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Leaching of silver contained in mining tailings, using sodium thiosulfate: A kinetic study

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ABSTRACT

Several years of mining in the Pachuca y Real del Monte mining district have led to the production of a great amount of mining tailings which is currently a great environmental problem. However, these residues contain metals of value and interest that cannot be recovered using harmful and aggressive reagents such as cyanide. Thiosulfate solutions represent a good alternative because of the advances made during the last few years of research on this subject. The kinetic study carried out indicates that the process involved in the leaching treatment of mining tailings for silver was only slightly affected by the stirring rate in the range studied; the reaction orders were 1 (oxygen partial pressure 0.2–1 atm), 0.074 (thiosulfate concentration 100–500 $\text{mol} \cdot \text{m}^{-3}$), 0.455 (pH 4–12) and 0.26 (Copper concentration 50–300 $\text{mol} \cdot \text{m}^{-3}$). The apparent activation energy of the process was 1.912 $\text{kJ} \cdot \text{mol}^{-1}$ in the temperature range from 288 to 318 K. A change of control seemed to occur above 318 K, possibly due to the destabilization of oxygen in the inner portion of the solution at higher temperatures. According to the results, kinetic is controlled by a mass transfer of oxygen at the solid–liquid interface. In the presence of copper ions and oxygen, the reaction rate increases, so the process was carried out using a stoichiometric excess of oxygen. The process was applied to a mining tailing, containing both metallic and silver sulfides, having a similar behavior to that observed by previous authors using silver powder and silver plate.

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1. Introduction

In Mexico, mining has been one of the most important economic activities since the pre-Hispanic era to the present day; traditionally, this activity has focused more on gold and silver ores. Processing of these types of ores has included technologies ranging from "The Benefit of Patio" and Pachuca tanks, to circuits of processing, which involve milling, froth flotation and cyaniding. In Hidalgo State (Mexico), during more than 458 years of mining, these technologies have led to the generation of a great amount of tailings. Today these technologies produce almost 110 million tons of tailings of economic importance (Hernández et al., 2007; Salinas et al., 2006), because these types of residues contain valuable gold and silver (25 to 120 g of Ag per ton and 0.3 to 1.5 g of Au per ton) (Espinosa de, 1984; Geyne and Fries, 1963; Hernández et al., 2007; Salinas et al., 2006). However, this type of waste presents some problems during its treatment, the most important being the presence of pyritic and quartz-type minerals where silver and gold contents are encapsulated in small particles (−75 μm) (Geyne and Fries, 1963). This causes difficulty in the extraction of such valuable metals. Furthermore, the presence of some elements and minerals that consume cyanide does not allow a suitable extraction of the valuable content in many cases. In the same way, the silver contained in the refractory ores, is a metallurgical problem for various conventional extraction processes (Abbruzzese et al., 1995; Geyne and Fries, 1963; Patiño and Ramírez, 1991).

To date, several studies on leaching have been carried out, and the most studied systems have been those based on cyanide use. Very few are based on thiosulfate media [$Na_2S_2O_3^{2-}$] for silver recovery, particularly in the treatment of tailings in Hidalgo State (Mexico). The cyaniding system has been used the most for more than 100 years principally due to the high capacity of the CN^- ions to form silver complexes. For this process, the oxidizing agent used is the oxygen or air. However, this system has two disadvantages: the first one is related to its environmental impact, and the second is related to the presence of some species inert to the cyaniding process, known as refractory ores. It is well known that cyanide is toxic, and the contamination due to this reagent is high with alarming figures in terms of its impact on human health. Thus, currently its use worldwide is very restricted (Jeffrey et al., 2002). Another reason to search for an alternative to the

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Table 1
Chemical composition of tailings (FRX, ICP and AAS).

Element	Pct weight
Ag	0.0055 (55 g/ton)
Au	0.000058 (0.58 g/ton)
Fe	2.690
Si	56.00
Mn	0.046
Ca	0.200
Na	0.300
K	2.320
Al	6.095
S	11.45
Zn	0.045
Cu	0.010
Pb	0.031
Cd	0.017
As	0.043
Sr	0.463
Cr	0.037
Ba	0.330
P	0.140
Ti	0.278
Traces	19.499

use of cyanide as a leaching reagent is the need to increase the extent of dissolution of precious metals from the refractory ores where cyanide is less selective and causes low metallic recovery. Systems based on leaching using thiosulfates are considered to be non-toxic alternatives to the conventional processes such as cyaniding (Hernández et al., 2013; Rivera, 2003; Schmitz et al., 2001) and an efficient alternative dissolution medium for refractory ores (Rivera, 1994). One of the advantages of this method compared to the use of cyanide is the high selectivity for silver extraction from refractory ores. The low stability of thiosulfate ions is a great disadvantage of the process. Some previous works have studied the solution of copper–ammonium–thiosulfate as a leaching system of great potential, where Cu^{2+} ions oxidize the noble metals while the thiosulfate forms stable complexes with them. At the same time, ammonium ions form a stable complex with copper ions avoiding their precipitation process. In addition to the role of ligands and oxidants during the thiosulfate leaching of gold, the effect of additives and electrolytes on the dissolution of gold in thiosulfate solutions has also been studied (Chandra and Jeffrey, 2004; Senanayake, 2005, 2012a, 2012b). However, the chemistry and kinetics of such processes actually present a challenge in the metallurgical industry. This is because recent studies have indicated that the use of thiosulfate as a leaching reagent could have important drawbacks, especially during silver leaching. Some researches (Rivera et al., 2015) have found that the kinetics of leaching of silver using thiosulfate are controlled by the mass transfer of oxygen to the solid–liquid interface. Other studies have also been conducted on silver and silver sulfide leaching in a thiosulfate–ammonium–cupric ion system (Briones and Lapidus, 1998; Deutsch and Dreisinger, 2013) and in the presence of EDTA (Puente-Siller et al., 2013, 2014). All of these authors concluded that for high and low concentrations of ammonia and thiosulfate, silver combines preferentially with thiosulfate. Therefore, in this work, the kinetics of dissolution of silver contained in the tailings of the mining industry was studied using O_2–$Na_2S_2O_3^{2-}$ as a silver dissolution medium instead of the conventional cyaniding process. The novelty of this work is related to the additional use of copper as an oxidizing reagent to improve silver leaching, and the system is now used to leach real minerals that were emitted as waste from the mining metallurgical industry.

2. Materials and experimental procedure

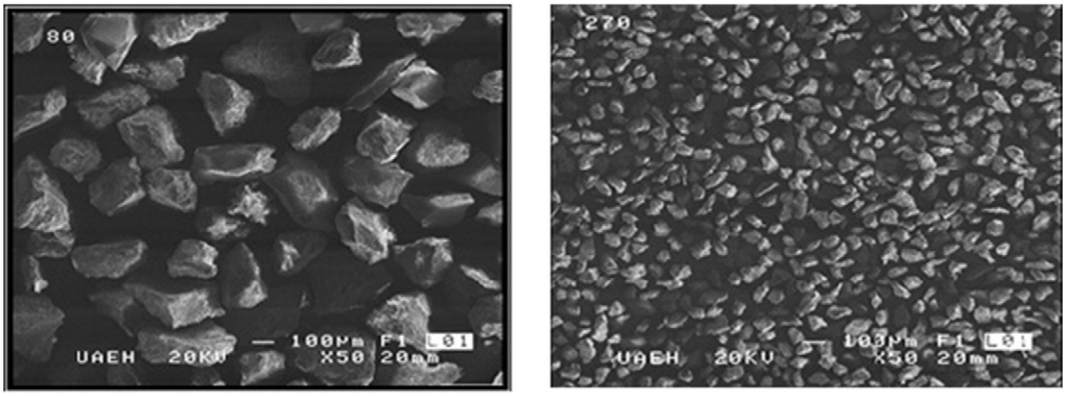
2.1. Materials

For this study, the dump "Dos Carlos", which is located in the urban zone of Pachuca city, Hidalgo (Mexico), was selected for sampling. Four representative samples, each of 50,000 g, were taken. The mineral used was previously subjected to a chemical and mineralogical characterization, by techniques such as X-ray diffraction (XRD), X-ray fluorescence (XRF), emission spectroscopy using inductively coupled plasma (ICP) and atomic absorption spectrometry (AAS). Then, the samples were ground for 480 s at a working speed of 71.87 s^{-1} (rpm) with a ball charge of 10,230 g, a pulp charge of 2097.77 g and a volume of 9.3×10^{-4} m^3 of water in the ball mill "Denver". Then, samples were collected for the leaching study.

2.2. Experimental procedure

All leaching experiments were carried out in a 0.001 m^3 flat-bottom glass reactor mounted on a hot plate with magnetic stirring (750 s^{-1}) and coupled to a pH meter. In this system, the pH was continuously measured and adjusted by the addition of controlled amounts of NaOH at a concentration of 200 $mol \cdot m^{-3}$. In the same way, ultra-high-purity oxygen was used to maintain a constant amount of oxygen dissolved in the solution and injected into the reactor. The flow was measured by a flow meter, and the partial O_2 pressures used were 1 and 0.2 atm. This was done to maintain a controlled atmospheric pressure inside the solution. The temperature was controlled by a thermocouple attached to the hot plate.

The kinetic study using thiosulfate was carried out under the following experimental conditions; concentration of [$Na_2S_2O_3$], 100 to 500 $mol \cdot m^{-3}$; temperature range, 288 to 333 K; mineral weight for each experiment, 40 $g \cdot m^{-3}$; pH range, 4 to 12; volume of reaction,



(a) (b)

Fig. 1. Overall image of the average particle size of, (a) 80 mesh (180 mμ) and (b) 270 mesh (53 mμ) (SEM, secondary electrons).

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