Study on Mechanism of Gold Leaching by Thiourea in the Presence of Sodium Sulphite

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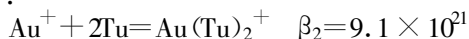
Abstract: The linear potential sweep voltammetry and electrochemical methods were used to study the mechanism and kinetics of gold dissolution in thiourea solution in the absence and presence of sodium sulphite. The results show that in the absence of sodium sulfite the dissolution rate of gold in thiourea solution is relatively slow and it increases with the increase of the concentration of thiourea and decreases with pH. Thiourea is easily oxidized to formamidine disulphide, which reduces the leaching efficiency and increases reagent consumption. In the presence of sodium sulphite, the effective concentration of thiourea is increased and the dissolution rate of gold in thiourea solution is greatly increased. The activation energy required for gold dissolution in thiourea solution with sodium sulphite is 20.9 kJ·mol^{-1} which is much lower than 55.0 kJ·mol^{-1} in the absence of sodium sulphite. It is evident that sodium sulphite has a significant effect on the electrochemical reaction kinetics of gold in thiourea solution.

Key words: gold leaching; thiourea; sodium sulphite; mechanism

Document code: A

Cyanidation has been used for more than one hundred years in gold industry since the first patent by MacArthur and the Forrests in 1889[1], and still remains the most popular option for processing gold ores because of its process simplicity and operation economy. Nevertheless, application of the technique has some disadvantages. Use of cyanide has generated environmental pollution in areas of high population density and the impreservation of water resources; reaction kinetics for gold leaching in a basic cyanide solution is quite slow; in some cases, it is not effective for refractory ores and concentrates. In order to overcome these disadvantages, seeking for noncyanide lixivints to treat gold ores and concentrates has received considerable attention. The noncyanide ligands mainly include thiosulfate[2-4], thiourea[5-9], halogen[10-12], and thiocyanate[13]. Of these noncyanide lixivints, thiourea is particularly interesting.

Thiourea is an organic compound and in acidic solution, thiourea can form a stable complex with gold (I)[14]:

$$Au^+ + 2Tu = Au(Tu)_2^+ \quad \beta_2 = 9.1 \times 10^{21}$$

In this way, it can be used to stabilize oxidized gold in solution.

Gold-bearing refractory ores and concentrates, by definition, exhibit high reagent consumption and low gold recovery because of the chemical and physical characteristics of the resources. It is imperative to pretreat the minerals before gold-leaching in order to improve recovery,

the most common methods for the pretreatment are roasting, pressure oxidation, and biooxidation. The products from pretreatment are predominantly acidic and in this regard acid thiourea leaching of gold is most reasonable and neutralization of the pretreated material would not be required.

The gold dissolution in acid thiourea solution can be described by the following anodic half-cell reaction:

$$Au + 2Tu = Au(Tu)_2^+ + e$$

The overall gold dissolution reaction requires an oxidant, such as hydrogen peroxide, manganese dioxide, ferric iron, formamidine disulfide, oxygen, and ozone etc. Comparative study on the kinetics of gold dissolution in different medium using these oxidants has shown that the initial rate of gold dissolution is the fastest when ferric iron is used as an oxidant in sulfuric acid solution. Unfortunately, the rate decreases with time. Another disadvantage of the use of thiourea for gold leaching is the high-level reagent consumption. It is generally believed that the high thiourea consumption mainly results from oxidation. One of thiourea degradation products from oxidation is elemental sulphur, which can passivate gold surface and inhibit its dissolution. Schulze[6] suggested a procedure that can effectively reduce thiourea consumption and also avoid the passivation of gold particles. The procedure involves adding SO$_2$ into the leaching solution thereby controlling the solution potentials; however the mechanism of its action is not clear. This paper studies the nature of

gold leaching by thiourea in the presence of sodium sulfite using electrochemical method.

1 Experimental

A gold foil of 99.99% purity (mass fraction) was used as working electrode, the area of which was 1 cm^2. Platinum and saturated calomel electrodes were used respectively as the accessory and reference electrode. The gold electrode was immersed in sulphuric acid solution for 5 min, washed and polished once before each test. The reagents used in the tests are all analytical grade. Double distilled water was used throughout the tests. The electrochemical measurements were conducted using a conventional three-electrode system with a PARC Model 173 potentiostat/galvanistat. The corrosion current density, J_{corr}, was used to express the dissolution rate of gold. In other experiments with a sulfide concentrate, the leaching efficiency was expressed by the percentage of gold dissolved. Thiourea was determined titrimetrically using potassium iodate with starch as an indicator.

2 Results and Discussions

2.1 Gold leaching from concentrate

Fig. 1 shows the effect of concentration of sodium sulfite on the leaching efficiency of a gold concentrate. It can be seen that sodium sulphite can greatly increase the leaching of gold by thiourea. Leaching for 60 min, the percentage of gold dissolved is increased from 25% in the absence of sodium sulphite to 60%, 75% and 92%, respectively, in the presence of 5×10^{-5}, 2×10^{-4}, 5×10^{-4} mol$\cdot$L^{-1} sodium sulphite, for a thiourea concentration of only 4 g$\cdot$L^{-1}. These data clearly show that sodium sulphite can increase the rate of gold leaching by thiourea and reduce the dosage for thiourea, which are consistent with those results reported by Schulze[6].
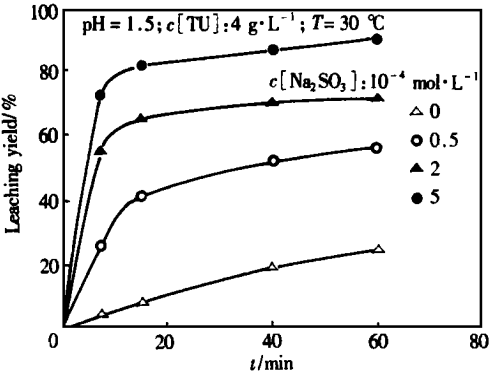
Fig. 1   Effect of concentration of sodium sulphite on leaching percentage of gold from flotation concentrate

2.2 Kinetics of gold leaching by thiourea in the presence of sodium sulphite

The dissolution rate of gold was examined using electrochemical method. The leaching rate of gold is expressed by the corrosion current density, J_{corr}. The range of potential scan was 40 mV relative to open circuit at a scan rate of 0.16 mV$\cdot$s^{-1}. The effects of concentration of sodium sulphite on the leaching rate (dissolution rate of gold) by thiourea are illustrated in Table 1. It shows that that the addition of sodium sulphite can greatly enhance the dissolution rate of gold in thiourea solution. According to the conventional rate equation, the relationship of gold dissolution rate (J_{corr}) and the concentrations of sulphite and TU (thiourea) are

$$J_{corr} = kc(TU)^m c^n \tag{1}$$

Table 1   Effect of concentration of sulphite on the dissolution rate of gold (pH: 0.8, c[TU]: 4 g$\cdot$L^{-1}, T: (298±2) K)

$[SO_3^{2-}]$ $(10^{-6}$ mol$\cdot$L$^{-1})$	0.5	2	5	10
$J_{corr}/(\mu A\cdot cm^{-2})$	21.3	29.8	48.5	65.4

When TU concentration is constant, then

$$\log J_{corr} = \log k_1 + n \log c \tag{2}$$

where n is the reaction order, and k_1 is the rate constant.

A replot of the date in Table 1 according to Eq. (2) is presented in Fig. 2. It is clear that a linear relation between $\log J_{coor}$ and $\log c$ exists. The slope of the line is about 0.5, showing that the gold dissolution rate exhibits half order dependence on the sulphite concentration.
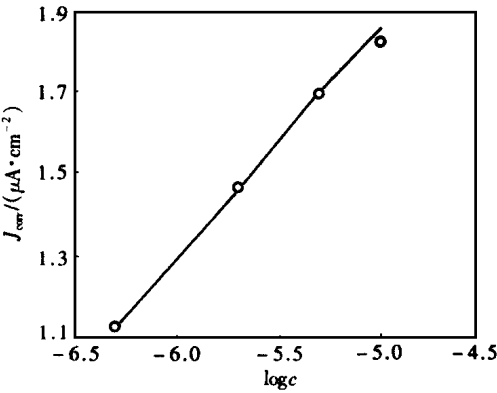
Fig. 2   Dissolution rate of gold *vs* concentration of sodium sulphite

To evaluate the catalyzing leaching of gold by sulphite, tests were conducted on the effect of temperature on gold dissolution rate in order to obtain the activation energy required for gold dissolution in thiourea solution in the absence and presence of sodium sulphite. The results are given in Table 2. It can be seen from Table 2 that the rate of gold dissolution is much higher in the presence than in

the absence of sodium sulphite at all temperatures. According to Arrenius' equation

$$\ln J_{\text{corr}} = k - \frac{E}{R} \cdot \frac{1}{T} \qquad (3)$$

Table 2　Effect of temperature on the dissolution rate of gold (pH: 0.8, c[TU] : 4 g·L⁻¹)

	T/ ℃	25	30	40	50
J_{corr}/ (μA·cm⁻²)	c[SO₃²⁻] : 0	12.3	28.7	45.6	53.2
	c[SO₃²⁻] : (10⁻⁵ mol·L⁻¹)	65.4	78.4	104	125

Plot $\ln J_{\text{corr}}$ against $(1/T)$ using the data in Table 2 as shown in Fig. 3. The activation energy required for gold dissolution in thiourea in the absence and presence of sodium sulphite can be obtained by the slope of lines in Fig. 3. In the absence of sodium sulphite the $E = 55.0$ kJ ·mol⁻¹, chemical reaction control; In the presence of sodium sulphite average $E = 20.9$ kJ·mol⁻¹, mixed control.
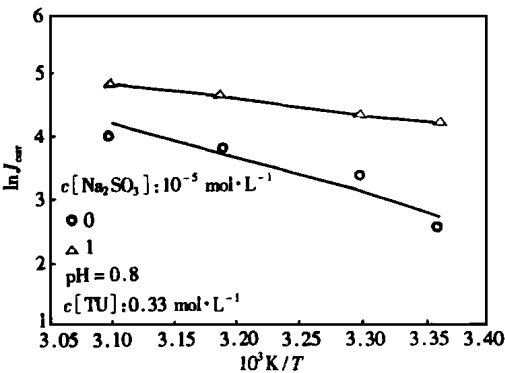

Fig. 3　Effects of temperature on the dissolution of gold in thiourea solution in the absence and presence of sodium sulphite

Evidently, the activation energy required for dissolution of gold in thiourea solution is greatly decreased in the presence of sodium sulphite (20.9 kJ·mol⁻¹) compared to that in absence of sodium sulphite (55.0 kJ·mol⁻¹), further indicating the catalyzing action of sodium sulphite on gold leaching by thiourea. Rewrite the relation between rate constant and activation energy based on Arrenius' equation as follows:

$$k = A\exp(-E/RT) \qquad (4)$$

In the absence of sodium sulphite, when leaching temperature is increased from 298K to 323K, the increase of gold dissolution rate is defined by

$$\frac{k_{323}}{k_{298}} = \exp\left[\frac{42150}{8.314}\left(\frac{1}{298} - \frac{1}{323}\right)\right] = \frac{4.5}{1} \qquad (5)$$

In the presence of sodium sulphite (1×10⁻⁵ mol· L⁻¹), when leaching temperature is increased from 298K to 323K, the increase of gold dissolution rate is defined by

$$\frac{k_{323}^{*}}{k_{298}^{*}} = \exp\left[\frac{29950}{8.314}\left(\frac{1}{298} - \frac{1}{323}\right)\right] = \frac{2.5}{1} \qquad (6)$$

The results above show that gold dissolution in thiourea solution without sodium sulphite is affected greatly by temperature and mainly controlled by chemical reaction. In the presence of sodium sulphite, dissolution rate of gold in thiourea solution is less affected by temperature, suggesting that the leaching of gold in thiourea solution in the presence of sulfite is controlled by diffusion and chemical reaction.

2.3　Electrochemical mechanism

The anodic current for gold dissolution in acidic thiourea solution in the presence of different concentration of sodium sulphite is presented in Fig. 4. The anodic current of gold dissolution is increased, indicating that the dissolution rate of gold in thiourea solution is increased with the increase of concentration of sodium sulphite. Even adding lower concentration of sodium sulphite, the dissolution rate of gold can be enhanced greatly. The dissolution rate of gold in the presence of 1×10⁻⁵ mol·L⁻¹ sodium sulphite is about 5 times as much as that in the absence of sodium sulphite. In order to know whether or not there is any adsorption of sulphite at gold surface, the current step experiments were conducted. When the current passes electrode, the total electrical quantity consumed is

$$Q = Q_a + Q_d = J\tau \qquad (7)$$

where Q_d is electrical quantity required for dispersion, Q_a is the electrical quantity consumed due to adsorption. According to Sand' equation[15]

$$Q_d = KJ^{-1} \qquad (8)$$

The relation between current and transit time is plotted by Q against J^{-1} as shown in Fig. 5. It shows that when $J^{-1} \to 0$, $Q = 0$. i. e. the intercept of the line in Fig. 5 is zero, $Q_a = 0$, showing no electrical quantity is consumed in adsorbed layer. It suggested that at gold electrode surface there is no adsorption of sodium sulphite. The only possible mechanism is the dispersion of reactants. Sodium sulphite catalyzes the dissolution rate of
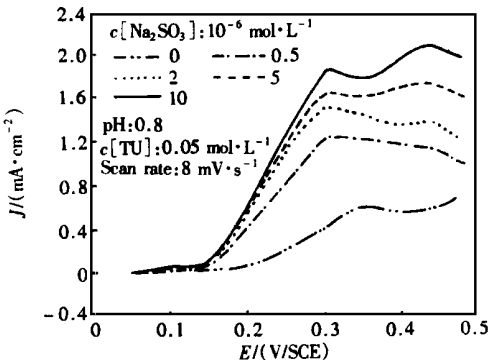

Fig. 4　Effects of concentration of sodium sulphite on the anodic current for gold dissolution
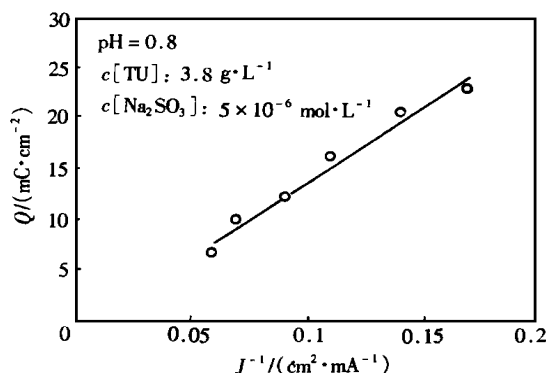
Fig. 5   Total electrical quantity consumed $vs\ J^{-1}$

gold in thiourea solution through taking part in redox reaction in solution.

The electrochemical reactions include the oxidation of thiourea into formamidine disulphide and then reduction by sodium sulphite, which decreases the oxidation of thiourea and increases the effective concentration of thiourea.

The experiment on the effect of leaching time on thiourea concentration shows that the concentration of thiourea is rapidly decreased with the increase of leaching time in the absence of sodium sulphite, which is consumed by gold dissolution and oxidation of thiourea itself. By adding $5 \times 10^{-6}\ mol \cdot L^{-1}$ sodium sulphite, the concentration of thiourea is gradually decreased with leaching time (as can be seen from Fig. 6). These results further demonstrate that sulphite may prevent the oxidation of thiourea and increase the effective concentration of thiourea for gold leaching giving rise to the increase of leaching rate of gold.
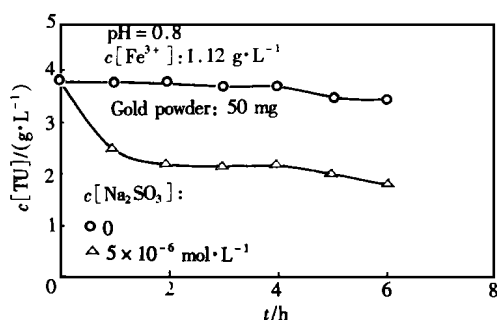

Fig. 6   The time dependence of the effective concentration of thiourea

3   Conclusions

The sodium sulphite in gold leaching by thiourea

plays an important role. Sodium sulphite participates in electrode reaction, which makes the oxidation of thiourea relatively reduce and maintain the effective concentration of thiourea. The activation energy required for gold dissolution in thiourea solution is greatly decreased by addition of sodium sulphite compared to no sodium sulphite addition, hence the dissolution rate of gold is greatly increased. The dissolution rate of gold in thiourea solution is mainly controlled by dispersion in the presence of sodium sulphite, whereas by temperature in the absence of sodium sulphite. The action electrochemical reduction-catalyzing leaching gold of sodium sulphite provides a possible way using thiourea as a reagent of gold leaching of noncyanide method.

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