

CATHODIC BEHAVIOR OF GOLD IN ACIDIC THIOUREA SOLUTIONS

C.M. Juarez¹ and A.J.B. Dutra²

¹National University of San Juan - Mining Research Institute
Av. San Martin, 1109 (O), San Juan, S.J. 5400 - ARGENTINA

²Federal University of Rio de Janeiro - Metallurgical and Materials Engineering Program
P.O. Box 68505 - Rio de Janeiro, RJ 21945-970 - BRAZIL - adutra@metalmat.ufrj.br

ABSTRACT

The extraction of gold with cyanide-free chemicals can be an attractive alternative to the traditional cyanidation process. The use of thiourea for gold leaching is very well known, however the electrowinning process has received little attention. In this paper, the influence of thiourea concentration and temperature on the cathodic behavior of gold, in acidic thiourea solutions, was studied with different electrochemical techniques. Results indicated that increasing amounts of thiourea impair the complex gold(I)-thiourea reduction, which is favored by higher temperatures, at least up to 65°C. The cathodic reaction mechanism involves the simultaneous reduction of the complex gold(I)-thiourea adsorbed on the electrode surface and in solution as well.

INTRODUCTION

In the last fifteen years environmental concerns about gold extraction have brought out a number of alternatives for the traditional gold leaching process [Deschênes, 1986; Hiskey and Atlury, 1988]. Among them, thiourea leaching was one of the most promising due to its faster kinetics, lower sensitivity to base metals and lower toxicity, although high thiourea consumption because of its degradation by the excessive presence of oxidizing agents. However, it is still attractive for certain refractory ores [Hisshion and Waller, 1984; Dupuis and Ghali, 1989; Lacoste-Bouchet *et al.*, 1998] and electronic gold scraps [Lin and Huarng, 1994].

Although a considerable amount of research has been carried out on gold leaching with thiourea, relatively little research has been done on electrowinning. Thus, the objective of this paper is to report the influence of temperature and potential on the cathodic behavior of gold in acidic thiourea solutions.

Previous work

It has been shown that gold could be electrowon onto titanium cathodes, from thiourea solutions, achieving around 98% extraction in a pilot plant (Maslii *et al.* (1973)).

Varentsov and Belyakova (1983) showed that the productivity increases and current efficiency decreases by increasing the current density for silver electrowinning from thiourea solutions. Additionally, they had shown that a drop in thiourea concentration lead to an increase in the silver extraction rate and in the current efficiency.

A two-stage electrolysis cell, for gold and silver electrowinning, from thiourea solutions, was developed by Zamyatin *et al.* (1983). A 98% extraction for silver and 90% for gold were reported. In a subsequent work, Zamyatin and Bek (1984) reported that hydrogen evolution limits the productivity of porous flow-through cathodes for gold electrowinning from thiourea solutions. For a carbon felt cathode, the maximum productivity was achieved with a current density of 0.12 A cm⁻², in a 0.25 M sulfuric acid solution containing 5 x 10⁻⁵ mol L⁻¹ of gold and 0.66 mol L⁻¹ of thiourea. In another paper, the same authors reported a dramatic decrease in the gold extraction due to the presence of dissolved oxygen in the electrolyte [Zamyatin and Bek, 1984].

Dupuis and Ghali (1989) investigated the gold recovery from thiourea solutions by direct electrowinning from leaching solutions in a flow-through cell with a carbon felt cathode and lead anode separated by a cationic membrane. A 99% gold recovery and current efficiencies lower than 10% were reported.

Conradie *et al.* (1994) showed that gold could be stripped from ion exchange resins by acidic thiourea solutions and electrowon onto a stainless steel mesh cathode with current efficiencies close to 100% at low current densities and gold concentrations around 1400 ppm.

Groenewald (1975) studied the behavior of a gold rotating disk electrode in acidic thiourea solutions. An

exchange current density of $1.2 \times 10^{-4} \text{ A cm}^{-2}$ and a transfer coefficient of 0.4, for cathodic overpotentials up to -0.1 V were reported. For an overpotential of 0.2 V the diffusion coefficient for the complex gold-thiourea, at 30°C , was reported as being $1.1 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ in 0.1 M sulfuric acid and 0.01 M thiourea solution.

Recently, Juarez and Dutra (2000) have studied the mechanism of the gold-thiourea complex reduction in a 0.1 M sulfuric acid and 0.0131 M thiourea solution. The proposed mechanism involved the adsorption of the electroactive species and the reduction of both adsorbed species and species in solution, being the first reduced more easily. The diffusion coefficient of the gold-thiourea complex, determined by chronopotentiometry, at 25°C , was $1.0 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$.

EXPERIMENTAL

The electrochemical measurements were done with a PAR/EG&G, model 273A, potentiostat/galvanostat connected to a microcomputer with the M270 software for data acquisition and further analysis. Additionally, a lock-in amplifier PAR 5210 and the M398 software were used for the impedance measurements. A conventional, 600 mL three-electrode cell, with a glass frit to separate the working and counter electrodes compartments, was used throughout the experiments. The working electrode was a 4 mm diameter gold disk (PAR, model 616); the counter electrode, a platinum spiral wire and the reference, a saturated calomel electrode in a Luggin probe. The electrolyte temperature was kept constant at the desired level with a thermostatic bath. All the chemicals used were analytically pure, except the formamidine disulphide, which, when used, was produced *in loco* by the reaction of thiourea with hydrogen peroxide. Prior to each test, the electrolyte was previously deaerated by purging oxygen-free nitrogen for at least two hours, to avoid the interference of dissolved oxygen in the measurements, and the working electrode was polished with a $0.25 \mu\text{m}$ alumina, to a mirror finishing, and cleaned with acetone and doubly distilled water, in order to provide always a fresh gold surface.

RESULTS AND DISCUSSION

The equilibrium of the species involved in this system is summarized by the Eh-pH diagram presented in Figure 1. The concentration chosen for the dissolved species are close to those that should be used for gold electrowinning, which means a very low formamidine disulfide concentration. For leaching, the formamidine disulfide concentration should be much higher,

increasing the predominance area of the complex gold (I)-thiourea, as can be observed in Figure 2.

A typical cathodic linear sweep voltammogram, for the reduction of gold(I)-thiourea complex, is presented in Figure 3. It can be observed that the cathodic current density increases up to -0.100 V , reaching a limiting current density plateau around -0.150 V vs. SCE followed by a passivation process, caused by the presence of adsorbed compounds on the electrode surface. For higher cathodic potentials, the hydrogen evolution becomes the main reaction, decreasing dramatically the current efficiency for gold electrowinning.

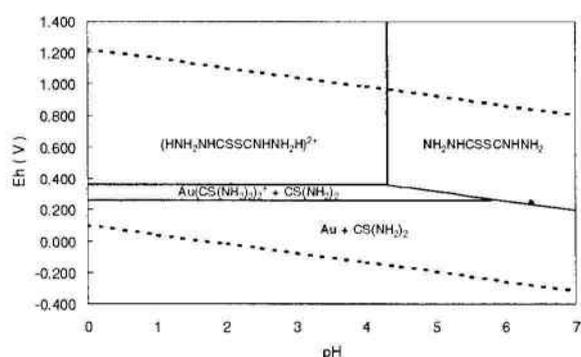


Figure 1 - Eh-pH diagram for Gold-Thiourea- H_2O system at 25°C . $[\text{CS}(\text{NH}_2)_2]=0.1 \text{ M}$, $[\text{NH}_2\text{NHCSSCNHNH}_2]=0.0001 \text{ M}$, $[(\text{H}_2\text{N})_2\text{NHCSSCNHNH}_2\text{H}_2]^{2+}=0.0001 \text{ M}$, $[\text{Au}(\text{CS}(\text{NH}_2)_2)_2^+]=0.0001 \text{ M}$.

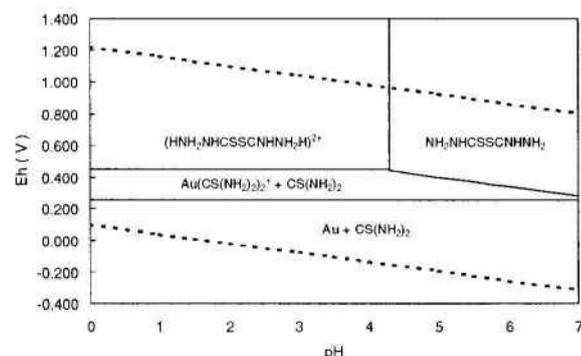


Figure 2 - Eh-pH diagram for Gold-Thiourea- H_2O system at 25°C . $[\text{CS}(\text{NH}_2)_2]=0.1 \text{ M}$, $[\text{NH}_2\text{NHCSSCNHNH}_2]=0.1 \text{ M}$, $[(\text{H}_2\text{N})_2\text{NHCSSCNHNH}_2\text{H}_2]^{2+}=0.1 \text{ M}$, $[\text{Au}(\text{CS}(\text{NH}_2)_2)_2^+]=0.0001 \text{ M}$.

The Nyquist diagrams for the potentials indicated in Figure 3 are shown in Figure 4. For cathodic potentials up to -0.050V vs. SCE, the plots indicated the presence of one semicircle at high frequencies associated to two semicircles for medium and low frequencies. The first semicircle was probably associated to the double layer charging and a slow charge transfer, while the others may be associated to an adsorption process. Additionally, it was observed that the size of the flattened semicircles had decreased with the increase of the electrode rotation speed, with the increase of gold concentration and with the increase of the cathodic potential, indicating a smaller charge transfer resistance. At potentials corresponding to the limiting current density plateau (-0.150V), and even more negative, the passivation characteristics were enhanced, making difficult the observation of mass transport features. This behavior was probably caused by the heterogeneous electrode surface due to adsorption of thiourea, and also gold-thiourea complex [Juarez and Dutra, 2000].

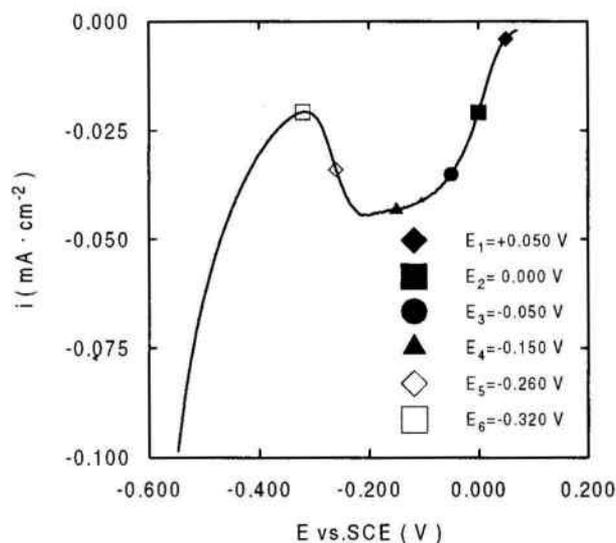


Figure 3 - Typical cathodic linear sweep voltammogram indicating the potentials used in the impedance tests in a solution containing $\text{Au}(\text{CS}(\text{NH}_2)_2)_2^+$ 5.08×10^{-5} M, $\text{CS}(\text{NH}_2)_2$ 0.0131 M and H_2SO_4 0.1 M. $\omega=2100$ rpm, $v=2.5$ $\text{mV}\cdot\text{s}^{-1}$.

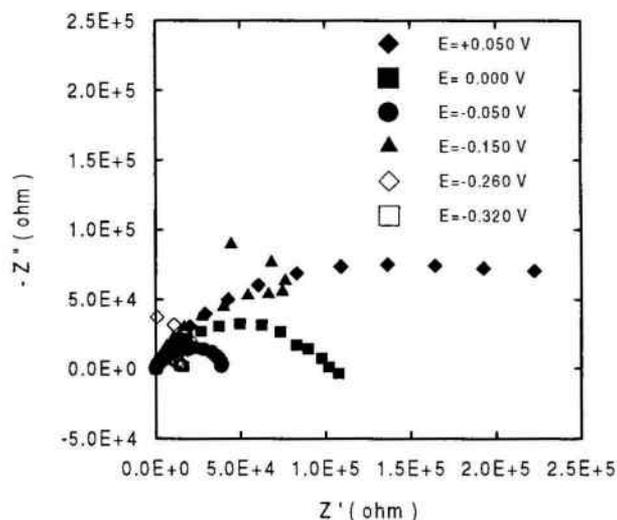


Figure 4 - Nyquist diagrams for the conditions indicated in Figure 3.

The influence of temperature on the current density vs. potential curves, for different thiourea concentrations, is shown in Figures 5, 6 and 7. It can be observed that, for all thiourea concentrations, a higher limiting current density plateau and a higher gold reduction rate is observed for the more elevated temperatures, which also favored the hydrogen evolution. For the lowest thiourea concentration (Figure 5), the cathodic current density drop, observed at -0.300V , tends to decrease gradually as temperature is increased, disappearing at 65°C .

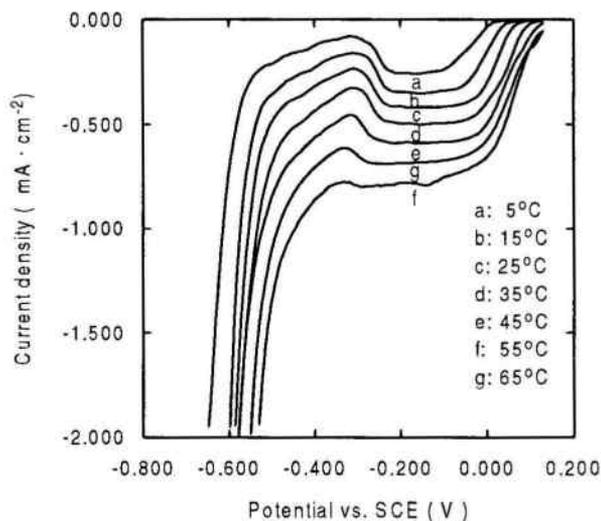


Figure 5 - Influence of temperature in current density vs. potential curves for solutions containing $\text{Au}(\text{CS}(\text{NH}_2)_2)_2^+$ 5.08×10^{-4} M, $\text{CS}(\text{NH}_2)_2$ 0.0131 M and H_2SO_4 0.1 M. $\omega=2100$ rpm; $v=2.5$ $\text{mV}\cdot\text{s}^{-1}$.

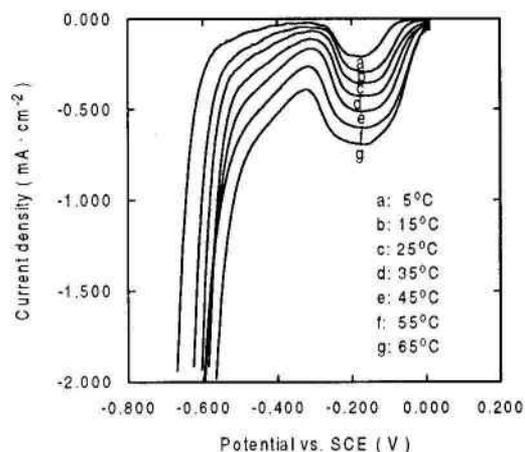


Figure 6 - Influence of temperature in current density vs. potential curves for solutions containing $\text{Au}(\text{CS}(\text{NH}_2)_2)_2^+$ 5.08×10^{-4} M, $\text{CS}(\text{NH}_2)_2$ 0.131 M and H_2SO_4 0.1 M. $\omega=2100\text{rpm}$; $v=2.5 \text{ mV}\cdot\text{s}^{-1}$.

This behavior may be attributed to an increase of thiourea degradation rate and/or to a decrease of the thiourea adsorption on the electrode surface at higher temperatures. For higher thiourea concentrations, the passivation persists even at 65°C , being more intensive for higher concentrations. This behavior indicates that the passivation observed for more cathodic potentials was caused by a strong thiourea adsorption on the gold electrode surface, as reported previously for silver electrodes [Bukowska and Jackowska, 1994], and not by the gold (I)-thiourea complex, which is also adsorbed on electrode surface before being reduced to metallic gold [Juarez and Dutra, 2000]. Furthermore, gold reduction is displaced to more cathodic potentials as thiourea concentration is increased.

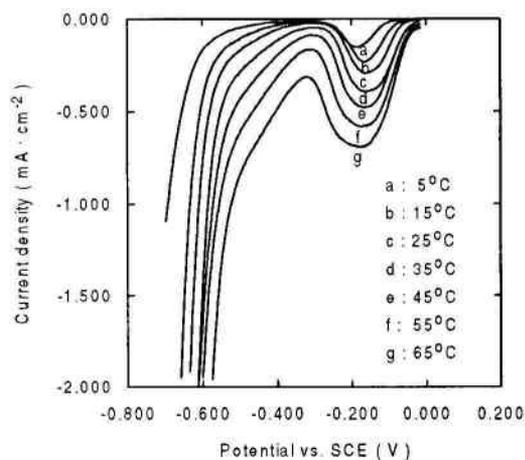


Figure 7 - Influence of temperature in current density vs. potential curves for solutions containing $\text{Au}(\text{CS}(\text{NH}_2)_2)_2^+$ 5.08×10^{-4} M, $\text{CS}(\text{NH}_2)_2$ 0.262 M and H_2SO_4 0.1 M. $\omega=2100\text{rpm}$; $v=2.5 \text{ mV}\cdot\text{s}^{-1}$.

The behavior of the effective activation energy at different constant potentials, calculated according to the method described by Antropov (1977) and Heitz and Kreysa (1986), with the inverse of temperature is shown in Figures 8 and 9. It can be observed that for less cathodic potentials the activation energy drops quickly as the temperature is increased, indicating a charge transfer control mechanism for the reduction of the complex gold (I)-thiourea, independently of thiourea concentration. For potentials in the range of -0.070 to -0.250V and thiourea concentration of 0.0131M , the activation energy smaller than 5kcal mol^{-1} indicates a mass transport control mechanism. For higher cathodic potentials the activation energy increases due to the intensive hydrogen evolution, which interferes strongly with the calculated activation energy.

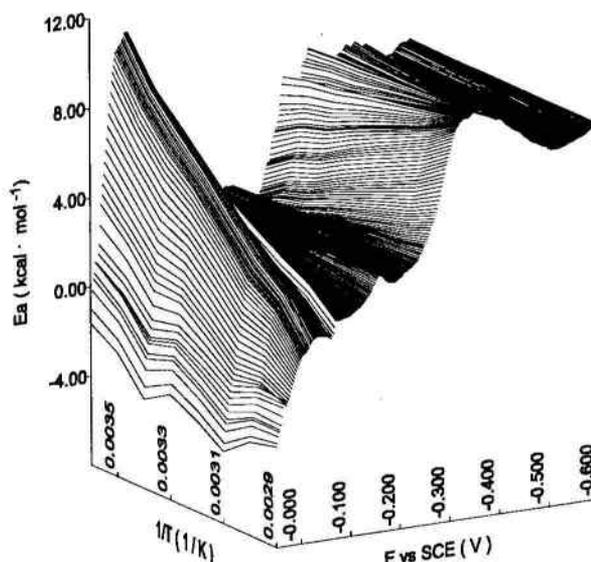


Figure 8 - Variation of effective activation energy with temperature and potential in a solution containing $\text{Au}(\text{CS}(\text{NH}_2)_2)_2^+$ 5.08×10^{-4} M, $\text{CS}(\text{NH}_2)_2$ 0.0131 M and H_2SO_4 0.1 M. $\omega=2100\text{rpm}$; $v=2.5 \text{ mV}\cdot\text{s}^{-1}$.

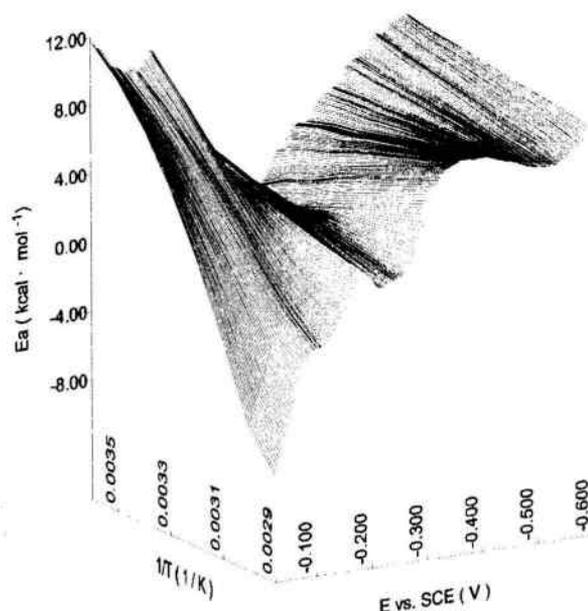


Figure 9 - Variation of effective activation energy with temperature and potential in a solution containing $\text{Au}(\text{CS}(\text{NH}_2)_2)_2^+$ 5.08×10^{-4} M, $\text{CS}(\text{NH}_2)_2$ 0.131 M and H_2SO_4 0.1 M. $\omega=2100\text{rpm}$; $\nu=2.5 \text{ mV}\cdot\text{s}^{-1}$.

The influence of the gold(I)-thiourea complex concentration on the exchange current density (i_0) and transfer coefficient (α) is presented in Table I. They were determined by the slope and intercept of the Tafel's plot of the cathodic polarization curve. The values determined for i_0 , around $1 \mu\text{A cm}^{-2}$, are indicative of pure charge transfer control for low overpotentials [Heitz and Kreysa, 1986]. The transfer coefficient figures greater than one indicate the presence of another reaction involving charge transfer occurring simultaneously with the gold complex reduction.

Table I - Exchange current density (i_0) and transfer coefficient (α) for different gold concentrations and solutions containing $\text{CS}(\text{NH}_2)_2$ 0.0131 M and H_2SO_4 0.1 M. $\omega=2100\text{rpm}$.

Gold concentration (M)	i_0 ($\mu\text{A}\cdot\text{cm}^{-2}$)	α
5×10^{-5}	1.104	0.97
1×10^{-4}	1.290	1.08
2×10^{-4}	1.304	1.30
5×10^{-4}	1.000	1.34

CONCLUSIONS

The electrochemical tests indicated that increasing amounts of thiourea displace gold(I)-thiourea reduction to more cathodic potentials.

The complex gold(I)-thiourea reduction is favored by low thiourea concentrations and high temperatures, up to 65°C .

The complex gold(I)-thiourea reduction is controlled by charge transfer for cathodic potentials up to 0.000V vs. SCE, then, the reaction becomes diffusion controlled up to approximately -0.200V . For even more cathodic potentials, the electrode surface is passivated, probably due to thiourea adsorption.

An intensive hydrogen evolution was observed at potentials below -0.400V vs. SCE.

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