

Thiosulphate as an Alternative to Cyanide for Gold Processing — Issues and Impediments

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ABSTRACT

Thiosulphate is an attractive alternative reagent to cyanide for processing gold ores. It is relatively cheap and non-toxic, forms relatively strong gold and silver complexes, and readily leaches gold ores in ammoniacal solutions, catalysed by Cu(II). It is particularly suited to carbonaceous ores where the recovery of gold by cyanide is poor. However research over the past 20 years has identified a number of issues and impediments that must be understood or overcome before an overall process can be demonstrated as practical and economic for typical oxidised gold ores.

This paper reviews our current understanding of thiosulphate chemistry and mechanism of gold dissolution, and discusses the stability of thiosulphate and polythionates. It then reviews the results of leaching various gold ores that have been reported in the literature, discusses gold recovery options, and considers environmental and toxicity issues. Some of the issues that require further research include decreasing the oxidation of thiosulphate by Cu(II) or other oxidants, increasing the extraction of gold compared to cyanide, and understanding the variation in gold recovery between ores. More work is also required to minimise the effect of polythionates on gold recovery using resins or alternative absorbents, to improve the elution of copper and gold from resins, and to recycle or minimise the concentration of reagents.

INTRODUCTION

The gold industry has been seeking alternative reagents for leaching gold from low-grade ores for the past 25 years. The cost and transport of cyanide, the poor recovery of gold from carbonaceous ores, the lack of selectivity of cyanide towards copper minerals and the cost of waste treatment are real factors which can make cyanide unattractive in some circumstances. However there are also perceived and real environmental concerns and pressures when dealing with cyanide solutions and waste streams in sensitive areas, which has an impact on the sustainability of the whole gold industry.

Compared to other industries like copper or oil, the gold industry has quite a good record. Few people realise that the gold mining industry only accounts for 13 per cent of total world cyanide consumption, and despite the widespread use and handling of cyanide in gold processing, the North American industry has recorded only three deaths attributed to cyanide over a period of 100 years (McNulty, 2001). What is remembered, are the 14 major incidents that have been recorded throughout the world over the past 25 years – ten involving tailings dams, two involving pipeline failures and two involving transportation accidents.

For this reason, the gold industry has been seriously looking for safer and cleaner reagents that not only meet chemical criteria but also toxicological and environmental criteria. Sparrow and Woodcock (1995) lists over 25 potential reagent types including polysulphides and various organics, but only a few attract serious attention. Alternative reagents that have been seriously considered for gold include chlorine, bromine, iodine, thiocyanate, thiourea, ammoniacal thiosulphate and ammoniacal copper cyanide. By necessity, all form strong complexes with gold enabling gold to be leached in a practical Eh range (Table 1). Thiosulphate provides the strongest alternative complex although this does not compare closely to cyanide.

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TABLE 1

Stability constants for gold complexes.

Gold species	Log K*	Standard potential (V)	Reference
Au(CN) ₂ ⁻	38.3	-0.67	Smith and Martell
Au(SCN) ₂ ⁻	16.98	0.66	Smith and Martell
Au(SCN) ₄ ⁻	10	0.64	Smith and Martell
AuCl ₄ ⁻	25.6	1.00	Wang
AuBr ₄ ⁻	32	0.85	Marsden and House
AuI ₄ ⁻	47.6	0.56	Marsden and House
Au(NH ₃) ₂ ⁺	26	0.16	Wang
Au(CS(NH ₂) ₂) ₂ ⁺	23.3	0.38	Marsden and House
Au(S ₂ O ₃) ₂ ³⁻	26.5	0.15	IUPAC

* Temperature 25°C, Ionic strength = 1.0

Initially in the 1970s, much research and development was carried out in the USA on halogen systems together with more limited work using thiourea and thiosulphate systems. However the halogens proved to be too reactive with other ore minerals and too expensive to operate. In the 1980s attention focussed more on acidic Fe(III)/thiourea leaching and significant R&D programs were carried out at CSIRO and at Murdoch University to investigate both the leaching and recovery of gold, and the degradation of thiourea. By 1991, thiourea was listed as a potential carcinogen and was considered too hazardous, so interest waned. Subsequent interest in thiocyanate was brief because of its instability in acidic Fe(III) solutions.

More recently, world industry attention has focussed on ammoniacal thiosulphate as a relatively cheap and non-toxic reagent. Research and development over the past 20 years has focussed on carbonaceous ores and copper-gold ores where gold recovery is poor or cyanide consumption is high. Newmont and Barrick have carried out extensive investigations to semi-commercial scale, using thiosulphate as an alternative lixiviant to cyanide. This was not driven by any particular environmental or health and safety concerns about using cyanide, but because cyanide was unable to effectively extract gold from a proportion of their ore resources.

However, increasing regulatory scrutiny of new gold projects and a lowering of what is considered acceptable levels of cyanide discharges are of considerable concern to the industry. It is anticipated that approval for any new gold project using cyanide would be extremely difficult in some parts of the world. In this case the political and environmental cost of using cyanide becomes too much and the establishment of an economic and environmentally viable option for extracting gold without the use of cyanide would seem essential.

Unfortunately no overall process has been piloted or costed using thiosulphate with typical oxidised gold ores. Hence in Australia, it was agreed by AMIRA sponsors to Project P420 'Gold Processing Technology' that a module on non-cyanide alternatives for gold should aim to develop an overall process for the leaching and recovery of gold from typical ores using

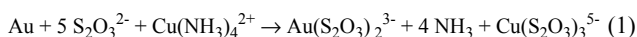
thiosulphate. To this end, researchers at Murdoch University and CSIRO Minerals working in the A J Parker CRC, have been studying the fundamental kinetics and mechanism of leaching; and the leaching of various simple and complex gold ores. They have also studied the *in situ* generation of thiosulphate from sulphide minerals and the adsorption/ stripping of gold thiosulphate with various ion-exchange resins.

This paper considers some of the issues that have been identified in various studies with thiosulphate that have been reported in the literature, and some of the impediments that must be overcome before a viable and economic process is ready to replace cyanide. Only brief mention is made of some of the sponsored work carried out by ourselves, and others in the Parker CRC, over the past three years which is yet to be publicly released.

THIOSULPHATE CHEMISTRY

Mechanism of gold leaching

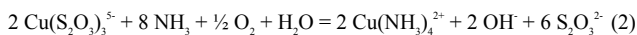
The oxidation of metallic gold to the aurous Au^+ ion in ammoniacal thiosulphate in the presence of Cu(II) , can be simply represented as follows, although a more complex mechanism no doubt exists and needs further investigation:



Oxidation of gold in equilibrium with 10^{-3} M Au(I) occurs at a potential of about 0 V.

Copper(II) is a catalyst to this reaction at concentrations around 10^{-3} – 10^{-4} M (60–6 ppm) and is believed to be the oxidant - with oxygen acting to re-oxidise Cu(I) to Cu(II) .

The redox equilibrium between the cuprous-cupric couple in ammoniacal solution and thiosulphate is represented by the following reaction (Abbruzzese *et al*, 1995; Wan, 1997)



In dilute (0.10 M) ammoniacal thiosulphate solutions, Cu(II) is rapidly reduced by thiosulphate to Cu(I) and an equilibrium ratio of $\text{Cu(II)}:\text{Cu(I)}$ is established which depends upon the relative concentrations of ammonia and thiosulphate and dissolved oxygen. The calculated standard potential of this couple, lies between 0.14 - 0.36 V depending upon the reagent composition and predominant species present (Table 2). However in the absence of Cu(II) , thiosulphate is reduced to sulphide ion resulting in the precipitation of Cu_2S .

TABLE 2

Standard potential for copper(II) ammonia/copper(I) thiosulphate and thiosulphate/tetrathionate couples.

Couple	Standard potential (V)
$\text{Cu}(\text{NH}_3)_4^{2+} / \text{Cu}(\text{S}_2\text{O}_3)_3^{5-}$	0.22
$\text{Cu}(\text{NH}_3)_4^{2+} / \text{Cu}(\text{S}_2\text{O}_3)_2^{3-}$	0.14
$\text{Cu}(\text{NH}_3)_3^{2+} / \text{Cu}(\text{S}_2\text{O}_3)_3^{5-}$	0.36
$\text{Cu}(\text{NH}_3)_3^{2+} / \text{Cu}(\text{S}_2\text{O}_3)_2^{3-}$	0.27
$\text{S}_2\text{O}_3^{2-} / \text{S}_4\text{O}_6^{2-}$	0.12

Figure 1 shows the overall speciation and Eh-pH diagram for copper and gold in ammoniacal thiosulphate whilst Figure 2a - c show the effect of pH, Eh and ammonia concentration on copper speciation in dilute (0.10 M) thiosulphate solutions (Aylmore and Muir, 2001b). It is clear from Figure 2 that the optimum Eh/pH window for stabilising Cu(II) and leaching gold becomes very

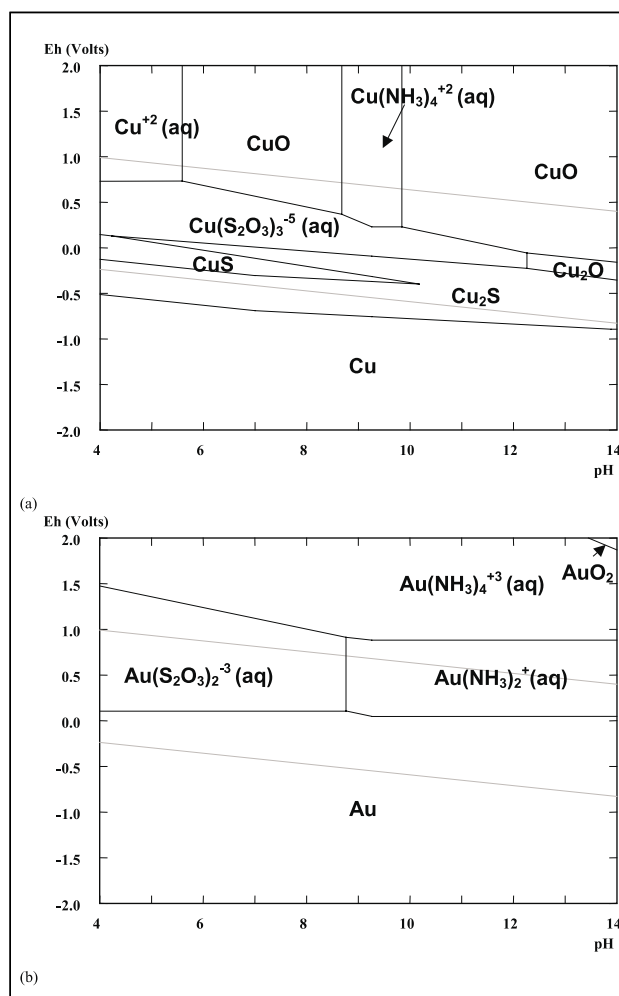


FIG 1 - Eh-pH diagram at low reagent concentrations for: (a) $\text{Cu-NH}_3\text{-S}_2\text{O}_3^{2-}$ system, and (b) $\text{Au-NH}_3\text{-S}_2\text{O}_3^{2-}$ system (conditions: 5×10^{-4} M Au ; 0.1 M $\text{S}_2\text{O}_3^{2-}$; 0.1 M $\text{NH}_3/\text{NH}_4^+$; 5×10^{-4} M Cu^{2+}).

small with dilute reagents. In 0.10 M $\text{NH}_3/\text{S}_2\text{O}_3^{2-}$ solutions containing 5×10^{-4} M Cu(II) the optimum pH is around 9 - 10 and the optimum Eh is around 300 mV(nHe). At higher pH and Eh, some copper precipitates from solution as tenorite (CuO), but this re-dissolves with increasing ammonia. Changing the ammonia concentration significantly affects the speciation and ratio of $\text{Cu(II)}:\text{Cu(I)}$ species in equilibrium. Thus much closer control of leaching conditions must be maintained compared to cyanide.

Kinetics of gold leaching

A recent series of papers by Jeffrey, Breuer and Choo (2001a, b), Breuer, Jeffrey and Choo (2001), Breuer and Jeffrey (2000) and Jeffrey (2001) discuss the fundamental kinetic and electrochemical aspects of gold and silver leaching with ammoniacal thiosulphate and compares alternative lixivants such as cyanide and chloride/hypochlorite. In general, the rate of leaching with 0.1 M thiosulphate containing 10 mM Cu(II) and 0.4 M NH_3 was similar to the rate with air saturated 5 mM cyanide (250 ppm NaCN), and significantly slower than 5 mM hypochlorite solution. The rate was dependent upon Cu(II) , thiosulphate and ammonia and was faster with higher reagent concentrations. Unfortunately reagent degradation was also much faster, and it was also found that the leach rate decreased upon ageing of reagents due to passivation of the gold surface by some unidentified reaction products (Breuer and Jeffrey, 2000).

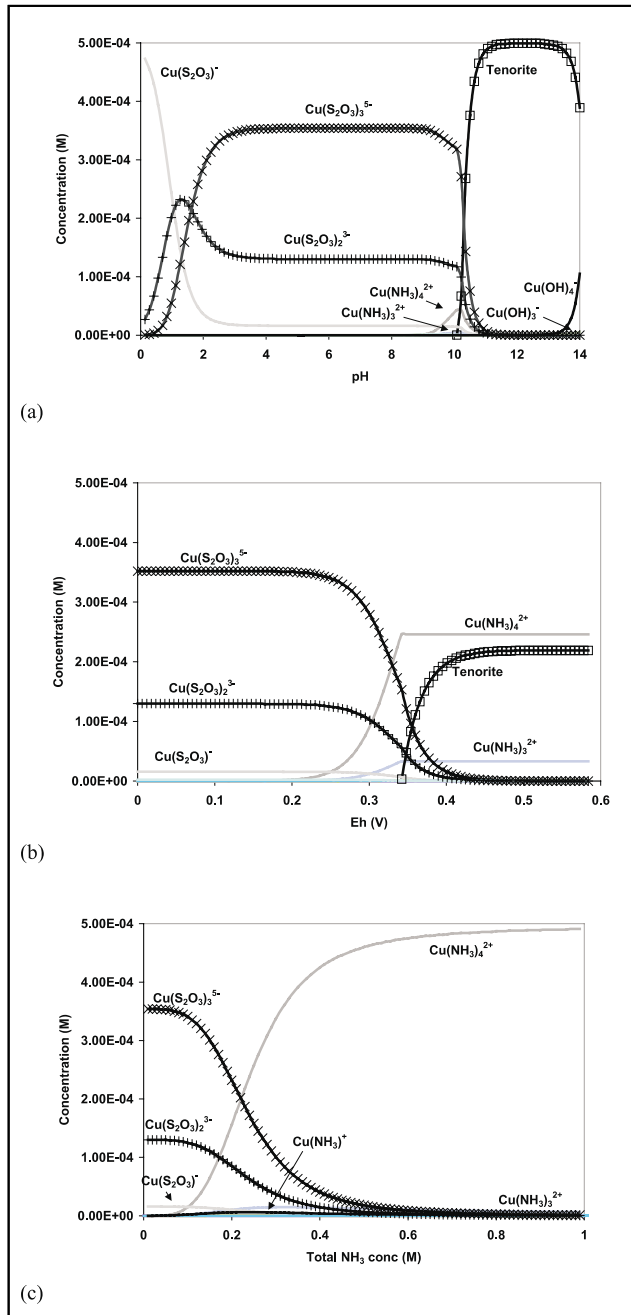


FIG 2 - Speciation diagrams for 5×10^{-4} M Cu, 0.10 M $\text{NH}_3/\text{S}_2\text{O}_3^{2-}$ for: (a) varying pH, (b) varying Eh and (c) varying NH_3 .

When the rate of gold dissolution in dilute reagent compositions was studied with a rotating disc electrode, Aylmore and Rae (2001) found that the rate increased with the addition of up to 1 mM Cu(II) (Figure 3). They also found that the rate was quite slow using equimolar 0.1 M ammonia and thiosulphate but increased significantly with addition of ammonia (Figure 4). However the addition of up to 0.01 M trithionate and tetrathionate had little effect on the rate.

Clearly the kinetics and mechanism of gold leaching is complex and under chemical control.

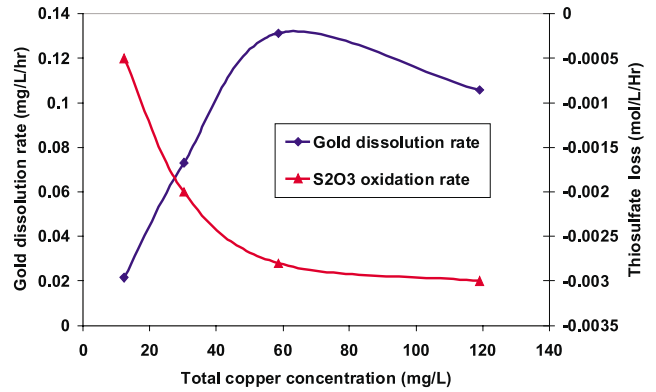


FIG 3 - Effect of copper concentration on rate of gold dissolution and thiosulphate decomposition (0.2 M $\text{NH}_3/\text{NH}_4^+$, 0.05 M $\text{S}_2\text{O}_3^{2-}$, pH 9.5, dissolved oxygen concentration at 5 mg/L).

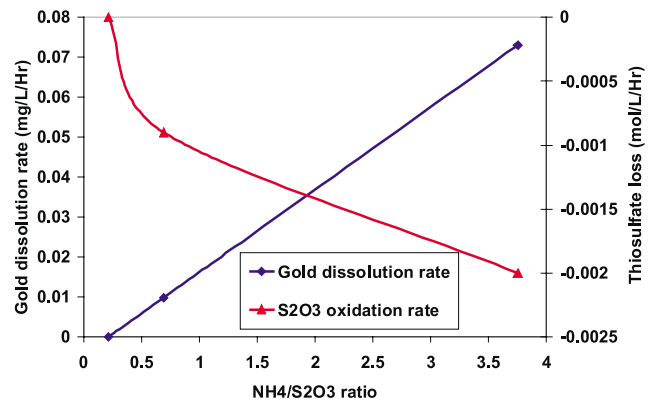


FIG 4 - Effect of ammonium/thiosulphate ratio on rate of gold dissolution and thiosulphate loss (32 mg/L Cu^{2+} , pH 9.5, dissolved oxygen set at 5 mg/L). NH_4 refers to the combined total NH_3 and NH_4^+ in solution.

Nevertheless there appears to be no evidence of complete passivation of the gold surface and no fundamental reason why the same overall gold recovery cannot be achieved with thiosulphate as with cyanide, provided the gold is liberated.

Stability of thiosulphate

Thiosulphate is a metastable anion that tends to readily undergo chemical decomposition in aqueous solutions. The factors that influence the stability of thiosulphate are the Eh and pH of solutions, the presence of copper, the presence of sulphur metabolising bacteria, and exposure to ultraviolet light (Dhawale, 1993).

Figure 5 presents the Eh-pH diagram for the metastable S-H₂O system (Kametani and Aoki, 1976; Osseo-Asare, 1989). The thermodynamically most stable species (ie HSO_4^- and SO_4^{2-}) are omitted from consideration to reveal the metastability domain of species such as thiosulphate ($\text{S}_2\text{O}_3^{2-}$), tetrathionate ($\text{S}_4\text{O}_6^{2-}$) and sulphite (SO_3^{2-}). Thermodynamically, the diagram shows that thiosulphate oxidises to tetrathionate between pH 4 to 10, otherwise it oxidises to other sulphur species, such as $\text{S}_2\text{O}_6^{2-}$ or SO_3^{2-} .

LEACHING STUDIES WITH AMMONIACAL THIOSULPHATE

Leaching ores

A review of the literature (Aylmore and Muir, 2001a) shows that thiosulphate has been used on occasions to leach gold and silver ores since 1900, but serious interest did not take place until a period around 1980. A summary of some published studies on various ores (Table 3) shows a wide range in the conditions and concentrations of reagents used with an emphasis on carbonaceous ores that give poor gold recoveries using cyanide, and copper-gold ores. The earlier studies, using relatively high concentrations of reagents, gave reasonable gold extraction but consumed up to 40 kg/t thiosulphate. Later studies (Langhans, Lei and Carnahan, 1992) established that comparable extraction of gold could be achieved with dilute ammoniacal thiosulphate and identified the catalytic role played by trace amounts of copper. Subsequent work carried out by Newmont (Wan, Levier and Clayton, 1995) showed that it was possible to heap leach low grade carbonaceous ores using dilute ammoniacal thiosulphate solutions with reasonable reagent consumption around 2 - 4 kg/t thiosulphate. In both cases no more than 0.2 M thiosulphate and ammonia were used for leaching with about 60 ppm Cu(II) as catalyst. It was recognised that it was necessary to limit the concentration of copper in solution because Cu(II) degrades thiosulphate and leads to high reagent losses.

Several research groups have studied gold-copper ores but generally find it difficult to control the extent of copper leaching and the degradation of thiosulphate (Dreisinger, 2000). Although 70 - 90 per cent Au could be leached from three Brazilian ores, each ore responded differently, and each required different leach conditions for optimum recovery. In some cases, copper partially precipitated from solution and gold extraction reached a maximum after about eight hours (Frietas, Trindade and Carageorgos, 2001).

Lakefield Research also examined pressure leached arsenopyrite ores from Barrick, and carried out a large number of stirred tank tests at pH 8 - 9. Up to 95 per cent Au was extracted from the finely divided gold left in the oxidised residue but the gold recoveries generally varied from 50 per cent to 95 per cent (Thomas *et al.*, 1998).

Recent unpublished studies have been made by ourselves and other colleagues on some relatively simple Australian oxide ores, using a range of dilute reagent compositions and conditions. These have showed that whilst most of the gold and silver were readily leached in two to four hours, a fraction of the cyanide-soluble gold always remained in the thiosulphate leach residue (Table 4). Although changes in reagent composition and leach conditions affected the kinetics and per cent gold recovery, no conditions were found that could match gold recovery by cyanide. Furthermore, the recovery of gold from different ores varied even more when similar leach conditions were used (Table 4), indicating other factors are more important.

Factors affecting gold recovery

Low gold recoveries from ores have been attributed to coarse gold, insufficient leaching time, the precipitation of gold on iron from grinding media and the absorption of gold onto some minerals. Decomposition of thiosulphate was also claimed to produce tetrathionate, polythionate and various unsaturated sulphur species that could passivate the gold surface.

Early work reported the precipitation of copper sulphide with high concentrations of reagents, but recent work by Frietas, Trindade and Carageorgos (2001) found that copper precipitated from solutions containing <0.3 M thiosulphate. Abbruzzese *et al.* (1995) found that increasing temperature decreased gold recoveries by 20 per cent which was ascribed to passivation by cupric sulphide. On the other hand, Bagdasaryan *et al.* (1983) and

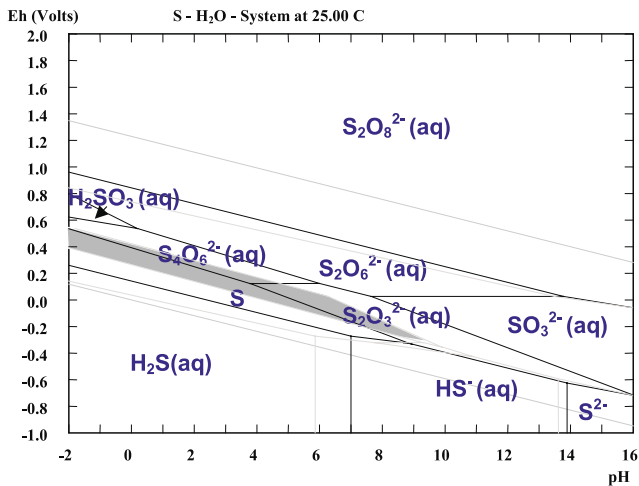
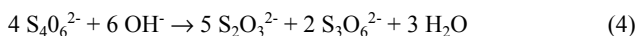
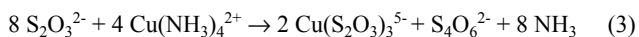


FIG 5 - Eh-pH diagram for the metastable S-H₂O system {S} = 1.0 M. The overall stability domain of tetrathionate is superimposed and shaded.

It can be concluded that the sulphur/water system is complicated because sulphur is multivalent and can exist in many species and oxidation states. To maintain thiosulphate in solution at ambient conditions, the solution has to be maintained in a narrow region of Eh at neutral to basic pH. However, once metal thiosulphate complexes are formed they are rather more stable.

Decomposition of thiosulphate and polythionates

Oxidative decomposition reactions of thiosulphate occur around 0.12 V (Table 2) which result in the formation of polythionates such as tetrathionate and trithionate (Equations 3 and 4) – dependent on reagent concentration, dissolved oxygen concentration, pH, Eh and temperature. In the presence of oxygen, direct oxidation of thiosulphate to sulphate and trithionate also occurs. By comparison, the oxidation of cyanide by air is negligible.



Fundamental studies by Byerley, Fouda and Rempel (1973, 1975) on the kinetics and mechanism of oxidation of thiosulphate ion in aqueous ammonia solution, established that the rate of oxidation and uptake of oxygen was dependent upon the concentration of Cu(II) and thiosulphate, and was inversely proportional to ammonia concentration. Similarly in our work, significant oxidation to trithionate and sulphate ion was measured in the presence of 10^{-3} M Cu(II) under the conditions used for leaching gold (Figures 3 and 4). Interestingly Wan (1997) and Li, Miller and Wan (1995) reported only tetrathionate as present in solution, with no mention of trithionate.

Studies on the kinetics of decomposition of tetrathionate and trithionate in alkaline solution (Naito, Sheh and Okabe, 1970; Rolla and Chakrabarti, 1982) showed that whilst tetrathionate can be readily decomposed to thiosulphate and trithionate by raising the pH to 11 (Equation 4), trithionate was more stable and required unacceptably higher pH or temperature to effect decomposition. This has practical significance because of the need to limit the concentration of these species when recovering gold using resins – as discussed below.

TABLE 3

Selection of ores and leaching conditions in literature (Aylmore and Muir, 2001a).

	Ore type	Gold (g/ton)	Temp	pO ₂ (kPa)	Retention (hrs)	S ₂ O ₃ ²⁻ (M)	NH ₃ (M)	Cu ²⁺ (M)	SO ₃ ²⁻ (M)	pH	% Recovery	Consumption
Tozawa <i>et al</i> , 1981	Gold plates	99.99 %	65	100	3	0.5	1	0.04	-	-		
Kerley, 1981, 1983	Sulphide 2 % Mn					18 %	2 %	4 g/L	2 %	7 - 9	95	4 kg/t
Block-Bolten and Torma 1985, 1986	Zn-Pb sulphide flotation 22.5 g/t Ag, 0.7 % Zn, 0.5 % Pb	1.75	21 - 50	air 2 L/ min	1	0.125 - 0.5	0.75	-	-	7 - 9	90	45 lb/t
Zipperian <i>et al</i> , 1988	Rhyolite ore 7 g/kg MnO ₂	3	50	atm	2	2	4	0.1	-	10	90 %	50 %
Hemmati <i>et al</i> , 1989	Carbonaceous 2.5 % org C	14.74	35	103	4	0.71	3	0.15	0.22	10.5	73 %	15 - 19%
Caixia and Qiang, 1991	Oxidised ore 0.05 % Cu _s	4.78	30 - 65	atm	2	1 - 22 %	1.36 - 8.86%	0.05 - 2 %	1 %	-	93.9	40 kg/t
Hu and Gong, 1991	0.048 % MnO ₂ 3.19 % Cu	50.4	40	1 L/min	1 - 2	1	2	0.016	0	-	95.6	-
Murthy, 1991	Pb-Zn sulphide 22.5 g/t Ag, 0.44 % Cu 0.68 % Zn, 0.54 % Pb	1.75	21 - 70	atm	3	0.125 - 0.5	1	-	-	6.9 - 8.5	95 %	-
Cao <i>et al</i> , 1992	Sulphide conc 3 % Cu	62	60	atm	1 - 2	0.2 - 0.3	2 - 4	0.047	-	10 - 10.5	95	4.8 kg/t
Langhans <i>et al</i> , 1992	Oxidised ore 0.02 % Cu	1.65	ambient	atm	48	0.2	0.09	0.001	-	11	90	2 kg/t
Wan <i>et al</i> , 1994	Carbonaceous 1.4 % C, 1.0 % S	2.4	ambient	atm	12 - 25 days	0.1 - 0.2	0.1	60 ppm	-	9.2 - 10		
Abbruzzese <i>et al</i> , 1995	Gold ore	51.6	25	atm	3	2	4	0.1	-	8.5 - 10.5	80	
Groudev <i>et al</i> , 1996	Bacteria leached ore 15.2 g/t, 0.14 % Cu, 0.91 % S	3.2	ambient	atm		15 g/l	added to pH 9.5	0.5 g/l	0.5 g/l	9.5 - 10.0	80	
Marchbank <i>et al</i> , 1996	Sulphide carbonaceous	3 - 7	55	atm	4	0.02 - 0.1	2000 ppm	500 ppm	0.01 - 0.05	7 - 8.7	70 - 85	
Yen <i>et al</i> , 1996	Gold-copper ore 1.4 g/t Ag, 0.3 % Cu	7.26	ambient	atm	24	0.4	0.2	0.03	-	11	90	
Wan, 1997	Sulphide carbonaceous	1 - 3	ambient	atm	-							
Wan and Brierley, 1997	Carbonaceous sulphide	1 - 3	ambient	atm	91 - 116 days	0.1	0.1	0.005	-	9	50.7 - 65.7	5.2 - 8.4
Yen <i>et al</i> , 1998,1999	Gold copper ores ~0.36 % Cu	7.2 - 7.9	ambient	atm	24	0.5	6	0.1	-	10	95 - 97	30 kg/t
Thomas <i>et al</i> , 1998	Pressure oxidised sulphide ore	2.5	45 - 55	atm	12	0.03 - 0.05	~500 - 1000 ppm	10 - 100 ppm	0.01 - 0.05	7.5 - 7.7	80 - 85	

TABLE 4

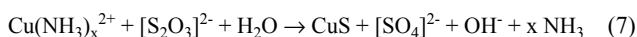
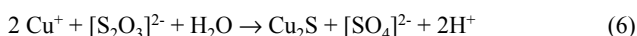
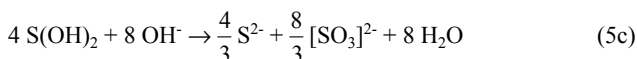
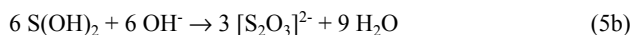
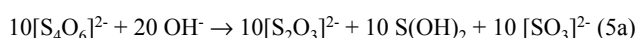
Leaching studies on Australian ores using dilute ammoniacal thiosulphate solutions.

Ore	Grade	% CN soluble	% Au	% Ag
N. Queensland A (oxide)	21 g/t Au 15 g/t Ag	95 88	77 - 90	75 - 95
N. Queensland B (oxide)	11 g/t 10 g/t	95 95	66 - 85	51 - 83
W.A. Goldfields (oxide + ~1 % sulphide)	3.8 g/t Au 2.8 g/t Ag	83 67	58 - 69	44 - 60
W.A. Goldfields (saline water/oxide)	3.3 g/t Au 0.3 g/t Ag	96 >90	25 - 35	50 - 65
N. Territory prospect (oxide/gravity tail)	1.1 g/t Au	90	58	ND

Pedraza *et al* (1988) observed a sulphur layer as well as copper sulphide in a thiosulphate-copper sulphate system. However, electrochemical impedance spectral studies have shown that gold passivation can occur in thiosulphate solution even in the absence of copper (MacDonald, 1990).

In some leach tests over an extended time there has been evidence of re-precipitation of gold, silver and copper and lower gold recovery. No doubt this reflects the build up of degradation products in solution and possible precipitation of gold and silver sulphide. Briones and Lapidus (1998) found precipitation of Ag₂S occurred at low thiosulphate concentrations. However Kerley (1981), and Perez and Galavis (1987), ascribe the precipitation of Ag₂S to the reaction of the silver thiosulphate complex with metal oxide minerals. Once Ag₂S is formed, it appears that the dilute thiosulphate solutions are unable to re-leach the sulphide. Recent studies on the leaching of pure silver sulphide (Briones and Lapidus, 1998) generally show <50 per cent Ag extraction with a range of ammoniacal thiosulphate compositions containing up to 0.10 M Cu(II).

Studies by Miura and Koh (1983) indicate that tetrathionate decomposes to thiosulphate and sulphite ion together with sulphylic acid (S(OH)₂) and some sulphide ion (Equation 5). Rabai and Epstein (1992) report that the fast redox reaction between Cu(II) and thiosulphate is followed by slower side reactions which produce Cu₂S (Equation 6). Abbruzzese *et al* (1995) claim that CuS is formed by the reaction between Cu(II) and thiosulphate (Equation 7) – similar to the ‘copper boil’ reaction used in the Sherritt-Gordon Process for refining nickel matte.



Clearly the mechanism and decomposition pathway of thiosulphate and tetrathionate species are complex and not well understood, and depend upon Eh and pH. There is evidence that some copper and silver sulphide can precipitate from solution, which could also contain gold, but the exact cause is not understood. It is not clear whether CuS can be avoided or re-leached by increasing the Eh of the solution.

Unfortunately many leach tests were carried out like cyanidation with little control of Eh, pH or reagent composition, and from the discussion above, it would appear that much closer control is required in this system to prevent undesirable side reactions.

GOLD RECOVERY OPTIONS

Activated carbon

Early researchers soon established that activated carbon does not selectively absorb the gold thiosulphate complex – unlike the gold cyanide complex. This is attributed to the high anionic charge of the thiosulphate complex and the distance of the gold atoms from the carbon surface when complexed with bulky thiosulphate ions (Ritchie, Nicol and Staunton, 2001). Hence most investigations have focussed on absorption onto resins and precipitation of gold from clarified solutions. However several patents include an alternative recovery option of adding trace amounts of cyanide to produce a stable gold cyanide complex, followed by quantitative absorption on activated carbon. This idea was first patented by Lulham and Lindsay (1991) who demonstrated that as little as 1.2 times the stoichiometric quantity of cyanide was required to complex the gold in solution. Furthermore the activated carbon was selective for gold cyanide over silver, copper and zinc in solution. In this case, cyanide is restricted to a small volume of eluate rather than a large volume of pulp.

Reduction and precipitation

Gold can be precipitated by reduction onto Zn, Cu, Al or Fe powder, by reduction with sodium borohydride, or by precipitation with sodium sulphide. Generally a large excess of metal powder is required to provide sufficient surface area to reduce gold in a reasonable time. Unfortunately, copper also co-precipitates from solution and must be recycled to leach – except when copper powder is used (Perez and Galviz, 1987; Guerra and Dreisinger, 1999). Interestingly, recent fundamental electrochemical studies by Breuer, Jeffrey and Choo (2001) report that gold(I) thiosulphate cannot be readily reduced to metallic gold in the potential region where copper dissolves. However the presence of both copper and silver in solution enhances gold deposition at a low overpotential, ie gold deposits readily on silver.

Clearly reduction and precipitation is best suited to heap leach liquors because of the soluble gold losses associated with filtering slurries. Unfortunately the precipitate is usually low grade with respect to gold and requires further processing.

Absorption on resins

Conventional strong base (SB) resins are able to load up to ten times more gold than weak base (WB) resins from pure solutions and slurries and have a capacity to load up to 100 000 ppm Au. But even low concentrations (0.01 M) of trithionate and tetrathionate in solution readily absorb onto the resin and significantly restrict gold uptake (Nicol and O'Malley (2001)). Furthermore, because of the large excess of copper over gold in typical leach solutions, and the limited selectivity of SB resins, the resins also load with copper as well as gold. Under optimum leaching conditions, resin loadings around 2000 - 4000 ppm Au have been reported (Wan, LeVier and Miller, 1993; Fleming, 1998) – which is comparable to gold cyanide loading onto activated carbon. However the performance of the resin is closely linked to the conditions of the leach and the relative amounts of polythionates produced.

Vernig and Serokowski (1997) have demonstrated the ability of WB guanidine function resins and solvent extractants to extract gold thiosulphate but the optimum loading of gold and

effect of copper and tetrathionate were not examined. Like other weak base resins its loading capacity is low in the pH 9 - 10 range generally used for leaching (Nicol and O'Malley, 2001).

Elution from resins

WB resins have the advantage of being readily stripped with dilute NaOH, but caustic solutions are known to decompose thiosulphate and this leads to precipitation of gold and silver sulphides on the resin. Stripping of gold from SB resins is more difficult. Thomas *et al* (1998) claims the use of ammonium thiosulphate to selectively elute the copper before gold, followed by elution of gold with concentrated thiocyanate solution. Gold was recovered preferentially by precipitation with sulphide ion – generated by the decomposition of thiosulphate at pH 11.5. More recent research at the Parker CRC has identified another simple eluant for gold and silver (O'Malley, 2001; Nicol and O'Malley, 2001), whilst researchers at Lakefield and Barrick have investigated the use of trithionate and tetrathionate as an eluant to avoid introducing other species into the process streams (Fleming, 2000).

ENVIRONMENT AND TOXICITY

Thiosulphate

Although thiosulphate is generally regarded as relatively non-toxic, it is also metastable and can decompose either to polythionates and sulphate whilst consuming oxygen, or to toxic sulphide ion under anaerobic or reducing conditions (Figure 2). Thus its uncontrolled release into the environment poses problems of de-oxygenation of waterways or the potential

formation of toxic species. Whilst this can be avoided by oxidation of thiosulphate to sulphate prior to release, the cost of oxidation is likely to be much higher than the oxidation of cyanide due to the relatively high concentration of thiosulphate used and the moles of oxygen required. (Gos and Rubo, 2000). Thus to be economic, it is necessary to minimise the release of thiosulphate and recycle as much as possible. But since recycling is limited by the build up of polythionates, it becomes important to leach gold with the minimum of thiosulphate.

Ammonia

Ammonia poses environmental and toxic problems both as a gas in air and as a soluble solution.

In air, the threshold limiting value (TLV) for ammonia gas is 14 mg/m³ (Gos and Rubo, 2000) which is classified similar to HCN. In water, free ammonia is classified similar to chlorine whilst ammonium ion has low toxicity. Unfortunately ammonia is difficult to breakdown and may eventually metabolise to nitrate, which has the potential to promote algae growth and to pollute groundwater. Thus even more strict precautions have to be taken to control ammonia emissions from tanks or heaps, and to prevent its release into the environment.

SUMMARY AND FUTURE RESEARCH

Table 5 summarises the issues and impediments discussed above with regard to the leaching gold ores, the recovery of gold from solution, the stability of the reagents and their release to the air or water. Clearly not all issues can be solved, but all criteria must be addressed and understood before an overall process can be developed, tested and costed.

TABLE 5

Summary of issues and impediments associated with thiosulphate leaching of gold ores and recovery from solution.

Aspects	Issues	Impediments
Kinetics and mechanism	Cu(II) catalyses both gold and thiosulphate oxidation. Complex leach kinetics. Chemically controlled Ag ₂ S partially leached.	High reagent consumption. Copper in ore difficult to control; Not understood. Dependent on Cu(II), T, NH ₃ , S ₂ O ₃ . Possible passivation of gold Au associated with Ag not leached.
Reagents	Relatively high S ₂ O ₃ , NH ₃ required. Relatively low copper required.	Cost of reagents. Recycling builds up impurities. Effluent treatment cost high. Ammonia hazard to health and environment. Copper associated with gold ores. Copper absorbed on minerals.
Stability	Thiosulphate oxidised to polythionates. Polythionates unstable.	Possible pptn of Au/Ag/Cu sulphide.
pH	Controls free NH ₃ , Cu(II), Eh near pH 9.5. High pH decomposes thiosulphate and tetrathionate.	Recovery sensitive to pH. Possible pptn of sulphides.
Dissolved oxygen	Controls Cu(II), Eh. Oxidises thiosulphate to trithionate.	Recovery sensitive to DO.
Temperature	Slow kinetics at 20°C. Degradation of reagents at > 40°C	Recovery sensitive to temperature.
Time	Rate of oxidation S ₂ O ₃ remains constant whilst gold extraction slows.	Large build up of polythionates for small increase in gold.
Gold deportment	Coarse gold and gold in sulphide minerals slow to leach.	Long leach time builds up polythionates.
Ore mineralogy	Possible preg-robbing of copper and gold by clays, sulphides. Reactive sulphides consume oxygen and Cu(II).	Recovery sensitive to ore type. Leaching impaired or stopped.
Pptn of gold	Copper and silver co-ppt.	Cost of reagents. Treatment cost of ppt.
Recovery on resins	Polythionates co-absorb on SB resin. Copper absorbs on resin.	Low resin loading increases cost. Copper competes for gold. Possible pptn sulphides in resin.
Elution of resin	Separation of Cu and polythionates. Recycling of eluant.	Two stage elution required. Impurity control.

There is no doubt that, despite its shortcomings, thiosulphate is an attractive alternative to cyanide for processing carbonaceous ores where the recovery of gold is poor. It may also be attractive for processing copper-gold concentrates and ores that consume significant cyanide. However for simple oxide ores further research is required to improve gold recovery and lower reagent costs to match that of cyanide.

Further research is now being carried out under AMIRA sponsorship in the Parker CRC at Murdoch University and CSIRO Minerals to examine a range of issues. This work aims to:

- understand the speciation and conditions controlling the oxidation of gold and thiosulphate to minimise reagent concentration and decomposition;
- examine alternative redox systems to ammoniacal copper to leach gold without oxidation of thiosulphate;
- understand why gold extraction varies with different ores;
- understand the effect of silver on extraction and recovery;
- examine whether particular minerals 'preg-rob' gold or copper, effect Eh/pH, or cause gold and copper to precipitate from solution;
- understand the effect of saline process water on leaching and recovery;
- examine means of removing or decomposing polythionates without affecting thiosulphate;
- optimise the loading of gold and silver onto resins, or modify the resin to minimise polythionate absorption;
- examine the selective elution of copper and gold from resin; and
- examine alternative methods of recovery of gold from eluates.

Until some of these issues are overcome, there is little current economic incentive to switch existing plants from cyanide to thiosulphate – except for the processing of carbonaceous ores. However the threat of increasing public concerns over cyanide management will ensure that companies will continue to strive for a viable alternative. The industry's first endeavour with the thiosulphate system is to develop a robust overall process flowsheet that can be realistically used and costed for a range of actual ores – including gold recovery, reagent recycling or destruction and impurity control.

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