



An electrochemical study of the dissolution of gold in thiosulfate solutions Part I: Alkaline solutions

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Abstract

The anodic dissolution of gold in alkaline thiosulfate solutions has been studied by using a rotating gold disc. Experimental results have shown that the gold dissolves at measurable rates in thiosulfate solutions at potentials above 0.2 V. It has been confirmed that dissolution occurs in parallel with oxidation of thiosulfate with a dissolution current efficiency that varies with time and with the experimental conditions and which is generally in the range of 0.3 to 0.6. Although oxygen could be used as an oxidant for gold in the thiosulfate system, the rate of the cathodic reduction of oxygen in the relevant potential region is too slow for practical purposes. It was found that in the potential region investigated, thiosulfate ions undergo oxidative decomposition leaving a sulfur-like film on the surface of gold, which inhibits the rate of dissolution of gold and results in a low anodic current efficiency for the dissolution of gold. The factors (temperature, pH, thiosulfate concentration and ammonia) have been found to have positive effects on the kinetics of gold dissolution. The rates of gold dissolution in oxygenated alkaline thiosulfate solutions have been estimated to be much lower than in the copper–ammonia–thiosulfate and cyanide systems.

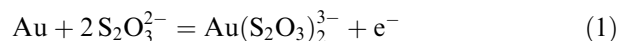
1. Introduction

The process for the extraction of gold and silver from their ores by cyanidation has been used for over a century and remains as the dominant process in the extractive metallurgy of gold in industry. However, there are increasing environmental concerns over its use, leading to considerable attention being devoted to the study of alternative non-cyanide lixiviants for leaching of gold. One of the most promising of these alternatives to cyanide is thiosulfate which is considered as a nontoxic alternative to cyanide especially for ores and concentrates which can not be economically treated because of excessive consumption of cyanide or which contain ‘pre-robbing’ components which adsorb the aurocyanide complex ion.

The recovery of precious metals using thiosulfate was first proposed early in the 1900s [1]. The process for gold extraction from gold ores by basic thiosulfate solutions containing ammonia and copper ions was developed by Berezowsky et al. [2, 3]. Since then, much work has been carried out with the aim of understanding and improving the ammoniacal thiosulfate leaching process. Alymore and Muir [1] have recently provided a comprehensive review of the chemistry involved. However, the thiosulfate leaching system has been found to be very complicated and the process is still not fully understood, which in turn hinders the development and application of the technology. In particular, the funda-

mental electrochemistry of the anodic oxidation of gold and of the cathodic reduction of oxygen and redox mediators such as the copper(II)/copper(I) couple have not been satisfactorily explored.

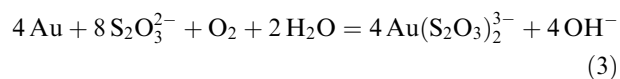
The dissolution of solid metallic gold is best described in terms of an electrochemical model that involves coupled anodic and cathodic reactions. For the leaching of gold in thiosulfate solutions, the anodic reaction is



The standard reduction potential for this anodic reaction is 0.153 V [4,5]. The cathodic reaction in the absence of a redox mediator is the reduction of dissolved oxygen:



This has a standard reduction potential is 0.401 V at pH 14. Thus, the overall stoichiometric reaction for the dissolution of gold in aqueous alkaline thiosulfate solutions in the presence of oxygen is



This reaction, however, has been found to be very slow [6, 7] and copper(II) ions were found to have a strong

catalytic effect on the rate of oxidation in the presence of ammonia that helps to stabilize copper(II) as the cupric tetramine complex ion.

There have been some studies of the fundamental chemistry of the leaching of gold in the thiosulfate leaching system. Jiang et al. [8, 9, 10] studied the anodic dissolution of gold in the presence of thiosulfate using electrochemical techniques. They found that a current peak in the anodic reaction appears at a potential of about 50 mV vs SCE suggesting that passivation of the reaction occurs in this potential region.

Zhu et al. [11] and Chen et al. [12] investigated the dissolution of gold in aqueous thiosulfate solutions with the methods of voltammetry and electrochemical impedance spectra (EIS). They established that the anodic voltammetric response of a gold electrode in the thiosulfate solutions includes reactions other than the dissolution of gold such as the oxidation of thiosulfate. Zhuchkov et al. [13,14] suggested that the dissolution of gold in thiosulfate solutions could be limited by the rate of chemical dissolution of a passive surface film, which was suggested as being a hydrated oxide.

Barbosa Filho et al. [15] investigated the dissolution of gold with a gold rotating disc in the presence of thiosulfate, copper and ammonia, while Jeffrey [16] studied the leaching of gold and silver in thiosulfate solutions containing copper and ammonia using a rotating electrochemical quartz crystal microbalance (REQCM) and suggested that the dissolution of gold is a complex process with the initial rate limited by the formation of a film of unknown composition.

During a current investigation into the oxidation of refractory gold ores containing arsenopyrite and pyrite, thiosulfate was detected as one of the major products of oxidation in strongly alkaline solutions. It is suspected that this species could be responsible for the observation that gold was found to dissolve simultaneously with oxidation of these minerals, that is, in the absence of cyanide. This study was therefore aimed at an investigation of the dissolution behaviour of gold in alkaline aqueous thiosulfate solutions at potentials in the region of the mixed potential of gold in oxygenated solutions in order to establish whether this process could be responsible for the dissolution of the gold.

2. Experimental details

Electrochemical experiments were carried out in a 100 ml water-jacketed glass electrochemical cell with three electrodes, i.e. silver–silver chloride reference electrode, platinum wire counter electrode, and a pure gold (99.99%) rotating disc working electrode (3.5 mm dia.). The cell was fitted with an entry port at the base for the Luggin capillary to pass through. The working gold electrode and the platinum counter electrode compartments were separated by a glass frit. Unless otherwise stated all the potentials are quoted with respect to the standard hydrogen electrode (SHE).

All the chemicals used in this study were of analytical grade and used without further purification. De-ionized water from a Millipore Milli-Q system was used for the preparation of the required solutions and rinsing purposes. The solutions for the experiments were purged with ultrahigh purity nitrogen gas before and during each experiment. Voltammetric experiments were performed at room temperatures while in the dissolution experiments the solutions in the cell were thermostated. The gold rotating disc electrode was polished using P2400 grade silicon carbide waterproof paper and rinsed with deionized water before each electrochemical experiment.

The electrochemical set-up consists of a Model 362 scanning potentiostat (from Princeton Applied Research Company, USA) linked to an X–Y or a Y–t recorder. The electrode was rotated using a stand and speed controller built at Murdoch University. Unless stated otherwise, a rotation rate of 200 rpm was used. In some of the experiments, the output of the potentiostat was linked to a data acquisition system using LabView™.

In some dissolution experiments, a solution sample of 3 mL was taken from the cell at intervals during the electrochemical oxidation of gold and a fresh 3 mL solution of same concentration of thiosulfate was returned to the cell to keep the solution volume constant. The solutions were analysed for gold by atomic absorption spectrometry (AAS). In other leaching tests, only final solutions were taken for analysis of the gold concentration.

3. Results and discussion

3.1. Open circuit potentials

To establish the relevant potential region for oxidative dissolution of gold in alkaline thiosulfate solutions, open circuit potential (o.c.p.) measurements were carried out by recording the potential of the rotating gold disc in alkaline thiosulfate solutions. Figure 1 shows the potential of the gold electrode in a solution containing 1 M $\text{Na}_2\text{S}_2\text{O}_3$ and 0.1 M NaOH with nitrogen and oxygen bubbling, respectively. It can be seen that the potential of gold increases from 0.02 to 0.05 V when exposed to solutions saturated with oxygen. The latter can be considered as a mixed potential which is within the potential range for the anodic region observed in the cyclic voltammogram obtained for gold in the same solution as shown in Figure 3. However, the relevant current at the mixed potential is extremely low and not suitable for coulometric measurements. Thus subsequent electrochemical dissolution experiments were performed at more positive potentials.

Mixed potentials of the gold electrode were also measured in the oxygenated thiosulfate solutions with a lower pH of 10.6 in the presence or absence of ammonia as shown in Figure 2. 0.1 M ammonium sulfate was used

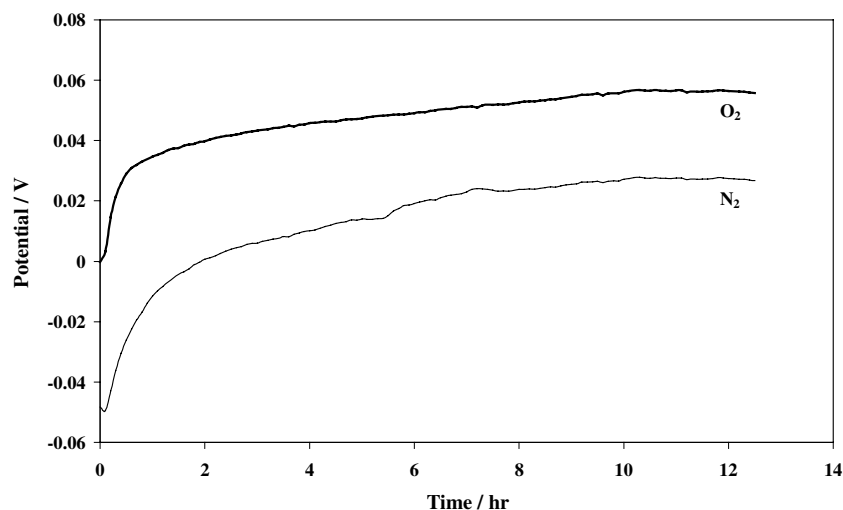


Fig. 1. OCP of a rotating (1000 rpm) gold electrode in solutions containing 1 M $\text{Na}_2\text{S}_2\text{O}_3$ and 0.1 M NaOH under nitrogen and oxygen at 23 °C.

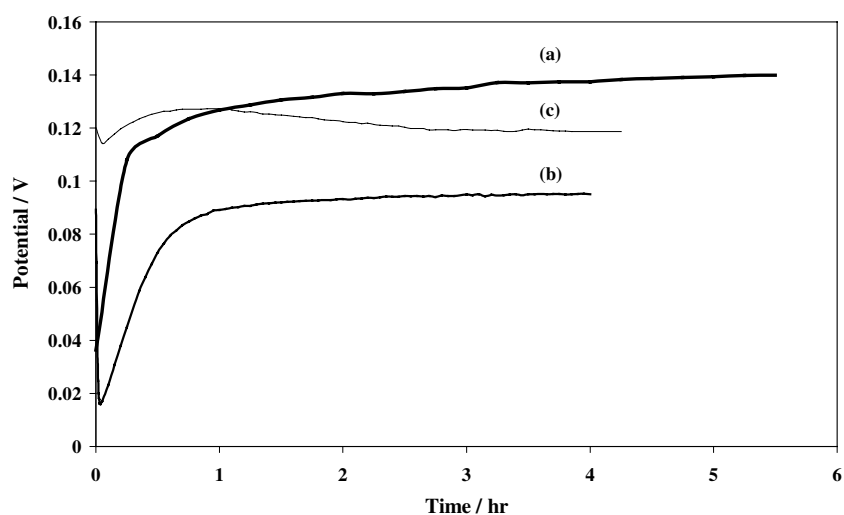


Fig. 2. Mixed potentials of a rotating gold disc electrode in oxygenated solutions at 25 °C containing: (a) 1 M $\text{Na}_2\text{S}_2\text{O}_3$, 0.1 M $(\text{NH}_4)_2\text{SO}_4$; (b) 1 M $\text{Na}_2\text{S}_2\text{O}_3$; (c) 0.1 M $(\text{NH}_4)_2\text{SO}_4$. Solutions (a) and (c) were adjusted to pH 10.6 with ammonia.

as a supporting electrolyte and to buffer the pH of the ammonia solutions.

Clearly, gold attains a higher potential in the solution containing ammonia alone than in the solution containing only thiosulfate at the same pH. More important is that in the presence of ammonium and ammonia, the potential of gold in the thiosulfate solution increased, which suggests that the addition of ammonia may increase the dissolution rate of gold with oxygen as an oxidant.

3.2. Cyclic voltammetry

Cyclic voltammograms of gold and platinum electrodes in 1 M $\text{Na}_2\text{S}_2\text{O}_3$ and/or 0.1 M NaOH solutions are shown in Figure 3. Gold oxidises in 0.1 M NaOH solutions at a potential higher than 0.6 V [17, 18] and no reactions take place on platinum in 0.1 M NaOH solutions in this potential range.

In the presence of thiosulfate there are noticeable oxidation currents on both gold and platinum electrodes at the potentials above about 0.4 V. In the case of gold there is a current peak at about 0.25 V for gold in the solution containing 1 M $\text{Na}_2\text{S}_2\text{O}_3$ and 0.1 M NaOH, which is similar to that reported in the literature [8–12]. By comparison with the thermodynamic potential, Jiang et al. [8, 9] suggested that the current peak at about 0.25 V responds to the anodic dissolution of gold, but they did not provide evidence for this conclusion. This current peak could be attributed to either oxidation of thiosulfate and/or dissolution of gold.

Cyclic voltammograms of gold and platinum electrodes in a more dilute solution containing 0.1 M $\text{Na}_2\text{S}_2\text{O}_3$ and 0.1 M NaOH are shown in Figure 4 from which it is apparent that the current at about 0.25 V is very small compared to that in the more concentrated solution. This result is in agreement with Zhu et al. [11] who indicated that there was no obvious anodic peak in

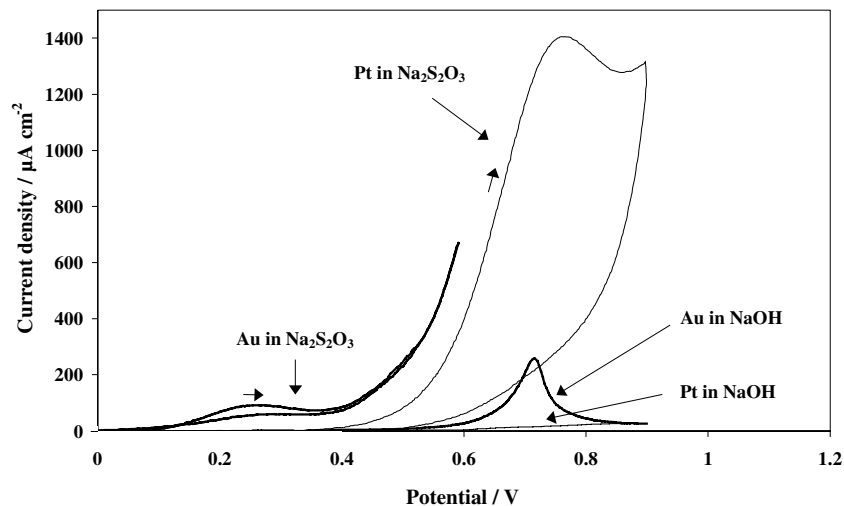


Fig. 3. Cyclic voltammograms at 5 mV s^{-1} of gold and platinum electrodes in deoxygenated 0.1 M NaOH solutions with and without $1 \text{ M Na}_2\text{S}_2\text{O}_3$. Sweeps were initiated in a positive direction from the rest potential.

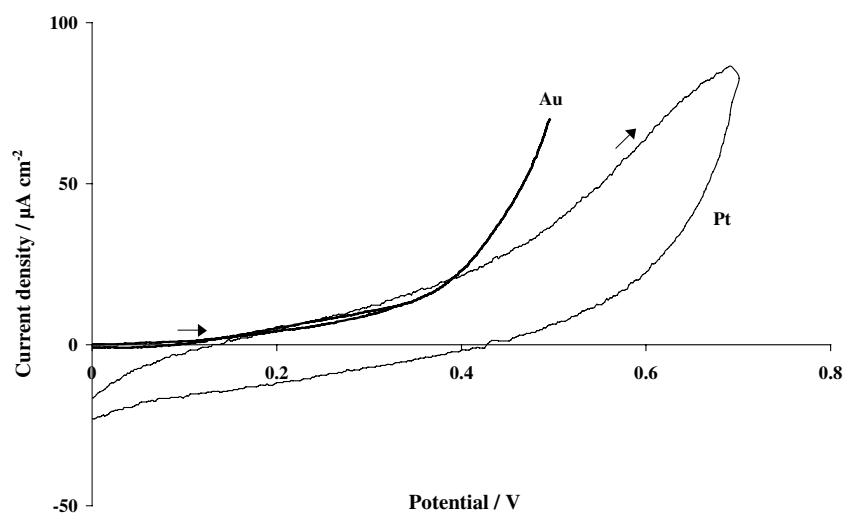


Fig. 4. Cyclic voltammograms at 5 mV s^{-1} of gold and platinum electrodes in deoxygenated solution containing $0.1 \text{ M Na}_2\text{S}_2\text{O}_3$ and 0.1 M NaOH .

dilute aqueous thiosulfate solution. The current at the same potential is somewhat higher on the gold than the platinum electrode.

From the viewpoint of thermodynamics, it is possible for thiosulfate to undergo many reactions in the potential region of interest. Some possible reactions

regarding thiosulfates in alkaline solutions are summarized in Table 1.

Anodic oxidation of thiosulfate to tetrathionate and sulfate has been found out in slightly acid or neutral solutions by Glasstone and Hickling [5]. Previous studies with regard to the electrochemical oxidation of thiosul-

Table 1. Some relevant reactions of thiosulfate and related species in alkaline solutions

Reaction	E° /V	$\Delta G^\circ_{298 \text{ K}}$ / kJ mol^{-1}	Equation
$\text{S}_4\text{O}_6^{2-} + 2 \text{e}^- = 2 \text{S}_2\text{O}_3^{2-}$	0.08		4
$2 \text{SO}_3^{2-} + 3 \text{H}_2\text{O} + 4 \text{e}^- = \text{S}_2\text{O}_3^{2-} + 6 \text{OH}^-$	-0.571		5
$\text{S} + 2 \text{e}^- = \text{S}^{2-}$	-0.447		6
$\text{S}_2\text{O}_3^{2-} + 2 \text{OH}^- = \text{SO}_4^{2-} + \text{H}_2\text{O} + \text{S}^{2-}$		-40.5	7
$4 \text{S}_4\text{O}_6^{2-} + 6 \text{OH}^- = 5 \text{S}_2\text{O}_3^{2-} + 2 \text{S}_3\text{O}_6^{2-} + 3 \text{H}_2\text{O}$		-258.5	8
$\text{S}_4\text{O}_6^{2-} + 2 \text{OH}^- = \text{S}_2\text{O}_3^{2-} + \text{SO}_4^{2-} + \text{S} + \text{H}_2\text{O}$		-174.6	9

Note: The standard free energy changes of these reactions are calculated by using standard free energy data of respective species at 25°C from Pourbaix [21].

fate on gold and platinum electrodes [19, 20] have shown that the thiosulfate ions are oxidized at the potential investigated with the formation of a film consisting of several sulfur-containing species on the electrodes.

Sulfide ions may be formed by disproportionation of thiosulfate (Equation 7 in Table 1) and oxidized to form sulfur on the gold surface at potential between 0 to 0.4 V as observed by Hamilton and Woods [22]. The sulfur film was found to be insulating and is therefore probably responsible for the reported inhibition of redox reactions on gold electrodes [18].

The formation of a sulfur-like film during the anodic oxidation of thiosulfate has been confirmed in this study by using the technique reported by Pedraza et al. [20]. After sweeping the potential of the gold electrode for three cycles from 0 to 0.35 V in a solution containing 1 M thiosulfate and 0.1 M NaOH, the gold electrode was transferred, after rinsing, to another electrochemical cell containing only 0.1 M Na₂SO₄ solution for a potential sweep in the negative direction from 0 V as shown in Figure 5. The cathodic processes at potential less than -0.5 V are due to the reduction of the sulfur film and the anodic peaks appearing at potentials greater than 1 V are also evidence of sulfur species according to Pedraza et al. [20]. Similar behaviour was reported by Wierse et al. [18] and Hamilton and Woods [22] for the reduction of a sulfur-covered gold electrode in alkaline solutions. Estimation of the charge for the oxidation of sulfur species indicates that there are multiple layers of sulfur on the surface in terms of the method proposed by Hamilton and Woods [22], which is consistent with results obtained by Loucka [19].

Since the sulfur film covers the surface of gold retarding the dissolution of gold in alkaline thiosulfate solutions, it would be desirable to eliminate or reduce the passivation of the gold in some way. Addition of ammonia has been found to increase the anodic current of gold in thiosulfate solutions as shown in Figure 6,

which confirms the conclusions of other researchers [10–12]. As seen in Figure 6, the anodic current in the solution containing only ammonia and ammonium ions is very low at potentials below 0.4 V, which is consistent with the results of Meng and Han [23]. However, when ammonia is added into the thiosulfate solution, the anodic current markedly increases as compared to that in the thiosulfate solution alone. The reason for this enhancement of the anodic current by ammonia is possibly due to elimination or reduction of the sulfur film on the surface of gold electrode.

3.3. Coulometric experiments

To verify the occurrence of gold dissolution in alkaline thiosulfate solutions, coulometric experiments were conducted by applying a constant potential to the gold rotating disc in the electrochemical cell containing alkaline thiosulfate solution for several hours. The current passed through the cell was recorded and the electric charge was obtained by integration of the current–time transient. After the run, the solution was analysed for gold by AAS.

3.3.1. Effect of potential

Figure 7 shows the average measured dissolution rates of gold over a period of 12.5 h in a solution containing 1 M Na₂S₂O₃ and 0.1 M NaOH for potentials in the range 0.20–0.35 V. Also shown are the rates calculated from the measured charge assuming a one-electron process. It is apparent that the trend in the data in Figure 7 is similar to that observed in the voltammogram shown in Figure 3 with a peak at about 0.25 V. This suggests that the partial passivation observed in Figure 3 is a steady-state effect.

It is reasonable to suppose that extrapolation of the data in Figure 7 to the mixed potential in an oxygenated thiosulfate solution will yield a rate less than

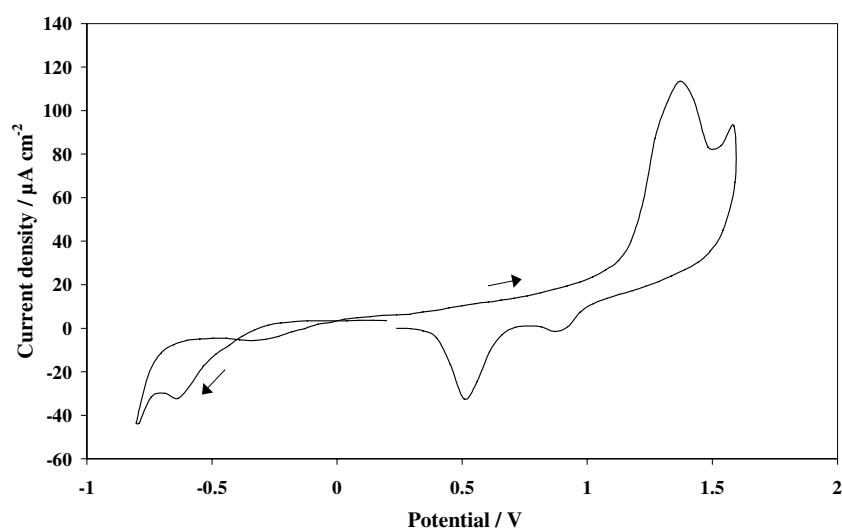


Fig. 5. Cyclic voltammograms at 10 mV s⁻¹ of a gold electrode in 0.1 M Na₂SO₄. Sweep starts at 0.2 V in a negative direction. Gold electrode was previously swept in 1 M Na₂S₂O₃ and 0.1 M NaOH between 0 V and 0.35 V for three cycles without rotation.

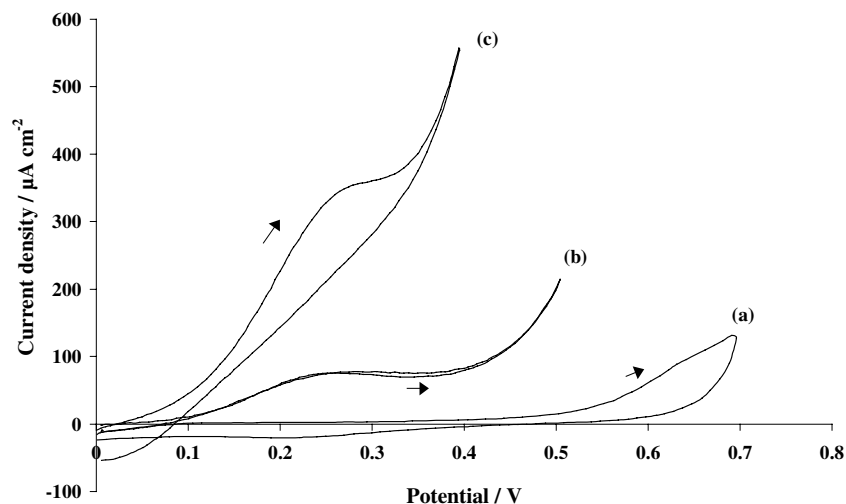


Fig. 6. Cyclic voltammograms at 5 mV s^{-1} of gold in deoxygenated solutions containing: (a) $0.1 \text{ M } (\text{NH}_4)_2\text{SO}_4$ plus NH_3 at pH 10.6; (b) $1 \text{ M } \text{Na}_2\text{S}_2\text{O}_3$ adjusted to pH 10.6 with NaOH ; (c) $1 \text{ M } \text{Na}_2\text{S}_2\text{O}_3$, $0.1 \text{ M } (\text{NH}_4)_2\text{SO}_4$ plus NH_3 at pH 10.6.

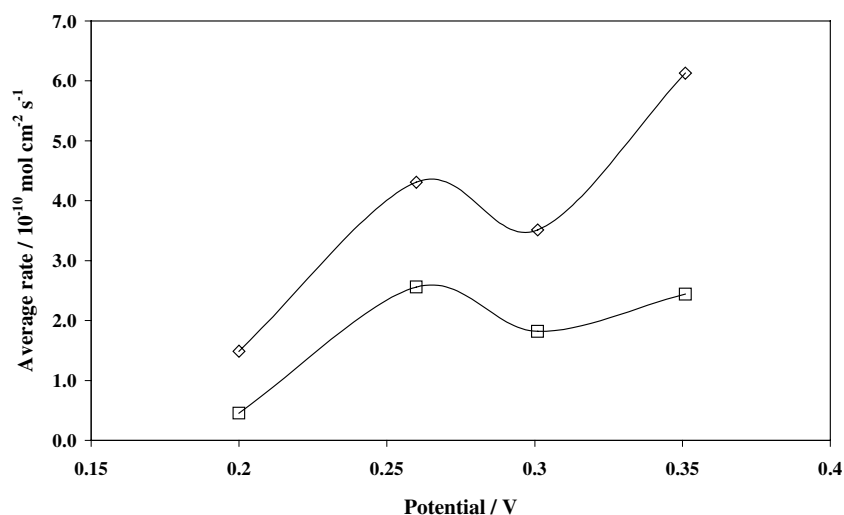


Fig. 7. Anodic dissolution of a rotating (1000 rpm) gold electrode in solutions containing $1 \text{ M } \text{Na}_2\text{S}_2\text{O}_3$ and $0.1 \text{ M } \text{NaOH}$ at different potentials at $23 \text{ }^\circ\text{C}$ for 12.5 h. Key: (\diamond) calculated from charge; (\square) measured from gold concentration.

$10^{-11} \text{ mol cm}^{-2} \text{ s}^{-1}$. This value suggests that gold may be oxidized by oxygen in alkaline thiosulfate solutions in the absence of copper ions and ammonia, although the dissolution rate of gold is very low as compared to that in aerated cyanide solutions of about $5 \times 10^{-9} \text{ mol cm}^{-2} \text{ s}^{-1}$ (Jeffrey et al. [24]). In the preliminary study reported by Webster [7], dissolution of gold was detected in 0.1 M thiosulfate solutions without ammonia and copper ions for nine weeks with oxygen. This estimated dissolution rate of gold in 1 M thiosulfate solution is much lower than that obtained by Jeffrey [16] of about $4 \times 10^{-9} \text{ mol cm}^{-2} \text{ s}^{-1}$ in ammoniacal thiosulfate solutions containing copper ions.

The average current efficiency for the dissolution of gold increases from 30% at 0.20 V to 59% at 0.25 V before decreasing to 40% at 0.35 V . The competing process involving the oxidation of thiosulfate therefore

becomes more prominent at the higher potentials as was suggested by the results in Figure 4.

The result shown in Figure 8 demonstrates that the current passed through the cell increases quickly at the start of the experiment achieving the plateau at about $60 \mu\text{A cm}^{-2}$, and then decreases progressively to about $15 \mu\text{A cm}^{-2}$ in 5 h, suggesting that the passivation process is relatively slow at this potential. The measured dissolution rate followed a similar pattern with a decrease after 5 h. Calculation of the ratio of gold dissolved to charge passed during this experiment showed that the oxidation of thiosulfate is favoured during the first 3 h after which the current efficiency for dissolution stabilized at about 55%. Visual and microscopic examination of the electrode after this experiment revealed that the presence of a brown film in addition to corrosion pits on the surface. The method of Pedraza

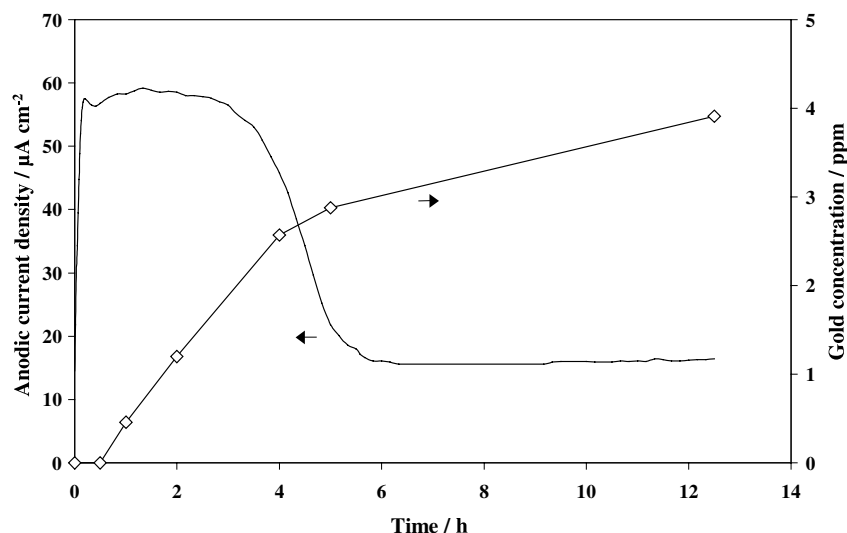


Fig. 8. Anodic dissolution of a rotating gold disc in a solution containing 1 M $\text{Na}_2\text{S}_2\text{O}_3$ plus 0.1 M NaOH at 0.25 V and 25 °C.

et al. [20] as described above was again utilized and confirmed the existence of a film on the gold electrode. Attempts to collect sufficient material for either chemical or X-ray diffraction analysis were not successful.

3.3.2. Effect of temperature

The effect of temperature was investigated by carrying out coulometric experiments at 0.25 V at various temperatures. The results shown in Table 2 demonstrate that a higher temperature results in higher average anodic currents and dissolution rates of gold. The coulombic efficiency does not have any consistent trend with temperature but is about 0.5, implying that oxidation of thiosulfate also increased with increase in temperature. It is well known that sodium thiosulfate is unstable in aqueous solutions, especially at higher temperatures [25]. At high temperatures, more sulfur could be produced on the surface of gold due to the oxidation of sulfide as shown in Equation 7, resulting in more rapid passivation of gold. However, the oxidation rate of gold in fact increases with temperature in this study. The reason for this is probably associated with the occurrence of the following disproportionation reaction of sulfur at high pH and high temperatures [25]:



Table 2. Effect of temperature on the average anodic dissolution rate of gold in 1 M $\text{Na}_2\text{S}_2\text{O}_3$ and 0.1 M NaOH solutions at 0.25 V over 12.5 h

Temperature / °C	Average charge / $\text{F cm}^{-2} \text{ s}^{-1}$	Dissolution rate / $\text{mol cm}^{-2} \text{ s}^{-1}$	Coulombic efficiency
25	3.13×10^{-10}	1.66×10^{-10}	0.53
35	7.42×10^{-10}	3.77×10^{-10}	0.51
45	15.6×10^{-10}	9.78×10^{-10}	0.63
55	42.0×10^{-10}	17.5×10^{-10}	0.42

Note: F = Faraday.

3.3.3. Effect of pH

The results in Table 3 indicate that the dissolution rate of gold increases markedly with increasing pH value of the thiosulfate solutions.

These results are in consistent with those of Jiang et al. [10] and Chen et al. [12] but are contrary to those of Zhuchkov et al. [14], who observed that the maximum dissolution current decreased with increasing pH of the reaction system. It is possible that the increase in the dissolution rate of gold with pH may be attributed to partial elimination of sulfur-like films from gold surfaces in solutions with high concentrations of hydroxyl ions.

3.3.4. Effect of the concentration of thiosulfate

The dissolution of gold in 0.1 and 0.5 M thiosulfate solutions with 0.1 M NaOH were performed at the potential of 0.25 V for 12.5 h in order to compare with the results conducted in 1 mol dm^{-3} thiosulfate solution under same conditions. The results shown in Table 4 indicate that there is little gold dissolution in 0.1 M thiosulfate solution confirming the result obtained by cyclic voltammetry in 0.1 M thiosulfate solution. As can be seen, the anodic dissolution rate at the constant potential increases with increasing the concentration of thiosulfate while the anodic current efficiency decreases as the thiosulfate concentration increases which suggests that the reaction order for thiosulfate oxidation is greater than that for the oxidation of gold.

Table 3. Effect of pH on the average anodic dissolution rate of gold in 1 M $\text{Na}_2\text{S}_2\text{O}_3$ solutions at 0.25 V and 25 °C for 12.5 h

pH	Average charge / $\text{F cm}^{-2} \text{ s}^{-1}$	Dissolution rate / $\text{mol cm}^{-2} \text{ s}^{-1}$	Coulombic efficiency
10.6	1.03×10^{-10}	0.66×10^{-10}	0.63
12	1.27×10^{-10}	0.88×10^{-10}	0.69
13	3.13×10^{-10}	1.66×10^{-10}	0.53

Table 4. Effect of concentration of Na₂S₂O₃ on the average anodic dissolution rate of gold in 0.1 M NaOH solutions at 0.25 V and 25 °C over 12.5 h

[Na ₂ S ₂ O ₃] /M	Average charge /F cm ⁻² s ⁻¹	Dissolution rate /mol cm ⁻² s ⁻¹	Coulombic efficiency
0.1	6.01 × 10 ⁻¹²	5.98 × 10 ⁻¹²	0.99
0.5	9.52 × 10 ⁻¹¹	7.44 × 10 ⁻¹¹	0.81
1	3.13 × 10 ⁻¹⁰	1.66 × 10 ⁻¹⁰	0.53

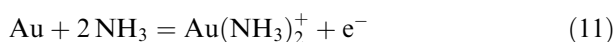
3.3.5. Effect of ammonia

The data in Table 5 show that the addition of ammonia leads to higher rate of anodic dissolution of gold at 0.25 V in the thiosulfate solution compared to the thiosulfate solution adjusted to the same pH of 10.6 with NaOH. The rate of oxidation of thiosulfate is also increased in the presence of ammonia. In the absence of thiosulfate, no gold was detected after 12.5 h at the potential of 0.25 V.

The current–time transients obtained during these experiments showed similar pattern as in Figure 8. The anodic oxidation current increased quickly to a maximum before decreasing over a period of several hours to a steady value that was significantly greater in the presence of ammonia. In the absence of thiosulfate, the anodic current was almost negligible in the aqueous ammoniacal solution.

The appearance of the electrode surface was different in that, without the addition of ammonia, a visible yellow–brown film was observed which can be easily rubbed from the surface. On the other hand, no visible film was present on the pitted surface after the experiment in the presence of ammonia.

According to Jiang et al. [8, 9], the effect of ammonia on the dissolution of gold is due to the following reactions:



in which gold is anodically oxidized to form the di-amine complex, Au(NH₃)₂⁺ which reacts with thiosulfate ions after entering the solution to form the aurous di-thiosulfate complex, Au(S₂O₃)₂³⁻. It is possible that this mechanism was suggested in the light of published data for the stability constants for the di-amine and di-thiosulfate gold complexes that appeared to be of a very similar magnitude of 10²⁶ [1]. However, some yet

unpublished work has shown that the stability constant for the formation of the di-amine complex has been overestimated by several orders of magnitude.

Furthermore, the cyclic voltammogram of gold in the ammonia plus ammonium sulfate solution at 25 °C shown in Figure 6 confirms that there is a negligible anodic current below 0.4 V. This was confirmed by the potentiostatic measurements at 0.25 V that resulted in no measurable dissolution of gold. Meng and Han [23] reported that the kinetics of the oxidative dissolution of gold is very poor at room temperatures but that significant gold dissolution in ammoniacal solutions occurred only at temperatures greater than 120 °C. Guan and Han [26] reported the occurrence of the dissolution of gold in during galvanostatic measurements in 1 M ammonia solutions at pH 10 and 135 °C.

Thus, it appears unlikely that the above mechanism is responsible for the role of the ammonia but that the primary role of the ammonia in enhancing dissolution of gold is associated with its ability to reduce partial passivation of the gold surface. The mechanism of such action has not, however, been established.

4. Conclusions

The cyclic voltammetric and coulometric studies have shown that anodic dissolution of gold can be measured in alkaline thiosulfate solutions at ambient temperatures at potentials above about 0.2 V. Thiosulfate ions undergo oxidative decomposition on the gold surface in the same potential region with the formation of a sulfur-like surface film that acts to partially passivate the surface for the dissolution of gold. The dissolution rate of gold at constant potential was found to be enhanced by increases in the pH, concentration of thiosulfate and temperature.

Addition of ammonia to the thiosulfate solution results in increased dissolution at fixed potential due to the elimination of the passivating film by some mechanism that is not understood.

Measurement of the mixed potential of a gold electrode in oxygenated thiosulfate solutions has shown that open circuit dissolution of the gold can occur with a rate which is significantly lower than that achieved by conventional cyanidation or the copper-catalyzed dissolution in ammoniacal thiosulfate solutions.

Table 5. Effect of ammonia on the anodic dissolution of gold in 1 M Na₂S₂O₃ solutions at pH 10.6 at 0.25 V and 25 °C over 12.5 h

Medium	Average charge /F cm ⁻² s ⁻¹	Dissolution rate /mol cm ⁻² s ⁻¹	Coulombic efficiency
1 MS ₂ O ₃ ²⁻ + 0.2 MNH ₄ ⁺ + NH ₃	2.13 × 10 ⁻¹⁰	1.42 × 10 ⁻¹⁰	0.66
1 MS ₂ O ₃ ²⁻ + NaOH	1.03 × 10 ⁻¹⁰	0.66 × 10 ⁻¹⁰	0.63
0.2 MNH ₄ ⁺ + NH ₃	5.17 × 10 ⁻¹⁰	<10 ⁻¹²	–

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