



An analysis of the efficiency and sustainability of the thiosulfate-copper-ammonia-monoethanolamine system for the recovery of silver as an alternative to cyanidation



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ABSTRACT

In this research, silver leaching experiments from pure phases of Ag and Ag₂S were done using the S₂O₃²⁻-Cu²⁺-MEA-NH₄ alternative system and varying the S₂O₃²⁻ and MEA concentrations. The results revealed that MEA can stabilize the cupric ions forming several Cu-MEA complexes. It was also found that MEA can form Ag-MEA complexes, and thus it can work as a co-leaching agent for silver, mainly when metallic silver is used.

Furthermore the leaching experiments with metallic silver showed a continuous oscillation process (silver dissolution-precipitation phenomenon), which was related to the formation of the redox couples Ag-MEA/Ag and Cu-NH₃/Cu-MEA, as well as with the oxidative decomposition of thiosulfate which could lead to the formation of copper sulfide species. The leaching experiments with silver sulfide revealed that the presence of MEA in the leaching system is advantageous in two ways: a) it decreases the precipitation of copper oxides and b) it assists the stabilization of silver in solution avoiding its precipitation.

Furthermore, the pregnant leaching solutions were treated by cementation using a metallic copper wire and the chemical and microstructural characterizations revealed that silver was deposited on the copper wire surface. When the leaching solution is re-utilized after the cementation step in a second leaching with Ag₂S, it is possible to dissolve 85% of silver. This paper presents an alternative-sustainable thiosulfate leaching system which permits the recovery of silver from metallic silver or silver sulfide at short processing times.

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1. Introduction

Since the 1980's the search of alternative-green processes to cyanidation has been intensified due to two issues: a) the environment i.e., nowadays the environmental regulations are becoming more severe with respect to the use of cyanide and b) the process kinetics, i.e., the enhancement of the gold and silver dissolution rates (Abbruzzese et al., 1995).

The recovery of precious metals using thiosulfate, was proposed for the first time in 1900, in a process known as "Von Patera" (Aylmore and Muir, 2001). Thiosulfate is an intermediate product of the oxidation of iron sulfides; due to this fact, many of the leaching solutions, used in the processing of sulfur minerals, contain thiosalts (S₂O₃²⁻, S₄O₆²⁻, S₃O₆²⁻), such compounds are produced from the degradation of the sulfur minerals (Senanayake, 2005a). The last fact, represents an interesting advantage, i.e., many of the worldwide reserves of iron and copper are found in the terrestrial cortex as sulfur minerals, which can be an important source to produce thiosulfate. Therefore, thiosulfate leaching

can be considered an alternative less toxic system to the conventional cyanidation (Abbruzzese et al., 1995).

Several investigations have been done for the leaching of gold and silver using thiosulfate solutions (Aylmore, 2001; Aylmore and Muir, 2001; Balaz et al., 2000; Breuer and Jeffrey, 2003; Fuentes-Aceituno et al., 2005; Lam and Dreisinger, 2003; Muir and Aylmore, 2005; Senanayake, 2005b; Zipperian et al., 1988); these researches showed that leaching solutions containing thiosulfate-copper-ammonia are efficient to dissolve the precious metals from sulfide ores in 48 h, approximately. Furthermore, Senanayake (2007) reported that thiosulfate is considered the most promising non-cyanide complexing agent for the recovery of precious metals from refractory ores. Thiosulfate needs to be in contact with co-leaching agents such as ammonia or thiourea, as well as in the presence of oxidizing agents such as copper (II) or iron (III) (Senanayake, 2007).

During the thiosulfate leaching of precious metals, several chemical and electrochemical reactions take place, such as: oxidation, dissolution and complexes formation. Only few oxidizing agents are adequate to work in ammoniacal solutions, such as cupric ions (Abbruzzese et al., 1995). Its catalytic power promotes the dissolution of gold in thiosulfate solutions, accelerating the dissolution rate from 18 to 20 times. However, the chemistry of this system is very complex and the presence of

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cupric ions in solution can promote the loss of thiosulfate up to 50% producing tetrathionate and other sulfur compounds (Aylmore and Muir, 2001).

Due to the persistent instability of the cupric ions in ammoniacal solutions, it is necessary to introduce additives to stabilize the copper in solution at high concentrations of ammonia, copper and thiosulfate (Feng and Van Deventer, 2010). EDTA is one of the most studied reactants to stabilize the cupric ions in the leaching solution (Feng and Van Deventer, 2010; Puente-Siller et al., 2013); however, Puente-Siller et al. (2013) reported the precipitation of copper sulfides and copper oxides in the system containing EDTA. Alternative complexing agents for cupric ions have been also studied, such as sodium citrate (Puente-Siller et al., 2014). These researchers found that the presence of sodium citrate favors the silver sulfide dissolution rate; however the precipitation of copper sulfides and copper oxides from the leaching solution persisted.

Due to the necessity to find a stabilizer agent for cupric ions in thiosulfate leaching solutions, this work proposes the use of monoethanolamine (MEA) in thiosulfate solutions. It is known that MEA can form Cu-MEA complexes. Shih et al. (2002) carried out a study on the dissolution of copper in MEA solutions at alkaline pH; they found that MEA can form complexes with copper ions. Furthermore, Kwang and Gyu (2010) studied the ability of MEA to solubilize copper oxides and stabilize copper ions as Cu-MEA complexes at different pH values. It has been also reported the ability of MEA as a complexing agent-inhibitor of corrosion, which avoids the formation of copper oxides on copper surfaces (Kwang and Gyu, 2010). Cho et al. (2014) used MEA as a copper complexing agent in the processing of thin films.

Copper oxides present an acceptable dissolution rate in MEA containing alkaline solutions at ($\text{pH} \geq 9$), it is important to mention that the solubility of copper oxides, in the presence of MEA, is decreased when the solution becomes more acid (Kwang and Gyu, 2010). The ability of MEA to complex cupric ions at pH values higher than 9 can be an advantage in this research. It is worth mentioning that thiosulfate leaching is carried out, in the most of cases, in alkaline solutions, due to the fact that thiosulfate can form more stable complexes with the precious metals when the leaching system is operated at pH values from 8.5 to 10.5 approximately.

This work presents a kinetic and thermodynamic study of the $\text{S}_2\text{O}_3\text{-Cu-NH}_4\text{-MEA}$ alternative system for the leaching of the pure species of silver and silver sulfide. This process would be able to dissolve silver in short processing times, to recover the silver in its metallic form, and to re-utilize the leaching solution.

2. Materials and methods

The experimental work was divided in three sections: Section 2.1, silver leachings from pure metallic silver with the thiosulfate-copper-ammonia-MEA system; Section 2.2, elaboration of the thermodynamic diagrams for the Ag-MEA- H_2O and Cu-MEA- $\text{NH}_3\text{-H}_2\text{O}$ systems, and; Section 2.3, silver leachings from pure silver sulfide followed by the cementation of metallic silver and re-utilization of the leaching solution with the thiosulfate-copper-ammonia-MEA system.

All leaching experiments were performed in an agitated batch reactor (250 mL glass beaker), magnetically stirred at 400 min^{-1} . The reactor was provided with a pH electrode (SENSOREX) and a redox potential electrode with calomel reference (Cole-Parmer); the pH and the redox potential were measured before the metallic silver or silver sulfide addition and during the leaching experiments. Samples of the leach solutions were withdrawn at different times during the leach period for analysis of silver by atomic absorption spectrophotometry (VARIAN Spectra AA 240). All samples were analyzed at the end of the experiments, and until the analysis they were kept in dark vessels to prevent the precipitation of silver by light. The quantification of the thiosulfate

decomposition was done in some leaching experiments, using the iodometric titration method reported by Paredes-Soto (2014).

It is worth mentioning that all experiments were performed at room temperature and all solutions were prepared with reagent grade chemicals and deionized water. The leaching experiments for silver and silver sulfide are described in the next sections.

2.1. Leaching tests using metallic silver with different thiosulfate and MEA concentrations

The leachings were carried out adding 0.125 g of metallic silver ($1-3 \mu\text{m}$, Alfa Aesar, 99.999%) in 200 mL of the leaching solution which contained 0.05 M Cu^{2+} , 0.1, 0.2 or 0.3 M thiosulfate and 0, 1.25×10^{-4} , 0.025 or 0.05 M MEA at room temperature and $\text{pH} = 10.20$ adjusted with ammonium hydroxide. The leachings were stirred at 400 min^{-1} during 6 h.

2.2. Elaboration of the thermodynamic diagrams

Thermodynamic diagrams for the Ag-MEA- H_2O and Cu-MEA- $\text{NH}_3\text{-H}_2\text{O}$ systems were constructed using the Medusa© Software. The diagrams were constructed considering the equilibrium data contained in the Hydra database of the Medusa© suite software (Puigdomenech, 2004), complemented with thermodynamic data for some silver and copper species reported by Aylmore and Muir (2001), and Smith and Martell (1975). The software is based in an algorithm developed by Eriksson (1979), which minimizes the Gibbs free energy of reactions in equilibrium that can occur in the aqueous leaching systems, and determines the predominating species under specific solution conditions. Table 1 presents the thermodynamic data used in this work.

2.3. Leaching of silver sulfide, cementation of metallic silver and re-utilization of the leaching solution (LCRL process)

The LCRL process i.e., the leaching of silver sulfide followed by the cementation of metallic silver and re-utilization of the solution in a second leaching of fresh silver sulfide, was studied employing two leaching solutions containing: 0.2 or 0.3 M thiosulfate, 0.05 M Cu^{2+} and 0.025 or 0.05 M MEA. Both leaching steps i.e., before and after the cementation process, used 0.1435 g of pure silver sulfide ($-400 + 500$ mesh, Alfa Aesar 99.99%) and 200 mL of the leaching solution at $\text{pH} = 10.20$ adjusted with ammonium hydroxide.

The total experimental time of the LCRL process corresponds to 6.5 h. The LCRL process was divided in three steps: a) silver sulfide leaching using both leaching solutions mentioned above during 3 h, b) after this time, the pregnant leaching solution was filtered and the silver cementation step was triggered immersing 10.95 g of copper wires (0.5 mm diameter) in the pregnant leaching solution during 30 min, c) after this time, the copper wires coated with metallic silver were withdrawn from the reactor, and the leaching solution was used to carry out a second leaching employing fresh silver sulfide (0.1435 g), in order to evaluate the performance of the system when the leaching solution is recycled. The copper wire coated with metallic silver was chemically and morphologically characterized by SEM (Phillips XL30ESEM). The local chemical composition on the wire surface was determined by EDXS (EDAX Genesis).

3. Results and discussion

The results of this research are presented and discussed in this section. The first section corresponds to the effect of thiosulfate and MEA concentrations on the metallic silver leaching; the second section shows a thermodynamic analysis focused to explain the phenomena observed in the first section, and the last section presents the silver sulfide leaching using this alternative thiosulfate system followed by a

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