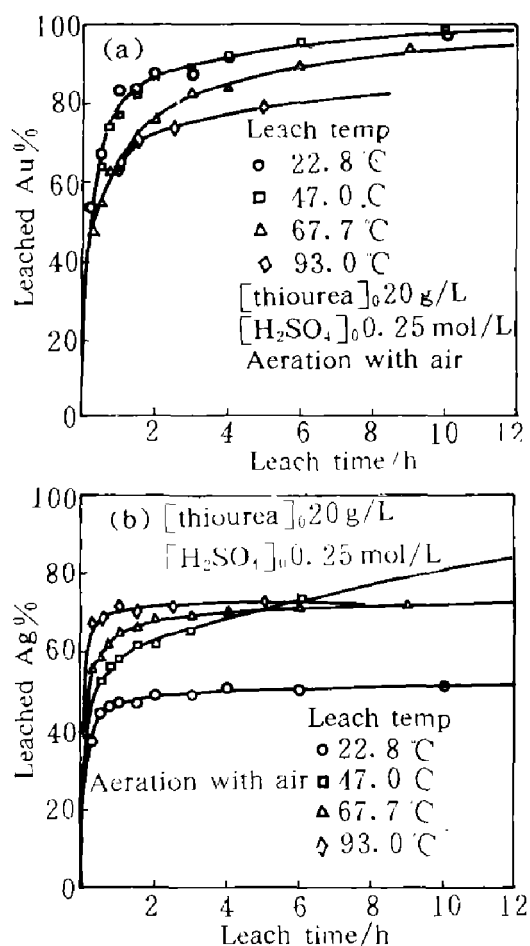
(a)—on gold dissolution;
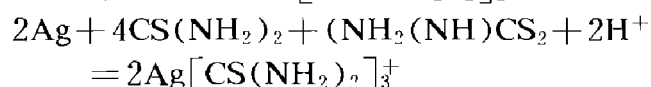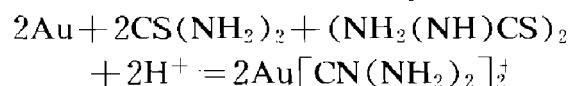
(b)—on silver dissolution

Fig. 5   Effects of leaching temperature

(a)—on gold dissolution ;

(b)—on silver dissolution

Under optimum conditions, about 40% of the gold is extracted in the first 30 min during cyanide leaching[7], while more than 60% of the gold is leached within 15 min during thiourea leaching. The accumulative recovery of gold in 10 h by thiourea leaching is little higher (2. 5%) than cyanide leaching. In contrast, the dissolution rate and accumulative recovery of silver in thiourea solutions are much higher than in cyanide solutions. The extracted yield of silver in acidic thiourea solutions is greater than 80% while it is lower than 36% in cyanide solutions. Formamine disulphide plays an important role as both an oxidant and a complex ligand in the dissolution of gold and silver by thiourea leaching. The

overall reactions can be expressed as[2,4]

$$2Au + 2CS(NH_2)_2 + (NH_2(NH)CS)_2$$
$$+ 2H^+ = 2Au[CN(NH_2)_2]_2^+$$
$$2Ag + 4CS(NH_2)_2 + (NH_2(NH)CS_2 + 2H^+$$
$$= 2Ag[CS(NH_2)_2]_3^+$$

The dissolution rates depend on the concentration of both thiourea and formamine disulphide. The formation of formamine disuphide is a reversible redox reaction in acidic solutions:

$$2CS(NH_2)_2 = (NH_2(NH)CS)_2 + 2H^+ + 2e^-$$
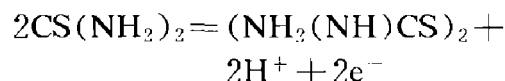
At proton concentrations from 0. 05 to 1. 0 mol/ L, the concentration and the conversion fraction of formamine sulphide depend only on the redox potential, and not on the proton concentration in solutions[5]. The fraction of thiourea converted to formamine disulphide, calculated from equilibrium, is greater than 99% when air acts as an oxidant in thiourea solutions, so that the elevation of oxygen pressure shows no effect on the conversion fraction. It is similar to other oxidants used in experiments. Meanwhile, it is reasonable that the rate of dissolution of gold is independent of the acidities of solutions except in the earliest period, in agreement with Ref. [4]. It has been pointed out that gold dissolution is a first-order reaction with respect to thiourea concentration[1]. The experimental results indicate that the initial rate of gold dissolution increases linearly with the increase of the thiourea concentration in the range of low concentration, and is almost independent of the concentration of thiourea when the concentration is higher than 20 g/L. Therefore, the process of gold dissolution is not controlled by chemical reaction under these experimental conditions.

The temperature has no effect on gold dissolution at low temperatures, and even a negative effect at higher one. Gold leaching with thiourea solutions is a complex process.

A passive film may be formed on the gold surface while gold dissolves in the process of thiourea leaching[1]. This film is destroyed simultaneously on the surface of gold particles as the dissolution process progresses and shrinks with the non-reacted core. Both formation of a passive film on the surface and diffusion of reagents through the film are the controlling step in the overall process of gold dissolution.

As for the dissolution of silver, similar conclusions can be drawn except for the effect of the reaction temperature. The experiments in this study indicate that, in the temperature range from ambient temperature to 93 C , the dissolution reaction for silver behaves as on the Arrhenius role. The apparent activation energy estimated from experimental data is 30. 0 kJ/mol, which indicates that the leaching process of silver in acidic thiourea solutions is controlled by the diffusion of the reacting ions, the oxidizing agent or thiourea. The cathodic reaction of formamine disulfide with proton on the surface is the controlling step in the redox reaction of silver dissolution. The diffusion rates for formamine and protons control the overall process.

6　CONCLUSIONS

The recovery of gold and silver from the sulphide concentrate are more than 95% and 80% respectively by using the acidic thiourea leaching. The dissolution rates are much higher than those in cyanidation. The oxidizing agent seems to have no significant effect on the recovery of the gold and silver in the experimental conditions under study. The initial acidity and the thiourea concentration are significant parameters only at the beginning of Au and Ag dissolution. The dissolution process for gold is controlled by both formation of a passive film and diffusion of reagents through the film during the thiourea leaching, while silver dissolution is controlled by reagent diffusion. The degradation of the thiourea is the most important factor affecting the consumption of thiourea, and a controlled redox potential in solutions may lead to optimization of reagent consumption. The optimum operation parameters under study may be as follows: solution pH = 0. 6 ~ 0. 8; 20 ~ 30 g/ L concentration of thiourea; 50 C or so; limited aeration with air, no further oxidant is required.

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