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Minerals Engineering 16 (2003) 21–30

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Copper catalysed oxidation of thiosulfate by oxygen in gold leach solutions

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Received 2 September 2002; accepted 23 October 2002

Abstract

The environmental and public concern over the continued use of cyanide in the recovery of gold has grown in recent times due to a number of recently publicised environmental incidents. Of the alternative lixiviants, thiosulfate appears to be the most promising, though the considerable amount of research conducted on thiosulfate leaching of gold over the last three decades has not resulted in its commercial introduction. Perhaps the largest contributing factor to this is the poor understanding of the thiosulfate leach solution chemistry, especially the oxidation of thiosulfate in the presence of copper(II) and oxygen. It has been shown in this research that the oxidation of thiosulfate in the presence of copper(II) and oxygen is very complex with the rates of copper(II) reduction and thiosulfate oxidation being significantly faster in the presence of oxygen. The higher initial rate of copper(II) reduction indicated that oxygen increases the rate of copper(II) reduction to copper(I) by thiosulfate, though the mechanism for this remains unclear. The rates of thiosulfate oxidation and copper(II) reduction were also shown to be affected differently by the presence of anions. This is consistent with thiosulfate oxidation occurring via two mechanisms, with one of these mechanisms involving the oxidation of thiosulfate by copper(II) and the other involving the oxidation of thiosulfate by the intermediate superoxide and hydroxide radicals formed as a result of copper(I) oxidation by oxygen. The effect of various parameters on the rate of thiosulfate oxidation and the copper(II) concentration are also shown.

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Keywords: Gold ores; Leaching; Oxidation

1. Introduction

Due to a number of recently publicised environmental incidents, there has become growing environmental and public concern over the continued use of cyanide as a lixiviant for gold recovery. Of the alternative lixiviants, thiosulfate appears to be the most promising, though the considerable amount of research conducted on thiosulfate leaching of gold over the last three decades has not resulted in its commercial introduction. Perhaps the largest contributing factor to this is the poor understanding of the thiosulfate leach solution chemistry. The importance of the leach solution chemistry has been clearly identified by the Newmont mining company who concluded that the solution chemistry was very complicated, having piloted thiosulfate heap leaching

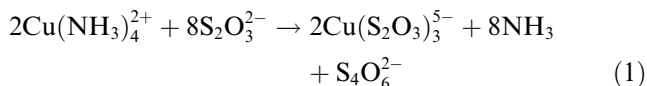
for a number of years without commercial success (Wan, 1997).

It has been shown recently that the presence of copper(II) in the thiosulfate leach solution does not solely act as the oxidant, but also significantly enhances the gold oxidation reaction (Breuer and Jeffrey, 2002). This is why copper(II) is more effective than other oxidants in the leaching process. As the leach solutions are alkaline in order to avoid thiosulfate decomposition, the addition of ammonia is required to stabilise the copper(II) as a copper(II)–ammine complex. The complexity of the thiosulfate leach solution chemistry is attributed to the undesirable reaction between copper(II) and thiosulfate. In the absence of oxygen the oxidation of thiosulfate occurs according to Eq. (1), which generates copper(I) and tetrathionate (Byerley et al., 1973a). The authors have recently studied this reaction in the absence of oxygen (Breuer and Jeffrey, submitted for publication) and it was shown that in addition to thiosulfate, copper(II) also oxidised tetrathionate, sulfite and trithionate under the conditions studied. Such a result is hardly

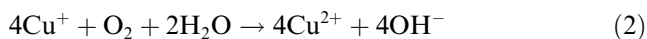
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surprising, as all the polythionates are only meta-stable, with sulfate being the only thermodynamically stable oxysulfur species.



In the presence of oxygen, the regeneration of copper(II) from copper(I) is known to occur readily according to the simplified reaction (copper ligands ignored) shown in Eq. (2).



Since the oxidation of thiosulfate directly by oxygen is known to be slow (Rolia and Chakrabarti, 1982), one would anticipate that the net result of such reactions would be the continual consumption of thiosulfate, at a rate limited by either Eq. (1) or (2). In addition, the copper(II) concentration will be dependant on the relative reaction rates of Eqs. (1) and (2); if the oxidation of copper(I) by oxygen were the fast step, then the copper would predominantly exist as copper(II). Limited attention has been given in the literature to the kinetics of reactions 1 and 2 despite their importance to the gold–thiosulfate leaching system. The only published kinetic study carried out on the oxidation of thiosulfate by copper(II) and oxygen in ammoniacal solutions was in the 1970s by Byerley et al. (1973b, 1975). Byerley et al. (1975) showed that the thiosulfate oxidation rate in the presence of oxygen was more than an order of magnitude faster than that estimated from the rate of reaction between copper(II) and thiosulfate in the absence of oxygen. The other key results from their study were:

- (a) the final reaction products were identified as trithionate and sulfate and not tetrathionate;
- (b) no decrease in the copper(II) concentration was observed for solutions maintained saturated with oxygen; and
- (c) the oxygen consumption was found to be independent of the initial copper oxidation state, as the copper(I) was rapidly oxidised to copper(II).

Thus, the concluding statement by Byerley et al. (1975) was that the “Stoichiometric and kinetic results indicated, however, that such a simple sequence was definitely not the major path for thiosulfate oxidation in the presence of oxygen.” The mechanisms thus proposed by Byerley et al. (1975) assumed that the copper(II) complexed both the oxidant (oxygen) and reductant (thiosulfate), providing a mechanism for electron transfer whereby the copper(II) itself was not reduced.

The objective of the work in this paper was to study in detail the kinetics of thiosulfate oxidation in the presence of oxygen for thiosulfate leach solutions ap-

plicable to gold leaching. This was achieved using a thiosulfate analysis technique previously published (Breuer et al., in press), and thus is not inferred from oxygen consumption measurements as used previously (Byerley et al., 1973b, 1975); oxygen consumption may not be directly related to thiosulfate oxidation due to the differing oxidation rates of the intermediate oxysulfur species formed during the oxidation of thiosulfate through to trithionate and sulfate. An important consideration in this work was the effect of oxygen on the copper(II) concentration as the presence of oxygen is shown in this paper not to maintain the copper in the copper(II) oxidation state as previously suggested (Byerley et al., 1975). Optimum conditions were also investigated in order to minimise the rate of thiosulfate oxidation whilst maintaining an acceptable copper(II) concentration for gold leaching.

2. Experimental

All experiments were carried out using solutions prepared from analytical grade reagents and distilled water. The concentration of the copper(II)–ammine complexes were monitored using UV–Vis spectrophotometry. The solution was stirred within a jacketed vessel (100 ml) maintained at a constant temperature ± 0.1 °C and purged with gas of known oxygen concentration before commencing experiments. Evaporation and volatilisation losses of ammonia were minimised by first equilibrating the sparged gas with a solution at the same temperature and having the same ammonia concentration as the experiment being conducted. A concentrated copper(II)–ammonia solution was injected into the vessel and after a short mixing time the solution was continually pumped through a UV cell. The UV cell was housed in a temperature controlled jacketed cell holder within a GBC UV–Vis spectrophotometer. The solution absorbance at 605 nm was recorded at regular time intervals via a computer. Other solution species gave zero absorbance at this wavelength. In order to convert absorbance readings to a copper(II) concentration the kinetics data was extrapolated back to zero time at which point the copper(II) concentration is known. The variation in the copper(II) absorbance with thiosulfate concentration was also corrected for using a linear correction between the extrapolated initial absorbance and the final absorbance. The thiosulfate concentration was monitored by withdrawing a sample at regular time intervals for analysis using a method previously developed by the authors (Breuer et al., in press). Unless otherwise specified, these experiments were conducted at 30 °C, air sparged at 1000 cm³ min^{−1} and the solutions initially contained 0.4 M ammonia, 0.1 M sodium thiosulfate, and 10 mM copper sulfate.

For experiments in which the copper was initially present as copper(I), a concentrated ammonia solution was injected into the vessel containing a solution of thiosulfate and copper(I). Unless otherwise specified, the solutions used in each of these experiments initially contained 0.4 M ammonia, 0.1 M sodium thiosulfate, and 10 mM copper(I) thiocyanate. In order to convert absorbance data to copper(II) concentrations the zero time absorbance for the same solution initially containing copper(II) instead of copper(I) was used.

3. Results and discussion

3.1. Copper(II) concentration

An initial experiment was conducted using a freshly prepared thiosulfate leach solution initially containing copper(II) in order to investigate the effect of oxygen on the copper(II) concentration in solution. Fig. 1 shows the measured copper(II) concentration for a thiosulfate leach solution which had been continuously sparged with air. Also shown in Fig. 1 for comparison is the measured copper(II) concentration for the same solution in the absence of oxygen (Argon). In this instance, the copper(II) concentration decreases due to its reaction with thiosulfate (Eq. (1)). After 1 h, around 2 mM of copper(II) had reacted with thiosulfate (obviously under these conditions, this reaction is slow). It should be clear for Fig. 1 that initially the copper(II) concentration in the thiosulfate solution decreases more rapidly in the presence of oxygen. Such a result is surprising given that copper(I) can be readily oxidised in the presence of oxygen to produce copper(II).

It can also be seen from Fig. 1 that the copper(II) concentration decreases to a minimum value at which point the rate of copper(II) reduction is matched by the

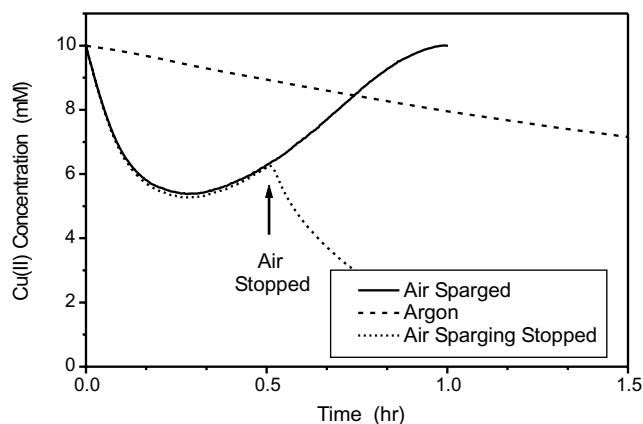


Fig. 1. Effect of oxygen (air sparging) on the copper(II) concentration in a typical thiosulfate leach solution: 0.1 M $\text{Na}_2\text{S}_2\text{O}_3$, 0.4 M NH_3 , 10 mM CuSO_4 , 30 °C, air sparged at $1000 \text{ cm}^3 \text{ min}^{-1}$.

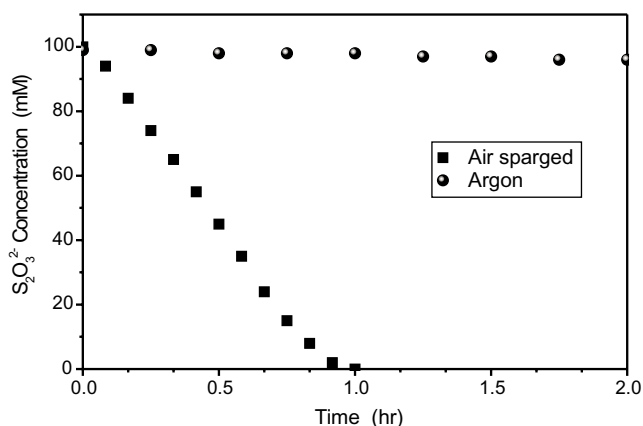


Fig. 2. Effect of oxygen (air sparging) on the rate of thiosulfate oxidation in a typical thiosulfate leach solution: 0.1 M $\text{Na}_2\text{S}_2\text{O}_3$, 0.4 M NH_3 , 10 mM CuSO_4 , 30 °C, air sparged at $1000 \text{ cm}^3 \text{ min}^{-1}$.

rate of copper(I) oxidation. The copper(II) concentration then increases, such that after 1 h, all the copper is again present as copper(II). This is shown in Fig. 2 to correspond with all the thiosulfate having been oxidised. The increase in the copper(II) concentration from the minimum is attributed to the decrease in thiosulfate concentration, since as will be shown in Fig. 8, a decrease in thiosulfate concentration results in a higher copper(II) concentration. In a separate experiment shown in Fig. 1, the air sparging was stopped after 0.5 h. At this point copper(I) is no longer being oxidised to copper(II) and the copper(II) concentration is observed to decrease rapidly. This indicates that the rate of copper(II) reduction occurs at a much higher rate in an air sparged thiosulfate leach solution than in the absence of oxygen. Obviously, the rate of copper(I) oxidation must also be rapid in order to maintain the copper(II) concentration above 5 mM.

One of the most important aspects of the data shown in Fig. 1 is that during the oxidation of thiosulfate, copper exists as both copper(I) and copper(II). In the work conducted by Byerley et al. (1975), the authors claimed that no decrease in the copper(II) concentration occurred. In addition, the mechanisms proposed by these authors do not account for the formation of copper(I) in solution. Another important point regarding the mechanisms involved in copper(II) reduction is that no induction period is observed for copper(II) reduction in the presence of oxygen. Hence, a mechanism that is consistent with oxygen increasing the rate of copper(II) reduction by thiosulfate to copper(I) is required. Subsequent to the work conducted by Byerley et al. (1973b, 1975) in the 1970s, studies into complexes formed between copper and oxygen has raised significant doubts over the existence or formation of copper(II)–oxygen complexes (Simandi, 1992). Also, catalytic oxidation processes involving copper and oxygen usually involve the autooxidation of copper(I)

complexes (Simandi, 1992; Zuberbühler, 1981, 1983). Therefore, the mechanisms proposed by Byerley et al. (1975) for the oxidation of thiosulfate in the presence of copper(II) and oxygen would appear to be questionable. Analysis of the kinetic data previously published by the authors for the copper(II) reduction by thiosulfate in the absence of oxygen (Breuer and Jeffrey, submitted for publication), showed that the reaction is generally second order with respect to copper(II). This indicates that the slow step in the mechanism is consistent with two $\text{Cu(II)}\text{-S}_2\text{O}_3^{2-}$ complexes reacting to give copper(I) and tetrathionate. As the formation of $\text{Cu(II)}\text{-O}_2$ complexes is considered highly unlikely (Simandi, 1992), it would appear that the presence of oxygen provides an alternative mechanism to this slow step.

3.2. Thiosulfate oxidation rate

Fig. 2 shows the measured thiosulfate concentrations as a function of time for a 0.1 M thiosulfate leach solution sparged with air or maintained under argon. Clearly, the rate of thiosulfate consumption is very rapid in the presence of oxygen (air); all of the thiosulfate is oxidised in 1 h. In comparison less than 5% of the thiosulfate was oxidised under argon for the same time period. Based on the initial copper(II) reduction rate under argon (0.58 mmol s^{-1}), it can be estimated that it would take at least two days to consume all the thiosulfate on the basis of the simple copper(II)/copper(I) redox cycle of Eqs. (1) and (2). A similar observation by Byerley et al. (1975) led to the conclusion that a simple copper(II)/copper(I) redox cycle as presented in Eqs. (1) and (2) was not the dominant cause of thiosulfate oxidation.

However, the initial rate of copper(II) reduction in the presence of oxygen is significantly faster than that observed in the absence of oxygen (Fig. 1). Based on this initial rate in the presence of oxygen, it can be estimated that all the thiosulfate will be oxidised in 2.3 h. Thus, it is conceivable that a redox cycle with an enhanced rate of copper(II) reduction plays an important role in the oxidation of thiosulfate in the presence of oxygen. The results presented in Figs. 1 and 2 clearly indicate that the presence of oxygen increases both the rate of thiosulfate oxidation and the rate of copper(II) reduction to copper(I). Thus, mechanisms other than those proposed by Byerley et al. (1975) are needed which explain both of these observations.

3.3. Effect of anions

The presence of anions has been shown previously to significantly reduce the rate of copper(II) reduction by thiosulfate (Breuer and Jeffrey, submitted for publication). Of the anions studied, phosphate was found to be the most effective. Fig. 3 shows the effect of 0.1 M so-

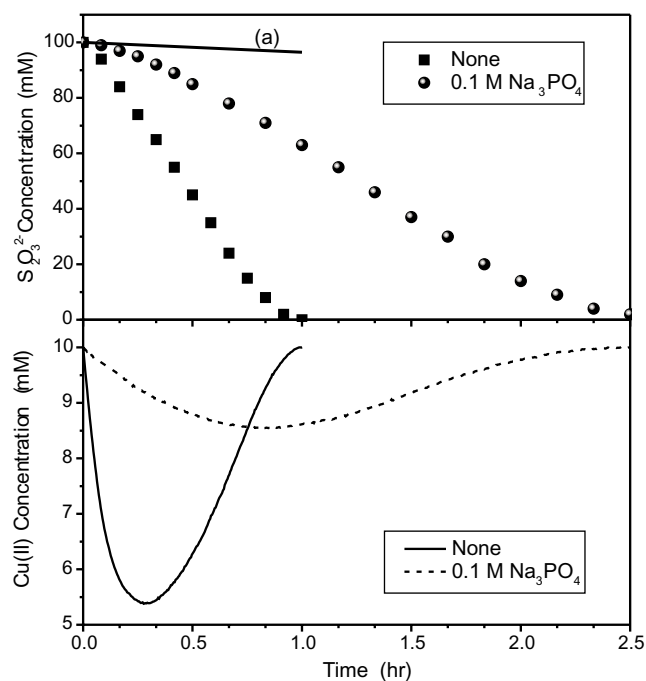


Fig. 3. Effect of phosphate ions on the rate of thiosulfate oxidation and the copper(II) concentration profile: 0.1 M $\text{Na}_2\text{S}_2\text{O}_3$, 0.4 M NH_3 , 10 mM CuSO_4 , 30 °C, air sparged at $1000 \text{ cm}^3 \text{ min}^{-1}$.

dium phosphate on the copper(II) concentration profile and the rate of thiosulfate oxidation. Clearly, the presence of phosphate dramatically reduces the initial rates of copper(II) reduction and thiosulfate oxidation. As the copper(II) concentration is shown to remain above 8.5 mM in the presence of 0.1 M phosphate, the rate of copper(II) reduction in the presence of anions is obviously much slower (initial rate approximately an order of magnitude lower). This is consistent with anions competing for coordination at the copper(II) axial sites and thus reducing the rate of copper(II) reduction by thiosulfate involving oxygen (Breuer and Jeffrey, submitted for publication).

The effect of anions on the initial rate of thiosulfate oxidation is also shown in Fig. 3 to be significant. Based on the initial rate of copper(II) reduction in the presence of 0.1 M sodium phosphate, the maximum rate of thiosulfate oxidation as a result of copper(II) reduction can be estimated (ignoring the thiosulfate complexed with copper(I) as this is small) and is indicated by line (a) in Fig. 3. The initial thiosulfate oxidation rate is similar to this line and thus is conceivably due to the rate of copper(II) reduction by thiosulfate in the presence of oxygen. However, the rate of thiosulfate oxidation increases significantly as evident by the deviation in the thiosulfate concentration from line (a) in Fig. 3. As a result of the increased rate of thiosulfate oxidation, the time taken for all the thiosulfate to be oxidised in the presence of 0.1 M phosphate is only 2.5 times longer than the time taken in the absence of added phosphate.

This clearly indicates that at least one other mechanism is involved in the oxidation of thiosulfate, via which the majority of the thiosulfate is oxidised.

3.4. Effect of initial copper oxidation state

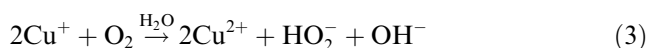
The effect of the initial copper oxidation state on the rate of thiosulfate oxidation by oxygen was also investigated. Fig. 4 shows a comparison of the copper(II) concentration measured for identical solutions with the exception that the copper was initially present as either copper(II) or copper(I). It should be clear from Fig. 4 that for the solution initially containing only copper(I), the copper(II) concentration increases rapidly due to the oxidation of copper(I) by oxygen. This clearly shows that the rate of copper(I) oxidation by oxygen to copper(II) is very fast for these conditions. Notably, the copper(II) concentration increases to a maximum value, before decreasing slightly to a minima. Such a result is consistent with an increase in the relative rate of copper(II) reduction to copper(I) oxidation during this time. It is worth noting that intermediate oxysulfur species formed during thiosulfate oxidation are likely to be reactive towards copper(II). Hence, it is possible that the decrease in the copper(II) concentration observed when starting with copper(I) is due to the increase in copper(II) reduction rate as a result of the increase in the concentration of the intermediate oxysulfur species.

The thiosulfate concentration profiles in Fig. 4 also indicate that the oxidation of thiosulfate is slightly faster

when the solution initially contains copper(I). In this instance, a faster initial increase in the concentrations of the reaction products from the oxidation of copper(I) by oxygen occurs. Such a result suggests that the reaction products of copper(I) oxidation by oxygen may be involved in the oxidation of thiosulfate. This is also consistent with the results shown in Fig. 3 for solutions containing phosphate, which suggests that another mechanism is responsible for most of the thiosulfate oxidation. Clearly, details regarding the mechanisms of copper(I) oxidation by oxygen need to be considered.

3.5. Copper(I) oxidation by oxygen

The oxidation of copper(I) complexes by oxygen has been studied extensively (Zuberbühler (1983, 1981) and Simandi (1992) and references within), especially in relation to biological systems. The second order rate constants for the autooxidation of copper(I) complexes with ammonia are roughly $1\text{--}20\text{ M}^{-1}\text{ s}^{-1}$ (Zuberbühler, 1983) indicating that the reactions involved are rapid. However, the rate of oxidation can be significantly lowered if the corresponding copper(I) and copper(II) complexes have significantly different structures where by extensive rearrangement of the coordination sphere is necessary before electron transfer can take place (Zuberbühler, 1983). It is well established that the first steps involved in the oxidation of copper(I) by oxygen (Eq. (2)) results in the formation of copper(II) and peroxide according to Eq. (3) (Zuberbühler, 1983).



The mechanisms for reaction 3 however are not clear. Based on kinetic results it is firmly established that the autooxidation of copper(I) complexes occurs via inner sphere mechanisms involving dioxygen adducts formed according to Eq. (4); this is believed to be common to the autooxidation of most if not all copper(I) complexes (Zuberbühler, 1983).



The Cu^+O_2 adduct may equally be viewed as a copper(II) superoxide complex, $\text{Cu}^{2+}\text{O}_2^-$ (Zuberbühler, 1983). However, superoxide has not been identified chemically or spectrophotometrically in its free or complexed form during copper(I) autooxidation (Zuberbühler, 1983). This is not surprising given that the superoxide reactivity (of the order $10^9\text{ M}^{-1}\text{ s}^{-1}$) is close to diffusion rates (Zuberbühler, 1983).

It has been known for about a century that the decomposition of hydrogen peroxide to oxygen and water is dramatically accelerated by the presence of metal ions, with the decomposition being the order of seconds in the presence of copper(II) (Luo et al., 1988). Byerley et al. (1975) however suggested that any peroxide formed in oxygenated thiosulfate solutions containing copper(II)

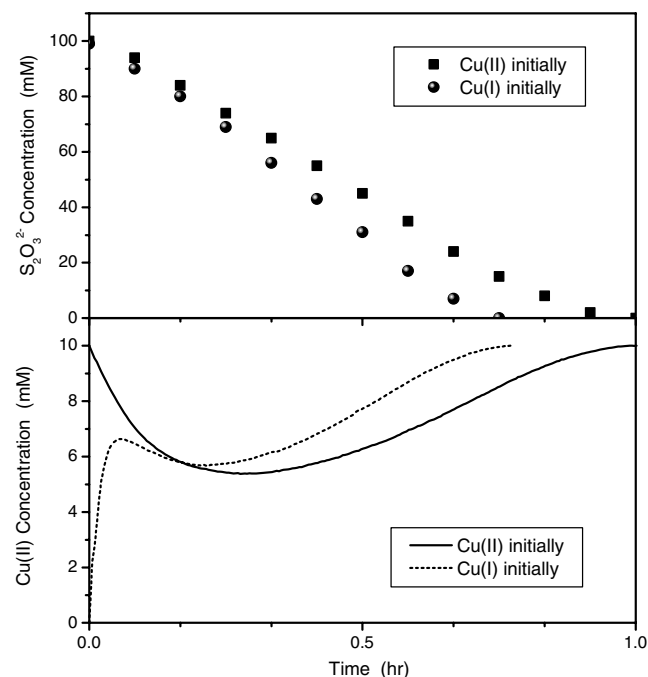


Fig. 4. Effect of initial copper oxidation state on the rate of thiosulfate oxidation and the copper(II) concentration profile: $0.1\text{ M Na}_2\text{S}_2\text{O}_3$, 0.4 M NH_3 , 10 mM Cu , 30°C , air sparged at $1000\text{ cm}^3\text{ min}^{-1}$.

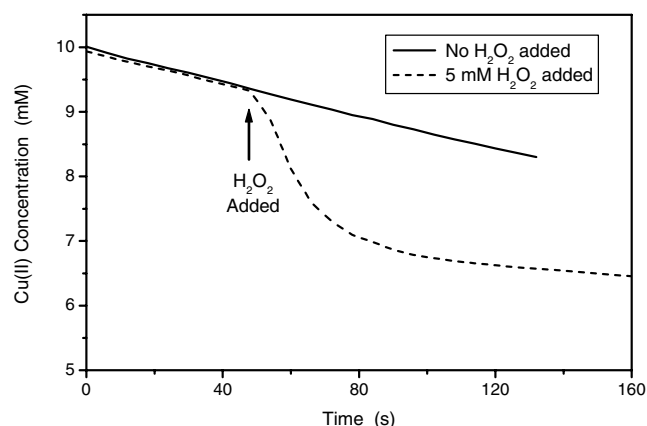
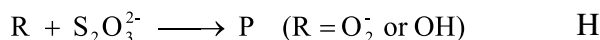
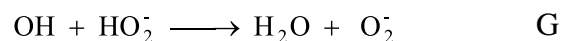
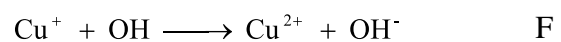
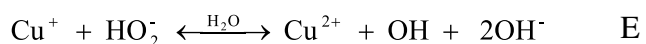
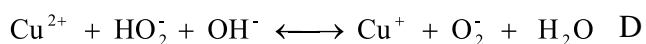
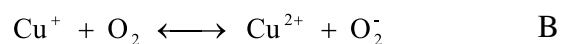
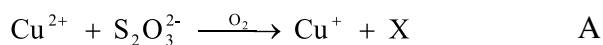


Fig. 5. Decomposition of hydrogen peroxide in thiosulfate leach solutions: 0.1 M $\text{Na}_2\text{S}_2\text{O}_3$, 0.4 M NH_3 , 10 mM CuSO_4 , 30 °C, air sparged at $1000 \text{ cm}^3 \text{ min}^{-1}$.

and ammonia directly oxidises thiosulfate. A series of experiments were therefore conducted in order to ascertain the effect of peroxide on the thiosulfate leach solution chemistry.

The addition of 50 mM hydrogen peroxide to a 0.1 M thiosulfate and 0.4 M ammonia solution (no copper) was found to result in less than 30% oxidation of thiosulfate after 1 h. Obviously this reaction does not occur at an appreciable rate. However, in the presence of copper(II) a very fast reaction occurs on the addition of peroxide. This is shown in Fig. 5, where the copper(II) concentration is observed to decrease rapidly on the addition of 5 mM hydrogen peroxide. A very rapid reaction was also observed on the addition of hydrogen peroxide to a thiosulfate leach solution containing copper only in the copper(I) oxidation state (not shown). The addition of hydrogen peroxide to a thiosulfate leach solution containing copper and ammonia was also found to result in a rapid decrease in the thiosulfate concentration. Such a result implies that the intermediates of peroxide decomposition oxidise thiosulfate and not peroxide directly as suggestion by Byerley et al. (1975).

Reaction mechanisms consistent with the results presented in this paper for thiosulfate oxidation and copper(II) reduction in thiosulfate leach solutions are shown in Scheme 1. Reactions B to G of Scheme 1 describe the copper catalysed decomposition of peroxide, which are obviously an integral part of the thiosulfate leach solution chemistry once copper(I) is formed in the presence of oxygen. The two paths for thiosulfate oxidation as predicted by the results of Fig. 3 are ascribed to Eqs. (A) and (H) of Scheme 1. Eq. (A) is the copper(II)–thiosulfate reaction that is catalysed by oxygen as evident in Fig. 1 by the higher initial rate of copper(II) reduction. Eq. (H) is the oxidation of thiosulfate by superoxide or hydroxide radicals as a result of cop-



Scheme 1. Proposed mechanisms for thiosulfate oxidation.

per(I) oxidation. Obviously a series of complex reactions are involved in copper(II) reduction and copper(I) oxidation (Eqs. (A), (B) and (D)–(F) of Scheme 1).

Even though it is shown in Fig. 2 that all the thiosulfate has been oxidised in 1 h, the oxidation of the other intermediate oxysulfur species, such as tetrathionate, may still be occurring. This has been shown to be the case in several of the references cited by Skorobogaty and Smith (1984). While these oxysulfur species may undergo further copper(II) catalysed oxidation involving similar mechanisms to those presented in Scheme 1 for the oxidation of thiosulfate (Eqs. (A) and (H)), this is beyond the focus of this paper.

A detailed study of the individual reactions involved in thiosulfate leach solutions in the presence of oxygen is beyond the focus of this paper. However, the copper(II) concentration and the rate of thiosulfate oxidation are of vital importance to the gold–thiosulfate leaching process. The $[\text{Cu(II)}]:[\text{Cu(I)}]$ ratio is also important as this essentially determines the potential at which gold leaching occurs. Hence, understanding the effect each of the various parameters have on the copper(II) concentration, the $[\text{Cu(II)}]:[\text{Cu(I)}]$ ratio and the rate of thiosulfate oxidation allows the conditions for gold leaching to be optimised.

3.6. Oxygen concentration

Fig. 6 shows the effect of oxygen concentration on the rate of thiosulfate oxidation and the copper(II) concentration. Clearly, the rate of thiosulfate oxidation is very rapid when the solution is sparged with pure oxygen; all the thiosulfate is consumed in less than 25 min, compared to 1 h for air. Also shown in Fig. 6 is the change in thiosulfate concentration when the solution is sparged using a gas composed of 1.9% oxygen in nitrogen. In this instance, the thiosulfate oxidation rate is

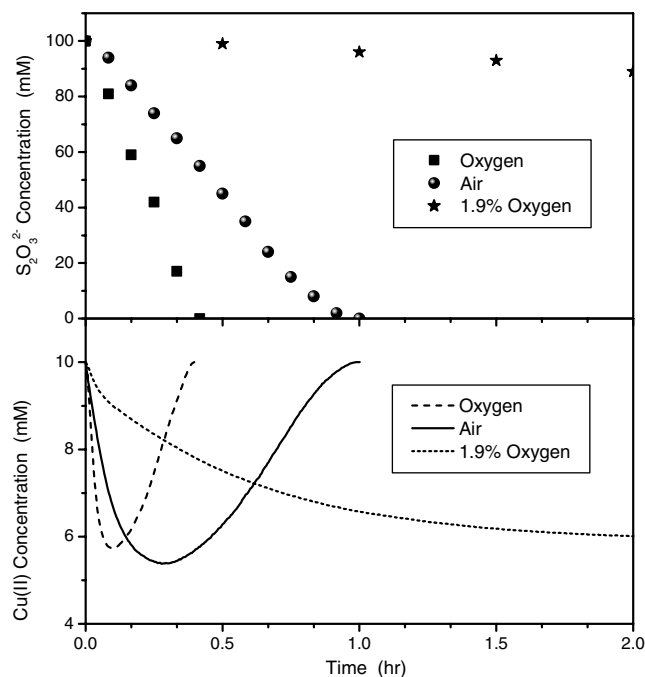


Fig. 6. Effect of oxygen concentration on the rate of thiosulfate oxidation and the copper(II) concentration: 0.1 M $Na_2S_2O_3$, 0.4 M NH_3 , 10 mM $CuSO_4$, 30 °C, gas sparged at 1000 $cm^3 min^{-1}$.

significantly reduced, and after 2 h only 10% of the thiosulfate has been destroyed.

It is evident from Fig. 6 that the copper(II) concentration is maintained above 5 mM for each of the three sparged gases used in the present study. As the sustainable copper(II) concentrations are similar, the effect of the oxygen concentration on the rate of copper(II) reduction must be very similar to the effect on the copper(I) oxidation rate. These results clearly show that increasing the oxygen concentration increases the copper(I) oxidation rate and associated reactions of Scheme 1, which increases the rate of thiosulfate oxidation. Thus, from an economic point of view, solutions sparged with low concentrations of oxygen are desirable, as the thiosulfate consumption rate will be low with little to no effect on the copper(II) concentration and hence the $[Cu(II)]:[Cu(I)]$ ratio.

Shown in Fig. 7 is the effect of air sparge rate on the thiosulfate oxidation rate and the copper(II) concentration. Clearly, the rate of thiosulfate oxidation decreases with decreasing sparge rate; such a result is hardly surprising, as the reaction is likely to be limited by the diffusion of oxygen to the solution–gas interface, and thus reducing the mass transfer rate of oxygen into solution significantly reduces the rate of thiosulfate consumption. The copper(II) concentrations are observed in Fig. 7 to decrease to a minimum value of around 5 mM before increasing again. These results are consistent with those presented in Fig. 6 and again indicate that decreasing the oxygen addition rate decreases both the rate

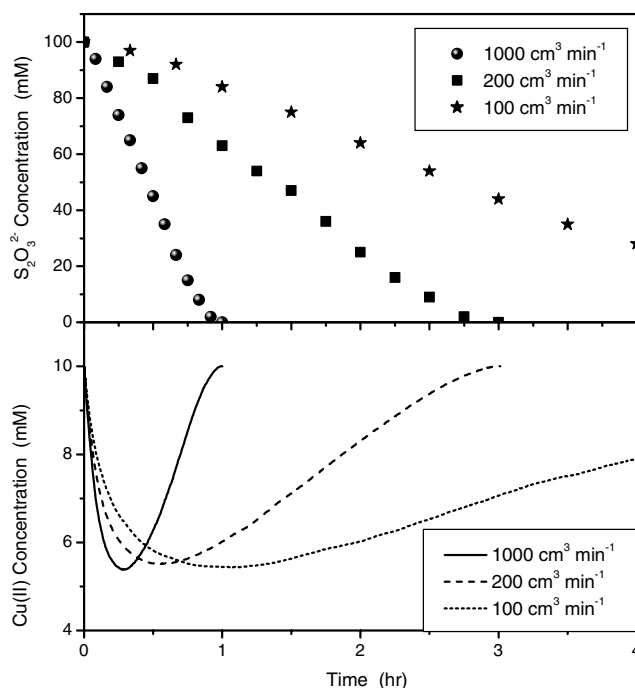


Fig. 7. Effect of air sparge rate on the rate of thiosulfate oxidation and the copper(II) concentration: 0.1 M $Na_2S_2O_3$, 0.4 M NH_3 , 10 mM $CuSO_4$, 30 °C, air sparged.

of copper(I) oxidation and copper(II) reduction. The net effect being almost no change in the copper(II) concentration and hence the $[Cu(II)]:[Cu(I)]$ ratio. However, at very low oxygen concentrations in solution (low gas phase oxygen concentration or sparge rate) the maintainable copper(II) concentration will be lower (not shown) as the rate of copper(II) reduction by thiosulfate and other oxysulfur species becomes significant in relation to the rates of the reactions shown in Scheme 1.

3.7. Thiosulfate concentration

Presented in Fig. 8 is the effect of thiosulfate concentration on the rate of thiosulfate oxidation and the copper(II) concentration. From this data, it can be seen that all the thiosulfate profiles show an induction period and have similar maximum thiosulfate oxidation rates. Hence, it would appear that the rate of thiosulfate oxidation is almost independent of thiosulfate concentration. However, the copper(II) concentration profiles in Fig. 8 indicate that increasing the thiosulfate concentration increases the rate of copper(II) reduction and reduces the sustainable copper(II) concentration and hence the $[Cu(II)]:[Cu(I)]$ ratio.

Obviously, in oxygenated solutions, any benefit of increasing the thiosulfate concentration on the gold dissolution process needs to be optimised against the decrease in copper(II) concentration and the $[Cu(II)]:[Cu(I)]$ ratio.

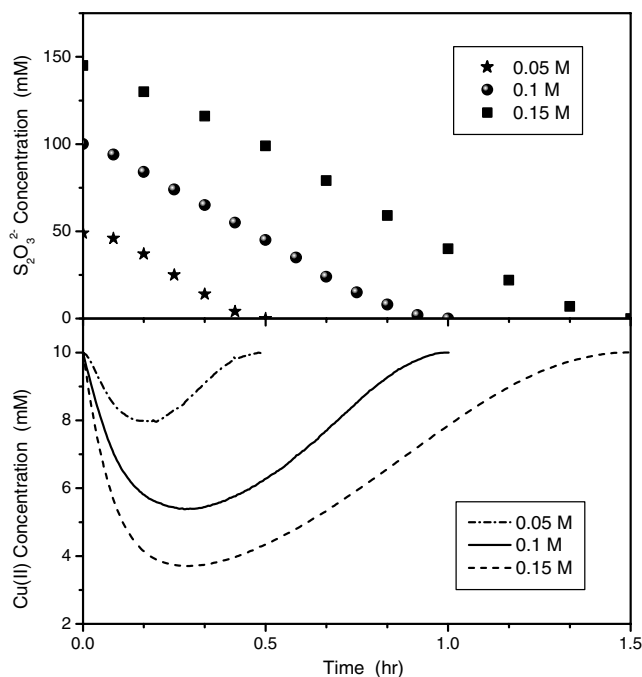


Fig. 8. Effect of thiosulfate concentration on the rate of thiosulfate oxidation and the copper(II) concentration: 0.4 M NH_3 , 10 mM $CuSO_4$, 30 °C, air sparged at 1000 $cm^3 min^{-1}$.

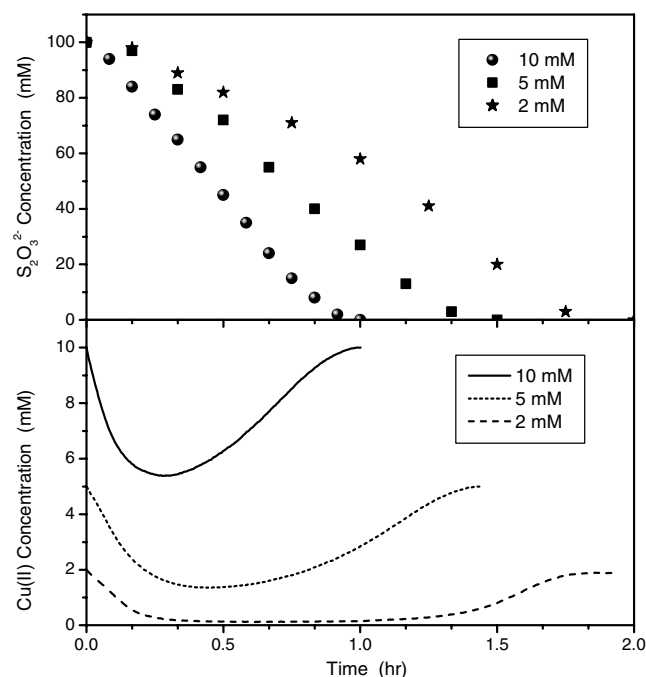


Fig. 9. Effect of copper concentration on the rate of thiosulfate oxidation and the copper(II) concentration: 0.1 M $Na_2S_2O_3$, 0.4 M NH_3 , 30 °C, air sparged at 1000 $cm^3 min^{-1}$.

3.8. Copper concentration

The effect of copper concentration on the rate of thiosulfate oxidation and the copper(II) concentration is shown in Fig. 9. It can be seen that a decrease in the copper concentration by a factor of 5 only decreases the rate of thiosulfate oxidation by a factor of 2. Fig. 9 also shows that the copper concentration has a significant effect on the observed sustainable copper(II) concentration and the $[Cu(II)]:[Cu(I)]$ ratio. As the copper concentration decreases, the $[Cu(II)]:[Cu(I)]$ ratio and hence the cathodic potential for gold leaching decreases significantly. Clearly, increasing the copper concentration, which benefits the cathodic potential, must be optimised against increased thiosulfate oxidation rates.

3.9. Ammonia concentration

Fig. 10 shows the effect of ammonia concentration on the rate of thiosulfate oxidation and the copper(II) concentration. It can be seen that the rate of thiosulfate oxidation for a solution containing 0.2 M ammonia is similar to that for a solution containing 0.4 M ammonia. Not surprisingly, the copper(II) concentration profile shows that the initial rate of copper(II) reduction increases with decreasing ammonia concentration and thus results in a lower sustainable copper(II) concentration. Thus, increasing the ammonia concentration has little effect on the thiosulfate oxidation rate, but

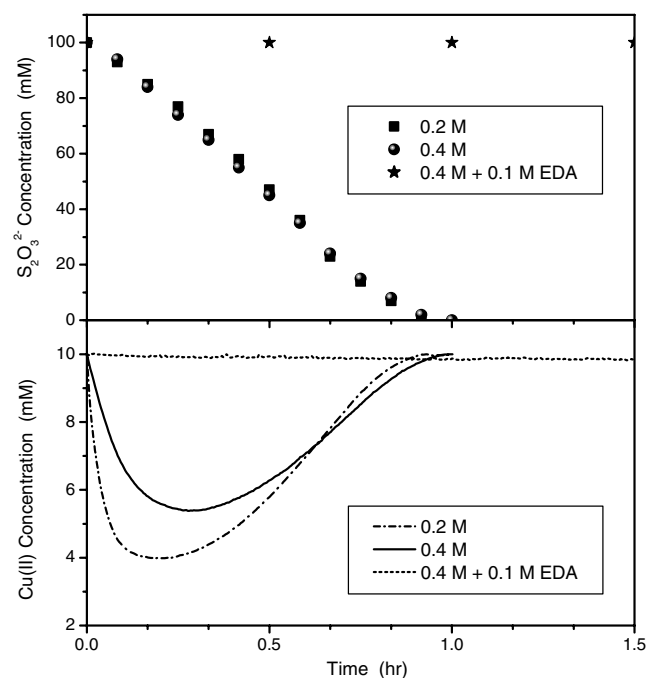


Fig. 10. Effect of ammonia concentration on the rate of thiosulfate oxidation and the copper(II) concentration: 0.1 M $Na_2S_2O_3$, 10 mM $CuSO_4$, 30 °C, air sparged at 1000 $cm^3 min^{-1}$ (EDA = ethylenediamine).

increases the sustainable copper(II) concentration and hence the $[Cu(II)]:[Cu(I)]$ ratio.

Also shown in Fig. 10 is the thiosulfate and copper(II) concentrations for a solution containing 0.4 M ammonia and 0.1 M ethylenediamine. It should be clear that for this solution, no decrease in either copper(II) or thiosulfate concentrations is observed. Such a result suggests that ethylenediamine forms a very strong complex with copper(II) which stops any copper(II) reduction and hence thiosulfate oxidation from occurring. According to the thermodynamic data (Smith and Martell, 1975, 1976), the copper(II)–ethylenediamine complex is significantly more stable than the copper(II)–amine complexes. The copper(II) is complexed by two ethylenediamine molecules at the four planar sites, with the axial sites available for possible thiosulfate complexation (Hathaway and Tomlinson, 1970). In studies previously published using various organic ligands for the copper(II) catalysed oxidation of thiosalts by molecular oxygen (Skorobogaty and Smith, 1984), the oxidation was only observed to occur at low ligand to copper(II) ratios. This suggests that only the two and three coordinated complexes were catalytically active and that the copper(II) complex must be able to be reduced in order for thiosulfate oxidation to occur. The addition of 50 mM hydrogen peroxide to a fresh thiosulfate leach solution containing ethylenediamine resulted in a 25% reduction in the thiosulfate concentration in less than 10 min. This is further evidence that the radicals involved in peroxide decomposition oxidise thiosulfate and hence supports the notion that thiosulfate oxidation results from the products of copper(I) oxidation. Obviously peroxide is strong enough to reduce copper(II) in the presence of ethylenediamine whereas thiosulfate with or without oxygen is not.

3.10. pH

The common use of ammonium thiosulfate in leaching studies results in a lower solution pH according to the equilibrium shown in Eq. (5); the pK_a for ammonia is 9.25 (Weast, 1974–75). Thus, at pH values below 9.25, more ammonium ions exist than ammonia and vice versa above this pH. This has significant implications to the copper(II) ion stability as it is ammonia that forms stable complexes and not ammonium ions.



Fig. 11 shows the effect of pH (constant ammonia concentration) on the copper(II) concentration and the thiosulfate oxidation rate. It has been previously shown that at low pH values, even though the ammonia concentration is constant, the copper(II) is much more reactive towards thiosulfate (Breuer and Jeffrey, submitted for publication). Hence it is not surprising that Fig. 11 shows that the sustainable copper(II) concentration is lower at the lower pH values. The thiosulfate

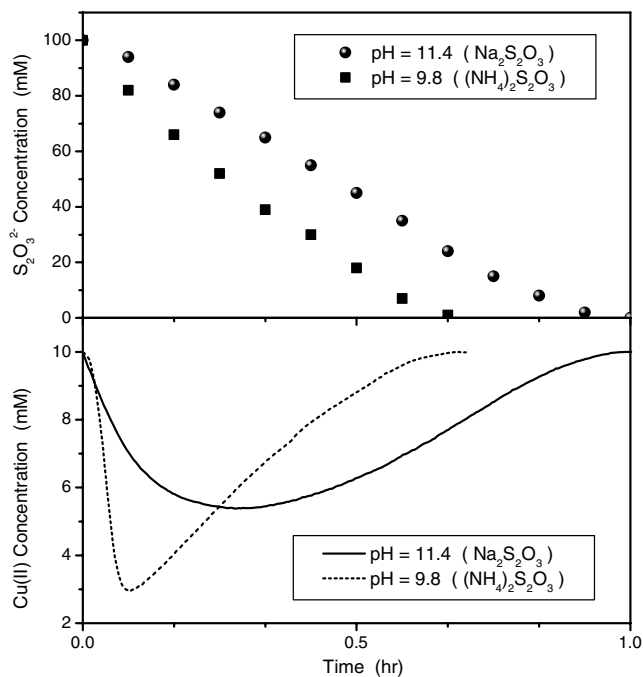


Fig. 11. Effect of pH on the rate of thiosulfate oxidation and the copper(II) concentration: 0.1 M $\text{Na}_2\text{S}_2\text{O}_3$, 0.4 M NH_3 , 10 mM CuSO_4 , 30 °C, air sparged at $1000 \text{ cm}^3 \text{ min}^{-1}$.

oxidation rate is also shown in Fig. 11 to be faster at lower pH.

4. Conclusions

Clearly, the results presented in this paper highlight the complexity of the thiosulfate leach solution chemistry, especially in the presence of oxygen. The rate of thiosulfate oxidation and copper(II) reduction were found to be significantly faster in the presence of oxygen. The initial rate of copper(II) reduction was higher in the presence of oxygen indicating that oxygen increases the rate of copper(II) reduction by thiosulfate to copper(I), though the mechanism for this remains unclear. The rates of thiosulfate oxidation and copper(II) reduction were also shown to be affected differently by the presence of anions. This indicated that thiosulfate oxidation may occur via two mechanisms. The main mechanism for thiosulfate oxidation was shown to be consistent with thiosulfate oxidation by the intermediate superoxide and hydroxide radicals formed as a result of copper(I) oxidation. A reaction scheme was also presented that is consistent with these results.

The thiosulfate oxidation rate was shown to be largely dependent on the oxygen addition rate (this being related to the oxygen mass transfer from the gas to the liquid). The ammonia and thiosulfate concentrations though were found to have little effect on the thiosulfate

oxidation rate. Surprisingly, the presence of anions only had a small effect on the overall rate of thiosulfate oxidation compared to the significant decrease observed in the copper(II) reduction rate. Thus, a possible advantage the presence of anions offer is the higher sustainable copper(II) concentration and hence a higher [Cu(II)]:[Cu(I)] ratio which is desirable for gold leaching. The sustainable copper(II) concentration and thus the [Cu(II)]:[Cu(I)] ratio was also increased by increasing the ammonia concentration but decreased with increasing thiosulfate concentration. Surprisingly, the [Cu(II)]:[Cu(I)] ratio was found to increase with increasing total copper concentration, though the rate of thiosulfate oxidation also increases.

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