

Article

Leaching of Chalcopyrite in Acidified Nitrate Using Seawater-Based Media

Pía C. Hernández ^{1,*} , María E. Taboada ^{1,2}, Osvaldo O. Herreros ³, Teófilo A. Graber ^{1,2} and Yousef Ghorbani ⁴ 

¹ Departamento de Ingeniería Química y Procesos de Minerales, Universidad de Antofagasta, Avda. Angamos 601, Antofagasta 1270300, Chile; mariaelisa.taboada@uantof.cl (M.E.T.); teofilo.graber@uantof.cl (T.A.G.)

² Centro de Investigación Científico Tecnológico Para la Minería (CICITEM), Sucre 220, Of. 602, Antofagasta 1270300, Chile

³ Departamento de Ingeniería en Minas, Universidad de Antofagasta, Avda. Angamos 601, Antofagasta 1270300, Chile; osvaldo.herreros@uantof.cl

⁴ School of Natural and Built Environment, Faculty of Science, Engineering and Computing, Kingston University, London KT1 2EE, UK; y.ghorbani@kingston.ac.uk

* Correspondence: pia.hernandez@uantof.cl; Tel.: +56-55-2-637-313

Received: 4 May 2018; Accepted: 30 May 2018; Published: 1 June 2018



Abstract: The leaching of copper from industrial copper ore with 4.8 wt % chalcopyrite by acidified nitrate with seawater based media was investigated. Water quality (pure water and seawater), temperature (25–70 °C), reagent concentration, and nitrate type (sodium and potassium) were studied variables. Leaching conditions were: 100 g ore/1 L solution; P₈₀ of 62.5 µm; 400 rpm and leaching time, varying between 3 and 7 days. Nitrates in sulfuric acid are known to be good oxidants for sulfide ores. This study showed that up to 80 wt % copper could be extracted at 45 °C in 7 days. In the absence of nitrate, under the same leaching conditions, only a 28 wt % copper extraction was achievable. The extraction rate increased to 97.2 wt % when leach temperature was increased to 70 °C in nitrate-chloride-acid media. The presence of chloride ions also increased the copper extraction rate. The copper extraction achieved in seawater systems were higher than in water systems under the same leaching conditions (increased by an average of 18 wt %). This effect can be attributable to the contribution of chloride that increases proton (H⁺) activity.

Keywords: nitrate; chalcopyrite; chloride; leaching; seawater

1. Introduction

Given that copper oxide minerals will probably be depleted in the near future and hydrometallurgical plants could then be left unused, hydrometallurgical methods to process copper sulfide represent an alternative use for solvent extraction and electro-winning plants.

Many researchers have argued that chloride ions are beneficial to leaching in the hydrometallurgical processing of chalcopyrite [1–7], owing to the formation of soluble copper chloro complexes [8,9]. Cupric and ferric ions have been tested as oxidants in chloride media [10–13] with beneficial results. Mining companies in desert areas (e.g., Las Luces, Taltal, Chile) use seawater in their operations because of limited access to freshwater [14–16]. The use of seawater in sulfuric acid leaching is expected to increase the dissolution rate of the copper sulfide ores as seawater contains approximately 19 g·L⁻¹ chloride [17,18].

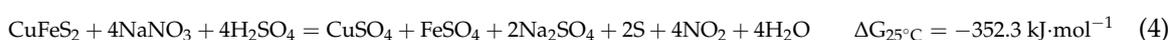
There are large reserves of nitrate (caliche) in Northern Chile [19–21]. Sodium nitrate is obtained by caliche leaching with water and then crystallizing the leaching solution by cooling or evaporation.

In the case of evaporation, discarded salts (tailings) from the solar pond still contains significant amount (4.6 wt % NaNO_3) of nitrate salts [22]. Such tailings can be used as oxidants in chalcopyrite leaching. Habashi [23] proposed the use of nitric acid (HNO_3) and indicated that in sulfide ore leaching nitrate ions act as an oxidant by forming NO or NO_2 gases and oxygen, from the decomposition of HNO_3 . Other researchers [24,25] related the better performance of HNO_3 as an oxidant due to its high redox potential. In a system of CuFeS_2 , HNO_3 and H_2SO_4 , the reaction products are Cu^{2+} , Fe^{3+} , S^0 and NO gas. This gas (NO) can be captured and oxidized with air and water to form HNO_3 . At higher temperatures, sodium nitrate converts to nitric acid in presence of sulfuric acid (Equations (1)–(2); Kazakov et al. [26]):

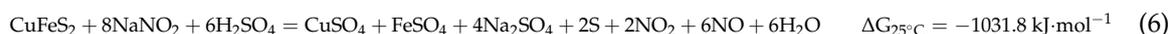


There are several leaching studies [27–31] that use nitrogen species (e.g., NO_3^- , nitrate, NO_2^- , nitrite, HNO_3 , nitric acid, or HNO_2 , nitrous acid, and NO_2 , nitrogen dioxide) as they increase the oxidization capacity, and enhance kinetics and/or dissolution of ores. Nitrogen species catalyzed (NSC) process uses nitric and sulfuric acid to leach sulfide ores at high temperature and pressure. This process has been successfully used in the mining industry for pressure leaching of copper sulfides [32]. The main advantage of this process is faster reaction rates. Tsogtkhankhai et al. [33] studied leaching copper concentrates using nitric acid, and determined the effects of nitric acid strength, liquid solid ratio, time and temperature on the copper extraction rate. Depending on the activation energy, temperature has a slight effect on the rate of copper extraction from chalcopyrite. The outset of leaching is controlled by an external diffusion regime. As time passes, the dissolution reaction is controlled by an internal diffusion regime due to the formation of a film around the particles. The same authors [34] determined optimal sulfide dissolution conditions for the Cu-Fe-S-N-O-H system in nitric acid at different temperatures (20 to 100 °C) using thermodynamic diagrams. They found that the best conditions were: high initial oxidizing potentials (high concentration of nitric acid), pH lower than 1 and high temperature. Arias [35] patented a hydrometallurgical process of copper sulfide heap leaching using H_2SO_4 and NaNO_3 at $\text{pH} \leq 2$, with a sulfide ore/nitrate ratio (by weight) of 1:1. Sodium nitrate was mixed with sulfuric acid and water. Prater and Queneau [36] patented a process for dissolving sulfide ores (copper, iron, cobalt, nickel, silver) using nitric acid which is continuously added during leaching. Iron (in the form of hydrogen jarosite) and sulfur compounds were precipitated; these products are highly filterable and are subsequently removed. It is mentioned that the formation of jarosites, which is followed by drop of pH, may cause losses of valuable ions from solution as a result of co-precipitation [37].

Leaching of copper ores in sulfuric acid with sodium nitrate/nitrite solutions resulted in copper extraction rates of 80–99 wt % [28,29]. Vračar et al. [30] leached Cu_2S at different temperatures, NaNO_3 and H_2SO_4 concentrations, stirring speeds and solid-liquid ratios. The authors determined that Cu_2S was leached in two stages, forming CuS , followed by elemental S , according to X-ray diffraction (XRD) analysis of leaching residues. The activation energy for the process was $60 \text{ kJ}\cdot\text{mol}^{-1}$. Ore leaching was a first order reaction and a second order reaction with respect to NaNO_3 and H_2SO_4 concentrations, respectively. Sokić et al. [28] leached a chalcopyrite concentrate and studied the effect of different temperatures, particle sizes, concentrations of NaNO_3 and H_2SO_4 and stirring speeds. The authors proposed the following reactions to explain the dissolution of chalcopyrite in acid-nitrate media (Equations (3)–(5)). These reactions are thermodynamically viable at 25 °C and atmospheric pressure due to the negative value of the Gibbs energy:



The authors found that the modeled kinetics of the reaction is dominated by a chemical surface reaction, followed by diffusion in the product layer with an activation energy of $83 \text{ kJ}\cdot\text{mol}^{-1}$. The residues produced were unreacted chalcopyrite and elemental sulfur. Gok and Anderson [29] leached chalcopyrite using an acidic solution containing a nitrite salt (Equation (6)). They obtained a 5 wt % increase in copper extraction rate by using nitrite instead of nitrate. The overall copper extraction rate was positively affected by the system temperature and the newly formed elemental sulfur in the residue.



This study considers the use of nitrate instead of nitrite because Chile has an industry based in nitrate production. Moreover, nitrite is more expensive than nitrate.

Shiers et al. [38] carried out leaching tests using nitrate as an oxidant in chalcopyrite concentrate and ore at 50°C . The authors determined the effect of nitrate, ferric nitrate, ferric chloride and ferric sulfate on copper extraction. A mixed chloride-nitrate system was favorable for extracting copper from chalcopyrite while the presence of ferric chloride was also beneficial.

However, the use of nitrate as an oxidant in an industrial process could be a problem in the solvent extraction stage (SX) due to the degradation of oxime-type extractants by nitration (nitration is the degradation of organic compounds caused by the presence of high nitrate concentration in pregnant leaching solution, PLS) [39–41]. Nowadays, chemical industries have developed nitration resistant reagents to solve this problem [42–44].

In this study, seawater and nitrate salts (NaNO_3 , KNO_3) were used to investigate the acid dissolution of commercial copper ore that contains 4.8 wt % chalcopyrite (1.6 wt % Cu). The effect of different physical and chemical conditions and variables were studied, including temperature, sulfuric acid and nitrate concentrations, nitrate sources, leaching time and water quality.

2. Materials and Methods

2.1. Ore Sample

In this study, an ore from the Atacama Region, Chile was used. Table 1 provides the mineralogical and chemical composition of the ore sample.

Table 1. Mineralogy and chemical composition of the ore sample.

Mineralogy		Chemical Analysis	
Minerals	(wt %)	Element	(wt %)
Magnetite (Fe_3O_4)	36.7	Iron (Fe)	33.6
Quartz (SiO_2)	17.1	Silicon (Si)	10.9
Plagioclase ((Ca,Na)(Al,Si)AlSi ₂ O ₈)	9.1	Calcium (Ca)	4.1
Pyrite (FeS_2)	8.1	Sulphur (S)	3.8
Chalcopyrite (CuFeS_2)	4.8	Aluminium (Al)	2.8
Calcite (CaCO_3)	4.6	Sodium (Na)	1.8
Kaolinite ($\text{Al}_4(\text{Si}_4\text{O}_{10})(\text{OH})_8$)	4.3	Copper (Cu) *	1.6
Garnet ($\text{Ca}_3\text{Fe}_2\text{Si}_3\text{O}_{12}$)	3.7	Magnesium (Mg)	0.9
Actinolite ($\text{Ca}_2(\text{Mg,Fe})_{2.5}\text{Si}_8\text{O}_{22}(\text{OH})_2$)	3.5	Manganese (Mn)	0.6
Amphibole ($\text{NaCa}_2(\text{Mg,Fe,Al})_5(\text{Si,Al})_8\text{O}_{22}(\text{OH})_2$)	3.5	Potassium (K)	0.6
Epidote ($\text{Ca}_2\text{Al}_2\text{FeSi}_3\text{O}_{12}(\text{OH})$)	2.6	Cobalt (Co)	0.4
Sericite ($\text{KAl}_2(\text{AlSi}_3\text{O}_{10})(\text{OH})_2$)	≤1.0	Chromium (Cr)	0.1
Chlorite ($(\text{Mg,Fe})_3(\text{AlSi})_4\text{O}_{10}(\text{OH})_2(\text{Mg,Fe})_3(\text{OH})_6$)	≤1.0	Nickel (Ni)	0.1
		Zinc (Zn)	<0.1
		Molybdenum (Mo)	<0.1
		Silver (Ag)	<0.1

* Chemical analysis by decomposing the ore in a nitric-perchloric acid solution and atomic absorption spectrometry (AAS).

The mineral characterization was carried out by semi-quantitative X-ray diffraction (Siemens/Bruker, Semi-QXRD, model D5000, Germany). The mineralogical data show that chalcopyrite is the only copper mineral present in the ore. Chemical analysis was performed by inductively coupled plasma atomic emission spectroscopy (ICP-AES, ICPE-9000, Shimadzu, Tokyo, Japan). The chemical analysis by atomic absorption spectrometry (AAS, Perkin-Elmer 2380, Perkin Elmer, Wellesley, MA, USA) measured the copper grade as 1.6 wt %. The particle size of the sample (P_{80}) in all tests was 62.5 μm , which was determined using a Microtrac Particle Analyzer (Microtrac S3500, Microtrac, Montgomeryville, PA, USA).

2.2. Reagents

Analytical grade H_2SO_4 , NaNO_3 , KNO_3 and NaCl were used in all leaching tests. Distilled water (referred to as “water” in the text) and seawater, obtained from San Jorge Bay, Antofagasta, Chile, were used to prepare dilute sulfuric acid. The seawater was filtered using quartz sand (50 μm) and a polyethylene membrane (1 μm). The seawater composition is shown in Table 2. One test used a synthetic saline solution composed of distilled water and 35 $\text{g}\cdot\text{L}^{-1}$ NaCl . That value was chosen because the salinity of seawater is 3.5%, so all salinity of seawater was considered as NaCl .

Table 2. Composition of seawater obtained from San Jorge Bay, Antofagasta, Chile.

Chemical Method	ICP-AES					AAS		Volumetric Analysis		Gravimetric Analysis
Ionic Species	Na^+	Mg^{2+}	Ca^{2+}	K^+	B^{3+}	Cu^{2+}	NO_3^-	Cl^-	HCO_3^-	SO_4^{2-}
$\text{mg}\cdot\text{L}^{-1}$	9480	1190	386	374	4.6	0.07	2.05	18,765	142	2771

2.3. Experimental Procedure

The leaching tests used 2 L jacketed glass reactors equipped with lids to prevent evaporative loss (the reactors are not hermetically sealed). Temperature was controlled by a thermostatic bath. Stirring was mechanical at 400 rpm, which provided stable suspension. The solid/liquid ratio used for all tests was 100 g ore in 1 L of solution. 1 L of leach solution was prepared by adding sodium nitrate (solid) and sulfuric acid to seawater or water. The tests were performed separately using both seawater and water. The stirring was periodically interrupted to collect 10 mL samples of supernatant solution from the reactors to analyze the copper content using AAS method. The copper extraction over time was calculated by dividing the copper concentration in the solution at time t and the initial copper concentration (1.6 wt %). The evaporation loss and the volume of samples removed during the tests are considered in calculating copper extraction (loss of mass). The redox potential (ORP) and pH were monitored during the leaching time. ORP was measured with a redox electrode (Ag/AgCl reference electrode with 3.5 M KCl as electrolyte) and pH was measured with a glass membrane electrode calibrated to buffers at pH 1 and pH 4. At the end of the leaching time, the pulp was filtered and washed with distilled water and dried at 60 °C. The leaching residues were characterized (Section 2.4). The total copper extracted from solid residues were compared with the leached copper extractions with an average standard deviation of $\pm 2\%$.

The performed leaching tests were summarized in Table 3. The variables studied were: sulfuric acid concentration (0.25, 0.5 and 1 M), sodium nitrate concentration (0, 0.25, 0.5 and 1 M), temperature (25, 30, 35, 40, 45 and 70 °C), nitrate sources (KNO_3 and NaNO_3), water type (water, seawater and saline solution) and leaching time (3, 5 and 7 days).

In test 14, a synthetic saline solution was used in the preparation of a H_2SO_4 (1 M) + NaNO_3 (1 M) leach liquor. The objective of the test was to determine whether NaCl is the only component of seawater that aids higher copper extraction.

Table 3. Experimental conditions used in chalcopyrite leaching tests

No.	H ₂ SO ₄ (M)	NaNO ₃ (M)	Water Type	T (°C)	t (Days)	Final Cu Extraction (wt %)
1	1.0	1.0	seawater	45	7	80.2
	1.0	1.0	water	45	7	63.9
2	1.0	0.0	seawater	45	7	27.9
	1.0	0.0	water	45	7	14.8
3	1.0	1.0	seawater	45	3	78.8
	1.0	1.0	water	45	3	61.0
4	1.0	1.0	seawater	40	3	65.3
	1.0	1.0	water	40	3	45.6
5	1.0	1.0	seawater	35	3	62.4
	1.0	1.0	water	35	3	37.2
6	1.0	1.0	seawater	30	3	57.1
	1.0	1.0	water	30	3	35.9
7	0.5	1.0	seawater	45	3	66.5
	0.5	1.0	water	45	3	49.4
8	0.25	1.0	seawater	45	3	52.6
	0.25	1.0	water	45	3	42.1
9	1.0	0.5	seawater	45	3	77.3
	1.0	0.5	water	45	3	47.4
10	1.0	0.25	seawater	45	3	68.6
	1.0	0.25	water	45	3	43.1
11	1.0	1.0	seawater	45	5	79.3
	1.0	1.0	water	45	5	62.9
12	0.5	0.5	seawater	45	5	61.2
	0.5	0.5	water	45	5	47.7
13	0.5	0.5 *	seawater	45	5	58.3
	0.5	0.5 *	water	45	5	49.1
14	1.0	1.0	saline solution	45	5	75.7
15	1.0	1.0	seawater	70	3	97.2
	1.0	1.0	water	70	3	83.2
16	1.0	1.0	seawater	25	3	31.8
	1.0	1.0	water	25	3	11.0

* 0.5 M as KNO₃.

2.4. Characterization of Ore Residues

The solid residues were characterized by AAS, optical microscopy with reflected light, scanning electron microscopy (SEM-EDX, JEOL 6260 LV, Tokyo, Japan) and semi-quantitative XRD (QXRD) methods.

3. Results and Discussion

3.1. Effect of Sodium Nitrate and Concentrations

Figure 1 shows copper extraction from the leach liquors using H₂SO₄ (1 M) with and without NaNO₃ in seawater and water-based media (tests 1 and 2 in Table 3).

It can be seen that the addition of NaNO₃ (1 M) to systems with H₂SO₄ (1 M), increased the copper extraction from 27.9 to 80.2% in seawater-based media and from 14.8 to 63.9% in water-based media. This improvement was related to the oxidizing potential of nitrate ions. The use of seawater

clearly had a positive effect on these two sets of tests, yielding higher copper extraction rates than with water. Copper extraction in seawater reached its maximum at about 96 h (4 days).

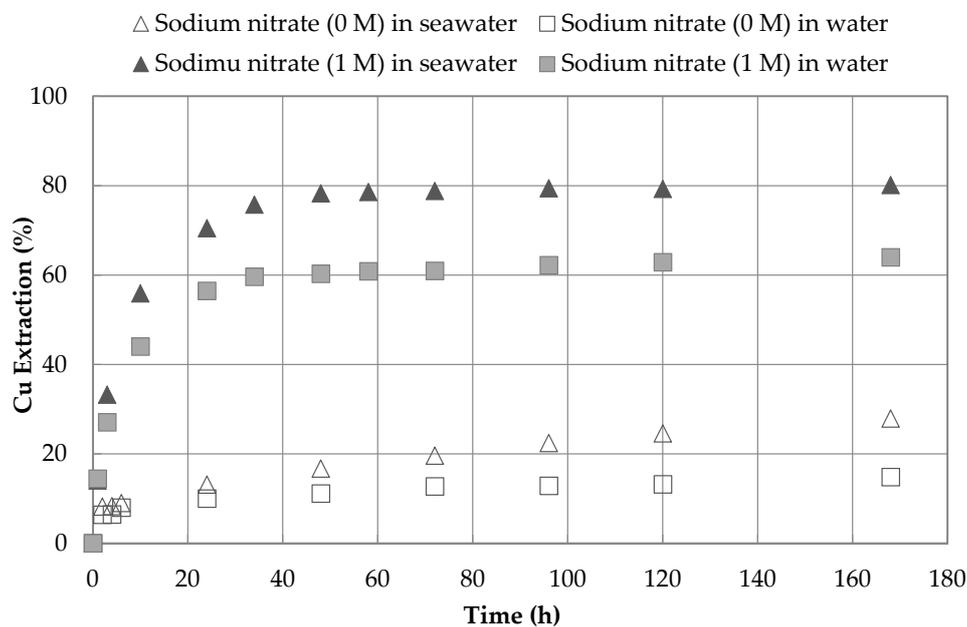


Figure 1. Copper extraction in the leach liquors using H₂SO₄ (1 M) + NaNO₃ (0 or 1 M) in seawater and water based media (at 45 °C and 7 days).

Figure 2a shows that a concentration of 0.5 M of sodium nitrate in seawater was sufficient to achieve a reasonably good level of copper extraction (77.3%) in 3 days. For the water system, a much higher concentration of nitrate (1 M) was needed to extract only 60.9% of copper in the same period (Figure 2b). This indicates that nitrate performs better with chloride ions during chalcopyrite leaching.

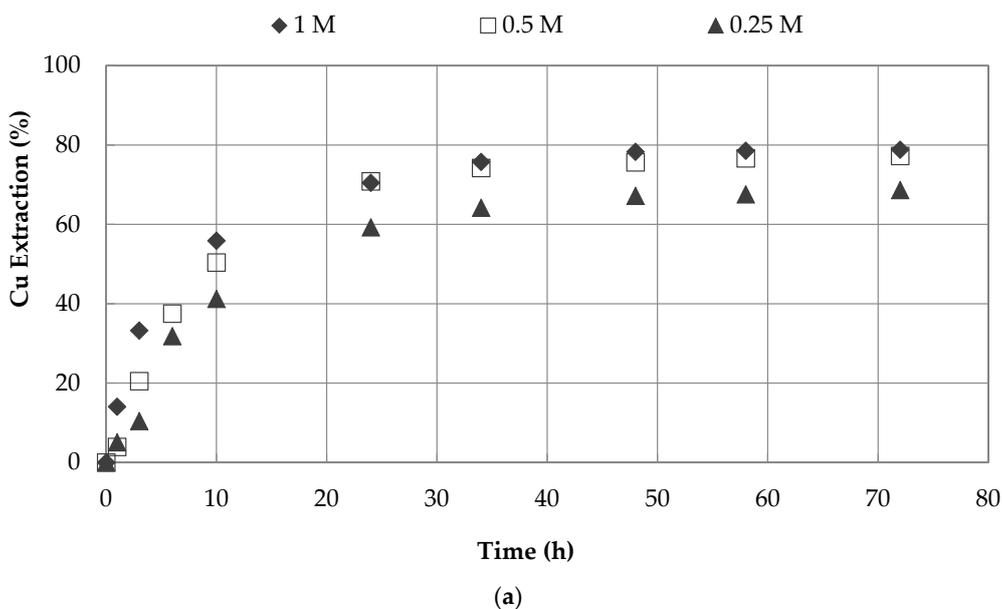


Figure 2. Cont.

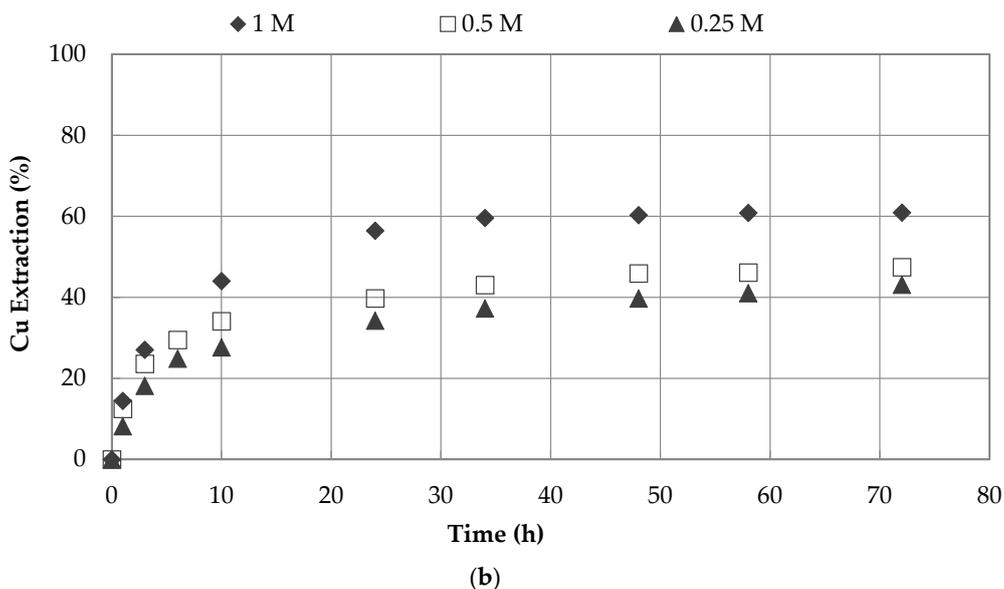


Figure 2. Effect of sodium nitrate concentration on copper extraction using H₂SO₄ (1 M), 3 days of leaching and 45 °C: (a) in seawater and (b) in water.

3.2. Effect of the Nitrate Source

Figure 3 shows the effect of the type of nitrate. Similar copper extraction rates were obtained when NaNO₃ or KNO₃ was used. Copper extraction reached 60% in seawater systems and 48% in water systems (0.5 M H₂SO₄) in 5 days. Thus, the type of nitrate (NaNO₃ or KNO₃) does not affect copper extraction, which is consistent with Shiers et al. [38].

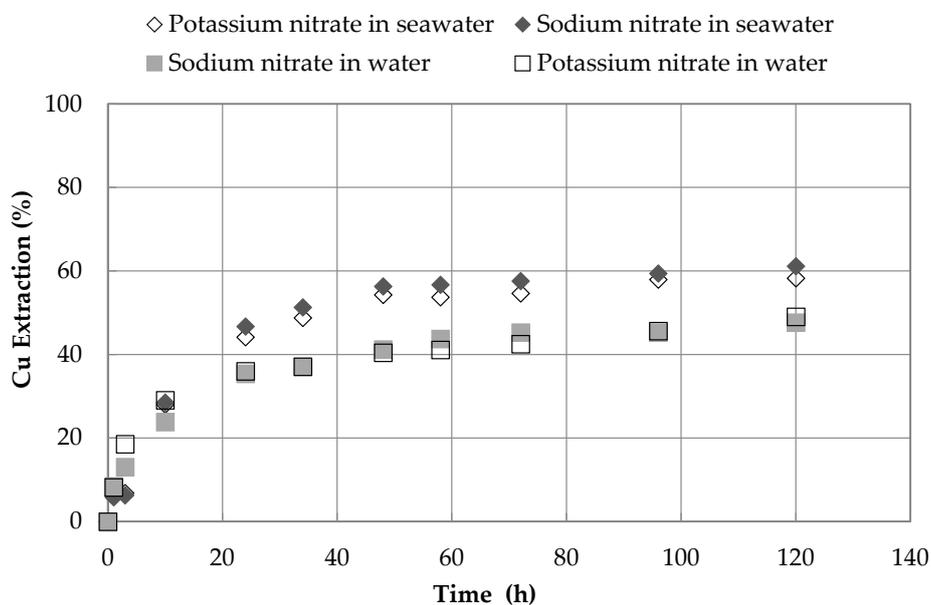


Figure 3. Effect of nitrate type on copper extraction. Experimental conditions: H₂SO₄ (0.5 M), NaNO₃ (0.5 M), KNO₃ (0.5 M), 5 days of leaching and 45 °C.

3.3. Effect of Sulfuric Acid Concentration

Figure 4a,b show the influence of sulfuric acid concentration. The highest copper extraction rate was obtained at higher concentrations of acid in seawater and water systems. The results indicate

that the oxidation power of nitrate ions increases with increased in sulfuric acid concentrations. This observation is in good agreement with the findings of Sokić et al. [28]. In this study, copper extraction increased by 50% and 45% when the sulfuric acid concentration increased from 0.25 to 1.0 M in seawater and water systems, respectively.

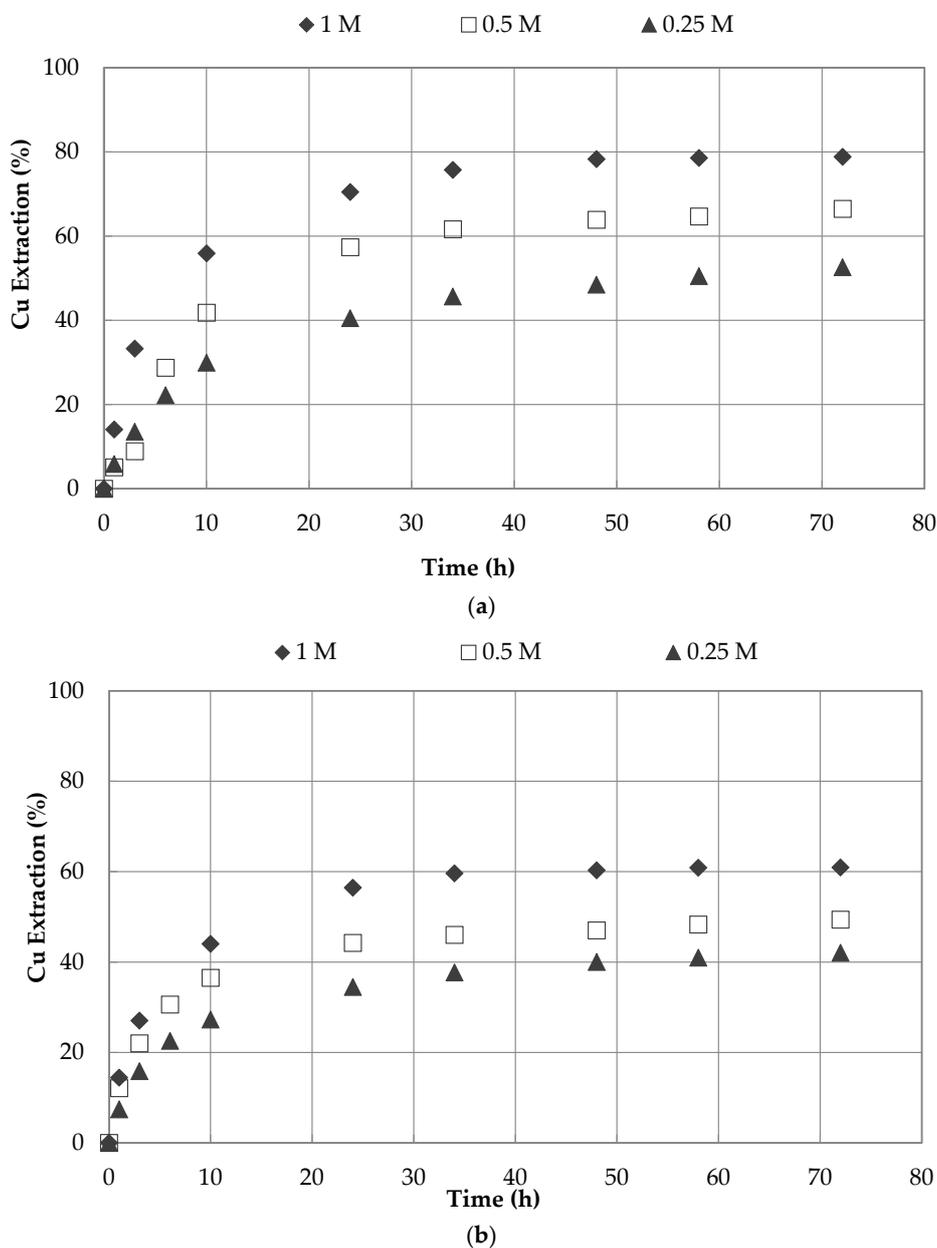


Figure 4. Effect of sulfuric acid concentration on copper extraction using NaNO_3 (1 M), 3 days of leaching and 45°C : (a) seawater and (b) water.

As Figure 5 shows, copper extraction using 0.5 M of H_2SO_4 in a seawater-based media is similar to that with 1 M of H_2SO_4 in a water-based media. The same behavior is observed in the kinetic curves of copper extraction using 0.25 M of H_2SO_4 in seawater and 0.5 M of H_2SO_4 in water. This confirms that chloride ions from seawater increase the acid activity of the systems. Puvvada et al. [45] and Senanayake [46] obtained similar results. These authors indicated that the presence of salts such as NaCl , CaCl_2 or MgCl_2 increase acid activity. This shows that a lower acid concentration can be used when seawater is present in the system.

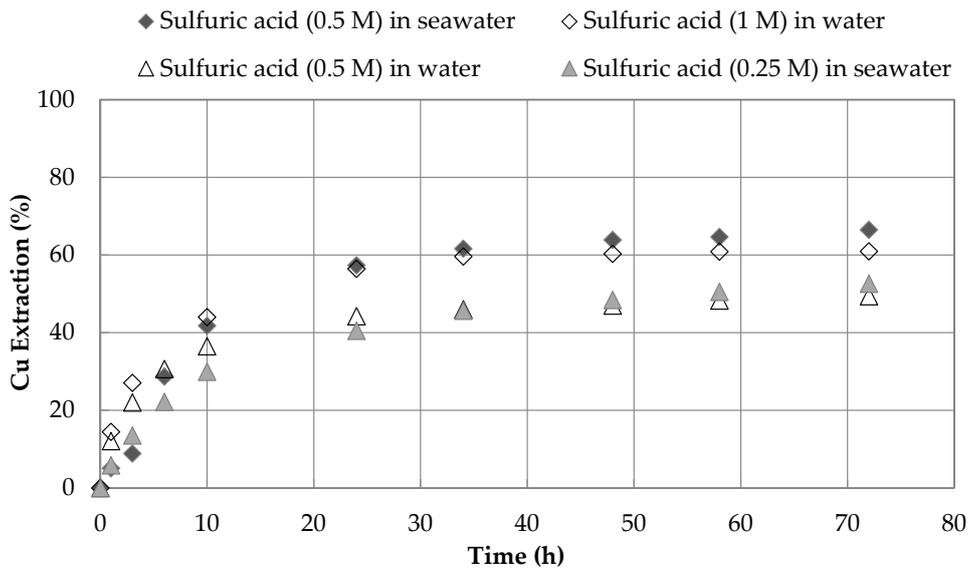


Figure 5. Copper extraction in the leach liquors with experimental conditions of: NaNO₃ (1 M), 3 days of leaching, 45 °C.

3.4. Redox Potential and pH

Figure 6 shows the copper extraction rates and redox potential values obtained during the tests at different concentrations of reagents (1 and 0.5 M of H₂SO₄ and NaNO₃). Because of the high acid concentrations (1 and 0.5 M) used in the tests, all the pH values were < 1. The redox potential (ORP) ranged from 742 mV to 793 mV in seawater and from 739 mV to 789 mV in water when 1 M of sulfuric acid and sodium nitrate were used. When 0.5 M was used, the range of redox potential was 701 mV to 738 mV in seawater and 696 mV to 729 mV in water. In both cases, the redox potential was higher in the seawater system than in water system. This indicates that copper leaching is more effective at higher redox potentials and in a strongly acid medium with seawater.

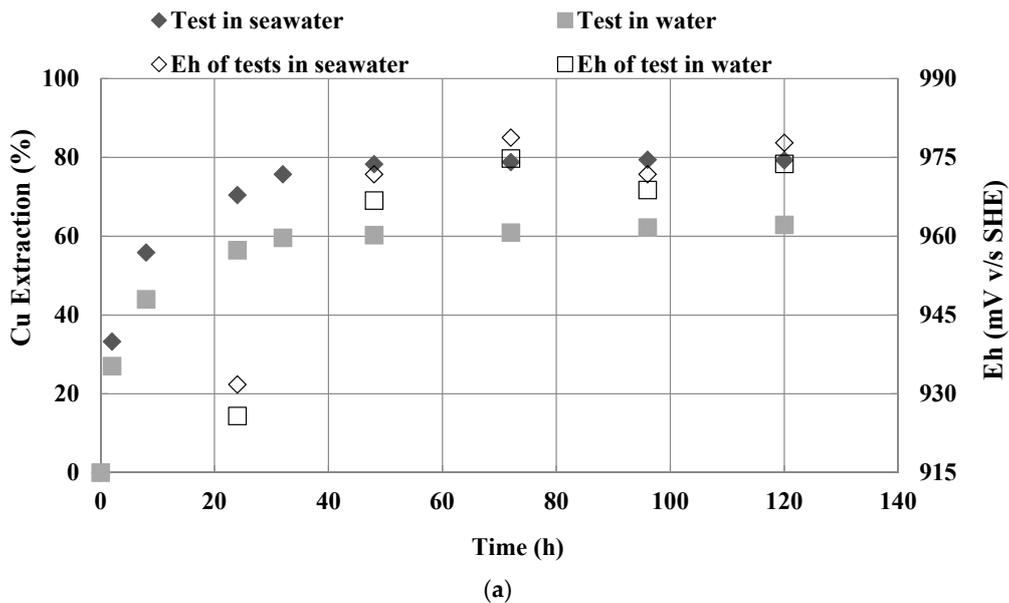


Figure 6. Cont.

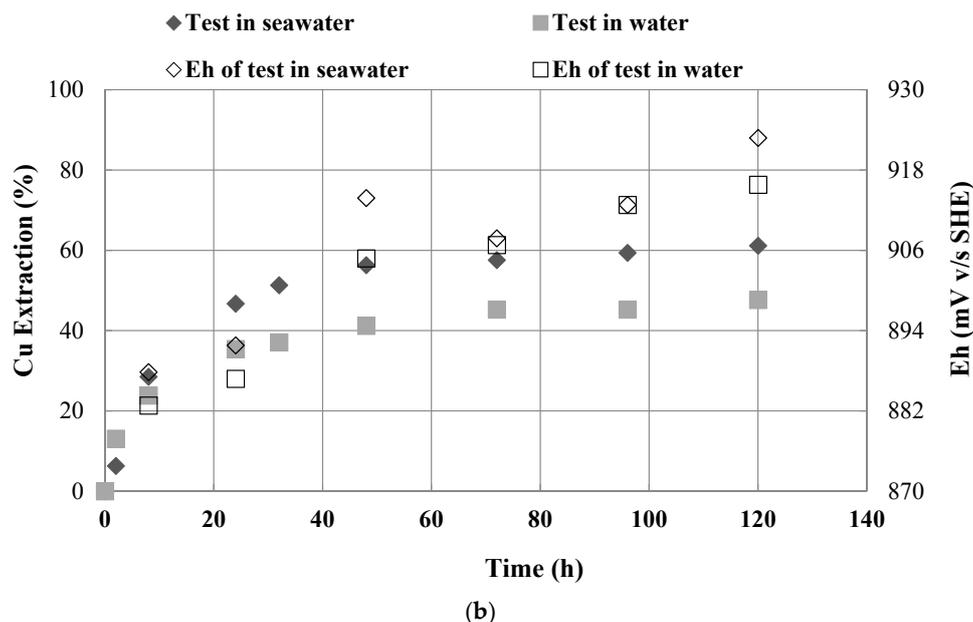


Figure 6. Values of redox potential (mV) against time (h) for the systems: (a) H₂SO₄ (1 M), NaNO₃ (1 M) in seawater and water and (b) H₂SO₄ (0.5 M), NaNO₃ (0.5 M) in seawater and water. Experimental conditions: 5 days of leaching and 45 °C.

3.5. Effect of Temperature

Figure 7a,b show the effect of temperature. The highest copper extraction rate of 97.2% was obtained at 70 °C after 3 days of leaching in a seawater media. This high rate of copper extraction was due to the presence of chloride in solution, higher acid and nitrate content, and higher temperature. The results obtained of the effect of the temperature are in agreement with the results reported in the literature [28,30].

Copper extraction was higher in the seawater-based media than in the water-based media independent of temperature. The increase in temperature from 25 to 70 °C resulted in an increase in the copper extraction rate from ≈31% to ≈97% when seawater was used.

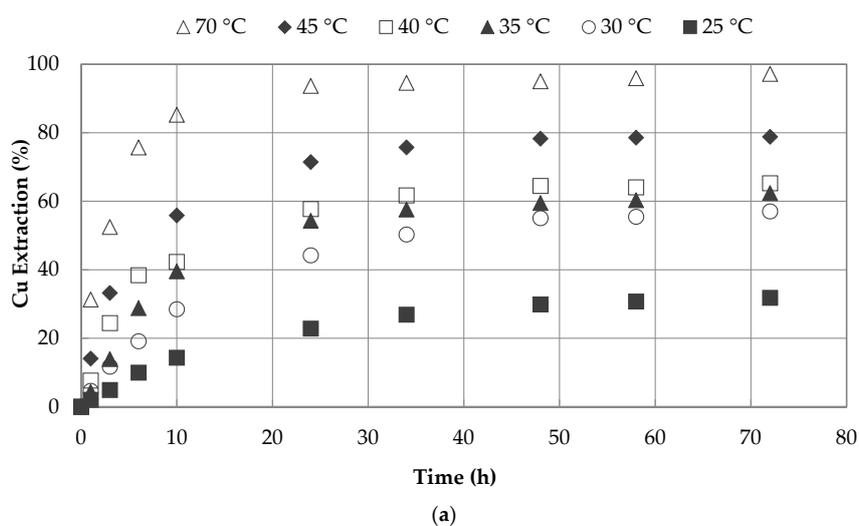


Figure 7. Cont.

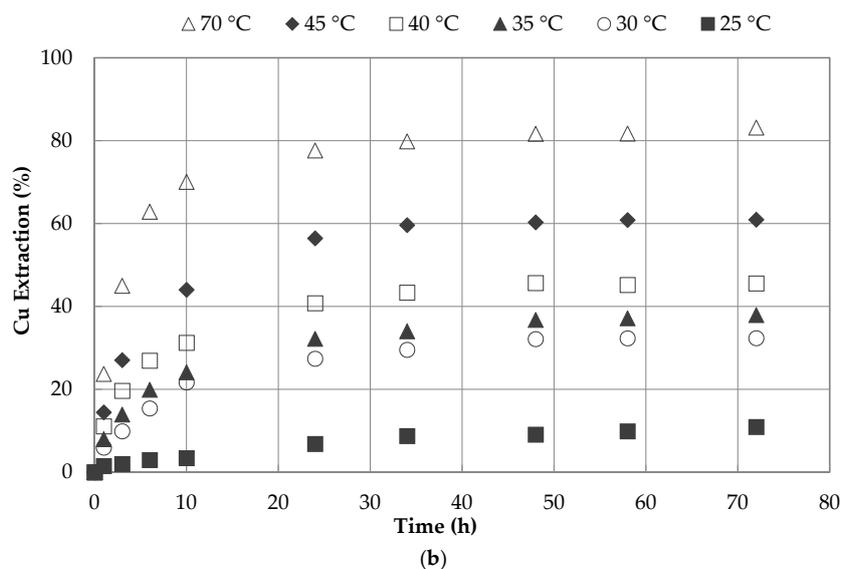


Figure 7. Effect of temperature on copper extraction using H_2SO_4 (1 M), NaNO_3 (1 M), 3 days of leaching: (a) seawater and (b) water.

3.6. Effect of Synthetic Saline Solution

Figure 8 compares the kinetic curves of copper extraction in seawater and a synthetic saline solution. The kinetics curves in Figure 8 show that the two extraction rates are similar. The small variations may be related to the presence of SO_4^{2-} ions in the seawater. Other ions in seawater, such as calcium, potassium, magnesium, do not contribute significantly to leaching under the conditions in this work. Figure 8 shows that chloride ions, present in both solvents, helped in the leaching process.

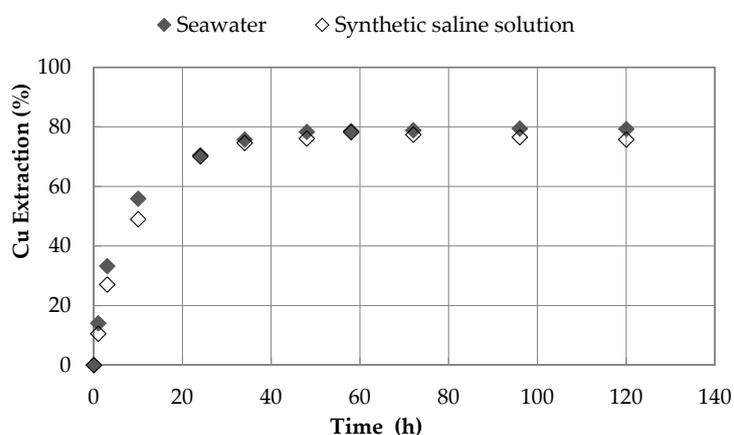


Figure 8. Comparison of copper extraction rates when leach solution was prepared in synthetic saline water and seawater. Experimental conditions: NaCl ($35 \text{ g}\cdot\text{L}^{-1}$), H_2SO_4 (1 M), NaNO_3 (1 M), 5 days of leaching and 45°C .

3.7. Characterization of Ore and Residue Samples

The residue characterization (test 11) confirms that chalcopyrite was significantly leached in the seawater media. Covellite was found in small quantities, 1% and 3%, in the solid residues of the leaching test in the seawater and water media, respectively (Figure 9). It is supposed that covellite in the solid residue is formed as an intermediate product during chalcopyrite dissolution.

The formation of elemental sulfur as a product of chalcopyrite leaching in both seawater and water-based media was confirmed by SEM-EDS analysis (red region, Figure 10).

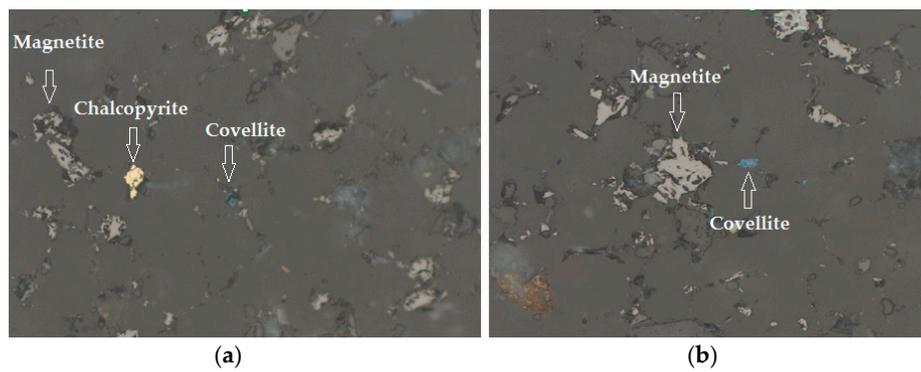


Figure 9. Optical microscope images of solid residue after leaching from (a) seawater, and (b) water system.

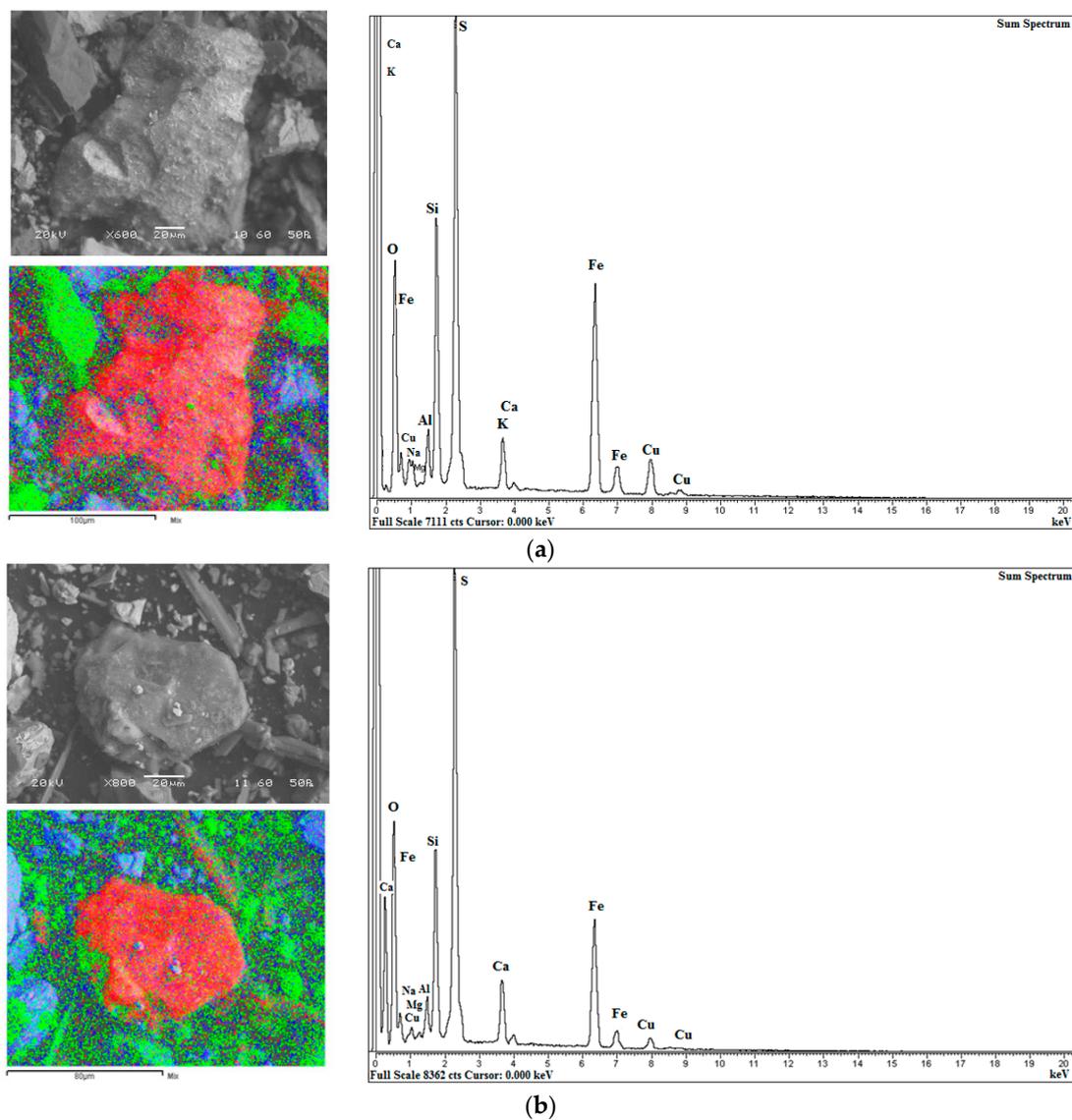
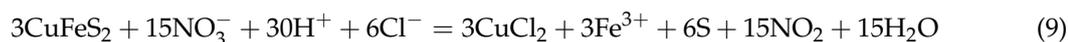


Figure 10. Results of scanning electron microscopy (SEM) analysis carried out using the solid residue. The ore sample was leached in: (a) seawater medium and (b) water medium. The false red color shows the sulfur presence.

3.8. Thermodynamic and Chemical Reactions

Equations (7)–(10) are chemical reactions proposed for the system $\text{CuFeS}_2\text{-NO}_3^- \text{-H}^+ \text{-Cl}^-$. In the literature, the system $\text{CuFeS}_2\text{-NO}_3^- \text{-H}^+$ was analyzed and respective chemical reactions were provided [28,47], but these studies did not include the presence of chloride ions.



The presence of covellite in the leached residue can be explained by Equations (11) and (12):



These equations have negative Gibbs energy (ΔG) indicating their thermodynamic viability at the temperatures used in this work (See Table 4).

Table 4. Gibbs energy (ΔG) value at different temperature

No.	$\Delta G_{25\text{ }^\circ\text{C}}$ ($\text{kJ}\cdot\text{mol}^{-1}$)	$\Delta G_{70\text{ }^\circ\text{C}}$ ($\text{kJ}\cdot\text{mol}^{-1}$)
(7)	−1195.8	−1205.8
(8)	−1351.5	−1338.8
(9)	−340.0	−413.6
(10)	−417.9	−480.2
(11)	−245.7	−274.8
(12)	−28.5	−38.2

4. Conclusions

In this study, leaching of chalcopyrite ore with 1.6 wt % Cu was investigated using a nitrate-acid-seawater system. A higher rate of copper extraction was obtained in an acid nitrate media when chloride ions were present in the leaching tests. The highest copper extraction rate of 97.2% was obtained at 70 °C with high sulfuric acid (1 M) and sodium nitrate (1 M) concentrations.

The addition of both nitrate types (NaNO_3 or KNO_3) to sulfuric acid in seawater or water-based media provided similar levels of copper extraction. The changes in the cation types did not affect copper extraction under the studied conditions.

Without chloride, in the form of seawater or synthetic brine, the nitrate system requires a higher acid concentration to extract the same amount of copper.

The residue characterization showed that sulfur formed during dissolution.

This study presents an alternative method of leaching chalcopyrite ores using seawater and/or brine with nitrate ions at moderate temperatures (45 °C). The main disadvantage of this method is the production of NOx gases that should be controlled in industrial leaching systems.

Proposals for future work include the use of discarded brines (liquid waste with high concentration of chloride ions) from reverse osmosis plants and discarded salts from caliche industry, as sources of oxidants and chloride media during chalcopyrite leaching.

Author Contributions: M.E.T. and P.C.H. designed the experiments; P.C.H. performed the experiments; P.C.H., M.E.T., T.A.G., O.O.H. and Y.G. analyzed the data; P.C.H. prepared and wrote the paper.

Acknowledgments: This work was financially supported by PAI/Concurso Nacional Insercion en la Academia, Convocatoria 2015 folio No. 79150003 and Fondecyt iniciación No. 11170179, CONICYT.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Liddicoat, J.; Dreisinger, D. Chloride leaching of chalcopyrite. *Hydrometallurgy* **2007**, *89*, 323–331. [[CrossRef](#)]
2. Lu, Z.Y.; Jeffrey, M.L.; Lawson, F. The effect of chloride ions on the dissolution of chalcopyrite in acidic solutions. *Hydrometallurgy* **2000**, *56*, 189–202. [[CrossRef](#)]
3. Velásquez-Yévenes, L.; Nicol, M.; Miki, H. The dissolution of chalcopyrite in chloride solutions: Part 1. The effect of solution potential. *Hydrometallurgy* **2010**, *103*, 108–113. [[CrossRef](#)]
4. Herreros, O.; Viñals, J. Leaching of sulfide copper ore in a NaCl-H₂SO₄-O₂ media with acid pre-treatment. *Hydrometallurgy* **2007**, *89*, 260–268. [[CrossRef](#)]
5. Ibáñez, T.; Velásquez, L. Lixiviación de la calcopirita en medios clorurados. *Rev. Metal.* **2013**, *49*, 131–144. [[CrossRef](#)]
6. Yoo, K.; Kim, S.-K.; Lee, J.-C.; Ito, M. Tsunekawa, and N. Hiroyoshi. Effect of chloride ions on leaching rate of chalcopyrite. *Miner. Eng.* **2010**, *23*, 471–477. [[CrossRef](#)]
7. Watling, H. Chalcopyrite hydrometallurgy at atmospheric pressure: 2. Review of acidic chloride process options. *Hydrometallurgy* **2014**, *146*, 96–110. [[CrossRef](#)]
8. Winand, R. Chloride hydrometallurgy. *Hydrometallurgy* **1991**, *27*, 285–316. [[CrossRef](#)]
9. Senanayake, G. A review of chloride assisted copper sulfide leaching by oxygenated sulfuric acid and mechanistic considerations. *Hydrometallurgy* **2009**, *98*, 21–32. [[CrossRef](#)]
10. Al-Harashsheh, M.; Kingman, S.; Al-Harashsheh, A. Ferric chloride leaching of chalcopyrite: Synergetic effect of CuCl₂. *Hydrometallurgy* **2008**, *91*, 89–97. [[CrossRef](#)]
11. Lundström, M.; Aroma, J.; Forsén, O.; Hyvärinen, O.; Barker, M.H. Leaching of chalcopyrite in cupric chloride solution. *Hydrometallurgy* **2005**, *77*, 89–95. [[CrossRef](#)]
12. Lundström, M.; Liipo, J.; Aroma, J. Dissolution of copper and iron from sulfide concentrates in cupric chloride solution. *Int. J. Miner. Process.* **2012**, *102–103*, 13–18. [[CrossRef](#)]
13. O'Malley, M.; Liddell, K. Leaching of CuFeS₂ by aqueous FeCl₃, HCl, and NaCl: Effects of solution composition and limited oxidant. *Metall. Mater. Trans. B.* **1987**, *18*, 505–510. [[CrossRef](#)]
14. Moreno, P.; Aral, H.; Cuevas, J.; Monardes, A.; Adaro, M.; Norgate, T.; Bruckard, W. The use of seawater as process water at Las Luces copper–molybdenum beneficiation plant in Taltal (Chile). *Miner. Eng.* **2011**, *24*, 852–858. [[CrossRef](#)]
15. Aroca, F.; Backit, A.; Jacob, J. CuproChlor®, a hydrometallurgical technology for mineral sulphides leaching. In *Hydroprocess 2012, Proceedings of the 4th International Seminar on Process Hydrometallurgy*; Casas, S.J.C., Ciminelli, V., Montes-Atenas, G., Stubina, N., Eds.; GECAMIN LTDA: Santiago, Chile, 2012; pp. 96–180.
16. COCHILCO. *Consumo de Agua en La minería del Cobre al 2016*; Gobierno de Chile, Ministerio de Minería, Ed.; Registro Propiedad Intelectual: Santiago, Chile, 2017.
17. Torres, C.; Taboada, M.; Graber, T.; Herreros, O.; Ghorbani, Y.; Watling, H. The effect of seawater based media on copper dissolution from low-grade copper ore. *Miner. Eng.* **2015**, *71*, 139–145. [[CrossRef](#)]
18. Hernández, P.; Taboada, M.; Herreros, O.; Torres, C.; Ghorbani, Y. Chalcopyrite dissolution using seawater-based acidic media in the presence of oxidants. *Hydrometallurgy* **2015**, *157*, 325–332. [[CrossRef](#)]
19. Taboada, M.; Hernández, P.; Galleguillos, H.; Flores, E.; Graber, T. Behavior of sodium nitrate and caliche mineral in seawater: Solubility and physicochemical properties at different temperatures and concentrations. *Hydrometallurgy* **2012**, *113*, 160–166. [[CrossRef](#)]
20. Valencia, J.A.; Méndez, D.A.; Cueto, J.Y.; Cisternas, L.A. Saltpeter extraction and modelling of caliche mineral heap leaching. *Hydrometallurgy* **2008**, *90*, 103–114. [[CrossRef](#)]
21. Ordóñez, J.I.; Moreno, L.; Gálvez, E.D.; Cisternas, L.A. Seawater leaching of caliche mineral in column experiments. *Hydrometallurgy* **2013**, *139*, 79–87. [[CrossRef](#)]
22. Torres, M.A.; Meruane, G.E.; Graber, T.A.; Gutiérrez, P.C.; Taboada, M.E. Recovery of nitrates from leaching solutions using seawater. *Hydrometallurgy* **2013**, *133*, 100–105. [[CrossRef](#)]

23. Habashi, F. Nitric Acid in the Hydrometallurgy of Sulfides. In *EPD Congress 1999*; TMS: Baltimore, MD, USA, 1999.
24. Peters, E. Hydrometallurgical process innovation. *Hydrometallurgy* **1992**, *29*, 431–459. [[CrossRef](#)]
25. Prasad, S.; Pandey, B. Alternative processes for treatment of chalcopyrite—A review. *Miner. Eng.* **1998**, *11*, 763–781. [[CrossRef](#)]
26. Kazakov, A.; Rubtsov, Y.I.; Andrienko, L.; Manelis, G. Kinetics and mechanism of thermal decomposition of nitric acid in sulfuric acid solutions. *Bull. Acad. Sci. USSR Div. Chem. Sci.* **1987**, *36*, 1999–2002. [[CrossRef](#)]
27. Baldwin, S.A.; van Weert, G. On the catalysis of ferrous sulphate oxidation in autoclaves by nitrates and nitrites. *Hydrometallurgy* **1996**, *42*, 209–219. [[CrossRef](#)]
28. Sokić, M.D.; Marković, B.; Živković, D. Kinetics of chalcopyrite leaching by sodium nitrate in sulphuric acid. *Hydrometallurgy* **2009**, *95*, 273–279. [[CrossRef](#)]
29. Gok, O.; Anderson, C.G. Dissolution of low-grade chalcopyrite concentrate in acidified nitrite electrolyte. *Hydrometallurgy* **2013**, *134–135*, 40–46. [[CrossRef](#)]
30. Vračar, R.Ž.; Vučković, N.; Kamberović, Ž. Leaching of copper(I) sulphide by sulphuric acid solution with addition of sodium nitrate. *Hydrometallurgy* **2003**, *70*, 143–151. [[CrossRef](#)]
31. Watling, H. Chalcopyrite hydrometallurgy at atmospheric pressure: 1. Review of acidic sulfate, sulfate-chloride and sulfate-nitrate process options. *Hydrometallurgy* **2013**, *140*, 163–180. [[CrossRef](#)]
32. Anderson, C.G. Treatment of copper ores and concentrates with industrial nitrogen species catalyzed pressure leaching and non-cyanide precious metals recovery. *JOM* **2003**, *55*, 32–36. [[CrossRef](#)]
33. Tsogtkhangai, D.; Mamyachenkov, S.V.; Anisimova, O.S.; Naboichenko, S.S. Kinetics of leaching of copper concentrates by nitric acid. *Russ. J. Non Ferr. Met.* **2011**, *52*, 469–472. [[CrossRef](#)]
34. Tsogtkhangai, D.; Mamyachenkov, S.V.; Anisimova, O.S.; Naboichenko, S.S. Thermodynamics of reactions during nitric acid leaching of minerals of a copper concentrate. *Russ. J. Non Ferr. Met.* **2011**, *52*, 135–139. [[CrossRef](#)]
35. Arias, J.A. Heap leaching copper ore using sodium nitrate. U.S. Patent US6,569,391B1, 27 May 2003.
36. Queneau, P.; Prater, J. Nitric acid process for recovering metal values from sulfide ore materials containing iron sulfides. U.S. Patent US3,793,429, 19 Februar 1974.
37. Antivachis, D.N.; Chatzitheodoridis, E.; Skarpelis, N.; Komnitsas, K. Secondary sulphate minerals in a cyprus-type ore deposit, Apliki, Cyprus: mineralogy and its implications regarding the chemistry of Pit Lake waters. *Mine Water Environ.* **2017**, *36*, 226–238. [[CrossRef](#)]
38. Shiers, D.; Collinson, D.; Kelly, N.; Watling, H. Copper extraction from chalcopyrite: Comparison of three non-sulfate oxidants, hypochlorous acid, sodium chlorate and potassium nitrate, with ferric sulfate. *Miner. Eng.* **2016**, *85*, 55–65. [[CrossRef](#)]
39. Alguacil, F.J.; Cobo, A.; Alonso, M. Copper separation from nitrate/nitric acid media using Acorga M5640 extractant: Part I: solvent extraction study. *Chem. Eng. J.* **2002**, *85*, 259–263. [[CrossRef](#)]
40. Eyzaguirre, D. Efecto del nitrato en la extracción por solventes de Cía. Minera Lomas Bayas. In *Proceedings of the VI Exposición Mundial Para la Minería Latinoamericana EXPOMIN, Seminario Innovación Tecnológica en Minería*; Instituto de Ingenieros de Minas de Chile: Santiago, Chile, 2000.
41. Yáñez, H.; Soto, A.; Soderstrom, M.; Bednarski, T. Nitration in copper SX? Cytec Acorga provides a new reagent. In *Hydrocopper 2009*; Domic, E., Casas, J., Eds.; GECAMIN LTDA: Antofagasta, Chile, 2009; pp. 332–341.
42. Zambra, R.; Quilodrán, A.; Rivera, G.; Castro, O. Use of NR®reagents in presence of nitrate ion in SX: A revision of the present moment. In *Hydroprocess 2013*; GECAMIN LTDA: Santiago, Chile, 2013.
43. Hamzah, B.; Jalaluddin, N.; Wahab, A.W.; Upe, A. Copper (II) Extraction from Nitric Acid Solution with 1-Phenyl-3-methyl-4-benzoyl-5-pyrazolone as a Cation Carrier by Liquid Membrane Emulsion. *J. Chem.* **2010**, *7*, 239–245. [[CrossRef](#)]
44. Virnig, M.J.; Mattison, P.L.; Hein, H.C. Processes for the recovery of copper from aqueous solutions containing nitrate ions. U.S. Patent 6,702,872, 9 March 2004.
45. Puvvada, G.V.K.; Sridhar, R.; Lakshmanan, V. Chloride metallurgy: PGM recovery and titanium dioxide production. *J. Miner. Met. Mater. Soc.* **2003**, *55*, 38–41. [[CrossRef](#)]

46. Senanayake, G. Review of theory and practice of measuring proton activity and pH in concentrated chloride solutions and application to oxide leaching. *Miner. Eng.* **2007**, *20*, 634–645. [[CrossRef](#)]
47. Narangarav, T.; Nyamdelger, S.; Ariunaa, G.; Azzaya, T.; Burmaa, G. Dissolution behavior of copper concentrate in acidic media using nitrate ions. *Mong. J. Chem.* **2014**, *15*, 79–84. [[CrossRef](#)]



© 2018 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<http://creativecommons.org/licenses/by/4.0/>).