Characterization of Minerals, Metals, and Materials 2016

Edited by

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CHARACTERIZATION AND STOICHIOMETRY OF THE CYANIDATION REACTION IN NaOH OF ARGENTIAN WASTE TAILINGS OF PACHUCA, HIDALGO, MÉXICO

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Abstract

The argentian resources of Pachuca, Hidalgo, México have suffered an extensive exploitation, resulting in more than 100 million tons of waste tailings located in several sites around the city of Pachuca and surrounding municipalities. Chemical, mineralogical and granulometric characterization of the waste tailings of Pachuca, Hidalgo, México, was carried out in this work. Characterization results indicate that these argentian wastes contain 56 g Ag ton^{-1}, and the silver is present in the forms of metal, argentite and argentian jarosite in a quartz matrix. Stoichiometry of the cyanidation reaction in NaOH media was analyzed, and the following conclusions were obtained: 1) both metal silver and silver present in the form of argentite can be quickly cyanidation, 2) Alkaline decomposition of argentian jarosite is the rate-control step in the cyanidation reaction.

Keywords*:* Characterization, Stoichiometry, Cyanidation reaction, Argentian waste tailings, Pachuca-Hidalgo-Mexico

Introduction

The mining district comprising Pachuca and Real del Monte in the State of Hidalgo, México, has been providing the world with silver for 470 years. This mining region has also been a pioneer in several technologies on the processing of argentian ores, such as the patio process and the Pachuca tanks. However, the argentian resources of this region have suffered an extensive exploitation, resulting in more than 100 million tons of waste tailings [1]. These tailings or *mine dumps* are becoming an environmental issue for the city of Pachuca and the Municipality of Mineral de La Reforma. There are mainly two causes for this: first, because, in periods of strong winds, dust clouds are formed which seriously affect the inhabitants' health; a second point is that these residues take up 1200 hectares, obstructing the city's proper and sustainable growth. Since the value of this precious metal is 15.21 dollars per troy ounce and these tailings contain 56 g

Ag ton^{-1}, it renders them appealing from an economic perspective (Monex Precious Metals, 2015) [2].

For these reasons, this piece of work presents an extensive reprocessing study of the Dos Carlos waste tailings of the city of Pachuca with the aim of: 1) recovering the silver contained in those residues through different silver leaching methods; 2) and using these residues as alternative construction material and in the glass industry. This paper presents only the results of the granulometric, mineralogical and chemical characterization, as well as the stoichiometry of the cyanidation reaction in NaOH of the Dos Carlos tailings located in the northeast area of the city of Pachuca. In spite of the toxic nature of the cyanidation, this process remains one of the most used processes in the extraction of silver and gold, either from natural deposits or mining wastes; and this process has undergone numerous improvements with the aim of improving efficiency, including the use of oxidizing and reducing agents such as ferricyanide and pyrite, cyanidation at high pressures, membrane processes and electrochemical processes [3-7]. Of the mining metallurgical district of the company Real del Monte y Pachuca, these tailings are the second richest in silver. It is found in different forms: quartz matrix, distributed as metal silver, as argentite and as argentian jarosite. This last ore is also called argentian potassium jarosite when it is synthesized in laboratories [8, 9]. This compound is also obtained in the metallurgical industry, where the precipitation of jarosite has been widely used in the hydrometallurgical circuits of zinc as a means to control the impurities of the solutions containing it, generating millions of tons of this jarosite type compound that has a high silver content [10].

Methods and materials

It is known that, for obvious reasons, the cyanidation of ores is practiced at alkaline pH levels between 9 and 12. The experiments were conducted in a conventional glass kettle coupled to a mechanical stirring system provided with an RPM meter, a thermometer and a pH meter to control the concentration of alkaline reagent. The kettle was also coupled to an electric heater that allows to dial temperature variations of ± 0.5 °C. The argentian tailings' cyanidation was conducted in a 500 cm^3 kettle under the following experimental conditions: 40 g argentian tailings sample, 25 °C, 1×10^{-2} mol L^{-1} [NaOH], 2.04×10^{-2} mol L^{-1} [NaCN], and a stirring rate of 750 min^{-1} in order to keep the solids suspended and to avoid the liquid film diffusion effect.

Since this study on the stoichiometry of alkaline cyanidation shows that silver ions are removed from the solids and diffuse towards the solution, the reaction was followed by analysis of silver ions in the liquid. The x fraction of cyanided silver was calculated with the following:

$$x = [Ag]_t / [Ag]_\infty \quad (1)$$

where $[Ag]_t$ is the concentration of silver at a time t, and $[Ag]_\infty$ is the concentration of Ag after the solids have been completely leached. The kinetic

models selected for the experimental data on the cyanidation in NaOH, were the following [11-13]:

$$1-(1-x)^{1/3} = k_{exp}t \quad (2)$$

$$1-3(1-x)^{2/3}+2(1-x) = k_{exp}t \quad (3)$$

Where k_{exp} is the experimental rate constant, x is the reacted fraction, and t is the reaction time.

Results and discussion

Figure 1 presents the X-ray Diffraction (XRD) spectrum, showing the presence of jarosite ($KFe_3(SO_4)_2(OH)_6$) in a quartz (SiO_2) matrix with other main species, such as orthoclase, albite ($NaAlSi_3O_8$) and berlinite ($AlPO_4$). Geyne reported this compound as argentian jarosite; it is original from the Paricutin mine in the mining district of Pachuca and Real del Monte [14].

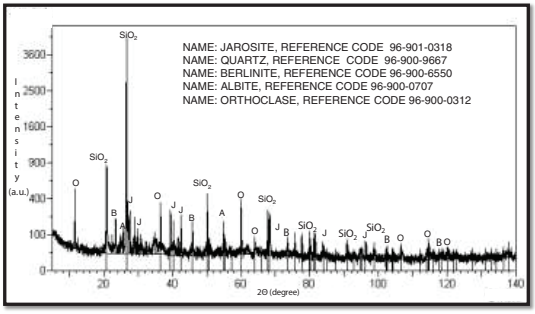

Fig. 1. X-ray diffractogram of the tailings sample (major phases: Quartz (SiO_2), O-Orthoclase ($KAlSiO_3$), A-Albite ($NaAlSi_3O_8$), B-Berlinite ($AlPO_4$), and J-Jarosite ($KFe_3(SO_4)_2(OH)_6$))

Table I summarizes the atomic absorption spectrophotometer (AAS) and inductively coupled plasma (ICP) chemical analysis data, where it can be observed that the gold and silver content is 56 g ton^{-1} and 0.60 g ton^{-1}, respectively. It can also be noted that the major elements are silicon, sulfur and aluminium, whereas the minor elements are iron, potassium, strontium, calcium, sodium, phosphorus and barium. The rest are considered trace elements. The problem is to explain how silver is distributed in the Dos Carlos waste tailings. In this respect SEM-EDS images show that the silver is distributed as follows: a) In metal form, as shown in Fig. 2a, where an 8 µm particle can be observed. Fig. 2b shows the same particle's X-ray microanalysis (EDS), showing the typical intensity peaks of metal silver. b) In the form of argentite, as observed on Fig. 3a, where argentite particles of up to 2 µm were obtained; Fig. 3b displays the EDS analysis of these particles, showing the typical intensity peaks of argentite. c) In

the form of argentian jarosite. Fig. 4a shows argentian jarosite particles finally scattered in the quartz matrix, and Fig. 4b presents the EDS analysis of the argentian jarosite particles, where the typical intensity peaks of this ore can be observed, with elements such as sulfur, iron, potassium and silver. This confirms that the peaks correspond to those of argentian jarosite, also known as silver potassium jarosite when it is obtained in the laboratory [8, 9].

Table I. Chemical composition of the waste tailings.

Elements	Wt %	Elements	Wt %
Au	0.60 g ton^{-1}	Ca	0.200
Ag	56 g ton^{-1}	Si	56.00
Cu	0.011	K	2.32
Bi	0.0002	Na	0.30
Ni	0.005	Al	6.095
Mn	0.046	Ti	0.278
Fe	2.69	P	0.14
Sn	0.0002	Mg	0.005

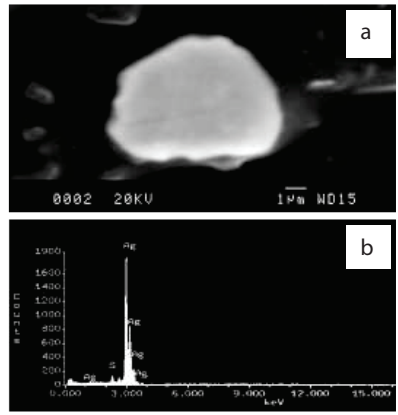

Fig. 2. a) SEM-backscattered electron image; and b) Energy dispersive X-ray microanalysis of a silver particle

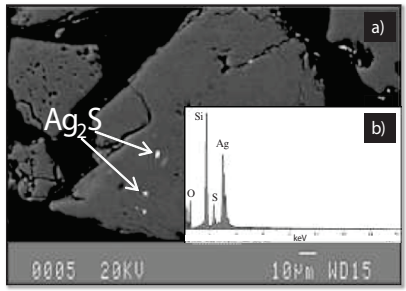

Fig. 3. a) SEM-backscattered electron image; and b) Energy dispersive X-ray microanalysis of argentite particles

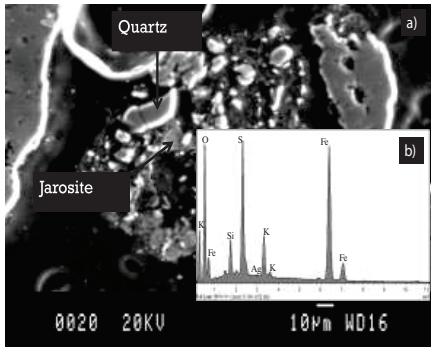

Fig. 4. a) SEM-backscattered electron image; and .b) Energy dispersive X-ray microanalysis of argentian potassium jarosite.

The results of the nature of the alkaline cyanidation reaction are summarized in Table II. The decomposition products of this ore are quickly cyanided; therefore, this second process consists of two consecutive phases, as previously observed in other studies on synthesized argentian jarosite-type compounds [9]. The reaction stoichiometry of the previously mentioned processes is described as follows:

Process 1- quick cyanidation of silver and argentite:

$$2Ag_{(S)} + 4NaCN_{(aq)} + \tfrac{1}{2}O_{2\,(g)} + H_2O_{(l)} \rightarrow 2Na[Ag(CN)_2]_{(aq)} + 2NaOH_{(aq)} \quad (4)$$

$$2AgS_{(S)} + 4NaCN_{(aq)} \rightarrow 2Na[Ag(CN)_2]_{(aq)} + NaS_{(s)} \quad (5)$$

Process 2- slow alkalination:

$$(K_xAg_{1-x})Fe_3(SO4)_2(OH)_{6\,(s)} + [3 + (1 - x)]OH^-_{(aq)} \rightarrow xK^+_{(aq)} + (1 - x)Ag(OH)_{(s)} + 3Fe(OH)_3 + 2SO^{2-}_{(aq)} \quad (6)$$

Process 3 – quick cynaidation of argentian jarosite:

$$(1-x)Ag(OH)_{(s)} + 2CN^-_{(aq)} \rightarrow (1-x)[Ag(CN)_2]^{2-}_{(aq)} + (1-x)OH^-_{(aq)} \qquad (7)$$

The chemical-control and diffusive-control kinetic models were then tested in order to determine the rate control steps of alkaline cyanidation. It was found that once the quick cyanidation (process 1) of metal silver and argentite takes place, the experimental results corresponding to process 2 adapt to both models with a similar regression coefficient, as shown in Figure 5. Therefore, it can be concluded that the global decomposition and cyanidation process of argentian jarosite is controlled in a mixed manner. The cyanidation rate constant obtained in this study for the naturally formed jarosite is calculated to be 0.007 min^{-1}, which is very similar to that of the synthetic jarosite obtained in previous studies [9].

Table II. Silver cyanidation at different time intervals: 40 g L^{-1}waste tailings, 2.04×10^{-2} mol L^{-1} [NaCN], 1×10^{-2} mol L^{-1} [NaOH], pH 11.71 and 298 K.

Time(min)	$X_{[Ag]}$	$1-(1-X_{Ag})^{1/3}$	$1-3(1-X)^{2/3}+2(1-X_{Ag})$
0	0.000	0.000	0.000
1	0.380	0.150	0.059
2.5	0.400	0.160	0.066
5	0.400	0.160	0.066
7.5	0.460	0.180	0.091
10	0.520	0.220	0.121
20	0.640	0.290	0.202
30	0.740	0.330	0.298
40	0.780	0.390	0.347
80	0.840	0.390	0.436
100	0.860	0.440	0.471
120	0.890	0.520	0.531
180	0.990	0.780	0.881
200	1.000	1.000	1.000

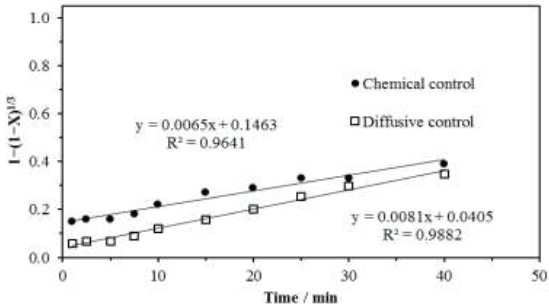

Fig. 5. Fitting of experimental data with chemical and diffusive control models

Conclusions

The Dos Carlos waste tailings located in Pachuca, Hidalgo, Mexico, are made of a quartz matrix that contains silver in the forms of metal, argentite and argentian jarosite. The silver content of these mining wastes is about 56 g Ag ton^{-1}. The stoichiometry of the alkaline cyanidation consists of: 1) quick cyanidation of both metal silver and silver present in the form of argentite, and 2) slow decomposition of the argentian jarosite and quick cyanidation of the silver contained in the decomposition products. The cyanidation rate constant of the naturally formed argentian jarosite is similar to that of the synthesized silver potassium jarosite.

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