



# Effect of ammoniacal thiosulfate solution composition on the gold dissolution rate: An electrochemical study

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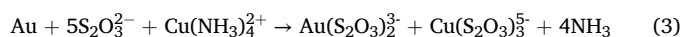
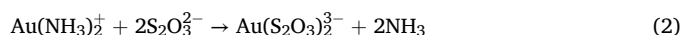
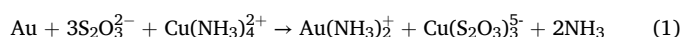
## ABSTRACT

The electrochemical behavior of ammoniacal thiosulfate solutions ( $S_2O_3^{2-}$ - $NH_3$ - $Cu^{2+}$ -EDTA) has been studied for varying electrolyte compositions in the gold electro-dissolution. A gold rotating disk electrode (RDE) was employed to measure anodic and cathodic polarization curves in alkaline thiosulfate solutions. Potentiodynamic polarization showed how thiosulfate, ammonia, and copper concentration influence the cathodic and anodic behavior of the electrolyte. Likewise, the influence of oxygen on the electrochemical behavior system was evidenced from the analysis of polarization curves, and using Koutecky – Levich equation (slope of 59.60 mV/decade), it was possible to determine the peroxide pathway for oxygen reduction reaction (ORR) with two-electron transference. Additionally, gold dissolution and thiosulfate degradation were evaluated using the gold foil leaching tests. It was found solutions with a  $0.2 \text{ mol l}^{-1}$  thiosulfate concentration favored the dissolution of gold and by maintaining an adequate ratio between thiosulfate/ammonium (1:3) or thiosulfate/copper (4:1) enable the attainment high gold dissolution and lower degradation of thiosulfate.

## 1. Introduction

The use of thiosulfate ammoniacal solutions for gold recovery has been extensively researched as an alternative to the traditional cyanide recovery process [1–9]. In addition to being a non-polluting alternative compared to the environmental toxicity of cyanide used in traditional mining, thiosulfate ammoniacal solution has shown gold dissolution of more than 80 % from refractory ores [10,11]. The different studies on this subject have focused on understanding the chemistry of the reactions involved in the electrolyte and defining the optimal conditions for achieving high gold dissolution. In this sense, different reaction mechanisms have been proposed to account for the leaching and dissolution of gold in solution using thiosulfate [4,12–14]. In a general form, the dissolution and leaching processes take into account the oxidation of gold and therefore its dissolution is catalyzed by cupric ion ( $Cu^{2+}$ ) in the presence of ammonia in the electrolyte [15–17]. Oxygen is required to compensate for the loss of  $Cu^{2+}$  during the dissolution process. Once the gold has been oxidized by  $Cu^{2+}$  ions in the solution, the formation of the gold-thiosulfate complex ( $Au(S_2O_3)_2^{3-}$ ) is favored [18, 19] by the combined interaction of ammonia ( $NH_3$ ) and thiosulfate ions ( $S_2O_3^{2-}$ ) present according to Eqs. (1–2). Eq (3) is the resulting global

equation.



Although the cupric ion catalyzes the oxidation and dissolution of gold in solution, if it is in excess in the electrolyte it could cause the oxidation of the thiosulfate ion ( $S_2O_3^{2-}$ ) to tetrathionate ( $S_4O_6^{2-}$ ) Eq. (4 and 5), reducing the possibility of dissolution and complexation of gold [20].

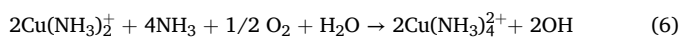


For this reason, it is necessary to add a ligand or chelate agents as ammonia ( $NH_3$ ) and EDTA [21,22] which form copper ion complexes with ammonia ( $Cu(NH_3)_4^{2+}$ ) and EDTA ( $Cu(EDTA)^{2-}$ ) respectively, diminishing the amount of free copper ions that can oxidize the thiosulfate ion.

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Each of the electrolyte components plays a particular role in the reactions that occur in the system, even the dissolved oxygen is important in the oxidation mechanism and dissolution of gold with thiosulfate solutions, the dissolved oxygen helps to the regeneration of the copper ion  $\text{Cu}(\text{NH}_3)_2^+$  to  $\text{Cu}(\text{NH}_3)_4^{2+}$  as it is shown in Eq (6) which is convenient to the reuse of the electrolyte; but also it promotes the degradation of thiosulfate through a redox reaction, where the oxygen is reduced and the thiosulfate is oxidized to species of sulfur of greater number of oxidation such as polythionates Eq (7). The oxygen reduction reaction (ORR) can be carried out by means of two reaction mechanisms,  $2e^-$  (8) and  $4e^-$  (9) pathway [23,24].



Different parameters can favor the gold dissolution such as the cation in the thiosulfate salt [25], the use of electrolyte stabilizers (ammonia or EDTA), and the control of solution pH [10,22,23,26].

Studies report that when ammonium thiosulfate salts are used in mineral leaching solutions, gold recovery is elevated, even more when these minerals have high sulfide contents [27]. Thiosulfate is a metastable species that can be easily oxidized. The presence of copper ( $\text{Cu}^{2+}$ ), as strong oxidant, increases the reaction rate, facilitating the leaching of gold and therefore can be said to increase the oxidation of thiosulfate which can favor its degradation [28]. Some authors have conducted experiments to investigate how different factors (temperature, time, concentration of reagents, among others) affect the degradation of thiosulfate [25,28]. Large amounts of ammonia, thiosulfate and copper greatly affect the degradation of thiosulfate dissolution, and it should be optimal conditions for each reagent in the dissolution in order to dissolve gold without largely affecting the stability of the lixiviant solution. For this reason, it is paramount to establish the limits of species concentrations in solution. Although some studies have been conducted to analyze the effect of solution components on gold dissolution and the stability of the lixiviant solution, there is no studies addressed to examine all the variables together from an electrochemical perspective, which is the prime novelty and the aim of the current study.

In this work, an electrochemical study of gold dissolution in ammoniacal thiosulfate solutions was conducted to evaluate the combined effects of different dissolution components on the gold dissolution kinetics and the degradation of thiosulfate. Anodic and cathodic polarization tests were carried out at different concentrations of their components and the response of the voltammograms obtained was evaluated. Hydrodynamic conditions were also evaluated and for that, polarization tests were performed on a gold rotating disk electrode (RDE). In addition, dissolution tests of a gold foil were implemented for monitoring the degradation of thiosulfate and the variation of the electrochemical potential of the metal. The influence of oxygen in the degradation of thiosulfate was analyzed through polarization curves and Koutecky – Levich equation.

## 2. Experimental

### 2.1. Chemicals and solutions

All solutions were prepared from Merck reagent analytical grade. The reagents used were anhydrous ammonium thiosulfate  $(\text{NH}_4)_2\text{S}_2\text{O}_3$ , copper (II) sulfate pentahydrate  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ , ammonia ( $\text{NH}_3$ ) solution 25 %, ethylenediaminetetraacetic acid (EDTA) anhydrous, and deionized water (18.2 MΩ cm).

### 2.2. Preparation of samples for the leaching test

Gold foils (99.9999 % Au, thickness 0.05 mm) with a surface area of approximately  $2 \text{ cm}^2$  (0.2 g), were used for leaching tests. Gold foils were washed with acetone, rinsed with distilled water and air dried before each leaching experiment. For each leaching test, a new gold foil was used.

### 2.3. Leaching essays

The gold leaching was carried out in a closed glass cell, using a magnetic stirrer and a stirring plate. For each test 100 mL of the leach solution was prepared with the desired amounts of the reagents. The gold foil was suspended at the top of the cell with a nylon thread. The leach solution system was left for 24 h with constant agitation at 500 rpm using a magnetic stirrer. The thiosulfate titration was performed at different times 6, 14, and 22 until 24 h of testing using the iodometric titration method, in order to evaluate its behavior on leaching process and its degradation over time. Through titration process thiosulfate concentration in solution  $[\text{S}_2\text{O}_3^{2-}]$  is quantified to determine how much it was oxidized during leaching of gold, that because during degradation process thiosulfate is oxidated to tetrathionates and sulfates ( $\text{S}_4\text{O}_6^{2-}$  and  $\text{SO}_4^{2-}$ ). The degradation percentage is obtained by the relationship  $100 \times [\text{S}_2\text{O}_3^{2-}]_t / [\text{S}_2\text{O}_3^{2-}]_{t=0}$ , where  $[\text{S}_2\text{O}_3^{2-}]_{t=0}$  is the initial concentration of thiosulfate and  $[\text{S}_2\text{O}_3^{2-}]_t$  is the thiosulfate concentration at any leaching time.

The dissolved gold records were made by taking the loss of mass of the gold foil (ppm). The weight of the gold foils was carried out on a 6-digit analytical balance, with 0.01 mg precision. This process was executed at different times, 6, 14, 22 and 24 h, in order to evaluate the dissolution of gold in time. The experimental conditions and the leaching solution components are shown in Table 1. They were chosen in order to analyze the effect of the different components of the leaching solution on the gold dissolution and on the degradation of thiosulfate solution taking into account the limits reported in [29–31] Randomization was performed using Computer program R [32], in order to balance or decrease the effect of external conditions such as temperature, humidity, raw material and even the operator himself that may influence the results of the experiment. Duplicate tests were performed in the same order. The leaching experiments were conducted at  $24 \pm 1$  °C. The pH solution was adjusted between 10.3 and 10.5 with drops of 25 % ammonia ( $\text{NH}_3$ ) solution. The temperature of the tests was maintained, unless otherwise stated, at 25 °C.

### 2.4. Electrochemical measurements

The electrochemical experiments were carried out in a conventional three-electrode cell, a gold sample (99.99 % Au) with an exposed area of  $0.071 \text{ cm}^2$  prepared as a rotating disc electrode (RDE) was used as working electrode (WE); an Ag/AgCl (3.0 M KCl) reference electrode (RE) and platinum mesh as counter electrode (CE) were used. Potentials were converted to the standard hydrogen electrode (SHE) scale, assuming Ag/AgCl electrode has a potential of 0.209 V versus the SHE.

Before each electrochemical test, the gold (Au) electrode was mechanically sanded with #600, #1000 and #1200 abrasive paper and polished in cloth with 1 and 0.5 μm alumina solution to a mirror finish. Anodic and cathodic polarization were carried out by using a 302 N Autolab potentiostat/galvanostat (Metrohm Autolab) controlled with the NOVA 1.11 software. All measurements were made in duplicate. Potentiodynamic polarization curves were performed using a scan rate of  $1.0 \text{ mV s}^{-1}$  from a cathodic overpotential of  $-600 \text{ mV}$  to anodic overpotential of  $+600 \text{ mV}$  in airtight solution unless the contrary been mentioned.

**Table 1**  
Composition of thiosulfate solutions for the study of the effect of concentration variation.

Assays	T (NH <sub>4</sub> ) <sub>2</sub> S <sub>2</sub> O <sub>3</sub> [mol l <sup>-1</sup> ]	A NH <sub>3</sub> [mol l <sup>-1</sup> ]	C Cu <sup>2+</sup> [mol l <sup>-1</sup> ]	E EDTA [mol l <sup>-1</sup> ]	T:A	T:C	T:E	A:C
E1	0.2	0.6	0.05	0.025	1:3	4:1	8:1	12:1
E2	0.1	0.6	0.05	0.025	1:6	2:1	4:1	12:1
E3	0.2	0.4	0.05	0.025	1:2	4:1	8:1	8:1
E4	0.1	0.4	0.05	0.025	1:4	2:1	4:1	8:1
E5	0.2	0.6	0.025	0.0125	1:3	8:1	16:1	24:1
E6	0.1	0.6	0.025	0.0125	1:6	4:1	8:1	24:1
E7	0.2	0.4	0.025	0.0125	1:2	8:1	16:1	16:1
E8	0.1	0.4	0.025	0.0125	1:4	4:1	8:1	16:1

T = Thiosulfate A = Ammonia C = Copper (II) E = EDTA.

The copper/EDTA (C:E) ratio is maintained at 2:1 in all solutions. pH = 10.3 - 10.5.

### 3. Results and discussion

#### 3.1. Electrochemical study of ammoniacal thiosulfate solution composition

##### 3.1.1. Effect of thiosulfate concentration

Fig. 1 shows the polarization curves for solutions with two different thiosulfate ammonium concentrations 0.2 and 0.1 mol l<sup>-1</sup>. For each thiosulfate concentration, was evaluated two copper concentrations 0.05 and 0.025 mol l<sup>-1</sup>. Those solutions are indicated in Table 1 as E1, E5 (Fig. 1a), and E2, E6 (Fig. 1b). At higher amount of thiosulfate in solution and T:C ratio of 4:1 (E1) (Fig. 1a), the current values of the anodic branch are slightly higher than the cathodic branch currents and Ecorr is lower compare with E2 (Table 2). Conversely, when it has a T:C ratio of 2:1 (E2) (Fig. 1b), the currents of the anodic branch are lower than the currents of the cathodic branch. These results suggest that the control of gold dissolution could change from cathodic to anodic control only with changes in the thiosulfate concentration in solution. When thiosulfate concentration is kept high, the cathodic reactions control the kinetics of gold dissolution. In that condition gold dissolution could be stimulated by the rise of the cathodic reaction rate. For instance, the increment of aeration or the stirring of the solution could play a positive role in gold dissolution, considering oxygen as an important oxidant in solution. On the other hand, at low thiosulfate concentration in solution, the gold dissolution is controlled by anodic process and passivation of the gold

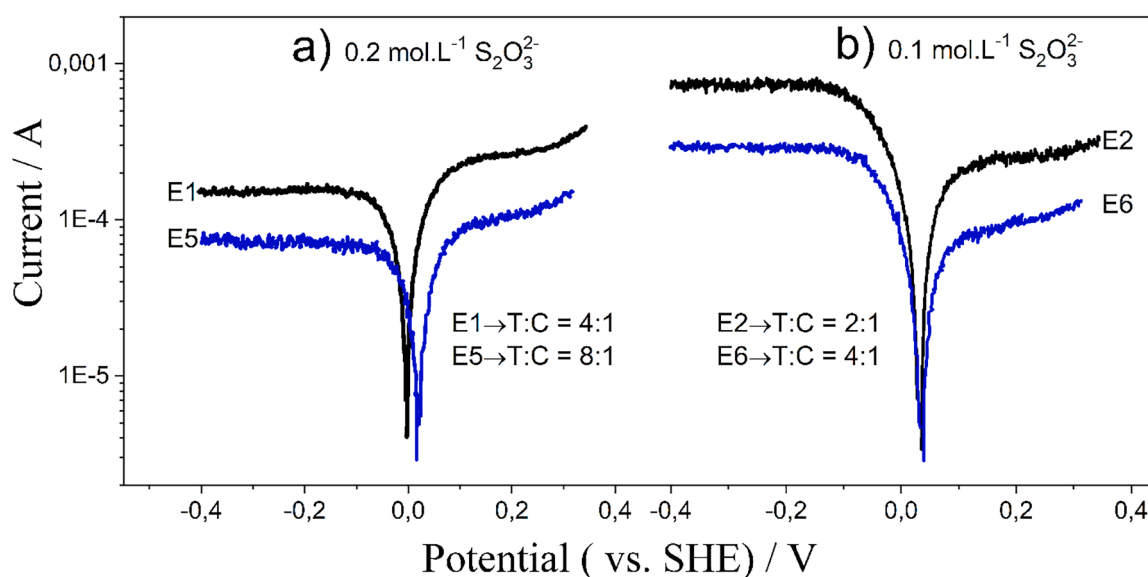
**Table 2**

Anodic and cathodic limit current values and corrosion potentials obtained from polarization curves for different solution ratios (Figs. 1–3).

Essay	I <sub>L</sub> anodic (A)	I <sub>L</sub> cathodic (A)	E <sub>corr</sub> (V)
E1	2.60E-4	1.55E-4	-0.003
E2	2.45E-4	7.55E-4	0.043
E3	6.30E-4	1.79E-4	0.005
E4	3.62E-4	3.85E-4	0.057
E5	9.80E-5	7.45E-5	0.015
E6	8.22E-5	3.02E-4	0.034

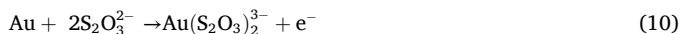
surface begins to be important in the oxidation reaction. In this situation, changes in the cathodic reaction rates do not have significant influence in the gold dissolution. According to the best knowledge of the authors these findings do not have precedents in literature reports.

At low overpotentials, between 0.1 V to 0.25 V vs SHE of the anodic branch of Fig. 1a, there is a limiting current and gradually current increases at potentials greater than 0.25 V. Chandra and Jeffrey [33], identified the gold oxidation process in thiosulfate solutions in a potential range between 0.1 V and 0.3 V according to Eq. (10). They also showed that at potentials greater than 0.3 V thiosulfate oxidation processes begins with a great increase in the current intensities. This behavior is consistent with that observed in the anodic branches of the polarization curves presented in Fig. 1, where increasing in the anodic



**Fig. 1.** Potentiodynamic polarization curves ( $v = 0.333 \text{ mV s}^{-1}$ ) on gold rotating disc electrode (RDE) in solutions of a)  $0.2 \text{ mol l}^{-1} (\text{NH}_4)_2\text{S}_2\text{O}_3$  and b)  $0.1 \text{ mol l}^{-1} (\text{NH}_4)_2\text{S}_2\text{O}_3$ . With (—)  $0.05 \text{ mol l}^{-1} \text{ Cu}^{2+}$ ,  $0.6 \text{ mol l}^{-1} \text{ NH}_3$ ,  $0.025 \text{ mol l}^{-1} \text{ EDTA}$  and (—)  $0.025 \text{ mol l}^{-1} \text{ Cu}^{2+}$ ,  $0.6 \text{ mol l}^{-1} \text{ NH}_3$ ,  $0.0125 \text{ mol l}^{-1} \text{ EDTA}$  pH between 10.1–10.3 and  $24^\circ\text{C}$ .

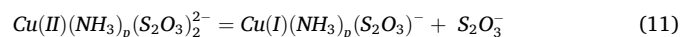
currents were observed at potential greater than 0.3 V.



At a T:C ratio of 2:1 (E2) (Fig. 1b) where cathodic currents are greater than anodic currents; the reduction reactions from Copper (II) to Copper (I) could be favored due to a greater amount of Copper (II) relative to thiosulfate in solution [34]. This behavior could stimulate some oxidation processes, such as gold dissolution.

In addition, when there is low concentration in all reagents (blue curves Fig. 1), low current values are obtained, indicating slow reaction rates in both anodic and cathodic processes. According to the analysis performed by Aylmore and Muir [35], low concentration in the reagents requires high gold oxidation potential.

Senanayake also argues that an increase in the concentration of thiosulfate and the presence of ammonia to stabilize copper (II) could slightly retard the degradation of thiosulfate when it reacts with copper (II) according to Eq. (11) where subindex  $p$  is 2 or 3 [13]. According to the above argument, a low concentration of thiosulfate facilitates the reduction of ammonia-thiosulfate-complex Cu (II), and higher cathodic current densities could be observed, as happened in Fig. 1b.



### 3.1.2. Effect of ammonia

Fig 2. shows the effect of ammonia concentration and different ratios T:A on the electrochemical behavior (polarization curves) of gold in thiosulfate solutions. In solutions with a thiosulfate/ammonia ratio (T:A) of 1:3 (Fig. 2a) exhibited anodic currents are greater than cathodic currents. However, when the T:A ratio is 1:6; the behavior changes and the cathodic current is larger than the anodic one (Fig. 2a). This means that a high relative concentration of ammonia in solution could stimulate the reduction of Cu(II); although the anodic reaction of gold dissolution will not be significantly affected. It was observed that when the thiosulfate/ammonia ratio is high ( $0.6 \text{ mol l}^{-1} \text{ NH}_3$ ) there are no major variations in the anodic currents; whereas when the ratio is lower ( $0.4 \text{ mol l}^{-1} \text{ NH}_3$ ) there is a variation in the anodic currents. A higher anodic current and lower  $E_{\text{corr}}$  (Table 2) were obtained in the lowest thiosulfate/ammonia ratio (E3) respect E4. In the same way, larger anodic currents concerning the cathodic ones are observed. This means that to stimulate the anodic dissolution of gold without affecting significantly the Cu(II) stability, low T:A ratio must be preserved.

In addition, with a thiosulfate/ammonia ratio of 1:2 with ammonia/copper of 8:1 (E3, Fig. 2b), the anodic currents are greater than the cathodic currents, with a large difference between the anodic and cathodic branches. Now, with a thiosulfate/ammonia ratio of 1:4 (E4, Fig. 2b), the anodic and cathodic curves have similar values of current intensities. These results indicate that concentration of ammonia has a greater effect on anodic gold dissolution with respect to the concentration of thiosulfate and copper in the solution. As mentioned above, the role of ammonia is to stabilize copper (II) [6,36,37]. Copper (II) should be necessarily preserved, because it is the main oxidizer in solution, Eqs. (1) and (3). However, the ammonia concentration should not be excessive, as this would increase the kinetics of the cathodic copper (II) reduction reaction. Accordingly, if there is a low concentration of thiosulfate with a high concentration of copper and ammonia (T:C ratio of 2:1), cathodic processes are favored (E2, Fig. 2a). In contrast, with T:C ratio of 4:1, anodic reactions prevail (E1, Fig. 2a).

### 3.1.3. Effect of copper (II)

Fig 3. shows the effect of Cu (II) concentration and different ratio T:C on the electrochemical behavior (polarization curves) of gold in thiosulfate solutions. When the concentration of  $\text{Cu}^{2+}$  is constant ( $0.05$  or  $0.025 \text{ mol l}^{-1}$ ), no effect on the anodic dissolution current at different thiosulfate concentrations was observed (Fig. 3); however, significant differences were presented in cathodic currents. When the T:C ratios were low, 2:1 (E2) (high  $\text{Cu}^{2+}$  concentration) and 4:1 (E6) (low  $\text{Cu}^{2+}$  concentration), the cathodic currents were higher than anodic ones. This behavior can be presented by the fact that having high concentration of copper (II) species in solution, the possibility that the ions of Cu(II) are reduced to Cu(I) increased [8]. It has been established that  $\text{Cu}^{2+}$  reacts rapidly with thiosulfate ions to form the  $\text{Cu}(\text{S}_2\text{O}_3)_3^{5-}$  complex (Eq. (1)); therefore, the concentration of copper(II) in solution is an important factor in maintaining the stability of the solution [38].

On the other hand, with T:C ratios of 8:1 and 4:1 (low  $\text{Cu}^{2+}$  concentration compared to thiosulfate, E1 and E5, Fig. 3), the cathodic currents were lower than the anodic ones, as well as lower  $E_{\text{corr}}$  were observed (Table 2), which indicate that higher anodic dissolution of gold can occur. These results indicate that copper (II) in solution should be maintained in low proportion with respect to thiosulfate concentration, that because the possibility to reduction to copper (I) will be restricted and the complexation power of thiosulfate ions preserved.

The cathodic branch of the polarization curves should be influenced

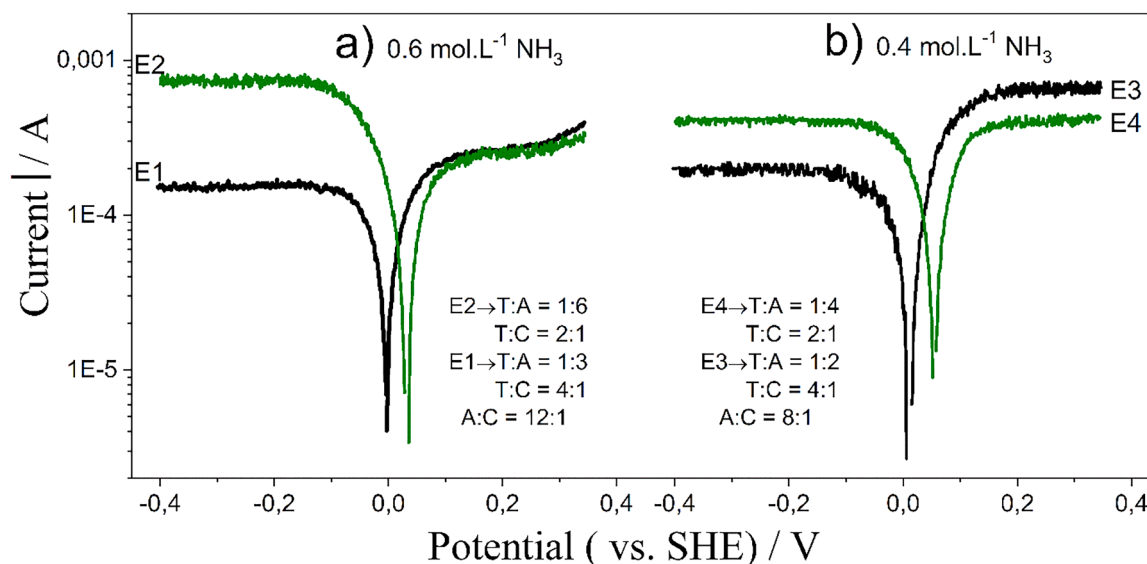
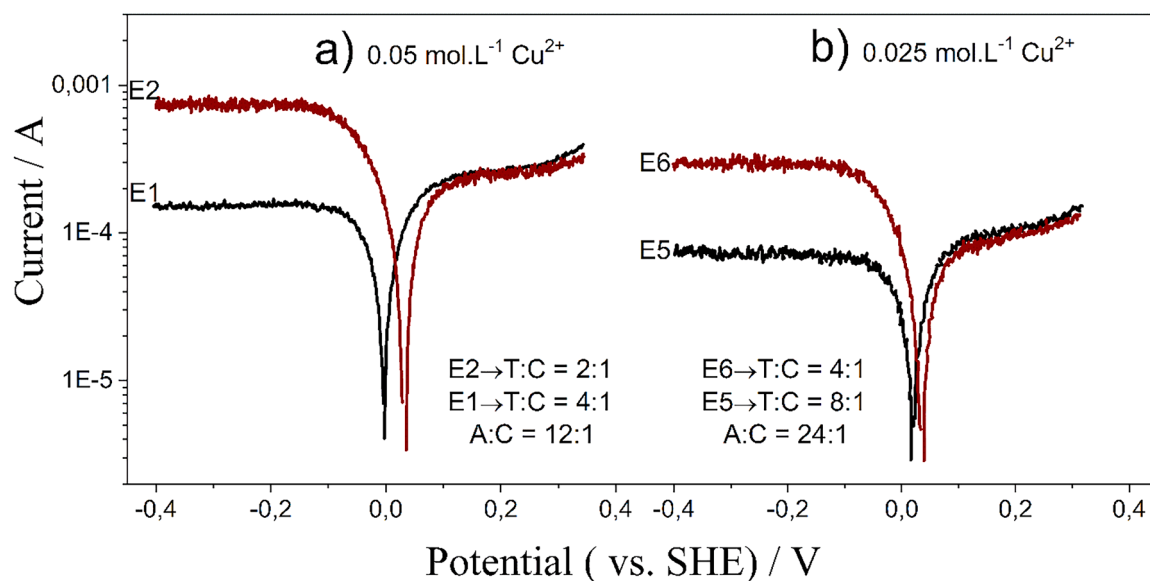


Fig. 2. Potentiodynamic polarization curves ( $v = 0.333 \text{ mV s}^{-1}$ ) of the gold rotating disc electrode (RDE) in solutions of a)  $0.6 \text{ mol l}^{-1} \text{ NH}_3$  and b)  $0.4 \text{ mol l}^{-1} \text{ NH}_3$ . With (■)  $0.2 \text{ mol l}^{-1} (\text{NH}_4)_2\text{S}_2\text{O}_3$ ,  $0.05 \text{ mol l}^{-1} \text{ Cu}^{2+}$ ,  $0.025 \text{ mol l}^{-1} \text{ EDTA}$  and (■)  $0.1 \text{ mol l}^{-1} (\text{NH}_4)_2\text{S}_2\text{O}_3$ ,  $0.050 \text{ mol l}^{-1} \text{ Cu}^{2+}$ ,  $0.025 \text{ mol l}^{-1} \text{ EDTA}$  pH between 10.1–10.3 and  $24^\circ \text{C}$ .



**Fig. 3.** Potentiodynamic polarization curves ( $\nu = 0.333 \text{ mV s}^{-1}$ ) on gold rotating disc electrode (RDE) in solutions of a)  $0.05 \text{ mol l}^{-1} \text{ Cu}^{2+}$  and b)  $0.025 \text{ mol l}^{-1} \text{ Cu}^{2+}$ . With (■)  $0.2 \text{ mol l}^{-1} (\text{NH}_4)_2\text{S}_2\text{O}_3$ ,  $0.6 \text{ mol l}^{-1} \text{ NH}_3$ ,  $0.025 \text{ mol l}^{-1} \text{ EDTA}$  and (■)  $0.1 \text{ mol l}^{-1} (\text{NH}_4)_2\text{S}_2\text{O}_3$ ,  $0.6 \text{ mol l}^{-1} \text{ NH}_3$ ,  $0.0125 \text{ mol l}^{-1} \text{ EDTA}$  pH between 10.1–10.3 and  $24^\circ \text{C}$ .

by either copper reduction and/or oxygen reduction reactions [16]. To clarify this issue, polarization tests were performed at three different copper concentrations and under hydrodynamic conditions (Fig. 4), evaluating the currents in the cathodic region.

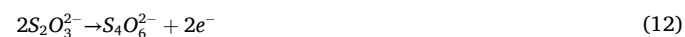
Fig. 4 shows polarization curves under hydrodynamic conditions, where an increase in cathodic currents is evident:  $I_{\text{cathodic}} = A [\text{Cu}^{2+} = 0.03 \text{ mol l}^{-1}] < B [\text{Cu}^{2+} = 0.05 \text{ mol l}^{-1}] < C [\text{Cu}^{2+} = 0.07 \text{ mol l}^{-1}]$  with increasing copper concentration. Also, the effect of hydrodynamics on the cathodic currents at different Cu(II) concentrations is observed. There were observed current-limit values of the Cu(II) reduction process at different Cu(II) concentrations and at different rotation rates of the electrode. Although the increase of the copper (II) concentration improves the kinetics of gold oxidation, an increase in the copper (II) concentration increases the deposition rate of copper on the substrate and increases the oxidation of thiosulfate [13]. However, the copper (II)

reduction is not the main cathodic process concerning the gold dissolution in thiosulfate media. That because, as was above mentioned, the copper (II) reduction should be limited in order to preserve the stability of the electrolyte and to avoid the oxidation of thiosulfate ions. The main cathodic process to be considered in the study is the oxygen reduction reaction (ORR), which is also hydrodynamic dependent. A more exhaustive study of the effect of hydrodynamics was conducted for ORR in the subsequent section of the paper.

Another important parameter to be taken into account, which can also influence the cathodic currents is the presence of dissolved oxygen in solution. That is because oxygen is considered a strong oxidant agent and contributes to the anodic process. Since the above tests (copper (II) reduction) were performed under aerated conditions (Fig. 4), the effect of oxygen under hydrodynamic conditions at an intermediate copper concentration [ $0.05 \text{ mol l}^{-1}$ ] was evaluated. The results are presented below.

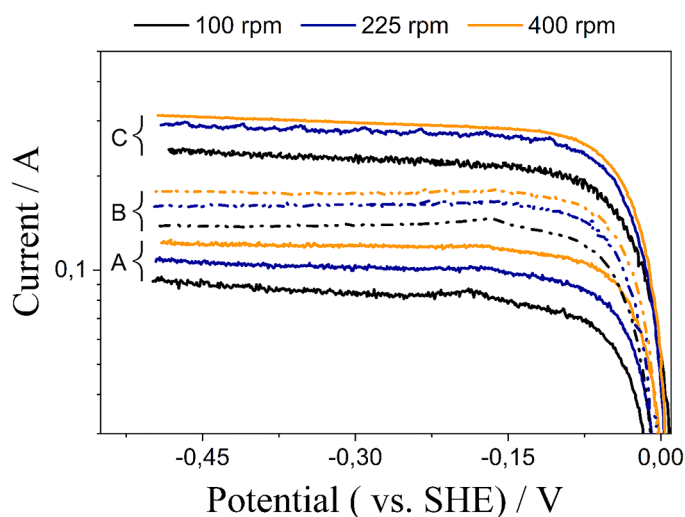
#### 3.1.4. Effect of dissolved oxygen

Dissolved oxygen plays an important role in the oxidation mechanism and dissolution of gold with thiosulfate solutions. On the one hand, it helps the regeneration of the copper ion ( $\text{Cu}(\text{NH}_3)_2^+/\text{Cu}(\text{NH}_3)_2^+$ ) which is convenient; but also it promotes the degradation of thiosulfate to tetrathionates (Eqs. (12)–(13) [23,24]. According to these reactions, a redox pair is established, where the oxygen is reduced, and the thiosulfate is oxidized to species of sulfur of greater number of oxidations such as polythionates until reaching the sulfate ion.

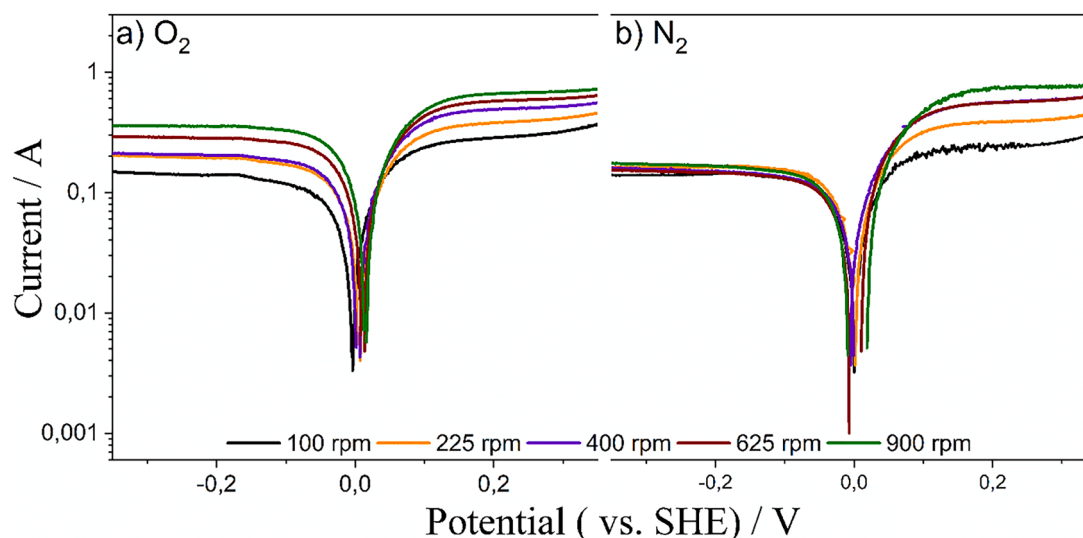


To evaluate the effect of the oxygen concentration in the cathodic and anodic currents of the polarization curves, tests were performed under hydrodynamic conditions with thiosulfate solutions under oxygen saturation conditions, i.e. 7–9 ppm [39], and solutions with nitrogen bubbling to remove dissolved oxygen, deaerated condition (Fig. 5b).

When polarization curves are made in thiosulfate solution with oxygen saturation (Fig. 5a) an increase in the current values in the cathodic region is observed when the rotation speed in the electrode is increased. This behavior is presented by greater mass transport because it moves

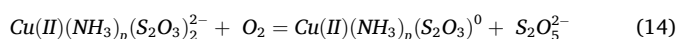


**Fig. 4.** Potentiodynamic polarization curves ( $\nu = 0.333 \text{ mV s}^{-1}$ ) on gold rotating disc electrode (RDE) to different  $\text{Cu}^{2+}$  concentrations [A =  $0.03 \text{ mol l}^{-1}$ ; B =  $0.05 \text{ mol l}^{-1}$  and C =  $0.07 \text{ mol l}^{-1}$ ] with  $0.2 \text{ mol l}^{-1} (\text{NH}_4)_2\text{S}_2\text{O}_3$ ,  $0.6 \text{ mol l}^{-1} \text{ NH}_3$ ,  $0.025 \text{ mol l}^{-1} \text{ EDTA}$  pH between 10.1–10.3,  $24^\circ \text{C}$  and rotating speeds of (■) 100 rpm, (■) 225 rpm y (■) 400 rpm.



**Fig. 5.** Potentiodynamic polarization curves ( $v = 0.333 \text{ mV s}^{-1}$ ) on gold rotating disc electrode (RDE) in a) aerated ( $\text{O}_2$ -saturated) and b) deaerated ( $\text{N}_2$ ) ammoniacal thiosulfate solution ( $0.2 \text{ mol l}^{-1} (\text{NH}_4)_2\text{S}_2\text{O}_3$ ,  $0.6 \text{ mol l}^{-1} \text{NH}_3$ ,  $0.025 \text{ mol l}^{-1} \text{EDTA}$  pH between 10.1–10.3,  $24^\circ \text{C}$ ) and different rotating speeds as indicated in the figure legends.

more oxygen to the electrode surface and thus a greater reduction of oxygen [40]. Senanayake stated that an increase in the percentage of oxygen or air increases the oxidation rate of thiosulfate [13,29]. Although oxygen is necessary for regeneration from Cu(I) to Cu(II), an excess of dissolved oxygen in the solution accelerates the reaction of copper(II) with thiosulfate promoting the oxidation of thiosulfate and the reduction of Cu(II) according to Eq. (14).



As can be seen in Fig. 5a and Fig. 4, the intensity of the currents in the cathodic region is influenced by the reduction reactions of copper and oxygen. However, in the absence of oxygen in solution (Fig. 5b) the influence of hydrodynamic conditions on this reaction are practically inexistent or negligible, being only detectable at high cathodic overpotentials. This means that the reduction of copper ions does not show appreciable hydrodynamics dependence on the cathodic process at low cathodic polarization conditions. At those conditions, the contribution of the copper reduction to the global cathodic current can be negligible (low polarization) and the analysis of the ORR as the main cathodic process can be performed. Furthermore, the presence of chelating ions in the electrolyte, EDTA,  $\text{NH}_3$ ,  $\text{S}_2\text{O}_3^{2-}$ , strongly coordinates the copper ions forming stable complex compounds, like  $\text{Cu(EDTA)}^{2-}$ ,  $\text{Cu(NH}_3)_3^{2+}$ ,  $\text{Cu(S}_2\text{O}_3)_3^{5-}$  and  $\text{Cu(S}_2\text{O}_3)_2^{3-}$ . The complexation decreases the activity of Cu(II) ions in solution, and consequently the reduction potential of copper is shifted to more negative potential. This has been reported by Alonso et al. [41], and similar polarization effect on copper reduction has been observed in other chelating ion solutions [42,43]. Breuer and Jeffrey's study [23] consider the relevant role of cathodic reactions on the gold and thiosulfate oxidation. The entire study of the cathodic reactions is done at a single and low electrode rotation speed (300 rpm). From the cathodic polarization curves at 300 rpm in the different electrolyte compositions, they observe that the cathodic overpotential for oxygen reduction is greater than for Cu(II) reduction, i. e. copper(II) is more readily reduced than oxygen and thiosulfate [23]. However, Breuer and Jeffrey's work lacks hydrodynamic analysis of the cathodic reactions involved. From the cathodic polarization curves at 300 rpm in the different electrolyte compositions, they observe that the cathodic overpotential for oxygen reduction is higher than for Cu(II) reduction, and concluded that the copper(II) is more readily reduced in a solution containing thiosulfate. In their work, they did not realize that the oxygen reaction is highly sensitive to hydrodynamic conditions, while the

reduction of Cu(II) to Cu(I) is not, both copper ions are stable in ammonia thiosulfate solution. Therefore at a low electrode rotation speed of 300 rpm, the cathodic oxygen reduction reaction may be less important than the Cu(II) reduction. However, when the rotation speed increases the hydrodynamic conditions for oxygen transport to the metal-electrolyte interface are favorable and the oxygen reduction reaction is more important than the reduction of Cu(II) to Cu(I).

When reaction in the cathodic region is hydrodynamics dependent, such as oxygen reduction, and assuming irreversible reaction, the Koutecky-Levich equation can be used to obtain a plot of  $1/I$  vs.  $1/\omega^{1/2}$ . From this relationship, we can establish data such as the direct constant of the cathodic process ( $\vec{k}$ ) and/or the global number of electrons transferred associated with the oxygen reduction reaction (ORR). It is important to highlight that kinetics parameters (Tafel slope and charge transfer coefficient) of the involved cathodic reactions are not easily obtained nor accurately by Tafel extrapolation method, either by the coexistence of at least two cathodic reactions (oxygen and  $\text{Cu}^{2+}$  reduction) or by the influence of the mass transport process, as has been seen in the potentiodynamic polarization curves already discussed. So, the Koutecky-Levich approach is currently the best alternative to estimating the kinetics parameters of the cathodic reaction.

In the mixed control zone (at low overpotentials) of the cathodic branch of Fig. 5a, for an irreversible process and assuming the diffusion of copper species close to zero; given that at low cathodic overpotentials, the copper reduction reaction is negligible, the Koutecky-Levich relationship can be obtained from Eq. (15) and  $\vec{k}$  can be calculated with the intercepts of the curves. With the relation  $\log \vec{k}$  vs potential, a Tafel curve can be obtained for the reduction of oxygen [44].

$$-\frac{1}{I} = \frac{1}{nF\vec{k}C_0^\infty} + \frac{1.61v^{1/6}}{nFC_0^\infty D_0^{2/3}} \frac{1}{\omega^{1/2}} \quad (15)$$

Where,  $F$ : Faraday constant (96,500 C/mol)  $n$ : Number of electrons transferred,  $\vec{k}$ : direct constant of the cathodic process,  $v$ : Kinematic viscosity ( $8.9 \text{ E-3 cm}^2/\text{s}$ ),  $\omega^{1/2}$  = rotation speed (radians/s),  $D_0$  = Diffusivity of oxygen in solution ( $0.5 \text{ E-5 cm}^2/\text{s}$ ),  $A$  = Electrode area,  $0.071 \text{ cm}^2$ ,  $C_0^\infty$ : Oxygen concentration in the solution.

Fig. 6a shows the plots obtained for  $|I|^{-1}$  vs  $\omega^{1/2}$ , where changes of the slopes were observed when the potential shifts. By plotting the values of  $\vec{k}$  and obtaining the linear fit to a Tafel curve, a slope of  $59.62 \text{ mV/dec.}$ ,

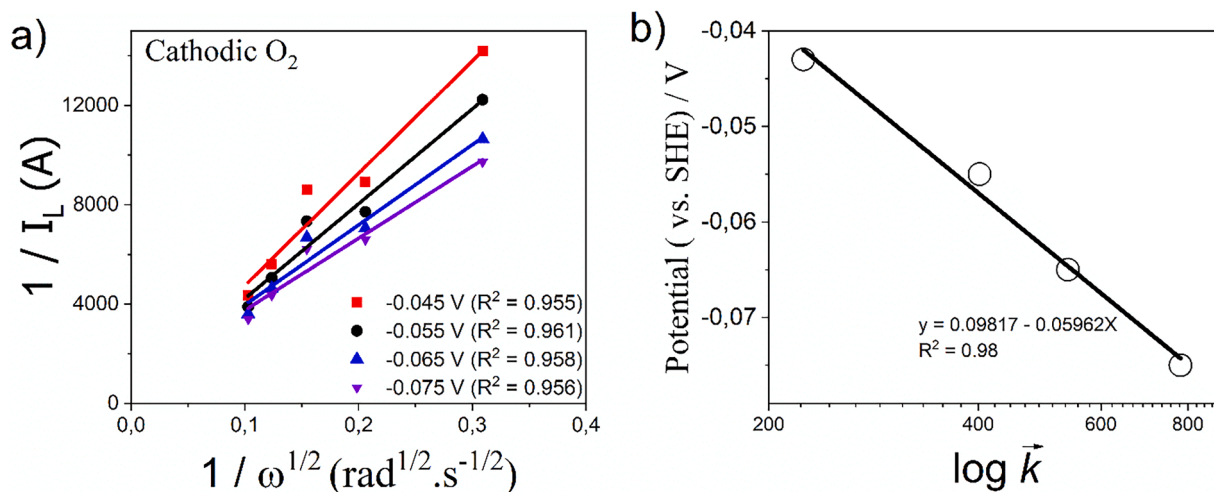
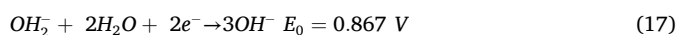
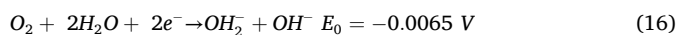


Fig. 6. (a) Plot of Koutecky–Levich equation for the cathodic branch of Fig. 5a obtained at different potentials as indicated in the figure. b)  $\log \bar{k}$  vs. Potential obtained from the intercepts of graph a).

is obtained (Fig. 6b). A similar value of cathodic Tafel slope for gold in thiosulfate solution (55.7 mV/dec) can be obtained from the work of Baron et al., how obtained the apparent charge transfer coefficient for the oxygen reduction reaction,  $\alpha = 0.53$  [45]. The kinetics and mechanism of the oxygen reduction reaction depend on factors such as the material of the cathode used and the conditions of the medium in which the reaction occurs. Similarly, oxygen reduction can occur in two ways, one involving 4 electrons and the peroxide way involving the transfer of 2 electrons. The reduction reaction of 4 electrons is favored on metals like Pt, Ir, Rh, Ru, Pd, Cu, on metallic oxides, and on some transition metals (Fe, Co) and graphite. On the other hand, the peroxide pathway is favored in most carbons, gold, mercury, and some transition metal oxides [46–48].

According to the mechanisms presented in the oxygen reduction, two different Tafel slopes can be obtained: 120 mV/decade (transfer of 4 electrons) and 60 mV/decade (transfer of 2 electrons). In noble metals and at low overpotentials a slope of 60 mV/decade is obtained. Thus, according to the slope of 59.60 mV/decade found with a gold RDE in an alkaline electrolyte (Fig. 6b); the reduction of oxygen occurs by peroxide pathway, according to Eqs. (16)–(18) [48]:



### 3.2. Effect of variation of the components concentration of ammoniacal thiosulfate solution on the gold leaching and thiosulfate degradation

Fig. 7 shows the results of dissolution of gold (Fig. 7a), degradation of thiosulfate (Fig. 7b) and gold potential in solution (Fig. 7c) during leaching of gold foil with ammonium thiosulfate solutions at different compositions according to Table 1 and pH 10.0. In Fig. 7a the plots E1, E3, E5 and E7, correspond to solutions with  $0.2 \text{ mol l}^{-1}$  of  $(NH_4)_2S_2O_3$  and the E2, E4, E6 and E8 to solutions with  $0.1 \text{ mol l}^{-1}$  of  $(NH_4)_2S_2O_3$ .

As can be seen in the Fig. 7, in general terms, the gold dissolution process, is accompanied by a decreasing in solution electrochemical potential and an increasing of thiosulfate degradation. During the first 6 h of leaching, an increase in dissolution of gold is observed in all solutions, been more accentuated for solutions E1, E3, E5, E8. Between 6 and 21 h the dissolution remains constant for E1 and E5 experiments; and a slight increase of gold dissolution with the time for E2, E3, E4, E6 and E7 was observed. From 21 to 24 h of leaching strong increase of gold

dissolution in E1, E3, E5 and E4 was found. Conversely, a decrease of gold dissolution for E6, E7 and E8 was observed.

Comparing the results for E1 ( $0.2 \text{ mol l}^{-1}$  of  $S_2O_3^{2-}$ ) and E2 ( $0.1 \text{ mol l}^{-1}$  of  $S_2O_3^{2-}$ ) the electrochemical potential of the solution for E2 decreases and is maintained in values where  $Cu^+$  species predominate (less than  $-0.02 \text{ V vs SHE}$ ) [49]. Consequently, gold dissolution rate is low because the oxidant agent  $Cu(II)$  is absent. Electrochemical potentials where free  $Cu(II)$  is promoted to reduce to  $Cu(I)$  are not beneficial for gold dissolution, since  $Cu(II)$  is required to catalyze gold oxidation [26]. By contrast, in E1 there is a shift to positive values of the electrochemical potential after 21 h to values close to  $0.0 \text{ V vs SHE}$ , where  $Cu(II)$  species predominate, and consequently an increase of gold dissolution is observed. This behavior was also observed in the E2, E4, E5, E6, E7 and E8 assays, where solution potentials fell to negative values ( $< 0.01 \text{ V vs SHE}$ ) affecting gold dissolution.

The sudden increase in gold leaching after 22 h, see Fig. 7a systems E1 and E3, is probably due to the recovery of  $Cu(II)$  ions in solution, which is associated with the increase in the electrochemical potential of the solution, Fig. 7c. It should be noted that the  $Cu(II)$  ion is a strong oxidizing agent. It can be observed that the systems that caused the greatest increase in the dissolution rate after 22 h (E1 and E3) are also those that experienced the greatest increase in electrochemical potential. During the leaching plateau, between 6 and 22 h, most of the systems experienced a decrease in the electrochemical potential in solution, due to the continuous reduction of  $Cu(II)$  to  $Cu(I)$ . However, the sudden recovery of  $Cu(II)$  in solution and the unusual increase in the gold dissolution rate after 22 h also brought about a considerable increase in the thiosulfate degradation rate, Fig. 7b. This is not advisable because thiosulfate degradation is irreversible and limits the possibilities of reusing the leaching solution for subsequent gold recovery processes. We do not know the causes of the sudden recovery of the  $Cu(II)$  ions in solution and the sudden increase in gold leaching after 22 h This may be a reason for future research.

A fact worth highlighting is that system E5 behaves in the opposite way to systems E1 and E3, i.e. in system E5 the sudden increase in gold leaching rates occurs after 22 h but it is accompanied by a decrease in the electrochemical potential of the solution, indicating that in this system  $Cu(II)$  recovery does not occur as in E1 and E3. However, in system E5 it is observed that the degradation of thiosulfate is minimal (Fig. 7b), so the chelating power of thiosulfate ions is maintained after 22 h, compensating for the loss of  $Cu(II)$  ions in solution, and preserving the dissolution power of the electrolyte.

The gold dissolution results obtained for E1 = 183 ppm versus E3 = 123 ppm and E5 = 68 ppm versus E7 = 6.3 ppm, with concentrations of

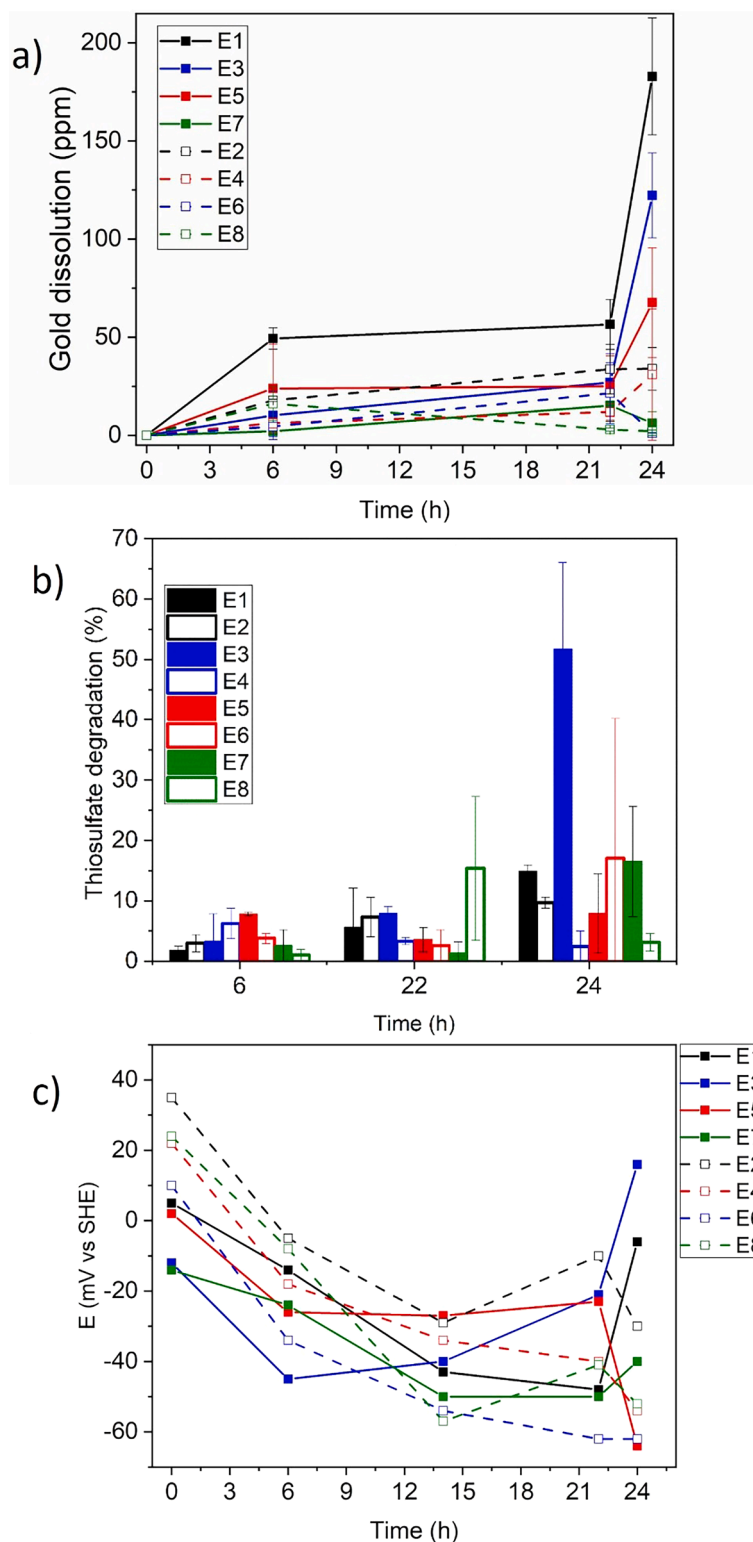


Fig. 7. Evaluation of gold foil dissolution (a), thiosulfate degradation (b) and solution potential (c) during gold leaching with ammonium thiosulfate solutions at pH 10.0 and compositions according to the tests described in Table 1.

0.2 mol l<sup>-1</sup> of S<sub>2</sub>O<sub>3</sub><sup>2-</sup> and Cu(II)/EDTA [0.05:0.025] for E1, E3; and Cu(II)/EDTA [0.025:0.0125] for E5 and E7, show that the increased concentration of thiosulfate and ammonia has a beneficial effect on gold dissolution. With a thiosulfate concentration of 0.2 mol l<sup>-1</sup> and ammonia of 0.6 mol l<sup>-1</sup> higher gold solutions are obtained than with a concentration of 0.2 mol l<sup>-1</sup> of S<sub>2</sub>O<sub>3</sub><sup>2-</sup> and 0.4 mol l<sup>-1</sup> of NH<sub>3</sub>. All this is consistent with the potentiodynamic polarization results shown in Figs. 1 to 3 and

in Table 2 where the highest anodic gold dissolution currents are obtained in the E1 and E3 assays.: I<sub>La</sub> E1 (2.60 E-4 A) > I<sub>Lc</sub> E1 (1.55 E-4 A) and I<sub>La</sub> E3 (6.30 E-4 A) > I<sub>Lc</sub> E3 (1.79 E-4 A) compared to the currents obtained in the E2 and E4 assays: I<sub>La</sub> E2 (62.45 E-4A) < I<sub>Lc</sub> E2 (7.55 E-4 A) and I<sub>La</sub> E4 (3.62 E-4 A) < I<sub>Lc</sub> E3 (3.85 E-4 A).

In terms of thiosulfate degradation (Fig. 7b), there is a general increase in the time; however, after 24 h the most abrupt increase is



presented to E3 solution.

As mentioned before, high copper concentration in the solution catalyzes the gold leaching, however an excess can promote the thiosulfate degradation [8]. The EDTA and  $\text{NH}_3$  form complexes with the copper ions [50]. In solution E1 to E4, the copper concentrations were  $0.05 \text{ mol l}^{-1}$ , but for E1 and E3 solutions the relation T:C and T:E were 4:1 and 8:1 respectively, but the difference is in terms of ammonium concentration E1  $0.6 \text{ mol l}^{-1}$  and E3  $0.4 \text{ mol l}^{-1}$ . If there is a high ammonium and EDTA concentration, copper ions can be complexes but a deficiency of these, promote the formation of free copper ions and therefore, more thiosulfate degradation.

In general, terms it is observed that the increase of gold dissolution is accompanied by the increase of thiosulfate degradation in solution and the decrease of gold potential in solution.

In the solution degradation process, thiosulfate is oxidated to tetrathionates and sulfates ( $\text{S}_4\text{O}_6^{2-}$  and  $\text{SO}_4^{2-}$ ) as was found in a previous study [51].

Fig. 8 presents the gold dissolution rates, and degradation percent of thiosulfate occurred after 24 h of leaching in the different electrolyte systems in study. The highest rates of gold dissolution (Fig. 8a) were obtained in solutions with concentrations of  $0.2 \text{ mol l}^{-1}$  of  $(\text{NH}_4)_2\text{S}_2\text{O}_3$ . The largest gold dissolution of 183 ppm was obtained in the E1 solution composed of  $0.2 \text{ mol l}^{-1}$   $(\text{NH}_4)_2\text{S}_2\text{O}_3$ ,  $0.05 \text{ mol l}^{-1}$   $\text{Cu}^{2+}$ ,  $0.6 \text{ mol l}^{-1}$   $\text{NH}_3$ ,  $0.025 \text{ mol l}^{-1}$  EDTA at pH 10.0 and a leaching time of 24 h (Fig. 8a). In this same solution (E1) the final degradation of thiosulfate reached 14.92 %.

According to the results at 24 h of leaching (Fig. 8a and 8b), the following behavior was found:

Gold foil dissolution (ppm): E1 > E3 > E5 > E2 > E4 > E7 > E2 > E6  
 Degradation of thiosulfate (%): E3 > E6 > E7 > E1 > E2 > E5 > E8 > E4

Although, the high dissolution rates were observed in the solution with high thiosulfate concentration, these solutions, except by E5, also experimented the largest degradation percentages after 24 h of leaching. This issue is important to consider, in order to preserve the integrity of the ammoniacal thiosulfate solution for further leaching processes. To keep the leaching power and avoid the degradation of the solution a compromise between the thiosulfate concentration, chelating anions and oxidizers ( $\text{O}_2$ ,  $\text{Cu(II)}$ ) should be done. According to that observed in Fig. 7, a continuous evolution of the electrochemical potential of the leaching solution to more negative values (Fig. 7c) was observed during the plateau, between 6h-22 h, of leaching. That occurs due to continuous reduction of  $\text{Cu(II)}$  to  $\text{Cu(I)}$ . Chelating compounds like EDTA and  $\text{NH}_3$

help to diminishing the reduction rate of  $\text{Cu(II)}$  during leaching (potential drops do not exceed 80 mV). A constant leaching power is maintained between 6 and 22 h, without appreciable degradation of thiosulfate solution after that period, see Fig. 7b. The use of less concentrated solutions of ammonium thiosulfate does not guarantee a lower rate of degradation of the thiosulfate ion. It could be observed that some solutions with low thiosulfate content, E2 and E8, Fig. 8b, experienced degradation rates similar to solutions with higher concentration.

#### 4. Conclusions

The electrochemical methodology used in this work shows that the method is able to identify the effects of variation of the components in an ammoniacal thiosulfate solution on anodic and cathodic processes, dissolution of and degradation of thiosulfate. The main results obtained can be summarized as follows:

Ammoniacal thiosulfate solution with a concentration of  $0.2 \text{ mol l}^{-1}$  thiosulfate, improves dissolution of gold which promotes the oxidation of gold to potential values between 0.1 V and 0.25 V vs SHE. Similarly, it is important to maintain an adequate ratio between thiosulfate/ammonium (T:A of 1:3) or thiosulfate/copper (T:C of 4:1) to maintain this condition and preserve the integrity of the ammoniacal thiosulfate solution for further leaching processes.

Copper (II) reduction reaction coexists with oxygen reduction during gold dissolution in thiosulfate solutions. However, it does not show appreciable hydrodynamics dependence on the cathodic process at low cathodic polarization conditions. In those conditions, the contribution of copper reduction to the global cathodic current can be negligible and the ORR becomes as the main cathodic process to be consider. It was found that the reduction of oxygen occurs by peroxide pathway, where 2 electrons are transferred, in ammoniacal thiosulfate solution.

A continuous evolution of the electrochemical potential of the leaching solution to more negative values occurs during the plateau, between 6h-22 h, of leaching. That occurs due to continuous reduction of  $\text{Cu(II)}$  to  $\text{Cu(I)}$ . Chelating compounds like EDTA and  $\text{NH}_3$  help to diminishing the reduction rate of  $\text{Cu(II)}$  during leaching (potential drops do not exceed 80 mV). A constant leaching power is maintained between 6 and 22 h, without appreciable degradation of thiosulfate solution after that period.

#### CRedit authorship contribution statement

**José A. Tamayo:** Writing – original draft, Validation, Investigation.  
**Carolina Ramírez-Sánchez:** Writing – original draft, Validation.  
**Jorge A. Calderón:** Writing – review & editing, Methodology, Funding

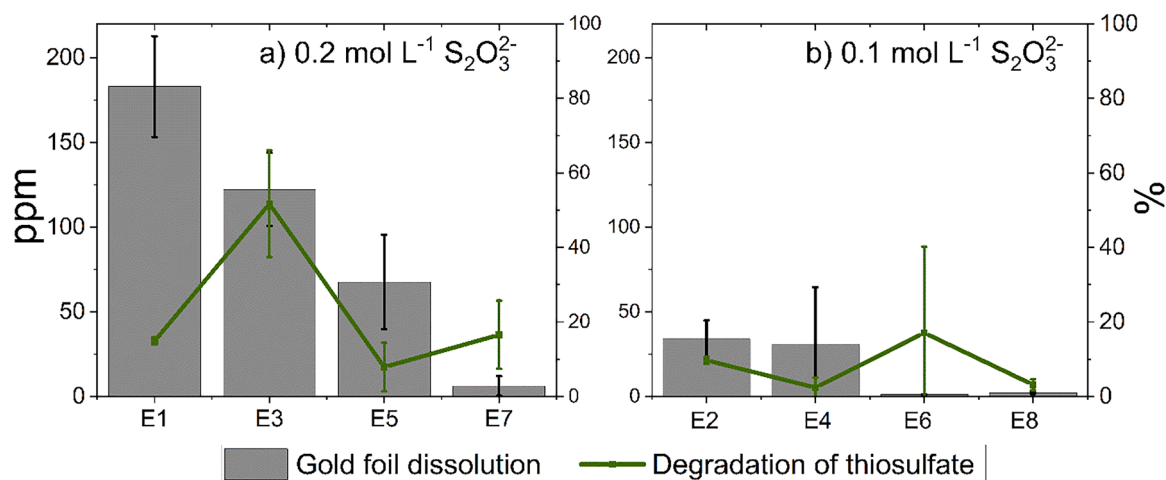


Fig. 8. Gold dissolution (ppm) y degradation of thiosulfate (%) at 24 h during leaching of gold foil with ammonium thiosulfate solutions: a)  $0.2 \text{ mol l}^{-1}$   $\text{S}_2\text{O}_3^{2-}$  [E1, E3, E5 y E7] and b)  $0.1 \text{ mol l}^{-1}$   $\text{S}_2\text{O}_3^{2-}$  [E2, E4, E6 y E8].

acquisition, Conceptualization.

### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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### Data availability

Data will be made available on request.

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