The role of ligands and oxidants in thiosulfate leaching of gold

Gamini Senanayake

A.J. Parker Cooperative Research Centre for Hydrometallurgy, Department of Mineral Science and Extractive Metallurgy, Murdoch University, Perth, WA 6150, Australia

Abstract

The widely used cyanidation technology is not applicable to some gold ores due to economic or technical reasons when the cyanidation gives very low gold extractions. Despite the fact that the gold mining industry accounts for only 13% of total cyanide consumption there is growing public concern over the use of toxic cyanide for gold extraction. Many researchers have identified that thiosulfate leaching is the most likely alternative to cyanidation due to non-toxicity, low cost and other benefits. This article describes the current information on stoichiometric relationships, equilibria, reaction rates and mechanisms related to anodic or chemical oxidation of gold in thiosulfate, ammoniacal thiosulfate and ammoniacal copper(II) thiosulfate solutions in the presence or absence of oxygen.

Introduction

Since the late 1970's (1), the oxidation of gold by thiosulfate ($S_2O_3^{2-}$) solutions has attracted renewed interest of researchers in the areas of hydrometallurgy, electrochemistry and solution chemistry (2-37). This is largely due to the following advantages of thiosulfate systems for leaching and recovery of gold compared to the conventional cyanidation process:

(i) fast leaching kinetics (12),

(ii) possibility of separating, concentrating and/or recovering dissolved gold using solvent extraction (7), anion exchange resins (13) or metal displacement (8),

(iii) applicability to gold ores that cannot be treated by the conventional cyanidation process due to high reagent costs and/or low gold recovery (19),

(iv) growing public concern on health, safety and environmental issues over the use of cyanide, especially after the recent accidents caused by failure of gold tailings dams (22).

However, there are issues which need to be addressed and impediments that must be overcome in order to develop a thiosulfate process to plant scale which in turn demands further investigations and a better understanding of the following aspects (21):

(i) the change in speciation during various stages of unit operations which would aid in minimizing the reagent consumption,

(ii) the effect of host minerals and their role in consumption of thiosulfate (29,33),

(iii) the beneficial or detrimental roles of metals such as copper, silver, lead and zinc in gold leaching and recovery (21,30),

(iv) the effect of particular minerals to adsorb or precipitate gold and/or copper or to affect solution parameters such as Eh and pH which in turn would affect the success of some unit operations (21,28),

(v) the effect of water quality on leaching and recovery of gold (21),

(vi) ways to remove or decompose some sulfur species which are detrimental to some unit operations used to separate and recover gold, such as the resin-in-pulp process (34),

(vii) alternative redox systems which would avoid the use of toxic ammonia and minimise thiosulfate degradation, but maintain the high leaching rates (19,35,36).

Recent research activities in this area have focused on understanding the leaching behaviour of different types of ores or concentrates, side reactions of thiosulfate and its degradation products, methods of separating, concentrating and recovering gold, chemical speciation, equilibria, rates and reaction mechanism(s) of gold oxidation (5-37). This article reviews some leaching results and the current status with respect to important stoichiometric relationships of chemical reactions, speciation, as well as detailed mechanisms for anodic or chemical oxidation of gold in thiosulfate solutions.

Selected leaching results

Unlike gold cyanidation, thiosulfate leaching involves relatively high concentrations of reagents, while the gold extraction is largely dependent on the presence or absence of various background reagents. The complexity of thiosulfate leaching of gold is exemplified in Figure 1 (14). It shows that sulfite, sulfide, sulfate glycine and ethylenediaminetetracetic acid (EDTA) have beneficial effects on gold extraction, compared to standard thiosulfate leaching with 0.03 M copper sulfate, 0.3 M sodium thiosulfate and 3 M ammonia (pH 10.2) in the absence of these additives. The oxidation of thiosulfate by copper(II) and/or oxygen during leaching produces tetrathionate ($S_4O_6^{2-}$), trithionate ($S_3O_6^{2-}$) and sulfate as by-products and increases thiosulfate consumption under some conditions. Reagents such as EDTA, sodium sulphide, and sodium sulfite lower the thiosulfate consumption (Fig. 1). While a moderate ammonia concentration up to 4 M is beneficial, a higher concentration of ammonia is detrimental for gold leaching (4).

As shown in Figure 2 the increase in pH from 9 to 10 is beneficial for gold extraction (12). However, the increase in pH also causes an increase in thiosulfate consumption as shown in Figure 3, especially at high thiosulfate dosages (2). Figure 4 shows the beneficial or detrimental effect of increasing temperature depending on the type of gold ore. The detrimental effect of high temperatures on gold extraction from an oxide ore (83 Au g/t + SiO_2, K, Na, Al, Mg, Si, AlOOH) has been related to the passivation caused by the reaction between copper(II) and thiosulfate, leading to the formation of copper(II) sulfide (4). The gold extraction from a sulfide concentrate reached a maximum at 60°C (3). However, the gold extraction from a low grade rhyolite ore which contained high grade silver (3 g/t Au, 113 g/t Ag) and MnO_2 was enhanced at a moderate temperature of 40°C (2). Mechanical activation has been used to improve the extraction of gold and silver from complex sulfide ores by using copper sulfate and ammonium thiosulfate at pH close to 6 and an elevated temperature of 70°C (31, 32).


Figure 2
Effect of pH on gold extraction from a mild-refractory copper-silver bearing sulphide concentrate (Data from Ref. 12)

Thiosulfate leaching is also sensitive to mineralogy because reactive sulfides consume oxygen and copper(II) while clays may adsorb (preg-rob) copper and gold from leach liquors (21). The presence of silver, lead and zinc can also affect gold extraction (21,30). Figure 5 compares and contrasts the effect of silver grade of the starting material on % gold and silver extraction during thiosulfate leaching and conventional cyanidation of oxide ores (21). In the case of gold ores of low silver grade (0.3 Ag g/t), thiosulfate leaching resulted low gold and silver extraction compared to cyanidation. However, in the case of gold ores with higher silver grades (2.8-15 Ag g/t), silver extraction with ammoniacal thiosulfate increased with increasing silver content. Although gold extraction also increased with increasing silver content, it remained 5-10% less than that by cyanidation (Fig. 5).

The concerns due to toxicity of ammonia and high thiosulfate consumption due to reactions with copper(II) have lead to investigations on non-ammoniacal thiosulfate processes. In the absence of added ammonia and copper(II) the thiosulfate leaching of gold has been carried out at high temperatures up to 80°C and at oxygen partial pressures up to 100 psig (19). For example, a carbonaceous ore of gold grade 9-10 Au g/t contained 81.8% of gold associated with

Figure 1
Effect of additives (0.1 M) on gold extraction and thiosulfate consumption during leaching of a mild-refractory copper bearing ore with 0.3 M $Na_2S_2O_3$, 0.03 M $CuSO_4$, 3M NH_3, pH 10.2, 24 hours (Original data from Ref. 14, reproduced from Ref. 48)
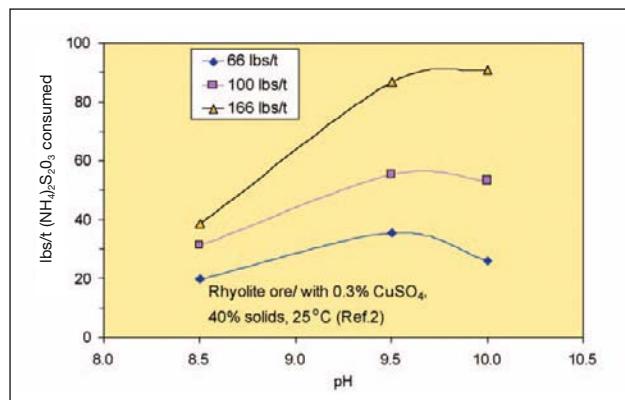

Figure 3
Effect of pH and thiosulfate dosage on thiosulfate consumption during gold leaching
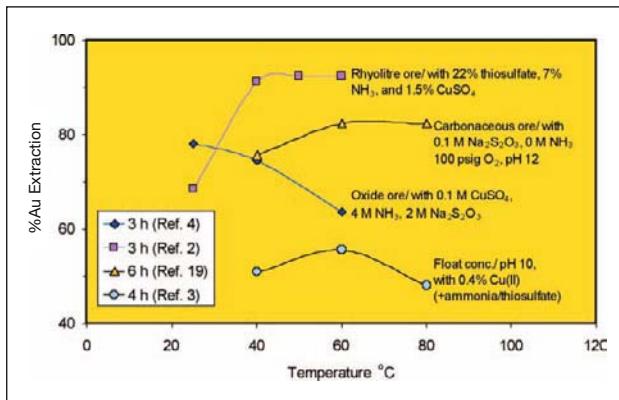
Figure 4
Effect of temperature on gold extraction from different material under different conditions

carbonaceous matter in the ore, 9.3% gold encapsulated in 0.36% sulphide, and 8.4% gold locked up in the gangue minerals. The diagnostic leaching indicated that only 0.5% gold was recoverable by direct cyanidation. However, the leaching of this material of particle size 75 μm (P_{80}) with 0.1 M sodium thiosulfate at 60°C, 100 psig O_2, 750 rpm, 33% pulp density at an initial slurry pH of 11-12 gave 82-83% gold extraction in 6 hours (19). The increase in temperature up to 60°C showed a beneficial effect (Fig. 4). Various additives decreased gold extraction and affected the amount of thiosulfate reacted and tetrathionate and trithionate formed during the 6h leaching period. Some of the results are shown in Figure 6. In addition to the decrease in gold extraction, Figure 6 also shows the amount of thiosulfate consumed, the amount of tetrathionate and trithionate formed and the quantity ΔS based on the sulfur balance:

$$\Delta S = 2[S_2O_3^{2-}]_{consumed} - 3[S_3O_6^{2-}]_{formed} - 4[S_4O_6^{2-}]_{formed}$$

The quantity ΔS represents the concentration of sulfur containing product(s) formed due to various background reactions. Sulfate is one of them which may precipitate as gypsum. It is clear that the gold extraction in non-ammoniacal oxygenated alkaline thiosulfate was decreased
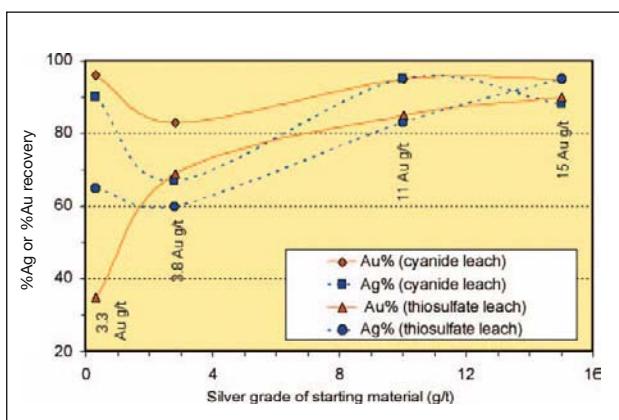
by various additives in the order FeS(s), Fe(II)<Fe(s)< Na_2CO_3. The carbonaceous ore used in these tests contained copper (50 g/t). The addition of 50 mg/L copper(II) as sulfate in a leaching test carried out at 10 psig O_2 and pH 11 caused no improvement in gold extraction. However, it increased thiosulfate consumption and produced more tetrathionate and trithionate and slightly enhanced the initial rate of gold extraction. A recent study has shown that the rate of gold leaching in non-ammoniacal thiosulfate solutions is enhanced by the presence of copper (26).

The increase in [trithionate]/[tetrathionate] caused a decrease in gold loading onto an anion exchange resin (19). Thus, a recent development includes the precipitation of gold metal from leach liquor by adding ammonium sulphide (34). Although a low gold recovery of 82-83% was achieved in non-ammoniacal thiosulfate at elevated temperatures and oxygen partial pressures (19), a recent study has shown the possible application of iron(III)-EDTA-thiosulfate-thiourea as a leaching agent for gold, to achieve a much higher gold extraction (> 90%) under ambient leaching conditions and neutral solutions (pH 6-7) (35). A fundamental study on the use of iron(III)-oxalate-thiosulfate-thiourea for gold leaching has also been reported (36).

Figures 1-6 clearly show the complex behaviour of thiosulfate leaching of gold from different ores under different conditions and highlights the importance of fundamental studies for a proper understanding of leaching processes, which in turn would be useful to minimise reagent consumption and maximise gold extraction.

Stoichiometry and equilibria

Table 1 lists the various stoichiometric relationships for the oxidation of gold by oxygen (R1-R7) or copper(II) (R8-R20) in solutions containing the three ligands ammonia, thiosulfate and hydroxide. The relevant stability constants (β) of gold(I) complexes defined by the following equations (charge


Figure 5
Effect of silver content in starting material on gold and silver extraction to compare leaching with cyanide and dilute ammoniacal thiosulfate (Original data from Ref. 21, reproduced from Ref. 48)
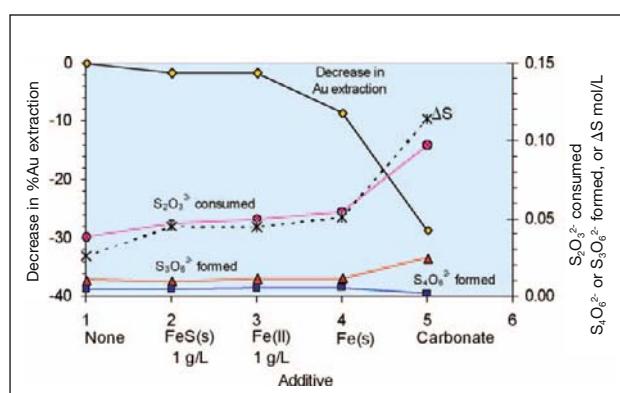
Figure 6
Effect of additives on non-ammoniacal gold extraction, thiosulfate consumption polythionates formation during leaching of a carbonaceous ore with 0.1 M $Na_2S_2O_3$, 100 psig O_2, at pH 11-12, and pulp density 33% over 6h(Ref. 19) (Gold extraction in the absence of additives was 82-83%, ΔS described in text)

ignored) and equilibrium constants for overall reactions (K) are also listed in Table 1:

$$Au^+ + 2X \leftrightarrows Au(X)_2$$
$$\beta = [Au(X)_2]/\{[Au^+][X]^2\}$$
$$Au^+ + X + Y \leftrightarrows Au(X)(Y)$$
$$\beta = [Au(X)(Y)]/\{[Au^+][X][Y]\}$$
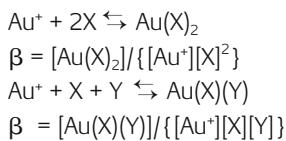
It is clear that the feasibility of gold dissolution is largely related to the stability of gold(I) and copper(I) complexes produced in each reaction. For example, gold dissolution is not feasible in the absence of ligands to stabilise Au^+ and Cu^+ ions as indicated by very low equilibrium constants of the order 10^{-22} or 10^{-26} in reactions R1 and R8. Thermodynamic studies based on half wave potential measurements, potentiometry, species distribution and Eh-pH diagrams in multi-ligand systems $S_2O_3^{2-}$-NH_3-OH^- have confirmed that $Au(S_2O_3)_2^{3-}$ is the most stable complex ion (23-25). Thus, in the presence of thiosulfate ligand, the equilibrium constant for oxidation of gold by oxygen or ammoniacal copper(II) is as large as 10^2 and 10^{-1}, respectively, as shown by reactions R7 and R13 in Table 1. However, the actual concentration of gold(I) in solution will depend on the thermodynamic activity of species involved in each reaction. Table 1 lists the equilibrium concentration of gold (mg/L) calculated from K values assuming unit activity of species and a unit activity ratio of Cu(II)/Cu(I). At such a high activity ratio of Cu(II)/Cu(I), the gold(I) concentration can vary from a low value of 2×10^{-21}

Table 1

Equilibrium data (β, K) for gold oxidation at 25°C

Reaction		log β			log K[c]	[Au(I)] (mg/L)[d]
		Au(I)[a]	Cu(I)[b]	Cu(II)[b]		
Oxidation by oxygen						
R1.	$Au + 0.25O_2 + 0.5H_2O = Au^+ + OH^-$				-22	
R2.	$Au + 0.25O_2 + 0.5H_2O = Au(OH)^0$	$10.2^e, 20.6^f$			-12,-1.4	
R3.	$Au + 0.25O_2 + OH^- + 0.5H_2O = Au(OH)_2^-$	22^f			0	
R4.	$Au + 0.25O_2 + 2NH_3 + 0.5H_2O = Au(NH_3)_2^+ + OH^-$	13			-9	
R5.	$Au + 0.25O_2 + NH_3 + 0.5H_2O = Au(NH_3)(OH)^0$	21^g			-1	
R6.	$Au + 0.25O_2 + S_2O_3^{2-} + NH_3 + 0.5H_2O = Au(NH_3)(S_2O_3)^- + OH^-$	20			-2	
R7.	$Au + 0.25O_2 + 2S_2O_3^{2-} + 0.5H_2O = Au(S_2O_3)_2^{3-} + OH^-$	24			2	
Oxidation by copper(II)						
R8.	$Au + Cu^{2+} = Au^+ + Cu^+$				-26	2×10^{-21}
R9.	$Au + Cu(NH_3)_4^{2+} = Au(NH_3)_2^+ + Cu(NH_3)_2^+$	13	10	13	-16	2×10^{-11}
R10.	$Au + S_2O_3^{2-} + Cu(NH_3)_4^{2+} = Au(S_2O_3)(NH_3)^- + Cu(NH_3)_2^+ + NH_3$	20	10	13	-9	2×10^{-4}
R11.	$Au + 2S_2O_3^{2-} + Cu(NH_3)_4^{2+} = Au(S_2O_3)_2^{3-} + Cu(NH_3)_2^+ + 2NH_3$	24	10	13	-5	2×10^0
R12.	$Au + 4S_2O_3^{2-} + Cu(NH_3)_4^{2+} = Au(S_2O_3)_2^{3-} + Cu(S_2O_3)_2^{3-} + 4NH_3$	24	12	13	-3	3×10^2
R13.	$Au + 5S_2O_3^{2-} + Cu(NH_3)_4^{2+} = Au(S_2O_3)_2^{3-} + Cu(S_2O_3)_3^{5-} + 4NH_3$	24	14	13	-1	8×10^3
R14.	$Au + 2S_2O_3^{2-} + Cu(OH)_2^0 = Au(S_2O_3)_2^{3-} + Cu(OH)_2^-$	24	12^h	13	-3	3×10^2
R15.	$Au + 2OH^- + Cu(OH)_2^0 = Au(OH)_2^- + Cu(OH)_2^-$	22	12	13	-5	2×10^0
R16.	$Au + 5S_2O_3^{2-} + Cu(OH)_2^0 = Au(S_2O_3)_2^{3-} + Cu(S_2O_3)_3^{5-} + 2OH^-$	24	14	13	-1	8×10^3
R17.	$Au + NH_3 + Cu(NH_3)_p(S_2O_3)^0 = Au(S_2O_3)(NH_3)^- + Cu(NH_3)_p^+$	20				
R18.	$Au + S_2O_3^{2-} + Cu(NH_3)_p(S_2O_3)^0 = Au(S_2O_3)_2^{3-} + Cu(NH_3)_p^+$	24				
R19.	$Au + Cu(S_2O_3)_2^{2-} + 2S_2O_3^{2-} = Au(S_2O_3)_2^{3-} + Cu(S_2O_3)_2^{3-}$	24	12	5^h	5	
R20.	$Au + Cu(S_2O_3)_2^{2-} + 3S_2O_3^{2-} = Au(S_2O_3)_2^{3-} + Cu(S_2O_3)_3^{5-}$	24	14	5^h	7	
Disproportionation of gold(I)						
R21.	$3Au(I)(NH_3)_2^+ = 2Au + Au(III)(NH_3)_4^{3+} + 2NH_3$				12^i	
	(Also see the reverse reactions of R2-R5).					

a. (23,24) if not stated otherwise;
b. (49,50)
c. Equilibrium constant for overall reaction
d. Calculated assuming unit activity of ligands and unit activity coefficients of Au(I) species
e. (51)
f. (52)
g. (46)
h. (39,42)
i. (47).

mg/L in the absence of ligands (R8) to 8×10^3 mg/L in the presence of ammonia and thiosulfate (R13). Equilibrium calculations have shown a decrease in gold(I) concentration with the decrease in [Cu(II)]/[Cu(I)] (9). Table 1 also shows that the equilibrium constant for gold oxidation by oxygen (R7) is 3-5 orders of magnitude larger than that by copper(II) in ammoniacal thiosulfate solutions (R12, R13).

Although the copper(II) ion is generally denoted by Cu^{2+}, $Cu(H_2O)_h^{2+}$ or $Cu(NH_3)_4^{2+}$, the species distribution diagrams show that it can exist as $Cu(X)_m^{-2(m-1)}$ and/or $Cu(NH_3)_p(X)_n^{-2(n-1)}$ depending on the medium and pH (38-40, 42-44), where:

   m = 1 or 2 for X = $S_2O_3^{2-}$,

   p = 2 or 3 and n = 1 or 2 for X = $S_2O_3^{2-}$, and

   p = 2 or 3, and n = 1 for X = SO_4^{2-}, $S_2O_5^{2-}$.

Likewise, the thiosulfate ion indicated by $S_2O_3^{2-}$ in Table 1 can exist in two other forms $NaS_2O_3^-$ and $NH_4S_2O_3^-$ in ammoniacal-sodium thiosulfate solutions (45,46). Thus, equilibrium calculations related to these systems should consider the following aspects:

   (i) activity coefficients of complex ions, ammonia, and ion-pairs,

   (ii) dependence of stability constants of complex ions and ion-pairs upon the type of medium and ionic strength,

   (iii) decomposition of copper(II)-thiosulfate complexes leading to thiosulfate degradation (37-40), and

   (iv) disproportionation/decomposition of unstable gold(I) complexes (41, 42, 47, 48) as shown by reaction R21 and the reverse reactions of R2-R6 in Table 1.

Moreover, these fundamental calculations need to be combined with the rates of gold oxidation in order to rationalise the relative effects of various oxidants/ligands.

Rates of gold oxidation

The following methods have been used in recent studies to determine the rates of gold oxidation in ammoniacal thiosulfate solutions:

   (i) anodic dissolution of freshly plated gold on quartz using a rotating electrode quartz crystal microbalance (REQCM), where the rate was monitored using the anodic current and/or the loss of mass of plated gold (5,10,16,17,18,20),

   (ii) anodic oxidation of a rotating gold disc, where the rate was measured by monitoring the concentration of gold in solution using atomic absorption spectrophotometry (15),

   (iii) chemical dissolution of colloidal gold, where the rate was measured by monitoring the concentration of residual colloidal gold using UV-Visible spectrophotometry (25), and

   (iv) chemical dissolution of gold powder, where the rates were measured by monitoring the concentration of dissolved gold in solution using atomic absorption spectrophotometry (17).

The first two methods allow the determination of rate per unit surface area but do not consider the effect of changes in surface roughness during reaction. The last two methods allow the rate measurements as a function of initial particle size and take into account the changes in surface area with time during the course of chemical oxidation. However, the analysis of rate of gold dissolution from a gold ore is more complex due to:

   (i) the range of shapes and sizes of ore/gold particles, where the gold particles may be completely liberated or embedded in the host minerals,

   (ii) the simultaneous reaction of oxidants with gold as well as ligands and host minerals,

   (iii) the change in chemical composition of solution with time due to side reactions, and

   (iv) the involvement of products from side reactions in gold oxidation.

Therefore, a systematic study would need to consider the kinetics of gold oxidation as well as the background reactions. Researchers have made attempts to address some of these issues on a qualitative and quantitative basis. The published rate data for gold oxidation in different lixiviant systems using different methods followed the ascending order given in Table 2. The rate of anodic oxidation of gold in alkaline sodium thiosulfate solutions increased with increase in concentration of sodium thiosulfate (15), and was affected by the nature of the cation in the order $Na_2S_2O_3 < K_2S_2O_3 << (NH_4)_2S_2O_3$ (16). In the case of colloidal gold, the highest % dissolution of 0.1 mM gold (97%) was achieved in the presence of copper(II) and both ammonia and thiosulfate as shown in Table 3 (25). Likewise, the results based on anodic oxidation (15) and REQCM (16,20) show that the rate of gold oxidation in thiosulfate solutions is faster in the presence of ammonia. Despite the low stability of gold(I) complexes with ammonia compared to the higher stability of complexes involving thiosulfate (Table 1), the results in Table 2 clearly show that the oxidation reaction is faster only in the presence of both ligands ammonia and thiosulfate. Thus, it is important to consider the chemical

Table 2

Relative rates of gold oxidation in different lixiviant systems (25-30°C)

Dissolution	Analysis	Relative rates in different systems	pH	Ref.
Electrochemical	dissolved Au(I)	$NH_3/(NH_4)_2SO_4 < Na_2S_2O_3 < Na_2S_2O_3/NH_3$	10.6	(15)
Electrochemical	anodic currents	$Na_2S_2O_3 < K_2S_2O_3 << (NH_4)_2S_2O_3$	< 7	(16)
Chemical	residual colloidal Au(0)	$Cu(II)/NH_3 < O_2/NH_3 < O_2/NH_3/S_2O_3^{2-} < Cu(II)/NH_3/S_2O_3^{2-}$	9.5	(25)

| Cu(II)(mM)	$[O_2]$/mM	$[NH_3+NH_4^+]$/mM	$[Na_2S_2O_3]$/mM	%Au (2 hours)
1.5	$0(N_2)$	240	0	5
0	0.25	0	50	10
0	0.25	240	50	9
0	0.5	240	50	22
1.5	$0(N_2)$	240	50	75
1.5	0.5	240	50	60
4.5	$0(N_2)$	240	50	97

speciation and reaction mechanism(s) which rationalise the role of thiosulfate, ammonia, and copper(II), as well as the nature of the cation.

Gold(I) speciation

Experiments which produced the results listed in Table 3 involved the oxidation of colloidal gold (0.1 mM) by dissolved oxygen (0.25 mM O_2) in the presence of ammonia and/or thiosulfate ligands in solutions maintained at pH 9.5 and 25°C. Some experiments were extended until the gold concentration reached an equilibrium value (25). Electrode potentials at equilibrium were measured using a gold wire and compared with the predicted values. The following forms of the Nernst equation were used to predict electrode potentials of the gold(I)/gold(0) couple representing the single-ligand or mixed-ligand complexes $Au(I)(X)_2$ or $Au(I)(X)(Y)$, where X and Y represent ammonia and thiosulfate, ignoring charge.

$$Au(I)X_2 + e \leftrightarrows Au(0) + 2X$$
$$E = E^o\{Au(I)(X)_2/Au(0)\} - 0.059 \log\{[X]^2/[Au(I)(X)_2]\}$$
$$Au(I)(X)(Y) + e \leftrightarrows Au(0) + X + Y$$
$$E = E^o\{Au(I)(X)(Y)/Au(0)\} - 0.059 \log\{[X][Y]/[Au(I)(X)(Y)]\}$$
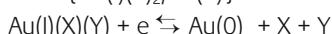
Figure 7 compares the measured and predicted potentials in solutions which contained sodium thiosulfate in the presence or absence of ammonia. The measured potentials agree well with the predicted values for $Au(I)(S_2O_3)_2{}^{3-}/Au(0)$, indicating that $Au(S_2O_3)_2{}^{3-}$ is the predominant complex even in the presence of ammonia. By contrast, Figure 8 shows poor agreement between the measured and predicted potentials in experiments carried out in ammonia solutions in the absence of thiosulfate. The predicted values closest to the measured values represent the $Au(OH)^0/Au(0)$ couple rather than $Au(NH_3)(OH)^0/Au(0)$ or $Au(NH_3)_2{}^+/Au(0)$, which involve NH_3 as a ligand.

Thus, gold(I) is unstable in alkaline ammoniacal solutions at 25°C in the absence of thiosulfate ions. It is also unstable in thiosulfate deficient alkaline solutions (42), leading to the disproportionation of gold(I). The reverse reactions of R2-R6 represent thermodynamically feasible disproportionation/ decomposition reactions of gold(I) in highly alkaline solutions that are deficient in appropriate ligand (especially $S_2O_3{}^{2-}$) concentration.

Role of ammonia and cations

The role of NH_3, Na^+ and K^+ is to stabilise the intermediate oxidation products of gold during anodic or chemical oxidation. Detailed analysis of literature data for anodic oxidation in non-copper solutions (45,46) led to the reaction mechanisms shown in Table 4 for non-ammoniacal thiosulfate (R22-R24) and ammoniacal-thiosulfate solutions
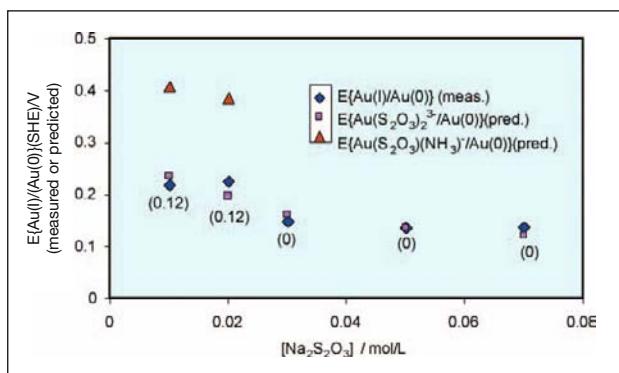

Figure 7
Comparison of measured and predicted electrode potentials of Au(I)/Au(0) couple at 25°C (15) in thiosulfate solutions in the absence or presence of ammonia (Ammonia concentration in each experiment is shown in brackets)
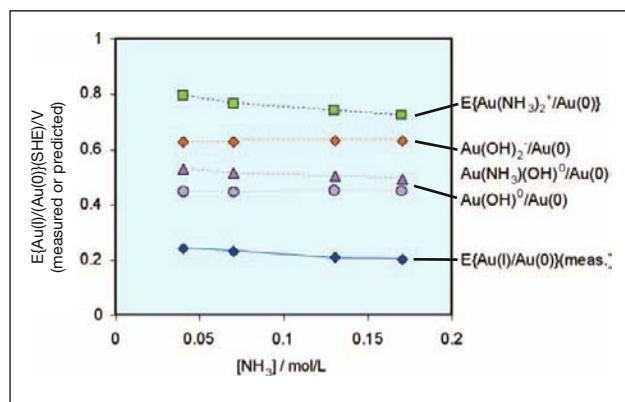
Figure 8
Comparison of measured (solid lines) and predicted (dashed lines) electrode potentials of Au(I)/Au(0) couple in ammonia solutions in the absence of thiosulfate at 25°C (15)

Table 4

Reaction mechanisms (40,45,46)

No.	Reaction
Anodic oxidation in thiosulfate media	
R22.	$Au + S_2O_3^{2-} = AuS_2O_3^{2-}(ads)$
R23.	$AuS_2O_3^{2-}(ads) = Au(S_2O_3)^-(ads/aq) + e$
R24.	$Au(S_2O_3)^-(ads/aq) + S_2O_3^{3-} = Au(S_2O_3)_2^{3-}$
Anodic oxidation in ammoniacal thiosulfate media	
R25.	$Au + S_2O_3^{2-} + NH_3 = Au(S_2O_3)(NH_3)^{2-}(ads)$
R26.	$Au(S_2O_3)(NH_3)^{2-}(ads) = Au(S_2O_3)(NH_3)^-(ads/aq) + e$
R27.	$Au(S_2O_3)(NH_3)^-(ads/aq) + S_2O_3^{2-} = Au(S_2O_3)_2^{3-} + NH_3$
Chemical oxidation by ammoniacal copper(II) thiosulfate	
R28.	$Au + S_2O_3^{2-} + Cu(NH_3)_p(S_2O_3)^0 = Au(S_2O_3)_2Cu(NH_3)_p^{2-}(ads/aq)$
R29.	$Au(S_2O_3)_2Cu(NH_3)_p^{2-}(ads/aq) = Au(S_2O_3)_2^{3-} + Cu(NH_3)_p^+$
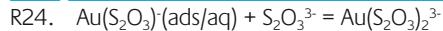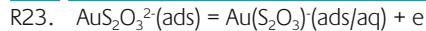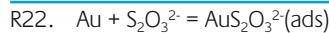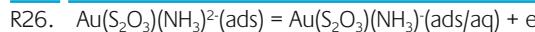
(R25-R27). Major steps in reaction mechanisms are described below:

(i) $S_2O_3^{2-}$ ion is adsorbed onto the gold surface to produce $Au(S_2O_3)^{2-}_{(ads)}$,

(ii) anodic oxidation of $Au(S_2O_3)^{2-}_{(ads)}$ produces $Au(S_2O_3)^-_{(ads/aq)}$,

(iii) $Au(S_2O_3)^-_{(ads/aq)}$ is re-equilibrated with thiosulfate ions to produce the most stable $Au(S_2O_3)_2^{3-}$ ion in solution,

(iv) interaction of alkali metal ion M^+ with thiosulfate ion leads to the formation of $Au(S_2O_3M)^0_{(ads/aq)}$ which stabilises the intermediate and hence increases the rate ($K^+ > Na^+$, Table 2),

(v) interaction of ammonia with Au(I) is much stronger and this leads to the formation of a more stable intermediate $Au(S_2O_3)(NH_3)^-_{(ads/aq)}$, which leads to a further increase in rate ($NH_4^+ >> K^+ > Na^+$, Table 2),

(vi) all intermediates are re-equilibrated to the most stable $Au(S_2O_3)_2^{3-}$ ion in solution.

The presence of ammonia prevents the precipitation of insoluble products (sulfur) on gold surface during anodic oxidation (15), indicating the formation of the mixed complex $Au(NH_3)(S_2O_3)^-_{(ads)}$ and thus preventing the oxidation/disproportionation of unstable $Au(S_2O_3)^-_{(ads)}$. Although the oxidation reaction takes place via intermediates such as $Au(S_2O_3)(NH_3)^-$, the measured equilibrium potentials of gold(I)/gold(0) couple in ammoniacal or non-ammoniacal thiosulfate solutions represent the dissolved species $Au(S_2O_3)_2^{3-}$ rather than the less stable $Au(S_2O_3)(NH_3)^-$ (Fig. 7). These facts support the catalytic role of ammonia during anodic oxidation described in Equations R25-R27 in Table 4.

Role of copper(II)

Recent speciation analysis data showed that copper(II) forms hydroxo complexes such as $Cu(OH)^+$, $Cu(OH)_2^0$, and $Cu(OH)_3^-$ in alkaline solutions in the absence of ammonia (42). As shown in Table 1 the equilibrium $Au(S_2O_3)_2^{3-}$ concentration in non-ammoniacal solutions (R16) is of the same order as that in ammoniacal solutions (R13). However, the low solubility of

Table 5

Background reactions of copper(II)/(I)-oxygen-thiosulfate system (2,4,27,28,40,43)

No.	Reaction
Oxidation of thiosulfate by copper(II) and copper(I) by oxygen	
R30.	$2Cu(II)(NH_3)_p(S_2O_3)^0 = 2Cu(I)(NH_3)_p^+ + S_4O_6^{2-}$
R31.	$Cu(II)(NH_3)_p(S_2O_3)^0 = Cu(I)(NH_3)_p^+ + S_2O_3^-$
R32.	$Cu(II)(NH_3)_p(S_2O_3)_2^{2-} = Cu(I)(NH_3)_p(S_2O_3)^- + S_2O_3^-$
R33.	$2S_2O_3^- = S_4O_6^{2-}$
R34.	$Cu(I)(NH_3)_p^+ + 0.25O_2 + 0.5H_2O + (m-p)NH_3 = Cu(II)(NH_3)_m^{2+} + OH^-$
R35.	$Cu^{2+} + S_2O_3^{2-} + H_2O = CuS$ or $(0.5Cu_2S + S) + SO_4^{2-} + 2H^+$
Copper catalysed oxidation of thiosulfate by oxygen	
R36.	$Cu(II)(NH_3)_p(S_2O_3)_2^{2-} + O_2 = Cu(II)(NH_3)_p(S_2O_3)^0 + S_2O_5^{2-}$
R37.	$Cu(II)(NH_3)_p(S_2O_3)_2^{2-} + O_2 = Cu(II)(NH_3)_p(S_2O_5)^0 + S_2O_3^{2-}$
R38.	$2S_2O_5^{2-} = S_3O_6^{2-} + SO_4^{2-}$
Oxidation of thiosulfate by oxygen	
R39.	$3S_2O_3^{2-} + 2O_2 + H_2O = 2S_3O_6^{2-} + 2OH^-$
R40.	$S_2O_3^{2-} + O_2 = 0.5S_3O_6^{2-} + 0.5SO_4^{2-}$
R41.	$S_2O_3^{2-} + 2O_2 + 2OH^- = 2SO_4^{2-} + H_2O$
R42.	$2S_2O_3^{2-} + 0.5O_2 + H_2O = S_4O_6^{2-} + 2OH^-$
Reactions of tetrathionate	
R43.	$4S_4O_6^{2-} + 6OH^- = 5S_2O_3^{2-} + 2S_3O_6^{2-} + 3H_2O$
R44.	$2S_4O_6^{2-} + HS^- + 4OH^- = 4.5S_2O_3^{2-} + 2.5H_2O$
R44.	$S_4O_6^{2-} + HS^- + OH^- = 2S_2O_3^{2-} + H_2O + S^0$
R45.	$4S_4O_6^{2-} + 2S^{2-} + 6OH^- = 9S_2O_3^{2-} + 3H_2O$
Reactions of trithionate	
R46.	$2S_3O_6^{2-} + 6OH^- = S_2O_3^{2-} + 4SO_3^{2-} + 3H_2O$
R47.	$S_3O_6^{2-} + S^{2-} = 2S_2O_3^{2-}$
R48.	$S_3O_6^{2-} + HS^- + OH^- = 2S_2O_3^{2-} + H_2O$
R49.	$S_3O_6^{2-} + H_2O = S_2O_3^{2-} + SO_4^{2-} + 2H^+ (pH\ 5.6\text{-}12,\ 50°C)$
R50.	$S_3O_6^{2-} + 2OH^- = S_2O_3^{2-} + SO_3^{2-} + H_2O$ (pH 13.4, 50°C)
R51.	$S_3O_6^{2-} + 2NH_3 = S_2O_3^{2-} + NH_2S_2O_3^- + NH_4^+$
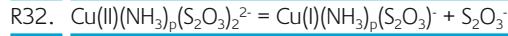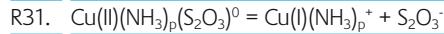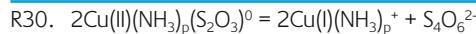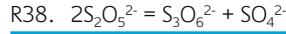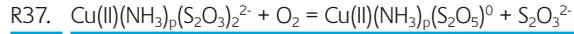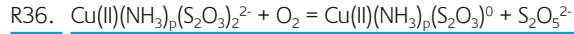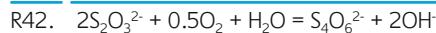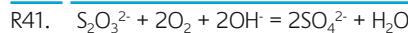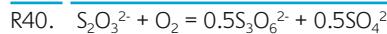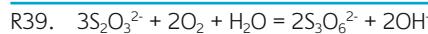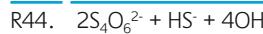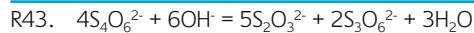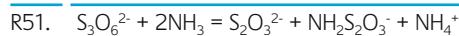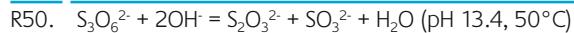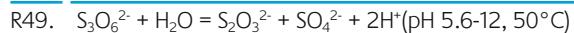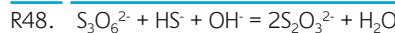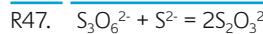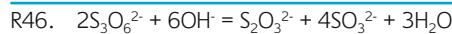
copper(II) in alkaline solutions in the absence of ammonia leads to low rates of gold oxidation. Since copper(II) rapidly oxidizes thiosulfate ions in the absence of ammonia (39,42), the role of ammonia is largely to stabilize copper(II) in alkaline solutions by forming the complex ion $Cu(NH_3)_4^{2+}$, which also leads to higher copper(II) concentrations.

Rate analysis has shown the involvement of $Cu(NH_3)_p(S_2O_3)_n^{-2(n-1)}$ in gold oxidation as well as thiosulfate oxidation (37,40,41). The relevant reactions are represented by R18 (Table 1) and R30-R32 (Table 5). Rate analysis has also supported the view that the reaction mechanism for gold oxidation by copper(II) involves the adsorption of both $S_2O_3^{2-}$ and $Cu(NH_3)_p(S_2O_3)^0$ onto gold surface. This produces the adsorbed complex $Au(S_2O_3)_2Cu(NH_3)_p^{2-}(ads)$, and is followed by the simultaneous anodic-cathodic reactions where gold(0) is oxidized to gold(I) while copper(II) is reduced to copper(I) (40,41,43,44). These two ions enter the solution as $Au(S_2O_3)_2^{3-}$ and $Cu(NH_3)_p^+$, as shown by equation R29 in Table

4. Copper(I) complexes, $Cu(NH_3)_p^+$ (p = 2, 3), produced in reactions R10-R11, R17-R18 in Table 1 and R29 in Table 4 are re-equilibrated to more stable $Cu(S_2O_3)_q^{-(2q-1)}$ complexes (q = 2,3) as shown by the higher equilibrium constants of R12-R13 compared to R11. The oxidation product of thiosulfate formed in Equations R30 and R33 reacts according to Equation R43 in Table 5.

Role of oxygen

Controlled aeration/oxygenation is beneficial for gold oxidation (1,11,17,25), showing the direct or indirect involvement of oxygen in surface reactions. Direct oxidation of gold by $O_2/NH_3/S_2O_3^{2-}$ is slower than that by $Cu(II)/NH_3/S_2O_3^{2-}$ (Table 2). Indirect involvement of oxygen is likely to be a result of:

(i) oxidation of $Cu(NH_3)_p^+$ to $Cu(NH_3)_m^{2+}$ by oxygen (R34 in Table 5) which would maintain a high concentration of Cu(II) and accelerate gold oxidation,

(ii) partial oxidation of $Cu(NH_3)_p(S_2O_3)_2^{2-}$ (R36 in Table 5) which would increase the concentration of $Cu(NH_3)_p(S_2O_3)^0$ and thus benefit gold oxidation (R18 in Table 1).

However, excess oxygen is detrimental to gold oxidation but beneficial for thiosulfate oxidation (11,17,18,25). This behaviour can be attributed to the decrease in concentration of $Cu(NH_3)_p(S_2O_3)^0$ (R37 in Table 5) leading to
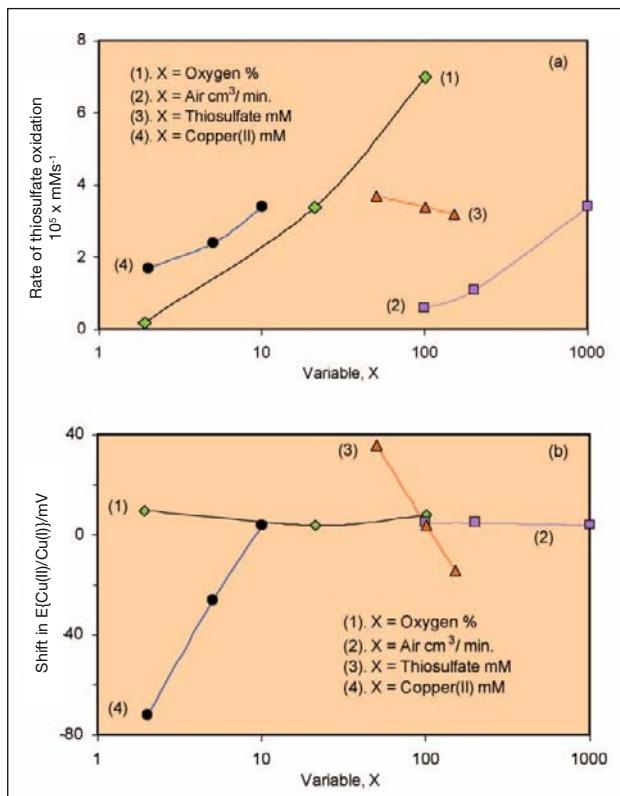
Figure 9

Effect of variables on (a) rate of thiosulfate oxidation, (b) Shift in copper(II)/copper(I) potentials : 10 mM copper(II) sulfate, 0.4 M ammonia, 0.1 M sodium thiosulfate, 30°C (Ref.18)

the production of $Cu(NH_3)_p(S_2O_5)^0$, which in turn enhances thiosulfate degradation (R38 in Table 5).

For example, Figure 9a shows the measured rate of thiosulfate oxidation by monitoring the decrease in thiosulfate concentration against time in experiments carried out with 0.1 M sodium thiosulfate, 10 mM copper(II) sulfate and 0.4 M ammonia at 30°C (18). An increase in copper(II) concentration enhances the rate of thiosulfate oxidation (line 4), but an increase in thiosulfate concentration has a negative effect on rate (line 3). The predicted changes in copper(II)/copper(I) reduction potential based on the measured residual copper(II) concentration using UV-Visible spectrophotometry and the Nernst equation (18):

$$E\{Cu(II)/Cu(I)\} = E^o\{Cu(II)/Cu(I)\} + (RT/F)\ln\{[Cu(II)/[Cu(I)]\}$$

are plotted in Figure 9b. They show trends similar to the relevant lines 3 and 4 in Figure 9a. A quantitative analysis of results in Figure 9a based on actual chemical speciation in solution would lead to a proper understanding of these results. Nevertheless, these observations support reactions R30-R32 (Table 5) which show that the reduction of copper(II) and oxidation of thiosulfate are interrelated.

Although the increase in oxygen percentage or air sparging rate enhances the rate of thiosulfate oxidation (lines 1 and 2, Figure 9a), the change in copper(II)/copper(I) potentials is negligibly small (lines 1 and 2 in Figure 9b). These observations support reactions R36-R38 in Table 5, which show that the main role of excess oxygen is to degrade thiosulfate, possibly via disulfite ($S_2O_5^{2-}$) ion (38). Moreover, an increase in thiosulfate concentration seems to slightly retard thiosulfate degradation (line 3 in Figure 9a) by reversing reaction R37, but the degradation would continue via reaction R32. Other reactions for the oxidation of thiosulfate by copper(II) and/or oxygen are shown by equations R39-R42 in Table 5, while the degradation of tetrathionate and trithionate is shown by equations R43-R51.

A recent study has revealed several important aspects of the stability of thiosulfate under typical leaching conditions (37):

(i) in the presence of dissolved oxygen, copper(I) thiosulfate complexes are oxidized at a slower rate than copper(I) diammine complex,

(ii) the reaction of copper(II) with thiosulfate is accelerated by dissolved oxygen, but retarded by ammonia,

(iii) the faster rate of reduction of copper(II) by thiosulfate compared to slow oxidation of copper(I) by oxygen allows the determination of rate of thiosulfate oxidation using pseudo-steady-state kinetics.

## Effect of reagent concentration and host minerals

The concentration of free ligands in a ammoniacal thiosulfate solutions depends on pH, ionic strength and temperature

Table 6

Possible reactions of gold(I) thiosulfate (28,34,43)

No.	Reaction
R52.	$2Au(S_2O_3)^- = Au_2S(s) + S_3O_6^{2-}$
R53.	$2Au(S_2O_3)^- = 2Au + S_4O_6^{2-}$
R54.	$Au(S_2O_3)_2^{3-} + 0.5SO_3^{2-} = Au + 1.5S_2O_3^{2-} + 0.5S_3O_6^{2-}$
R55.	$Au(S_2O_3)_2^{3-} + 0.5SO_3^{2-} + OH^- = Au + 2S_2O_3^{2-} + 0.5SO_4^{2-} + 0.5H_2O$
R56.	$2Au(S_2O_3)_2^{3-} + HS^- + OH^- = 2Au + 4S_2O_3^{2-} + H_2O + S^0$
R57.	$Au(S_2O_3)_2^{3-} + Fe(OH)_2 + OH^- = Au + 2S_2O_3^{2-} + Fe(OH)_3$
R58.	$Au(S_2O_3)_2^{3-} + X + OH^- = Au + 2S_2O_3^{2-} + Fe(OH)_3$
	X = intermediate dissolved iron(II) species such as Fe^{2+} and $Fe(OH)^+$ or defected sulfide surface (28)

Table 7

*Possible reactions of host minerals with copper(II) and oxygen (29)*

No.	Reaction
R59.	$2FeS_2 + 6.5O_2 + 4Cu(NH_3)_4^{2+} + (6+n)H_2O + 4NH_3$ $= Fe_2O_3.nH_2O + 4(NH_4)_2SO_4 + 4Cu(NH_3)_2^+ + 4NH_4^+$
R60.	$2CuFeS_2 + 6.5O_2 + 6Cu(NH_3)_4^{2+} + (6+n)H_2O + 4NH_3$ $= Fe_2O_3.nH_2O + 4(NH_4)_2SO_4 + 8Cu(NH_3)_2^+ + 4NH_4^+$
R61.	$ZnS + 2Cu(NH_3)_4^{2+} + 1.5O_2 + 2NH_3 + H_2O$ $= Zn(NH_3)_4SO_4 + 2Cu(NH_3)_2^+ + 2NH_4^+$
R62.	$2FeS + 4O_2 + 2Cu(NH_3)_4^{2+} + (3+n)H_2O + 2NH_3$ $= Fe_2O_3.nH_2O + 2(NH_4)_2SO_4 + 2Cu(NH_3)_2^+ + 2NH_4^+$

which affect the relevant equilibrium constants as shown by the equations described below:
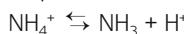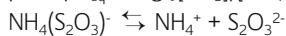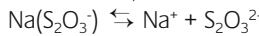
$$NH_4^+ \leftrightarrows NH_3 + H^+$$
$$pH = pK_{eq} + \log\{[NH_3]/[NH_4^+]\}$$
$$NH_4(S_2O_3)^- \leftrightarrows NH_4^+ + S_2O_3^{2-}$$
$$pS_2O_3 = pK_{eq} + \log\{[NH_4^+]/[NH_4(S_2O_3^-)]\}$$
$$Na(S_2O_3^-) \leftrightarrows Na^+ + S_2O_3^{2-}$$
$$pS_2O_3 = pK_{eq} + \log\{[Na^+]/[Na(S_2O_3^-)]\}$$
$$Cu(NH_3)_q(S_2O_3)^0 \leftrightarrows Cu(NH_3)_q^{2+} + S_2O_3^{2-}$$
$$pCu(NH_3)_q = pK_{eq} + \log\{[S_2O_3^{2-}]/[Cu(NH_3)_q(S_2O_3)^0]\}$$
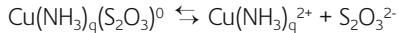
where $pK_{eq} = -\log K_{eq}$ and K_{eq} = equilibrium constant in each case, pS_2O_3 and $pCu(NH_3)_q$ represents the $-\log[S_2O_3^{2-}]$ or $-\log[Cu(NH_3)_q^{2+}]$. It is clear that pH and the total concentration of ammonia, thiosulfate or copper(II) will control the concentration of free ligands and other species such as the gold oxidant $Cu(NH_3)_q(S_2O_3)^0$ noted in the equations described above.

Like thiosulfate, the sulfate ions also form ion-pairs while hydroxide ions form mixed copper(II)-ammonia-hydroxide complexes (49,50). Thus, it is important to consider the effect of pH and the concentration of various reagents on species distribution and reaction mechanisms via intermediates in order to rationalise the kinetics of thiosulfate degradation and gold leaching (37,40,41,44). For example, anions such as chloride and sulfate decreases the concentration of copper(II)-ammonia-thiosulfate intermediate(s) due to the competition of these anions to form ion-pairs with ammoniacal copper(II) by replacing thisoulfate and thus retard the thiosulfate degradation (37). This would also affect the rate of gold oxidation according to equation R28 in Table 4.

Dissolved gold can re-precipitate in ageing leach liquors due to the deficiency of thiosulfate or due to the presence of other reagents such as sulfite or sulphide, according to the reactions shown in Table 6. Although thermodynamics predict the formation of Au_2S, the recent X-ray diffraction analysis has provided evidence for the precipitation of elemental gold (34). Thus, while reaction R56 is useful for the recovery of gold (34) reactions such as R57 and R58 may explain the decrease in gold extraction in non-ammoniacal thiosulfate leaching in the presence of FeS and Fe(II) shown in Figure 6. Silver (53) and chloride (20) catalyse the dissolution of gold in thiosulfate solutions. Host minerals can react with copper(II) and oxygen and also affect thiosulfate and gold oxidation (11,29,30,33,) (Table 7). A recent review (54) has described the successful heap leaching processes using thiosulfate and the effect of sulfide minerals on gold extraction. It is important to consider the possible extension of kinetic models for gold leaching (40,41) to consider the effect of host minerals.

Summary

- Fundamental studies based on equilibria, rates and chemical speciation are vital for the understanding of the role of ligands, oxidants, stoichiometry and reaction mechanism of gold oxidation in thiosulfate solutions.
- Although $Au(S_2O_3)_2^{3-}$ is the most stable complex, anodic oxidation takes place via unstable intermediates such as $Au(S_2O_3)^-$ and $Au(NH_3)(S_2O_3)^-$.
- Chemical oxidation of gold by copper(II) takes place via the adsorbed species $Au-S_2O_3^{2-}-Cu(NH_3)_p(S_2O_3)^0$.
- Controlled aeration/oxygenation enhances the concentration of $Cu(NH_3)_p(S_2O_3)^0$ and thus benefits gold oxidation.

About the author

Dr. Gamini Senanayake received his PhD from Murdoch University. He is a senior lecturer in the Department of Mineral Science and Extractive Metallurgy. Gamini received the Extraction & Processing Science Award by the Minerals, Metals & Materials Society in 2006.

References

1   R.M.G.S. Berezowsky, V.B Sefton, AIME, New Orleans, LA, 1979, 102

2   D. Zipperian, S. Raghavan, J.P. Wilson, *Hydrometallurgy* 1988, **19**, 361

3   T. Jiang, J. Chen, S. Xu, *Hydrometallurgy, Fundamentals, Technology and Innovations* (ed. J.B. Hiskey, G.W. Warren), AIME, 1993, 119

4   C. Abbruzzese, P. Fornari, R. Massidda, F. Veglio, S. Ubaldini, *Hydrometallurgy* 1995, **39**, 265

5 P.L. Breuer, M.I. Jeffrey, *Miner. Engng*., 2000, **13**, 1071

6 M.G. Aylmore, D.M. Muir, *Miner. Engng*., 2001, **14**, 135

7 L. Kejun, W.T. Yen, A. Shibayama, T. Miyazaki, T. Fujita, *Hydrometallurgy* 2002, **73**, 41

8 J.B.Hiskey, J.Lee, *Hydrometallurgy* 2003, **69**, 45

9 I.M. Ritchie, M.J. Nicol, W.P. Stauton, In: *Cyanide Social, Industrial and Economic Aspects* (Ed. C.A. Young, L.G. Tidwell, C.G. Anderson), TMS, Warrendale, 2001, 427

10 M.I. Jeffrey, *Hydrometallurgy*, 2001, **60**, 7

11 E. Molleman, D.B. Dreisinger, *Hydrometallurgy*, 2002, **66**, 1

12 P. Navarro, C. Vargas, A. Villarroel, F.J. Alguacil, *Hydrometallurgy*, 2002, **65**, 37

13 M.J. Nicol, G.P. O'Malley, *J. Metals* 2002, **54**, 44

14 C. Xia, W.T. Yen, G. Deschenes, *Minerals and Metallurgical Processing* 2003, **20**, 68

15 S. Zhang, M.J. Nicol, *J Appl. Electrochem*., 2003, **33**, 767

16 I. Chandra, M. Jeffrey, *Hydrometallurgy* 2003, TMS, Warrendale, 169

17 M.I. Jeffrey, P.L. Breuer, C.K. Chu, *Int. J. Miner. Process*., 2003, **72**, 323

18 P.L. Breuer, M.I Jeffrey, *Hydrometallurgy* 2003, TMS, Warrendale, 139

19 J. Ji, C. Fleming, P.G. West-Sells, R.P. Hackl, *Hydrometallurgy 2003*, TMS, Warrendale, 2003, 227

20 I. Chandra, M.I. Jeffrey, *Hydrometallurgy*, 2004, **73**, 305

21 D.M. Muir, M.G. Aylmore, *Mineral Processing and Extractive Metallurgy (Trans. Inst. Min. Metall. C)* 2004, **113**, C2

22 C.A. Young, L.G. Tidwell, C.G. Anderson, *Cyanide: Social, Industrial and Economic Aspects*, TMS, Warrendale, 2001

23 G. Senanayake, W.N. Perera, M.J. Nicol, *Hydrometallurgy* 2003, TMS, Warrendale, 155

24 W.N. Perera, G. Senanayake, *Inorg. Chem*. 2004, **43**, 3048

25 X.M. Zhang, G. Senanayake, M.J. Nicol, *Hydrometallurgy*, 2004, **74**, 243

26 S. Zhang, M.J. Nicol, *J. Applied Electrochem*. 2005, *35*, 339-345

27 N. Ahern, D.B. Dreisinger, G. Van Weert, *Treatment of Gold Ores*, (Ed. G. Deschenes, D. Hodouin, L. Lorenzen), 2005, CIM, 295

28 C. Xia, W.T. Yen, *Treatment of Gold Ores*, (Ed. G. Deschenes, D. Hodouin, L. Lorenzen), 2005, CIM, 259

29 D. Feng, J.S.J. van Deventer, *Hydrometallurgy*, 2002, **63**, 189-200

30 D. Feng, J.S.J. van Deventer, *Hydrometallurgy*, 2002, **64**, 231-246

31 J. Ficeriova, P. Balaz, E. Boldizarova, S. Jelen, *Hydrometallurgy*, 2002, **67**, 37-43

32 J. Ficeriova, P. Balaz, C.L. Villachica, *Hydrometallurgy 2005*, **77**, 35

33 D. Feng, J.S.J. van Deventer, *Treatment of Gold Ores*, (Ed. G. Deschenes, D. Hodouin, L. Lorenzen), 2005, CIM, 129

34 P.G. West-Sells, R.P. Hackl, *Treatment of Gold Ores*, (Ed. G. Deschenes, D. Hodouin, L. Lorenzen), 2005, CIM, 209

35 H. Zhang, M.J. Nicol, W.P. Staunton, *Treatment of Gold Ores*, (Ed. G. Deschenes, D. Hodouin, L. Lorenzen), 2005, CIM, 243

36 I. Chandra, M.I. Jeffrey, *Hydrometallurgy* 2005, **77**, 191

37 C. van Wensveen, M.J. Nicol, *Treatment of Gold Ores*, (Ed. G. Deschenes, D. Hodouin, L. Lorenzen), 2005, CIM, 193

38 J.J. Byerley, S.A. Fauda, G.L. Rempel, *J Chem. Soc. Dalton Trans*., (a).1973, 889, (b). 1975, 1329

39 G. Rabai, I.R. Epstein, *Inorg. Chem*. 1992, **31**, 3239

40 G. Senanayake, *Hydrometallurgy*, 2004, **75**, 55

41 G. Senanayake, *Miner. Engng*. 2004, **17**, 785

42 G. Senanayake, *Miner. Engng*. 2005, **18**, 409

43 G. Senanayake, *Miner. Engng*. 2005, **18**, 995

44 G. Senanayake, *Colloid Interface Sci*., 2005, **286**, 253

45 G. Senanayake, *Hydrometallurgy*, 2005, **76**, 233

46 G. Senanayake, *Hydrometallurgy*, 2005, **77**, 287

47 L.H. Skibsted, J. Bjerrum, *Acta Chem. Scand*., 1974, A(28), 740

48 G. Senanayake, Green Processing 2004, AusIMM. Melbourne, 113

49 L.G. Sillen, E. Martell, Stability constants of metal-ion complexes, special publication Nos. 17 and 26. Chemical Society, London, 1964.

50 E. Hogfeldt, Stability constants of metal-ion complexes, 2nd supplement, IUPAC Chemical Data Series No. 2: Part A. Inorganic Ligands. Pergamon, Oxford, 1982

51 R. Kissner, G. Welti, G. Geier, The hydrolysis of gold(I) in aqueous acetonitrile solutions. *J. Chem. Soc., Dalton. Trans*. 1997, 1773

52 A. Stefansson, T.M. Seward, The hydrolysis of gold(I) in aqueous solutions to 600°C and 1500 bar. *Geochim. et Cosmochim. Acta,* 2003, **67**, 1677

53 J.G. Webster, *Geochimica et Cosmochemica Acta* 1986, **50**, 1837

54 R.Y. Wan, K.M. LeVoer, *Int. J. Miner. Process*. 2003, **72**, 311