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Silver leaching with the thiosulfate–nitrite–sulfite–copper alternative system

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ABSTRACT

In the recent years, several silver leaching technologies have been investigated in order to find out an alternative and sustainable leaching process; one of these alternatives is the thiosulfate. The main research line is focused in the use of thiosulfate with copper as a catalyst and ammonia as a cupric ion stabilizer; however, the ammonia is also another toxic reagent. For that reason, an alternative-new leaching system using thiosulfate–nitrite and copper ions was investigated in this work. This new leaching system is able to dissolve silver without the use of cyanide or ammonia due to the cupric–ammonia complexes in-situ production, which is possible through the reaction of the nitrite and the cupric ions at neutral pH and NO_2:Cu molar ratio of 30:1, according to silver leaching experiments and thermodynamic predictions.

On the other hand, the effect of sulfite concentration was studied in the leaching solution revealing that the reductive ability of the sulfite ions has a negative effect on the silver leaching kinetics and recovery. It was also found that an increase in the pH of the leaching solution from 7 to 9.6 promotes the precipitation of copper hydroxide species which inhibits the silver leaching kinetics.

Finally, copper–ammonia complex formation was also confirmed in the silver leaching by the UV–Visible spectroscopy technique. The solid leaching residues obtained at neutral pH were analyzed by X-ray diffraction and scanning electron microscopy showing the formation of a copper hydroxysulfate species called antlerite; this result was also confirmed by species distribution diagrams.

1. Introduction

Cyanidation is the process traditionally employed worldwide for the extraction of silver and gold. This method is simple, economic and efficient; for that reason, it has been used for more than 100 years. At the present time, the mining industry has been involved in solving new technological and environmental challenges (Aylmore and Muir, 2001; Ahern et al., 2006). In this sense, the thiosulfate is an excellent alternative to replace the cyanide from the leaching systems.

1.1. Leaching with thiosulfate

The thiosulfate system has been studied extensively in the last years due to the fact that it is a very attractive and cheap reagent for the silver and gold leaching, furthermore, this reagent has the ability to produce strong complexes with these metals and easily leach the ores when is catalyzed with cupric ions (Aylmore and Muir, 2001); however, the understanding of the reaction mechanism for the precious metals leaching has shown to be very complex; consequently, the industrial application has been limited (Zhang and Nicol, 2003).

On the other hand, the proper maintenance of the pH and potential conditions and the control of the thiosulfate, ammonia and copper concentrations in the leaching solution can achieve high extractions of gold and silver with low consumption of reagents (Ji et al., 2003).

1.2. Effect of the copper and ammonia in the thiosulfate leaching

As mentioned above, the catalytic effect of the cupric ions in the leaching solution of thiosulfate–copper–ammonia favors the silver and gold leaching kinetics from 18 to 20 times; this increase is mainly attributed to the formation of a copper–ammonia complex, the so-called cupric tetraamine $Cu(NH_3)_4^{2+}$ (Aylmore and Muir, 2001).

On the other hand, an excessive increase of the cupric ion concentration in the leaching solutions has the disadvantage of promoting the thiosulfate degradation to polythionates that compromises the gold recovery and the process profitability (Ji et al., 2003). In this sense, a wide number of metastable sulfur species such as sulfite (SO_3^{2-}), thiosulfate ($S_2O_3^{2-}$), dithionate ($S_2O_6^{2-}$), trithionate ($S_3O_6^{2-}$), tetrathionate ($S_4O_6^{2-}$), sulfur (S^0) and polysulfides ($S_n{}^{2-}$), have been found in pregnant thiosulfate alkaline solutions (Aylmore and Muir, 2001; Zhang and Dreisinger, 2002; Ahern et al., 2006).

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In addition, ammonia has other important implications in the precious metal leaching kinetics: the ammonia absence causes a decrease in the leaching kinetics due to the accumulation of sulfur layers on the precious metal particle as a result of the thiosulfate degradation. This suggests that the ammonia prevents the gold passivation due to its preferential adsorption on the gold surface, generating a gold–ammonia complex (Aylmore and Muir, 2001).

1.3. Effect of sulfite in thiosulfate leaching solutions

One way to partially reduce the thiosulfate degradation is adding a small amount of sulfite ion to the leaching solution to react with the polythionates as shown in the next reaction (Tanriverdi et al., 2000):

$$SO_3^{2-} + S_xO_6^{2-} \leftrightarrow S_{x-1}O_6^{2-} + S_2O_3^{2-}. \qquad (1)$$

From a mechanistic point of view, the presence of the sulfite or bisulfite ions in alkaline solutions can cause an equilibrium reaction between the hydrogen sulfide ions and thiosulfate contained in the leaching solution, according to the next equation (Aylmore and Muir, 2001; Grosse et al., 2003):

$$2HS^- + 4HSO_3^- \leftrightarrow 3S_2O_3^{2-} + 3H_2O. \qquad (2)$$

This equilibrium is important because without the presence of the sulfite ion, the reaction would be favored to the left, producing hydrogen sulfide (HS^-) which promotes the precipitation of silver as an insoluble sulfur compound (Kerley, 1983; Ji et al., 2003; Gudkov et al., 2010a, 2010b).

For this reason, reaction (2) shows the necessity to have sulfite ions in the leaching solution in order to direct the reaction to the right and prevent the thiosulfate degradation (Kerley, 1983; Gudkov et al., 2010a, 2010c; Aylmore and Muir, 2001; Grosse et al., 2003).

However, an excess of sulfite can decrease significantly the oxidation ability of the leaching solution and have a negative effect in the silver leaching kinetics (Wan and LeVier, 2003).

1.4. The role of sodium nitrite in alternative leaching systems

In the last decades, the leaching process with nitrogen species catalyzed (NSC) with pressure has been studied for the recovery of silver, copper, zinc and iron from refractory sulfide ores, this method is an alternative to the cyanidation process (Anderson, 1995; Anderson et al., 1996a).

This process uses a leaching aqueous solution that contains: sulfuric acid and sodium nitrite under oxygen pressure (Anderson, 1995; Anderson et al., 1996b). From a mechanistic point of view, the sodium nitrite produces unstable nitrous acid according to next reaction (Anderson, 1995; Anderson and Nordwick, 1996):

$$NaNO_{2(aq)} + H^+ \rightarrow HNO_{2(aq)} + Na^+. \qquad (3)$$

The nitrous acid reacts in the acid medium to form NO^+ (Anderson, 2003):

$$HNO_{2(aq)} + H^+ \rightarrow NO^+_{(aq)} + H_2O. \qquad (4)$$

The NO^+ reacts with the sulfide mineral (MeS) (Anderson, 2003):

$$2MeS_{(s)} + 4NO^+_{(aq)} \rightarrow 2Me^{2+}_{(aq)} + 2S^0 + 4NO_{(g)}. \qquad (5)$$

The main objective of this research was to evaluate the thiosulfate–nitrite–sulfite–copper alternative leaching system for silver dissolution in order to find the optimal conditions to accelerate the silver dissolution kinetics and to improve the understanding of the phenomena that controls the silver leaching process.

2. Materials and methods

This section describes all the materials, equipment, reagents, leaching solution composition and the experimental methodologies used in this research work.

Leaching solutions were prepared with analytical grade reagents and deionized water. The reagents were: metallic silver (99.999%, 1–3 μM, spherical, Alfa Aesar), sodium sulfite (98%, Jalmek), sodium nitrite (97.2%, Analytyka), cupric sulfate pentahydrate (99%, Merck) and sodium thiosulfate pentahydrate, crystals (100%, J.T. Baker). For the pH adjustment and UV/Vis characterization, sodium hydroxide flakes (97%, J.T. Baker) and ammonium hydroxide (28–30%, Jalmek) were employed, respectively.

The experimental work was divided in four main sections: Section 2.1. Thermodynamic study, Section 2.2. Leaching tests, Section 2.3. Chemical and morphological characterization of the solid residues and Section 2.4. Ultraviolet/Visible spectroscopy study.

2.1. Thermodynamic study

In order to elucidate the predominant species in the thiosulfate–nitrite–copper–silver system, nitrite system and nitrite–copper system, Pourbaix and species distribution diagrams were calculated at room temperature using the Medusa© Software and considering the equilibrium data contained in the Hydra database of the same software (Puigdomenech, 2004).

These diagrams were used to determine all the species that can be formed in the leaching solutions at different pH and potential conditions.

2.2. Leaching tests

All silver leaching experiments were performed in an agitated batch reactor (250 mL glass beaker); the reactor was provided with a pH meter (pH 538 WTW), a pH electrode (SENSOREX), a redox potential electrode with Ag/AgCl reference (Cole–Parmer) and a magnetic plate (for stirring). The general procedure for the leaching experiments was as follows: 200 mL of the leaching solution (Table 1) and 0.1266 g of

Table 1
Leaching solutions.

Concentration (M)				
Thiosulfate	Sulfite	Nitrite	Copper	pH
Effect of copper on silver leaching with the thiosulfate–nitrite–sulfite system				
0.018	0.005	0.009	–	9.9
0.018	0.005	0.009	0.004	10
Silver leaching with the thiosulfate–copper, sulfite–copper and nitrite–copper systems at different pH				
0.018	–	–	0.004	7.8
0.018	–	–	0.004	9.9
–	0.005	–	0.004	5.46
–	0.005	–	0.004	9.9
–	–	0.009	0.004	5.5
–	–	0.009	0.004	9.9
Effect of the NO_2–Cu molar ratio on silver leaching with the thiosulfate–nitrite–sulfite–copper system				
0.018	0.005	0.009	0.008	9.9
0.018	0.005	0.009	0.008	7.6
0.2	0.005	0.6	0.02	9.6
0.2	0.005	2.6	0.04	9.6
Effect of thiosulfate and sulfite on silver leaching with the thiosulfate–nitrite–sulfite–copper system				
0.07	0.005	1.5	0.05	6.5
0.1	0.005	1.5	0.05	7.4
0.1	0.2	1.5	0.05	8.4
0.1	0.005	1.5	0.05	7.4
0.1	–	1.5	0.05	7.27