

Role of copper(II), carbonate and sulphite in gold leaching and thiosulphate degradation by oxygenated alkaline non-ammoniacal solutions

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Abstract

Researchers have been unable to incorporate the copper(II)–thiosulphate complexes in Eh-pH or species distribution diagrams due to the unreliability of the reported stability constants. The present work describes a concurrent thermodynamic and kinetic analysis of literature data to show that the reaction between copper(II) and thiosulphate ions takes place via the formation of an unstable $\text{Cu}(\text{S}_2\text{O}_3)_n(\text{H}_2\text{O})_p^{-2(n-1)}$ complex followed by its first or second order decomposition. The oxidation of thiosulphate to tetrathionate, predominantly via the second order disproportionation with a rate constant of $1.2 \times 10^5 \text{ l mol}^{-1} \text{ s}^{-1}$ produces $\text{Cu}(\text{S}_2\text{O}_3)^-$, which is stabilized as $\text{Cu}(\text{S}_2\text{O}_3)_n^{-(2n-1)}$ ($n = 2$ or 3). This analysis allows the calculation of two stability constants $10^{2.4}$ and $10^{5.2}$ for $\text{Cu}(\text{S}_2\text{O}_3)^0$ and $\text{Cu}(\text{S}_2\text{O}_3)_2^{2-}$ respectively, which predict the predominant species: $\text{Cu}(\text{S}_2\text{O}_3)_2^{2-}$ ($\text{pH} < 9$), $\text{Cu}(\text{OH})_2^0$ ($9 < \text{pH} < 11$) and $\text{Cu}(\text{OH})_3^-$ ($\text{pH} > 11$). The disproportionation of $\text{Cu}(\text{S}_2\text{O}_3)^0$ and $\text{Cu}(\text{S}_2\text{O}_3)^-$ leads to the precipitation of Cu, CuS and Cu_2S .

The calculated equilibrium constants predict that copper(II) complexes such as $\text{Cu}(\text{S}_2\text{O}_3)^0$, $\text{Cu}(\text{S}_2\text{O}_3)_2^{2-}$, $\text{Cu}(\text{OH})_2^0$ and $\text{Cu}(\text{OH})_3^-$ can leach gold to produce $\text{Au}(\text{S}_2\text{O}_3)_2^{3-}$, $\text{Au}(\text{OH})^0$, and $\text{Au}(\text{OH})_2^-$, where the latter two are converted to the more stable $\text{Au}(\text{S}_2\text{O}_3)_2^{3-}$ complex. The rate of thiosulphate oxidation by oxygen during gold leaching from copper gold ores in alkaline media is of the order $\approx 10^{-6} \text{ mol l}^{-1} \text{ s}^{-1}$, irrespective of the presence or absence of ammonia. This is three orders of magnitude smaller than the rate of oxidation of thiosulphate by copper(II) in acid media, indicating the involvement of mixed complexes of the type $\text{Cu}(\text{II})\text{-(L)}_n(\text{S}_2\text{O}_3)_m(\text{O}_2)$ in ammoniacal ($\text{L} = \text{NH}_3$) and non-ammoniacal ($\text{L} = \text{OH}^-$) media, compared to the disproportionation of $\text{Cu}(\text{II})(\text{S}_2\text{O}_3)_{1-2}$ in acid media with no oxygen. The gold leaching in oxygenated alkaline thiosulphate media obeys a shrinking core kinetic model with an apparent rate constant of the order 10^{-5} s^{-1} . In the presence of 0.4 M total carbonate in alkaline media, the predominant copper(II) complex is $\text{Cu}(\text{CO}_3)_2^{2-}$. This minimizes thiosulphate degradation to tetrathionate via the disproportionation of $\text{Cu}(\text{II})(\text{S}_2\text{O}_3)_{1-2}$. However, the presence of carbonate enhances the overall thiosulphate consumption and trithionate and sulphate formation, leading to a lower gold extraction. In a thiosulphate deficient leach liquor, such as that produced in the presence of carbonate, gold precipitation takes place via disproportionation reactions. The addition of sulphite reproduces thiosulphate from tetrathionate, but slowly precipitates gold.

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1. Introduction

Thiosulphate is an intermediate product of the oxidation of iron sulphides (Mishra and Osseo-Asare, 1988). Thus, mill tailings waters from sulfide leaching

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operations contain thiosalts ($S_2O_3^{2-}$, $S_4O_6^{2-}$, $S_3O_6^{2-}$) produced by the degradation of sulphide minerals. When discharged, the mill waters cause environmental problems due to the oxidation of thiosalts to sulphuric acid. Oxidation of thiosulphate by copper(II) in acid media is faster than that in oxygen alone (Rábai and Epstein, 1992). This led to investigations of methods of complete oxidation of thiosalts to sulphuric acid by chemical means, using oxidants such as copper(II); and neutralization of the acid prior to discharge of the effluent (Chanda and Rempel, 1987).

However, the oxygenated thiosulphate system has been recognized as a promising non-cyanide gold lixiviant in the presence of ammonia. Recent research publications have highlighted the advantages and problems associated with the use of the oxygenated thiosulphate system as a non-cyanide gold lixiviant in the presence of copper(II) and ammonia (Berezowsky and Sefton, 1979; Zipperian et al., 1988; La Brooy et al., 1994; Abbruzzese et al., 1995; Ritchie et al., 2001; Aylmore and Muir, 2001; Molleman and Dreisinger, 2002; Grosse et al., 2003; Muir and Aylmore, 2004). Ammonia forms stable complexes with copper(II) and slows down thiosulphate oxidation. Thus, the oxygenated ammoniacal copper(II)–thiosulphate system for gold leaching based on the redox reaction $Cu(II) + Au(0) = Cu(I) + Au(I)$ is proven to offer environmental, economic, and other benefits compared to leaching with oxygenated alkaline cyanide, especially with refractory, carbonaceous (preg-robbing), and copper–gold ores. Although the role of oxygen is expected to be the re-oxidation of copper(I) to copper(II), the rate of oxidation of thiosulphate by ammoniacal copper(II) is also enhanced by oxygen (Byerley et al., 1973a, 1975). Thus, Ji et al. (2003) reported current research interest to develop an oxygen–thiosulphate leaching system for gold ores without using copper(II) to minimize thiosulphate degradation and to avoid toxic ammonia.

The thiosulphate degradation and consumption is unavoidable and detrimental to overall gold leaching due to high reagent cost, precipitation of gypsum, metallic gold and/or Au_2S , and the interference of degradation products in subsequent separation and recovery using ion exchange processes (Nicol and O'Malley, 2001, 2002; West-Sells et al., 2003; Ji et al., 2003; Muir and Aylmore, 2004). Thus, despite long term interest and some success in recent years (Wan and LeVier, 2003), thiosulphate processes for gold extraction are at developmental stages with limited understanding of the (i) leach and pulp (slurry) chemistry, (ii) reaction mechanism of gold oxidation, and (iii) degradation chemistry of thiosulphate.

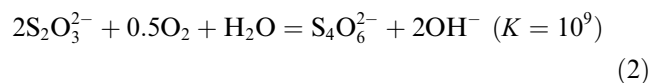
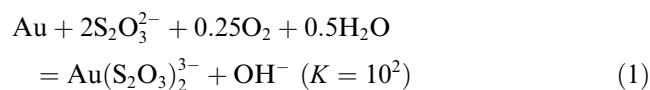
A proper analysis of leaching kinetics requires reliable information on chemical speciation based on stability constants of copper(II)/(I) complexes listed in Table 1. Although the Eh-pH and species distribution dia-

grams provide useful information on chemical speciation and reactions involved in hydrometallurgical systems, the lack of reliable information on stability constants of relevant complex species has hampered the construction of such diagrams for the thiosulphate systems. For example, there are two values for stability constants of $Cu(II)(S_2O_3)_2^{2-}$ reported in the literature ($\log\beta_2 = 4.6$ and 12.3 , Table 1) and the higher value is closer to that of $Cu(I)(S_2O_3)_2^{3-}$, as noted by Rábai and Epstein (1992). This shows the difficulties in obtaining reliable stability constants for complexes such as $Cu(II)(S_2O_3)^0$ and $Cu(II)(S_2O_3)_2^{2-}$ due to the fast reaction between copper(II) and thiosulphate in acid media.

The aim of the present investigation is to (i) carry out a concurrent thermodynamic and kinetic analysis of the data reported by Rábai and Epstein (1992) for the reaction between copper(II) and thiosulphate in non-ammoniacal media, (ii) to determine reliable stability constants for $Cu(II)(S_2O_3)^0$ and $Cu(II)(S_2O_3)_2^{2-}$, and to construct species distribution diagrams for the $Cu(II)/(I)-S_2O_3^{2-}-OH^- -CO_3^{2-}$ system, (iii) to summarize evidence that suggests the possible involvement of copper(II) as an oxidant for gold and/or thiosulphate in alkaline non-ammoniacal media, and (iv) to rationalise reported results (Ji et al., 2003) that show the effect of copper(II) sulphate, sodium carbonate and sodium sulphite on gold extraction and thiosulphate degradation in oxygenated non-ammoniacal alkaline media.

2. Thiosulphate degradation products

In the case of non-ammoniacal gold leaching by oxygenated thiosulphate, it is expected that the concentration of thiosulphate (ligand) and oxygen (oxidant) would control the kinetics of gold leaching and thiosulphate degradation that involve a series of reactions (Eqs. (1)–(9)) as noted by previous researchers (Rolia and Chakrabarti, 1982; Zipperian et al., 1988; Abbruzzese et al., 1995; Aylmore and Muir, 2001; Molleman and Dreisinger, 2002; Zhang and Dreisinger, 2002; Grosse et al., 2003). The equilibrium constants (K) based on the reported values of standard free energy of formation for various sulphur species (Aylmore and Muir, 2001; Molleman and Dreisinger, 2002) are also shown along with Eqs. (1)–(9) in order to examine the thermodynamic feasibility of these reactions.



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