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Original Article

Dissolution of pure chalcopyrite with manganese nodules and waste water

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ARTICLE INFO

ABSTRACT

Chalcopyrite is the most abundant copper ore and, consequently, the most utilised to produce metallic copper. The main route of treatment is through pyrometallurgical processes, but these emit significant quantities of SO_2 into the atmosphere (e.g. 182,000 t/year among all Chilean smelters), producing mighty concern in the community. In this context, hydrometallurgy is presented as an alternative that may be more environmentally friendly; however, the difficulties of processing sulphide minerals prevent achieving sustainable efficiencies for the industry. In this research, a pure chalcopyrite mineral is leached at 25 °C with the addition of manganese nodules as an oxidizing agent, and wastewater with a high concentration of chloride that both enhances the dissolution and avoid the passivation of the chalcopyrite. The high concentrations of MnO_2 (4/1 and 5/1) allows that the potential values can be between 580 and 650 mV, which favors the dissolution of $CuFeS_2$. The XRD showed the formation of non-polluting species and, besides, they do not cause obstacles to the copper dissolution. High concentrations of chloride enable increasing copper solutions from $CuFeS_2$, attaining favorable outcomes when working with wastewater instead of seawater.

1. Introduction

Chalcopyrite is the most abundant copper mineral in the world [1–3], representing nearly 70 % of the reserves [4–6]. For this reason, this copper mineral is the most adopted to provide metallic copper [7]. Currently, around 80–85% of the world's copper production is conducted by conventional pyrometallurgical methods, which consists of flotation, smelting, refining, and electrorefining [8]. However, despite the high levels of production, deep concerns arise about the significant emissions of sulfur dioxide caused by these operations; for example, the Chilean smelters produce about 188 kt of SO_2 per year [9]. In this context, extending hydrometallurgy to sulfide minerals is presented as a promised option to reduce environ-

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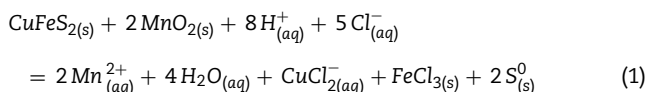E-mail: ntoro@ucn.cl (N. Toro).

mental impacts [10]; however, the perplexity lies in the low efficiency of the operations, especially at room temperature and atmospheric pressure [11]. Diverse studies have been carried out for the recovery of copper from chalcopyrite in acid media utilising varied oxidising agents such as dissolved oxygen [12,13], ferric chloride [14–16], ferric sulfate [17,18], cupric ions [19], and manganese nodules [20,21].

Polymetallic nodules, called manganese nodules as well, are rock concretions formed by concentric layers of Fe and Mn hydroxides [22]. These are a good alternative for the recovery of Mn, which is essential for the production of steel [23–25]. Its economic interest is due to the high grades of base, critical, and rare metals [26,27], such as Co, Ni, Te, Ti, Pt, and rare earth elements [28].

In previous trials [20,21,29], it was disclosed that MnO_2 is a good oxidizing for the leaching of chalcopyrite in acid media, especially at HCl concentration ranges between 3−4 mol/L. Three routes were discovered for the copper dissolution of copper: (i) the galvanic interaction between chalcopyrite and MnO_2, (ii) the action of the Fe^{3+}/Fe^{2+} ratio, and (iii) the action of chloride gas formed by the reaction between MnO_2 and HCl in chalcopyrite. Beside, Havlik et al. [21] gotten low copper solutions for 3 mol/L HCl, indicating that the optimal results may be reached at 4 mol/L HCl and a ratio of $4/1 MnO_2/CuFeS_2$.

Several investigations have reported that chloride stabilizes cuprous ions forming soluble complexes that improve chalcopyrite dissolution [12,30–32]. The reason, leaching with sulfuric acid and sodium chloride forms porous crystals of sulfur on the mineral surface rather than a layer of passive sulfur that blocks the flow [33,34].

The proposed reaction for chalcopyrite leaching with manganese nodules is next expressed:

$$CuFeS_{2(s)} + 2\,MnO_{2(s)} + 8\,H^+_{(aq)} + 5\,Cl^-_{(aq)}$$

$$= 2\,Mn^{2+}_{(aq)} + 4\,H_2O_{(aq)} + CuCl^-_{2(aq)} + FeCl_{3(s)} + 2\,S^0_{(s)} \tag{1}$$

$$\Delta G^0 = -202.6\,kJ$$

$$Ca^{2+}_{(aq)} + SO^{2-}_{4(aq)} = CaSO_{4(s)} \tag{2}$$

$$\Delta G^0 = -28.0 kJ$$

The Mn^{4+} (MnO_2) presented in the manganese nodules was used as the oxidizing agent. Eq. (1) describes the copper dissolving in a sulphate-chloride medium, owing to the sulfuric acid and the high presence of chloride (wastewater). The principal benefits of leaching in a chlorinated environment are related to: i) enhanced leaching kinetics, ii) generation of elemental sulfur and not residual sulfate, and iii) the cupric and/or cuprous ions are stable as chloride complexes. The Gibbs free energy of Eq. (1), being negative, is considered spontaneous under normal conditions, allowing a stable copper product and a non-contaminating elemental sulfur residue. While the calcium in both wastewater and manganese nodules reacts with the sulfate (Eq. (2)), insoluble calcium sulfate is formed because the cation precipitates when it comes into contact with sulfate, nitrates, and other elements. Eq. (1)

shows a $2/1 MnO_2/CuFeS_2$ ratio for leaching copper using manganese nodules as an oxidizing agent, but the best conditions to leach copper is at a $4/1 MnO_2/CuFeS_2$ ratio. The values of the Gibbs free energy were calculated using the software HSC 5.1 (Outotec Company, Espoo, Finland).

Overall, the studies attest that mixing intensity in stirring reactors with chloride media does not alter the rate of copper dissolution [35]. Other researches indicated that mixing does not affect oxidization of chalcopyrite [30,36,37]. The explanation is that the dissolution speed is not controlled by mass transfer through the liquid border layer [30]. Otherwise, some authors stated positive results in dissolving copper from $CuFeS_2$ by increasing stirring speed [11,38].

The oceans and other saline waters are the most significant water resource on the planet, representing 97.4 % of the available water. The additional 2.5 % for freshwater includes 1.7 % in the polar ice caps and glaciers, making it difficult to use. Traditional sources (groundwater, lakes, wetlands, rivers, among others) are only 0.8 % [39]. The shortage of freshwater is more noticeable in arid areas, where it becomes an economic, environmental and social problem [40], especially given the demand of the large-scale mining for this resource. Mining is the fourth largest consumer of water in Chile, occupying 3 % of the total. The first user is agriculture, which requires 82 %; then human consumption with 8 %; and the remaining 7 % is for industries other than mining. Total mining occupied 14.9 m^3/s in 2016, being 13.6 m^3/s utilised by copper, smelters, and refineries, while other minerals consumed 1.3 m^3/s, such as gold, iron, silver, polymetallic, and non-metallic mining [41]. The General Water Directorate extended the prohibition zones for water extraction, restricting the water rights for mining companies. Besides, authorities in Chile indicated that large-scale mining projects would not be longer authorized for using water from aquifers. This prompted the new facilities to consider seawater or desalinated water [42], especially in the north of the country [43]. Therefore, it is vital to find new alternatives that can improve water availability, wherein a valid option is associativity between mining companies and desalination plants.

In the present research, the leaching of chalcopyrite was studied, considering manganese nodules as an oxidising agent and the reuse of wastewater with a high chloride content. Varied $MnO_2/CuFeS_2$ proportions, mixing intensity, H_2SO_4 concentration, and chloride concentration were examined.

2. Materials and methods

2.1. Chalcopyrite mineral

The sample of chalcopyrite was obtained from Minera Michilla, located in Antofagasta (north of Chile). The sample was taken selectively from a copper deposit (800 g) and then crushed in a porcelain mortar to get a size range between 38 and 47 μm (−47 + 38 μm). We removed the impurities by hand (with the help of a microscope). The homogenisation of the material was done by sampling techniques, selecting a representative fraction of 40 g (20 g for chemical analysis and 20 g for mineralogical analysis). The chemical analysis was performed by atomic emission spectrometry via

Table 1 – Chemical analysis of chalcopyrite.

Component	Cu	Fe	S
Mass (%)	33.89	30.62	35.49

induction-coupled plasma (ICP-AES), developed in the Applied Geochemistry Laboratory of the Department of Geological Sciences of the Universidad Católica del Norte. Table 1 shows the chemical composition of the samples.

In addition, the sample was analyzed mineralogically using a Bruker brand X-ray diffractometer, automatic and computerized model of D8. According to the initial qualitative analysis of XRD, the primary mineral phase present in the samples was chalcopyrite, which showed 99.9 % purity, and whose main peaks are at 29,372, 48,975 and 48,684°. These peaks correspond to those given in the reference pattern PDF 35-0752 (ICDD, 2004). Fig. 1 gives the results that indicate a purity of 99.90 %.

2.2. Manganese nodules (MnO_2)

The manganese nodule was collected during the 1970s from the deep ocean on the Blake Plateau (Atlantic Ocean). The sample was crushed with a porcelain mortar to reach a particle size between 53 and 75 μm ($-75 + 53$ μm). The mineralogical composition is presented in Table 2. The material was analyzed using a Bruker® tabletop M4-Tornado μ-FRX (Fremont, CA, USA). The interpretation of the μ-XRF data shows that the nodules were composed by fragments of preexisting nodules that formed their nucleus, with concentric layers that precipitated around the nucleus in later stages.

2.3. Reactant and leaching tests

The sulfuric acid (Merck Millipore) used for the leaching tests had analytical grade, purity 95–97%, and density 1.84 kg/L. The wastewater from Aguas Antofagasta Desalination Plant had a concentration of 39.16 g/L of chloride. Tables 3 and 4 shows the chemical composition of wastewater and seawater, respectively.

Leaching assays were conducted in a 50 mL glass reactor with a 0.01 S/L ratio. A total of 200 mg of chalcopyrite and MnO_2 (Manganese nodules) at different concentrations were maintained in suspension with a 5-position magnetic stirrer (IKA ROS, CEP 13087-534, Campinas, Brazil) at 600 rpm. The temperature was controlled at 25 °C with an oil-heated circulator (Julabo). All tests were triplicated, and measurements were carried out in 5 mL undiluted samples, using atomic absorption spectrometry with a coefficient of variation ≤ 5 %, and a relative error between 5 and 10%. Measurements of pH and oxidation-reduction potential (ORP) of leaching solutions were made using a pH-ORP meter (HANNA HI-4222). The ORP solu-

Table 3 – Chemical composition of waste water.

Compound	Concentration (g/L)
Fluoride (F-)	0.002
Calcium (Ca^{2+})	0.8
Magnesium (Mg^{2+})	2.65
Bicarbonate (HCO_3^-)	1.1
Chloride (Cl^-)	39.16
Calcium carbonate ($CaCO_3$)	13

Table 4 – Reference composition of seawater (data from Cisternas and Gálvez [39]).

Solute	g/kg of solution	Solute	g/kg of solution
Na^+	10.78145	Br-	0.06728
Mg^{2+}	1.28372	CO_3^{2-}	0.01434
Ca^{2+}	0.41208	$B(OH)_4^-$	0.00795
K^+	0.3991	F-	0.0013
Sr^{2+}	0.00795	OH-	0.00014
Cl^-	19.35271	$B(OH)_3$	0.01944
SO_4^{2-}	2.71235	CO_2	0.00042
HCO_3^-	0.10481	Total	35.16504

tion was measured using a redox electrode (internal Ag/AgCl with electrolyte 3.5 mol/L KCl).

2.4. Effect on the $MnO_2/CuFeS_2$ ratio

In previous studies, it was demonstrated that at higher concentrations of MnO_2 concerning $CuFeS_2$, better extractions of copper can be obtained from chalcopyrite [20,29].

This research seeks to optimize the $MnO_2/CuFeS_2$ ratio for the leaching of chalcopyrite in chloride media. The work is done with a particle size of $-47 + 38$ μm for chalcopyrite, and $-75 + 53$ μm for manganese nodule, using varied proportions of both samples, 20 mL of leaching solution (1 M of H_2SO_4), 39.16 g/L of chloride, 600 rpm, and 25 °C.

2.5. Effect of mixing

The present work investigates the effect mixing intensity (200–1,000 rpm) on the copper dissolution rate from chalcopyrite, considering a 5/1 of MnO2/CuFeS2 ratio, 1 M of H_2SO_4, 39.16 g/L of chloride (wastewater), and 25 °C.

2.6. Effect of H_2SO_4

Different concentrations of H_2SO_4 were evaluated for chalcopyrite leaching using MnO_2. We worked at a chalcopyrite particle size of $-47 + 38$ μm and manganese nodule of $-75 + 53$ μm at different concentrations of sulfuric acid (1, 2, and 3 mol/L), a $MnO_2/CuFeS_2$ ratio of 5/1, 600 rpm, 20 mL of leaching solution and temperature of 25 °C.

Table 2 – Mineralogical analysis of the manganese nodule.

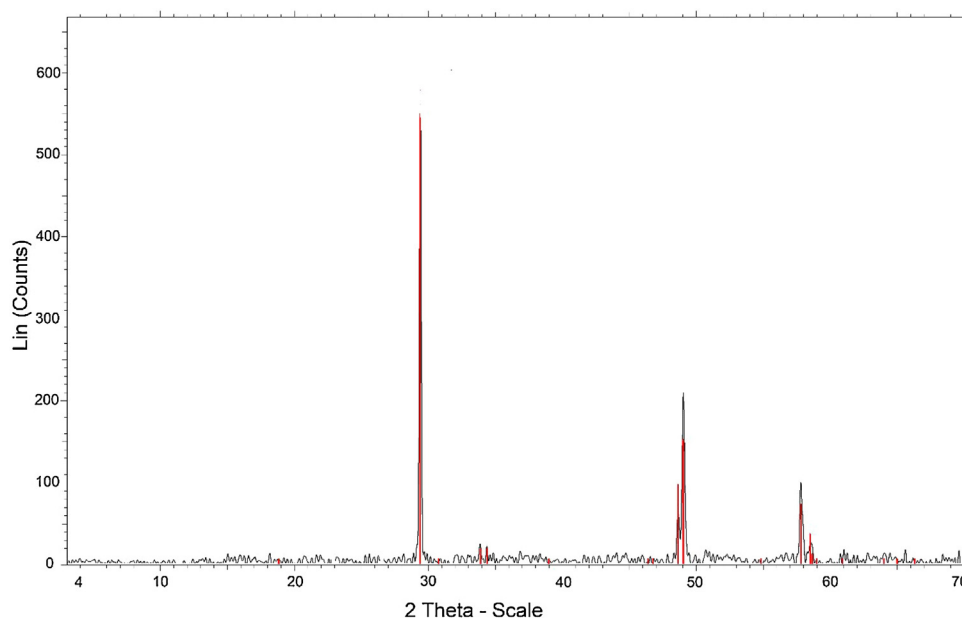| Component	MgO	Al_2O_3	SiO_2	P_2O_5	SO_3	K_2O	CaO	TiO_2	MnO_2	Fe_2O_3
Mass (%)	3.54	3.69	2.97	7.20	1.17	0.33	22.48	1.07	29.85	26.02

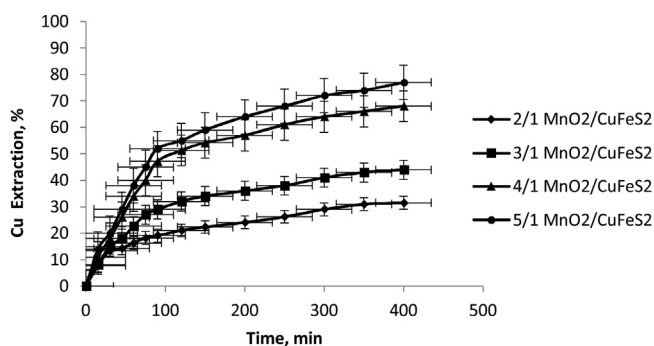**Fig. 1 – X-ray powder diffraction patterns for the chalcopyrite.**

Fig. 2 – Effect of the $MnO_2/CuFeS_2$ ratio on Cu extraction (25 °C, $CuFeS_2$ size: $-47+38\,\mu m$, MnO_2 size: $-75+53\,\mu m$, 1 mol/L H_2SO_4 and 39.16 g/L of chloride).

2.7. *Effect on different chloride concentrations*

The effect of chloride was evaluated for chalcopyrite particle size of $-47+38\,\mu m$ and manganese nodule of $-75+53\,\mu m$, a $MnO_2/CuFeS_2$ ratio of 5/1, 600 rpm, a H_2SO_4 concentration of 1 mol/L, and different chloride concentrations (seawater: 20 g/L and wastewater: 39.16 g/L).

3. Results and discussion

3.1. *Effect on the $MnO_2/CuFeS_2$ ratio*

Fig. 2 shows the evolution of copper dissolution from chalcopyrite at different $MnO_2/CuFeS_2$ proportions. For low $MnO_2/CuFeS_2$ (2/1), passivation of the mineral appeared, and little Cu solutions were obtained (31 % in 400 min). For the 3/1 ratio, there was a considerable increase in the Cu extractions (approximately 10 %) but still slow kinetics of dissolution. In both previous conditions, the low copper extractions were due to a deficient amount of oxidising agent (Mn^{4+}) for its dissolution. The best results for this investigation were obtained at the 4/1 and 5/1 ratios, where Cu solutions of 68 and 77 % were sequentially achieved at 400 min. The results agree with Havlik et al. [21], who indicated that $MnO_2/CuFeS_2$ at 4/1 present good outcomes for the dissolution of Cu from chalcopyrite. However, in this study, it was noted that 4/1 is an optimum for dissolution and over this proportion, no higher extractions could be gotten. It should be remarked that, unlike previous studies [20,21], the chalcopyrite used here had high purity. Dutrizac [30] stated the challenge of determining the effects of additives when working with chalcopyrite in chlorinated media, since small amounts of secondary copper mineralisations may affect the interpretation of the results. Then, it can be established that our dissolution is specific for chalcopyrite. Fig. 3 shows the potential for the tests performed in Fig. 2. For the lower $MnO_2/CuFeS_2$ ratios (2/1 and 3/1), lower potential were obtained (between 500−570 mV), while having higher contents of MnO_2 the potentials were between 580–650 mV. For all the experimental assays, the pH ranged between -0.6 and 1.5. These results agree with the study of Velásquez-Yévenes et al. [13]. The authors worked with a chalcopyrite, concentrated in chloride media, and concluded that the best potential window in which the chalcopyrite dissolution rate is linear is between 550 and 620 mV. Additionally, the authors indicated that at high concentrations of chloride, the potential range might increase.

3.2. *Agitation evaluation*

Fig. 4 shows that the stirring promotes the copper extraction. The best results were obtained at 800 rpm (54 % copper extraction); however, the extraction rate at 600 rpm is not significantly differing (52 %). This concurs with other studies [13,18] where the mixing intensity did not affect the copper
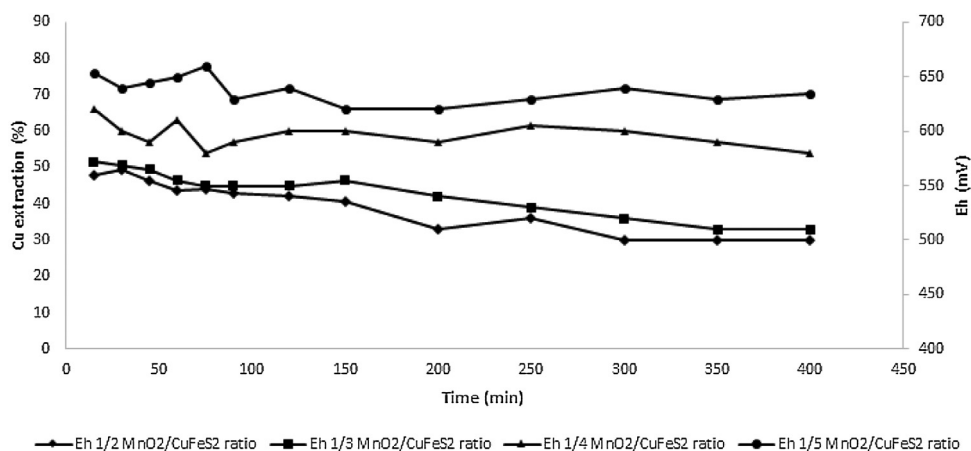
Fig. 3 – Effect of the potential in the solution of Cu at different ratios of $MnO_2/CuFeS_2$.

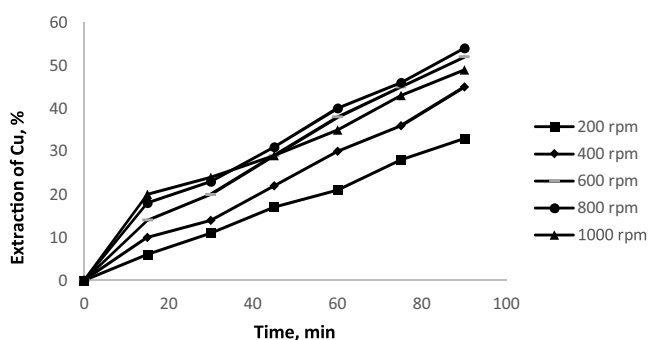**Fig. 4 – Effect of mixing on the copper extraction (25 °C, MnO_2/CuFeS2 ratio of 5/1, chalcopyrite size to −47 + 38 μm, 1 mol/L H_2SO_4 and 39.19 g/L de cloruro).**
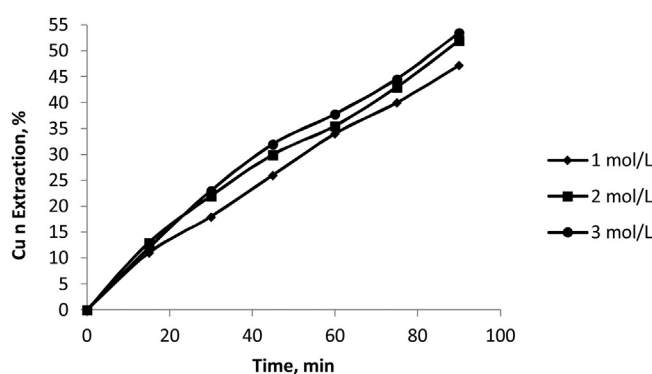

Fig. 5 – Effect on the acid concentration in chalcopyrite leaching with the addition of MnO_2 (25 °C, $CuFeS_2$ size: −47 + 38 μm, MnO_2 size: −75 + 53 μm, $MnO_2/CuFeS_2$ to 4/1 and 39.16 g/L chloride).

dissolution rate from chalcopyrite. More lowering dissolution rates were obtained with slower agitation (200 and 400 rpm), wherein not all the particles remained in suspension, having a significant influence on the results. Velásquez-Yévenes [35] pointed out that once keeping the mineral particles dispersed (near to 600 rpm), the mixing intensity does not play a significant role in copper extraction. Ultimately, the copper dissolution rate at 1000 rpm was below that reached at 800 rpm. This coincides with Sokic et al. [44] who found that the chalcopyrite leaching rate declined slightly by an increase in mixing, since a lessened contact occurs between the particles and the oxidant. Also, extremely high agitation make the mineral particles adhere to the reactor wall [22].

3.3. Effect of H_2SO_4

Fig. 5 shows the dissolution of chalcopyrite in time with the addition of MnO_2 and Cl- at different concentrations of H_2SO_4. As the concentration of the acid increases, the copper solutions enhance. For 1 mol/L, the final extraction of Cu was 47 %. For 2 mol/L, there was an increase of 6 %; however, for 3 mol/L, there was no significant increase in the copper extraction from chalcopyrite. These results in Fig. 5 and those presented in Fig. 2, indicate that it is not necessary to have a high concentration of H_2SO_4 while having high ratios of $MnO_2/CuFeS_2$ and chloride.
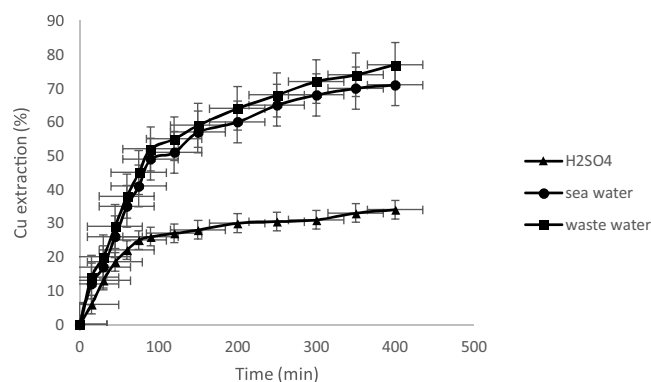

Fig. 6 – Effect on the chloride concentration in the leaching of chalcopyrite with the addition of MnO_2 (25 °C, $CuFeS_2$ size: −47 + 38 μm, MnO_2 size: −75 + 53 μm, $MnO_2/CuFeS_2$ to 5/1 and H_2SO_4 concentration of 1 mol/L).

3.4. Effect of different chloride concentrations

Fig. 6 shows the effect on chloride concentration for leaching chalcopyrite by adding MnO_2 as an oxidizing agent. The best results were obtained when working with high concentrations of chloride (wastewater, 39.19 g/L of chloride) achieving
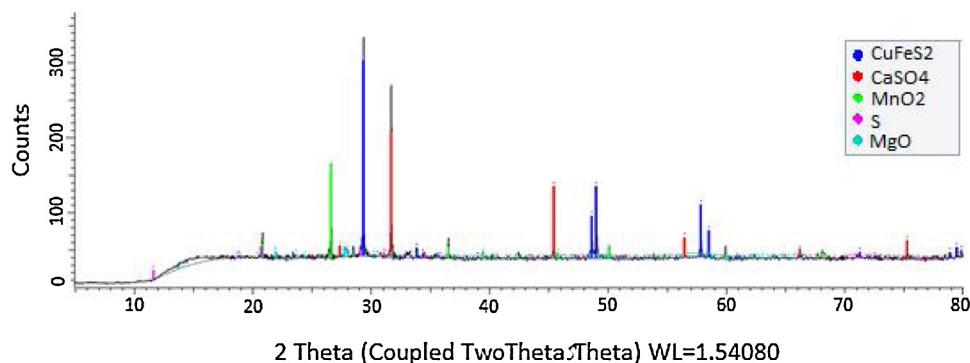
Fig. 7 – X-ray powder diffraction patterns for the residue mineral after being leached with waste water at 25 °C in a time of 90 min. CuFeS$_2$ size: −47 + 38 µm, MnO$_2$ size: −75 + 53 µm, MnO$_2$/CuFeS$_2$ to 5/1 and 39.16 g/L chloride).
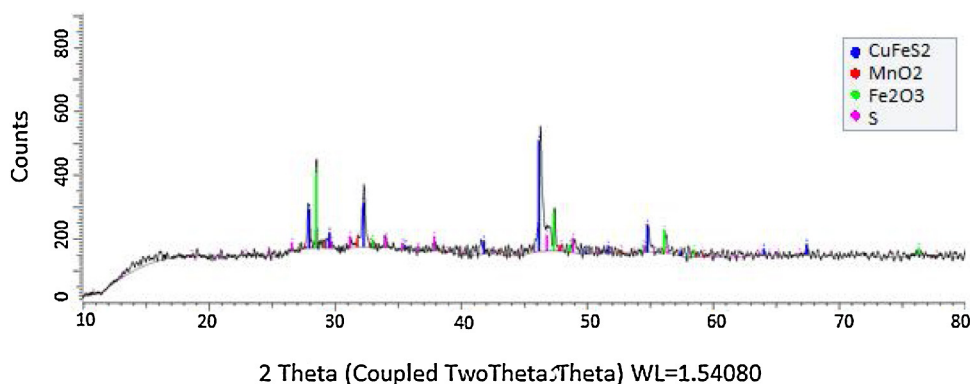

Fig. 8 – X-ray powder diffraction patterns for the residue mineral after being leached with H$_2$SO$_4$ at 25 °C in a time of 90 min. CuFeS$_2$ size: −47 + 38 µm, MnO$_2$ size: −75 + 53 µm, MnO$_2$/CuFeS$_2$ to 5/1 and 39.16 g/L chloride).

extractions of 77 % Cu at the end of the experiment. The outcomes matches with the research of Devi et al. [20], who achieved Cu extractions of up to 77 % after 60 min, although with higher concentrations of HCl (4 mol/L). Havlik et al. [21] got better copper extraction while increasing the concentration of HCl up to 4 Mol/L, but further levels led to a decay of Cu removal. Cu solutions decrease (71 %) when working at lower concentrations of chloride (seawater), what agrees with what was expected: the lower amount of chloride, the lower the extraction of Cu. In the case of leaching with wastewater, the solution was not negatively affected by the presence of impurities, nor was it affected by contaminants contribution from the manganese nodules. According to several authors, phosphate precipitates and forms coatings in the sulfides generating passivation, but in this case, it was not a retardant in the dissolution of copper [45,46]. When not adding chloride, the dissolution decreases and, besides, there was a tendency to passivation after 90 min. This is possibly because the chloride ions promote the formation of long sulfide crystals. Then, the reactants penetrate the sulfide layer, preventing the passivation of the mineral [47]. In future works, it is necessary to study the optimal ratios of MnO$_2$/CuFeS$_2$, H$_2$SO$_4$ and chloride. Moreover, it would be interesting to evaluate other industrial waters that have high concentrations of chloride.

3.5.   Mineralogy of the residue

Fig. 7 shows an x-ray diffractogram of the mineral residue that was leached with wastewater. It was found that the calcium precipitate in the form of sulfate, but it did not affect the copper extraction (comparing with seawater in Fig. 6). The copper remaining in the residue was in the form of chalcopyrite (approximately 20 mg), while small quantities of elemental sulfide were established as a stable residue. The rest was composed of magnesium oxide and manganese, where the last one is of interest since it is the oxidizing agent. In Fig. 8, the residues that worked with H$_2$SO$_4$ were analyzed, without the addition of chloride (Fig. 6). It was found that the remaining is mostly composed of chalcopyrite and pyrolusite (MnO$_2$). The unreacted chalcopyrite is explained by passivation since at not having chloride, a film of sulfur ash can cover the mineral surface. This layer prevents the contact between the oxidizing agent with copper, mitigating its reaction. Hematite residues were also found from manganese nodules used as an oxidizing agent. Dutrizac [31] explained the morphological formations of sulfur around a chalcopyrite mineral leached with FeCl$_3$ and HCl. It was observed granular formations, hemispherical globules, crystallised aggregates, and irregular globular masses, which tend to cover the entire mineral surface. However, the crystal formation has enough space to allow the

leaching solution to enter into the mineral. Havlik et al. [14] leached chalcopyrite using $FeCl_3$ and HCl. The researchers found elemental sulfur on the surface of mineral residues, which realize on chlorine and its effects on morphological formation. Carneiro and Leao [17] analysed the effect of NaCl in a chalcopyrite concentrate. Considering the mineralogical analysis of the residues, the authors evaluated the porosity, which increased with the presence of NaCl, facilitating the diffusion of the leaching solution through the mineral. The formation of a solid compound of elemental sulfur with a high porosity converges to what was obtained in this research. The assays conducted with H_2SO_4 (Fig. 6) reported low copper extractions, while the mineralogical analyses (Fig. 8) indicated the presence of sulfur around the mineral. Despite not analysing the porosity of this residue, it is theoretically expected that the lack of chlorine was fundamental in the non-formation of elongated and porous sulfur crystals [33]. This prevented a high extraction of copper. The analysis and identification of the crystalline phases were obtained using the DIFFRAC.EVA V4.2.1 program, with the Powder Diffraction File of ICDD database (PDF-2 (2004)) (Manganese Oxide PDF 65-1298(ICDD, 2004), Sulfur PDF 08-0247 (ICDD, 2004), Magnesium Oxide, PDF 04-0829(ICDD, 2004), Calcium Sulfate PDF 86–2270 (ICDD, 2004) and Iron Oxide PDF 89-8103(ICDD, 2004)).

4.   Summary and conclusions

This research displays the results of the copper dissolution from chalcopyrite by adding MnO_2 as an oxidizing agent (manganese nodules), using wastewater at 25 °C. The MnO_2 present in the marine nodules proved to be an excellent oxidizing agent for the dissolution of chalcopyrite. The main findings of this study are the following:

- High concentrations of MnO_2 (4/1 and 5/1) allow the potential values to be between 580 and 650 mV, favoring the dissolution of $CuFeS_2$.
- The mixing intensity did not have a significant effect on the copper dissolution rate from chalcopyrite.
- The best results for high ratios of $MnO_2/CuFeS_2$ (5/1), in chloride media, were obtained 2 mol/L of H_2SO_4.
- High concentrations of chloride allow to significantly increase the copper dissolution from $CuFeS_2$, achieving better results when working with discard (waste) water compared to seawater.
- The waste analysed for leaching with wastewater did not reveal the formation of pollutants elements like stable elemental sulfur (S^0). Besides, the elements present as MgO and $CaSO_4$ did not significantly affect the copper extraction
- The best results of this investigation (77 % of Cu) were obtained when working at $MnO_2/CuFeS_2$ ratios of 5/1 and a concentration of 1 mol/L of H_2SO_4 at 25 °C.

Wastewater proved to be an excellent contribution to the process as well as a reusable water resource that provides high amounts of chloride. It is necessary to investigate: i) hydrometallurgical alternatives for the information of secondary and primary sulfides, since these are a more environmentally friendly alternative, and ii) to provide solutions for the water scarcity.

Author contributions

All of the authors contributed to analyzing the results and writing the paper.

Conflicts of interest

The authors declare no conflicts of interest.

Acknowledgments

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