

Solution chemistry factors for gold thiosulfate heap leaching

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Abstract

Thiosulfate is an alternative lixiviant for the leaching of precious metals. Research and development of thiosulfate leach technology has been prompted by environmental concerns with the use of cyanide and problems associated with the processing of difficult-to-treat ores. The Newmont Mining, Nevada, operation has successfully developed a combined biooxidation–thiosulfate heap-leaching process for carbonaceous/high sulfide ores and a direct thiosulfate heap-leaching process for carbonaceous/low sulfide ores. The chemistry of copper catalytic thiosulfate leach is a complicated system due to the simultaneous presence of ammonia, thiosulfate and Cu(II)–Cu(I) redox couple, especially for a heap leach operation. In this paper, factors affecting both the leach reaction and the stability of the lixiviant are discussed relating to heap-leaching operation from a solution chemistry perspective.

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1. Introduction

Since 1980, mine production of gold has steadily increased. Primary gold mine production accounts for most of the total US production. The most common leaching process for gold dissolution involves cyanidation, a process that has been practiced for over a century. During the past three decades, the development of heap-leaching technology for low-grade ore has extended the world resource base considerably.

Most gold production from primary resources is still achieved by cyanidation; many research activities have been focused on alternative processes using non-cyanide lixivants. Such research has been prompted by environmental concerns and problems associated with the processing of so-called difficult-to-treat ores or refractory gold ores. Among the non-cyanide lixivants, thiosulfate as an alternative leaching reagent has received much attention in recent years. Ammonium thiosulfate is an inexpensive, nontoxic reagent, used mostly for fertilizer. Acceptable leaching rates using thiosulfate are achieved in the presence of ammonia with cupric ion acting as the oxidant.

Newmont has developed a heap leach process using ammonium thiosulfate for gold recovery from low-grade carbonaceous sulfidic gold ores. Gold

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cannot be heap leached with cyanide due to high preg-robbing characteristics of the carbonaceous matter in the ores. It has been found that activated carbon has a very low affinity for gold–thiosulfate complex ion (Gallagher et al., 1990). The reasons for the very low adsorption of gold onto the carbon from the thiosulfate system have not been fully explained. Various possibilities exist including the relatively high negative charge of the complex ion and steric limitations due to the molecular structure or specific interactions of the ligand group with carbon active sites. The very low affinity of gold–thiosulfate ion to activated carbon indicates that gold extraction from carbonaceous ore is possible using a thiosulfate lixiviant. Based on this, the thiosulfate leach technology on carbonaceous ores has been studied extensively in laboratory, pilot plant tests and in demonstration scale (Wan, 1997; Wan et al., 1994). A total of 1.24 million tonnes low-grade refractory gold ore has been processed with ammonium thiosulfate at Newmont's operation near Carlin, Nevada. The carbonaceous refractory ores have also been studied by other researchers including Barrick Gold (Marchbank et al., 1996; Schmitz et al., 2001), and other research consortia.

The copper–ammonia–thiosulfate solution used for precious metal leaching was reported to be a very complicated system. Many interactions may occur among the system constituents, not to mention that the system itself is thermodynamically unstable. Unlike cyanide, thiosulfate is metastable and tends to undergo chemical decomposition under improper leach conditions. Numerous factors affect the system's stability. Thiosulfate solution applied to a heap leach operation is more complicated since it requires a long duration leach period. Leach solution after gold recovery is required for recycling and it forms aging solutions after an extended leach period. Heap leaching is applied to low-grade ores associated with various minerals. Most of the sulfide minerals react with thiosulfate and affect gold dissolution and thiosulfate stability. Maximum control of the stability of the leaching system is a key factor for success, especially for a heap leach operation. In this paper, factors affecting a thiosulfate leaching system are discussed. Solution chemistry related to gold recovery from thiosulfate so-

lution using copper cementation will be discussed on another occasion.

2. Thiosulfate heap-leaching application

Since the cyanidation process has been very successful in treating oxide ores and non-preg-robbing ores over the years, from a technical point of view, it is still the preferred process for the recovery of precious metals whenever possible. However, cyanide has problems leaching gold occurring in carbonaceous ores. Newmont's Nevada operation has refractory ores in which sulfide locking of gold occurs with preg-robbing carbon. The high-grade refractory ore was treated by roasting the ores at high temperatures, followed by a cyanidation carbon-in-leach (CIL) process. For low-grade sulfidic and carbonaceous refractory gold ores, Newmont has used the capabilities of sulfide-oxidizing bacteria as a pretreatment process (Brierley, 1994; Brierley et al., 1995). This biooxidation process results in the oxidation of the sulfide minerals that increases the exposure of gold for subsequent extraction. Following biooxidation, the ores are neutralized with lime and placed on pads for leaching. The biooxidized carbonaceous sulfidic ores cannot be treated with cyanide solution because of the preg-robbing characteristics of the ore. A combined biooxidation–thiosulfate heap process was developed for high sulfide carbonaceous ores and a direct thiosulfate leach process for low sulfide carbonaceous ores. From 1996 to 1999, a total of 1.24 million tonnes of low-grade carbonaceous refractory ore was heap leached at Carlin, Nevada, with ammonium thiosulfate. The thiosulfate demonstration plant started in 1996; each campaign processed about 320,000 tonnes of low-grade (Au, 1.3–2.7 g/tonne) carbonaceous refractory ores (Table 1).

Table 1
Thiosulfate leach plant at Newmont, Nevada, operation

Campaign year	Leach type	Tonnes	Gold produced	
			(oz)	(kg)
1996	Bio/Thio	326,500	11,850	368.5
1997–1998	Direct Thio	324,000	20,100	625.1
1998	Bio/Thio	331,100	11,370	353.6
1998–1999	Direct Thio	259,800	12,470	387.8
Total CSR ore treatment		1,241,400	55,790	1735

Gold recovery from thiosulfate pregnant solution was achieved with copper powder cementation. After gold recovery, the barren solution was recycled back to the heap. A total of 55,790 oz (1.735 tonne) of gold was produced from the thiosulfate leach technology as shown in Table 1.

Pilot plant tests and several demonstration field tests have been reported (Brierley et al., 1995; Wan and Brierley, 1997). The last batch demonstration operation (Table 1) was performed on a highly preg-robbing sulfide ore with ammonium thiosulfate leaching without sulfide pre-oxidation (Bhatka, 1999). The ore contained 2.5–2.8 g Au/tonne. Cyanide leach yielded zero gold extraction. In laboratory batch tests, the highest gold extraction that was achieved on a fine-ground sample using ammonium thiosulfate was 71%. For the demonstration operation, 259,800 tonnes of ores were crushed to P₈₀ of 1.9 cm. Lime addition averaged 13.7 kg/tonne. The high lime consumption was due to the sulfide content and the acidic nature of the ore. The pad was loaded by end dumping to an average height of 10 m before settling. The leach pad contained eight leach cells with a leaching cycle averaging 176 days, which included a 30-day rest period. The ore was leached at an average solution application rate of 0.005 gpm/ft² (12 l/h/m²). The solution applied to the heap was initiated with 40 g/l (NH₄)₂S₂O₃ with pH around 9.2. After complete solution breakthrough, ammonium thiosulfate concentration in the pregnant solution dropped to 10–13 g/l; this concentration level was maintained for the entire leach cycle. The copper concentration in the leach solution was 30–60 ppm and solution pH was 8.8–9.2 for the whole leach period. The final solution potential was about 100 mV with a silver–silver chloride electrode. A total of 12,470 oz (387.8 kg) of gold was produced. Ammonium thiosulfate consumption for this campaign was high, 9.7 kg/tonne ore. Other reagent consumptions were ammonium hydroxide, 0.75 kg/t;

CuSO₄, 0.03 kg/t; and copper dust, 0.015 kg/t (Bhatka, 1999).

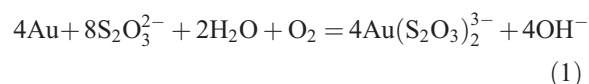
Demonstration plant tests confirmed that higher gold recoveries and a lower reagent consumption were obtained from carbonaceous, low-sulfide (or oxide) ores compared with carbonaceous high-sulfide ores even with biooxidation pretreatment.

Though it has been confirmed in laboratory tests that oxygen is an important factor for increasing gold reaction kinetics, the Newmont thiosulfate demonstration facility did not have the capability to add air into the heap. Depending upon the ore characteristics, air permeability within the heap and the lift height of the heap, gold leach kinetics may be limited due to the availability of oxygen in the heap.

After the demonstration plant tests, implementation of the thiosulfate leach technology to a commercial operation was initiated. However, the construction of a commercial plant has been postponed due to low gold prices and limited carbonaceous ore reserves.

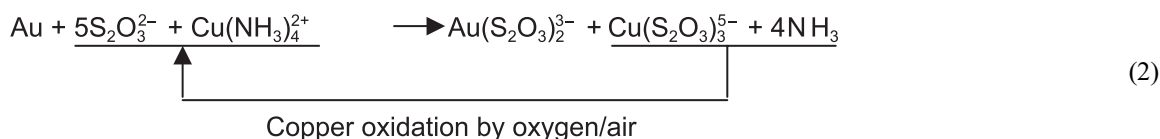
3. Thiosulfate leaching of gold

Gold dissolution in ammonium thiosulfate solution is described by the following reaction:

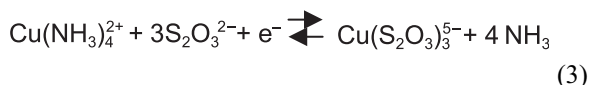


The dissolution of gold in the presence of oxygen was found to be very slow. Cupric ion was found to have a strong catalytic effect on the rate of oxidation. The presence of ammonia helps to stabilize the Cu(II) state as the cupric tetra-ammine complex ion acting as an oxidant.

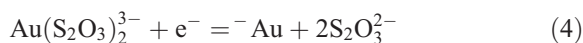
Li et al. (1995) modified the above reaction to reflect the influence of the copper during gold dissolution:



The relevant copper half-cell reaction appears to involve both the ammonia and thiosulfate ligands:



The Cu(II) cation can act as an oxidant for the leaching of gold when this half-cell reaction is coupled with the appropriate half-cell reaction (4) for gold.



It is due to this electrochemical process involving copper that gold can be dissolved. In the absence of copper ions, the limited solubility of oxygen in the thiosulfate solutions and its slow reductions at the gold surface resulted in unsatisfactory gold dissolution.

During the leaching reaction, copper ions in solution transfer back and forth from Cu(II) ammine to Cu(I) thiosulfate as shown in reaction (2). Maintaining Cu(II) tetra-ammine complex ion in the system is very important for the Cu(II) to serve as a catalytic oxidant. The Cu(I) existing in the leach solution is also important for the next step of gold recovery from the thiosulfate solution using cementation. The Cu(I) from the barren solution after cementation reacts with ammonia and oxygen (in the air) and transfers back to Cu(II) ammine. Regeneration of the Cu(II) to sustain the oxidation reaction is an important feature of the leaching reaction. Thus, the concentration ratio of ammonia to thiosulfate should be maintained in a certain range to have copper ammonia and thiosulfate complexes to coexist.

4. Behavior of sulfide minerals in thiosulfate solutions

Gold in carbonaceous refractory ores is associated with various minerals. Many of these minerals are conductors and semiconductors and are also electrochemically active in the thiosulfate system.

Newmont's refractory gold ores contain sulfide minerals with preg-robbing carbon. The most common sulfide minerals associated with gold are pyrite, arsenopyrite and pyrrhotite, with minor amounts of copper sulfides (chalcopyrite, chalcocite, covellite, etc.). The

behavior of these sulfide minerals in thiosulfate solution affects the thiosulfate stability and gold leaching kinetics.

4.1. Thermodynamic considerations

Eh–pH diagrams for copper and iron sulfide minerals in an ammonia–thiosulfate system are shown in Figs. 1 and 2. The diagrams indicate that thermodynamically, copper and iron sulfide minerals are not stable in ammonium thiosulfate solutions as long as the solution potential is high enough. Comparing Figs. 1 and 2 with the Eh–pH diagram of Au–NH₃–S₂O₃²⁻ system (Fig. 3), the potentials required for sulfide dissolution are about the same as for gold leaching. Stronger oxidizing conditions are necessary when the pH becomes lower. Therefore, thermodynamically, the iron and copper sulfide minerals would become unstable in the thiosulfate solutions at certain oxidizing potentials.

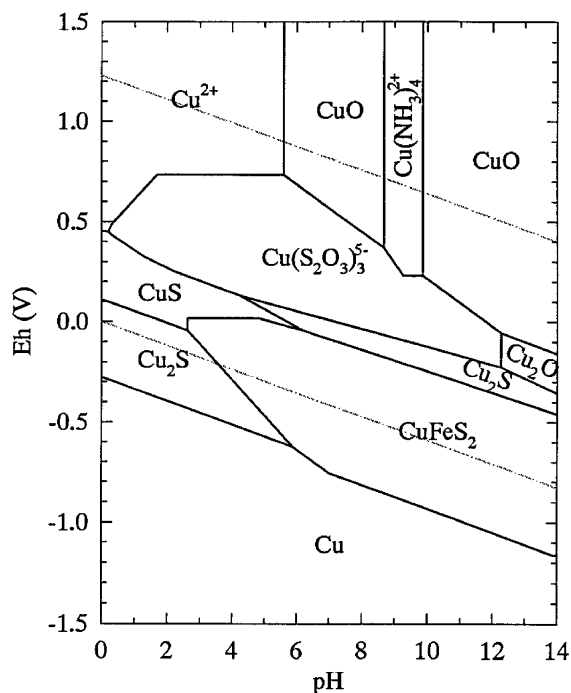


Fig. 1. Eh–pH diagram of copper–iron–ammonia–thiosulfate system at 25 °C, 0.1 M ammonia, 0.1 M ammonium thiosulfate, 5×10^{-4} M copper, 1×10^{-6} M iron.

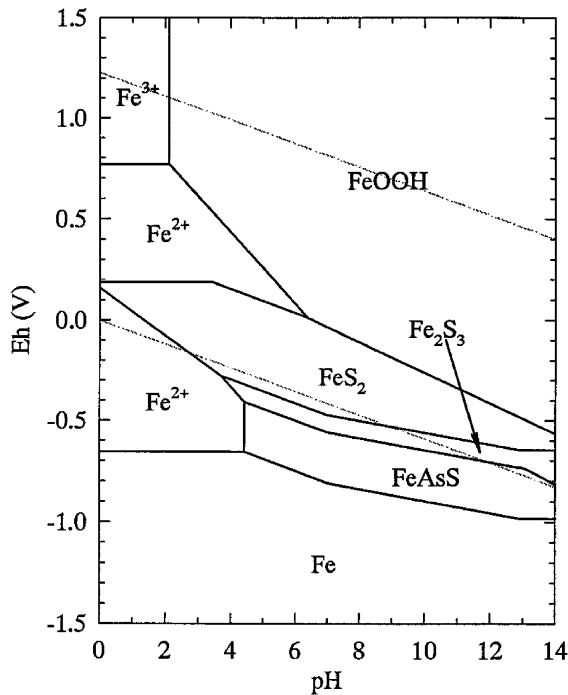


Fig. 2. Eh–pH diagram of iron–arsenic–ammonia–thiosulfate system at 25 °C, 0.1 M ammonia, 0.1 M ammonium thiosulfate, 1×10^{-6} M iron, 1×10^{-5} M arsenic.

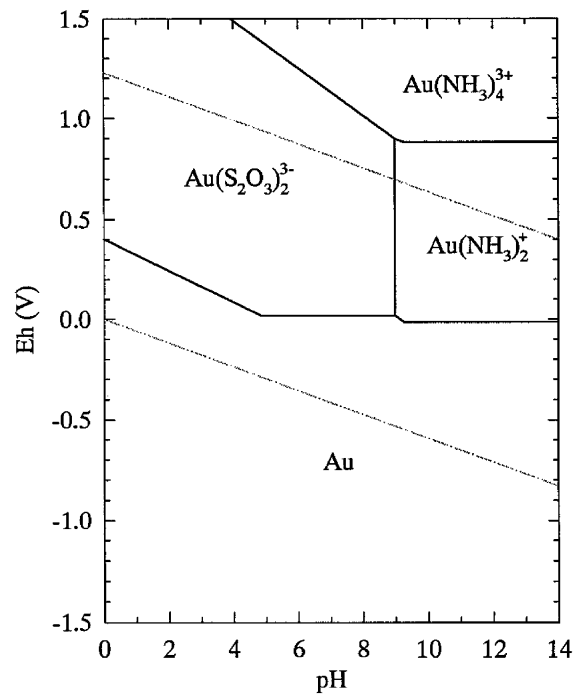


Fig. 3. Eh–pH diagram of gold–ammonia–thiosulfate system at 25 °C, 0.1 M ammonia, 0.1 M ammonium thiosulfate, 5×10^{-5} M gold.

4.2. Electrochemical measurements

The dissolution of iron and copper sulfide in the ammonium thiosulfate solutions has been demonstrated by electrochemical study (Miller and Li, 1995). Steady-state polarization curves were measured with the potentiodynamic technique at a voltage scan rate of 1 mV/s. The scan started from the rest potential (open circuit potential) of the working electrode and ended at 840 mV (SHE). Each measurement was repeated three times and was conducted under an argon atmosphere. Important findings from the measurements of gold, pyrite, arsenopyrite, chalcopyrite, chalcocite and covellite are summarized as follows

(1) The rest potentials of gold and sulfide minerals, which were directly measured in thiosulfate solutions, are compared in Table 2. Though the physical properties of these pure sulfide specimens, used as working electrodes, could be different from the minerals associated with gold in the refractory gold ores, their rest

potentials should give the comparable thermodynamic stability in the thiosulfate solution. Materials with a lower rest potential have a greater tendency to be oxidized. From Table 2, the measured rest potentials, which indicate the thermodynamic stability in ammonium thiosulfate solution, are in the following order:

Chalcocite < gold < chalcopyrite ~ arsenopyrite
< covellite < pyrite.

The most difficult minerals to be oxidized in the thiosulfate solution are pyrites, while gold has a relatively strong tendency to be dissolved.

Table 2
Rest potentials (mV vs. SHE) of gold and sulfide minerals

	Cu ₂ S	Au	CuFeS ₂	FeAsS	CuS	FeS ₂
0.5 M Na ₂ S ₂ O ₃	–141	–40	57	62	75	76
0.5 M (NH ₄) ₂ S ₂ O ₃	–137	–45	0	26	44	69

Measured in thiosulfate solutions: 0.2 M NH₄OH.

Table 3

Current densities ($\mu\text{A}/\text{cm}^2$) of gold and sulfide minerals at 340 mV (SHE)

	Cu ₂ S	FeAsS	FeS ₂	CuFeS ₂	CuS	Au
0.5 M Na ₂ S ₂ O ₃	9938.0	277.7	143.0	483.6	22.3	64.2
0.5 M (NH ₄) ₂ S ₂ O ₃	11,750.0	5292.0	1335.0	708.6	225.0	162.6

Measured in thiosulfate solutions: 0.2 M NH₄OH.

(2) The current densities, which were measured at 340 mV (SHE) are given in Table 3. The measured current densities that indicate the reaction rate are much higher for sulfide oxidation than for gold dissolution. The kinetic order at 340 mV (SHE) is

Chalcocite > arsenopyrite > pyrite > chalcopyrite
> covellite > gold.

It should be pointed out that in these measurements, the measured current of anodic oxidation includes two reactions: the decomposition of a sulfide mineral (or the dissolution of gold) and the decomposition of thiosulfate. Nevertheless, results indicate that these sulfide minerals may oxidize in thiosulfate solutions.

Many applications have been reported using the thiosulfate leach technology for gold and silver extraction from sulfide ores and complex sulfide concentrates without pretreatment (Li et al., 1995; Yen et al., 1996, 1998). In leaching practice, the sulfide minerals would interact with the gold leaching reaction, affecting the thiosulfate stability, and resulting in high reagent consumption. The operation of thiosulfate leaching for oxide ores should be more easily controlled than for sulfide refractory ores. The thiosulfate leaching performance could be predicted based on sulfide content and mineralogy characteristics in refractory gold ores. Depending on sulfide content and sulfide mineral activities, a pre-oxidation process may be necessary prior to thiosulfate leaching, in order to reduce thiosulfate degradation.

5. Important aspects of solution chemistry

The copper catalytic ammonium thiosulfate system is a complicated system due to the simultaneous presence of thiosulfate, ammonia and the Cu(II)/Cu(I) redox couple. While both leaching and cementation are carried out in the same solution, the ions in the solution may go through a series of changes. An

important difference between the cyanide system and the ammonium thiosulfate system is the stability of the lixivants. While the cyanide is relatively stable throughout the production cycle, ammonia and thiosulfate are not so stable if the operation conditions are not properly controlled. The escape of free ammonia from the leaching solution is unavoidable. Thiosulfate ions are metastable and tend to undergo chemical decompositions in aqueous solutions, especially in the presence of copper (Byerley et al., 1973). The factors that influence the thiosulfate stability are the concentration and pH of solutions, the presence of certain metals, the presence of sulfur-metabolizing bacteria and the exposure to ultraviolet light (Dhawanale, 1993). The continuous loss of ammonia and thiosulfate increases the cost of production and decreases the productivity.

In copper–ammonia–thiosulfate solution, many interactions may occur among the system constituents, not to mention that the system itself is thermodynamically unstable. The successful development and utilization of the thiosulfate leach technology will depend upon a detailed knowledge of the system, an understanding of the reaction mechanisms and control of the solution chemistry. In recent years, a significant amount of research has been carried out using thiosulfate for gold leaching. Recently, fundamental studies of thiosulfate leach technology were reported (Aylmore and Muir, 2001a,b; Jeffrey, 2001; Breuer and Jeffrey, 2002; Arima et al., 2002), and information related to thiosulfate leaching of precious metals was reviewed (Aylmore and Muir, 2001a).

For practical applications, in order to achieve a sustainable and acceptable leach rate along with acceptable thiosulfate consumption, a balance of parameters or conditions is important.

5.1. Gold passivation and retardation

It was observed in column tests and field tests that gold leaching kinetics in copper–ammonia–thiosulfate solution was gradually decreased after leaching an extended time. The decreasing leach rate may occur if the gold is not exposed to the solution and is encapsulated in the particles.

The gold leaching kinetics was further examined in the laboratory using a gold foil. After the foil had been leached for a number of leaching cycles, the leaching

rate was also found to decrease. The surface of the gold foil became tarnished and passivated. XPS, XRD, Raman spectroscopy and microprobe analysis techniques were employed to determine the species on the gold surface. Sulfur and copper sulfides were identified by XPS and microprobe analysis. According to XRD and Raman spectroscopy, the sulfur on the gold surface was either elemental sulfur or in the sulfide form combined with copper. Since not all peaks from either XRD data or Raman spectra agreed with the references, the species on the gold surface may be amorphous or incompletely crystallized. Sulfur and sulfide species on the gold surface appear to form a new interface between gold and solution, preventing thiosulfate from diffusing to the gold surface, thus inhibiting gold leaching reaction.

The gold passivation phenomenon in thiosulfate solution was also confirmed from electrochemical measurements (Miller and Li, 1995) of gold electrode in copper–ammonia–thiosulfate solution. The rest potential (or open circuit potential) of gold increased gradually during thiosulfate leaching, indicating gold passivation and a decrease in the driving force for further gold dissolution.

Therefore, with the presence of ammonia and oxygen, desirable working conditions, such as solution oxidizing potential and pH value, must be maintained, so as to eliminate sulfur/sulfide formation while decelerating the thiosulfate decomposition. The gold passivation can be reduced to a minimum amount with the presence of ammonia and oxygen under proper Eh–pH conditions as discussed below. It has been suggested that ammonia prevents gold passivation by being preferentially adsorbed on gold surfaces over thiosulfate (Jiang et al., 1993).

5.2. Copper concentration and the ratio of ammonia to thiosulfate

From past experience, under certain conditions, the copper catalytic oxidation reaction may be limited: (1) inappropriate concentration ratio of ammonia to thiosulfate may stabilize the copper in either the Cu(I) or Cu(II) state, (2) high pH values lead to the precipitation of copper from solutions as oxides and (3) the amount of copper used could be too high. Control of the copper concentration is an important factor to achieve optimum leaching conditions and to

minimize thiosulfate decomposition especially for a heap leach operation. High copper concentration increases the gold leaching rate especially for gold extraction from sulfide minerals or concentrates. However, the high concentration of copper also increases the oxidation decomposition rate of thiosulfate. The optimum concentration of copper in the leach solution depends on ore characteristics and the concentration of thiosulfate used. In Newmont's heap-leaching practice, the copper concentration in the initial leach solution was about 30 ppm and increased to 60 ppm after several months of operation. Increasing the copper concentration to 200 ppm resulted in high reagent consumption.

As discussed above, maintaining Cu(II) tetra-ammine in the system is very important for the copper(II) ion to serve as an oxidant. The concentration ratio of ammonia to thiosulfate must be maintained for copper ammine and thiosulfate complex ions to coexist. The influences of ammonia and thiosulfate concentrations on the distribution of copper species are presented in Figs. 4 and 5. These figures indicated that the necessary condition for the copper ammonia and thiosulfate complexes to coexist is that the ligand concentration ratio has to be maintained in a certain range. Increasing the concentration of either ammonia or thiosulfate will have a negative effect for gold leaching, since an inappropriate concentration ratio of ammonia to thiosulfate may stabilize the copper ions in either the Cu(I) or Cu(II) state and may change reaction (3) from reversible to irreversible (Li et al., 1996).

It has been observed that the recycled solution after gold cementation sometimes reduces its leaching capability. Part of the reason is due to an inappropriate concentration ratio of ammonia to thiosulfate. Another situation in which this ammonia/thiosulfate ratio may play a role is in the solution aging that occurs during heap leaching after an extended period. In heap leach operation, loss of ammonia due to evaporation and loss of thiosulfate due to degradation are unavoidable. The process design may consider the removal of a bleed stream for better control of solution chemistry.

In general, Cu(I) thiosulfate is the predominate species in solution at most common potentials and appears to be in equilibrium with Cu(II) ammine.

Potential influences the equilibrium between Cu(I) and Cu(II) ions as shown in Fig. 6. As potential

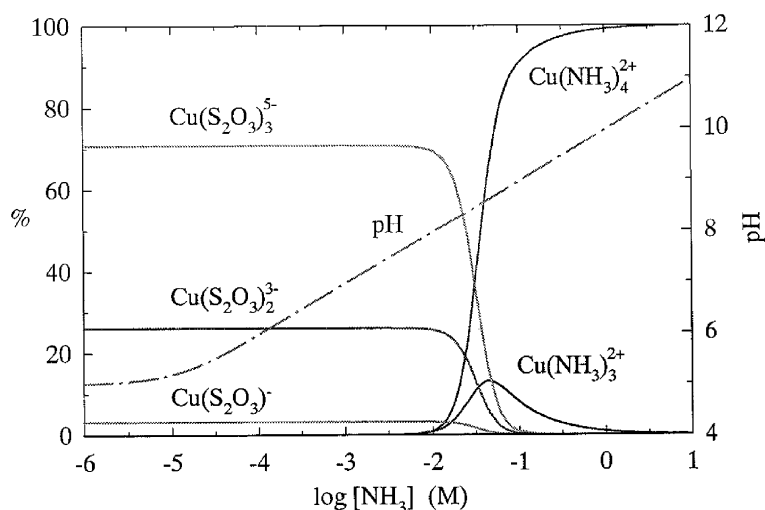


Fig. 4. Effect of ammonia concentration on the distribution of copper species, 0.1 M ammonium thiosulfate, 5×10^{-4} M copper.

increases, more copper ions will exist at the higher valence state, i.e., the Cu(II) state. Either Cu(I) or Cu(II) species will dominate if the potential is too low (<200 mV, SHE) or too high (>400 mV, SHE). Note that this exact potential is also dependent upon ammonia and thiosulfate concentrations.

Moderate changes in copper concentration do not affect the species distribution diagram significantly. However, it is not recommended that high copper concentrations (>0.003 M) be used. Though high

copper concentration will increase the gold leaching rate, on the negative side, copper ions will not only decrease the lixiviants availability for gold dissolution but will also accelerate the decomposition of thiosulfate.

5.3. Maintain proper pH/Eh in heap leach solution

It was confirmed experimentally that ammonium and ammonia constituted a pH buffer solution

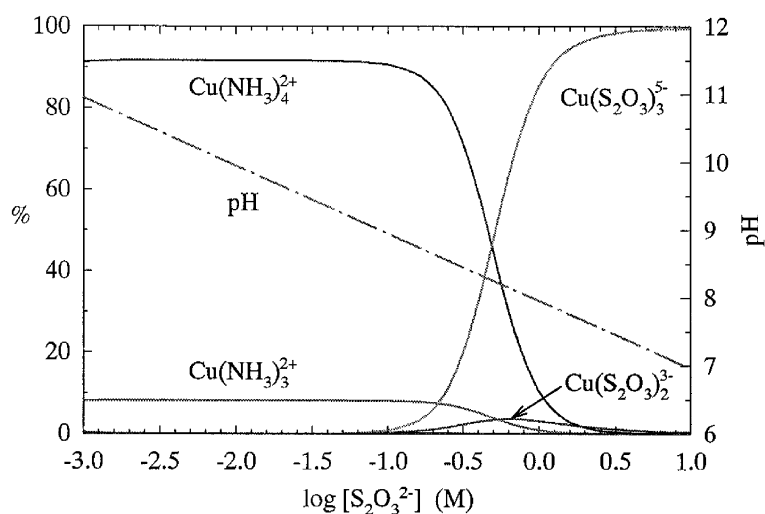


Fig. 5. Effect of thiosulfate concentration on the distribution of copper species, 0.1 M ammonia, 5×10^{-4} M copper.

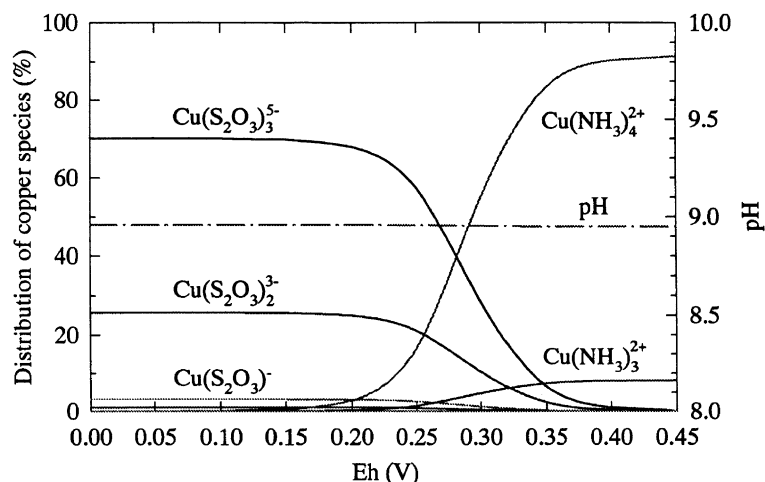


Fig. 6. Effect of potential on the distribution of copper species, 0.1 M ammonia, 0.1 M ammonium thiosulfate, 5×10^{-4} M copper.

($pK_a = 9.26$). Not only was the solution pH stabilized, but also the free ammonia concentration could be estimated based on pH measurements and total ammonia analysis.

Though the solution pH of the lixiviant is stabilized based on the concentrations of ammonia and thiosulfate, many factors affect pH value of solutions from the heap. Depending on ore characteristics (especially sulfide content) and acidity/alkalinity level prior to thiosulfate leaching, pH of the initial leach solutions drained from the heap may be low, even acidic sometimes (in the case of high sulfidic ores). Ammonia with lime or soda ash has been used to adjust the solution pH prior to recycling to heap. Depending upon operation parameters and thiosulfate concentration, leach solution pH ranged from 8.5 to 9.5. Under normal conditions, solution pH was maintained at 8.8–9.2 without any problems. It is not desirable to have solution pH below 8, since the solution would change to acidic dramatically. However, high pH values should be avoided. At high pH (>11), copper will be removed from the leaching solution as oxide species and loss of ammonia will be significant. In general, thiosulfate leach on oxide ore is much easier to operate. Both solution potential and pH can be easily controlled.

Depending on the potential (Fig. 3), gold may remain in the metallic form or precipitate from the solution if potentials are too low. In a real system,

solution potentials will vary depending on concentrations of ammonia, thiosulfate, oxygen and Cu(II)/Cu(I), as well as interference by sulfide minerals. The oxidative and reductive of thiosulfate reaction also affected the solution potential. In Newmont's heap-leaching practice, the pregnant solution potential after months of leaching was measured at about 50–100 mV with silver–silver chloride electrode.

Potential influences the equilibrium between Cu(I) and Cu(II) ions as it has been discussed in the previous section. Either Cu(I) or Cu(II) will dominate if the potential becomes too low or too high. At low potentials, where oxidants are deficient, the decomposition of thiosulfate also leads to the precipitation of copper sulfides. In the absence of air, black precipitates were observed to form in solutions containing ammonia, thiosulfate and copper. The precipitates had been identified as copper sulfides by XRD analysis. Under these circumstances, gold extraction may be limited and gold will coprecipitate with sulfides from the solution.

In Newmont's heap leach operation, based on solution potential and pH value, a small stream of ammonia is added to the barren solution (if necessary) to control the pH and convert Cu(I) to Cu(II) prior to recycling the solution to the leach pad.

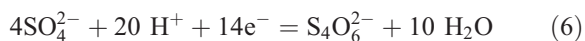
5.4. Importance of oxygen/air in the heap-leaching system and thiosulfate stability

The stability of the system is another key factor for normal production. The following facts were observed in our study:

- (1) dilute solution of ammonium thiosulfate (0.01 M or lower) decomposes more rapidly than concentrated solutions (0.1 M or higher);
- (2) thiosulfate is more stable in stirred solutions than in stagnant solutions;
- (3) thiosulfate decomposes immediately in a closed system in the presence of copper and produces black precipitation; and
- (4) high copper concentration accelerates the thiosulfate decomposition.

It has been shown that oxygen availability in the system is of vital importance. Oxygen does not participate directly in the gold leaching reaction as in the case of cyanidation. However, its presence in the system is absolutely necessary. In the absence of oxygen, Cu(I) ions cannot return to the Cu(II) state and, in fact, will precipitate copper sulfides from solution. Under these conditions, the leaching reaction will cease.

Depending on the solution potential and pH value, two types of thiosulfate degradation may occur in the system: oxidative and reductive. For the oxidative decomposition of thiosulfate, a series of stable or metastable sulfur–oxygen species may form. The existence of $\text{S}_4\text{O}_6^{2-}$ (major) and $\text{S}_3\text{O}_6^{2-}$ (minor) in the pregnant solution has been detected by ion chromatography. Although the oxidative degradation appears to be rather complicated due to the existence of many species, the reaction can be simply described as follows:



Sulfate is the most stable and is the final degradation product in the thiosulfate solution under leaching conditions. The sulfate in the heap leach solution reacts with lime-forming calcium sulfate or with

ammonia-forming ammonium sulfate. It has been observed during cold weather operations that the crystallized ammonium sulfate formed on the heap surface. The concentration of sulfate (SO_4^{2-}) for demonstration heap leach solution averaged about 35–38 g/l after months of operation.

For the reductive decomposition, a possible reaction is



Copper sulfides and elemental sulfur, the intermediate of thiosulfate decomposition, were observed to form as confirmed by XRD analysis. The reductive degradation of thiosulfate was of concern in the heap-leaching operation since the dissolved oxygen concentration in thiosulfate–ammonia solution was very low. The Cu(II) tetra-ammine concentration may be limited because of the availability of oxygen in the heap. The degradation of thiosulfate not only results in loss of the lixiviants, but also leads to the formation of sulfides which, in turn, passivates gold and limits the leaching rate. In the worst case, gold was precipitated from the solution. It is highly recommended to improve air permeability and have an air ventilation system within the heap. This is especially important in the design and construction of a heap leach system.

The addition of sulfite has been suggested to stabilize the ammonium thiosulfate system (Kerley, 1981, 1983). In a heap leach operation, an excess of sulfite may significantly change the redox potential of the system and have a detrimental effect on gold extraction. From our experience, in the late stage of the leaching period, the addition of a very small amount of sulfite (<0.02%) to the aged solution gave some benefits for preventing sulfide formation and improving thiosulfate stability.

6. Summary

Cupric–ammonia–thiosulfate leaching has proved to be a promising alternative process for precious metals recovery. Newmont Mining has successfully developed a heap leach process using ammonium thiosulfate for gold recovery from low-grade carbonaceous sulfidic gold ores. A combined biooxida-

tion–thiosulfate heap process was developed for high sulfide ores and a direct thiosulfate leach process for low-sulfide ores. A total of 1.24 million tonnes of low-grade carbonaceous sulfidic ores has been heap leached at Carlin, Nevada, with ammonium thiosulfate. Gold recovery was achieved with copper cementation. After gold recovery, the barren solution was recycled back to the heap for leaching. A total of 55,790 oz of gold was produced from the thiosulfate leach technology.

In this paper, the solution chemistry factor for gold leaching with ammonium thiosulfate was discussed. The chemistry of the copper–ammonia–thiosulfate system was found to be complex. Thiosulfate formed complex ions with a variety of metals. Sulfide minerals associated with gold are electrochemically active in the thiosulfate solution. Their behavior affects gold leaching kinetics and thiosulfate stability.

The Cu(II) ions in solution participate in a catalytic oxidation reaction and their presence enhances the gold dissolution. For copper to play this role, the leaching solution has to meet certain conditions. It was explained why the concentration ratio of ammonia to thiosulfate is important for successful leaching. The critical point lies in the formation of a solution that allows for both Cu(II) and Cu(I) complex ions to coexist at appropriate concentrations. High copper concentrations accelerate thiosulfate decomposition, and therefore, copper concentration should be controlled.

Maximum control of the stability of the thiosulfate leaching system is a key factor for success, especially for a heap leach operation. Proper control of solution pH and potential decreases the tendency for thiosulfate degradation. The loss of ammonia from the leach system is unavoidable. The rate of ammonia loss may be decreased to some extent by maintaining a proper solution pH. Solution potential influences the equilibrium between cuprous and cupric ions. At low potential, where oxidants are deficient, the decomposition of thiosulfate leads to the precipitation of copper sulfides. The reductive degradation of thiosulfate was more concerned for a heap leach operation since oxygen is limited within the heap. Oxygen availability in the system is another important factor. Appropriate access of air must be maintained.

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References

- Arima, H., Fujita, T., Yen, W.T., 2002. Thermodynamic evaluation on gold oxidation and reduction mechanisms in ammonium thiosulfate solution. Presented at 2002 SME Annual Meeting, Phoenix, Arizona. SME Preprint 02-39.
- Aylmore, M.G., Muir, D.M., 2001a. Thiosulfate leaching of gold—a review. *Minerals Engineering* 14 (2), 135–174.
- Aylmore, M.G., Muir, D.M., 2001b. Thermodynamic analysis of gold leaching by ammoniacal thiosulfate using Eh/pH and speciation Diagrams. Presented at SME Annual Meeting, February 26–28, Denver, Colorado. SME Preprint 01-142.
- Bhatka, P.N.H., 1999. Ammonium thiosulfate leaching Batch IV metallurgical report, Refractory Leach Demonstration Facility, November 1999, Newmont Interior Report.
- Breuer, P.L., Jeffrey, M.I., 2002. An electrochemical study of gold leaching in thiosulfate solutions containing copper and ammonia. *Hydrometallurgy* 65, 145–157.
- Brierley, J.A., 1994. Biooxidation-heap technology for pretreatment of refractory sulfidic gold ore. *Proceedings Biomine'94*. Australasian Mineral Foundation Inc., Glenside, SA. Chapter 10.
- Brierley, J.A., Wan, R.Y., Hill, D.L., Logan, T.C., 1995. Biooxidation-heap pretreatment technology for processing lower grade refractory gold ores. *Proceedings of the International Biohydrometallurgy Symposium*, Vina del Mar, Chile, Nov. 19–22.
- 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.
- Dhawale, S.W., 1993. Thiosulfate. *Journal of Chemical Education* 70 (1), 12–14.
- Gallagher, N.P., Hendrix, J.L., Milosavyevic, E.B., Nelson, J.H., Solujic, L., 1990. Affinity of activated carbon towards some gold (I) complexes. *Hydrometallurgy* 25, 305–316.
- Jeffrey, M.I., 2001. Kinetic aspects of gold and silver leaching in ammonia–thiosulfate solutions. *Hydrometallurgy* 60, 7–16.
- Jiang, T., Chen, J., Xu, S., 1993. Electrochemistry and mechanism of leaching gold with ammoniacal thiosulfate. *Proceeding of XVII International Mineral Processing Congress*, May 23–28, Sydney, Australia. The Australasian Institute of Mining and Metallurgy, Carlton, Victoria, Australia, pp. 1141–1146.
- Kerley Jr., B.J., 1981. Recovery of precious metals from difficult ores. US Patent 4,269,622.

- Kerley, B.J., 1983. Recovery of precious metals from difficult ores. US Patent, 4,369,061.
- Li, J., Miller, J.D., Wan, R.Y., LeVier, K.M., 1995. The ammoniacal thiosulfate system for precious metal recovery. Proceedings of the XIX IMPC, Chapter 7. SME, Littleton, CO, USA, pp. 37–42.
- Li, J., Miller, J.D., Wan, R.Y., 1996. Important solution chemistry factors that influence the copper-catalyzed ammonium thiosulfate leaching of gold. 125th SME Annual Meeting, Phoenix, Arizona, March 11–14.
- 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.
- Miller, J.D. and Li, J., 1995. Unpublished Research Report.
- Schmitz, P.A., Duyvesteyn, S., Johnson, W.P., Enloe, L., McMullen, J., 2001. Ammoniacal thiosulfate and cyanide leaching of preg-robbing Goldstrike Ore carbonaceous matter. Hydrometallurgy 60, 25–40.
- Wan, R.Y., 1997. Importance of solution chemistry for thiosulfate leaching of gold. World Gold '97 Conference, Singapore, September 1–3. The Australasian Institute of Mining and Metallurgy, Carlton, Victoria, Australia, pp. 159–162.
- Wan, R.Y., Brierley, J.A., 1997. Thiosulfate leaching following biooxidation pretreatment for gold recovery from refractory carbonaceous–sulfidic ore. Mining Engineering, 76–80 (August 1997).
- Wan, R.Y., LeVier, K.M., Clayton, R.B., 1994. Hydrometallurgical process for the recovery of precious metals values from precious metals ores with thiosulfate lixiviant. US Patent 5,354,359.
- Yen, W.T., Stogran, K., Fujita, T., 1996. Gold extraction from a copper bearing ore by thiosulfate leaching. Resources Treatment Technology 43 (2), 83–87.
- Yen, W.T., Aghamirian, M., Deschenes, G., Theben, S., 1998. Gold extraction from mild refractory ore using ammonium thiosulfate. Proceedings of the International Symposium on Gold Recovery, Montreal, Canada, May 3–6, CIM, Montreal, Quebec, Canada Paper No. THAM61.1.