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Leaching of White Metal in a NaCl-H_2SO_4 System under Environmental Conditions

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Abstract: The effect of NaCl on the leaching of white metal from a Teniente Converter was investigated in NaCl-H_2SO_4 media under environmental conditions. The copper dissolution from white metal was studied using ferric ions in the range of 1–10 g/L, NaCl in the range of 30–210 g/L, and sulfuric acid in the range of 10–50 g/L. The test without NaCl produced a dissolution of 55%; through the addition of NaCl, the dissolution increased to nearly 90%. The effect of sulfuric acid on the copper dissolution was not significant in the studied range, as the excess sulfuric acid simply increased the iron precipitation. The positive effect of NaCl seems to be related to the action of chloro-complex oxidizing agents in relation to the Cu^{+2}/Cu^{+} couple. A simplified two-stage mechanism is proposed for the leaching of white metal. In the first stage, the white metal produces covellite and Cu^{2+}, and in the second stage it produces elemental sulfur and Cu^{2+}. The first stage is very rapidly compared to the second stage.

Keywords: metal extraction; acid leaching; white metal; ferric ion; chloride ion

1. Introduction

In the pyrometallurgical processing of copper concentrates, iron is eliminated through the formation of two immiscible phases called slag and matte; the iron reports to the slag as oxide, and the copper remains in the matte as sulfide. In particular, a Teniente Converter (TC) produces high-grade matte called "white metal" (74–76% Cu) that is further processed in a Peirce-Smith converter or similar furnace, to produce so-called blister copper (99% Cu) [1–3]. There are alternatives to Peirce-Smith converting that can greatly reduce the apollution in copper smelters [2,3]. Indeed, the hydrometallurgical treatment of copper matte is supported by a series of experimental tests carried out by different authors, who have achieved the total dissolution of copper under different operating conditions. In most cases, these conditions are chemically aggressive or very energetic, achieving the total dissolution in a few hours by agitation leaching, under a high pressure and high temperature [4–6].

Studies in copper matte leaching (also applicable to studies with chalcocite) are divided into two main areas: high temperature and pressure with an oxidizing agent, and the use of molecular chlorine [6–8].

In the literature, there are several cases of white metal leaching that apply a high temperature, high pressure, and oxidizing agents, to obtain a high recovery within a few hours; these systems are very effective even for other sulfides like chalcopyrite. Some variables considered in the studies are the temperature, oxygen pressure, concentration of sulfuric acid and iron, and particle size [4,6,9,10]. A high temperature white metal leaching has a faster rate of oxidation of Fe^{2+} to Fe^{3+} than a low temperature oxidation (Equations (1) and (2)) and tends to promote sulfate formation instead of elemental sulfur (Equation (3)) [4,11].

$$Cu_2S + 2Fe^{3+} = CuS + Cu^{2+} + 2Fe^{2+}, \tag{1}$$

$$CuS + 8Fe^{3+} + 4H_2O = Cu^{2+} + 8Fe^{2+} + SO_4^{2-} + 8H^+, \tag{2}$$

$$CuS + 2Fe^{3+} = Cu^{2+} + 2Fe^{2+} + S^0. \tag{3}$$

In contrast, the oxidative leaching of white metal occurs in two stages, with CuS as an intermediate product (Equations (4) and (5)), with the possible presence of nonstoichiometric sulfides, such as djurleite or digenite [4,9,12]. Although this mechanism changes in atmospheric conditions, to produce elemental sulfur instead of sulfate (Equation (6)) the intermediate product CuS remains the same [4,13].

$$Cu_2S + 0.5O_2 + 2H^+ = CuS + Cu^{2+} + H_2O, \tag{4}$$

$$CuS + 2O_2 = Cu^{2+} + SO_4^{2-}, \tag{5}$$

$$CuS + 0.5O_2 + 2H^+ = Cu^{2+} + S^0 + H_2O. \tag{6}$$

The literature suggests that molecular chlorine may be an appropriately strong leaching agent for several complex ores, including refractory gold and platinum ores, as well as copper sulfides. However, chlorine leaching requires extreme care, in order to avoid the health risks of chlorine gas. In some tests, the molecular chlorine was provided by chlorine gas; other tests applied an in-situ generation. The in-situ generation consists in producing molecular chlorine through a reaction between sodium hypochlorite and hydrochloric acid (Equation (7)), the addition of MnO_2 in the presence of hydrochloric acid (Equation (8)), or the electro-generation of Cl_2 (Equation (9)) [7,14–22].

$$NaClO + 2HCl = NaCl + Cl_2 + H_2O, \tag{7}$$

$$MnO_2 + 4HCl = MnCl_2 + 2H_2O + Cl_2, \tag{8}$$

$$2Cl^- = Cl_2 + 2e^-. \tag{9}$$

Several authors propose the following mechanism for Cu_2S leaching with chlorine [7,15,23]:

$$Cu_2S + 5Cl_{2(g)} + 4H_2O = 2Cu^{2+}_{(aq)} + SO_4^{2-} + 10Cl^-_{(aq)} + 8H^+. \tag{10}$$

This method for copper recovery is effective but is very sensitive to the particle size and initial chlorine concentration.

The mechanism for the leaching of copper matte in strong chlorine media can be approximated to have two stages: the first is the transformation of chalcocite into covellite and Cu^{2+}, and the second is the formation of Cu^{2+} in the presence of elemental sulfur or sulfate. However, the real mechanism may be more complex, involving several transformations of nonstoichiometric compounds [24,25] through the following scheme:

$$Cu_2S \rightarrow Cu_{1.93}S \rightarrow Cu_{1.8}S \rightarrow Cu_{1.6}S \rightarrow Cu_{1-1.2}S. \tag{11}$$

This paper presents the experimental results of white metal leaching in NaCl-H_2SO_4 media, because the hydrometallurgical processing of white metal may be an attractive alternative to pyrometallurgical processing, but most research efforts have used aggressive methods such as a high pressure and temperature with an oxidizing agent, as well as the use of chlorine gas. These aggressive methods are centered on chemical considerations for copper recovery, but not on the other problems faced by the mining industry, such as sustainability, strong environmental regulations, the scarcity of fresh water, high-energy costs, and low ore grades [26].

2. Materials and Methods

2.1. White Metal Characterization

Representative white metal from a Teniente Converter reactor was supplied by the Hernán Videla Lira smelter in Copiapó, Chile. Pieces weighing 250 g were collected, crushed, milled and sieved to produce a fine powder with an average size of 64 µm.

The chemical characterization by Atomic absorption spectroscopy (AAS) (PerkinElmer PinAAcle^{TM} 900F, Waltham, MA, USA) and sulfur analyzer (LECO) of white metal shows 74.03% Cu, 2.01% Fe and 20.5% S.

In order to identify the mineralogical species, the sample was analyzed by X-ray diffraction (XRD), and the result is shown in Figure 1. The species in the white metal are chalcocite (Cu_2S with a tetragonal structure), Spinel ($Fe_{2.57}Si_{0.43}O_4$ with an orthorhombic structure) and Cristobalite (SiO_2 with a tetragonal structure).

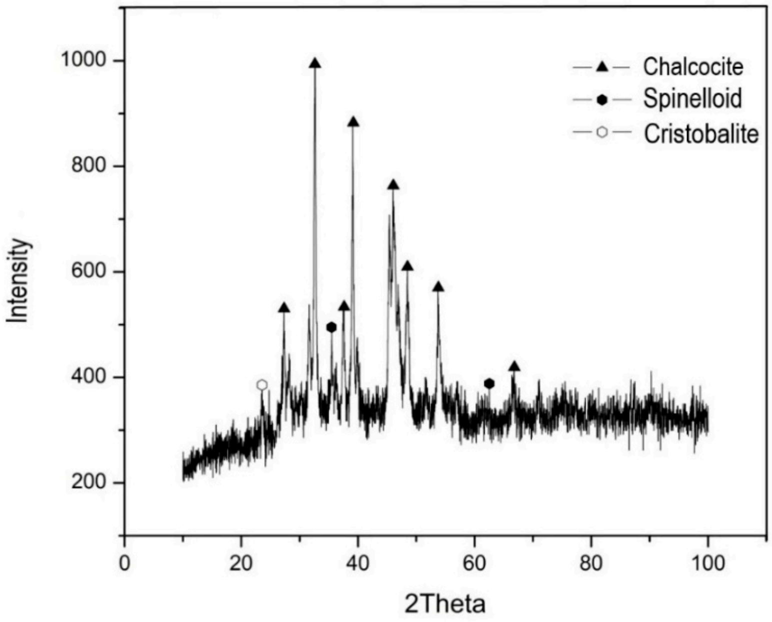


Figure 1. White metal diffractogram.

Scanning electron microscopy with energy dispersive spectroscopy (SEM-EDS) was performed in order to study the morphology of the particles and chemical composition. Mapping SEM-EDS suggests a majority presence of copper and sulfur, and small amounts of iron and oxygen (Figure 2), which reaffirms the XRD analysis. The morphology is similar to that of ceramic materials, with small irregular particles; crystallized structures or regular forms are not observed.

Finally, an optical microscopic observation of the white metal was carried out in order to corroborate the aforementioned results. In Figure 3, traces of metallic copper are observed by optical inspection in the white metal matrix. Metallic copper was not observed by SEM-EDS and XRF analysis, because these techniques are limited to trace levels of species.

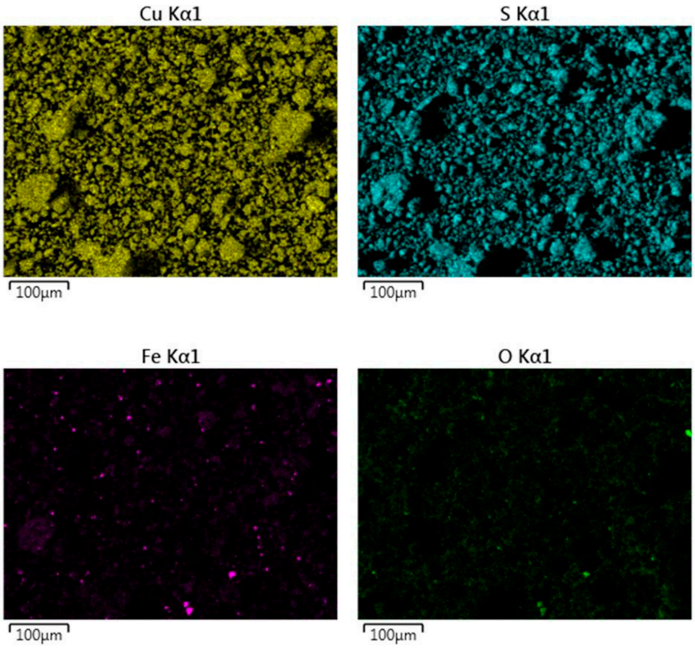
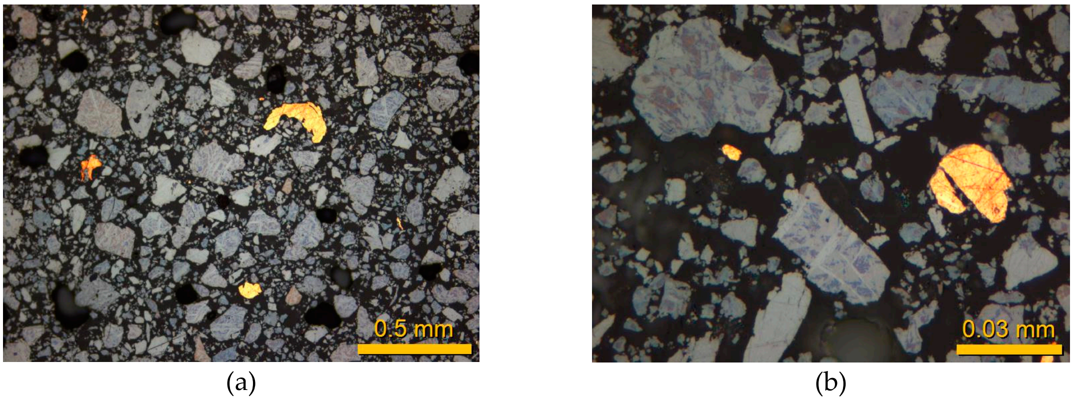


Figure 2. Analysis by scanning electron microscopy with energy dispersive spectroscopy SEM-EDS to the white metal with mapping to 200×.



(a) (b)

Figure 3. Optical microscopy of white metal with magnification (**a**) 20× and (**b**) 100×.

2.2. Leaching Tests

The tests were conducted in shake flasks, at an ambient temperature, with magnetic stirring set to 200 rev/min. 500 mL of leach solution was put in contact with 2.5 g of white metal for 4 days. The pH, electrical potential and temperature were measured regularly. Aliquots of 10 mL of leached solution were collected and filtered to perform the copper and iron analyses. The concentration of copper and iron in the aqueous solution was quantified by Atomic absorption spectroscopy. After the leaching test, the residues were filtered, dried, and analyzed by SEM-EDS, XRD, and AAS.

The aqueous solutions were prepared using High performance liquid chromatography (HPLC) water from Merck. All chemical reagents that were used were of analytical grade, supplied by Merck.

3. Results and Discussion

The leaching tests were performed to evaluate the influence of the ferric ion, sodium chloride and sulfuric acid concentration on the copper dissolution. The tests considered the concentration ranges of 0–10 g/L, 0–210 g/L and 10–50 g/L, for Fe^{3+}, NaCl and H_2SO_4, respectively.

3.1. Baseline

The first test was performed to establish a baseline, evaluating the dissolution of white metal using a solution containing only water and sulfuric acid. The experiments were carried out with a stirring speed of 400 rpm, and with 20 g/L H_2SO_4 at room temperature for 4 days. As shown in Figure 4, copper leaching occurs very fast on the first day, in comparison to the other three days. Copper dissolution in the first day is 37.8%, ending with a 54.9% extraction on the fourth day. This asymptotic trend is attributed to a limited quantity of oxygen dissolved in the leaching solution. Consider that white metal is artificial chalcocite; thus, if the dissolved oxygen is the only oxidizing agent that is present, the following mechanism is proposed [4,9,24].

$$Cu_2S + 0.5O_2 + 2H^+ = CuS + Cu^{2+} + H_2O. \tag{12}$$

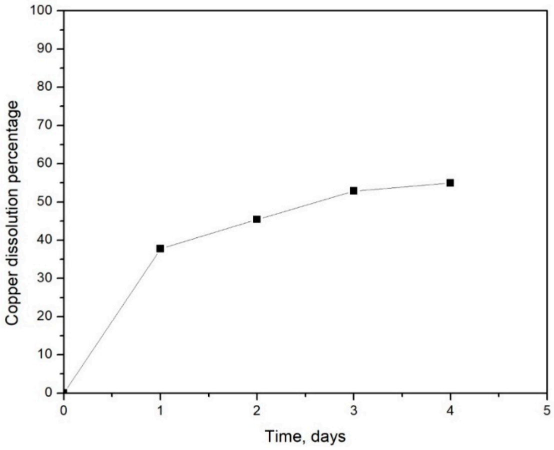


Figure 4. Copper leaching of white metal with a leaching solution containing 20 g/L H_2SO_4 at 1 atm, 22 °C and 400 rpm.

According to the mechanism, cupric ions are dissolved, and covellite is generated. Covellite is difficult to dissolve without a strong oxidizing agent; however, in this case, the copper dissolution is more than 50%, which may be due to the dissolved iron. The white metal contains 2% iron, which contributes to an iron concentration of 0.06 g/L in the final solution.

The residue characterization is shown in Figure 5, showing only covellite (hexagonal crystalline system). This is evidence of the mechanism of white metal leaching of Equation (12), since elemental sulfur is not detected.

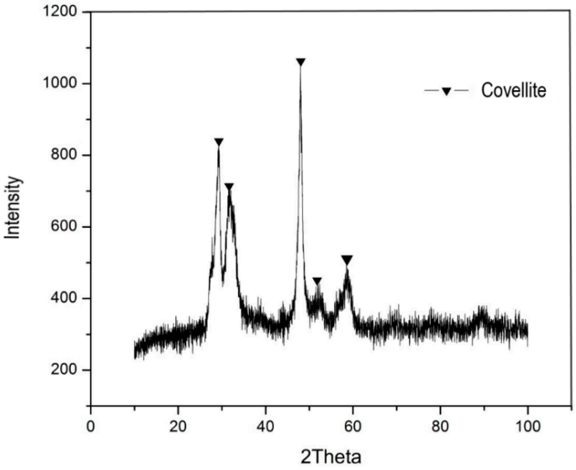


Figure 5. XRD analysis of residue for the baseline test.

3.2. *Effect of Ferric Ion*

The addition of ferric ions has a positive effect on the leaching in comparison to the baseline. The copper dissolution increased to a maximum of 75.3%, from the baseline value of 54.9%. As shown in Figure 6, the copper dissolution has a moderate increase with 1 g/L of Fe^{3+} (60.8%). With 4 and 10 g/L of Fe^{3+}, the effect is similar, at 73.5% and 75.3% respectively.

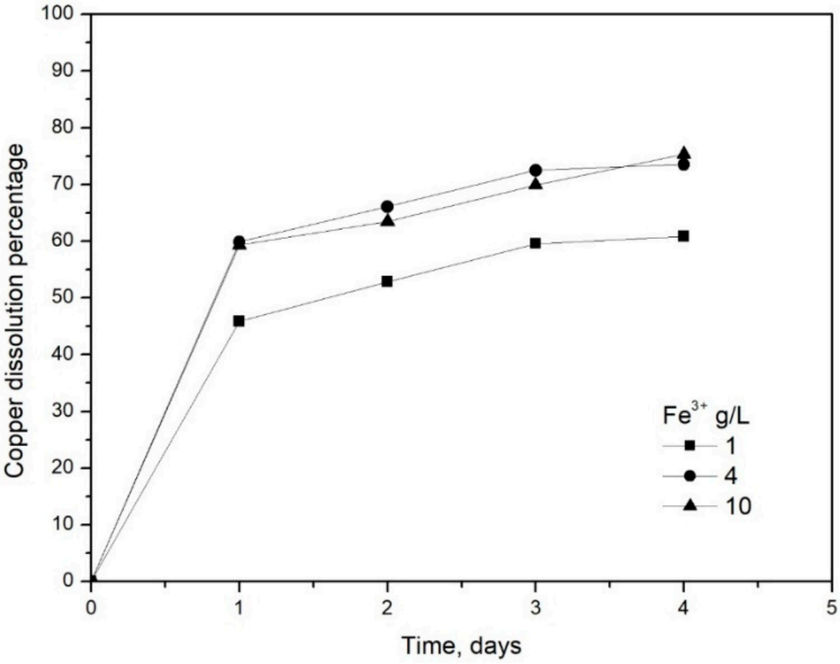


Figure 6. Copper recovery curves in leaching with a variation of Fe^{3+}, 20 g/L H_2SO_4 under conditions of 1 atm, 22 °C, and 400 rpm.

Ferric ions increase the kinetics and dissolution of copper in comparison to the baseline, but the curves show two distinct steps in the reaction. The copper dissolution is very fast within the first day; but from the second day onward, the copper dissolution is slower, tending toward an asymptote. The two-step behavior of the white metal dissolution is comparable to the leaching of chalcocite ores. Indeed, chalcocite is dissolved in the presence of Fe^{3+} in two steps; the first step is fast, but the second step is slow at room temperature. The mechanism is shown in the following equations:

$$Cu_2S + 2Fe^{3^+} = Cu^{2^+} + 2Fe^{2^+} + CuS, \tag{13}$$

$$CuS + 2Fe^{3^+} = Cu^{2^+} + 2Fe^{2^+} + S^0. \tag{14}$$

Equation (13) shows the chemical dissolution of white metal (synthetic chalcocite) in the presence of Fe^{3+}, with a molar ratio of 1:2 between Cu_2S and Fe^{3+} to carry out a transformation from synthetic chalcocite to covellite and Cu^{2+}. The stoichiometry of Equation (13) explains the result for the slower kinetics and recovery at low Fe^{3+}, resulting from an insufficient amount of oxidizing agent. Indeed, a low concentration of ferric ion, added to the formation of elemental sulfur, is a barrier to copper leaching. The analysis of the residues by XRD indicates the presence of covellite and elemental sulfur, as shown in Figure 7, which supports the proposed mechanisms of Equations (13) and (14), which are similar to the leaching of natural chalcocite in the presence of ferric ions.

The additional ferric ions successfully increase the copper dissolution, but also lead to the contamination of the leaching solution with ferrous ions or precipitates; in an industrial setting, this would require auxiliary operations to purify the solution.

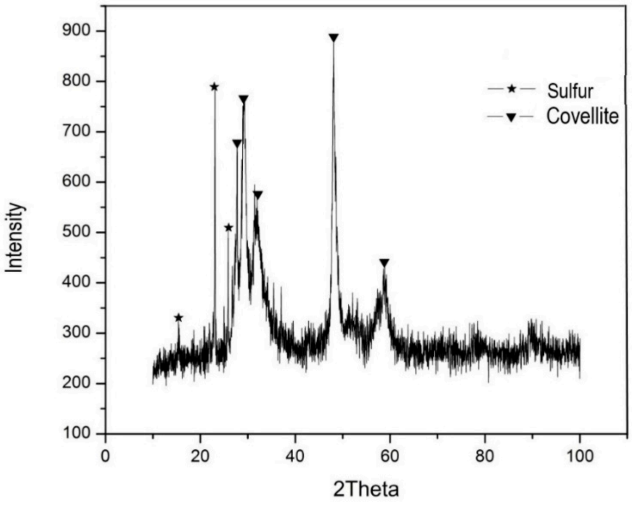


Figure 7. Residue diffractogram 4 days of leaching with 4 g/L of Fe^{3+}, 20 g/L of H_2SO_4 in conditions of 1 atm, 22 °C and 400 rpm.

3.3. *Effect of Strong Chloride Media*

The testing of a high chloride media similar to seawater is motivated by the scarcity of fresh water and the potential use of this resource in copper leaching [27–29]. There are no other studies in the literature that use a media similar to seawater for copper leaching, although there has been extensive research reported for copper ores with chloride, even for the leaching of concentrates and primary sulfides copper ores [26,30–35].

Within the current study, the effect of the NaCl concentration was tested from 30 to 210 g/L; these values consider seawater feed and high recirculating solutions that would be typical of copper leaching plants. As shown in Figure 8, the addition of chloride produces an important increase in copper dissolution compared to the test without NaCl. At concentrations over 30 g/L NaCl, the effect on the final recovery was not significant (although the rate of reaction seems to be affected). At 30 g/L of NaCl, the copper dissolution was 84.23%. Increasing this concentration to 210 g/L, the copper dissolution was 84.49%. This agrees with the observations of Miki et al. [13] who reported that the copper recovery from synthetic covellite increased marginally with an increasing chloride concentration in the range of 7–90 g/L.

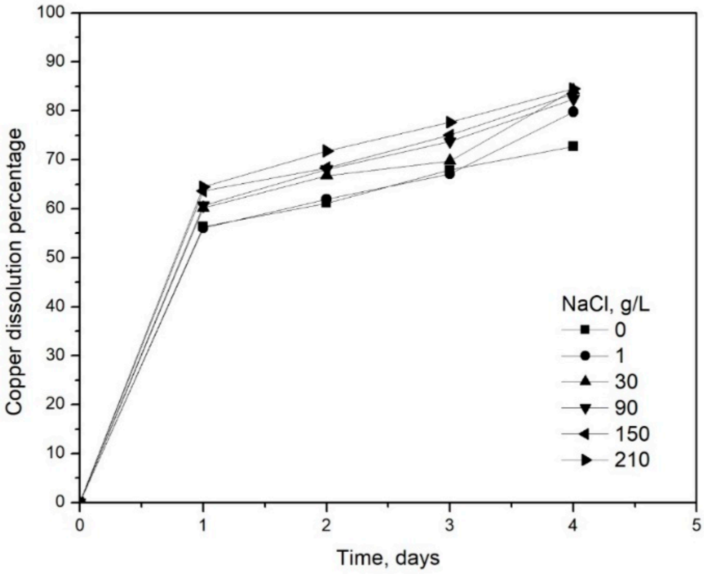


Figure 8. Copper recovery curves in leaching with a variation of NaCl, 20 g/L H_2SO_4, 4 g/L Fe^{3+} under conditions of 1 atm, 22 °C and 400 rpm.

The positive effects of strong chloride media in white metal leaching are shown in Figure 8. Interestingly, white metal is a high purity synthetic chalcocite, that has a similar leaching behaviour to chalcocite ores. The differences between both products (natural and synthetic) are the structure and morphology, which show a rough and slightly crystalline character (Figures 1–3), which could be significant for the copper recovery.

The efficiency of the chloride system for copper leaching from white metal is possibly attributed to the action of several chloro-complexes. As listed in Table 1, the leaching of copper sulfides in chloride media involves several stables species. Nonetheless, the speciation of the system is strongly conditioned by the pH, temperature and chloride concentration.

Table 1. Ion distribution as a function of the chloride concentration [36–38].

	Low Cl^-					**High Cl^-**
Cu(II)	Cu^{2+}	$CuCl^+$		$CuCl_2$	$CuCl_3^-$	$CuCl_4^{2-}$
Cu(I)	$CuCl_2^-$		$CuCl_3^{2-}$		$CuCl_4^{3-}$	
Fe(III)	Fe^{3+}			$FeCl^{2+}$		$FeCl_2^+$
Fe(II)	Fe^{2+}					$FeCl^+$

Although there are numerous stable species within the chloride medium, as shown in Table 1, the main ions that are present in strong chloride solutions are Cu^{2+} and $CuCl^+$. In the literature, it is proposed that $CuCl^+$ is generated constantly from reoxidized CuCl (formed by Cu_2S leach) to $CuCl^+$, thus continuously regenerating the oxidizing agent [27,39–41].

On the other hand, another possible beneficial effect of chloride is located at the residue surface. Reports in the literature suggest that chloride increases the surface area and porosity of residues, which tends to favor a higher copper dissolution. A high porosity sulfur layer facilitates the diffusion of leachants and products to and from the reaction surface [42,43].

The identification of species that are present in the residue is shown in Figure 9. According to the XRD analysis, the residue is composed of covellite and elemental sulfur. The diffraction pattern is similar to the leaching system in the absence of chloride ions; however, in this case, the intensities of the species are higher, especially the elemental sulfur. This result agrees with the higher recoveries obtained in the strong chloride system, since more elemental sulfur is produced as more copper is leached.

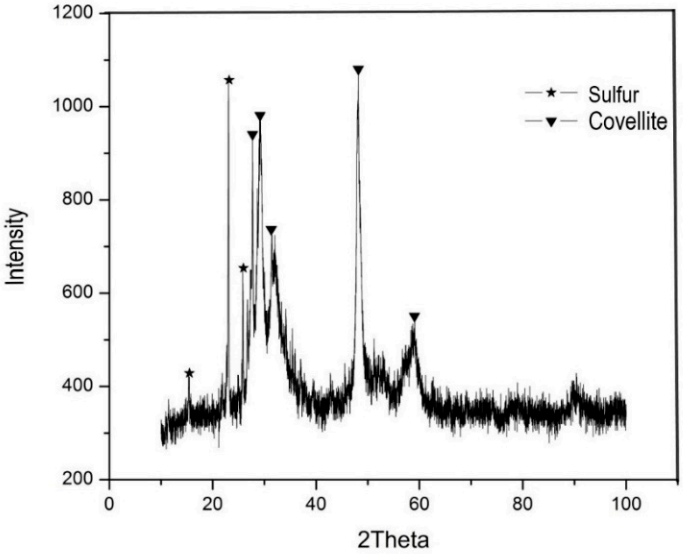


Figure 9. Residue diffractogram after 4 days of leaching with 4 g/L of Fe^{3+}, 20 g/L H_2SO_4, and 30 g/L NaCl in conditions of 1 atm, 22 °C and 400 rpm.

Based on the literature reports and the results obtained in this study, the leaching of white metal in strong chloride media at ambient conditions involves several chloride species, but the mechanism can be adequately described by:

$$Cu_2S + \frac{1}{2}O_2 + 2H^+ + Cl^- = CuS + CuCl^+ + H_2O, \quad (15)$$

$$CuS + \frac{1}{2}O_2 + 2H^+ + Cl^- = CuCl^+ + S^0 + H_2O. \quad (16)$$

For the system studied in this research, the mechanism for the first stage (Equation (15)) is valid only at the initial stage (in the absence of Cu^{2+} ions); later, when the copper is dissolved, the cupric and chloride ions are oxidizing agents of white metal, as shown by the following equations:

$$Cu_2S + Cu^{2+} + 2Cl^- = CuS + 2CuCl, \quad (17)$$

$$Cu_2S + CuCl^+ + Cl^- = CuS + 2CuCl. \quad (18)$$

3.4. *Effect of Sulfuric Acid*

The effect of the concentration of sulfuric acid from 10 to 50 g/L is shown in Figure 10. It is observed that a substantial increase in the concentration of H_2SO_4 does not imply a significant increase in the dissolution of the copper; rather, there is a slight decrease at the end of the leaching test. Indeed, the increase in sulfuric acid causes a decrease in the oxygen solubility. This agrees with the observations of Ruiz et al. [9] who reported that the copper recovery from white metal increased marginally with an increasing sulfuric acid concentration in the range of 0.05–0.5 M.

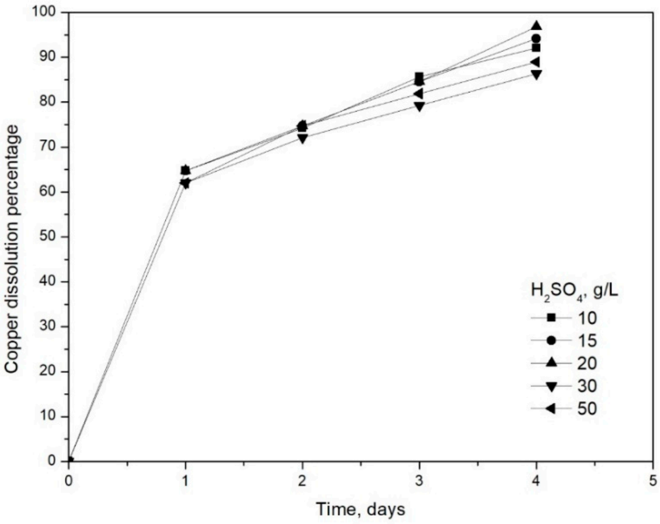


Figure 10. Copper recovery curves in leaching with a variation of H_2SO_4, 30 g/L NaCl and 4 g/L Fe^{3+} under conditions of 1 atm, 22 °C and 400 rpm.

Another important observation is that, for low levels of sulfuric acid, the dissolution of copper decreases slightly, while a significant iron hydroxide precipitation occurs (Table 2). This is a promising result from an industrial perspective, since a lower iron content in the leaching solution is favorable for solvent extraction [44].

Table 2. Total iron concentration in leach residues at different concentrations of H_2SO_4.

H_2SO_4, g/L	**10**	**15**	**20**	**30**	**50**
%Fe	3.14	2.99	2.67	2.35	2.11

A similar result was reported by Lu et al. [44], who in a study of chalcopyrite leaching in an acid medium with chloride ions, obtained more iron precipitation at low concentrations of acid. The iron precipitation is shown by the following equation:

$$3Fe^{3+} + 2SO_4^{2-} + 6H_2O + Na^+ = Na[Fe(OH)_2]_3(SO_4)_2 + 6H^+. \tag{19}$$

The pregnant solution with cupric ions can be purified by solvent-extraction, to then obtain metallic copper by electrowinning [45,46]. The raffinate can be recycled to the leaching process.

4. Conclusions

The results of white metal leaching in the NaCl-H_2SO_4 system under environmental conditions indicate that white metal leaches in two stages. The first stage consists of the transformation of chalcocite into covellite and Cu^{2+}, and the second stage consists in the transformation of covellite into Cu^{2+} and elemental sulfur; on average, the first stage is about 5 times faster than the second.

In the baseline test, only a partial dissolution of white metal was observed, with a relatively fast first stage and a much slower second stage, with an asymptotic tendency close to a 55% dissolution. The residue showed no evidence of an elemental sulfur formation; this can be attributed to the presence of naturally dissolved oxygen in the solution, which acted as an oxidizing agent. The low concentration of oxygen in the solution and the room temperature limited the efficiency of the second dissolution stage.

The inclusion of chloride ions strongly increases the copper dissolution, approaching a dissolution of approximately 90%. The positive effect of the chloride is attributed to the Cu^{2+}/Cu^+ redox pair and the action of the oxidizing agents Cu^{2+}, $CuCl^+$, $CuCl_2$, and $CuCl_3$.

The effect of the sulfuric acid addition is not significant; in fact, the high sulfuric acid concentration causes an iron precipitation rather than increasing the copper dissolution.

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