Hydrometallurgy 160 (2016) 98–105

Contents lists available at ScienceDirect

Hydrometallurgy

journal homepage: www.elsevier.com/locate/hydromet

Silver leaching with the nitrite–copper novel system: A kinetic study

G. Alvarado-Macías [a], J.C. Fuentes-Aceituno [a,*], F. Nava-Alonso [a,b], Jae-chun Lee [c]

[a] *Centro de Investigación y de Estudios Avanzados del IPN, Unidad Saltillo, Av. Industria Metalúrgica # 1062, Parque Industrial Ramos Arizpe, Ramos Arizpe, Coahuila, 25900, México*
[b] *On sabbatical leave at Department of Mining, Metallurgical and Materials Engineering, Laval University, Quebec, QC, Canada G1K 7P4*
[c] *Mineral Resources Research Division, Korea Institute of Geoscience and Mineral Resources (KIGAM), Daejeon 305-350, Korea*

ARTICLE INFO

Article history:
Received 3 September 2015
Received in revised form 18 December 2015
Accepted 22 December 2015
Available online 23 December 2015

Keywords:
Sodium nitrite
Silver nitrite
Copper nitrite complex
Silver leaching

ABSTRACT

This work presents a novel leaching system involving NO_2–Cu to oxidize and complex silver without the use of cyanide, ammonia or thiosulfate. It is possible to oxidize metallic silver through the reduction reaction of the nitrite ions, the cupric-nitrite complexes seem to be responsible for increasing the silver leaching kinetics; the nitrite ions act as a complexing agent for the silver ions in the solution. The effect of cupric ions concentration (0.05 M, 0.1 M and 0.2 M) and nitrite ions concentration (1.0 M, 1.35 M and 1.5 M) on the dissolution kinetics of silver was evaluated. Based on the results the best leaching conditions were worked out as: 1.5 M nitrite ions and 0.2 M copper ions at a natural pH of 5.0. This leaching solution dissolves 80% of silver within 6 h. The effect of temperature on the dissolution kinetics of silver was studied at the room temperature till 30, 45, 50 and 55 °C, showing a progressive increase in silver recovery from 7.69% to 10.38%, 28.62%, 44.7% and 53.93%, respectively in 30 min. The kinetic analysis revealed that silver leaching depends on the temperature and rate controlling step corresponds to the silver dissolution through the chemical reaction. The apparent activation energy of the reaction is found to be 50.92 kJ/mol, along with the enthalpy and entropy of activation values of 48.34 kJ/mol and −139.05 J/mol K, respectively. The kinetic model corresponding to the silver leaching can be represented by the expression: $1 - (1 - x)^{1/3} = k_0 \exp.(-50.92/RT)\, t$. The analysis of solid residue obtained after leaching at pH 5 by XRD and SEM with elemental mapping showed the formation of a copper-hydroxysulfate species, brochantite, formed in the bulk solution and not on the silver particle surface. The leaching results of silver by the NO_2–Cu system were also ratified by the species distribution diagrams.

1. Introduction

Cyanidation is the process traditionally employed worldwide for the extraction of silver and gold from different sources. Metallic silver can be found in different wastes. For example in the so-called urban ores, it is of environmental and economic importance to leach metallic silver from printed circuit boards (PCB's), electronics, spent catalysts and fabrics containing silver nanoparticles (Ficeriová et al., 2008; Manju Gurung et al., 2013; Jadhav and Hocheng, 2012; Pasricha et al., 2012). Presently the mining and recycling industry has been involved in solving new technological and environmental challenges (Aylmore and Muir, 2001; Ahern et al., 2006). Some of the main alternatives to replace the cyanide from the leaching systems includes the use of thiourea (Jing-ying et al., 2012) and thiosulfate as the lixiviant (Abbruzzese et al., 1995; Tanriverdi et al., 2000; Aylmore and Muir, 2001; Breuer and Jeffrey, 2000, 2002; Wan and LeVier, 2003; Zhang and Nicol, 2003; Grosse et al., 2003; Ji et al., 2003; Senanayake, 2005; Gudkov et al., 2010a, 2010b, 2010c; Puente-Siller et al., 2014; Alvarado-Macías et al., 2015). The leaching of metallic silver has been studied by different researchers using alternative leaching systems in the presence of thiosulfate or ozone (Puente-Siller et al., 2013, 2014; Alvarado-Macías et al., 2015; Rivera et al., 2015; Viñals et al., 2005). The thiosulfate system seems to be the most promising for the extraction of precious metals, because of its capability to increase the metal dissolution rate from 18 to 20 times (Aylmore and Muir, 2001). However, one of the main disadvantages of the thiosulfate system relates to its oxidative degradation to tetrathionates (Aylmore and Muir, 2001). Therefore, in order to reduce such degradation, researches are being carried out using different additives such as citrate, EDTA and amino acids (Puente-Siller et al., 2013, 2014; Feng and Van Denventer, 2010, 2011). These investigations have shown the possibility of decreasing the oxidative degradation of the thiosulfate ions by lowering the redox potential of the system. However, the drawback is yet to be overcome.

Recently, Alvarado-Macías et al. (2015) examined an alternate process for silver leaching involving S_2O_3-NO_2-Cu which avoids the use of cyanide or ammonia in the thiosulfate process and minimizes the environmental impact. However, the formation of a Cu-S coating on the surface of silver particles (Alvarado-Macías et al., 2015) due to the degradation of thiosulfate has retarded the leaching (Aylmore and Muir, 2001) due to the hindered contact between the lixiviant and unreacted

---

* Corresponding author.
E-mail address: juan.fuentes@cinvestav.edu.mx (J.C. Fuentes-Aceituno).

http://dx.doi.org/10.1016/j.hydromet.2015.12.014
0304-386X/© 2015 Elsevier B.V. All rights reserved.

silver. In addition, the Cu-S catalyzes the oxidative decomposition of thiosulfate in solution by air resulting in low silver extraction (Chanda and Rempel, 1985; Puente-Siller et al., 2014).

In view of the above, the current researches have aptly focused on exploring a new system to dissolve the precious metals from different resources without the use of cyanide, thiosulfate or thiourea. Mention may be made of a recent study in which Oraby and Eksteen (2015) used glycine-peroxide for the gold and silver leaching. The gold leaching rate of 0.322 μmol/m^2.s was achieved using a solution of 0.5 M glycine and 1% peroxide at pH 11 in 48 h. In fact, this result was better as compared to the gold leaching rate obtained after six days with thiosulfate–EDTA or thiosulfate–oxalate systems in the presence of thiourea. Other systems that do not use cyanide for the leaching of silver/precious metals are based on the nitric acid (Holloway et al., 2004; Pan-Pan et al., 2014), the nitrogen species catalyzed (NSC) (Anderson, 1995; Anderson and Nordwick, 1996; Anderson et al., 1996a; Anderson et al., 1996b; Anderson, 2003a, 2003b), and the bisulfide (Hunter et al., 1998) in the conventional leaching operations. However, the use of nitrite ions as oxidant and complexing agent for silver has not been investigated systematically until the present work.

In this work, use of a novel leaching system involving NO_2–Cu^{2+} solution has been investigated to understand the dissolution behavior of silver and establish the most suitable conditions to accelerate the leaching kinetics, with the aim of using it in future, this information would be valuable to dissolve metallic silver contained in different wastes (mining industry or urban mines). The research is based on the premise that nitrite ions can oxidize the metallic silver. In fact, nitrite reduction can produce ammonia and ammonium ions as previously reported by Alvarado-Macías et al. (2015) according to the reactions (1 and 2) depending on the pH of the solution. The formation of ammonia and ammonium ions may cause oxidative dissolution of the precious metals as a result of the redox process.

Thus at pH >9 ammonia is predominantly generated as Eq. (1):

$$NO_2^- + 5H_2O + 6e^- \rightarrow NH_3 + 7OH^- \quad (1)$$

Whereas, at pH < 9 ammonium ions are predominantly formed (2):

$$8H^+ + 6e^- + NO_2^- \rightarrow NH_4^+ + 2H_2O \quad (2)$$

2. Materials and methods

The leaching solutions were prepared with analytical grade reagents and deionized water. The reagents used were: metallic silver (99.999%, 1–3 μm, spherical, Alfa Aesar), sodium nitrite (97.2%, Analytyka) and cupric sulfate pentahydrate (99%, Merck).

2.1. Leaching tests

All silver leaching experiments were performed in an agitated batch reactor (250 mL glass beaker) which 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 stirring plate. The general procedure for the leaching experiments was as follows: 200 mL of the leaching solution with sodium nitrite, cupric sulfate and 0.1266 g of metallic silver were placed in the reactor at room temperature. The effect of cupric sulfate concentration (0.05 M, 0.1 M and 0.2 M), sodium nitrite concentration (1.0 M, 1.35 M and 1.5 M) and temperature (19, 30, 45, 50 and 55 °C) on the silver leaching kinetics was tested during 6 h of experiments. The pH and redox potential were measured before the silver addition and during the leaching experiments at an interval of 60 min. Samples of the leaching solution were withdrawn at each 5 min or 30 min, during the leaching test of 6 h. Silver in the aliquot was analyzed by atomic absorption spectrophotometry (Varian SpectrAA 220FS). All samples were stored in dark vessels to prevent the silver precipitation caused by light. Once the experiments were concluded, the residues were filtered, rinsed with deionized water and air dried.

2.2. Chemical and morphological characterization of the solid residues

The solid residues formed at 6 h were microstructurally characterized in order to elucidate their morphology and local chemical composition by scanning electron microscopy (SEM) (Phillips, XL30ESEM), X-ray mapping and energy-dispersive X-ray spectroscopy (EDS) (EDAX, Genesis). Some of the solid residues were also analyzed by X-ray diffraction (XRD) (Phillips, X'PERT PW3040) in order to identify the predominant and other minor phases.

3. Results and discussion

Silver leaching tests at different temperatures and kinetic aspects could be complemented with the thermodynamic analysis of the nitrite–copper system and characterization of the solid residue.

3.1. Thermodynamic study

In order to elucidate the predominant species (solid and liquid phase) formed in the nitrite-copper-silver system, Pourbaix and species distribution diagrams were constructed at different pH and room temperature representing the potential leaching conditions with the help of Medusa Software using the equilibrium data contained in the Hydra database (Puigdomenech, 2004). As reported previously (Alvarado-Macías et al., 2015), silver can be leached in S_2O_3-NO_2-Cu-SO_3 system through the formation of $[Ag(S_2O_3)_x]^{1-2x}$ complexes, where x = 1, 2 or 3. It is also possible to produce silver–nitrite complexes using the nitrite ions as a co-leaching agent without using the thiosulfate ions. The species distribution diagram for the NO_2-Ag-H_2O system constructed and presented in Fig. 1 reflects the formation of nitrite-silver complexes in a range of pH and redox conditions. Thus metallic silver can be oxidized at the anodic potential >0.49 V_{SHE} in the pH range 5.0–6.5. The stabilization of silver with nitrite ions producing predominantly the $Ag(NO_2)_2^-$ complex can proceed according to the oxidation reaction (3):

$$Ag + 2NO_2^- \rightarrow Ag(NO_2)_2^- + e^- \quad (3)$$

This anodic reaction must occur simultaneously with a reduction reaction, which is likely at the acidic pH [Eq. (2)] through the reduction of nitrite ions to NH_4^+ ions (Alvarado-Macías et al., 2015).

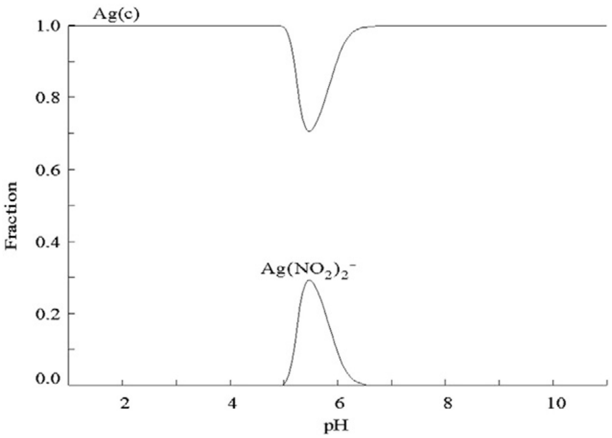

Fig. 1. Silver species distribution diagram for the Ag-NO_2-H_2O system with 6×10^{-3} M Ag and 1.5 M NO_2^- at 0.49 V vs SHE.