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. The above due to the negative effect of its components which cause 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 is 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 is assisted by glycine, the latter decreases 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 increase the silver recovery of 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 alkalinizing 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. have 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. have carried out tests of oxidizing acid leaching of materials with pyrargirite using O\(_3\) and H\(_2\)SO\(_4\), 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 \(D_{80} = 100 \mu m\)) 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 Graphitec 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 occurs, as seen later once the acid has 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

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:

\[
\% \text{ Extraction} = \frac{\text{Initial material} - \text{Final material}}{\text{Initial material}} \times 100
\]

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,

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**Figure 1. Schematic presentation of experimental procedure.**
The experimental procedure was carried out as follows: first the DLR without any treatment was leached with glycine (C$_2$H$_5$NO$_2$ under certain conditions (C$_2$H$_5$NO$_2$ =1M, pH=11, H$_2$O$_2$=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, C$_2$H$_5$NO$_2$ =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.

| 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.

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

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

| Identified species | Composition (wt. %) |
|--------------------|---------------------|
| Natrojarosite      | NaFe₃(SO₄)₂(OH)₆    | 58      |
| Sulfur             | S⁰                 | 24      |
| Sphalerite         | ZnS                | 7       |
| Lead sulfate       | PbSO₄              | 1       |
| Pyrite             | FeS₂               | 1       |
| Anhydrite          | CaSO₄              | 4       |
| Others             |                     | 5       |

SEM characterization of the DLR is shown in Fig. 3, where it is observed that the DLR is formed by natrojarosite and elemental sulfur. The elemental sulfur is generated during the direct leaching of the zinc concentrate, a process from which the DLR comes.

Figure 3. SEM images of DLR formed by natrojarosita and elemental sulfur.
The total reaction of direct leaching of the ZnS concentrate can be presented by Eq. 2 [27]:

\[
\text{ZnS} + \text{H}_2\text{SO}_4 + \frac{1}{2} \text{O}_2 \rightarrow \text{ZnSO}_4 + \text{S}^\circ + \text{H}_2\text{O} \quad \Delta G^\circ_{95^\circC} = -420.27 \text{ kJ}
\]  

(2)

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

\[
1.5 \text{Fe}_2(\text{SO}_4)_3 + \text{NaOH} + 5\text{H}_2\text{O} \rightarrow \text{NaFe}_3(\text{SO}_4)_2(\text{OH})_6 + 2.5\text{H}_2\text{SO}_4
\]

(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.

**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$_3$SbS$_3$            | 0.05       |
|                            | Freibergite     | (Ag$_{0.3}$Cu$_{0.6}$Fe$_{0.1}$)$_3$Sb$_2$S$_{13}$ | 0.01 |
| Gangues and other oxides   | Natrojarosite   | NaFe$_3$(SO$_4$)$_2$(OH)$_6$ | 51.82 |
|                            | Sulfur          | S$^\circ$                | 22.2       |
|                            | Others          |                          | 16.12      |

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]:

\[
3\text{Ag}_2\text{S-Sb}_2\text{S}_3 \rightarrow 2\text{Ag}_3\text{SbS}_3
\]

(4)

Laufek et al. found that, in the crystal structure of pyrargyrite, antimony atoms form a pyramidal unit of SbS$_3$, which is a characteristic feature of sulfosal structures. These pyramids are oriented in one direction, which explains the polar character of pyrargyrite. Ag atoms are found between these pyramids and connected by short S-Ag-S bonds. Because there is not much data in the literature about pretreatments of materials containing pyrargyrite, a possible approach would be to consider that pyrargyrite consists of the Ag$_2$S and Sb$_2$S$_3$ species, this in order to elucidate the mechanism through which silver it is 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$_2$S and Sb$_2$S$_3$ individually [28]:

**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 are refractory (extraction less than 80%) to the different leaching media. Although, comparatively, cyanidation is 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 on 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.

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.

Fig. 4a shows the results of gold and silver extraction through cyanidation from the DLR subjected to the different treatments. In the case of DLR without treatment, it can be observed that this is refractory since the extraction of gold and silver is less than 80%, it is known that pH control during cyanidation is important to avoid excessive loss of cyanide by hydrolysis, which occurs at pH values lower than 9.4, this pH control is usually performed using lime (Ca(OH)₂). As mentioned above, the DLR is mainly formed by natrojarosite and elemental sulfur, these components consume lime according to the following equations:

\[
\text{NaFe}_3\text{(SO}_4\text{)}_2\text{(OH)}_6 + 2\text{Ca(OH)}_2 + 4\text{H}_2\text{O} \rightarrow 3\text{Fe(OH)}_3 + 2\text{CaSO}_4 \cdot 2\text{H}_2\text{O} + \text{NaOH}
\]

\[\Delta G^{\circ} = -162.03 \text{ kJ} \] (5)

\[
3\text{S}^\circ + 3\text{Ca(OH)}_2 \rightarrow 2\text{CaS} + \text{CaSO}_3 + 3\text{H}_2\text{O}
\]

\[\Delta G^{\circ} = -29.17 \text{ kJ} \] (6)

Based on the above equations, it can be inferred that conventional cyanidation of DLR without treatment is not an appropriate process because its main components are 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° occurs (35 and 38% respectively) during
cyanidation. Also, an excess of lime would cause the increase of H$_2$O$_2$ (according to the Eq. 7), which accumulates on the surface of the metal and prevents reaction with cyanide [29].

$$\text{Ca(OH)}_2 + \text{H}_2\text{O}_2 \leftrightarrow \text{CaO}_2 + 2\text{H}_2\text{O} \quad \text{(7)}$$

Another factor to consider is the silver that is present as pyrargyrite, 37.2% associated with natrojarosite and 62.8% free. It is known that when silver is contained in Ag$_2$S, it easily dissolves in cyanide, however, when it is associated with Sb as pyrargyrite it is hardly extracted [29]. During cyanidation, antimony dissolves to form antimonates, delaying the dissolution of gold and silver [30].

In the process of alkaline leaching with cyanide Sb$_2$S$_3$ increases the consumption of OH$^-$, CN$^-$ and O$_2$ [31], then, the equations proposed by these researchers are presented:

$$\text{Sb}_2\text{S}_3 + 6\text{OH}^- \rightarrow \text{SbO}_3^{3-} + \text{SbS}_3^{3-} + 3\text{H}_2\text{O} \quad \text{(8)}$$

$$\text{SbS}_3^{3-} + 6\text{OH}^- \rightarrow \text{SbO}_3^{3-} + 3\text{S}_2^{2-} + 3\text{H}_2\text{O} \quad \text{(9)}$$

$$4\text{SbS}_3^{3-} + 6\text{CN}^- + 6\text{H}_2\text{O} + 3\text{O}_2 \rightarrow 2\text{Sb}_2\text{S}_3 \downarrow + 6\text{CNS}^- + 12\text{OH}^- \quad \text{(10)}$$

Sb$_2$S$_3$ is 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 leads to a low extraction. Some researchers propose certain treatments for this type of refractory materials such as alkaline leaching with NaOH or Na$_2$S [32-33], or roasting [34].

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

$$\text{CN}^- + 2\text{Fe}^{3+} + \text{OH}^- \rightarrow 2\text{Fe}^{2+} + \text{HCNO} \quad \Delta G^{\circ}_{30^\circ C} = -286.84 \text{ kJ} \quad \text{(11)}$$

$$\text{Fe}^{2+} + 6\text{CN}^- \rightarrow \text{Fe(CN)}_6^{4-} \quad \Delta G^{\circ}_{30^\circ C} = -245.52 \text{ kJ} \quad \text{(12)}$$

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

$$\text{S}^0 + \text{CN}^- \rightarrow \text{CNS}^- \quad \Delta G^{\circ}_{30^\circ C} = -21.67 \text{ kJ} \quad \text{(13)}$$

The formation of thiocyanate was checked by contacting 10 grams of S$^0$ in a 0.06 M solution of NaCN, subsequently detecting the formation of sodium thiocyanate through the Alpha method 4500 CN$^-\text{M. Thiocyanate}$. According to Eq. 14, the silver and cyanide complex can react with S$^0$ and subsequently the dissolved silver can precipitate again as silver thiocyanate.

$$\text{Ag(CN)}_2^- + \text{S}^0 \rightarrow \text{AgSCN} + \text{CN}^- \quad \Delta G^{\circ}_{30^\circ C} = -32.02 \text{ kJ} \quad \text{(14)}$$
In the case of cyanidation with glycine, according to some researchers, glycine forms complexes with iron and consumes OH\(^-\) radicals, according to Eq. 15 [36].

\[
\text{Fe}^{2+} + \text{H-glycine} + \text{OH}^- \rightarrow \text{Fe(glycine)}^{3+} + \text{H}_2\text{O} \tag{15}
\]

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

Considering that the components of the residue cause 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).

| 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

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).

| Sample               | Chemical analysis | Species, Composition (wt. %) |
|----------------------|-------------------|----------------------------|
|                      | Au (g/t) | Ag (g/t) | Fe (%) | S°       | NaFe\(_3\)(SO\(_4\))\(_2\)(OH)\(_6\) | 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

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 consists of Ag\(_2\)S and Sb\(_2\)S\(_3\), based on the above, the equation of pyrargyrite with NaOH during the alkaline treatment occurs as follows:

\[
\text{Ag}_2\text{S} + 2\text{OH}^- \rightarrow 2\text{AgOH(aq)} + 3\text{S}^0 + 2\text{e}^- \quad \Delta G^\circ_{50\text{°C}} = 166.73 \text{ kJ} \tag{16}
\]

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

\[
\text{Sb}_2\text{S}_3 + 2\text{NaOH} \rightarrow \text{NaSbOS} + \text{NaSbS}_2 + \text{H}_2\text{O} \tag{17}
\]
However, Eq. 18 calculated using HSC Chemistry 6 software is proposed:

$$\text{Sb}_2\text{S}_3 + 8\text{OH}^- \rightarrow 2\text{SbO}_2^- + 3\text{S}^\circ + 4\text{H}_2\text{O} + 6\text{e}^- \quad \Delta G^\circ_{50^\circ C} = -190.42 \text{ kJ} \quad (18)$$

In Eq. 16 the $\Delta G^\circ$ is positive, so perhaps thermodynamically it is not feasible to occur; however, the negative $\Delta G^\circ$ of the equation of the antimony sulfide in alkaline medium indicates that the NaOH probably contributes to dissolve the antimony of the pyrargyrite leaving only $\text{Ag}_2\text{S}$.

Then, the dissolution of $\text{Ag}_2\text{S}$ can be occur according to the following reaction:

$$\text{Ag}_2\text{S} + 4\text{NaCN} + 2\text{O}_2 = 2\text{NaAg(CN)}_2 + \text{Na}_2\text{SO}_4 \quad \Delta G^\circ_{50^\circ C} = -770.75 \text{ kJ} \quad (19)$$

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

$$\text{NaFe}_3(\text{SO}_4)_2(\text{OH})_6 + 3\text{NaOH} + 14\text{H}_2\text{O} \rightarrow 2\text{Na}_2\text{SO}_4*7\text{H}_2\text{O} + 3\text{Fe(OH)}_3 \quad \Delta G^\circ_{50^\circ C} = -314.6 \text{ kJ} \quad (20)$$

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 is observed, which possibly corresponds to the decomposition of the natrojarosite into hydroxides of iron ($\text{Fe(OH)}_3$) amorphous.

As mentioned earlier, iron hydroxides can coat gold and silver particles or part of the iron that dissolves from the natrojarosita or the insoluble hydroxides can be reduced by cyanide and then form iron hexacyanide, which possibly inhibits 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 dissolves and complexes with cyanide and elemental sulfur does 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 is observed (Fig. 4c), as can be seen also there was an increase in the extraction of iron compared to that obtained in conventional cyanidation, possibly because glycine dissolves the iron hydroxides deposited on the particles as $\text{Fe}^{2+}$ and forms 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 $\text{Fe}^{2+}$
system and glycine, as can be seen in this diagram, glycine in alkaline medium consumes OH-radicals and forms the glycinate (gly⁻) ion, which reacts with Fe²⁺ to form the complex of iron and glycine.

\[
\text{[gly}^\text{-}]_{\text{TOT}} = 60.00 \text{ mM} \\
\text{[Fe}^2\text{+}]_{\text{TOT}} = 950.00 \text{ mM}
\]

![Diagram of distribution of species of the Fe²⁺-glycine system.](image)

It is inferred that the complex remains stable in the leaching solution, which allows for greater cyanide availability and a better dissolution of gold and silver. However, removing the iron hydroxides layer increases the dissolution of elemental sulfur, which is a cyanide consumer and inhibits 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 coincides with the low iron extraction during the cyanidation (Fig. 4b) since this remains in the residue. As mentioned above the formation of iron oxides can coat gold particles and can reduce the leaching efficiency so that they could coat the gold and Ag₂S particles by inhibiting the dissolution of gold and silver, which would explain the low gold and silver extraction during conventional cyanidation.

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

| Sample          | Au (g/t) | Ag (g/t) | Fe (%) | ZnS | Fe₃O₄ | Fe₂O₃ | ZnFe₂O₄ | U.M* |
|-----------------|----------|----------|--------|-----|-------|-------|----------|------|
| DLR-TT          | 1.08     | 334.59   | 29.6   | 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

In the cyanide medium with glycine there is a greater extraction of gold and silver because as mentioned above (Fig. 4c), the complexes formed by glycine allow the gold and silver particles to be released and that the iron does not consume cyanide. On other hand, the elemental sulfur was decomposed during the thermal treatment, which allowed to increase the extraction of the values in the cyanide medium with glycine. In the case of S⁰, it has been reported that this element at temperatures above 393 K, sulfur melts and to 719 K, SO₂ 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 ($\text{Ag}_3\text{SbS}_3$) depending on the temperature, and found that from 536 K the crystalline structure of the pyrargyrite seems to be disordered to the maximum and the material decomposes in $\text{Ag}_2\text{S}$ leaving residual silver and sulfides on the surface of the sample. This is indicative that the pyrargyrite was decomposed in $\text{Ag}_2\text{S}$ 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 $\text{S}^0$ 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 $\text{Na}_2\text{S}_2\text{O}_8$), DLR -AHO, to ensure the oxidation of the pyrargyrite.

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).

| 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

As observed in Table 7, the elemental sulfur from the residue was removed and the natrojarosite was decomposed, therefore, the unidentified material corresponds 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 $\text{S}^0$ on the DLR particles.

$$\text{NaFe}_3(\text{SO}_4)_2(\text{OH})_6 + 3\text{Na}_2\text{S}_2\text{O}_8 + 13\text{NaOH} \rightarrow 9\text{Fe(OH)}_3 + 11\text{Na}_2\text{SO}_4 + \text{S}^0 + \text{H}_2\text{O} + 3\text{O}_2$$

$$\Delta G^{\circ}_{50^\circ\text{C}} = -1400.92 \text{ kJ} \quad (21)$$

As observed in Fig. 3 in the SEM characterization of the DLR, elemental sulfur covers the residual natrojarosite and sphalerite particles. The fact that the removal of elemental sulfur increases the extraction of gold and silver indicates that the values are possibly "adsorbed or trapped" by it, therefore, when it is eliminated from the residue, it allows them to be released and increases 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 explains the high consumption of cyanide, which was evaluated in both cyanide and cyanide with glycine, Fig. 7 shows the results of cyanide consumption, which was between 15 and 9 kg/t respectively.
Figure 7. Cyanide consumption in leaching tests of DLR-AH (leaching medium cyanide and cyanide with glycine).

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

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 inhibits the latter from reacting with cyanide, therefore, the consumption of cyanide decreases when glycine is added.

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 is not information on waste treatments with this composition or mixture of components. Individually, as mentioned in the introduction, both elemental sulfur and jarosite have been 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 is 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, Na₂S₂O₈ = 0.1 M, T = 323 K, RPM = 350, pH = 10, t = 3 h
3. Cyanidation:
\[ \text{pH} = 11, \text{NaCN} = 0.06 \text{ M}, T = 298 \text{ K}, t = 24 \text{ h}, \text{reactor} = \text{bottles} \]

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

Additionally, it was found that glycine helps reduce cyanide consumption, determining that it possibly forms complexes with iron and sulfur, which are known cyanide consumer. This finding allows us to assess glycine as an inhibitor of the solubility of some elements and compounds that increase 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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