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Effects of pretreatment and leaching medium on the extraction efficiency of Au and Ag from a chalcopyrite leaching by-product

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Abstract

Precious metals such as gold (Au) and silver (Ag) are essential to our modern society due to their unique properties, such as high conductivity and physical and chemical resistance. They are often concentrated in by-products during the extraction of base metals. In the present work, a chalcopyrite leaching residue, constituted mainly of elemental sulfur and jarosites, was subjected to different pretreatments and leached with different leaching media to recover Au and Ag. The solid residue was pretreated by desulfurization, peroxidation, desulfurization+peroxidation and leached with cyanide, cyanide+glycine, and glycine. For comparison, samples without pretreatment were also leached using the same leaching media. Changes in the mineralogical species were followed to explain the effects of pretreatment and leaching medium on the dissolution of Au and Ag. Results indicate that the highest extraction of gold and silver (Au:99.50%, Ag:46.71%) is achieved by using a combined desulfurization+peroxidation pretreatment and cyanide as leaching medium.

Keywords: cyanidation; glycine; precious metals; chalcopyrite leaching by-product.

Efectos del medio de pretratamiento y lixiviación sobre la eficiencia de extracción de Au y Ag de un subproducto de la lixiviación de calcopirita

Resumen

Los metales preciosos como el oro (Au) y la plata (Ag) son esenciales para nuestra sociedad moderna debido a sus propiedades únicas como alta conductividad, resistencia física y química. A menudo se concentran en subproductos durante la extracción de metales básicos. En el presente trabajo, un residuo de lixiviación de calcopirita constituido principalmente por azufre elemental y jarositas fue sometido a diferentes pretratamientos y lixiviación con diferentes medios de lixiviación para recuperar Au y Ag. El residuo sólido se pretrató mediante desulfuración, peroxidación, desulfuración + peroxidación y se lixivió con cianuro, cianuro + glicina y glicina. A modo de comparación, las muestras sin tratamiento previo, también se lixiviaron utilizando el mismo medio de lixiviación sobre la disolución de Au y Ag. Los resultados indican que la mayor extracción de oro y plata (Au: 99,50%, Ag: 46,71%) se logra mediante el uso de un pretratamiento combinado de desulfuración + peroxidación y cianuro como medio de lixiviación.

Palabras clave: cianuración; glicina; metales preciosos; subproducto de la lixiviación de calcopirita.

1. Introduction

Mexico is considered one of the top producers of gold (Au) and silver (Ag) in the world, which has been possible due to its great mining potential in terms of mineral

resources. The cyanide leaching process is the most widely used method for recovery of Au and Ag and is considered an efficient hydrometallurgical technology [1]. However, the hydrometallurgical extraction of these high value elements from copper iron-sulfide mineral by-products becomes

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difficult in the presence of jarosites and/or elemental sulfur (products of leaching reactions) [2], since they act as cyanicides, thus affecting the effectiveness of cyanide to leach Au and Ag from sulphide ores [3].

Several works have been conducted to remove elements that cause a negative effect on the extraction efficiency of Au and Ag, for instance, the selective dissolution process toward removing elemental sulfur using organic solvents such as perchlorethylene, kerosene, clear oil, trichlorethylene, ethylcyclohexane, carbon tetrachloride, tetrachloroethane, and mixtures of these. This process is based on the chemical affinity between sulfur and organic solvents, which allows the formation of organosulfur compounds [4].

Other authors have reported the hydrothermal decomposition of jarosites in alkaline and acid media [5, 6]. It was found that in acid medium, the hydrothermal decomposition of jarosites in the range 90-250 °C promotes the formation of soluble sulfate species [5]. On the other hand, the hydrothermal decomposition of an industrial Najarosite (150 g/t Ag) was conducted in alkaline medium at 60 °C; NaOH and Ca(OH)₂ were employed as alkalizing agents to obtain different pH (8, 9, 10, and 11). Best results were obtained at pH 11 for both alkalizing agents. Hydrothermal decomposition of the jarosite was completed after 3 min and 40 min, when NaOH and Ca (OH)₂ were used to adjust pH to 11, respectively. In the former, the decomposition process was controlled by the chemical reaction, while in the second, the decomposition process was controlled by diffusion. This latter was supported by the formation of a product layer, which renders the reaction between hydroxyl ions and the unreacted jarosite core difficult [6].

It is noteworthy that Au and Ag may be present in refractory species (for example, pyrargyrite); for this reason, some researchers have proposed an oxidation pretreatment process with ozone for the extraction of such metals (O_3) [3,7]. Sodium persulfate (Na₂S₂O₈) has been utilized as an oxidizing agent for the recovery of metals in alkaline solutions [8,9]; in addition, it has been employed to dissolve copper sulphides in acidic pH solutions [8].

Although the conventional cyanidation process is known to be the most efficient in gold extraction, cyanide nevertheless has the disadvantage of being harmful to the environment and health. Based on the above, other researchers have searched for alternative leaching agents to cyanide, among which glycine is highlighted. Glycine has the advantage of not being toxic, and it has been demonstrated that a mixture of glycine and cyanide can enhance the efficiency of Au and Ag extraction from copper ores and concentrates [10,11]. In this context, the present work was aimed at investigating the effect of the pretreatment (desulfurization, peroxidation, desulfurization+peroxidation) and the leaching medium (cyanide, glycine, and cyanide+glycine) on the efficiency of Au and Ag extraction from a chalcopyrite leaching by-product.

In this work, the effect of the composition of a direct leaching residue of chalcopyrite (composed mainly of jarosite, elemental sulfur, and valuable metals such as gold and silver) is analyzed. It is important to mention that there are no studies, to our knowledge, that report information on waste treatments with the composition or mixture of components employed in this work. Individually, as previously mentioned, elemental sulfur and jarosite have been studied, since they affect the extraction of gold and silver. In this regard, this work exposes the effect of jarosite and elemental sulfur and the impact of the pre-treatments for their removal or transformation into compounds that do not inhibit the extraction of gold and silver. Cyanide is used as leaching agent, and glycine, as an assistant of cyanide in the recovery of gold and silver, with the aim of reducing the use of cyanide.

2. Experimental procedure

The residue used in the present investigation was obtained from the leaching process of a chalcopyrite concentrate (particle size D90 = 47.61 μ m), Table 1 shows the chemical analysis of the chalcopyrite concentrate and Table 2, the mineralogical reconstruction of this concentrate.

The leaching experiments were carried out in a 200-L, 316-L stainless steel reactor, which can operate at 0.15 MPa. It was equipped with a chemical seal, a stirring system and four deflectors, a controlled cooling/heating jacket, a pressure transmitter and a resistance temperature detector, and a Graphtec Data logger.

The experimental procedure began with the addition of hot water (80 °C) to the reactor and the initiation of the agitation system, which was set at a low revolution speed; then, the chalcopyrite concentrate was fed into the reactor, followed by sulfuric acid. After the addition of these materials, a 2-min air purge was performed; then, the reactor was closed and pressurized to 1 kg/cm² with medicinal oxygen, and the agitation velocity was set at 550 rpm.

The chalcopyrite leaching by-product obtained in the leaching of chalcopyrite (particle size $D90 = 16.92 \mu m$), used in the present work is mainly constituted of plumbojarosite, hydroniumjarosite, and elemental sulfur; this solid residue will be referred hereafter as Material M1. The solid residue was characterized by inductively coupled plasma optical emission spectroscopy (ICP-OES), X-ray fluorescence spectrometry (XRF), and X-ray diffraction (XRD) using a PerkinElmer Optima ICP-OES spectrometer, a Rigaku Primus XRF spectrometer, and a Panalytical Emperyrean X-ray diffractometer, respectively. The mineralogical reconstruction of Material M1 was determined from the results of ICP, XRF, and XRD using HSC 8.0 software and the Species Converter module.

Table 1.

(Chemical analysis of the chalcopyrite concentrate (wt. %).											
	Ag (g/t)	Au (g/t)	Cu	Si	Cu	Fe	Ca	Zn	S°			
	493.7	1.5	23.76	1.06	23.76	24.3	1.28	6.22	32.4			

Source: The authors.

Table 2.

Mineralogical reconstruction of the chalcopyrite concentrate.

	Species	Composition (wt.%)
Chalcopyrite	CuFeS ₂	70.7
Galena	PbS	3.4
Sphalerite	ZnS	9.4
Gypsum	$CaSO_4$	4.2
Pyrite	FeS_2	7.7

Source: The authors.



Figure 1. Schematic flow diagram of the methodology used in the present work. Source: The authors.

Solid products were characterized in each processing step for mass balance. Experiments consisted of two steps: pretreatment of the chalcopyrite leaching by-product and recovery of precious metals (Au, Ag) from the solid residue.

The experimental procedure was carried out as follows: first, the Material M1 without any treatment was leached with glycine ($C_2H_5NO_2$ under certain conditions ($C_2H_5NO_2 = 1M$, pH=11, H₂O₂=1%, T=50 °C, t= 24 h), this to determine whether glycine would be used in combination with cyanide.

Subsequently, Material M1 was subjected to three treatments, whose experimental conditions are shown in Fig. 1:

- a) Desulfurization treatment. The samples were placed in a vessel and perchloroethylene was added following the procedure describe by Haver and Wong (1971) [12].
- b) Preoxidation. Material M1 sample (S/L=10%) was treated with NaOH 1M, Na₂S₂O₈ 0.1M, at a temperature of 323 K and pH=1.
- c) Desulfurization + Preoxidation. The desulfurized sample was treated with NaOH 1M, Na₂S₂O₈ 0.1M, at a temperature of 323 K and pH=1.

Each treated residue was subjected to cyanide and glycine cyanide leaching, where 300 g of material was leached into bottles, under the following conditions: pH=11, NaCN=0.06 M, T=298 K, t=24 h, C₂H₅NO₂=0.06 M.

Finally, chemical analysis was realized using a PerkinElmer ICP optical emission spectrometer

Fig. 1 shows a schematic flow diagram of the experimental procedure used in the present investigation.

3. Results and discussion

3.1 Characterization of the as-received chalcopyrite leaching by-product

Table 3 shows the chemical composition of Material M1 determined by XRF (elemental sulfur, S°) and ICP (the rest of the elements).

Table 5.										
Chemical analysis of the as-received chalcopyrite leaching by-product (wt. %).										
Ag (g/t)	Au (g/t)	Cu	Si	Cu	Fe	Ca	Zn	S°		
1608.69	4.66	1.64	2.25	2.55	13.61	2.55	0.38	31.75		
Source: The a	authors.									

Table 4.

Mineralogical reconstruction of the as-received chalcopyrite leaching byproduct.

SI	pecies	Composición (wt. %)
Plumbojarosite	$PbFe_6(SO_4)_4(OH)_{12}$	25
Hydroniumjarosite	$Fe_3(SO_4)_2(OH)_5(H_2O)_2$	17
Elemental sulfur	S°	26
Unidentified material	-	32

Source: The authors.

A characteristic of the residue that was utilized in the present work is that it is constituted, for the most part, by elemental sulfur, which we can observe in another research works [13,14].

Table 4 shows the mineralogical reconstruction of Material M1 obtained from the results of ICP, XRD and XRF, with HSC 8.0 software and the Species Converter module.

The mineralogical reconstruction of the materials in the characterization tables is determined by the results of X-ray diffraction and chemical analysis, using HSC 8.0 software in the Species Converter module.

As mentioned previously, the as-received chalcopyrite leaching by-product (Material M1) was subjected to different pretreatments and leached with different leaching media to recover Au and Ag. For comparison, an experiment without pretreatment was also conducted. The results obtained from these experiments are presented in the following sections.

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Figure 2. Extraction of Au, Ag and S° from the as-received chalcopyrite leaching by-product without pretreatment, by leaching with: cyanide (black), cyanide+glycine (dark gray), and glycine (light gray). Source: The authors.

Table 5.

Mineralogical analysis of chalcopyrite leaching by-product, before (M1) and after leaching with cyanide (CN M1), cyanide+glycine (CN+GLI M1), glycine (GLI M1).

C	Chemical analysis					Species, composition (wt. %)					
Sample	Ag (g/t)	Au (g/t)	Fe (%)	PJ	HJ	S°	Others	AM			
M1	1608.6	4.66	13.61	25	17	26	0	32			
CN M1	23.89	0.22	1.51	25	0	19	5	51			
CN+GLI M1	19.85	0.22	7.07	27	0	26	6	41			
GLI M1	0.01	0.01	0.60	26	18	26	4	26			

Source: The authors.

3.2 Characterization of the as-received chalcopyrite leaching by-product: without pretreatment

To investigate the effect of pretreatments, the as-received chalcopyrite leaching by-product (Material M1) was firstly leached with cyanide, cyanide+glycine, and glycine, without being subjected to any pretreatment. Fig. 2 shows the recovery of Au and Ag from the solid residue with the different leaching media; as can be observed, highest extraction efficiency is obtained with cyanide.

As can be observed in Table 4, the chalcopyrite leaching byproduct is constituted mainly of elemental sulfur (S°), plumbojarosite (PJ), hydroniumjarosite (HJ), and amorphous material (AM), the latter composed mainly of sulfur and amorphous iron and, to a lesser extent, quartz (SiO₂) and molybdenite (MoS₂). These latter two species are designated as "others" in Table 5.

It is important to mention that species designated as "others" in Table 5 do not have a significant effect on the efficiency of the leaching process. In addition, it is noteworthy to indicate that the chemical analysis of the solid residue leached with glycine was not available; thus, the chemical analysis of the liquid used to extract Au and Ag was considered.

As observed in Fig. 2, the extraction of Au and Ag is low. Some authors have reported that, during the cyanidation process, Ag is frequently associated with Au, resulting in cyanide and oxygen consumption and in a simultaneous dissolution of Au and Ag, as shown in Equations 1 and 2 [15]:

$$4Au + 8CN^{-} + O_2 + 2H_2O \leftrightarrow 4Au(CN)^{-}_2 + 4OH^{-}$$
(1)

$$4Ag + 8CN^{-} + O_2 + 2H_2O \leftrightarrow 4Ag(CN)_2^{-} + 4OH^{-}$$
(2)

It has been also reported that sulphur minerals are soluble in solutions with cyanide and oxygen; some sulfur-based species may be present in the leaching solution. A high consumption of the reagent occurs due to the presence of these species under conventional gold-cyanide leaching conditions; in addition, the dissolution rate of silver is usually slower than that of gold, which affects the leaching kinetics and the extraction of the desired metals [1]. Sulfur-containing solids can react with cyanide, forming thiocyanate, thus negatively affecting the availability of cyanide to leach precious metals [16]; this reaction is described by Equation 3 [17]:

$$S^{\circ} + CN^{-} \rightarrow CNS^{-} \qquad \Delta G^{\circ}_{30^{\circ}C} = -21.67 \ kJ$$
 (3)

Silver (Ag) dissolution is affected by the presence of elemental sulfur (S°), since this latter promotes the precipitation of silver thiocyanate [18], as shown in Equation 4 [17]:

$$Ag(CN)_2^- + S^\circ \rightarrow AgSCN + CN^- \Delta G^\circ = 32.02 \, kJ$$
 (4)

Fig. 3 shows the species distribution diagram calculated as a function of pH using the Medusa computer program [19], considering the species concentrations employed in the experiments. As can be observed, thiocyanate is thermodynamically stable in the pH range of 1-12.

When glycine is added to the leaching medium, the extraction of S° is low; this could be indicative of the adsorption of glycine on the S° surface, which may inhibit its dissolution; therefore, the reactions of Equations 3 and 4 will occur, to a lesser degree, in the presence of glycine. Regarding the presence of jarosite in Material M1, some studies have reported that the low recovery of Ag in mine tailings is due to that silver is occluded within the plumbojarosite lattice structure [20]. One of the problems involved in the jarosite precipitation process is the loss of significant amounts of silver, lead, zinc, and copper, which can be incorporated or assimilated into the jarosite structure. In this context, jarosite-type compounds represent an attractive source of silver and other precious metals, in that the amount of silver in these compounds is about 250 g/t Ag [21].



Figure 3. Species distribution diagram calculated for the system CN--SCN-[19]. Source: The authors.



Figure 4. Extraction of Au, Ag and Fe from Material M2 by leaching with cyanide (black), cyanide+glycine (dark gray) and glycine (light gray). Source: The authors.

Table 6.

Chemical composition and species of chalcopyrite leaching by-product (M1), with desulfurization pretreatment, before (M2) and after leaching with cvanide (CN M2), cvanide+glycine (CN+GLI M2) and glycine (GLI M2).

	Cher	nical an	alysis	Species, composition (wt. %						
Sample	Ag (g/t)	Au (g/t)	Fe (%)	PJ	HJ	S°	Others	AM		
M1	1608.6	4.66	13.6	25	17	26	0	32		
M2	5729.2	5.22	18.6	42	0	7	10	41		
CN M2	3202.1	0.56	17.6	40	24	0	17	19		
CN+GLI M2	4206.3	1	17.4	41	26	1	19	13		
GLI M2	0.01	0.01	0.57	41	0	0	7	52		

Source: The authors.

*Note: Species designated as "others" correspond to those elements that do not affect the leaching process efficiency.

Chalcopyrite leaching by-product subjected to 3.3 desulfurization pretreatment

The solid residue was then subjected to a desulfurization pretreatment, which was conducted under the experimental conditions shown in Fig. 1; this material was identified hereafter as Material M2. After performing this pretreatment, Material M2 was leached with the different media (cvanide, cyanide+glycine, glycine).

Fig. 4 shows the effects of the leaching medium on the recovery of silver and gold from Material M2. As can be observed, the highest recovery of Au and Ag (90.50% and 46.71%, respectively), is achieved in the cyanide-only leach system. The recoveries of these precious metals in the combined cyanide+glycine and glycine-only leach systems were 82.22% and 34.16%, and 1.91% and 0%, respectively. In addition, the amounts of Fe dissolved in the cyanide-only, cyanide+glycine, and glycine-only leach systems were about 12.98%, 16.13% and 16.46%, respectively.

Table 6 shows the chemical composition and mineralogical species of Material M2. As can be observed, this material is mainly constituted of plumbojarosite, elemental sulfur, and amorphous material. This latter contains mostly sulfur and amorphous iron.

As can be observed, the recovery of precious metals from Material M2 is higher than that obtained from Material M1; this behavior can be related to the significant reduction of elemental sulfur by the desulfurization pretreatment. The

decrease in the amount of sulfur improves the extraction of gold and, to a lesser extent, the extraction of silver. However, these results were not expected; therefore, the low extraction of silver in the presence of jarosites is attributed to the occlusion of the silver within the jarosite crystal structure.

On the other hand, the formation of iron oxides and/or insoluble hydroxides may occur either before or during leaching with cyanide (Equations 5 and 6) [17], but this is not always desirable, since these products can surround gold particles, significantly reducing the effectiveness of the gold recovery [21].

$$CN^{-} + 2Fe^{3+} + OH^{-} \rightarrow 2Fe^{2+} + HCNO \ \Delta G^{\circ} \ 30^{\circ}C \qquad (5)$$
$$= -286.84 \ kj$$

$$Fe^{2+} + 6CN^{-} \to Fe(CN)_{6}^{-4} \ \Delta G^{\circ}_{30^{\circ}C} = -245.52 \, kJ$$
 (6)

Fig. 5 shows the species distribution diagram for the Fe^{2+} -Fe³⁺ - CN⁻ system calculated by Medusa software, considering the species concentrations employed in the experiments. As can be observed, the reaction of iron with cyanide decreases the availability of cyanide [19].

As observed in Figs. 2 and 4, the extractions of Au and Ag in the glycine-only leach system are marginal compared to those obtained in the combined cyanide+glycine leach system. This behavior suggests that the recovery of these precious metals with the lixiviant mixture of cyanide and glycine is mainly attributed to the effect of cyanide. For this reason, to evaluate the effectiveness of gold and silver extraction in further experiments, only leach systems with either cyanide or glycine were considered.

Chalcopyrite leaching by-product subjected to 3.4 peroxidation pretreatment

The as-received chalcopyrite leaching by-product was subjected to peroxidation pretreatment; this sample is referred hereafter as Material M3. After conducting peroxidation pretreatment, Material M3 was leached using cyanide and glycine as leaching media. As observed in Fig. 6, the extractions of Au and Ag in the cyanide-only leach system were 99.50% and 6.04%, respectively, which were significantly higher than those obtained in the glycine-only leach system (0% Au and 8% Ag). These results indicate that glycine is less effective than cyanide in gold and silver recovery.



Figure 5. Species distribution diagram calculated by Medusa for the system Fe3+- Fe2+- CN- system. Source: The authors.



Figure 6. Effect of leaching media on the extraction of Au, Ag, S^o and Fe from Material M3: cyanide (black) and glycine (gray). Source: The authors.

Table 7.

Chemical composition and species of chalcopyrite leaching by-product (M1), with peroxidation pretreatment, before (M3) and after leaching with cyanide (CN M3) and glycine (GLI M3).

(Chemical analysis						Species, composition (wt. %)						
Sample	Ag (g/t)	Au (g/t)	Fe (%)	PJ	HJ	S°	Others	AM					
M1	1608.6	4.66	13.61	25	17	26	0	32					
M3	4730	1.86	15.8	0	0	30	13	57					
CN M3	4834.5	< 0.01	16.74	0	0	23	23	54					
GLI M3	4988	3.23	15.50	0	0	25	8	67					

Source: The authors.

Regarding the dissolution of S°, the amounts obtained by cyanide leaching and glycine leaching were 29.52% and 27.30%, respectively. In the case of Fe dissolution, the values obtained were 3.48% and 0.23%, respectively, when leaching was conducted with cyanide and glycine. As can be observed in Table 7, there is a significant amount of amorphous material in the solid residue. From the mineralogical reconstruction of Material M3, it was found that the predominant species is argentojarosite.

It is notable that the extraction of gold from Material M1 (without pretreatment) is higher than that obtained from Material M3 (with peroxidation pretreatment). This result suggests that peroxidation occurring in alkaline medium allows the release of gold from elemental sulfur due to the reaction of this later with NaOH, which promotes the formation of Na₂S according to Equation 7:

$$S^{\circ}+2NaOH \leftrightarrow \frac{2}{3}Na_2S + \frac{1}{3}Na_2SO_3 + H_2O$$

$$\Delta G^{\circ}_{30^{\circ}C} = -151.03 \text{ kJ}$$

$$\tag{7}$$

Leaching of Material M3 with glycine causes a reduction of the unidentified material (Table 7), which may allude to the low silver extraction, since this latter is commonly associated with one or more minerals such as potassium jarosite, plumbojarosite, iron oxides and fine-grained silica. The recovery of silver usually decreases during hydrometallurgical processes such as cyanidation, when silver is often found as argentojarosite or as different varieties of oxides and sulfides [22]. Some materials are depleted after leaching; however, jarosite is not affected.

3.5 Chalcopyrite leaching by-product subjected to a combined desulfurization-peroxidation pretreatment

Material M2 (with desulfurization) was subjected to a peroxidation pretreatment, obtaining a sample with a desulfurization+peroxidation pretreatment, which is referred hereafter as Material M4. Subsequent leaching of Material M4 was conducted with cyanide and glycine, considering that, in the combined cyanide+glycine leach system, only one of the lixiviants (cyanide) acts as the metal complexing agent of the precious metal. As observed in Fig. 7, about 69.84% Au and 1.93% Ag were extracted in the cyanide-only leach system; however, the extractions of Au and Ag in the glycine-only leach system were 30.53% and 0%, respectively.

The iron-dissolution percentages obtained in the cyanideonly and glycine-only leach systems were 6.699% and 0%, respectively. According to Table 8, this material is mainly composed of elemental sulfur and unidentified material. As previously mentioned, sulfur does not affect the extraction of Au; however, it does affect the extraction of Ag. The mineralogical reconstruction corresponding to the unidentified material suggests that this is mainly composed of sulfohydroxides



Figure 7. Effect of leaching media on the extraction of gold and silver from Material M4: cyanide (black) and glycine (gray). Source: The authors.

Table 8.

Chemical composition and of chalcopyrite leaching by-product with desulfurization+peroxidation pretreatment, before (M4) and after leaching with cyanide (CN M4) and glycine (GLI M4).

C	hemical	analysis		Species, composition (wt. %)					
Sample	Ag (g/t)	Au (g/t)	Fe (%)	PJ	HJ	S°	Others	AM	
M1	1608.6	4.66	13.61	25	17	26	0	32	
M4	6811.9	5.43	22.17	0	0	0	18	57	
CN M4	7465.6	1.83	24.22	0	0	0	23	54	
GLI M4	8139.6	4.48	26.81	ND	ND	ND	8	67	

Source: The authors.

*Note: Species designated as "others" are elements that do not affect the leaching process. NA: Chemical analysis not available.

^{*}Note: Species designated as "others" correspond to those elements that do not affect the leaching process.



Figure 8. Effect of pretreatment on the gold and silver extraction from the chalcopyrite leaching by-product in the cyanide-only leach system: asreceived (M1), desulfurization (M2), peroxidation (M3) and desulfurization+peroxidation (M4). Source: The authors.

3.6 Summary

The results of the present investigation show that cyanide is the best leaching medium for the extraction of Au and Ag from the chalcopyrite leaching by-product. Fig. 8 presents a comparison of the gold and silver percentages extracted under the different leaching systems.

As can be observed, desulfurization is the most effective pretreatment to achieve the highest extraction of gold and silver from the chalcopyrite leaching by-product. As mentioned previously, the presence of elemental sulfur during cyanidation is undesirable because it contributes to the precipitation of silver and affects cyanide permeability, thus affecting the recovery of precious metals.

4. Conclusions

The following conclusions can be drawn from the results of the present investigation:

- In general, all of the pretreatments investigated enhance the extraction of gold and silver. However, they have different impacts on the elements affecting the leaching performance.
- Desulfurization is the most effective pretreatment to achieve the highest extraction of gold and silver, which is indicative of that a certain amount of these metals is occluded in the elemental sulfur, affecting cyanide permeability. Therefore, sulfur removal can enhance gold and silver extraction.
- The increase in the recovery of gold (99.50%) by the peroxidation pretreatment is possibly related with the sulfur- to-Na₂S transformation in alkaline medium. On the other hand, the peroxidation pretreatment apparently is not capable of releasing the silver present in plumbojarosite, thus decreasing the amount of silver recovered. This jarosite-type compound is refractory for cyanidation; in addition, silver associates strongly with lead, but not with gold.
- From the comparison between the effectiveness of desulfurization and the combined desulfurization+peroxidation pretreatment, it is

concluded that this latter is less effective for the recovery of precious metals. This observation is supported by the lower gold and silver extraction obtained with the combined pretreatment. In addition, peroxidation of Material M1 has a detrimental effect mainly on the extraction of silver.

• Highest extraction of gold and silver from the chalcopyrite leaching by-product is obtained when Material M1 is subjected to the desulfurization pretreatment and subsequent leaching with cyanide. Independently of material type or mineralogical species, cyanide leaching significantly improves gold extraction from the solid residue; however, glycine does not have any significant effect either on the extraction of gold or of silver.

On many occasions, residues with higher gold and silver grades are obtained; such is the case of the chalcopyrite leaching by-product that was used in the present work, which contained 1,608.9 g/t of silver and 4.66 g/t of gold. Therefore, it can be economically profitable to apply the procedures and results obtained in this article.

This project was carried out with the objective of studying the extraction of gold and silver contained in these two materials using cyanide, glycine, and a mixture of cyanide and glycine. Although glycine did not have a significant effect on the extraction of gold and silver, it does have a significant effect on cyanide consumption, which has an environmental impact, since the use of glycine would allow the generation of cleaner waste.

References

- Zhang, P., Guo, Q., Wei, Q., Meng, L., Han, L., Qu, J. and Qi, T., Leaching metals from saprolitic laterite ore using a ferric chloride solution. Journal of Cleaner Production, 112, pp. 3531-3529, 2016. DOI: 10.1016/j.jclepro.2015.10.134
- [2] Cháidez-Félix, J., Estudio cinético y termodinámico de la recuperación de oro, plata y cobre de minerales sulfurosos, Tesis Doctorado en Ciencias de la Ingeniería, Instituto Tecnológico de Saltillo, México, 2018, 108 P.
- [3] Salinas, E., Rivera, I., Carrillo, F., Patiño, F. y Hernandez, L., Mejora del proceso de cianuración de oro y plata mediante la preoxidación de minerales sulfurosos con ozono. Rev. Soc. Química Méx, 48, pp. 315-320. 2004.
- [4] Jorjani, E. and Ghahreman, A., Challenges with elemental sulfur removal during the leaching of cooper and zinc sulfides, and from the residues. A review. Hydrometallurgy, 171, pp. 333-343. 2017. DOI: 10.1016/j.hydromet.2017.06.011
- [5] Calla, D., Nava, F. and Fuentes, J., Acid decomposition and thiourea leaching of silver from hazardous jarosite residues: effect of some cations on the stability of the thiourea system. Journal of Hazardous Materials, 317, pp. 440-448. 2016. DOI: 10.1016/j.jhazmat.2016.05.085.
- [6] González, A., Nava, F., Fuentes, J. and Uribe, A., Hydrothermal decomposition of industrial jarosite in alkaline media: the rate determining step pf the process kinetics. Journal of mining and metallurgy, Section B: Metallurgy, 52, pp. 135-142. 2016.
- [7] Rodríguez, C., Nava, F., Uribe, A. and Viñals, J., Pyrargyrite (Ag₃SbS₃): Silver and antimony dissolution by ozone oxidation in acid media. Hydrometallurgy, 164, pp. 15-23. 2016. DOI: 10.1016/j.hydromet.2016.04.014
- [8] Liu, Z., Yin, Z., Hu, H. and Chen, Q., Leaching kinetics of low-grade copper ore containing calcium-magnesium carbonate in ammoniaammonium sulfate solution with persulfate. Hydrometallurgy, 22, pp. 2822-2830. 2012. DOI: 10.1016/S1003-6326(11)61538-0
- [9] Reed, W., Garnov, A., Rao, L. and Nash, K., Oxidative alkaline

leaching of americium from simulated high-level nuclear waste sludges. Separation Science and Technology, 40, pp. 1029-1046. 2007. DOI: 10.1081/ss-200049860.

- [10] Eksteen, J., Oraby, E. and Tanda, B., A conceptual process for copper extraction from chalcopyrite in alkaline glycinate solutions. Minerals Engineering, 108, pp. 53-66. 2017. DOI: 10.1016/j.mineng.2017.02.001
- [11] Perea, C. and Restrepo, O., Use of amino acids for gold dissolution. Hydrometallurgy, 177, pp. 79-85. 2018. DOI: 10.1016/j.hydromet.2018.03.002
- [12] Haver, J. and Wong, M., Recovery of copper, Iron, and sulfur from chalcopyrite goncentrate using a ferric chloride leach. Journal of Metal, pp. 25-29, 1971. DOI: 10.1007/BF03355683
- [13] Lv, C., Wu, H., Lin, W., Illerup, J., Karcz, A., Ye, S. and Damo, A., Characterization of elemental sulfur in chalcopyrite leach residues using simultaneous thermal analysis. Hydrometallurgy, 188, pp. 22-30. 2019. DOI: 10.1016/j.hydromet.2019.05.020
- [14] Wu, J., Ahn, J. and Lee, J., Gold deportment and leaching study from a pressure oxidation residue of chalcopyrite concentrate. Hydrometallurgy, 201, pp. 105-583, 2021. DOI: 10.1016/j.hydromet.2021.105583
- [15] Muhammad, K. and Faical, L., Impact of silver sulphides on gold cyanidation with polymetal sulphides. Trans. Nonferrous Met. Soc. China, pp. 542-555, 2017. DOI: 10.1016/S1003-6326(18)64687-4
- [16] Liu, G. and Yen, W., Effects of sulphide minerals and dissolved oxygen on the gold and silver dissolution in cyanide solution. Minerals Engineering, 8, pp. 111-123. 1995. DOI: 10.1016/0892-6875(94)00107-N
- [17] Roine, A. HSC Chemestry 6. [online]. [Accessed on March 22th of 2019]. Available at: www.outotec.com/hsc.
- [18] Picazo-Rodríguez, N., Recuperación de valores de los insolubles procedentes de la lixiviación directa de los sulfuros de zinc, Tesis Dr. en Ciencia y Tecnología de los Materiales, Universidad Autónoma de Coahuila, México, 2019, 206 P.
- [19] Puigdomeneach, I., Medusa Software, Version 6. [online]. Available at: http://www.kemi.kth.se/medusa. 2010.
- [20] Reyes, I., Patiño, F., Flores, M., Pandiyan, T., Cruz, R., Gutiérrez, E., Reyes, M., Flores, V., Nuñez, C. and Yen, W., Dissolution rates of jarosite-type compounds in H₂SO₄ medium: a kinetic analysis and its importance on the recovery of metal values from hydrometallurgical wastes. Hydrometallurgy, 167, pp. 16-29. 2017. DOI: 10.1016/j.hydromet.2016.10.025
- [21] Salinas, E., Reyes, M., Patiño, F., Méndez, M., Rivera, I., Martínez, A. y Hernández, L., Factores que afectan el crecimiento de partículas de jarosita de amonio argentífera sintética. Rev. Soc. Quimica Mex, 46, pp. 67-72, 2002.
- [22] May, A., Sjoberg, J. and Baglin, E., Synthetic argentojarosite: physical properties and thermal behavior. American Mineralogist, 58, pp. 930-941, 1973.

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