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S^o AND JAROSITE BEHAVIOR DURING RECOVERY OF VALUES FROM THE DIRECT LEACHING RESIDUE OF SPHALERITE USING CYANIDE AND GLYCINE

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Abstract

This paper reports the effect of the components of a direct leaching residue (jarosite and elemental sulfur), on the recovery of valuable metals such as gold and silver. Leaching media such as cyanide and mixtures of cyanide with glycine were used to recover the gold and silver from the residue; however, a low recovery of these metals was obtained. This occurred due to the negative effect of its components which caused problems in the extraction process such as encapsulation of silver (due to jarosite) and the formation of thiocyanate and re-precipitation of silver (due to sulfur). Various treatments prior to leaching were tested, finding that when the residue was desulfurized with perchlorethylene and subjected to an oxidizing alkaline hydrothermal treatment, the gold extraction increased from 39.73 to 88% and the silver extraction of 64.76 to 94.29%. Additionally, it was determined that when cyanide was assisted by glycine, the latter decreased the cyanide consumption by inhibition of the dissolution of iron and sulfur in cyanide.

Keywords: *Gold; Silver; Treatments; Jarosite; Elemental sulfur*

1. Introduction

Gold is widely scattered in nature, although it is scattered in small quantities. Its presence has been detected in a great diversity of minerals; and occurs frequently in nature accompanied by silver [1].

However, gold and silver are also present in residues that come from leaching processes, such is the case of the direct leaching process of sphalerite which generates waste containing valuable concentrations of zinc, lead, iron, silver, and gold. Additionally, the waste generated from this process contains elemental sulfur (S°) as a product of sulfur oxidation [2], and jarosite [3].

When gold or silver are contained in waste composed of elemental sulfur, it is difficult to recover these metals through the hydrometallurgical route, since this is considered a cyanicide, decreasing the profitability of the cyanidation process for the recovery of leaching residue values [4]. However, there are selective dissolution processes of elemental sulfur with organic solvents such as perchlorethylene, kerosene, diaphanous oil, trichlorethylene, ethyl-cyclohexane, carbon tetrachloride, tetrachloroethane, and mixtures between them. The mechanism refers to the chemical affinity between organic solvents forming organosulfurous compounds [5].

In the case of residues composed of jarosite, some researchers have focused on conducting tests to stabilize the residue [6] and others in recovering valuable metals [7-10]; however, the stability of the jarosite hinders the recovery of the silver by the standard leaching method and a decomposition process must be applied before the leaching of this type of materials [11]. Some researchers have proposed two types of decay processes of jarosite: hydrothermal decomposition (acidic or alkaline) [12, 13] and thermal decomposition [14, 15].

In the case of acid hydrothermal decomposition, Dandy Calla et al. propose that acid decomposition of jarosite with heat (363-523 K), promotes the formation of sulfate species soluble in acidic media [11]. With regard to alkaline hydrothermal decomposition, several studies have also been carried out [16]. Deqing Zhu et al. performed tests of alkaline decomposition of jarosites using $Ca(OH)_2$ for 1 hour at 363 K and subsequently leached the treated material in a 1M solution of NaCN, they achieved an

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increase of the silver recovery from 25% (extraction of silver from jarosite without treatment) to 85%. Tests of alkaline hydrothermal decomposition for 2 hours were performed by researchers, at 363 K and 333 K using $Ca(OH)_2$ and NaOH respectively, the amount of alkali used in these tests was the necessary to obtain a solution at pH of 11.5. They then subjected the treated material to leaching in a 0.02 M solution of NaCN for 24 hours, achieving a recovery of silver greater than 90% in both materials [17].

Adrian Gonzalez et al. carried out tests of alkaline hydrothermal decomposition of an industrial sodium jarosite, which contained 150 g/t of silver, these used NaOH and $Ca(OH)_2$ as alkalizing agents at different pH (8, 9, 10, and 11) at a temperature of 333 K and determined that the best pH to carry out the tests was 11 with both reagents. The results of their investigation showed that the total hydrothermal decomposition of jarosite was completed in 3 minutes when NaOH was used to adjust the pH to 11 [18].

It should be mentioned that gold and silver may be contained in refractory species, such as pyrargirite, Carolina Rodriguez et al. proposed the performance of an oxidative treatment with O_3 prior to the recovery of gold and silver in a 1.8 M solution of NaCN improving the extraction of these metals by 50% and 10%, respectively [19]. Eleazar Salinas et al. carried out tests of oxidizing acid leaching of materials with pyrargirite using O_3 and H_2SO_4, managing to extract 80% of the silver [20]. As for the use of other oxidants, it is known that persulfate is a strong oxidant in basic solutions and has been used as a leaching agent for the recovery of metals in alkaline solutions [21, 22]. On the other hand, persulfate has been used to dissolve copper sulphides at acidic pH [21].

In this paper, the effect of the composition of a direct leaching residue of sphalerite (DLR) (consisting mainly of jarosite, elemental sulfur and valuable metals such as gold and silver) on the subsequent recovery of gold and silver is analyzed. Since there is limited information in the literature on waste treatments with this composition, it was decided to design a series of treatments based on what other researchers have done with materials that share at least one component with the DLR. Regarding the leaching media, compounds such as cyanide and glycine were chosen. This last leaching has been used individually, as well as an assistant of cyanide in the recovery of gold and silver by some researchers [23, 24], with the aim of reducing the use of cyanide.

2. Experimental procedure

In this work, residue from a direct leaching process of sphalerite and the precipitation of iron in one stage (DLR), was used. The residue used in the present investigation was obtained from a leaching process of a sphalerite concentrate (particle size D_{80} = 100 μm) 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 4 deflectors, a controlled cooling/heating jacket, a pressure transmitter and resistance temperature detector, and a Graphtec Data logger. For the experiments, deionized, distilled water was used; boiling water was added to the reactor to reach a temperature of 368 K, followed by a low speed stirring and the addition of all the materials needed for leaching. A 2-min air purge was made after adding the materials, and industrial grade oxygen (99.5%) was used to increase the pressure of the reactor to 0.096 MPa. It is worth mentioning that in these tests, NaOH was added in such an amount that iron precipitated as jarosite. Such precipitation occurred, as seen later once the acid decreased (from pH 2) by its consumption in the leaching reaction of sphalerite. The stirring speed was set at 500 rpm.

This residue was characterized by inductively coupled plasma optical emission spectrometry, X-ray diffraction and scanning electron microscopy. This later was performed in a FEI Quanta 600 scanning electron microscope. In addition, the association and chemical composition of the DLR particles was determined by using the system MLA (Mineral Liberation Analyzer) adapted to a FEI Quanta 600 scanning electron microscope. All solid products of the different experimental stages were characterized to carry out the final balances. To obtain the extraction percentages, the following data were used:

Initial material = (concentration based in chemical analysis of initial material) * initial sample weight for testing and

Final material = (concentration based in chemical analysis of final material) * final test sample weight.

After the results of the previous data were substituted in Eq. 1:

$$\%Extraction = \frac{Initial\ material - Final\ material}{Initial\ material} \cdot 100 \quad (1)$$

The experimental development consisted of two stages: 1.-DLR treatments and 2.- DLR gold and silver recovery.

Fig. 1 shows an outline of the experimental procedure that was followed in the present investigation

The experimental procedure was carried out as follows: first the DLR without any treatment was leached with glycine ($C_2H_5NO_2$ under certain conditions ($C_2H_5NO_2$=1M, pH=11, H_2O_2=1%, T=323 K, t= 24 h), this to determine if glycine would be used in combination with cyanide.

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

a) Alkaline hydrothermal treatment (DLR-AH). DLR sample (S/L=10%) was treated with NaOH 1M, at a temperature of 323 K and pH equal to 1.

b) Thermal treatment (DLR-TT). This treatment was carried out in a muffle, at a temperature of 550 ° C for 1 hour.

c) Desulfurization treatment and oxidizing alkaline hydrothermal treatment (DLR-AHO). The sample were put in a vessel and perchloroethylene was added following the procedure describe by Haver and Wong, 1971 [25].

Each treated residue was subjected to cyanide and glycine cyanide leaching, where 300 g of material were leached in bottles, under the following conditions: pH=11, NaCN=0.06 M, T=298 K, t=24 h, and $C_2H_5NO_2$ =0.06 M.

Finally, chemical analysis was realized using a Perkin Elmer ICP optical emission spectrometer.

It is important to mention that the management and control of chemical reagents used in the experimental tests were carried out based on the Official Mexican Standard NOM-010-STPS-2014 [26].

3. Results and Discussion

3.1. DLR characterization

The chemical composition of the DLR determined by inductively coupled plasma optical emission spectrometry in a Perkin Elmer ICP optical emission spectrometer is shown in Table 1.

The pattern of X-ray diffraction of leaching residues without any treatment is shown in Fig. 2.

Table 2 shows the main species of the DLR determined by X-ray diffraction in a Panalytical Empyrean X-ray diffractometer.

SEM characterization of the DLR is shown in Fig.

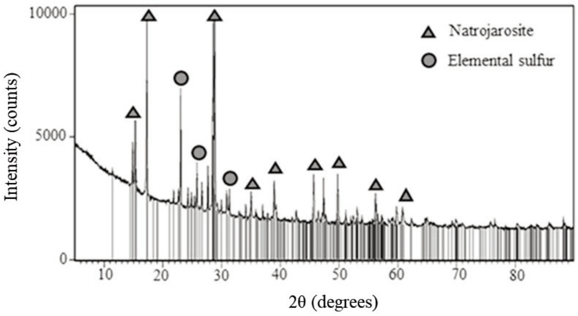

Figure 2. *Diffraction pattern of DLR*

Table 2. *Mineralogical reconstruction of the DLR (wt. %)*

Identified species		Composition (wt. %)
Natrojarosite	$NaFe_3(SO_4)_2(OH)_6$	58
Sulfur	S°	24
Sphalerite	ZnS	7
Lead sulfate	$PbSO_4$	1
Pyrite	FeS_2	1
Anhydrite	$CaSO_4$	4
Others	-	5

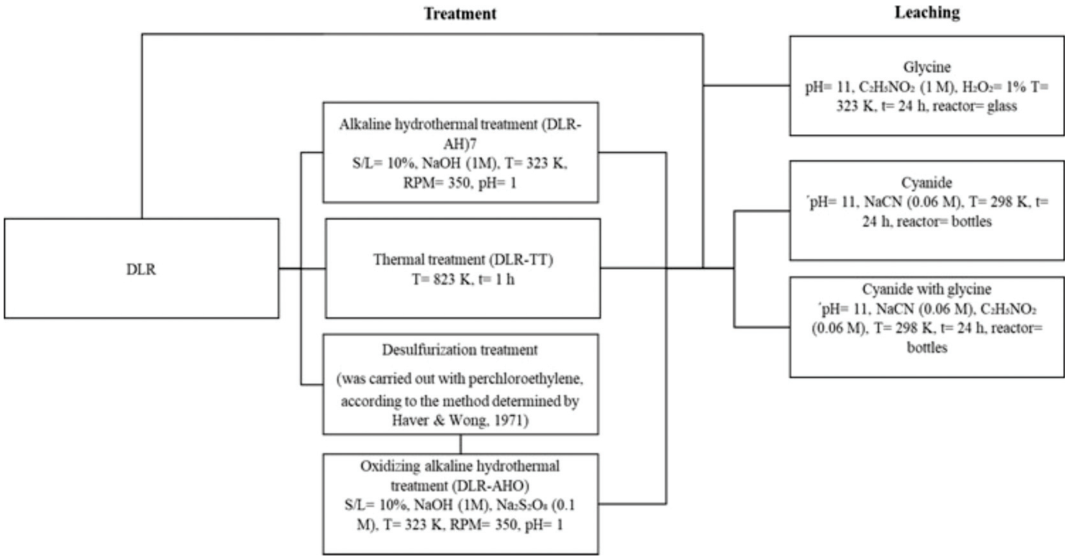

Figure 1. *Schematic presentation of experimental procedure*

Table 1. *Chemical analysis of DLR*

Ag (g/t)	Au (g/t)	Fe (%)	Zn (%)	As (%)	S (%) *	Pb (%)	Ca (%)	Cd (%)
192.2	0.78	17.94	4.76	0.22	35	0.67	0.65	0.04

** Sulfur was determined through X-ray fluorescence*

3, where it was observed that the DLR was formed by natrojarosite and elemental sulfur. The elemental sulfur was generated during the direct leaching of the zinc concentrate, a process from which the DLR came.

The total reaction of direct leaching of the ZnS concentrate can be presented by Eq. 2 [27]:

$$ZnS + H_2SO_4 + \frac{1}{2}O_2 \rightarrow ZnSO_4 + S^o + H_2O \qquad (2)$$
$$\Delta G^0_{95^o C} = -420.27\ kJ$$

Natrojarosite was formed during the leaching process according to the following equation.

$$1.5Fe_2(SO_4)_3 + NaOH + 5H_2O \rightarrow NaFe_3(SO_4)_2(OH)_6 + 2.5H_2SO_4 \qquad (3)$$

Table 3 shows the main species determined by MLA; the analysis methodology consisted in the acquisition of images with backscattered electrons to delineate the mineral particles for later identification through X-ray analysis.

The results of the gold and silver recovery experiments are shown below, these were conducted considering the composition of DLR (mainly of elemental sulfur, natrojarosite, gold, and silver present as pyrargyrite).

The chemical formula of pyrargyrite can be expressed as follows [28]:

$$3Ag_2S \cdot Sb_2S_3 \rightarrow 2Ag_3SbS_3 \qquad (4)$$

Laufek et al. found that, in the crystal structure of pyrargyrite, antimony atoms formed a pyramidal unit of SbS_3, which was a characteristic feature of sulfosal structures. These pyramids were oriented in one direction, which explained the polar character of pyrargyrite. Ag atoms were found between these pyramids and connected by short S-Ag-S bonds. Because there was not much data in the literature about pretreatments of materials containing pyrargyrite, a possible approach would be to consider that pyrargyrite consisted of the Ag_2S and Sb_2S_3 species, this in order to elucidate the mechanism through which silver was extracted according to the pretreatments and leaching media, therefore, in the present work some of the reactions involving pyrargyrite will be addressed using the Ag_2S and Sb_2S_3 individually [28].

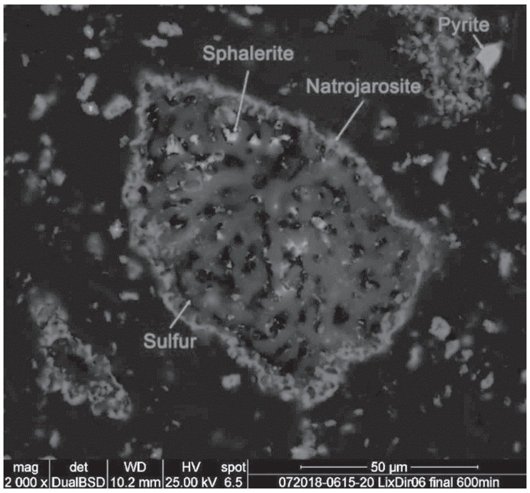

Figure 3. SEM images of DLR formed by natrojarosita and elemental sulfur

3.2. Dissolution of gold and silver from the DLR with and without treatments using cyanide, cyanide with glycine, and glycine

First, cyanide, cyanide with glycine, and glycine leaching media were used to carry out the recovery of gold and silver from DLR without treatments. However, the results indicated that the gold and silver were refractory (extraction less than 80%) to the different leaching media. Although, comparatively, cyanidation was the method that dissolved the greatest amount of silver and gold.

Based on the previous results, it was decided to study the conventional cyanidation and glycine-assisted cyanidation to visualize the effect of the latter on the extraction of values compared with cyanidation. In this sense, a comparative analysis was conducted using average extractions of the gold and silver obtained by main factor (the variables considered, such as leaching media), this to evaluate the effectiveness of the leaching media in the extraction of the gold and silver. Fig. 4 shows the results of gold and silver extraction of DLR submitted to the different treatments shown in Fig. 1 and leached in mediums of cyanide and cyanide with glycine, as well as the interaction of other elements present in the DLR, such as Fe and S° with the leaching medium and which can interfere with the extraction of the values.

Fig. 4a shows the results of gold and silver

Table 3. Results of the analysis of association and chemical composition of the DLR by the SEM-MLA system

Group	Mineral	Formula	Weight (%)
Sulfides	Sphalerite	ZnS	8.68
	Pyrite	FeS_2	1.12
Silver species	Pyrargyrite	Ag_3SbS_3	0.05
	Freibergite	$(Ag_{0.3}Cu_{0.6}Fe_{0.1})_{12}Sb_4S_{13}$	0.01
	Natrojarosite	$NaFe_3(SO_4)_2(OH)_6$	51.82
Gangues and other oxides species	Sulfur	S°	22.2
	Others	-	16.12

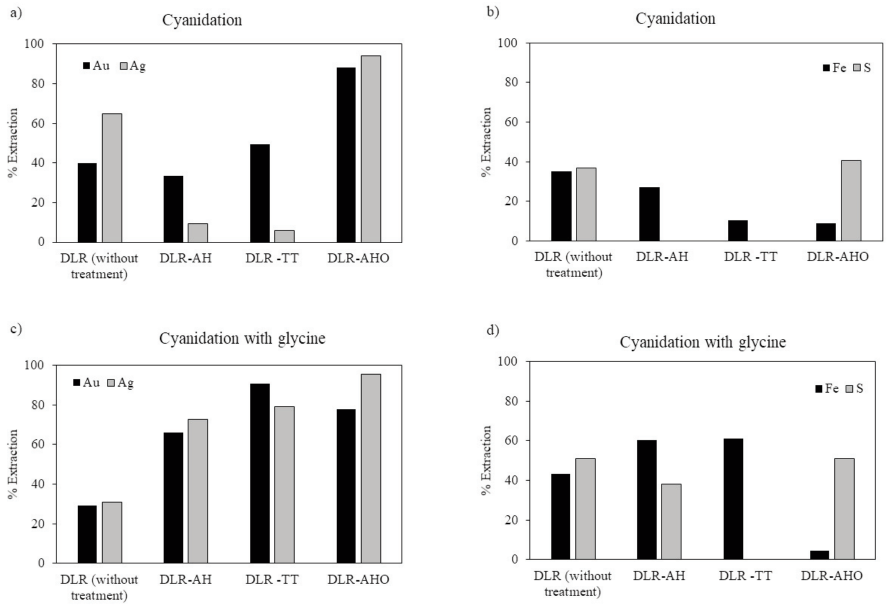

Figure 4. *Extraction of Au, Ag, Fe, S ° and % of natrojarosite decomposition of the DLR without and with treatments (DLR-AH (hydrothermal alkaline treatment), DLR-TT (heat treatment), DLR-AHO (hydrothermal alkaline oxidant treatment) during cyanidation and cyanidation with glycine*

extraction through cyanidation from the DLR subjected to the different treatments. In the case of DLR without treatment, it can be observed that this was refractory since the extraction of gold and silver was less than 80%, it was known that pH control during cyanidation was important to avoid excessive loss of cyanide by hydrolysis, which occurred at pH values lower than 9.4. This pH control was usually performed using lime ($Ca(OH)_2$). As mentioned above, the DLR was mainly formed by natrojarosite and elemental sulfur, and these components consumed lime according to the following equations:

$$NaFe_3(SO_4)_2(OH)_6 + 2Ca(OH)_2 + 4H_2O \rightarrow 3Fe(OH)_3 + 2CaSO_4 \cdot 2H_2O + NaOH \quad \Delta G^o_{50^o C} = -162.03\ kJ \tag{5}$$

$$3S^o + 3Ca(OH)_2 \rightarrow 2CaS + CaSO_3 + 3H_2O \quad \Delta G^o_{50^o C} = -29.17\ kJ \tag{6}$$

Based on the above equations, it can be inferred that conventional cyanidation of DLR without treatment was not an appropriate process because its main components were avid lime consumers. On the other hand, adding an excess of lime in the cyanidation, in search of accelerating the decomposition of natrojarosite and elemental sulfur at the same stage would not be adequate. As can be seen in Fig. 4b a high extraction of Fe and S° occurred (35 and 38% respectively) during cyanidation. Also, an excess of lime would cause the increase of H_2O_2 (according to the Eq. 7), which accumulated on the surface of the metal and prevented reaction with cyanide [29].

$$Ca(OH)_2 + H_2O_2 \leftrightarrow CaO_2 + 2H_2O \tag{7}$$

Another factor to consider was the silver that was present as pyrargyrite, 37.2% associated with natrojarosite and 62.8% free. It is known that when silver was contained in Ag_2S, it easily dissolved in cyanide, however, when it was associated with Sb as pyrargyrite it was hardly extracted [29]. During cyanidation, antimony dissolved to form antimonates, delaying the dissolution of gold and silver [30].

In the process of alkaline leaching with cyanide Sb_2S_3 increased the consumption of OH^-, CN^- y O_2 [31], then, the equations proposed by these researchers were presented:

$$Sb_2S_3 + 6OH^- \rightarrow SbO_3^{3-} + SbS_3^{3-} + 3H_2O \tag{8}$$

$$SbS_3^{3-} + 6OH^- \rightarrow SbO_3^{3-} + SbS_3^{3-} + 3H_2O \tag{9}$$

$$4SbS_3^{3-} + 6CN^- + 6H_2O + 3O_2 \rightarrow 2SbS_3 \downarrow + 6CNS^- + 12OH^- \tag{10}$$

Sb_2S_3 was deposited on the surface of the gold particles, forming a dense product layer, and preventing the diffusion of CN^- and O_2 to the gold particles, which led to a low extraction. Some researchers proposed certain treatments for this type of refractory materials such as alkaline leaching with NaOH or Na_2S [32-33], or roasting [34].

On the other hand, the formation of iron oxides and/or insoluble hydroxides was not always desirable, either before or during cyanide leaching, in accordance with Marsden (2005) these products coat gold particles and significantly reduce leaching efficiency [35]. Also, part of the iron that dissolved from the natrojarosita or the insoluble hydroxides was reduced by cyanide and then formed iron hexacyanide according to the following equations:

$$CN^- + 2Fe^{3+} + OH^- \rightarrow 2Fe^{2+} + HCNO \qquad \Delta G^o_{30^o C} = -286.84\ kJ \tag{11}$$

$$Fe^{2+} + 6CN^- \rightarrow Fe(CN)_6^{-4} \qquad \Delta G^o_{30^o C} = -245.52\ kJ \tag{12}$$

In the case of elemental sulfur, this also affected the recovery of the values because it consumed cyanide to form thiocyanate according to the following equation.

$$S^o + CN^- \rightarrow CNS^- \qquad \Delta G^o_{30^o C} = -21.67\ kJ \tag{13}$$

The formation of thiocyanate was checked by contacting 10 grams of S° in a 0.06 M solution of NaCN, subsequently detecting the formation of sodium thiocyanate through the Alpha method 4500 CN^- M. Thiocyanate.

According to Eq. 14, the silver and cyanide complex reacted with S° and subsequently the dissolved silver could precipitate again as silver thiocyanate.

$$Ag(CN)_2^- + S^o \rightarrow AgSCN + CN^- \qquad \Delta G^o_{30^o C} = -32.02\ kJ \tag{14}$$

In the case of cyanidation with glycine, according to some researchers, glycine formed complexes with iron and consumes OH^- radicals, according to Eq. 15 [36].

$$Fe^{2+} + H - glycine + OH^- \rightarrow Fe(glycine)^+ + H_2O \tag{15}$$

The results of cyanidation with glycine shown in Fig. 4c, indicated that glycine did not impact gold extraction, iron extraction was superior to that obtained in conventional cyanidation (Fig. 4d). It was inferred that glycine only influenced the consumption of OH^- radicals.

Considering that the components of the residue caused its refractoriness, to evaluate the effect of glycine and optimize conventional cyanidation, it was decided to evaluate different types of treatments based on the literature reviewed before leaching.

Table 4 shows how the chemical composition and the DLR phases in these leaching media; cyanide (DLR-CYA) and cyanide with glycine (DLR-CYA-GLY).

Later, the first treatment to DLR was the hydrothermal alkaline (DLR-AH) and subsequently leaching of waste was carried out. Table 5 shows as a change the chemical composition and phases of the residue after alkaline treatment (DLR-AH) and leaching in the leaching media used cyanide (DLR-AH-CYA) and cyanide with glycine (DLR-AH-CYA-GLY).

According to Fig. 4a, during the cyanidation of this residue there was a decrease in the extraction of gold and silver compared to the DLR without treatment. As mentioned earlier, this investigation worked on the assumption that pyrargyrite consisted of Ag_2S and Sb_2S_3, based on the above, the equation of pyrargyrite with NaOH during the alkaline treatment occurred as follows:

$$Ag_2S + 2OH^- \rightarrow 2AgOH(aq) + 3S^o + 2e^- \qquad \Delta G^o_{50^o C} = 166.73\ kJ \tag{16}$$

In the case of antimony sulfide, the leaching of antimony in alkaline medium with NaOH was carried out according to Eq. 17 [37]:

$$Sb_2S_3 + 2NaOH \rightarrow NaSbOS + NaSbS_2 + H_2O \tag{17}$$

However, Eq. 18 calculated using HSC Chemistry 6 software was proposed:

$$Sb_2S_3 8OH^- \rightarrow 2SbO_2^- + 3S^o + 4H_2O + 6e^- \qquad \Delta G^o_{50^o C} = -190.42\ kJ \tag{18}$$

In Eq. 16 the ΔG° was positive, so perhaps thermodynamically it was not feasible to occur; however, the negative ΔG° of the equation of the antimony sulfide in alkaline medium indicated that the NaOH probably contributed to dissolve the antimony of the pyrargyrite leaving only Ag_2S.

Then, the dissolution of Ag_2S can occur according to the following reaction:

Table 4. *Chemical composition and species in the DLR without treatment before and after leaching with cyanide and cyanide with glycine*

	Chemical analysis			Species, composition (wt. %)			
Sample	Au (g/t)	Ag (g/t)	Fe (%)	S°	$NaFe_3(SO_4)_2(OH)_6$	ZnS	U.M*
DLR	0.78	192	17.94	24	58	7	6
DLR-CYA	0.51	73.48	16.03	14	40	8	0
DLR-CYA-GLY	0.6	144.05	16.5	17	50	10	6

** Unidentified material*

$$Ag_2S + 4NaCN + 2O_2 = 2NaAg(CN)_2 + Na_2SO_4 \quad (19)$$
$$\Delta G^o_{50^o C} = -770.75\ kJ$$

As can be seen in Table 5, natrojarosite was decomposed during alkaline treatment. According to Eq. 20, natrojarosite was broken down into iron hydroxides.

$$NaFe_3(SO_4)_2(OH)_6 + 3NaOH + 14H_2O \rightarrow$$
$$2Na_2SO_4 \cdot 7H_2O + 3Fe(OH)_3 \quad (20)$$
$$\Delta G^o_{50^o C} = -314.6\ kJ$$

The diffraction pattern of the DLR-AH is shown in Fig. 5, where the disappearance of the natrojarosite phase and the presence of unidentified material in its place was observed, which possibly corresponded to the decomposition of the natrojarosite into hydroxides of iron ($Fe(OH)_3$) amorphous.

As mentioned earlier, iron hydroxides could coat gold and silver particles or part of the iron that dissolved from the natrojarosita or the insoluble hydroxides could be reduced by cyanide and then form iron hexacyanide, which could possibly inhibit their recovery. Probably due to the above, in the case of conventional cyanidation of the DLR treated in medium alkaline, the extraction of gold and silver decreased compared to the cyanidation of the DLR without treatment. On the other hand, part of the DLR -AH iron dissolved and became a complex with cyanide and elemental sulfur did not dissolve during conventional cyanidation, possibly because of iron hydroxides.

In the medium of cyanide with glycine, a substantial increase in the extraction of gold and silver was observed (Fig. 4c), there was also an increase in the extraction of iron compared to that obtained in conventional cyanidation, possibly because glycine dissolved the iron hydroxides deposited on the particles as Fe^{2+} and formed a complex. As observed in Fig. 4d in cyanidation with glycine, a greater extraction of Fe occurred, which is indicative that glycine formed complexes with iron. The following diagram shows the distribution of species of the Fe^{2+} system and glycine, as can be seen in this diagram, glycine in alkaline medium consumes OH- radicals and formed the glycinate (gly^-) ion, which reacted with Fe^{2+} to form the complex of iron and glycine.

It is inferred that the complex remained stable in the leaching solution, which allowed for greater cyanide availability and a better dissolution of gold and silver. However, removing the iron hydroxides layer increased the dissolution of elemental sulfur, which was a cyanide consumer and inhibited the extraction of gold and silver.

On the other hand, during the cyanidation of DLR-TT, a low gold and silver extraction was obtained as shown in Fig. 4a. In the case of DLR-TT, as can be seen in Table 6, Au and Ag were concentrated during the heat treatment, in addition the natrojarosita possibly was decomposed into iron oxides. This coincided with the low iron extraction during the cyanidation (Fig. 4b) since this remained in the residue. As mentioned above the formation of iron oxides could coat gold particles and reduce the leaching efficiency so that they could coat the gold and Ag_2S particles by inhibiting the dissolution of gold and silver, which would explain the low gold and

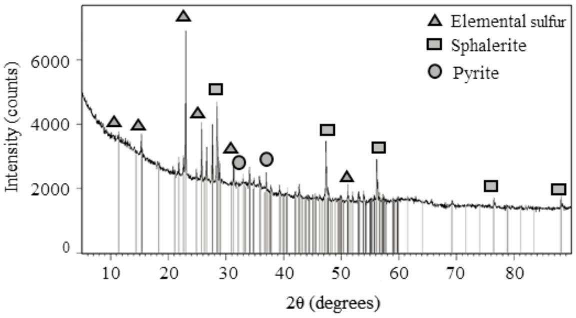

Figure 5. *Diffraction pattern of DLR-AH*

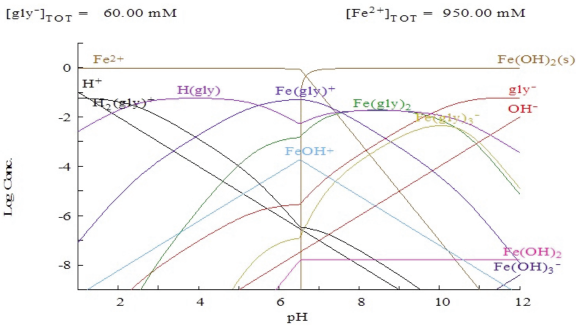

Figure 6. *Diagram of distribution of species of the Fe^{2+}-glycine⁻ system*

Table 5. *Chemical composition of the residue and species identified of the DLR-AH, before and after leaching with cyanide and cyanide with glycine*

	Chemical analysis			Species, Composition (wt.%)		
Sample	Au (g/t)	Ag (g/t)	Fe (%)	S°	ZnS	U.M*
DLR-AH	0.76	236.83	20.34	17	17	56
DLR-AH-CYA	0.51	216.85	21.5	22	1	55
DLR-AH-CYA-GLY	0.49	121.63	22.1	23	17	48

* *Unidentified material*

silver extraction during conventional cyanidation.

In the cyanide medium with glycine there was a greater extraction of gold and silver because as mentioned above (Fig. 4c), the complexes formed by glycine allowed the gold and silver particles to be released and that the iron did not consume cyanide. On other hand, the elemental sulfur was decomposed during the thermal treatment, which allowed the increase of extraction of the values in the cyanide medium with glycine. In the case of S°, it was reported that at temperatures above 393 K, sulfur melts and to 719 K, SO_2 is formed [38]. However, the thermal treatment of materials containing jarosite has certain disadvantages, since to carry out this treatment high temperatures are required, which generates gases, such as SO_2 [39].

On other hand, some researchers [40], studied the phase transitions in the pyrargyrite (Ag_3SbS_3) depending on the temperature, and found that from 536 K the crystalline structure of the pyrargyrite seemed to be disordered to the maximum and the material decomposed in Ag_2S leaving residual silver and sulfides on the surface of the sample. This indicated that the pyrargyrite was decomposed in Ag_2S during the heat treatment that was performed, so this specie of silver was leached into cyanide and cyanide with glycine. It should be mentioned that the thermal treatment that was carried out at the DLR was carried out to know the effect of eliminating the elementary S ° of the material. However, as the objective of the present work was to evaluate the hydrometallurgical pathway, it was decided to carry out a desulfurization treatment to the residue followed by a hydrothermal decomposition (using $Na_2S_2O_8$), DLR -AHO, to ensure the oxidation of the pyrargirite.

Table 7 shows the phases present and the chemical composition of DLR -AHO treated before and after leaching with cyanide (DLR-AHO-CYA) and cyanide with glycine (DLR-AHO-CYA-GLY).

As observed in Table 7, the elemental sulfur from the residue was removed and the natrojarosite was decomposed, therefore, the unidentified material corresponded to the decomposition of the natrojarosite. As can be seen in Fig. 4b and Fig. 4c, the extraction of gold and silver increased substantially in both leaching media. The removal of elemental sulfur inhibited the equations of thiocyanate formation and re-precipitation of silver that was proposed earlier, and the use of persulfate allowed to reduce iron consumption by inhibiting its dissolution in the leaching media, since according to Eq. 21, it could form a layer of elementary S° on the DLR particles.

$$NaFe_3(SO_4)_2(OH)_6 + 3Na_2S_2O_8 + 13NaOH \rightarrow$$
$$9Fe(OH)_3 + 11Na_2SO_4 + S^o + H_2O + 3O_2 \qquad (21)$$
$$\Delta G^o_{50^o C} = -1400.92\ kJ$$

As observed in Fig. 3 in the SEM characterization of the DLR, elemental sulfur covered the residual natrojarosite and sphalerite particles. The fact that the removal of elemental sulfur increased the extraction of gold and silver indicated that the values were possibly “adsorbed or trapped” by it, therefore, when it was eliminated from the residue, it allowed them to be released and increased the recovery of gold and silver.

3.3. Cyanide consumption in gold and silver leaching tests from DLR-AHO

Normal commercial operation to recovery gold results in consumption of 1.5-2.5 kg/t of sodium cyanide [41]. However as can be seen in the Table 7 the DLR-AHO, is composed mostly of iron, which is an avid consumer of cyanide, which explained the high consumption of cyanide, which was evaluated in

Table 7. *Chemical composition and identified species of the DLR-AHO before and after leaching with cyanide and cyanide with glycine*

Chemical analysis				Species, composition (wt.%)
Sample	Au (g/t)	Ag (g/t)	Fe (%)	U.M*
DLR-AHO	1.18	309.12	28.12	100
DLR-AHO-CYA	0.22	28.92	30.17	100
DLR-AHO-CYA-GLY	0.25	62.5	18.96	100

** Unidentified material*

Table 6. *Chemical composition and species of the DLR-TT before and after leaching with cyanide and cyanide with glycine*

	Chemical analysis			Species, Composition (wt.%)				
Sample	Au (g/t)	Ag (g/t)	Fe (%)	ZnS	Fe_3O_4	Fe_2O_3	$ZnFe_2O_4$	U.M*
DLR-TT	1.08	334.59	29.06	10	18	9	7	56
DLR-TT-CYA	0.61	352.58	32.2	13	24	10	14	55
DLR-TT-CYA-GLY	0.26	178.61	32.62	11			24	48

** Unidentified material*

both cyanide and cyanide with glycine. Fig. 7 shows the results of cyanide consumption, which was between 15 and 9 kg/t respectively.

It is important to highlight that the metal contents in these materials were much higher, and that, in addition, there was a higher consumption due to the presence of compounds that were the product of the treatments, which were more likely to react with cyanide than species present in the leaching residue.

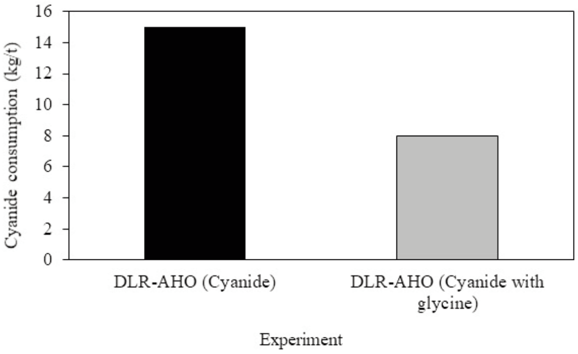

Figure 7. *Cyanide consumption in leaching tests of DLR-AH (leaching medium cyanide and cyanide with glycine)*

On the other hand, a lower consumption of cyanide was obtained where cyanide assisted with glycine was used. Possibly the formation of a glycine and iron complex inhibited the latter from reacting with cyanide, therefore, the consumption of cyanide decreased when glycine was added.

4. Conclusions

In this work the effect of the composition of a direct leaching residue of sphalerite (DLR) (composed mainly of jarosite, elemental sulfur, and valuable metals such as gold and silver) is analyzed. In the literature there was not information on waste treatments with this composition or mixture of components. Individually, as mentioned in the introduction, both elemental sulfur and jarosite were studied since they affect the extraction of gold and silver (which was corroborated by leaching the residue without any treatment). In this sense, this work exposes the behavior of jarosite and elemental sulfur as a whole, and the impact of the treatments necessary for their removal or transformation into compounds that do not inhibit the extraction of gold and silver.

Based on the above, a series of DLR treatments were carried out to establish the best conditions in which the gold and silver present in this material could be recovered. Below are the treatments with their respective conditions, under which the DLR gold and silver can be recovered:

1.- Desulfurization.

This process was carried out in two stages:

a) DLR was dissolved in perchlorethylene under the following conditions: S / L ratio = 10%, T = 333 K, t = 1h.

b) The solution from the dissolution was cooled to a temperature of 269.16 K to precipitate elemental sulfur, which was finally filtered later.

2.- Oxidation:

a) Thermal route: T = 823 K, t = 1 h

b) Hydrothermal route: S / L = 10%, NaOH = 1 M, $Na_2S_2O_8$ = 0.1 M, T = 323 K, RPM = 350, pH = 10, t = 3 h

3.- Cyanidation:

pH = 11, NaCN = 0.06 M, T = 298 K, t = 24 h, reactor = bottles

Using the above route, at least the following can be recovered: 94.29% Ag and 88% Au.

Additionally, it was found that glycine helped reduce cyanide consumption, determining that it possibly formed complexes with iron and sulfur, which were known cyanide consumer. This finding allowed us to assess glycine as an inhibitor of the solubility of some elements and compounds that increased cyanide consumption, in addition to that reported as a precious metals complexing. However, the cost of using glycine will have to be considered versus the cost of consuming cyanide.

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PONAŠANJE ELEMENTARNOG SUMPORA I JAROZITA PRILIKOM EKTRAKCIJE DRAGOCENIH METALA IZ TALOGA DOBIJENOG DIREKTNIM LUŽENJEM SFALERITA U PRISUSTVU CIJANIDA I GLICINA

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Apstrakt

U ovom radu se govori o uticaju komponenata taloga dobijenog direktnim luženjem (jarozit i elementarni sumpor) na ekstrakciju dragocenih metala poput zlata i srebra. Mediji, kao što su cijanid i smeša cijanida i glicina, korišćeni su prilikom luženja za odvajanje zlata i srebra iz taloga, međutim, stepen iskorišćenja ovih metala je bio nizak. Do toga je došlo zbog negativnog dejstva komponenti koje su se nalazile u talogu, a koje su uzrokovale probleme tokom postupka ekstrakcije, kao što su kapsulacija srebra (koja se dogodila zbog jarozita) i stvaranje tiocijanita i novo taloženje srebra (koje se dogodilo zbog sumpora). Ispitivani su različiti postupci pre luženja i ustanovljeno je da je iz taloga podvrgnutog postupcima desulfurizacije perhloretilenom i oksidaacionom alkalno hidrotermalnom postupku, ekstrakcija zlata povećana sa 39,73 na 88%, a ekstrakcija srebra sa 64, 76 na 94,29%. Pored toga je utvrđeno i da, kada je uz cijanid prisutan i glicin, potrošnja cijanida je smanjena zbog inhibicije rastvaranja gvožđa i sumpora u cijanidu.

Ključne reči: *Zlato; Srebro; Postupak; Jarozit; Elementarni sumpor*