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LEACHING OF GOLD IN ACID THIOUREA-THIOCYANATE SOLUTIONS USING FERRIC SULFATE AS OXIDANT

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Abstract

The leaching of gold in ferric-thiourea-thiocyanate solutions has been studied by the rotating-disk technique. The effects of initial concentrations of ferric, thiourea (Tu), thiocyanate, temperature and pH value on gold leaching rate were studied. Determinations of apparent activation energy indicate that the process was controlled by a combination of chemical reaction and diffusion in the mixed lixiviant system. The gold leaching rate in the mixed ligand solution is higher than either lixiviant alone, even the sum of individual lixiviant. In the presence of thiourea, thiocyanate shows considerable stability towards oxidation.

Introduction

A possible alternative reagent to cyanide for gold leaching is thiocyanate, as first reported in 1905 by White [1]. However, that pioneering work was forgotten during the following decades because cyanidation was established as the predominant gold extraction process worldwide. It was more than 80 years before thiocyanate was revisited when Fleming published the results of an investigation of the simultaneous extraction of gold and uranium from South African pyrite ores using acid ferric sulfate solution for oxidation [2]. Since then, research efforts have been made to further understand the thiocyanate system. A thermodynamics study of thiocyanate system for leaching gold and silver ores was investigated by Barbosa-Filho and Monhemius[3].

Thiocyanate is a technically viable and interesting lixiviant for gold [4]. Development has been reported by Newmont with application to low-grade refractory gold ores after bio-oxidation [5]. One of the important features of the thiocyanate system is that leaching is usually performed

between pH 1 and 2, which allows the use of ferric sulfate as an oxidizing agent. The mechanism of dissolution of gold by ferric-thiocyanate solutions is directly linked with autoreduction process, in which ferric is spontaneously reduced to ferrous while oxidizing SCN^- . This oxidation proceeds through the formation of several intermediate species, particularly $(\text{SCN})_3^-$ and $(\text{SCN})_2$, which act both as oxidants and, upon reduction, as complexants for gold. The formation of $(\text{SCN})_3^-$ and $(\text{SCN})_2$ must be continuous due to their relatively fast decomposition by hydrolysis into more stable oxidation products. The instability of $(\text{SCN})_3^-$ and $(\text{SCN})_2$ towards hydrolysis is a major drawback of the ferric-thiocyanate leaching system. Experimental results with this system at 25 °C yielded initial gold leaching rate of the order of $10^{-10} \text{ mol cm}^{-2} \text{ s}^{-1}$. Rates as high as 10^{-9} or even $10^{-8} \text{ mol cm}^{-2} \text{ s}^{-1}$, depending on reagent concentrations, could be obtained by raising the temperature to 85 °C, but this was seen as a limitation to the commercial use of thiocyanate as a gold lixiviant, as it would add costs to conventional agitated leaching [6-9].

Occasionally, the combination of lixiviants can produce a synergistic effect. Copper sulfate is a good coordinator for gold dissolution in thiosulfate solution compared to other oxidants [10]. The presence of Tu can improve the gold oxidation half reaction in thiosulfate solutions [11]. The addition of a small amount of Tu into a thiocyanate solution may catalyze the gold dissolution leading to significant benefits such as a faster leaching rate [12-13]. The aim of this paper is to determine the effect of major parameters on the dissolution rate associated with mixed thiocyanate/Tu leaching system using ferric sulfate as oxidant.

Experimental

The rotating disc technique was employed for leaching experiments. A gold disc (99.9% purity, 14.0 mm diameter) was purchased from Pine Instrument. An analytical rotator (Model: ASR, Pine Instrument) was used, and the rotational speed was controlled by the ASR Speed Control (Pine Instrument). Before each experiment, the disc surface was carefully ground and polished with successively finer grades of alumina powder of size 1.0, 0.3 and 0.05 μm . After rinsing with deionized water, dipping in 0.5 M HCl for more than 10 min, and rinsing with water again, the disc was ready for the leaching experiments.

The gold leaching experiments were carried out in a cylindrical reactor immersed in a thermostatically controlled water bath. A solution was freshly prepared for each experiment and it was left open to the atmosphere during the experiment. The volume of the solution was 1000 mL. The pH was adjusted by addition of NaOH or sulfuric acid. Ferric sulfate was used as the oxidant. Solution samples, about 5 mL, were taken at selected time intervals and analyzed for gold with a model IRIS intrepid II XSP ICP(Thermo Electro Corporation).

The standard conditions employed were a thiourea concentration of 5 mM, a ferric sulfate concentration of 0.055 M, a thiocyanate concentration of 0.02 M, pH 1.5, temperature 25 °C and a disc rotational speed of 200 rpm. Variations from these conditions are noted in the text and in

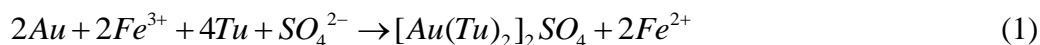
figure captions. All the chemicals were analytical grade and used as received.

Potentials measurements between gold disc and reference electrode (SCE) were made through a Luggin capillary using a Gamry Instrument PCI4G750 Potentiostat. The solution was 200mL and deaerated with nitrogen before open circuit potential measurements.

Results and Discussion

Effect of ferric sulfate concentration

The effect of ferric sulfate concentration on the gold leaching rate is shown in Figure1. As can be observed, gold leaching rate slightly increases with increasing ferric sulfate concentration from 0.0055 M to 0.022M. Further increasing ferric sulfate concentration to 0.055M has only a minor effect on the rate of gold dissolution. In thiourea only solutions, gold dissolves according to reaction (1), gold leaching rate is independent on ferric concentrations and remains constant with time when thiourea concentration is below 12 g/L[14].



In thiocyanate only solutions, gold dissolves according to reaction (2). Gold leaching rate decreases with time and ferric concentrations have only a minor effect on the rate of gold dissolution.

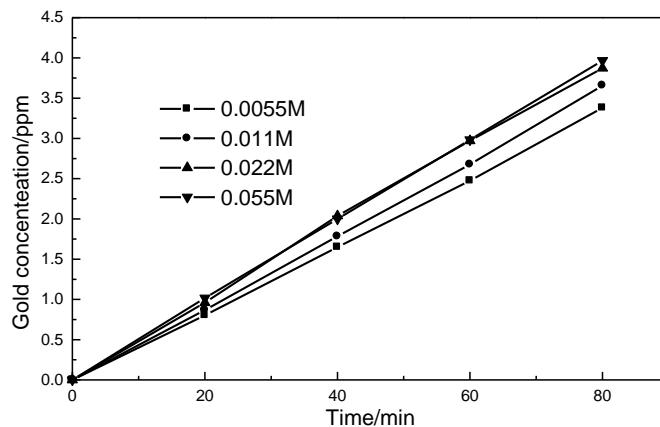
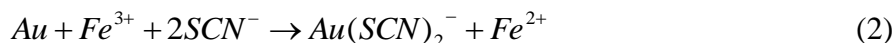


Figure1 Effect of ferric sulfate concentration on leaching of gold. Conditions: Tu 0.005 M, thiocyanate 0.02 M, pH 1.5, temperature 25 °C, 200 rpm.

In thiourea-thiocyanate solution, the gold leaching rate remains constant with time, which means the mixed ligand exhibits similar behavior as thiourea solutions. In our previous experiment, SERS results suggests a possible formation of a mixed ligand complex involving the interaction

of $Au(Tu)_2^+$ and SCN^- [13-14]. Now it is suggested again that gold dissolves according to reaction (3). Increasing ferric concentration leads to a small increase in gold leaching rate when ferric sulfate concentration is from 0.0055 M to 0.022M and no increase above 0.022 M. It is suggested that this response to ferric ions is similar to those observed by Li and Miller [14] when leaching in thiourea only solution.



Effect of thiocyanate and thiourea concentration

The rates of dissolution of gold obtained at different thiourea and thiocyanate concentrations are listed in Table 1. It is apparent that increasing thiocyanate concentration from 0.005M to 0.05 M decreases gold leaching rate. Increasing thiocyanate concentration appears to favor reaction (2) rather than reaction (3). Due to the slow reaction kinetics of reaction (2) compared to reaction (3), gold leaching rate decreases with increasing thiocyanate concentration. This may be caused by thiocyanate anions covering the surface of the gold electrode and hindering the interaction of thiourea with gold. Additional research will be needed to verify this hypothesis.

It can be seen that gold leaching rate increases with increasing Tu concentration, which is similar to previous reports in Tu only solutions [14]. The mixed solution with a Tu / SCN^- ratio of 1:4 to 1:1 leads to a higher gold leaching rate than either lixiviant alone or the sum of the two individual lixiviants.

The rates observed are the same magnitude with those of cyanide (typically, $10^{-9} \text{ mol cm}^{-2}\text{s}^{-1}$) or thiourea (0.1 molL^{-1} thiourea and 0.01 molL^{-1} formamidine disulphide) and one magnitude higher than those obtained with thiocyanate [8,15-16]. The dissolution in thiocyanate only solution is very slow, which means that thiocyanate does not participate significantly by directly dissolving gold, it must be assisting Tu to increase its rate of dissolution, which again suggests that Tu and thiocyanate have some synergistic effects and gold dissolves according to reaction (3).

Table 1 Gold leaching rate at various concentrations of thiourea and thiocyanate
 (25 °C, pH 1.5, 0.055 M ferric, 200 rpm)

Tu, M	Thiocyanate, M	Tu/SCN ⁻	Initial Rate, J, mol cm ⁻² s ⁻¹ (J×10 ⁹)
0.005	0.005	1:1	4.30
0.005	0.02	1:4	2.79
0.005	0.05	1:10	2.22
0.001	0.01	1:10	0.93
0.005	0.01	1:2	3.44
0.01	0.01	1:1	4.21
0.005	0	/	2.50
0	0.01	0	0.22

The synergistic effects can be illustrated by the open circuit potential shown in Figure2 and 3. It is interesting to note that there is a decrease in the potential readings in the ferric thiocyanate solution due to the oxidation of thiocyanate, resulting in the formation of the intermediate thiocyanate species such as (SCN)₂ and (SCN)₃⁻. Increasing thiocyanate concentration accelerates the decrease of potential. While in thiourea system (0 M NaSCN), The mixed potentials are low at zero time (shortly after the insertion of gold disc) and then increase and tend to plateau due to the production of the species formamidine disulphide, generated by the oxidation of thiourea by Fe³⁺ [17]. The adsorption of formamidine disulphide and thiourea on gold surface increases the potential initially [18-19]. Formamidine disulphide acts as oxidant for gold dissolution and is reduced to thiourea again. After some period, the system reaches a stable state and the potential tends to plateau [8,15].

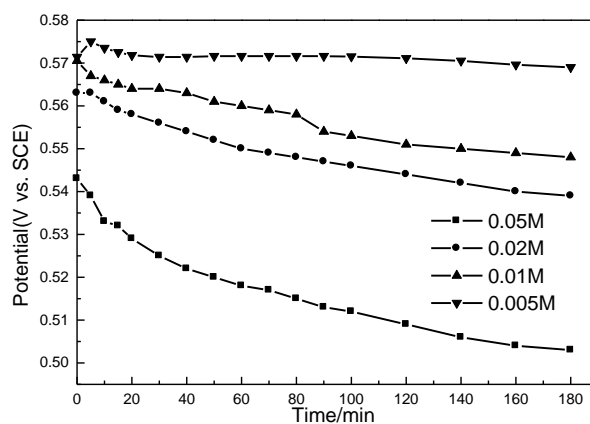


Figure2 Effect of thiocyanate concentration on open circuit potential reading in thiocyanate only solution on gold disc. Conditions: pH 1.5, temperature 25 °C, 200 rpm.

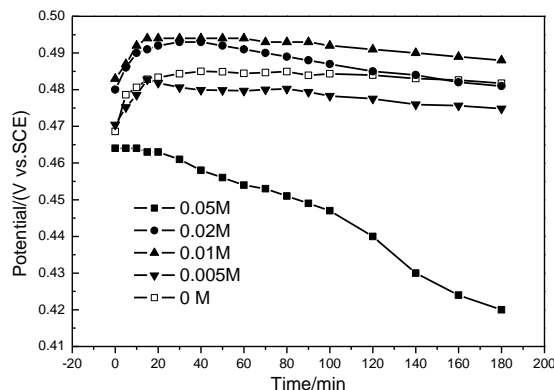


Figure 3 Effect of thiocyanate concentration on open circuit potential reading for Tu/thiocyanate mixed solution on gold disc. Conditions: Tu 0.005 M, pH 1.5, temperature 25 °C, 200 rpm.

In the mixed system containing 0.005 to 0.02 M thiocyanate, potential initially increases and then tended to a plateau or slowly decreases, which is similar to thiourea only system. By comparing the potentials for thiocyanate concentration from 0.005 to 0.02 M, it was found that the potential in thiocyanate only solution decreases more than that in the mixture at the same thiocyanate concentration. When thiocyanate concentration is increased to 0.05 M, the potentials decrease 60 mV within 180 min for the two systems. Since the decrease in the potential is related to thiocyanate oxidation, it is concluded that the mixture shows considerable stability towards oxidation in comparison with the corresponding thiocyanate solution.

Effect of pH value and temperature

The effect of pH value and temperature on gold leaching rates in a mixed Tu/thiocyanate solution is shown in Table 2. Increasing the pH value does not affect the gold leaching rate significantly for the mixed lixiviant system. What is observed is the gold leaching rate for pH 1.5 is a little higher than that for pH 1.0 and 1.9. In thiourea only solution, high pH value is favorable to gold dissolution [14]. In thiocyanate only solution, low pH value is favorable to thiocyanate stability [6]. From reaction (1) to (3), it is known that hydrogen ions do not take part in the reaction. The small effect is interpreted as pH value is related to thiocyanate stability and reaction kinetics of thiourea.

Table 2 Gold leaching rate at various pH value and temperature
(5 mM Tu, 0.01M NaSCN, 0.055 M ferric, 200 rpm)

pH	Temperature/°C	Initial Rate, J, mol cm ⁻² s ⁻¹ (J×10 ⁹)
1.5	20	2.5
1.5	25	3.44
1.5	30	4.56
1.5	35	6.17
1.0	25	2.98
1.9	25	3.07

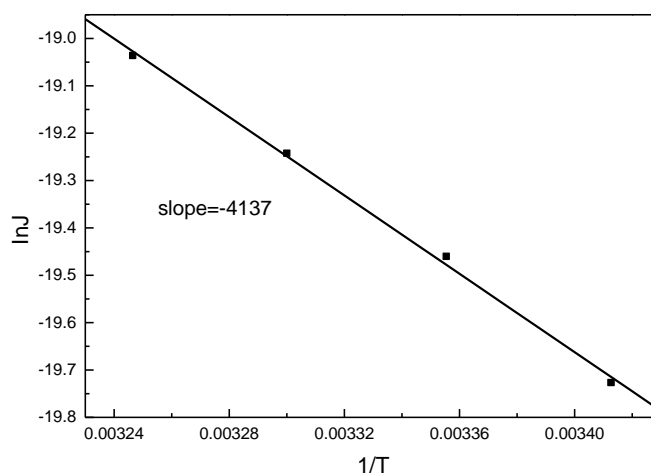


Figure 4 Arrhenius plot of ln J vs. 1/T. Data taken from Table 2.

Gold leaching rate increases with increasing temperature in the mixed Tu/thiocyanate solution. To better understand the mechanisms, activation energy was determined. The activation energy is simply calculated from logarithm of the initial rate against 1/T (e.g. Arrhenius plot) shown in Figure 4. The slope is -4137 . The apparent activation energy is calculated as 34.40 KJmol^{-1} according to Arrhenius theory. An activation energy of 34.40 KJmol^{-1} suggests that the process is controlled by a combination of surface reaction and mass transfer.

Conclusions

The addition of small amounts of Tu to thiocyanate-ferric solutions reveals a synergistic effect on the dissolution of gold. The dissolution rate are higher than those obtained when either ferric-thiocyanate or ferric-thiourea solutions are used separately at the concentrations used in the mixture. The mixture has the advantage of being more stable towards oxidation in comparison with single thiocyanate. Determinations of apparent activation energies indicate that gold dissolution is a mixed-control process unlike surface controlled reaction observed in thiocyanate solutions. Initial gold leaching rate of the order of 10^{-9} mol $\text{cm}^{-2}\text{s}^{-1}$ was obtained. Thiourea to thiocyanate ratio has a significant effect on gold leaching rate and thiocyanate stability.

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