

The treatment of copper–gold ores by ammonium thiosulfate leaching

Ellen Molleman, David Dreisinger*

Department of Metals and Materials Engineering, The University of British Columbia, 309-6350 Stores Road, Vancouver, BC, Canada V6T 1Z4

Received 6 July 2001; received in revised form 23 April 2002; accepted 31 May 2002

Abstract

The application of ammonium thiosulfate for the treatment of copper–gold ores has been investigated. Copper minerals and copper–gold samples were leached in an ammonium thiosulfate solution under varying experimental conditions, i.e. aeration, temperature and reagent addition. The behaviour of thiosulfate, tetrathionate and sulfate in solution was studied using ion chromatography. Experiments showed that both gold extraction and thiosulfate stability are affected by a combination of aeration and cupric ions in solution. It is important to establish a balance between providing sufficient air and cupric ions for fast gold dissolution, and at the same time minimize the amount of air in the presence of cupric ions to prevent excessive thiosulfate degradation. Promising results, i.e. high gold extractions and low thiosulfate consumption, were obtained during a 24-h leach without forced aeration.

© 2002 Elsevier Science B.V. All rights reserved.

Keywords: Copper; Minerals; Gold

1. Introduction

The application of alternative lixiviants, such as thiourea, chloride, bromide and ammonium thiosulfate, for gold recovery has been extensively researched in the last few years. These lixiviants would be particularly attractive if they improve the gold recovery or result in a savings in reagent cost (von Michaelis, 1987). Ideally, the lixiviant should be cheap or recyclable, selective, nontoxic and compatible with downstream recovery processes (Avraamides, 1982). In practice, meeting all these criteria is difficult.

Thiosulfate has the ability to complex gold and silver. Moreover, ammonium thiosulfate is relatively nontoxic and has been used for many decades as a fertilizer and, consequently, from an environmental standpoint, has a definite advantage over cyanide (Atluri, 1987). Comparing reagent unit costs, ammonium thiosulfate is far cheaper than sodium cyanide (US\$0.13/kg vs. US\$1.80/kg). Consequently, with similar or even slightly higher lixiviant consumption, the application of thiosulfate for gold recovery can be economical and compete directly with cyanidation.

Copper–gold ores form a type of refractory gold ore. Large quantities of this ore type are available for processing. Cyanide treatment of ores with a high cyanide soluble copper to gold ratio is unfavourable due to high cyanide consumption resulting from the formation of copper–cyanide complexes.

* Corresponding author. Fax: +1-604-822-3619.

Ammonium thiosulfate is particularly attractive as an alternative to cyanide for the treatment of copper–gold ores. The presence of copper is desirable in a thiosulfate leach, whereas it is detrimental in a cyanide leach. Moreover, it might be possible to recover both gold and copper provided enough lixiviant and economical copper and gold recovery methods are available.

2. Theoretical background

The chemistry of the ammoniacal thiosulfate system for gold recovery involves many interrelated chemical equilibria which are not yet fully understood. This complexity can be attributed to the presence of three essential components, which define the ammoniacal thiosulfate leaching environment: ammonia, thiosulfate and copper. Thiosulfate stabilizes gold in solution, while copper and ammonia accelerate the leach reaction. Many reactions may occur between these species, dissolved metal ions, atmospheric gases and ore minerals. Another complication of the system is that thiosulfate is prone to oxidative degradation; thiosulfate is a metastable sulfur species which will eventually decompose in aqueous solutions.

2.1. Aqueous chemistry of thiosulfate

Thiosulfates are compounds containing the $\text{S}_2\text{O}_3^{2-}$ group, which is a structural analog of sulfate with one oxygen atom replaced by a sulfur atom. The two sulfur atoms are not equivalent (Fig. 1).

The unique chemistry of the thiosulfate ion, $\text{S}_2\text{O}_3^{2-}$ or SSO_3^{2-} , is dominated by the sulfide-like sulfur atom, which is responsible for the reducing properties and complexing abilities of thiosulfates

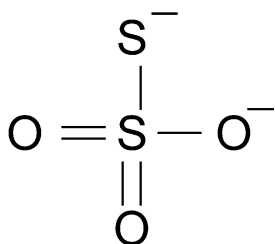


Fig. 1. Structure of the thiosulfate ion (Othmer, 1983).

(Othmer, 1983). Chemical properties of thiosulfate include:

- Tendency to be oxidized (by O_2 , Cu^{2+} , etc., see Section 2.3.3).
- Tendency to hydrolyse at $\text{pH} < 5.5$ to S^0 and HSO_3^{2-} at mildly acid pH (Skoog and West, 1976) and to more complex mixtures in strong acid (Smith and Hitchen, 1976).
- Moderately good hydrolytic stability in basic solution (Pryor, 1960).
- Ability to form complexes with a variety of metals, e.g. gold, silver, copper (Cu^+ and Cu^{2+}), iron (Fe^{3+}), etc. (Burns et al., 1981). The stability of these complexes depends on the solution conditions.
- Formation of metal sulfides, e.g. with copper, silver, mercury (Burns et al., 1981).
- Stability toward reduction to free sulfide; the E^0 of Eq. (1) is $-0.643 \text{ V}_{\text{SHE}}$



2.2. Overview of thiosulfate technology for gold extraction

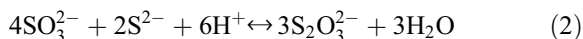
The use of thiosulfate for the recovery of precious metals was first proposed in the 19th century and is known as the “Patera Process.” It was applied in 1858 by Von Patera for silver recovery. The process utilizes the solubility of silver chloride in a solution of sodium thiosulfate. The ore was treated by a chloridizing roast followed by a sodium thiosulfate leach. Sodium sulfide was then used to precipitate silver sulfide (Liddell, 1945).

Berezowsky and Gormely (1978) revived interest in the thiosulfate leaching system for precious metals recovery by developing an atmospheric ammoniacal thiosulfate leach system to recover gold and silver from ammoniacal oxidative pressure leach residues of sulfidic copper concentrates. Extractions of 88–95% for gold and 83–98% for silver were achieved after 2–4-h leaching with 0.4–0.8 M $\text{S}_2\text{O}_3^{2-}$ at 40–60 °C. The parameters affecting the gold solubilization were thiosulfate, ammonia and cupric ion concentrations, temperature and residence time. To minimize oxidation of thiosulfate, initial testwork was performed under a nitrogen atmosphere.

In some experiments, a decrease in gold extraction with time was observed. Berezowsky and Gormely (1978) attributed this phenomenon to thiosulfate degradation; thiosulfate decomposition in the presence of copper causes the precipitation of copper sulfide, which coats the gold particles and, thus, inhibits gold leaching and recovery. Therefore, an optimal leach time exists; the leach time should not be needlessly prolonged. A direct thiosulfate leaching test was performed on a chalcopyrite concentrate with 3–5 g/L Cu^{2+} addition and mild air sparging. A gold extraction of 97% was obtained after 1 h. Analysis of the leach liquors for thiosulfate indicated that 90–95% of the thiosulfate was accounted for and could be recycled (Berezowsky and Sefton, 1979).

Kerley (1981, 1983) patented a process for the recovery of precious metals from refractory ores, particularly those containing manganese and/or copper, by lixiviation using an ammonium thiosulfate leach solution. The patent claims to improve upon the thiosulfate leaching of the patent of Berezowsky and Gormely (1978) by providing better control of the stability of the thiosulfate ion. The Kerley leach solution contained 1.2–1.35 M $\text{S}_2\text{O}_3^{2-}$, 1–4 g/L Cu^{2+} , sufficient ammonia to maintain a pH of 7.5 or higher and a minimum of 0.05% sulfite ions to control the stability of the solutions during leaching.

Kerley (1981) claims that sulfite ions inhibit the decomposition of thiosulfate according to Eq. (2) and, thus, prevent precipitation of metal sulfides.



This reaction is, however, unlikely to occur at pH 7.5, since the sulfide ion is not stable in this pH region (see Fig. 2 and Section 2.3.3).

The process patented by Kerley was carried out in a plant in Mexico, but the scale-up from laboratory to plant-size failed. Perez and Galaviz (1987) describe the modifications required to make plant operation feasible. The most important process adjustment was the pH value, which should be maintained at a minimum level of pH 9.5, instead of 7.5 as suggested by Kerley (1981).

Zipperian and Raghavan (1988) identified the parameters of importance in the dissolution of gold and silver values from a rhyolite ore with a high manganese content using ammoniacal thiosulfate solutions containing copper. The effects of thiosulfate, ammonia concentration, temperature and copper sulfate addition were researched. Optimum conditions were established at 2 M $\text{S}_2\text{O}_3^{2-}$, 4.1 M NH_3 , 6 g/L Cu^{2+} , 50 °C and 2-h leaching in the absence of oxygen. In the absence of cupric ions, only 14% gold

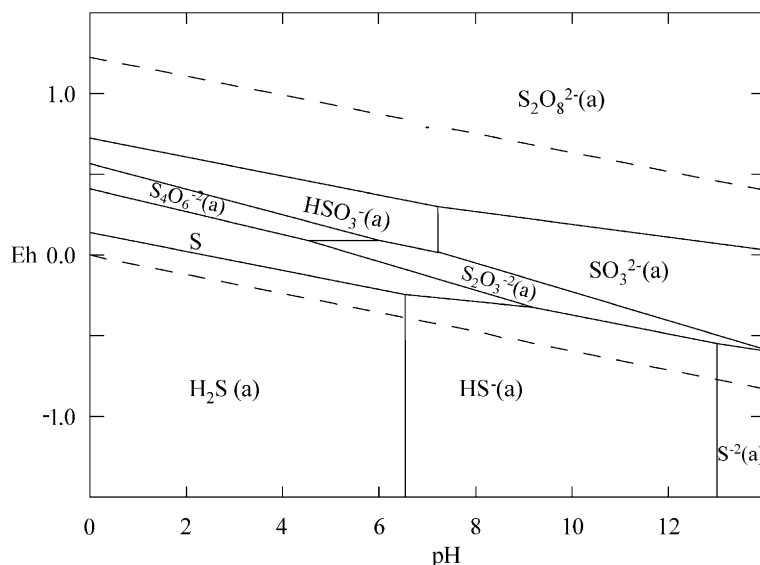


Fig. 2. Eh–pH diagram for the metastable system S–H₂O at 25 °C. The activity of sulfur species is 0.4 M [$\Delta G_f^\circ(\text{S}_2\text{O}_3^{2-}) = -518.8$ kJ/mol].

was solubilized. Initial rates of gold extraction were enhanced by increasing cupric ion concentration, but the ultimate extraction was not influenced by the cupric ion concentration in the range investigated (up to 6 g/L Cu). Further, it was concluded that maintaining optimal pH and Eh conditions (pH 10 and 200 mV) is necessary to prevent precipitation of copper as Cu_2S . Half of the thiosulfate in the lixiviant solution at pH 9.5–10 was reported to be consumed during the dissolution process.

Langhans et al. (1992) focused on maximizing gold extraction while minimizing thiosulfate consumption at low reagent concentrations and ambient temperatures and pH between 9 and 11. The research was conducted on low-grade oxidized gold ores with application to heap, dump or in situ leaching techniques. The range of the thiosulfate concentration tested was 0.05–0.2 M. After leaching for 48 h, 83% gold extraction was achieved with 0.2 M $\text{S}_2\text{O}_3^{2-}$ with 0.4 kg $\text{S}_2\text{O}_3^{2-}$ consumed per ton of ore.

The effectiveness of low thiosulfate concentrations was confirmed by Cao et al. (1992), who studied the effects of the concentrations of thiosulfate, copper and ammonia on the extraction of gold and silver from a sulfide concentrate. Leaching was performed with a 0.2-M thiosulfate solution at 2-h retention time, which yielded 95% gold extraction. The sparge air was treated with ammonia in order to keep the ammonia concentration constant. Cao et al. (1992) also researched the influence of sulfate addition to the system, in order to reduce the thiosulfate consumption, but found no effect (see Section 2.3.3).

Newmont Gold evaluated the application of ammonium thiosulfate on a demonstration heap leach of 327,000 metric tons of low-grade carbonaceous sulfidic ore that was pretreated by biooxidation. The average gold recovery for thiosulfate heap leach at a particle size of minus 1.9 cm was found to be approximately 55%. Ammonium thiosulfate consumption was about 5 kg/ton for low sulfide carbonaceous ores (without biooxidation) and 12–15 kg/ton for biooxidised ores. Typical leach solutions used contained 0.1 M $\text{S}_2\text{O}_3^{2-}$, 0.1 M NH_3 and 30 ppm Cu^{2+} (Wan, 1997).

The application of a thiosulfate salt lixiviant to recover gold from an oxidative pressure leach slurry is described in a patent granted to Marchbank et al. (1996). A slurry of refractory sulfidic and refractory

carbonaceous ore is subjected to pressure oxidation in an autoclave under neutral or alkaline conditions followed by leaching with a thiosulfate salt in stirred tank reactors. Typical leaching conditions are 0.025–0.1 M $(\text{NH}_4)_2\text{S}_2\text{O}_3$, 50–100 ppm Cu^{2+} , 40–55 °C and a minimum sulfite concentration of 0.001 M, while maintaining a pH between 7 and 8.7.

2.2.1. Summary of literature

Little research is available regarding the treatment of copper–gold ores by ammonium thiosulfate. The research reported by Berezowsky and Sefton (1979) concerned the treatment of ammonia pressure oxidation residues, which contained 0.54–2.58% copper. Several studies were performed by Gong and Hu (1990) and Cao et al. (1992) on a gold sulfide concentrate containing 3.16% Cu.

All of these studies were performed at high thiosulfate concentrations (0.4–1 M), and high ammonia concentrations (1–2 M). The catalytic effect of copper on gold extraction was recognized by these researchers, but only Berezowsky and Sefton (1979) mentioned the detrimental effect of copper on thiosulfate stability. None of the studies attempted to investigate the behaviour of copper and thiosulfate during the leach.

Kerley (1981, 1983) described a cupric addition of 1–4 g/L and Berezowsky and Gormely (1978) mention an addition of 1–10 g/L. Cupric ion concentrations of 50–100 ppm are mentioned in the patents granted more recently (Marchbank et al., 1996; Wan et al., 1994). Low cupric ion concentrations seem to be favourable, since high cupric ion concentrations accelerate thiosulfate degradation.

The pH of the recently developed ammonium thiosulfate leaching processes is generally maintained between 9 and 10. This pH range is dictated by the ammonia/ammonium buffer point (9.25 at 25 °C), since the presence of ammonia has to be ensured in order to solubilize copper as the copper(II)–ammonia complex. The thiosulfate stability will decrease at higher temperatures and lower pH values. Therefore, a pH of 9–10 is generally preferred at ambient temperature because thiosulfate appears to be less prone to degradation in this region and the copper(II)–ammonia complex is stable.

When evaluating the optimum ammonia concentration, two factors should be considered. Firstly, there

has to be sufficient ammonia present in the leaching system to solubilize the copper partially as an ammonia complex. Secondly, the ammonia to thiosulfate mole ratio should be kept in a certain range, preferably around 1–2 (see Section 2.3.2).

In conclusion, ammonium thiosulfate leaching for gold recovery preferably should be performed at:

- low thiosulfate concentrations, ranging from 0.1 to 0.2 M;
- an ammonia to thiosulfate ratio of 1–2;
- copper concentrations ranging from 50 to 100 ppm;
- an alkaline pH, preferably 9–10;
- ambient temperature to 50 °C.

2.3. Chemistry of the ammonium thiosulfate system

This section reviews some fundamental aspects of the ammonium thiosulfate system: thermodynamics, copper catalysis and the degradation pathways of thiosulfate.

2.3.1. Thermodynamic considerations

Thermodynamically, the ammonium thiosulfate system is not stable. Both ammonia and thiosulfate will be lost through volatilization or decomposition. Therefore, true equilibrium diagrams cannot be constructed for this system. By omitting the more stable species such as sulfate ions from the system, the features of the metastable species can be examined

(see Fig. 2). The species considered are: NH_4^+ , NH_3 , $\text{S}_2\text{O}_3^{2-}$, S^0 , $\text{S}_x\text{O}_6^{2-}$ ($x \geq 2$), SO_3^{2-} , HSO_3^{2-} , H_2S , HS^- and S^{2-} . The stability of the thiosulfate ion will be discussed in Section 2.3.3.

Eh–pH diagrams reflecting the experimental conditions used in this research were constructed with the use of the computer program CSIRO Thermochemistry (Turnbull and Wadsley, 1986). Thermodynamic data for the various copper and gold species expected to be present in these solutions are presented in Table 1. The pH range was chosen between 6 and 14, below pH 6 complex reactions involving the hydrolysis of thiosulfate start to take place which were not pertinent to this research. The diagrams were constructed using molarities, since representative activity coefficients are not readily available due to the complex nature of the solutions in this system.

The Eh–pH diagram for the gold–thiosulfate–ammonia–water system appears in Fig. 3. The gold activity is 2.5×10^{-5} (5 ppm), the thiosulfate activity is 0.2 and the ammonia/ammonium activity is 0.4. It can be seen that the gold(I)–thiosulfate complex is stable in the whole pH range shown.

Comparing Fig. 3 with the Eh–pH diagrams given in the literature (see Fig. 4), it can be observed that the gold(I)–ammonia complex has no region of stability in Fig. 3, while Fig. 4 shows a region of stability for this complex. A closer examination of the literature revealed that a different value was used for the free energy of formation of the thiosulfate species.

Table 1
Thermodynamic data of relevant species

Formula	ΔG_f^0 (kJ/mol)	Formula	ΔG_f^0 (kJ/mol)	Formula	ΔG_f^0 (kJ/mol)
H_2O	–237.18	$\text{S}_2\text{O}_3^{2-}$	–518.8	HSO_3^-	–527.81
OH^-	–157.29	$\text{S}_2\text{O}_3^{2-}$	–532.2 ^{a,b}	Au	0
NH_3	–26.6	$\text{S}_2\text{O}_4^{2-}$	–600.4	Au^+	176
NH_4^+	–79.37	$\text{S}_2\text{O}_5^{2-}$	–791	Au^{3+}	440
S^{2-}	86.31	$\text{S}_2\text{O}_6^{2-}$	–966	AuO_3^{3-}	–51.9
S_2^{2-}	79.5	$\text{S}_2\text{O}_8^{2-}$	–1110.4	HAuO_2^-	–142
S_3^{2-}	73.6	$\text{S}_3\text{O}_6^{2-}$	–958	H_2AuO_3^-	–218
S_4^{2-}	69	$\text{S}_4\text{O}_6^{2-}$	–1022.2	Au(OH)_3 (aq)	–283.5
S_5^{2-}	65.7	$\text{S}_5\text{O}_6^{2-}$	–956	Au(OH)_3 (s)	–317
SO_3^{2-}	–486.6	HS^-	12.05	$\text{Au(NH}_3)_2^+$	–41.1 ^c
SO_4^{2-}	–744.63	H_2S (aq)	–27.87	$\text{Au(S}_2\text{O}_3)_2^{3-}$	–1048 ^c

All data without footnotes are from Bard et al. (1985).

^a From the CRC Handbook of Chemistry and Physics (Weast, 1975).

^b From Duby (1977).

^c From Atluri (1987) and Wang (1992).

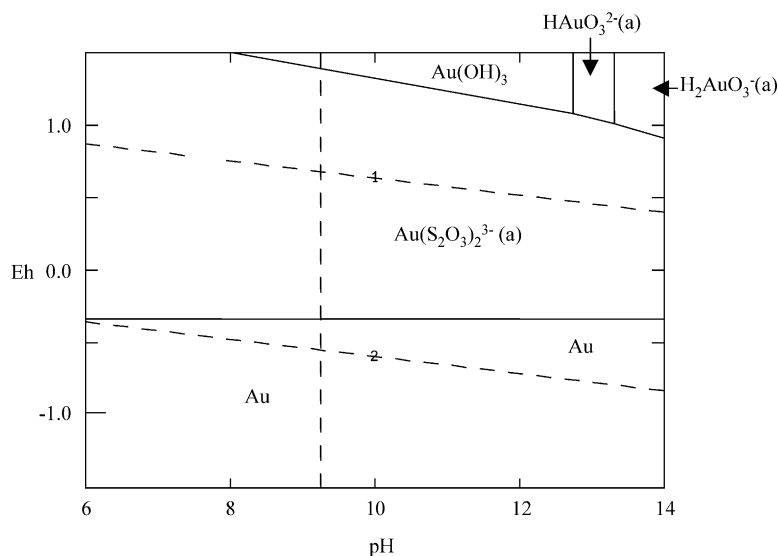


Fig. 3. Eh–pH diagram of the gold–thiosulfate–ammonia–water system at 25 °C. The activities of the species are 2.5×10^{-5} M Au (5 ppm), 0.2 M $\text{S}_2\text{O}_3^{2-}$ and 0.4 M $\text{NH}_3/\text{NH}_4^+$ [$\Delta G_f^0(\text{S}_2\text{O}_3^{2-}) = -518.8$ kJ/mol].

In Fig. 3, a value of -518.8 kJ/mol was used for the thiosulfate species (Bard et al., 1985). The Handbook of Chemistry and Physics (Weast, 1975) lists a value of -532.2 kJ/mol for thiosulfate, resulting in the

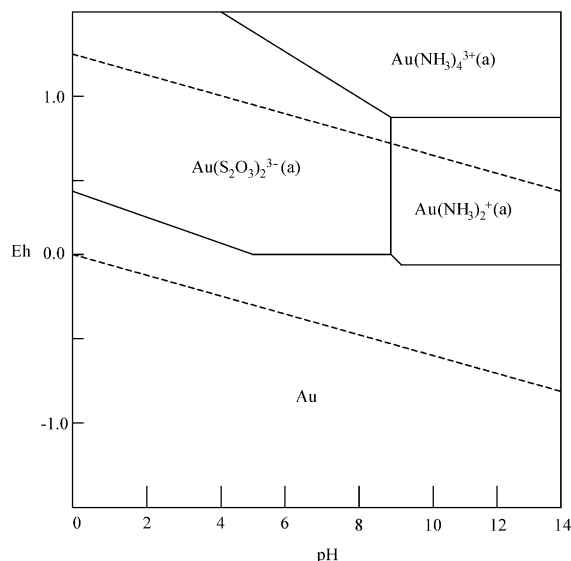
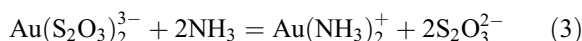


Fig. 4. Eh–pH diagram for the gold–ammonia–thiosulfate–water system at 25 °C. Activity of species: 0.1 M thiosulfate, 0.1 M ammonia, 5×10^{-4} M gold (Li et al., 1995).

Eh–pH diagram presented in Fig. 5, which resembles Fig. 4.

The gold(I)–ammonia complex now appears next to the gold(I)–thiosulfate complex. The large effect of this relatively small change in free energy is explained when the following equation is considered:



The free energy change for this reaction, calculated using the ΔG_f^0 value of -518.8 kJ/mol for thiosulfate, is $+22.5$ kJ, which indicates that this reaction is not favoured. When the free energy change is recalculated using the ΔG_f^0 value of -532.2 kJ/mol for thiosulfate, the value -4.3 kJ is obtained, which indicates that the formation of the gold(I)–ammonia complex is now slightly favoured. It can be concluded that a small change in the free energy of the thiosulfate species has a great impact on the thermodynamic equilibria of the gold–thiosulfate–ammonia–water system. As Li et al. (1996) remarked, it is generally accepted that the gold(I)–thiosulfate species is the more stable species at pH 10 and this was confirmed by rest potential measurements (see Fig. 6). The above discussion shows that there is a need

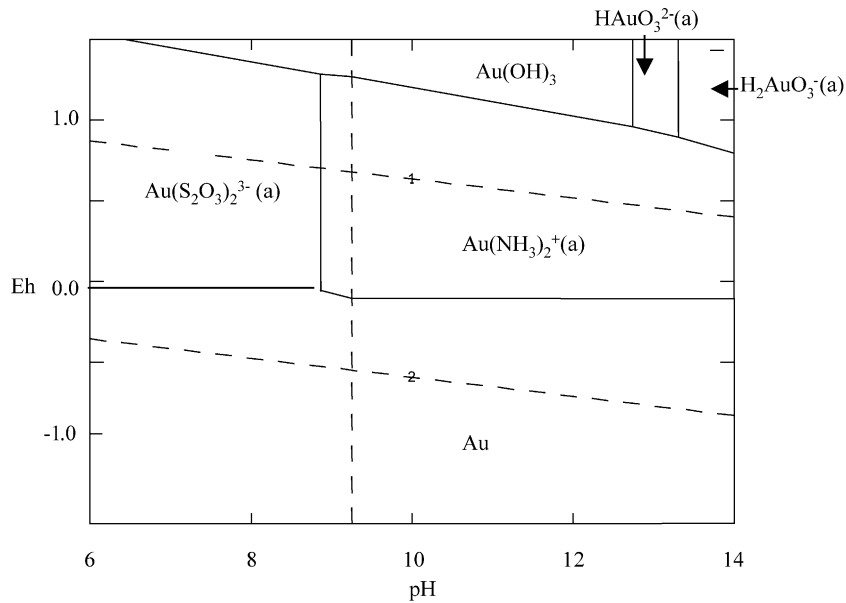


Fig. 5. Eh–pH diagram of the gold–thiosulfate–ammonia–water system at 25 °C. The activities of the species are 2.5×10^{-5} M Au (5 ppm), 0.2 M $\text{S}_2\text{O}_3^{2-}$ and 0.4 M $\text{NH}_3/\text{NH}_4^+$ [$\Delta G_f^\circ(\text{S}_2\text{O}_3^{2-}) = -532.2$ kJ/mol].

for more thermodynamic data for the Au/NH₃/S₂O₃ system.

Fig. 7 shows the copper–ammonia–water system. This Eh–pH diagram represents the leaching

conditions when thiosulfate is no longer present in solution. The copper(I)–ammonia complex appears as a stable species in the area of interest. The areas of the copper(I)–ammonia and copper(II)–ammonia

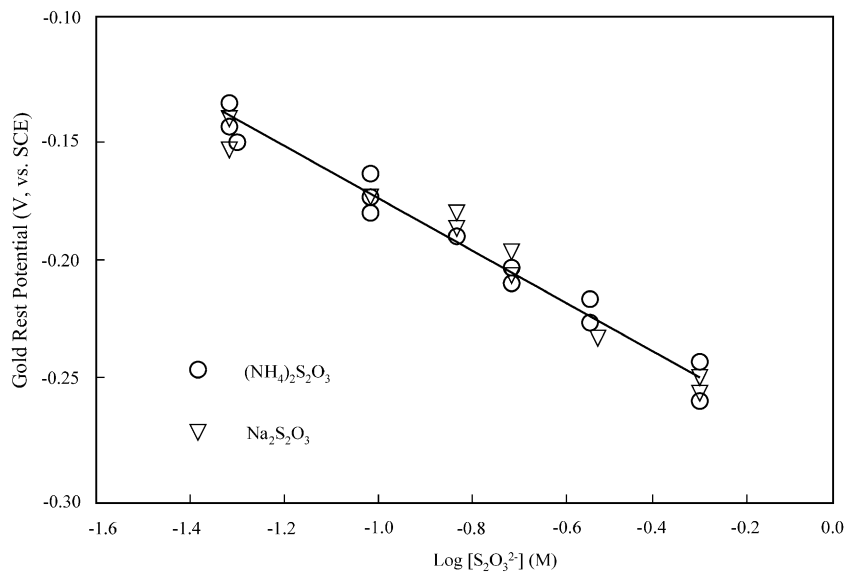


Fig. 6. Effect of thiosulfate concentration on the rest potential of gold (Li et al., 1996).

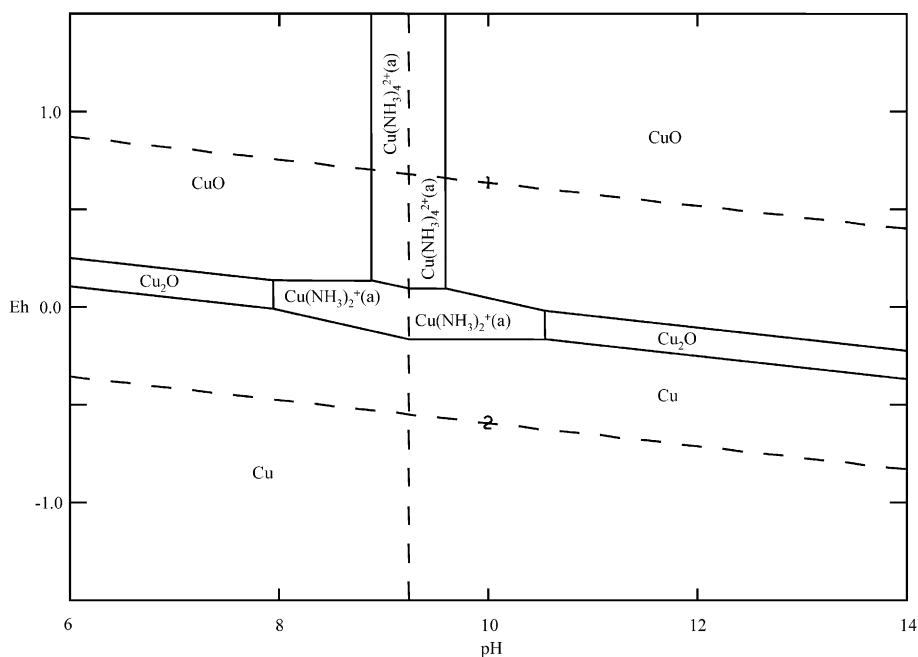


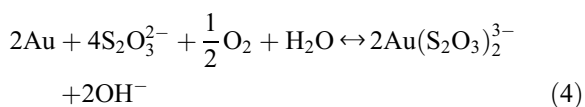
Fig. 7. Eh–pH diagram of the copper–ammonia–water system at 25 °C. The activities of the species are 0.015 M Cu (0.95 g/L) and 0.4 M NH_3 .

decrease in width with higher copper concentrations and lower ammonia concentrations. At very low ammonia concentrations, the stability region of the copper(II)–ammonia complex completely disappears.

2.3.2. Copper catalysis

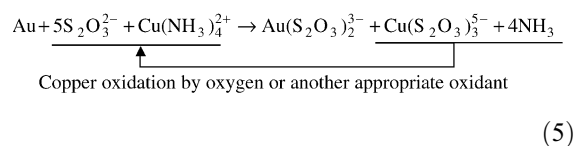
The rate of gold leaching in an ammoniacal thio-sulfate solution is enhanced greatly by a catalytic copper reaction (Berezowsky and Sefton, 1979; Zipperian and Raghavan, 1988; Tozawa et al., 1981). However, conflicting opinions exist on the exact role of the copper in the leach chemistry.

Agreement does exist concerning the dissolution reaction of gold in thiosulfate solutions in the presence of oxygen (Eq. (4)).

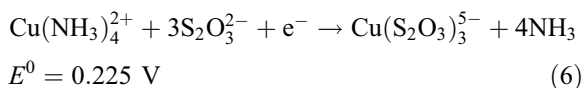


The above reaction can be modified to incorporate the influence of the catalytic action of the cupric ion

during gold dissolution (Marchbank et al., 1996; Li et al., 1995):



Copper minerals in some ores can act as a source of cupric ion or copper sulfate may be added to the leach solutions. The appropriate copper half-cell reaction is:



Li et al. (1996) state that oxygen in the absence of a catalyst may be an oxidant for gold leaching, but with much slower kinetics. It was found that in the absence of copper, the gold leaching rate in ammonium thiosulfate becomes negligible.

At low copper levels, an increase in the copper concentration results in a dramatic rise in the gold

dissolution rate. However, too high copper concentrations significantly inhibit gold leaching. Li et al. (1996) explained this by a deficiency of lixiviant for complexing gold because the copper combines with most of the ammonia and thiosulfate in solution. Furthermore, thiosulfate degradation is accelerated by high copper concentrations (see Section 2.3.3). Either way, loss of reactants results in slower leaching kinetics.

It is evident from Eq. (6) that to enable the regeneration of the cupric ion, it is necessary to keep the concentration ratio of ammonia to thiosulfate in a certain range. Increasing the concentration of only one of the ligands will have a limited positive effect on the gold leaching process. However, this may have a negative effect, as a too high ammonia concentration might stabilize copper as the copper(II)–ammonia complex. A too high thiosulfate concentration might result in the stabilization of copper as the copper(I)–thiosulfate complex, thus, limiting the catalytic action on gold extraction (Eq. (6)).

Jiang et al. (1993) proposed a model for gold dissolution in ammoniacal thiosulfate solutions on the basis of electrochemical investigations. According to this study, ammonia preferentially complexes gold, and the $\text{Au}(\text{NH}_3)^+$, which forms at the anodic surface then reacts with $\text{S}_2\text{O}_3^{2-}$ and is converted to the more stable $\text{Au}(\text{S}_2\text{O}_3)_2^{3-}$. The $\text{Cu}(\text{NH}_3)_4^{2+}$ gains an electron at the cathodic surface and is reduced to $\text{Cu}(\text{NH}_3)_2^+$, which is then oxidized by oxygen into $\text{Cu}(\text{NH}_3)_4^{2+}$ after entering the bulk solution. In this model, a prominent role is ascribed to oxygen in the system, and the effect of the ratio of ammonia to thiosulfate does not seem to play a role on the regeneration of the cupric ion. This is in contradiction to the observations of Li et al. (1996). The two models display the complexity of the ammonia thiosulfate leaching system and the need for more fundamental research.

2.3.3. Thiosulfate degradation reactions

The variables affecting the stability of thiosulfate solutions are (Skoog and West, 1976):

- pH,
- the presence of microorganisms and redox catalysts,
- the thiosulfate concentration of the solution,

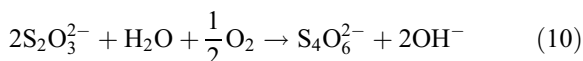
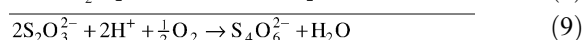
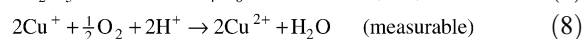
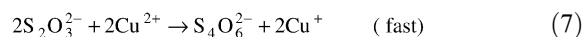
- the presence of oxygen and
- exposure to sunlight.

Experiments indicate that in the absence of strong oxidants or catalysts, the stability of thiosulfate solutions is at a maximum in the pH range between 9 and 10 (Skoog and West, 1976). Bacterial activity appears to be at a minimum at this pH, which explains the maximum stability in this pH region since bacterial activity is reported to be the most prominent cause of instability. Thiosulfate decomposition is catalyzed by copper(II) and iron(III) ions, as well as by the reaction products of the decomposition. Skoog and West (1976) report that the decomposition rate is greater in more dilute solutions.

In the case of oxidative decomposition of thiosulfate, sulfur may exist in many different oxy-sulfur species in the +2 or higher oxidation states. These include $\text{S}_5\text{O}_6^{2-}$ (+2), $\text{S}_2\text{O}_3^{2-}$ (+2), $\text{S}_4\text{O}_6^{2-}$ (+5/2), $\text{S}_2\text{O}_4^{2-}$ (+3), $\text{S}_3\text{O}_6^{2-}$ (+10/3), SO_3^{2-} (+4), $\text{S}_2\text{O}_6^{2-}$ (+5), SO_4^{2-} (+6), $\text{S}_2\text{O}_8^{2-}$ (+7), SO_5^{2-} (+8). Thermodynamically, sulfate is the most stable sulfur species under the preferred leaching conditions (alkaline pH, oxidative potential). This is visible in Fig. 8—the oxidation state diagram for sulfur at several pH values. By drawing a line between HS^- and SO_4^{2-} at pH 10, it is visible that most sulfur species are unstable (all species lie above the line). The nearest species to the line are S^0 and $\text{S}_2\text{O}_3^{2-}$, which indicates the relative stability for these species in the pH 10 range.

Smith and Hitchen (1976) described the oxidation of thiosulfate to tetrathionate in the presence of cupric ion:

or in basic solution:



Tetrathionate may then decompose according to a variety of pathways, leading to the following stoichi-

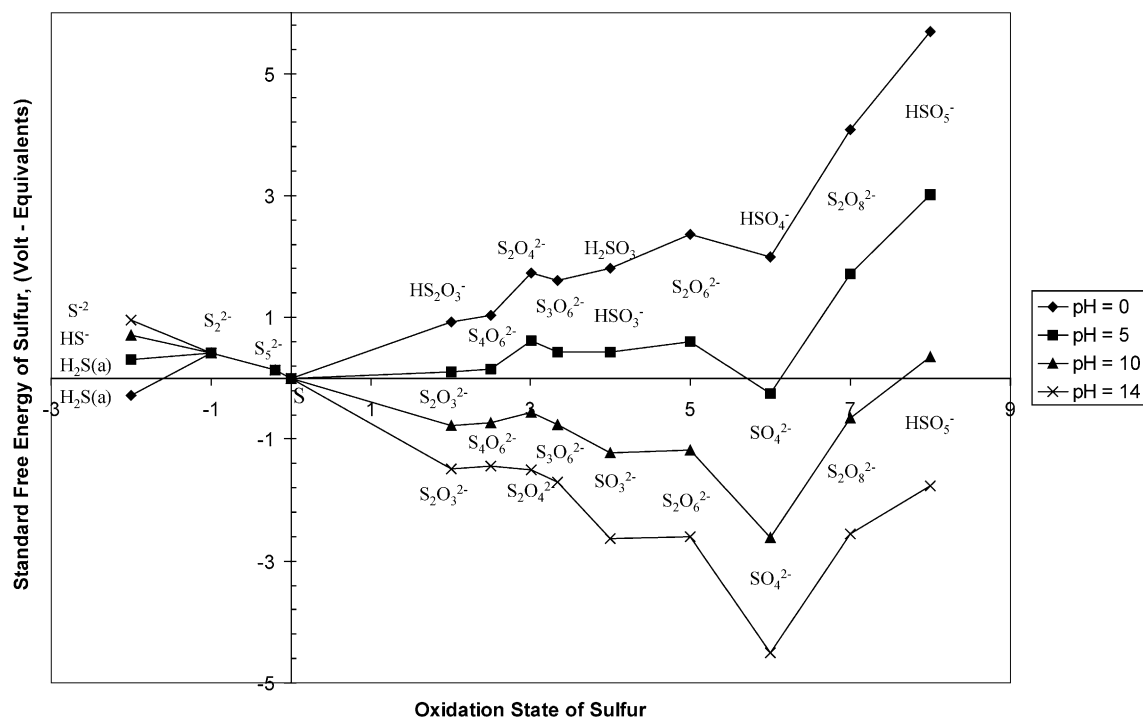
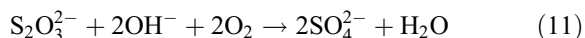
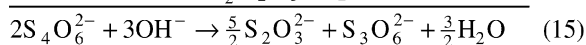
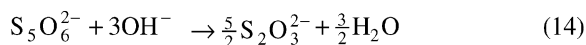
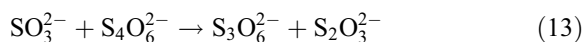
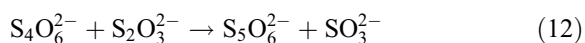


Fig. 8. Oxidation state diagrams for sulfur at several pH values (Peters).

ometry for the overall oxidation of thiosulfate via the tetrathionate pathway:



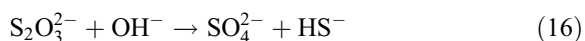
Byerley et al. (1973) cited the following reactions to describe the disproportionation of $\text{S}_4\text{O}_6^{2-}$ to higher and lower polythionates:



These reactions will take place at $\text{pH} > 7$ (Smith and Hitchen, 1976). The trithionate ($\text{S}_3\text{O}_6^{2-}$) species

only decomposes under harsh conditions ($\text{pH} > 13$ and boiling) to form thiosulfate and sulfite. Marsden and House (1992) used Eq. (15) to explain why $\text{S}_2\text{O}_3^{2-}$ is relatively stable under basic conditions.

Pryor (1960) showed that $\text{S}_2\text{O}_3^{2-}$ is relatively stable in basic solution, i.e. in the absence of catalysts. The disproportionation of thiosulfate in water or aqueous buffers at 250–280 °C follows Eq. (16) and is irreversible.

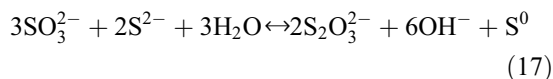


This base hydrolysis was found to be very slow in basic solution, even at 250 °C, and sulfite was found not to be an intermediate in the reaction.

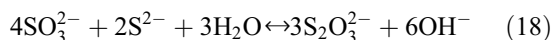
According to several authors the addition of sulfite ions (SO_3^{2-}) to an ammoniacal thiosulfate solution has a beneficial effect on the stability of thiosulfate (Kerley, 1981, 1983; Perez and Galaviz, 1987; Zipperian and Raghavan, 1988; Gong and Hu, 1990). The sulfite ions react with sulfide to regenerate thiosulfate and consequently prevent the precipitation of precious

metal values with the sulfide ions. Different reactions are proposed to explain this effect:

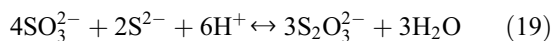
- Zipperian and Raghavan (1988):



- Gong and Hu (1990):



- Kerley (1981, 1983) and Perez and Galaviz (1987):



It is questionable that the reactions described in Eqs. (17)–(19) take place under typical thiosulfate leaching conditions (around pH 9–10, Eh 150–250 mV_{SHE}). Little free sulfide ions and hydrogen sulfide ions will exist at these pH and Eh values (Fig. 2). Eq. (19) describes the formation of thiosulfate under acidic conditions. This is unlikely since thiosulfate tends to hydrolyze under acidic conditions (Skoog and West, 1976).

There are a few reactions in which sulfite can participate. An advantage of sulfite addition can be the oxidation of sulfite to sulfate (Eq. (20)). When this reaction is kinetically favored over the oxidation of thiosulfate to sulfate, sulfite can improve the stability of thiosulfate in solution. However, lowering of the oxygen input would achieve the above also.



A further beneficial effect of sulfite addition is described by Wasserlauf and Dutrizac (1982). Sulfite ions accelerate the decomposition of $\text{S}_x\text{O}_6^{2-}$, $x \geq 4$, in alkaline to mildly acidic solutions. The products are trithionate, thiosulfate and protons. The reaction with tetrathionate is given in Eq. (13). Also, elemental sulfur may react with sulfite under alkaline conditions, to form thiosulfate (Eq. (21)) (Wasserlauf and Dutrizac, 1982):



Several authors described the substitution of sulfate for sulfite, in order to stabilize thiosulfate (Cao et al., 1992; Gong and Hu, 1990). Since sulfate is quite

stable toward reduction (Burns et al., 1981), no effect of sulfate with respect to thiosulfate degradation would be anticipated.

2.3.4. Summary of the ammonium thiosulfate system chemistry

From the above overview on the chemistry of the ammonium thiosulfate system, it is apparent that the chemistry is very complex and poorly understood. More data are required to accurately describe the Au/Cu/NH₃/S₂O₃ system. Similar observations can be made regarding the exact role of copper in the leach chemistry. It is generally accepted that the cupric ion catalyses the dissolution of gold in an ammonium thiosulfate solution. However, at the same time, it has to be remembered that copper catalyses the degradation of thiosulfate in solution. The exact degradation pathways of thiosulfate are very complex, many reactions are possible between existing and generated species in solution. The reactions quoted by the literature do not reflect this complexity, and even tend to simplify the reactions taking place.

3. Materials

To study the application of ammonium thiosulfate for the treatment of copper–gold ores an experimental program consisting of three different sets of experiments was performed. First, the leaching behaviour of sulfide (chalcocite, covellite, chalcopyrite and enargite) and oxide (cuprite and malachite) copper minerals in the ammonium thiosulfate system was studied. It has been reported that copper plays a catalytic role during a thiosulfate leach. However, no information is available regarding the leaching of copper minerals in an ammonium thiosulfate solution.

Samples of naturally occurring copper minerals were obtained. The copper and iron content, and main mineral phases present, determined by XRD, are summarized in Table 2.

To observe the behaviour of gold in combination with the copper minerals, soluble gold (from a nitric acid reference standard solution) was added to the leach solutions in a second set of experiments. The experimental program was completed by subjecting several copper–gold samples of different copper and gold grades to the ammonium thiosulfate system. The

Table 2
Composition of copper mineral samples for testwork

Mineral sample	Cu (%)	Fe (%)	Mineral phases
Covellite (CuS)	63.1 (66.4)	2.5 (0)	Covellite, Chalcocite
Chalcocite (Cu ₂ S)	53.9 (79.8)	8.43 (0)	Chalcocite, Bornite (Cu ₅ FeS ₄)
Chalcopyrite (CuFeS ₂)	28.5 (34.6)	27.7 (30.4)	Chalcopyrite
Enargite (Cu ₃ AsS ₄)	23.2 (48.4)	7.0 (0)	Enargite, Chalcopyrite
Cuprite (Cu ₂ O)	38.9 (88.8)	13.9 (0)	Cuprite, Goethite (FeOOH)
Malachite (Cu ₂ (CO ₃)(OH) ₂)	47.7 (57.5)	0.6 (0)	Malachite

Values in brackets represent the percentage of Cu or Fe in a 100% pure mineral.

following copper–gold concentrates and ores were obtained for the leaching studies:

- Overall Lobo Composite from Teck
- Guanaco Composite from Amax Gold
- M10 Pyrite Concentrate from Newcrest Mining

Gold and copper content and the copper mineral phases present in the samples are listed in Table 3.

The Overall Lobo Composite and Guanaco Composite are whole ores, whereas the M10 Pyrite Concentrate is a flotation product. Mineralogical examination of the Overall Lobo Composite revealed that the ore was characterized by highly altered rock fragments and lesser granular vein quartz with minor

finely disseminated sulfides and iron oxides/oxyhydroxides. Copper mineralization was dominated by chalcopyrite (CuFeS₂, 76%), with minor covellite (CuS, 24%), trace chalcocite (Cu₂S, <1%) and rare bornite (<0.2%). Trace gold/electrum was identified as small grains (<15 µm), and was found associated with silicates and iron oxides/oxyhydroxides (Lakefield Research, 1997).

The Guanaco Composite was comprised of rather strongly oxidized ore with minor remnant pyrite (FeS₂), enargite (Cu₃AsS₄) and sphalerite (ZnS). The oxidation suite includes goethite (FeOOH), with lesser amounts of psilomelane (BaMn²⁺Mn⁴⁺₈O₁₆(OH)₄), cuprite (Cu₂O) and copper oxysalts minerals (malachite (Cu₂(CO₃)(OH)₂), azurite (Cu₃(CO₃)₂(OH)₂) and olivenite (Cu₂(AsO₄)(OH)) (Honea, 1998). No information is available about the gold occurrence or association in this composite.

The M40 Pyrite Feed was characterized by 78% pyrite (FeS₂) and 10% quartz (SiO₂). Some minor chalcopyrite (CuFeS₂, 1.6%) and calcite (CaCO₃, 1%) was present and the remainder was comprised of mainly clay minerals. The M10 Pyrite Concentrate was found to be similar with 76% pyrite and 7% quartz as the main minerals present. Minor chalcopyrite (1.6%) and calcite (2.5%) and some dolomite (CaMg(CO₃)₂, 5.0%) were identified (Oretest, 1997). Details regarding gold association are not available for these concentrates.

For comparative purposes, the cyanide consumption and copper and gold extraction of the copper–gold materials were determined by a 24-h cyanide leach at a constant 1 g/L cyanide level. The results are summarized in Table 4.

Table 3
Composition of copper–gold concentrate and ore samples

Copper–gold samples	Au (ppm)	Cu (ppm)	Cu mineral phases
Overall Lobo Composite (Lakefield Research Limited, 1997)	2.11	1120	Chalcopyrite, Covellite, Chalcocite
Guanaco Composite (Honea, 1998)	2.06	3320	Enargite, Cuprite, Malachite
M10 Pyrite Concentrate (Molleman, 1998)	45.5	16,600	Chalcopyrite

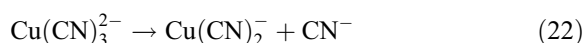
Table 4
Results of 24-h cyanide leach of the copper–gold samples

Copper–gold samples	Gold extraction (%)	Copper extraction (%)	Cyanide consumption (kg/t ore)
Overall Lobo Composite	81.4	41.4	4.38
Guanaco Composite	84.3	70.4	6.77
M10 Pyrite Concentrate	47.5	28.3	9.91
M10 Pyrite Concentrate ^a	81.2	50.3	n.a.

^a Data obtained from Newcrest Mining.

Cyanide leaching of all copper–gold samples resulted in high cyanide consumption and, consequently, a high reagent cost must be anticipated when treating these samples with cyanide. It can be seen that a substantial amount of the copper in all samples is cyanide soluble.

Two test numbers are listed for the M10 Pyrite Concentrate. The first was obtained during the leach described, the second was provided by Newcrest Mining, a 24-h cyanidation at an initial cyanide concentration of 1.25 g/L cyanide, maintained at 0.75 g/L cyanide. The first number for gold extraction is believed to be low because of the following reaction:



During the test, the free cyanide concentration was determined by titration. Because of the above reaction, the presence of free cyanide was observed, while in reality it was complexed with copper and consequently unavailable for leaching.

4. Experimental

A schematic diagram of the experimental set-up used for the batch leaching tests is given in Fig. 9. The experiments were carried out in a 1500-ml cylindrical glass vessel with a removable high-density polyethylene lid. The vessel was vertically baffled with a baffle width of 1/10 the tank diameter. The baffles were made of acrylic. The solutions were stirred by a stainless steel Rushton impeller (35 mm diameter, 1/3 of the vessel diameter, six blades) on a stainless steel shaft connected to a variable speed DC motor. All experiments were performed at an impeller speed of 1700 RPM. It was experimentally determined that this was the minimum impeller speed required for complete particle suspension.

Unless otherwise stated, experiments were performed at 35 °C. The glass vessel was placed in a water bath heated by an immersion heater connected to a PID controller. A thermocouple was placed in the reactor to provide temperature control. Air was added to the solutions via a stainless steel sparger placed directly under the Rushton impeller. A gas flowmeter controlled the flow of air into the

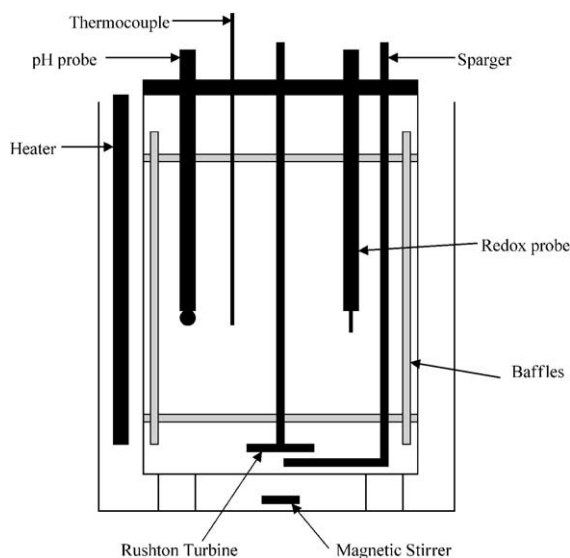


Fig. 9. Schematic diagram of the batch leaching experimental set-up.

reactor. A gel-filled combination pH probe with a silver/silver chloride reference electrode was used to monitor the pH of the solutions. The redox potential was measured using a platinum combination redox electrode with a silver/silver chloride reference electrode.

4.1. Experimental procedure

4.1.1. Leaching test

The testwork involved the leaching of the copper minerals in 1 L of deionized water. Depending on the copper content of the different minerals (Table 2), sufficient mineral feed was added to the solution such that upon 100% copper dissolution, the copper concentration would be either 5 or 1 g/L copper. A narrow particle size range of 53–63 µm was used. The 5 g/L value was initially chosen as a representative amount for an industrial application. This amount was later adjusted to 1 g/L to enable the observation of the leaching of copper with both thiosulfate and ammonia.

The initial slurry of copper mineral feed was heated to the desired temperature. Once the desired temperature was attained, aeration of the slurry was initiated (0.23 L/min), and the ammonium thiosulfate was added. The pH of the slurry was adjusted to 10 for all experiments with concentrated sodium hydroxide.

Table 5

Overview of experiments with copper minerals and gold addition

Copper mineral	Baseline	No aeration	Temperature 20 °C	0.4 M NH ₃	0.05 M SO ₃ ²⁻	0.05 M SO ₄ ²⁻
Covellite	×					
Chalcocite	×	×	×	×	×	×
Chalcopyrite	×					
Enargite	×					
Cuprite	×	×	×			
Malachite	×					

This marked time zero. The pH was allowed to drift in all experiments. The experimental procedure for the series of experiments with gold addition is similar to that described above with the exception that 5 ppm of gold from the standard reference was added to the deionized water. The experiments involving the concentrates were performed at a pulp density of 30% by weight.

Slurry samples were withdrawn at 30, 60, 120, 180, 240 and 360 min, centrifuged and prepared for copper, gold, thiosulfate, tetrathionate and sulfate analysis. Unless otherwise stated, the experiments lasted 6 h, after which the solution was filtered. The residues and the wash water were collected. The amount of residue remaining after the experiments involving the copper minerals was not deemed sufficient for copper analysis. For the experiments involving the copper–gold samples, the wash water samples were analysed for gold content and the residues were analysed for copper and gold. The following parameters were evaluated in the different test series: aeration, leach temperature, reagent addition (copper as cupric, sulfate, sulfite and ammonia).

4.1.2. Experimental design

Test conditions for the experiments with the copper minerals tests incorporated: aeration of the system, 0.2 M ammonium thiosulfate, pH 10 (uncontrolled), a

copper mineral addition, which would achieve 5 or 1 g/L copper upon 100% dissolution and 35 °C. The experiments lasted 6 h. Two experiments were performed without aeration.

The experiments with copper minerals and gold addition were performed under the same conditions as the copper mineral experiments. However, several other parameters were evaluated in this test series; aeration, leach temperature, ammonia concentration, sulfite concentration and sulfate concentration (Table 5).

Baseline experiments of the copper–gold samples included: aeration of the system, 0.2 M ammonium thiosulfate, pH 10 (uncontrolled), 30% pulp density and 1 g/L copper addition (as cupric (CuSO₄·5H₂O)) and 6 h. The parameters studied in this series are (see Table 6): aeration of the system, leaching time, ammonia thiosulfate concentration, copper addition and ammonium thiosulfate grade.

4.1.3. Analysis

All solution samples were analysed for thiosulfate, tetrathionate and sulfate by high performance liquid chromatography (HPLC) methods directly following the experiment. A Dionex Series 4500i Chromatograph was used for the analysis. The IonPac AS4A-SC analytical column and IonPac AG4A-SC guard column combined with a conductivity detector and

Table 6

Overview of experiments with copper–gold samples

Copper–gold samples	Baseline	No aeration	No aeration (24 h)	No cupric	No aeration, no cupric	Extra ATS ^a	Thiogold™ Grade
Overall Lobo Composite	×	×		×			
Guanaco Composite	×	×		×			×
M40 Pyrite Feed	×	×		×	×		
M10 Pyrite Concentrate	×	×	×	×		×	

^a Ammonium thiosulfate.

anion micro membrane suppressor were used for sulfate analyses. An OmniPac PAX-100 analytical and OmniPac PAX-100 guard column with a UV detector was used for thiosulfate and tetrathionate determination (Molleman, 1998).

Atomic absorption spectrophotometry (AAS) was used to determine the copper and gold content of the solution samples. The copper content of the residues was determined by acid digestion and AAS analysis of the resulting solution. Gold content of the residues was determined by fire assay, cupellation and AAS.

5. Results

5.1. Copper minerals

The recorded pH and Eh data for the experiments with chalcocite at 1 g/L copper addition are presented in the left graph of Fig. 10. The corresponding sulfur species in solution and copper extraction and gold solubilization are shown in the right graph. Gold solubilization is represented, not extraction, since soluble gold was added. The negative time on this plot reflects the heating of the solution to 35 °C, in the absence of reagents. The large increase of pH and sharp decrease of the Eh result from the reagent addition.

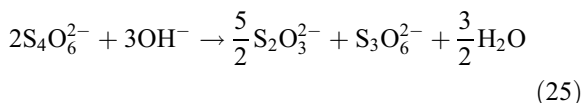
The solution pH is influenced by several reactions, which occur simultaneously.

- The oxidation of thiosulfate to tetrathionate (Eq. (23)), coupled with the reduction of oxygen to

hydroxide (Eq. (24)), resulting in the production of hydroxide ions:



- Concurrently, hydroxide will be consumed by the hydrolysis of tetrathionate in a basic solution:



- Hydroxide is also consumed because ammonia is removed from the system due to evaporative losses and complexation reactions. The equilibrium depicted in Eq. (26) changes accordingly:



The reactions depicted in Eqs. (23) and (24) are dominant while thiosulfate is present. When the thiosulfate is gone, the hydroxide consuming reactions become more prominent and consequently, the pH decreases. The pH rise and fall in Fig. 10 are consistent with this sequence of reactions. The pH increases as long as thiosulfate is present, followed by a pH decrease around the same time that thiosulfate was no longer detected in solution.

A closer look at Fig. 10 reveals that the Eh remains constant for a long time and then suddenly increases around 230 min. This time coincides with the instant

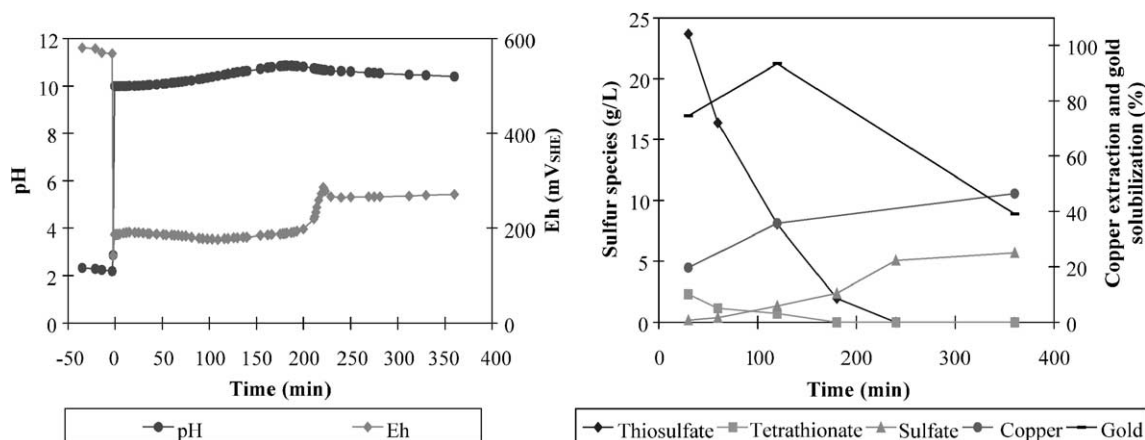


Fig. 10. Leaching results for chalcocite, 5 ppm gold, 1 g/L copper, 0.20 M $(\text{NH}_4)_2\text{S}_2\text{O}_3$, aeration, 35 °C.

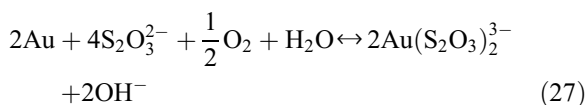
that the pH starts to drop and thiosulfate is no longer present. Further, the colour of the leach solution changed: after about 180 min the solution colour changes from colourless to light blue indicating that the copper(II)–ammonia complex has formed. Moreover, the copper extraction curve shows a steady increase after thiosulfate has disappeared, which can only be explained by copper complexing with ammonia, since there is no thiosulfate present in solution. It can be remarked that the copper extraction is low.

Fig. 7, showing the Eh–pH diagram of the copper–ammonia system at 25 °C, can be used to interpret these results. However, one has to remember that the EMF value was measured in an air-agitated system and represents a mixed potential of all redox couples sensed by the platinum electrode. Therefore, direct comparison with the theoretical EMF value must be made with caution. It can be seen from Fig. 10 that the copper concentration is about 0.006 M. Therefore, the stability regions of the copper(I)–ammonia and copper(II)–ammonia complexes are slightly larger than represented in Fig. 7. The pH and Eh values measured indicate that it is likely that the copper(I)–ammonia complex forms under these conditions. The copper(I)–ammonia complex oxidizes rapidly, in the presence of sufficient oxygen, to form the copper(II)–ammonia complex, explaining the colour change of the solution and the Eh increases.

For most of the experiments, the pH and Eh trends described above are applicable, except for the leaching of enargite (Fig. 11). However, this figure also confirms the reactions suggested above. No decrease

in pH is observed, which indicates that thiosulfate was present throughout the entire experiment, which was confirmed by solution analysis. Consequently, no change in Eh value should occur, which is confirmed by the Eh curve in Fig. 11.

At the moment that thiosulfate is no longer present in solution, the following reaction is driven to the left and gold precipitates, unless it is complexed by something else in solution:



Thermodynamically, ammonia should be able to complex the gold. However, Meng and Han (1993) have shown that the formation of the gold ammonia complex under atmospheric conditions is slow. Gold extraction drops once thiosulfate disappears. The discussion in Section 2.3.1 already indicated that it is likely that Fig. 3 represents the actual solution conditions more accurately than Fig. 4. However, Fig. 10 indicates that some gold stays solubilized, although it appears that there is no free thiosulfate present in solution. Several explanations can be given for this phenomenon:

- Ammonia complexes gold to a certain extent. The literature reports 10–20% gold extraction in the presence of ammonia and cupric ions (Kerley, 1983; Cao et al., 1992).
- Gold precipitates as colloidal gold and is, therefore, detected in solution.

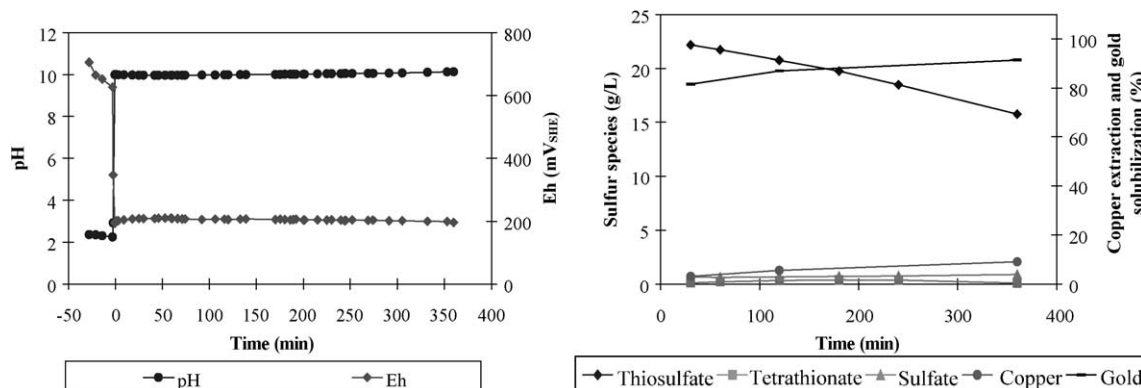


Fig. 11. Leaching results for enargite, 5 ppm gold, 1 g/L copper, 0.20 M (NH₄)₂S₂O₃, aeration, 35 °C.

- There is still a small amount of thiosulfate left in solution not detected by ion chromatographic analysis, providing enough background for gold to remain in solution to a certain extent.

Some results of the experiments involving the copper minerals are presented in Table 7. All extraction calculations are based on solution volume, solution analytical data and head assays of the copper minerals. Table 8 reports the results of the leaching of chalcocite under various conditions.

It can be observed that the leaching of chalcopyrite, enargite and covellite results in low copper extractions. Significant thiosulfate concentrations were detected in solution after 360 min with corresponding high gold solubilizations (see as example Fig. 11).

Leaching of chalcocite, cuprite and malachite gave higher copper extractions, but insignificant thiosulfate concentrations were detected in solution, which correlates to the lower gold solubilizations detected (see as example Fig. 10). The higher copper concentrations achieved during the leaching of those three minerals increased the presence of cupric ion in solution, which enhances the degradation of thiosulfate.

No beneficial effect of lower temperature, sulfite and sulfate addition on thiosulfate stability was observed (see Table 8). Lower copper extractions with 1 g/L copper addition were observed compared to the copper extractions achieved with 5 g/L copper addition. Extra addition of ammonia did improve copper extraction but indications are that the thiosulfate stability decreased (Table 8).

Table 7

Copper extractions and thiosulfate concentrations of copper minerals at different times (5 ppm soluble gold addition, 0.20 M $(\text{NH}_4)_2\text{S}_2\text{O}_3$, aeration)

Mineral	Feed addition (g/L Cu)	Percent copper extracted at time (min)			Thiosulfate concentration (g/L) at time (min)		
		30	120	360	30	120	360
Covellite	1	8.8	14.3	15.1	21.2	18.9	2.93
Chalcocite	5	29.5	26.3	18.3	3.3	3.8	0.1
Chalcocite	1	19.7	35.7	46.4	23.7	8.0	0
Chalcopyrite	1	3.78	9.9	14.5	22.2	21.1	12.7
Enargite	1	3.19	5.7	9.2	22.2	20.8	15.8
Cuprite	5	80.9	32.2	24.4	1.95	2.7	0.1
Malachite	1	87.0	86.1	83.5	0.2	2.8	0

Table 8

Copper extractions and thiosulfate concentrations of chalcocite at different times

Mineral	Feed addition (g/L Cu)	Percent copper extracted at time (min)			Thiosulfate concentration (g/L) at time (min)		
		30	120	360	30	120	360
Chalcocite, aeration	5	29.5	26.3	18.3	3.3	3.8	0.1
Chalcocite, aeration	1	19.7	35.7	46.4	23.7	8.0	0
Chalcocite, no aeration	5	3.2	5.7	12.6	21.2	19.1	19.8
Chalcocite, 20 °C	5	18.2	36.5	39.3	19.9	8.6	0
Chalcocite, 0.05 M SO_3^{2-}	5	14.6	34.9	47.4	20.2	7.7	0
Chalcocite, 0.05 M SO_4^{2-}	5	19.7	35.7	44.6	21.4	12.2	0
Chalcocite, 0.4 M NH_3	5	39.6	38.4	51.0	15.9	1.9	0

It can be concluded that for the gold–thiosulfate–ammonia–water system Fig. 3 (using the free energy value of -518.8 kJ/mol for thiosulfate) gives a more accurate representation of the actual leaching conditions compared to Fig. 5 (using the free energy value of -532.2 kJ/mol for thiosulfate).

5.2. Copper–gold samples

The leaching of the Overall Lobo Composite results in moderate gold extractions (Table 9). The absence of both aeration and cupric ion addition has a positive effect on the thiosulfate stability and results in the case of no cupric ion addition (with aeration), in a gold extraction of 74%. Copper in this composite seems to be unreactive towards ammonium thiosulfate leaching, which confirms the testwork described in Section 5.1 since chalcopyrite, covellite and chalcocite are the copper mineral phases in the sample.

From Table 9, when comparing the aerated, de-aerated and no-cupric addition testwork results, indications are that most of the copper(II) sulfate initially added to the leach solution precipitates. Compared to the cyanidation results (81.4% Au, 41.4% Cu after 24 h) similar gold extractions are achieved in the experiment with aeration and no cupric ion addition. Copper extractions with the ammonium thiosulfate leach are very low compared to the cyanidation.

Table 9

Gold and copper extraction (%) of Overall Lobo Composite at different times

Experimental conditions	Percent gold extracted at time (min)				Percent copper extracted at time (min)		
	30	120	360	Total ^a	30	120	360
Aeration	42.0	41.6	41.2	62.1	36.9	20.4	11.6
Aeration, duplicate	16.2	15.9	15.5	44.8	35.0	13.8	11.3
No aeration	b.d.	b.d.	35.8	n.a.	48.0	48.6	48.7
Aeration, no cupric	34.6	67.9	66.0	73.5	9.3	11.7	12.6
Aeration, no cupric, duplicate	b.d.	34.2	66.5	74.3	7.9	10.4	12.6

b.d. = below detection limit, n.a. = not available.

^a Total represents total gold extraction, including wash water.

A 24-h experiment was performed with no forced aeration. The thiosulfate consumption was around 15.7 kg/ton ore, which results in a reagent cost of US\$2.04/ton ore ((NH₄)₂S₂O₃ at US\$0.13/kg). The concentrate contains 2.11 g/ton gold, which yields US\$20.3/ton (at US\$300/oz gold). Thus, the reagent cost constitutes about 10% of the total metal value. Cyanidation would result in a reagent cost of US\$7.88 (cyanide consumption of 4.38 kg/ton ore). Thiosulfate leaching compares favourably to cyanidation for this experiment.

Table 10 lists the results of the leaching of the Guanaco Composite. Initial gold extractions are higher in an aerated system, while final extractions are higher in a nonaerated system. In the presence of thiosulfate (nonaerated system) higher copper extractions are

Table 10

Gold and copper extraction (%) of Guanaco Composite at different times

Experimental conditions	Percent gold extracted at time (min)				Percent copper extracted at time (min)		
	30	120	360	Total ^a	30	120	360
Aeration	33.6	33.0	b.d.	0.0	47.0	34.9	32.5
No aeration	b.d.	b.d.	39.6	44.0	9.0	28.7	59.2
Aeration, no cupric	51.6	50.6	24.6	30.7	30.4	31.5	24.7

b.d. = below detection limit.

^a Total represents total gold extraction, including wash water.

achieved. The copper extractions achieved are higher compared to the copper extractions of the Overall Lobo Composite, confirming the testwork described in Section 5.1: cuprite and malachite are the copper mineral phases present in the sample. Compared to the cyanidation results (84.3% Au, 70.4% Cu at 24-h cyanidation) the gold extractions are low. For this composite, the experiment with no forced aeration should be extended to a 24-h leach, enabling a more accurate comparison with the cyanidation test results.

Table 11 summarizes the copper and gold extractions achieved with the M10 Pyrite Concentrate. The combination of aeration and cupric addition results in high gold extraction (80%) early in the experiment (around 120 min), but is followed by gold precipitation due to the degradation of thiosulfate. Similar gold extractions were obtained in a 24-h leach without aeration and a leach with a total addition of 0.72 M thiosulfate.

Low copper extractions were expected since chalcopyrite is the main copper mineral. The slightly higher copper concentrations compared to the Overall Lobo Composite can be explained by the higher chalcopyrite concentrations in the M10 sample (16,600 vs. 1120 ppm). Total copper extraction is not significantly influenced by any of the variables tested: cupric addition, aeration, leaching time, reagent concentration.

A 24-h leach was performed. The gold extractions achieved during the 24-h leach compare very well to the cyanidation test results (81.4% Au, 50.3% Cu at 24 h). It should be noted that the resulting copper

Table 11

Gold and copper extraction (%) of M10 Pyrite Concentrate at different times

Experimental conditions	Percent gold extracted at time (min)				Percent copper extracted at time (min)		
	30	120	360	Total ^a	30	120	360
Aeration	39.2	87.1	5.9	7.2	21.2	20.5	27.4
No aeration	14.1	29.7	50.0	55.6	20.1	20.8	21.0
No aeration, 24 h	13.2	29.8	76.1 ^b	83.3	20.3	21.6	21.7 ^b
Aeration, no cupric	39.8	49.3	3.99	5.8	11.9	12.9	23.6
0.72 M (NH ₄) ₂ S ₂ O ₃	49.1	74.3	76.1	84.4	23.6	25.5	29.2

^a Total represents total gold extraction, including wash water.^b At time 1440 min (24 h).

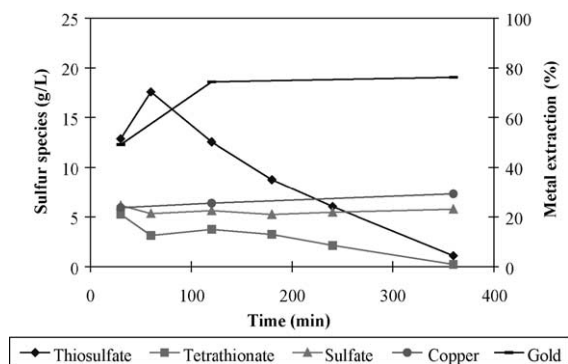


Fig. 12. M10 Pyrite Concentrate, 0.72 M $(\text{NH}_4)_2\text{S}_2\text{O}_3$, 1 g/L cupric addition, aeration, 35 °C.

extractions are very low. The thiosulfate consumption for the 24-h experiment was around 40 kg/ton ore, which results in a reagent cost of US\$5.2/ton ore. The concentrate contains 45.5 g/ton gold, which yields US\$436/ton (at US\$300/oz gold). Thus, the reagent cost constitutes about 1.2% of the total metal value.

5.3. Sulfur balance

A closer examination of the curves representing the sulfur species of the experiments discussed above, reveals that not all the sulfur that was added to the solution (0.2 M ammonium thiosulfate) is accounted for by the sulfur species detected by the ion chromatograph. A good example is given in Fig. 12, the leaching of the M10 Pyrite Concentrate with a total addition of 0.72 M ammonium thiosulfate. After 360 min, a negligible amount of thiosulfate and tetrathionate is detected and about 5 g/L sulfate. Since the experiment indicates that thiosulfate degrades, it was expected that a large amount of tetrathionate and sulfate would be present. If all the thiosulfate converts to sulfate, 138 g/L of sulfate should be present. However, the ion chromatography analyses did not detect high concentrations of either sulfate or tetrathionate.

The sulfur balances for all experiments were calculated, which clearly indicated that the sulfur accounting for most experiments was not correct. To investigate

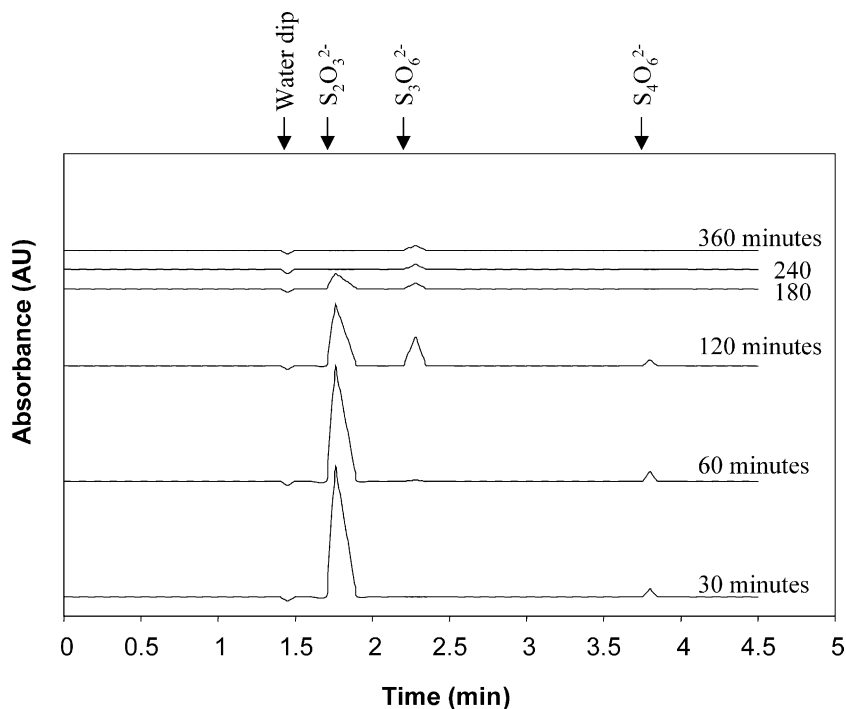


Fig. 13. Ion chromatograms showing thiosulfate, trithionate and tetrathionate peaks at different times during the leaching of 1g/L chalcocite with 5 ppm gold addition.

where the sulfur reported to, several leach solutions were analyzed for sulfate using barium chloride (Jefrey et al., 1989). The experiments indicated that the sulfate levels were not significantly different from the ion chromatograph analyses. Several copper mineral residues were analysed for sulfur species (S^{total} , S^0 and S^{2-}) to determine whether the sulfur reported to the residues. The analyses showed that the sulfur levels did not increase significantly in the residues.

Several solutions were also analyzed for total sulfur and these results indicated that the sulfur was still present in solution. The ion chromatograph detected along with the thiosulfate, tetrathionate and sulfate species, two other sulfur species: sulfite (SO_3^{2-}) and trithionate ($S_3O_6^{2-}$). The sulfite peak appears just before the sulfate peak on the ion chromatogram and the trithionate appears between the thiosulfate and tetrathionate peak (Fig. 13).

At first glance, it seems unlikely that these ions are present at high concentrations, since their peak area is very small (Fig. 13). However, a study by Steudel and Holdt (1986) indicated that the response factor of trithionate is about 18 times lower than that of tetrathionate. This means that when trithionate and tetrathionate have the same area, the trithionate concentration is 18 times larger. Using this knowledge, the sulfur balance was recalculated for several experiments. This recalculation essentially closed the sulfur mass balance.

This indicates that the decomposition of tetrathionate to higher and lower polythionates, as presented in Eq. (15) takes place (Section 2.3.3):

Further work on thiosulfate and tetrathionate degradation is required to support the above.

6. Conclusions

The experiments indicate that aeration is a key control parameter during the leaching of a copper–gold ore in an ammonium thiosulfate solution. High initial gold extractions but low final gold concentrations were achieved in a forced aerated system. Extended retention times and surface aeration of the leach slurry resulted in increased gold extractions.

The gold extractions depend on the presence of thiosulfate in solution. Ammonia is known as a complexing agent for gold, but does not appear to play a role under the experimental conditions inves-

tigated. Forced aeration of the leach solution results in the generation of cupric ions, which catalyze thiosulfate degradation with subsequent decreasing gold extractions. Thiosulfate degradation is reduced in the absence of forced aeration, even in the continuing presence of high copper concentrations. Therefore, it can be concluded that a balance has to be found between providing enough oxidant for fast gold dissolution, and minimizing the amount of oxidant in the presence of cupric ions to prevent excessive thiosulfate degradation. The alternative is slow gold dissolution and low thiosulfate consumption in a surface aerated system with extended residence time.

Leach temperatures of 20 °C instead of 35 °C did not result in a measurable effect on thiosulfate degradation, copper extraction and gold solubilization. Furthermore, the addition of sulfite and sulfate was not observed to affect thiosulfate stability in this study, as suggested in the literature.

The copper–gold samples tested did not show appreciable coextraction of copper during an ammonium thiosulfate leach. Compared to the cyanidation test results, the ammonium thiosulfate treatment of the Overall Lobo Composite and M10 Pyrite Concentrate showed that similar gold extractions were achieved at lower reagent cost.

Acknowledgements

The financial support provided by Barrick Gold, Kinross Gold, Newcrest Mining Normandy Mining, Placer Dome, Teck and Tessenderlo Kerley is gratefully acknowledged.

References

- Atluri, V.P., 1987. Recovery of gold and silver from ammoniacal thiosulfate solutions containing copper by resin ion exchange method. Masters of Science thesis, University of Arizona.
- Avraamides, J., 1982. Prospects for alternative leaching systems for gold, "a review". Carbon-in-Pulp Technology for the Extraction of Gold. The Australasian Institute of Mining and Metallurgy, Melbourne, Murdoch, Australia, pp. 369–391, July.
- Bard, A.J., Parsons, R., Jordan, J., 1985. Standard potentials in aqueous solution. International Union of Pure and Applied Chemistry.
- Berezowsky, R.M., Gormely, L.S., 1978. Recovery of precious metals from metal sulfides. US Patent 4,070,182, January 24.

- Berezowsky, R.M.G.S., Sefton, V.B., 1979. Recovery of gold and silver from oxidation leach residues by ammoniacal thiosulfate leaching. 108th AIME Annual Meeting, New Orleans, TMS, Warrendale, PA, February 18–22.
- Burns, D.T., Townshend, A., Carter, A.H., 1981. Reactions of the Elements and their Compounds: Part. B. Osmium to Zirconium. Inorganic Reaction Chemistry, vol. 2. Ellis Horwood, Chichester, UK, pp. 421–423.
- Byerley, J.J., Fouda, S.A., Rempel, G.L., 1973. Kinetics and mechanism of the oxidation of thiosulfate ions by copper-II ions in aqueous ammonia solution. Journal of the Chemical Society. Dalton Transactions, 889–893.
- Cao, C., Hu, J., Gong, Q., 1992. Leaching of gold by low concentration thiosulfate solution. Transactions of Nonferrous Metals Society of China 2 (4), 21–25. Nov.
- Duby, P., 1977. The Thermodynamic Properties of Aqueous Inorganic Copper Systems International Copper Research Association, USA.
- Gong, Q., Hu, J., 1990. Treatment of copper-containing gold sulfide concentrate using thiosulfate solution. Journal of Engineering Chemistry and Metallurgy 2 (11), 145–151.
- Honea, R.M., 1998. Polished Section Examination of P2509 Guanaco Composite. AMAX Gold, Denver, CO, February 6.
- Jeffrey, G.H., Bassett, J., Mendham, J., Denney, R.C., 1989. Vogel's Textbook of Quantitative Chemical Analysis, 5th ed. Longman, Great Britain, p. 490.
- Jiang, T., Chen, J., Xu, S., 1993. Electrochemistry and mechanism of leaching gold with ammoniacal thiosulfate. XVIII Int. Mineral Processing Congress, vol. 5. The Australasian Institute of Mining and Metallurgy, Australia, pp. 1141–1146.
- Kerley, B.J., 1981. Recovery of precious metals from difficult ores. US Patent 4,269,622, May 26.
- Kerley, B.J., 1983. Recovery of precious metals from difficult ores. US Patent 4,369,061, Jan. 18.
- Lakefield Research, 1997. Mineralogical Examination of Overall Lobo Composite. Lakefield Research, Lakefield, Canada, May 15.
- Langhans Jr., J.W., Lei, K.P.V., Lei, Camahan, T.G., 1992. Copper-catalyzed thiosulfate leaching of low-grade gold ores. Hydrometallurgy 29, 191–203.
- Li, J., Miller, J.D., Wan, R.Y., Le Vier, M., 1995. The ammoniacal thiosulfate system for precious metal recovery. Proceedings of the 19th International Mineral Processing Congress, San Francisco. SME, Littleton, CO, Chap. 7.
- Li, J., Miller, J.D., Wan, R.Y., 1996. Important solution chemistry factors that influence the copper-catalyzed ammonium thiosulfate leaching of gold. Presented at the 125th SME Annual Meeting Phoenix, Arizona, March 11–14. SME, Littleton, CO.
- Liddell, D.M., 1945. Handbook of Non-Ferrous Metallurgy. Recovery of Metals, vol. 2. McGraw-Hill, New York, p. 1052.
- Marchbank, A.R., Thomas, K.G., Dreisinger, D., Fleming, C., 1996. Gold recovery from refractory carbonaceous ores by pressure oxidation and thiosulfate leaching. US Patent 5,536,297, July 16.
- Marsden, J., House, I., 1992. The Chemistry of Gold Extraction. Ellis Horwood, New York.
- Meng, X., Han, K.N., 1993. The dissolution behaviour of gold in ammoniacal solutions. Hydrometallurgy, Fundamentals, Technology and Innovation. SME, Littleton, CO, pp. 205–221.
- Molleman, E., 1998. The treatment of copper–gold ores by ammonium thiosulfate leaching. MASC thesis, University of British Columbia.
- Oretest, 1997. Metallurgical Testwork on Telfer M40 and M10 Flotation Samples. Oretest Pty, Perth, Australia, August 18.
- Othmer, K., 1983. Encyclopedia of Chemical Technology, 3rd ed., vol. 22. Wiley, New York, pp. 974–988.
- Perez, A.E., Galaviz, H.D., 1987. Method for recovery of precious metals from difficult ores with copper–ammonium thiosulfate. US Patent 4,654,078, March 31.
- Peters, E., 1988. Oxidation state diagrams. Short course notes, Department of Metals and Materials Engineering, University of British Columbia.
- Pryor, W.A., 1960. The kinetics of the disproportionation of sodium thiosulfate to sodium sulfide and sulfate. Analytical Chemistry, vol. 82. The American Chemical Society, Columbus, Ohio, pp. 4794–4797.
- Skoog, D.A., West, D.M., 1976. Fundamentals of Analytical Chemistry, 3rd ed. Holt, Rinehart and Winston, New York, pp. 363–366.
- Smith, C.W., Hitchen, A., 1976. Aqueous solution chemistry of polythionates and thiosulfate: a review of formation and degradation pathways. CANMET.
- Steudel, R., Holdt, G., 1986. Ion-pair chromatographic separation of polythionates $S_nO_6^{2-}$ with up to thirteen sulfur atoms. Journal of Chromatography 361, 379–384.
- Tozawa, K., Inui, Y., Umetsu, Y., 1981. Dissolution of gold in ammoniacal thiosulfate solution. TMS Paper Selection, A81-25.
- Turnbull, A.G., Wadsley, M.W., 1986. The CSIRO Thermochemistry System Institute of Energy and Earth Resources, Division of Mineral Chemistry, Australia (version V).
- von Michaelis, H., 1987. Gold processing update. The prospects for alternative leach reagents, can precious metals producers get along without cyanide? Engineering and Mining Journal, 42–47, June.
- Wan, R.Y., 1997. Importance of solution chemistry for thiosulfate leaching of gold. Unpublished.
- Wan, R.Y., LaVier, K.M., Clayton, R.B., 1994. Hydrometallurgical process for the recovery of precious metal values from precious metal ores with thiosulfate lixiviant. United States Patent 5,354,359, Oct. 11.
- Wang, X., 1992. Thermodynamic equilibrium calculations on Au/Ag lixiviant systems relevant to gold extraction from complex ores. Electrochemistry in Mineral and Metal Processing III, St. Louis, Missouri, 17–22 May. The Electrochemical Society, USA, pp. 452–477.
- Wasserlauf, M., Dutrizac, J.E., 1982. The chemistry, generation and treatment of thiosalts in milling effluents—a non-critical summary of Canmet investigations 1976–1982. CANMET Report 82-4E (March).
- Weast, R.C., 1975. CRC Handbook of Chemistry and Physics CRC Press, Ohio.
- Zipperian, D., Raghavan, S., 1988. Gold and silver extraction by ammoniacal thiosulfate leaching from a rhyolite ore. Hydrometallurgy 19, 361–375.