An electrochemical study of the dissolution of gold in thiosulfate solutions. Part II. Effect of Copper

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Abstract

Thiosulfate has been considered as one of the most promising of the non-toxic alternatives to cyanide for the leaching of gold and much work has been carried out with the aim of understanding and improving the ammoniacal thiosulfate leaching process. In particular the behaviour of gold in thiosulfate solutions containing copper in the absence of ammonia has received little attention. It has been shown in this study involving electrochemical and leaching tests that copper ions catalyze not only the oxidation of thiosulfate but also the dissolution of gold in alkaline thiosulfate solutions. Electrochemical studies have shown that copper has a positive effect on the anodic dissolution of gold with increasing concentrations of copper resulting in higher dissolution rates of gold at a potential of 0.3 V. Studies on the dissolution of gold powder in alkaline oxygenated thiosulfate solutions containing low concentrations of copper have shown that the role of copper in enhancing the dissolution rate of gold is possibly associated with the formation of a copper–thiosulfate–oxygen intermediate which is more reactive in terms of cathodic reduction than dissolved oxygen. The electrochemical experiments have been complemented by a leaching study which has shown that milling of gold powder in the presence of copper (added as ions, metal, or oxide) assists with the dissolution of gold in thiosulfate solutions.

1. Introduction

Thiosulfate appears to be the most promising nontoxic alternative to cyanide for the leaching of gold, especially from ores and concentrates which cannot be economically treated because of excessive consumption of cyanide or which contain 'pre-robbing' components which adsorb the aurocyanide complex ion. Although much research work on thiosulfate leaching of gold over the last three decades has been carried out, commercial introduction of the process has not yet been achieved [1]. One of the reasons for this is the poor understanding of the thiosulfate leaching system which has been found to be very complex [2]. In particular, the fundamental 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 overall stoichiometric reaction for the dissolution of gold in aqueous alkaline thiosulfate solutions in the presence of oxygen is

$$4Au + 8S_2O_3^{2-} + O_2 + 2H_2O = 4Au(S_2O_3)_2^{3-} + 4OH^- \tag{1}$$
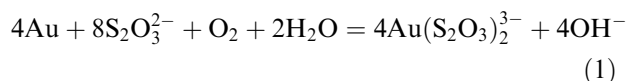
However, this reaction has been found to be very slow in the absence of ammonia due to formation of a sulfur-like film as a result of decomposition of thiosulfate on the gold surface [3–5]. It has been known that for leaching to occur at a reasonable rate, thiosulfate, ammonia and copper(II) must be present in solution [2, 6–8]. Copper(II) ions have been found to have a strong catalytic effect on the dissolution rate of gold in the presence of ammonia [2, 6, 9–11]. The main role of copper(II) ions during the dissolution of gold is believed to be the oxidation of metallic gold by cupric tetra-ammine complex ions as expressed in the following reaction:

$$Au + 5S_2O_3^{2-} + Cu(NH_3)_4^{2+}$$
$$= Au(S_2O_3)_2^{3-} + 4NH_3 + Cu(S_2O_3)_3^{5-} \tag{2}$$
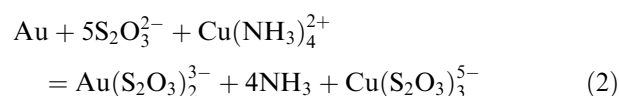
On the other hand, it is well known [12] that cupric tetra-ammine ions can also be reduced to cuprous complex ions by thiosulfate

$$2Cu(NH_3)_4^{2+} + 8S_2O_3^{2-}$$
$$= 2Cu(S_2O_3)_3^{5-} + 8NH_3 + S_4O_6^{2-} \tag{3}$$
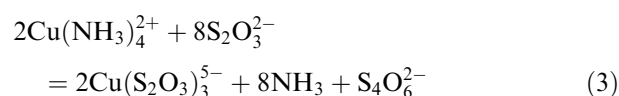
Although this reaction is written with the thiosulfate complex as the product, depending on the relative concentrations of ammonia and thiosulfate, copper(I) exists as both ammine and thiosulfate complexes.

Consequently, the concentration of copper(II) ions present in the leaching solution is an important factor in determining both the stability of thiosulfate and the rate of leaching of gold. Oxygen is required to convert copper(I) to copper(II) for further gold leaching. The oxidation of copper(I) by oxygen in ammoniacal thiosulfate solutions is known [13, 14] to occur readily and represented by the reaction

$$2Cu(NH_3)_2^+ + 4NH_3 + 1/2\ O_2 + H_2O$$
$$= 2Cu(NH_3)_4^{2+} + 2OH^- \qquad (4)$$
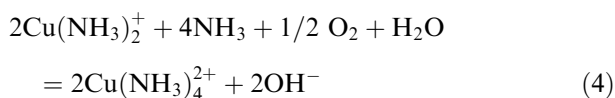
Recent results (Wensween and Nicol, unpublished) have shown that the copper(I) thiosulfate complexes are only oxidized at very slow rates relative to those of the copper(I) ammine complexes.

A freshly prepared solution of sodium thiosulfate containing copper(I) ions is known to be able to dissolve silver metal and sulfides from sulfidic ores even in the absence of ammonia [15, 16]. The dissolution rate of silver metal in a solution of sodium cuprous thiosulfate is nine times higher than that in a solution of sodium thiosulfate alone [15]. The enhanced solvent power of sodium cuprous thiosulfate for silver metal compared with that of sodium thiosulfate alone has been attributed to the redox mediating effect of the copper ions. On the other hand, gold apparently does not dissolve in sodium cuprous thiosulfate solutions any more rapidly than in a solution of sodium thiosulfate alone [15]. Although the above described role of copper ions in the copper–ammonia–thiosulfate leaching system for gold is generally accepted, the behaviour of gold in thiosulfate solutions containing copper without ammonia is less clear despite some published work on the leaching of gold in thiosulfate solutions [8, 11, 17].

During an ongoing investigation into the oxidation of refractory gold ores containing arsenopyrite and pyrite, thiosulfate was detected as one of the major oxidation products of sulfide minerals in strongly alkaline solutions. In addition, up to 1 mM copper was also detected in the leaching solutions. It is suspected that these species could be responsible for the observation that gold was found to dissolve simultaneously with oxidation of these minerals and dissolution of copper in the absence of cyanide and ammonia. This study was therefore aimed at investigating 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. An electrochemical study of the dissolution of gold in alkaline thiosulfate solutions without copper has been reported as Part I of this study [5].

1.1. Chemistry of copper in thiosulfate solutions

Rabai and Epstein [18] have reported that copper(II) ions in aqueous solutions containing excess thiosulfate are converted to stable (thiosulfato)copper(I) complexes by reduction of copper(II) by thiosulfate. The overall reaction has been described as occurring with the formation of an intermediate copper(II) thiosulfate complex ion

$$Cu^{2+} + 2S_2O_3^{2-} = Cu(S_2O_3)_2^{2-} \qquad (5)$$

$$2Cu(S_2O_3)_2^{2-} = 2CuS_2O_3^- + S_4O_6^{2-} \qquad (6)$$
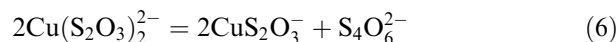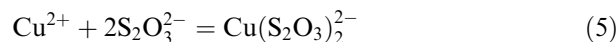
where reaction (5) is a very fast complex-forming process and reaction (6) a rapid but relatively slower redox process with a half life of the order of seconds. With excess thiosulfate, nearly all the copper ions are present in the form of either mono-, bis- or tri(thiosulfato) copper(I) complexes which have stability constants of $10^{10.4}$, $10^{12.3}$ and $10^{13.7}$, respectively [19]. In the absence of excess thiosulfate, the fast redox reaction is followed by slower side reactions that result in the formation of sulfate and precipitation of cuprous sulfide [18]. Thus, it can be assumed that the cuprous thiosulfato complexes are the stable forms of soluble copper during the dissolution of gold in alkaline thiosulfate solutions.

It has been long known that copper(II) can greatly catalyze the homogeneous oxidation of thiosulfate by a variety of oxidizing agents, including oxygen in aqueous solutions. The oxidation of thiosulfate by oxygen under ambient conditions in the absence of copper ions is known to be extremely slow [18, 20]. The catalytic activity of copper is usually explained by assuming that the copper(II) ion rapidly oxidises thiosulfate by the above reaction, followed by re-oxidation of copper(I) to copper(II) by dissolved oxygen.

2. Experimental

Electrochemical instrumentation and detailed experimental procedures can be found in Part I of this study [5]. Unless otherwise stated, all electrochemical experiments were carried out in solutions containing 0.2 M thiosulfate at 25 °C using a gold disk electrode rotated at 400 rpm. The potential scan rate in the electrochemical experiments was 5 mV s^{-1}. The potentials are reported with respect to the standard hydrogen electrode (SHE).

Tests on the dissolution of fine gold powder in thiosulfate solutions were carried out in a specially designed 1-l glass reactor with a water jacket and a plastic lid on which a stationary direct current motor was mounted to control the stirring speed. The lid of the reactor also includes ports for measurement of pH, oxygen concentration and the potential of a gold wire electrode. The measurement of these parameters was accomplished using a computer-based data acquisition system operated using LabView^{TM} software (National Instruments Corporation, USA). The reactor is also equipped with an inlet for oxygen injection and a

cooling condenser. The temperature in the reaction system was controlled through the water jacket by using a thermostatted water bath.

Before running the dissolution experiments, a known amount of gold powder (1.5–3 μm spherical, 99.9 + % purity, Aldrich Chemical Company, USA) was added into the reactor unmilled or after wet-milling in a small porcelain ball mill (Retsch GmbH & Co. KG, Germany) for 30 min. 600 ml of a solution of 0.2 M sodium thiosulfate was then added and nitrogen gas bubbled into the reactor. The required amount of concentrated cupric sulfate solution was added before adjusting the pH of the aqueous solution. When the required temperature of 25 °C was achieved, oxygen was bubbled into the solution to initiate the dissolution of gold. The agitation was controlled at 800 rpm. During the leaching experiments, samples (about 5 ml) of the reaction solution were taken at given intervals and filtered through 0.45 μm nylon membrane filter paper for analysis of gold by Atomic Absorption Spectrometry (AAS). In some tests, gold powder was wet milled together with copper metal or copper oxide before addition to the reactor. All the chemicals used were of analytical grade. Distilled or deionized water was used and the oxygen and nitrogen gases were of industrial and high purity grade respectively.

3. Results

3.1. *Mixed potential measurements*

Figure 1 shows the mixed potentials of a rotating gold disk electrode in aerated 0.2 M $Na_2S_2O_3$ solutions containing different copper concentrations at pH values of 7 and 12 at room temperature. In the solutions at pH 7, the potential of the gold electrode reaches a maximum before decreasing to a steady value of about 0.1 V at longer times. Initially, the potential increases with an increase in the concentration of copper. In the solutions at pH 12, the initial potential of the gold similarly increases with copper concentration but this is
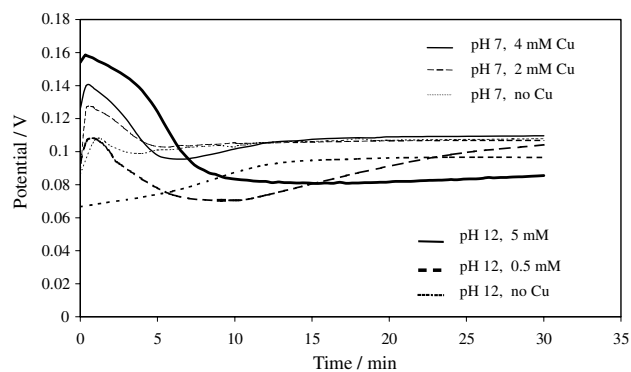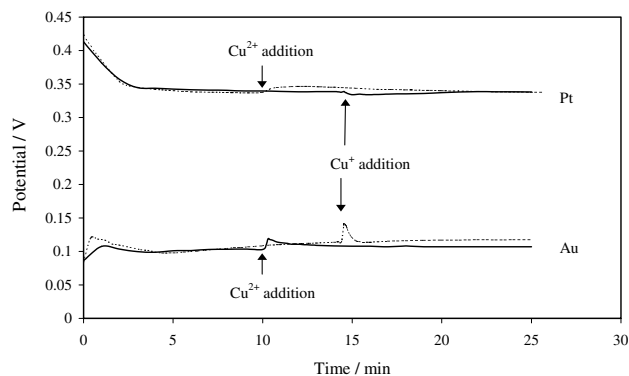
Fig. 2. Effect of copper ions (2 mM Cu) on the mixed potentials of rotating gold and platinum electrodes in aerated 0.2 M thiosulfate solutions at pH 7.

not true after longer times. It also appears that the final potential is lower at the higher pH value. At pH 7, the final potentials are very similar suggesting that there could be little effect of copper on the rate of dissolution at this pH value. At pH 12, the trend with copper concentration is not clear. These results suggest that copper could initially increase the dissolution rate of gold in thiosulfate solutions and that a higher pH may have a negative effect on the rate of dissolution.

The effect of copper on the mixed potential of a gold electrode can be clearly seen in aerated 0.2 M $Na_2S_2O_3$ solutions at pH 7 as shown in Figure 2. In these experiments, a given amount of cupric sulfate or cuprous thiosulfate solution was added to the solution at the times indicated to produce a concentration of 2 mM copper. The mixed potential of gold increases immediately to a higher value and then gradually decreases to the normal level. By comparison, the mixed potential of a platinum electrode under same conditions does not change measurably on addition of copper ions. It is also obvious that platinum has a higher potential than gold in thiosulfate solutions, suggesting that platinum is more inert than gold in aerated thiosulfate solutions. It is possible that the increase in the potential of gold is associated with the formation of an intermediate copper(II) complex which can act to oxidize the gold. It is well known that the oxidation of thiosulfate by copper(II) ions involves the intermediate formation of a metastable copper(II) thiosulfate complex, $Cu(S_2O_3)_2^{2-}$ [18].

3.2. *Anodic polarization*

Anodic polarization experiments were carried out to investigate the behaviour of gold and platinum in thiosulfate solutions with and without copper ions. The results are shown in Figures 3 and 4.

It is apparent that the anodic reactivity increases in the presence of copper on both gold and platinum electrodes. The increase in anodic current is more obvious on the gold electrode. Clearly, with 5 mM copper the anodic current appears to increase with

Fig. 1. Variation of the potential of a rotating gold electrode in aerated 0.2 M thiosulfate solutions at different pH values and copper concentrations.
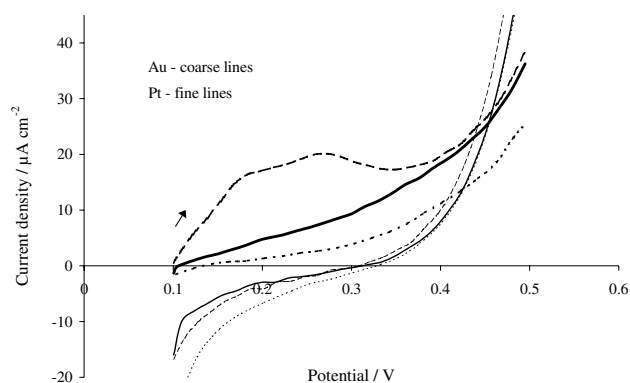
Fig. 3. Anodic polarization of rotating gold (coarse lines) and platinum (fine lines) electrodes in deoxygenated 0.2 M thiosulfate solutions containing 0 mM (······), 0.5 mM (——) and 5 mM (- - - -) Cu ions at pH 7.
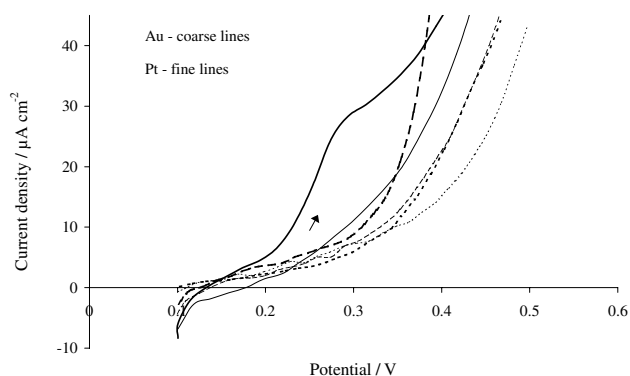

Fig. 4. Anodic polarization of rotating gold (coarse lines) and platinum (fine lines) electrodes in deoxygenated 0.2 M thiosulfate solutions containing 0 mM (······), 0.5 mM (——) and 5 mM (- - - -) Cu ions at pH 12.

potential with a peak at a potential of about 0.28 V. This result indicates that the surface may become partially passivated during oxidation.

The effect of pH on the anodic oxidation of gold electrode in 0.2 M thiosulfate solutions with 0.5 mM copper is summarized in Figure 5. It is apparent that pH has a significant influence only at potentials above about 0.3 V. The overall effect of copper ions on the anodic behaviour in the region of the mixed potential in aerated solutions does not appear to be significant.

3.3. Coulombic measurements

It has been reported that gold dissolves during anodic oxidation in alkaline thiosulfate solutions in the absence
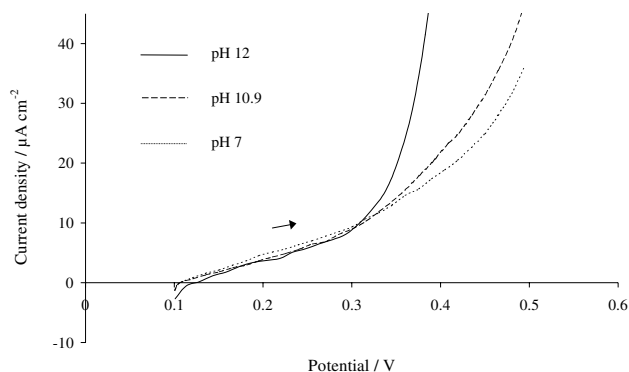

Fig. 5. Anodic polarization curves of a rotating gold electrode in deoxygenated 0.2 M thiosulfate solutions containing 0.5 mM Cu ions at various pH values.

of copper and ammonia [5]. The anodic current at the gold electrode in thiosulfate solutions containing copper shown above could be associated with either the oxidative dissolution of gold, the oxidation of copper(I) to copper(II) and/or the oxidation of thiosulfate. Coulometric measurements were therefore carried out in 0.2 M thiosulfate solutions containing copper ions at pH 12 by applying a constant potential of 0.3 V to the gold electrode and recording the anodic current as a function of time. After potentiostatic oxidation, the solutions were analyzed for gold by AAS. The average dissolution rates of gold and the coulombic efficiencies (assuming a one-electron process) were calculated and are shown in Table 1.

It is apparent that the dissolution rate of gold increases slightly with increasing concentration of copper ions at 0.3 V. However, the coulombic efficiency decreases with increasing copper concentration. This fact suggests that the presence of copper in thiosulfate solutions enhances not only the rate of dissolution of gold but also the rate of oxidation of thiosulfate. The potentiostatic current-time transients shown in Figure 6 reveal that the anodic currents are high initially and then decrease gradually to very low levels, suggesting that passivation of both the oxidation of gold and of thiosulfate occurs in this potential region.

3.4. Dissolution of gold in thiosulfate solutions containing copper

To further investigate the effect of copper on the dissolution of gold, experiments were performed with gold powder in oxygenated thiosulfate solutions in the presence or absence of copper. The effect of milling of the gold particles on the rate of dissolution was also

Table 1. Average rates of anodic dissolution of gold at 0.3 V in 0.2 M thiosulfate solutions at pH 12

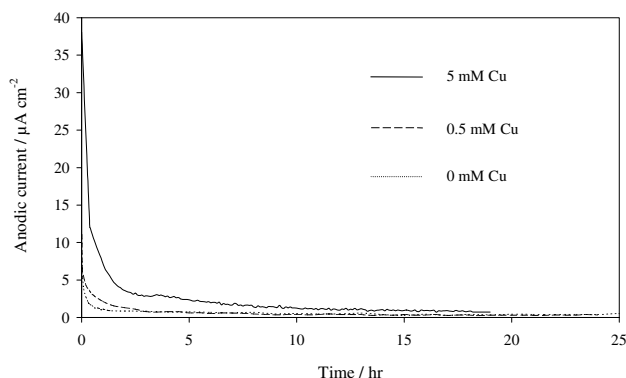| Copper concentration/mM	Average charge/F cm^{-2} s^{-1}	Au Dissolution Rate/mol cm^{-2} s^{-1}	Coulombic efficiency
0	5.17×10^{-12}	2.07×10^{-12}	0.40
0.5	6.46×10^{-12}	2.11×10^{-12}	0.33
5	2.50×10^{-11}	6.50×10^{-12}	0.26

Fig. 6. Current-time transients at a gold electrode in 0.2 M thiosulfate solutions at pH 12 with and without copper ions.
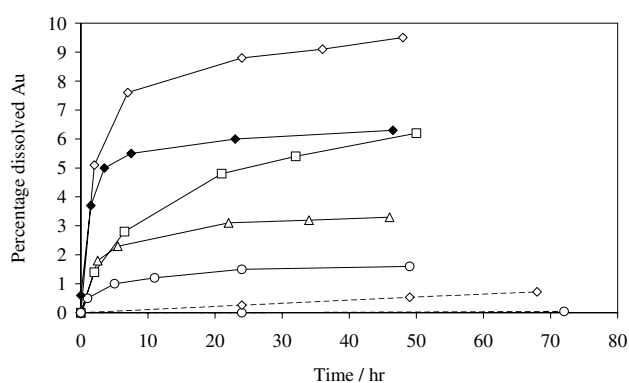

Fig. 7. Dissolution of gold powder in oxygenated 0.2 M thiosulfate solutions at pH 12 with (solid line) and without (dashed line) copper. Fine gold powder (0.1 g) was wet-milled (diamond, triangle or square) or added without milling (circles). The copper was added as ($\Diamond$, o) 0.5 mM CuSO$_4$, ($\blacklozenge$) 2 mM CuSO$_4$, ($\square$) 20% CuO (by mass, milled with gold) and ($\triangle$) 20% Cu powder (by mass, milled with gold) respectively.

investigated. Figure 7 shows the dissolution rates of unmilled and milled fine gold powder in thiosulfate solutions with or without copper. Obviously, copper (in the form of either ions, metal or oxide) enhances the rate of gold dissolution. The effect appears to be greatest with dissolved copper although higher concentrations of copper ions appear to be disadvantageous, which is possibly due to the instability of copper in alkaline solutions. It is apparent that the rate of gold dissolution decreases significantly after a rapid initial reaction which is consistent with the results in Figure 6. The appreciable effect of milling on the dissolution of gold is probably associated with the increased surface area of gold. The potential of a gold electrode in the leach solutions was found to be about 0.11 V which is similar to the mixed potential of gold reported in Figure 1.

4. Discussion

4.1. Electrochemical oxidation

Electrochemical experiments have shown that even without ammonia, copper in thiosulfate solutions has a positive effect on the anodic behaviour of gold. The presence of copper in thiosulfate solutions enhances not only the dissolution of gold but also the oxidation of thiosulfate which is similar to that observed in the presence of ammonia [11]. In the presence of ammonia, the role of copper in providing an alternative cathodic reaction is relatively well understood in terms of the chemistry of the copper ammine complexes. However, in the absence of ammonia, the role of copper is not obvious.

A stability constant (3.6×10^4 M^{-2}) for the unstable bis(thiosulfato)copper(II) complex, Cu(S$_2$O$_3$)$_2^{2-}$, has been determined by Rabai and Epstein [18]. Using this stability constant and relevant thermodynamic data from Aylmore and Muir [1], the standard free energy of formation of Cu(S$_2$O$_3$)$_2^{2-}$ can be calculated as -998.7 kJ mol^{-1}. By using this value, standard reduction potential for the reduction of this species can be calculated as

$$\text{Cu(S}_2\text{O}_3)_2^{2-} + \text{e}^- = \text{Cu(S}_2\text{O}_3)_2^{3-} \quad E^\circ = 0.611\text{V} \quad (7)$$
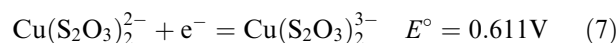
Thus in the present electrochemical studies with copper ions in 0.2 M thiosulfate solutions, the equilibrium concentration of the copper(II) complex, Cu(S$_2$O$_3$)$_2^{2-}$ at a solution potential of 0.35 V (Figure 2) can be calculated to be very low. Thus, assuming that reaction (7) is operative at the platinum electrode, the ratio of Cu(S$_2$O$_3$)$_2^{3-}$ to Cu(S$_2$O$_3$)$_2^{2-}$ is $10^{4.4}$. Although not stable under the conditions of our experiments, it is nevertheless possible that it could be formed by oxidation of copper(I) by dissolved oxygen and therefore account for the enhanced rate of oxidation of thiosulfate.

The higher currents and lower current efficiencies for gold dissolution shown in Table 1 in copper-containing thiosulfate solutions are possibly associated with the oxidation of copper(I) to copper(II) followed by rapid reactions of the copper(II) species with thiosulfate, i.e. catalysis of the anodic oxidation of thiosulfate by copper.

On the other hand, the role of copper is possibly also associated with the partial elimination or reduction of a sulfur-like passivating film on the surface of gold. As suggested in the previous study [5], a gold surface at these potentials in thiosulfate solutions is covered by a sulfur-like film. It is possible that copper ions could act to scavenge any sulfide ions which may be formed at the gold surface thereby reducing the extent of film formation.
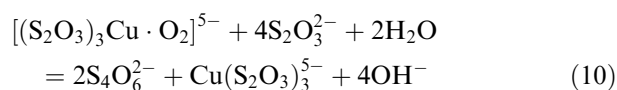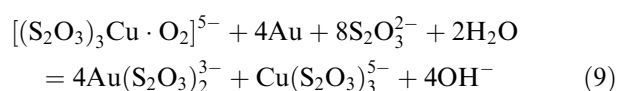
4.2. Dissolution of gold with oxygen

Leaching experiments have confirmed the catalytic effect of copper on the dissolution of gold in thiosulfate solutions without ammonia. The role of copper in the dissolution of gold in oxygenated thiosulfate solutions could be due to formation of a copper–thiosulfate–oxygen intermediate which has a higher reduction

potential. Figure 1 shows that gold attains a higher potential when initially contacting an aerated thiosulfate solution in the presence of copper. Figure 2 shows that after copper ions (either cuprous or cupric) are added into aerated thiosulfate solutions, the potential of gold electrode immediately increases to a higher value before gradually decreasing to a lower value of about 0.1 V. The increase in the potential of gold electrode probably implies the formation of an intermediate which has a higher reduction potential. The intermediate could be formed from a cuprous thiosulfate complex and oxygen as suggested by Rabai and Epstein [18].

$$Cu(S_2O_3)_3^{5-} + O_2 = [(S_2O_3)_3Cu \cdot O_2]^{5-} \qquad (8)$$
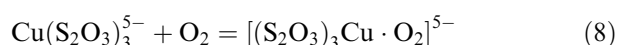
in which oxygen molecule is bound to copper(I) which has an apparent coordination number of 4. In this way cuprous thiosulfate acts as a carrier of oxygen to expedite redox reactions as in the case of dissolution of silver metal in cuprous thiosulfate solutions [15]. Similar intermediates have been suggested in the reactions between oxygen and other cuprous complex ions in copper-catalyzed autoxidation reactions in aqueous solutions [21–24]. However, these intermediates have not been identified chemically or spectrophotometrically in their free or complexed forms during copper(I) autoxidation [25]. This is not unexpected given the high reactivity of these intermediates [25, 26]. In the current study, the increase in the potential of the gold electrode could be an indicator of the presence of this intermediate. Possible overall reactions between this intermediate and gold or thiosulfate could be given by the reactions:

$$[(S_2O_3)_3Cu \cdot O_2]^{5-} + 4Au + 8S_2O_3^{2-} + 2H_2O$$
$$= 4Au(S_2O_3)_2^{3-} + Cu(S_2O_3)_3^{5-} + 4OH^- \qquad (9)$$

$$[(S_2O_3)_3Cu \cdot O_2]^{5-} + 4S_2O_3^{2-} + 2H_2O$$
$$= 2S_4O_6^{2-} + Cu(S_2O_3)_3^{5-} + 4OH^- \qquad (10)$$

Another possible reason should be considered for the enhancement of gold dissolution in thiosulfate solutions containing copper. Webster [4] has suggested that gold might substitute into the silver–thiosulfate complex to form a mixed complex of the type $(Au,Ag)(S_2O_3)_2^{3-}$ in his study on the solubility of gold and silver in thiosulfate solutions. In the current study, it is possible that a similar mixed gold–copper–thiosulfate complex of the type $(Au,Cu)(S_2O_3)_2^{3-}$ could be formed which may assist in the dissolution of gold in thiosulfate solutions. However, evidence for this possible gold–copper–thiosulfate complex needs to be obtained.

Figure 7 has shown that gold initially dissolves relatively rapidly in copper bearing thiosulfate solutions but that the rate gradually decreases with time, which is consistent with results in Figure 6. As suggested in a previous study [5], it is possible that a sulfur-like film could be formed on the oxidized gold surface in thiosulfate solutions, which inhibits further dissolution of gold. Some unidentified yellowish-brown spots were observed under the microscope on a gold disk after it had been reacted with oxygenated copper bearing thiosulfate solutions at room and elevated temperatures.

The initial dissolution rate of wet-milled gold powder in oxygenated alkaline 0.2 M thiosulfate solution in the presence of 0.5 mM copper ions can be estimated to be 3.5×10^{-11} mol cm^{-2} s^{-1}, assuming that all the gold particles are spherical and uniform in size. The rate of dissolution of wet-milled gold powder in oxygenated 0.2 M thiosulfate solution without copper can be estimated to be about 1.5×10^{-13} mol cm^{-2} s^{-1}. These values indicate that a small amount of copper can significantly accelerate the initial rate of dissolution of gold. However, these estimated rates are low compared with that obtained by Jeffrey [27] of about 4×10^{-9} mol cm^{-2} s^{-1} in ammoniacal thiosulfate solutions containing copper ions.

5. Conclusions

Both electrochemical and dissolution experiments have shown that copper ions enhance the rate of gold dissolution in the absence of ammonia at ambient temperatures. Electrochemical studies have shown that copper has a positive effect on the anodic dissolution of gold with increasing concentrations of copper resulting in higher dissolution rates of gold at a potential of 0.3 V. Studies on the dissolution of gold powder in alkaline oxygenated thiosulfate solutions containing low concentrations of copper have shown that the role of copper in enhancing the dissolution rate of gold is possibly associated with the formation of a copper–thiosulfate–oxygen intermediate which is more reactive in terms of cathodic reduction than dissolved oxygen, but this mechanism remains to be proven. On the other hand, the possibility of the formation of mixed copper–gold–thiosulfate complexes can not be ruled out and this possibility needs to be further investigated using other techniques. As expected, milling of gold powder assists with the dissolution of gold in thiosulfate solutions, especially in the presence of copper.

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