Thiourea-thiocyanate leaching system for gold

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Abstract: The leaching of gold in thiourea-thiocyanate solutions has been studied by the rotating-disk technique using ferric sulfate as oxidant. The effects of initial concentrations of ferric, thiourea (Tu) and thiocyanate as well as temperature and pH values on gold leaching rates were studied. An initial gold leaching rate in the order of 10^{-9} mol cm^{-2} s^{-1} was obtained at 25℃, which was higher than rates obtained when either ferric-thiocyanate or ferric-thiourea solutions were used separately. The synergistic effect was attributed to the formation of a mixed ligand complex $Au(Tu)_2SCN$. Determinations of apparent activation energy indicate that the process was controlled by a combination of chemical reaction and diffusion in the mixed lixiviant system. Open circuit potentials show that thiocyanate stability is increased in the mixture.

Keywords: Gold dissolution; Thiourea; Thiocyanate; Synergistic effect

1. Introduction

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A possible alternative reagent to cyanide for gold leaching is thiocyanate, as first reported by White (1905). However, it was not until 1986 that research on the subject was resumed by Fleming (1986). A thermodynamics study of the thiocyanate system for leaching of gold and silver ores was published by Barbosa-Filho and Monhemius (1989).

Thiocyanate is a technically viable and interesting lixiviant for gold (Broadhurst and Du Preez, 1993). Leaching is performed between pH 1 and 2, which allows the use of ferric sulfate as an oxidizing agent (Barbosa-Filho and Monhemius, 1994a). The mechanism of dissolution of gold by ferric-thiocyanate solutions is directly linked to the auto-reduction process, in which ferric is spontaneously reduced to ferrous while oxidizing SCN^-. This oxidation proceeds through the formation of several intermediate species, particularly $(SCN)_3^-$ and $(SCN)_2$, which both act as oxidants and, upon reduction, as complexants for gold(Barbosa-Filho and Monhemius, 1994b). The formation of $(SCN)_3^-$ and $(SCN)_2$ must be continuous due to their relatively fast decomposition by hydrolysis into more stable oxidation products. The instability of $(SCN)_3^-$ and $(SCN)_2$ towards hydrolysis is a major drawback of the ferric-thiocyanate leaching system. Experimental results with this system at 25° yielded an initial gold leaching rate in the order of 10^{-10} mol cm^{-2} s^{-1} (Barbosa-Filho and Monhemius, 1994c). Rates as high as 10^{-9} or even 10^{-8} mol cm^{-2} s^{-1}, depending on reagent concentrations, could be obtained by raising the temperature to 85°, but this was seen as a limitation to the commercial use of thiocyanate as a gold lixiviant, as it would add cost to conventional agitated leaching (Barbosa-Filho and Monhemius, 1994d).

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 (Breuer and Jeffrey, 2002; Li, et al., 1995). The presence of Tu can improve the gold oxidation half reaction in thiosulfate solutions (Chandra and Jeffrey, 2004). The addition of a small amount of Tu into a thiocyanate solution appears to catalyze the gold dissolution leading to significant benefits such as a faster leaching rate (Yang et al., 2010a). The aim of this paper is to determine the effect of major parameters on the dissolution rate associated with mixed a thiocyanate/Tu leaching system using ferric sulfate as an oxidant.

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

The FTIR Transmission spectra were recorded in the range of 4000-400 cm^{-1} on a Bio-Rad 6000 FTIR spectrometer with a broadband MCT detector. A cell with two CaF_2 windows and a 0.05 cm Teflon spacer was used in this study. All the spectra were obtained at room temperature from the average of 500 scans with a resolution of 4 cm^{-1}. The solutions examined included 0.4 M Tu, 0.4 M Tu + 0.1M $AuCl_3$ and NaSCN + 0.4 M Tu + 0.1 M $AuCl_3$, the NaSCN concentration was controlled at 0.4 M, 0.8M and 1.8 M, respectively. To diminish the interference of water and to avoid as much as possible that from the acid, deuterated oxide was used as solvent and the spectrum of 0.03 M H_2SO_4 in deuterated oxide was used as a baseline.

3. Results and discussion

3.1 Effect of ferric sulfate concentration

The effect of ferric sulfate concentration on the gold leaching rate in the presence of thiourea and thiocyanate is shown in Fig.1. As can be observed, the gold leaching rate slightly increases with increasing ferric sulfate concentration from 0.0055 M to 0.022 M. Further increasing the ferric sulfate concentration to 0.055M has only a minor effect on the rate of gold dissolution. In sulfuric acid solutions with ferric and thiourea present (e.g. thiourea only solutions), gold dissolves according to reaction (1). The gold leaching rate is independent of ferric concentration and keeps constant with time when thiourea concentration is below 12 g L^{-1} and ferric is above 0.1 g L^{-1} (Li and Miller, 2007).

$$2Au + 2Fe^{3+} + 4Tu + SO_4^{\ 2-} \rightarrow [Au(Tu)_2]_2SO_4 + 2Fe^{2+} \tag{1}$$

In sulfuric acid solutions with ferric and thiocyanate present (e. g. thiocyanate only solutions), gold dissolves according to reaction (2) (Li et al., 2008). The gold leaching rate decreases with time and ferric concentration has only a minor effect on the rate of gold dissolution.

$$Au + Fe^{3+} + 2SCN^- \rightarrow Au(SCN)_2^{\ -} + Fe^{2+} \tag{2}$$

In thiourea-thiocyanate solutions, the gold leaching rate remains constant with time, which means the mixed ligand exhibits behavior similar to thiourea solutions. Increasing ferric concentration leads to a small increase in the gold leaching rate when ferric sulfate concentration increases from 0.0055 M to 0.022 M with no increase above 0.022 M. It is suggested that this response to ferric ions is related to mass transport. Ferric ion forms complexes with SCN$^-$ (Barbosa-Filho and Monhemius, 1994a) and thiourea (Li and Miller, 2007). When ferric is in the concentration range of 0.0055 M to 0.022 M, free ferric ion is limited and increasing ferric concentration increases the mass transfer, which is similar to the results reported by Li and Miller (2007). When ferric is above 0.022M, ferric is excess with respect to thiourea or thiocyanate, the gold dissolution reaction is independent on ferric concentration. It is reported that high ferric concentration is favorable to thiocyanate stability (Broadhurst and Preez, 1993) and thus ferric was fixed at 0.055 M for subsequent experiments.

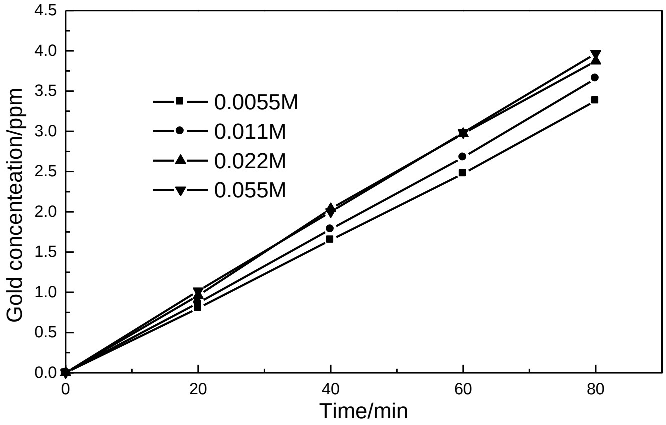

Fig.1 Effect of ferric sulfate concentration on the leaching rate of gold. Conditions: Tu 0.005 M, thiocyanate 0.02 M, pH 1.5, temperature 25°C, 200 rpm.

3.2 FTIR measurements

Previously, SERS results suggested a possible formation of a mixed ligand complex involving the interaction of $Au(Tu)_2^+$ and SCN^- to form $[Au(Tu)_2]SCN$ (Yang et al., 2010a). To further support the formation of the mixed ligand complex, FTIR measurements were performed in Tu, Tu-$AuCl_3$ and SCN^--Tu-$AuCl_3$ solutions. The results are shown in Fig.2. The spectrum of deuterated Tu shows bands at 1378 and 1466 cm^{-1} related to the stretching of C-S and C-N bonds. The band at 1515 cm^{-1} has been assigned to the bending mode of the ND_2 groups. The band at 1625 cm^{-1} that becomes stronger upon the addition of auric chloride is related to formamidine disulfide (FDS). The gold is predominantly stable as an aurous ion when complexed with thiourea. Auric is reduced to aurous by the oxidation of thiourea to FDS. The band at 3407 cm^{-1} can be assigned to the stretching mode of ND_2 groups. When $AuCl_3$ was added, a new band at 1561 cm^{-1} can be seen, which indicates the formation of the gold-thiourea complex in the presence of sulfuric acid [Bolzan et al., 2003].

When thiocyanate was added into the above solution, a band related to the stretching mode of sulfur in SCN^- appears at 2063 cm^{-1} [Bron and Holze, 1999]. With increasing thiocyanate concentration, the band of ND_2 stretching mode at 3047 cm^{-1} shifts toward higher wavenumbers likely due to concentration increase. The C-N stretching mode at 1466 cm^{-1} shifts toward lower wavenumbers. The band at 1561 cm^{-1} associated with the gold-thiourea complex disappears into the shoulder of the increasing C-N stretching peak at 1466 cm^{-1}.

The red shift of the C-N stretching mode band upon the addition and increase of thiocyanate indicates the increased character of the bond of C-N. This is interpreted as being caused by an interaction between $Au(Tu)_2^+$ and SCN^- complex. Because the stability constant for the soluble species of $Au(Tu)_2^+$ is higher than that for $Au(SCN)_2^-$ (Groenewald, 1975; Barbosa-Filho and Monhemius, 1994c), the most probable complex is $Au(Tu)_2SCN$ involving the interaction of $Au(Tu)_2^+$ and SCN^-. It is suggested again that gold dissolves according to reaction (3).

$$Au + Fe^{3+} + SCN^- + 2Tu \rightarrow Au(Tu)_2SCN + Fe^{2+} \qquad (3)$$

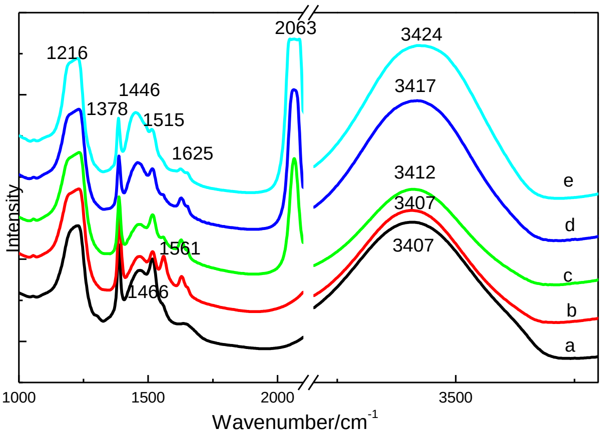

Fig.2 FTIR spectra in (a) 0.4 M Tu; (b) 0.4 M Tu + 0.1 M $AuCl_3$; (c) 0.4 M SCN^- + 0.4 M Tu + 0.1 M $AuCl_3$; (d) 0.8 M SCN^- + 0.4 M Tu + 0.1 M $AuCl_3$ and (e) 1.8 M SCN^- + 0.4 M Tu + 0.1 M $AuCl_3$ solutions.

3.3 Effect of thiocyanate concentration

The effect of thiocyanate concentration on the gold leaching rate is shown in Fig.3. It is apparent from Fig.3 that increasing the thiocyanate concentration from 0.005M to 0.05 M decreases the gold leaching rate. When thiocyanate concentration is below

0.02 M, gold concentration increases linearly with time indicating that leaching rate is not time dependent over the range studied. When the thiocyanate concentration is 0.05 M the gold leaching rate decreases with time, which is similar to the behavior observed in thiocyanate only solutions.

Due to the low thiourea concentration used (0.005 M), the required thiocyanate concentration for reaction (3) to proceed is also low. Thus, the added thiocyanate appears to decrease the rate of reaction and eventually lead to passivation at high thiocyanate concentration.

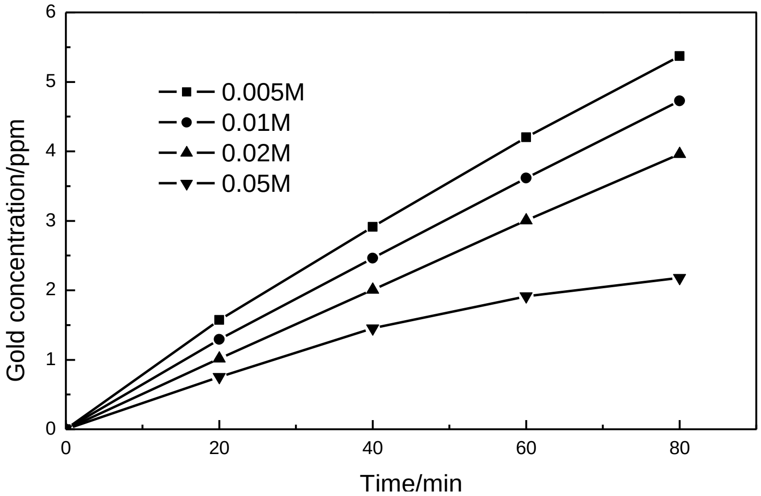

Fig.3 Effect of thiocyanate concentration on the leaching rate of gold. Conditions: Tu 0.005 M, ferric 0.055 M, pH 1.5, temperature 25°C, 200 rpm.

3.4 Effect of thiourea concentration

The results at various concentration of thiourea at a fixed thiocyanate concentration of 0.01 M are shown in Fig.4. The gold leaching rate increases with increasing Tu concentration, which is similar to previous reports in Tu only solutions (Li and Miller, 2007).

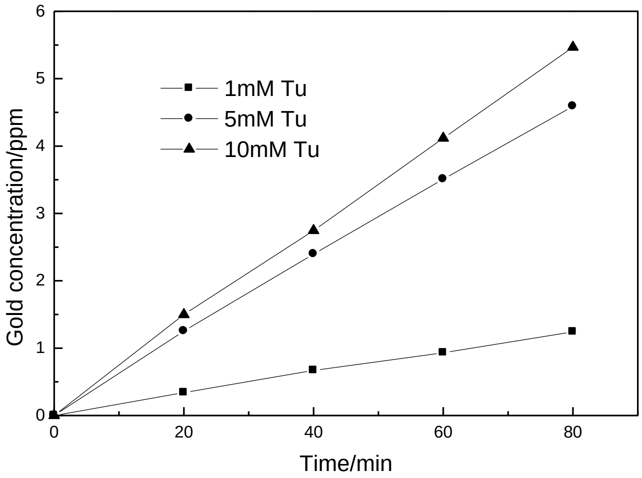

Fig.4 Effect of Tu concentration on the leaching rate of gold. Conditions: ferric 0.055 M, thiocyanate 0.01 M, pH 1.5, temperature 25°C, 200 rpm.

To better understand the leaching process, the gold leaching rate for the mixed Tu/thiocyanate solution compared with that in Tu or thiocyanate only solutions is shown in Fig.5. The sum of gold concentration with two individual lixiviants is also presented. It can be seen that the mixed solution leads to a higher gold leaching rate than either lixiviant alone or the sum of the two individual lixiviants.

It is easy to get the initial gold leaching rate from the results presented previously. These results are summarized in Table 1 and indicate that the dissolution rate is strongly dependent on the concentration of thiourea and the ratio of thiourea to thiocyanate. A higher ratio and thiourea concentration are favorable to enhanced leaching kinetics.

Table 1 Gold leaching rate at various concentrations of thiourea and thiocyanate.

Tu, M	Thiocyanate, M	Tu/thiocyanate	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

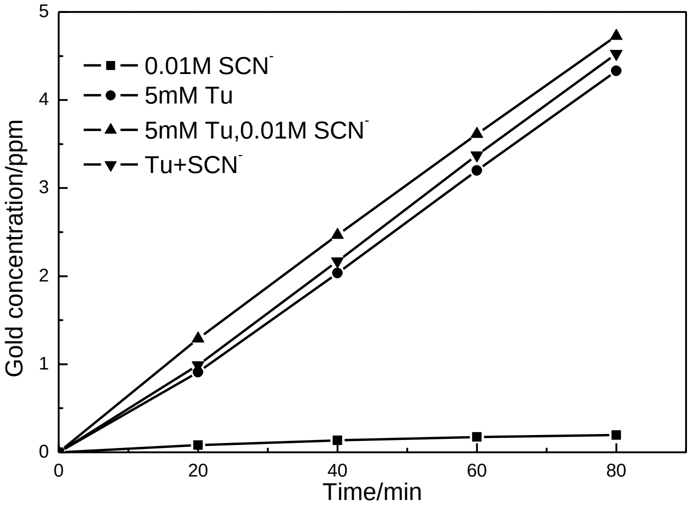

Fig.5 Effect of ligand on gold dissolution and the sum of gold concentration in 5 mM Tu and 0.01 M NaSCN individually. Conditions: ferric 0.055 M, pH 1.5, temperature 25°C, 200 rpm.

3.5 Electrochemical measurements

Previous electrochemical results indicate the lowest polarization resistance for gold dissolution at potentials of 0.3 and 0.4 V vs. SCE was observed at SCN$^-$ to Tu ratios between 5:1 and 10:1 (Yang et al., 2010b). The leaching results in the presence of ferric indicate 1:1 is better than 5:1 to 10:1. One possible explanation for this apparent discrepancy is that the leaching was performed in the presence of the ferric ion and the electrochemical studies were not.

Ferric ion forms complexes with SCN^- (Barbosa-Filho and Monhemius, 1994a) and thiourea (Li and Miller, 2007). Due to differences in complex stability constants, it is likely that the actual free SCN^- to Tu ratio is different from the SCN^- to Tu ratio based on the initial addition. While a rigorous calculation of stability constants has not been performed, a quick examination of the relative magnitude of stability constants indicates that ferric ion is likely to complex more with thiourea than with thiocyanate. This would result in the actual SCN^- to Tu ratio in the ferric solution being higher than what appears to be added in the form of the chemicals. Thus, the optimal free SCN^- to Tu ratio for the ferric-thiourea-thiocyanate leaching solution is probably similar to those measured electrochemically.

The rates observed are the same magnitude as reported for cyanide leaching of gold (typically, 10^{-9} mol cm^{-2} s^{-1}) or thiourea (0.1 M thiourea and 0.01 M formamidine disulphide) and one magnitude higher than those obtained with thiocyanate (Barbosa-Filho and Monhemius, 1994c; Li and Miller, 2002; Groenewald, 1976).

The dissolution in thiocyanate only solution is very slow, which means that thiocyanate does not participate significantly in the direct dissolution of gold, rather thiocyanate must be assisting Tu to increase the rate of dissolution, which again suggests that Tu and thiocyanate have some synergistic effects and gold dissolves according to reaction (3).

To understand the synergistic effect further, the open circuit or mixed potential of gold was measured over time. Fig.6 shows the open circuit potentials of gold in ferric thiocyanate solutions with various thiocyanate concentrations. 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 $(SCN)_3^-$ (Barbosa-Filho and Monhemius,1994c) and reduction of ferric ion.

The reverse occurs in the thiourea system as shown in Fig.7 (0 M NaSCN). The mixed potentials are low at zero time and then increase and tend to plateau due to the production of the species formamidine disulphide, generated by the oxidation of thiourea by Fe^{3+}. The weak adsorption of formamidine disulphide and thiourea on the gold surface slight increases the potential initially (Yang et al, 2010; Zhang et al., 2001). Formamidine disulphide acts as oxidant for gold dissolution and is reduced to thiourea again (Li and Miller, 2002). After some period, the system reaches a stable state and the potential tends to plateau.

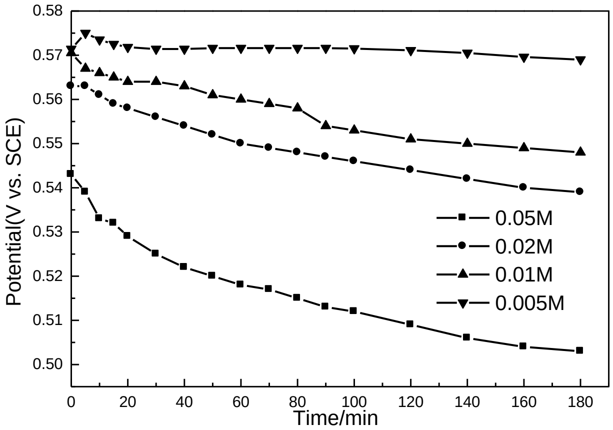

Fig.6 Effect of thiocyanate concentration on open circuit potential reading in thiocycanate only solution on gold disc. Conditions: ferric 0.055 M, pH 1.5, temperature 25°C, 200 rpm.

In the mixed system with thiocyanate concentration from 0.005 to 0.02 M, the potentials show the same tendency with thiourea while 0.05 M thicyanate appears more similar to the response in thiocyanate only solutions.

The mixed or potential measured at 20 minutes (From Fig.7) is compared to the calculated current density for gold dissolution in Fig.8. The current density was calculated from the leaching rate given in Table 1 using Faraday's law and a one electron transfer reaction ($Au \rightarrow Au^+ + e$).

It appears that several competing reactions are occurring simultaneously making a mechanistic determination difficult at this time. The authors believe the addition of small amounts thiocyanate is activating the gold surface by alleviating some surface passivation possibly caused by $[Au(Tu)_2]_2SO_4$ (Zhang et al., 2001). Further addition of thiocyanate can lead to surface blocking (e.g. deactivation) by the proposed formation of Au(SCN) (Li et al., 2008). Additionally, thiocyanate can also complex ferric ion and thus reduce the oxidation power of the leaching solution. How these three mechanisms interact to generate the response observed in this study need further investigation.

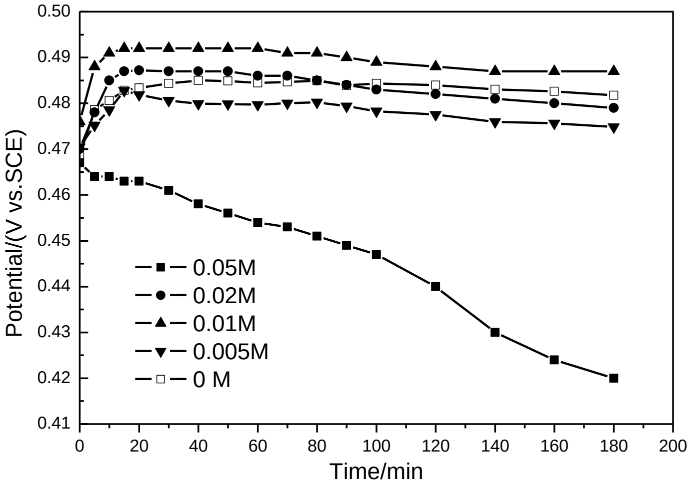

Fig.7 Effect of thiocyanate concentration on open circuit potential reading for Tu/thiocyanate mixed solution on gold disc. Conditions: ferric 0.055 M, Tu 0.005 M, pH 1.5, temperature 25°, 200 rpm.

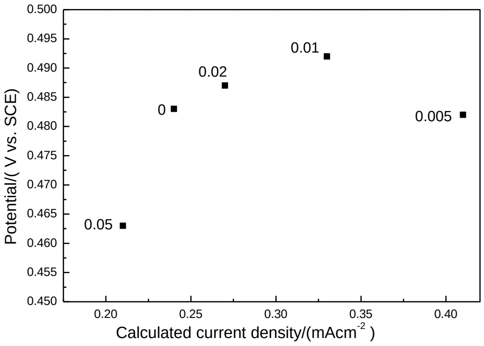

Fig.8 Mixed potential at 20 min vs. calculated current density from gold dissolution rate as a function of thiocyanate concentration (M as listed in plot). Conditions: ferric 0.055 M, Tu 0.005 M, pH 1.5, temperature 25°, 200 rpm.

3.6 Effect of pH value

The effect of pH on gold dissolution in a mixed Tu/thiocyanate solution is shown in Fig.9. 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 the thiourea only solution, a high pH value is favorable for gold dissolution (Li and Miller, 2007). In the thiocyanate only solution, a low pH value is favorable for thiocyanate stability (Barbosa-Filho and Monhemius, 1994a). From reaction (1) to (3), it is known that hydrogen ions do not take part in the reaction. The small effect of pH value appears to be related to thiocyanate stability and reaction kinetics of thiourea.

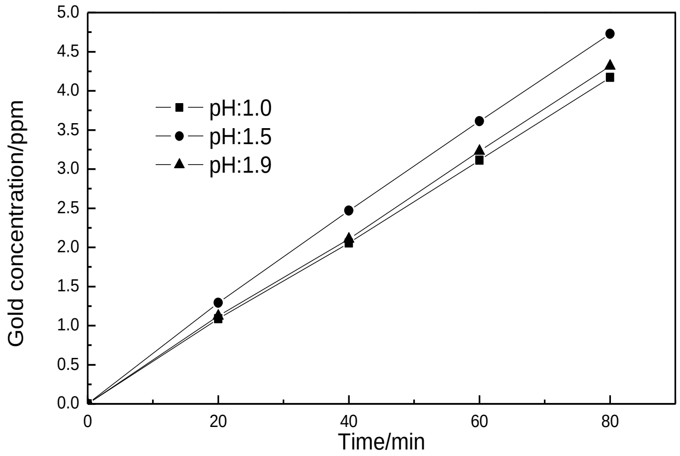

Fig.9 Effect of pH value on the leaching rate of gold. Conditions: ferric 0.055 M, thiocyanate 0.01 M, thiourea 0.005 M, temperature 25°, 200 rpm.

3.7 Effect of temperature

The effect of temperature on gold dissolution is presented in Fig. 10. It is shown that the gold leaching rate increases with increasing temperature in the mixed Tu/thiocyanate solution. To better understand the leaching mechanisms, the activation energy was determined. The activation energy is simply calculated from the slope of the logarithm of the rate deduced from experimental results against 1/T (e.g. Arrenhius plot) as shown in Fig.11. The slope is –4137. The apparent activation energy is calculated as 34.40 KJ mol $^{-1}$ according to the Arrenhius theory and suggests that the process is either controlled by a surface reaction or a combination of surface reaction and mass transfer.

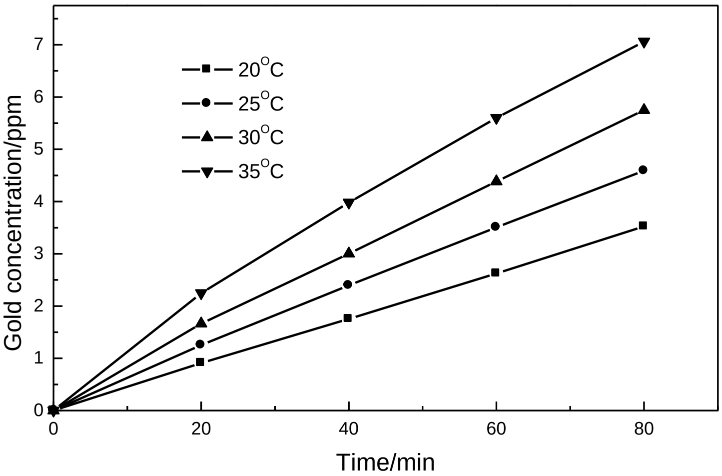

Fig.10 Effect of temperature on the leaching rate of gold. Conditions: ferric 0.055 M, thiocyanate 0.01 M, thiourea 0.005 M, pH 1.5, 200 rpm.

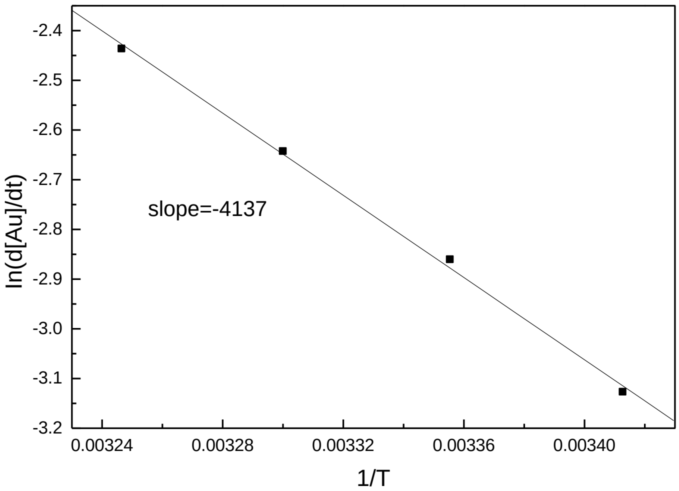

Fig.11 Arrhenius plot of In(d[Au]/dt) vs. 1/T. Data taken from Fig. 10.

To confirm the rate-controlling step, the effect of rotating speeds on gold dissolution was studied and the results are shown in Table 2. It can be seen that increasing the rotating speed does increase the gold leaching rate. According to Levich (1962), for reactions at a rotating disk that are controlled by the diffusion of reactants or products, there is a linear dependence between the flux of a given species to or from the disk and the square root of the disk's angular velocity. The data in Table 2 indicates that there is no linear relationship between the gold leaching rate and the square root of the disk's angular velocity. This analysis is in agreement with the calculated activation energy, which indicates gold dissolution is a mixed-control process where mass transfer control is present. In thiocyanate solutions, the process is controlled by surface reaction (Barbosa-Filho and Monhemius, 1994c). It seems that the addition of small amounts of thiourea into thiocyanate solutions leads to the control step changing from surface reaction to a mixed process. In fact such a transition in rate control was suggested by Li and Miller for the acid thiourea system (Li and Miller, 2007).

Table 2 Gold leaching rates observed at several disk rotating speeds.

Rotation speed, ω, rpm	$\omega^{1/2}$	Rate, J, mol $cm^{-2}s^{1}(J\times10^{9})$
100	10	2.43
200	14.1	3.44
400	20	3.51

4. Conclusions

The addition of small amounts of Tu to thiocyanate-ferric solutions reveals a synergistic effect on the dissolution of gold. The dissolution rate is higher than those obtained when either ferric-thiocyanate or ferric-thiourea solutions are used separately at the concentrations used in the mixture. The synergistic effect is ascribed to the formation of a mixed ligand complex $Au(Tu)_2SCN$. Determinations of apparent activation energies indicate that gold dissolution is a mixed-control process unlike the surface controlled reactions observed in thiocyanate solutions. An initial gold leaching rate in the order of 10^{-9} mol $cm^{-2}s^{-1}$ was obtained and dependent on the thiourea to thiocyanate ratio. These initial dissolution rates compare favorably to cyanide leaching rate.

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