



Chalcopyrite dissolution using seawater-based acidic media in the presence of oxidants



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ABSTRACT

Due to water shortages and depletion of both surface water and underground aquifers, seawater is now used increasingly in the mining industry in northern Chile as a main alternative water resource. In this paper, the use of seawater in leaching of the chalcopyrite ore samples with copper grade of 1.6% in acidic media is investigated. Different leach solutions were prepared using different acids (H_2SO_4 , HCl and HNO_3) with and without seawater. Cupric chloride and ferric chloride were added as oxidant in the leaching process.

Leaching tests were conducted in the agitated leaching reactors with 400 RPM using 100 g of the representative ore sample and 1 L of leach solution at 45 °C, with duration of 7 days. The ore was ground to P_{80} of 62.5 μm . The maximum copper extraction of 37.7% was obtained in the test performed using hydrochloric acid in the seawater-based media and in the presence of cupric chloride. In the leaching test conducted using sulfuric acid in the seawater-based media and in the presence of sodium chloride and cupric chloride, the maximum copper recovery of 34.2% obtained. In all of the different designed leaching approaches, the highest copper extraction was obtained in the tests performed with addition of the cupric ions (Cu^{2+}). In general, copper extraction in the leaching tests performed using seawater-based acidic media, were higher than those conducted in the pure water-based leaching media. Only exceptions observed when chloride ions (sodium chloride) were added externally. This indicated the importance of chloride ions presence in the leach solution.

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1. Introduction

Chalcopyrite is known to resist sulfuric acid leaching. Many investigators have concluded that when sulfuric acid was used as leaching solution, a passivating layer forms on the surface of the mineral during leaching which hinders the copper dissolution. A large number of sulfate (sulfuric acid)-based processes have been developed to overcome the slow rate of leaching chalcopyrite. A review of acidic sulfate, sulfate-chloride and sulfate-nitrate process options was provided by Watling (2013). One approach was to increase the temperature and pressure. For instance, the Total Pressure Oxidation Process proposed by King and Dreisinger (1995), operates under high temperature (220 °C) and high pressure (30–40 atm) to achieve higher copper extractions. This process has the advantage of rapid and complete copper dissolution and a high degree of iron hydrolysis, mainly as hematite (Glen et al., 2003). However, the oxygen consumption is high due to the total conversion of sulfur to sulfate (Peacey et al., 2003). Another approach is

activation of the mineral surfaces by ultrafine grinding ($P_{80} = 5\text{--}10\ \mu\text{m}$). Activox and Albion are sulfate-based processes that employ ultrafine grinding to accelerate the kinetics and increase the level of copper dissolution from chalcopyrite (Hourn and Halbe, 1999; Corrans and Angove, 1993). Other methods to improve chalcopyrite leaching have also been investigated, including adding activated carbon (Nakazawa et al., 1998), coal (Barta et al., 1999), silver (Carranza et al., 1997), nitrate or nitrite (Gok and Anderson, 2013; Sokić et al., 2009) or iron powder (Sanchez et al., 1996) and adjusting the redox potential (Hiroyoshi et al., 2002). The technical viability of the BRISA process (Biolixiviación Rápida Indirecta con Separación de Acciones: Fast Indirect Bioleaching with Simultaneous Separation) for the dissolution of copper from chalcopyrite concentrates was investigated by Romero et al. (2003). However, an effective chalcopyrite bio-leaching required elevated temperatures.

Additions of chloride ions (e.g., hydrochloric acid) are also known to increase the kinetics of chalcopyrite leaching (Defreyne and Cabra, 2009; Carneiro and Leão, 2007; Skrobjan et al., 2005; Lu et al., 2000a; Lawson et al., 1992; Cheng and Lawson, 1991a, 1991b). The leaching of chalcopyrite in chloride media has been reviewed and advanced by Dutrizac (1992). Early processes were focused on the leaching of concentrates under aggressive conditions (Lunt et al., 1997). Kinnunen and Puhakka (2004) reported that the presence of 0.25 g/L of Cl^-

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enhanced the copper yield at temperatures between 67 and 90 °C but decreased the copper yield at 50 °C. Lu et al. (2000b) focused their electrochemical studies on the leaching of chalcopyrite in mixed sulfate-chloride (sulfuric acid - hydrochloric acid) media and found that the presence of chloride enhances the oxidation of chalcopyrite. The presence of chlorides has been shown to produce a porous layer around the leached particle, allowing better diffusion of the liquid into the solid (Carneiro and Leão, 2007; Lu et al., 2000a; Lawson et al., 1992; Cheng and Lawson, 1991a; Hirato et al., 1987). Redox potential is a very important variable due to the creation of a potential range where the chalcopyrite is not passive. Many researchers have worked carefully controlling this variable (Velásquez-Yévenes et al., 2010; Lundström et al., 2009; Córdoba et al., 2008a, 2008b; Hiroyoshi et al., 2008; Parker et al., 1981). The utilization of chloride solutions in chalcopyrite leaching is advantageous due to the aggressive nature of the leaching and to the stability of cuprous ions due to the formation of chloro-complex ions. Nicol and co-workers (Miki and Nicol, 2011; Nicol et al., 2010; Velásquez-Yévenes et al., 2010; Velásquez et al., 2010) conducted a wide-ranging study of the dissolution of chalcopyrite in chloride solutions containing cupric ions and dissolved oxygen. Initially, the rate of chalcopyrite dissolution was shown to be enhanced when leaching was conducted in a redox potential range of 550 to 620 in reference to standard hydrogen electrode at 35 °C in a solution containing 0.2 M HCl, 0.008 M Cu^{2+} and 5–15 $\text{mg}\cdot\text{L}^{-1}$ dissolved O_2 (Velásquez-Yévenes et al., 2010). Leaching at a redox potential of <540 mV reduced the dissolution rates of chalcopyrite and covellite or chalcocite formation on some chalcopyrite surfaces. Further details of the chalcopyrite leaching in chloride have been discussed in the recent review by Watling (2014).

Seawater, an alternative to freshwater, has been used in some mining companies. For example, Batu Hijau (Indonesia), Texada Mill, Raglan (Canada), BHP Nickel (Australia), Lipesed, Michilla, Esperanza, Algorta Norte, Mantos de la Luna, Las Luces (Chile) use raw (unprocessed) seawater in their processes (González et al., 2012; Philippe, 2012; Castro and Laskowski, 2011; Moreno et al., 2011; Aral et al., 2010; Quinn et al., 2007). In Chile, copper deposits are found mainly in the north of the country where the weather is arid with slight or no rainfall. The Antofagasta region is responsible for 36% of the production of copper concentrates and 72% of the production of copper cathodes at the national level. The mining industry in this region therefore has high water consumption. Comisión Chilena del Cobre (Cochilco) reported that 18% of the water used in mining processes in this region comes from seawater (Comisión Chilena del Cobre, C., 2013).

Moreover, systems of copper-chlorine, copper-chloride and copper-seawater have been researched (Glasby and Schulz, 1999; Beverskog and Puigdomenech, 1998; Plyasunova et al., 1997; Wang et al., 1997a, 1997b; Nila and Gonzalez, 1996; Winand, 1991; Berger and Winand, 1984; Fritz, 1980; Bianchi and Longhi, 1973). Torres et al. (2013) worked on copper leaching using hydrochloric acid mixed with seawater, and found out that the amount of copper extraction was similar to the amount of copper extraction when hydrochloric acid was mixed with tap water. It was concluded that seawater could be beneficial to the hydrometallurgical processing of copper sulfides, especially chalcopyrite, due to the presence of chloride ions in the seawater (Torres et al., 2015).

The aim of this research is to investigate the dissolution of copper from chalcopyrite using acids mixed with seawater. Tests have been performed using various system designs in order to be able to clearly illustrate the comparison of variable factors. Acids (H_2SO_4 , HCl, and HNO_3), added chloride (NaCl) and oxidants (cupric chloride – Cu^{2+} and ferric chloride – Fe^{3+}) were the variables studied.

2. Materials and methods

2.1. Ore sample

Ore samples used in this work were obtained from the Atacama region of Chile. The ore was crushed and milled to a fine particle size

with a P_{80} of 62.5 μm , determined using a Microtrac Particle Size Analyzer. The chemical and mineralogical composition of the test sample is shown in Table 1.

The ore mineralogy was determined using quantitative X-ray diffraction (QXRD). Chalcopyrite was the only copper-bearing mineral that was detected in the ore sample. The ore sample contained a high concentration of iron minerals including magnetite (36.7 wt.%), pyrite (8.1 wt.%) and chalcopyrite (4.8 wt.%). Quartz was the main silicate gangue mineral (17.1 wt.%). Chemical analysis (Table 1) using inductively coupled plasma atomic emission spectroscopy (ICP-AES) showed the presence of 1.63% Cu total in the sample.

2.2. Leaching reagents and oxidants

All chemicals (NaCl , CuCl_2 , FeCl_3 , H_2SO_4 , HCl and HNO_3) were analytical-grade reagents (AR) unless otherwise stated, and all solutions were prepared either with distilled water (named as “pure water” or simply “water” in the text) or seawater that was obtained from San Jorge Bay, Antofagasta, Chile. As shown in Table 2, different analytical chemistry methods including volumetric, gravimetric, atomic absorption spectrometry (AAS) and ICP-AES were used to determine the chemical composition of the seawater. The total dissolved ion content of the seawater was measured as approximately 33,115 $\text{mg}\cdot\text{L}^{-1}$ of which 18,765 $\text{mg}\cdot\text{L}^{-1}$, was chloride.

2.3. Comparison experimental approach

The experimental setup was designed and performed under three groups (system A - sulfuric acid, system B - hydrochloric acid and system C - nitric acid). Overall 12 tests were performed to obtain a clear evaluation of the variable parameters. The test details are shown in Table 3. The initial pH for all tests was 0.5, except test 2 in system A. To investigate the effect of the acid concentration on the copper extraction, a high acid concentration was used in test 2 in system A. The total copper concentration in the solution and the residue was measured using atomic absorption spectrometry (AAS). Copper extraction was calculated based on the dissolved copper concentration at a given time t and the initial copper present in the ore sample (values obtained by solution). Evaporation of solutions during the test was

Table 1
Chemical and mineralogical composition of the ore samples.

Chemical analysis		Mineralogical analysis	
Element	Amount (wt.%)	Mineral	Amount (wt.%)
Iron (Fe)	33.6	Magnetite (Fe_3O_4)	36.7
Silicon (Si)	10.9	Quartz (SiO_2)	17.1
Calcium (Ca)	4.1	Plagioclase ((Ca,Na)(Al,Si)AlSi ₂ O ₈)	9.1
Sulfur (S)	3.8		
Aluminum (Al)	2.8	Pyrite (FeS_2)	8.1
Sodium (Na)	1.8	Chalcopyrite (CuFeS_2)	4.8
Copper (Cu)	1.6	Calcite (CaCO_3)	4.6
Magnesium (Mg)	0.9	Kaolinite ($\text{Al}_4(\text{Si}_4\text{O}_{10})(\text{OH})_8$)	4.3
Element	Amount ($\text{mg}\cdot\text{kg}^{-1}$)	Garnet ($\text{Ca}_3\text{Fe}_2\text{Si}_3\text{O}_{12}$)	3.7
Potassium (K)	600	Actinolite ($\text{Ca}_2(\text{Mg,Fe})_{2.5}\text{Si}_8\text{O}_{22}(\text{OH})_2$)	3.5
Manganese (Mn)	600	Epidote ($\text{Ca}_2\text{Al}_2\text{FeSi}_3\text{O}_{12}(\text{OH})$)	2.6
Cobalt (Co)	407		
Chromium (Cr)	150	Amphibole ($(\text{NaCa}_2(\text{Mg,Fe,Al})_5(\text{Si,Al})_8\text{O}_{22}(\text{OH})_2$)	3.5
Nickel (Ni)	100		
Zinc (Zn)	59	Sericite ($\text{KAl}_2(\text{AlSi}_3\text{O}_{10})(\text{OH})_2$)	≤1.0
Molybdenum (Mo)	47	Chlorite ($((\text{Mg,Fe})_3(\text{Al,Si})_4\text{O}_{10}(\text{OH})_2(\text{Mg,Fe})_3(\text{OH})_6$)	≤1.0
Silver (Ag)	22		

Table 2
Chemical composition of seawater as determined using different chemical analysis techniques.

Chemical analysis 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⁻
Amount (mg·L ⁻¹)	9480	1190	386	374	4.6	0.07	2.05	18,765	142	2771

considered on the calculation. These values were checked by analysis of the remaining copper in the respective leaching residues. The average standard deviation of $\pm 2\%$ was obtained in calculation of copper extraction using solid and solution phases in all tests performed. The values for the total copper extraction obtained by solution are given in the Table 3.

Agitated leaching was performed using double-jacketed glass reactor (2 L) fitted with a lid (this system is not hermetic). A thermostatic bath was used for set at a constant temperature of approximately 45 °C. To provide a stable suspension of ore particles inside the leach reactors, a stirring speed of 400 RPM (based on the preliminary experiments) was used in all tests. When the desired temperature was achieved, 100 g of ore was added to the reactor. The leaching tests continued for 7 days (determined in preliminary tests).

The initial Cl⁻ concentration given in the Table 3 are in fact total Cl⁻ concentration including the Cl⁻ concentration within solvent (seawater) and in the leaching reagents (NaCl, HCl, CuCl₂ and/or FeCl₃) used in the different tests. All the tests performed with the initial pH of 0.5 and the average of standard deviation of 0.86 was obtained for pH changes during the experiments. In the case of the redox potential the changes were not significant and the maximum changes were measured in the tests 7 and 8 of system B. As shown in the Table 3, this could be due to addition of ferric as oxidant in the experiments.

Table 3
Systems and tests using seawater and pure water as solvent (45 °C, 7 days, 400 RPM, P₈₀ of 62.5 μm, 100 g ore in 1 L of solution, initial pH ≈ 0.5).

Systems	Test N°	Test Characteristics	Initial	Final	
			[Cl ⁻]/M	% Cu Ext.	
A	1	H ₂ SO ₄ (0.32 M) + seawater	0.6	28.8	
		H ₂ SO ₄ (0.32 M) + water	0.0	17.8	
	2	H ₂ SO ₄ (1.0 M) + seawater*	0.5	27.9	
		H ₂ SO ₄ (1.0 M) + water*	0.0	14.8	
	3	H ₂ SO ₄ (0.32 M) + Cl ⁻ (0.16 M) + seawater	0.8	21.8	
		H ₂ SO ₄ (0.32 M) + Cl ⁻ (0.16 M) + water	0.3	18.3	
	4	H ₂ SO ₄ (0.32 M) + Cl ⁻ (0.16 M) + Cu ²⁺ (0.08 M) + seawater	1.0	34.2	
		H ₂ SO ₄ (0.32 M) + Cl ⁻ (0.16 M) + Cu ²⁺ (0.08 M) + water	0.4	36.7	
	B	5	HCl (0.32 M) + seawater	1.3	33.7
			HCl (0.32 M) + water	0.9	13.9
6		HCl (0.32 M) + Cl ⁻ (0.16 M) + seawater	1.6	25.3	
		HCl (0.32 M) + Cl ⁻ (0.16 M) + water	1.2	32.1	
7		HCl (0.32 M) + Cl ⁻ (0.16 M) + Fe ³⁺ (0.09 M) + seawater	1.9	30.8	
		HCl (0.32 M) + Cl ⁻ (0.16 M) + Fe ³⁺ (0.09 M) + water	1.5	31.5	
8		HCl (0.32 M) + Fe ³⁺ (0.09 M) + seawater	1.7	15.0	
		HCl (0.32 M) + Fe ³⁺ (0.09 M) + water	1.2	15.8	
9		HCl (0.32 M) + Cl ⁻ (0.16 M) + Cu ²⁺ (0.08 M) + seawater	1.8	27.6	
	HCl (0.32 M) + Cl ⁻ (0.16 M) + Cu ²⁺ (0.08 M) + water	1.3	26.7		
10	HCl (0.32 M) + Cu ²⁺ (0.08 M) + seawater	1.5	37.7		
	HCl (0.32 M) + Cu ²⁺ (0.08 M) + water	1.0	35.6		
C	11	HNO ₃ (0.32 M) + seawater	0.6	15.5	
		HNO ₃ (0.32 M) + water	0.0	5.5	
	12	HNO ₃ (0.32 M) + Cl ⁻ (0.16 M) + seawater	0.8	23.7	
		HNO ₃ (0.32 M) + Cl ⁻ (0.16 M) + water	0.3	28.7	

* Initial pH ≠ 0.5.

3. Results and discussion

3.1. Experimental approach

3.1.1. System A-effect of chloride and cupric ions on the H₂SO₄ and seawater leaching media

In system A, the effect of Cl⁻ and Cu²⁺ ions on chalcopyrite leaching using a mixture of H₂SO₄ and seawater and/or pure water was investigated. Four sets of tests were performed as shown in Table 3. In the first two tests, leaching was done using 0.32 M H₂SO₄ (pH ≈ 0.5) prepared once in seawater and once in pure water. The second test was the same as the first but the leach solution was prepared at a higher concentration of H₂SO₄ (1.0 M) in seawater and pure water. Test number three was the same as the first but with the addition of 0.16 M Cl⁻ in the form of NaCl. In test four, CuCl₂ was added as oxidant and at a concentration of 0.08 M Cu²⁺. Cumulative copper extractions are presented in Figs. 1–3 for these experiments.

Fig. 1, test 1, shows a pronounced difference in copper extraction when using a seawater-based acid leach solution compared with pure water-based acid leach solution under the same experimental conditions. This indicates that the presence of seawater in the system has a positive effect on the copper extraction from chalcopyrite. This positive effect could be due to the formation of copper chloro-complexes as suggested by O'Malley and Liddell (1987).

Fig. 1 also presents the results of the test 2 which was conducted under the same condition as test 1 but at the different acid concentrations (see Table 3). The result was almost the same as the result presented in Fig. 1 for test 2 (for more details, see Section 3.2.1).

The addition of NaCl at a concentration of 0.16 M Cl⁻ also slightly increased (approximately 0.5%) the copper extraction in the pure water-based leach solution but deteriorated the extraction rate when acid was prepared using seawater (Fig. 2). This difference is tentatively attributed to the increase in the ionic strength of the solution as a result of the high Cl⁻ concentration and subsequent decrease in the mobility of the individual ions of solution to solid. In Fig. 3, the addition of Cu²⁺ significantly increased the amount of copper extraction in both seawater and pure water-based acid solution. The positive role of Cu²⁺ as an oxidant has been previously mentioned in the literature by

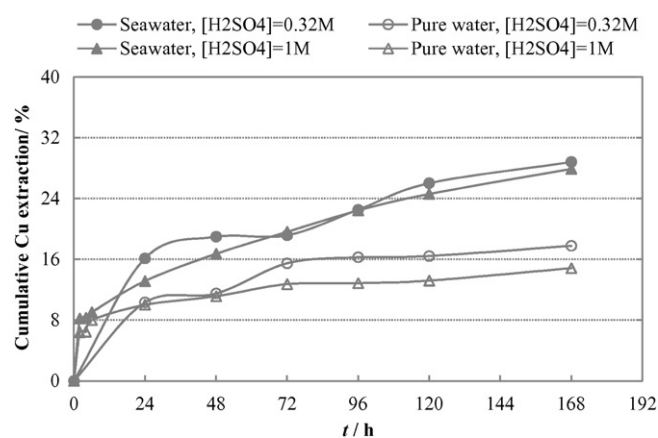


Fig. 1. Kinetic curves of H₂SO₄ system in seawater and pure water. Test 1 (●), initial pH ≈ 0.5 and test 2 (▲), initial pH ≈ 0.5, [H₂SO₄] initial = 1 M. (Test conditions for both systems: 7 days, 45 °C, 400 RPM, S/L = 100 g/L, P₈₀ of 62.5 μm).

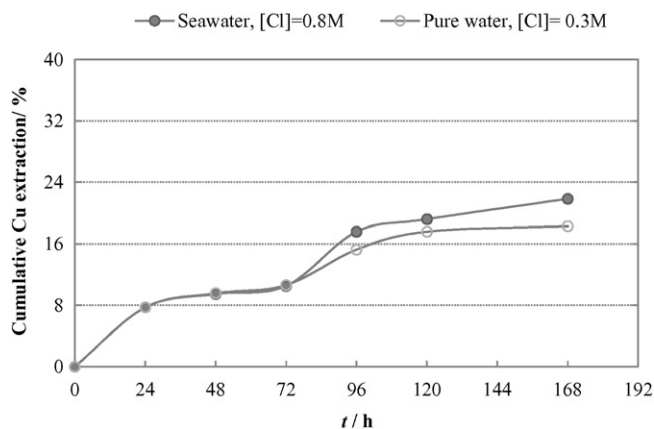


Fig. 2. Kinetic curves of $\text{H}_2\text{SO}_4 + \text{NaCl}$ system in seawater and pure water, test 3 (Test Conditions: $[\text{Cl}^-]$ added = 0.16 M, 7 days, 45 °C, 400 RPM, S/L = 100 g/L, P_{80} of 62.5 μm , initial pH \approx 0.5).

several authors (Al-Harabsheh et al., 2008; Lundström et al., 2005; Hirato et al., 1987; Guy et al., 1983). The effect of the oxidant on copper extraction in the pure water-based acid solution was slightly higher than in the seawater-based acid solution. This finding may also be attributed to the increase in the ionic strength in terms of increase in the Cl^- concentration.

3.1.2. System B-effect of chloride and cupric and/or ferric ions on the HCl and seawater leaching media

In system B, six sets of tests were performed to investigate the effect of Cl^- and Cu^{2+} and/or Fe^{3+} ions on chalcopyrite leaching using HCl and seawater and/or pure water. Test number 5 was performed using 0.32 M HCl (pH \approx 0.5) prepared in either seawater or pure water. Test number 6 was the same as test 5 but with the addition of NaCl at a concentration of 0.16 M Cl^- . Test number 7 was similar to test number 6, but with the further addition of 0.09 M ferric chloride (FeCl_3). Test number 8 was the same as test 5 with the addition of FeCl_3 at a concentration of 0.09 M Fe^{3+} . No additional NaCl was present in test 8. In test number 9, CuCl_2 at a concentration of 0.08 M Cu^{2+} was added to test 6. Test number 10 was the same as test 5 but with the addition of 0.08 M Cu^{2+} . As in test 8, no additional NaCl was present in test 10. Cumulative copper extractions are shown in Figs. 4–6 for the system B experiments.

Fig. 4 (test 5) presents a \approx 20% more copper extraction in seawater than in the pure water-based leach solution, indicating that the increased Cl^- concentration (Cl^- from acid and seawater) helps to improve the copper extraction rate. However, Fig. 4 (test 6) shows a contrary result, where the pure water-based acid leach extracts more

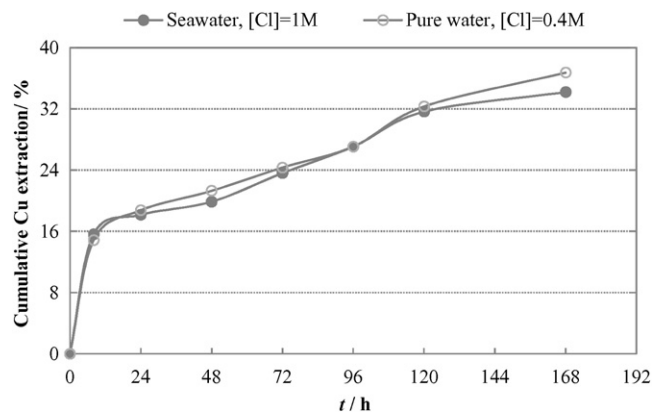


Fig. 3. Kinetic curves of $\text{H}_2\text{SO}_4 + \text{NaCl} + \text{CuCl}_2$ system in seawater and pure water, test 4 (Test Conditions: $[\text{Cu}^{2+}] = 0.08$ M, $[\text{Cl}^-]$ added = 0.16 M, 7 days, 45 °C, 400 RPM, S/L = 100 g/L, P_{80} of 62.5 μm , initial pH \approx 0.5).

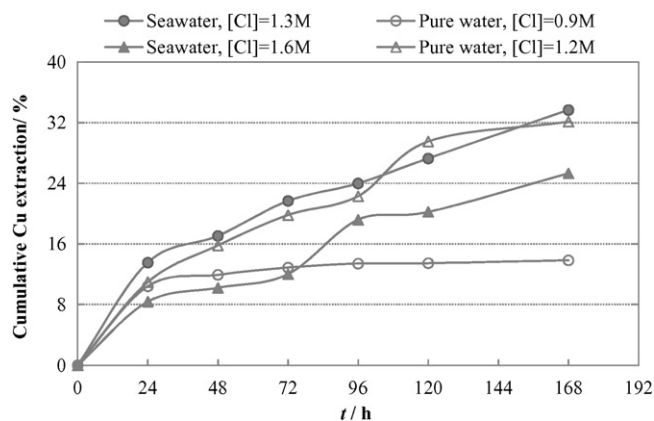


Fig. 4. Kinetic curves of HCl system in seawater and pure water, test 5 (●) and kinetic curves of HCl + NaCl system in seawater and pure water, test 6 (▲). (Test conditions for both systems: 7 days, 45 °C, 400 RPM, S/L = 100 g/L, P_{80} of 62.5 μm , initial pH \approx 0.5).

copper than the seawater-based acid leach, 32.1% versus 25.3% Cu. This is tentatively related to the presence of additional Cl^- (addition of NaCl to seawater) in the leach solution and the concomitant increase in the ionic strength. The comparison of the results of tests 5 and 6, both performed with pure water-based acid solution, indicated that the addition of NaCl increases copper extraction from 13.9% to 32.1% Cu. Conversely, in systems with seawater-based acid solution, the addition of NaCl decreases the copper extraction from 33.7% to 25.3% Cu. The same trend was observed in tests 1 and 3 when conducted using H_2SO_4 (see Section 3.1.1., Figs. 1 and 2).

As shown in Fig. 5 (test 7), leaching using HCl with seawater in the presence of NaCl and FeCl_3 does not significantly affect the copper dissolution rate. This finding indicates that there is an optimum Cl^- concentration to increase the copper extraction rate under the given test conditions.

Fig. 5 (test 8) shows the result of adding Fe^{3+} instead of Cl^- addition. It is interesting that the trends of the kinetic curves in both seawater- and pure water-prepared acid leach solutions are similar. This in turn even suggests a strong role for the Fe^{3+} ion in improving the leaching kinetics compared with the Cl^- ion. The same trend is observed with the addition of the Cu^{2+} ion, where the kinetic curves based both on seawater and pure water were similar only with a slight difference in the first 3 days of the test (Fig. 6).

Fig. 6 (test 10) shows very similar trends in the copper extraction where both curves show a positively increasing trend against the increasing leach time.

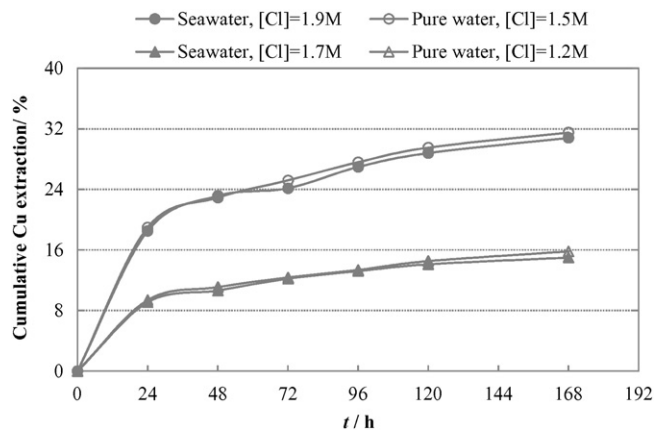


Fig. 5. Kinetic curves of HCl + NaCl + FeCl_3 system in seawater and pure water, test 7 (●), ($[\text{Cl}^-]$ added = 0.16 M), and kinetic curves of HCl + FeCl_3 system in seawater and pure water, test 8 (▲). (Test conditions for both systems: $[\text{Fe}^{3+}] = 0.09$ M, 7 days, 45 °C, 400 RPM, S/L = 100 g/L, P_{80} of 62.5 μm , initial pH \approx 0.5).

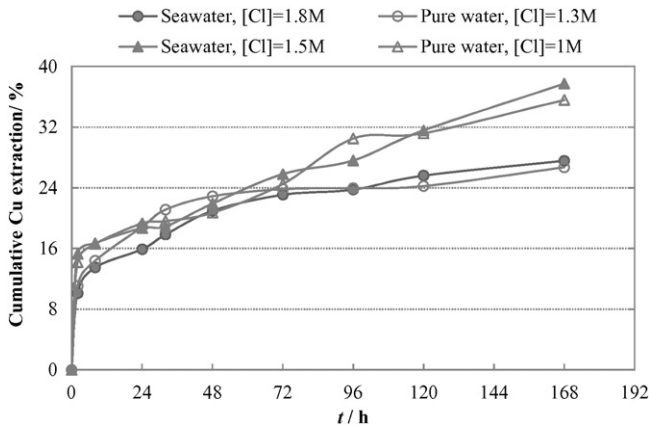
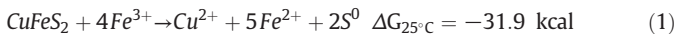


Fig. 6. Kinetic curves of HCl + NaCl + CuCl₂ system in seawater and pure water, test 9 (●), ([Cl⁻] added = 0.16 M), and kinetic curves of HCl + CuCl₂ system in seawater and pure water, test 10 (▲). (Test conditions for both systems: [Cu²⁺] = 0.08 M, 7 days, 45 °C, 400 RPM, S/L = 100 g/L, P₈₀ of 62.5 μm, initial pH ≈ 0.5).

The results of the experimental setups (Figs. 5 and 6) performed using tests 7–10 showed that seawater- or pure water-based acid leach brings about almost the same amount of copper extraction. Both seawater- and pure water-based leach solution in test 7 show higher copper extraction (15.5% more) compared with test 8, indicating that the presence of additional Cl⁻ ions helps to increase the copper extraction in the presence of Fe³⁺. However, the same trend was not observed in tests 9 and 10 in the presence of Cu²⁺ ion. The high Cl⁻ concentration in test 9 with both seawater- and pure water-based acid leaches was detrimental to copper extraction, as the copper extraction decreased approximately 9.5% compared to test 10.

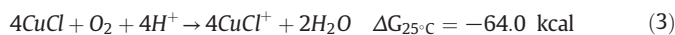
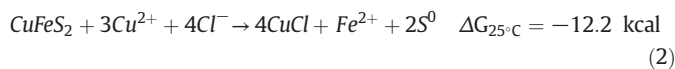
The results obtained performing tests 7 and 9 indicated that in the Cl⁻ media, leaching with the Fe³⁺ ion as an oxidant shows slightly higher copper extraction than using the Cu²⁺ ion as an oxidant (≈4%). In the absence of the Cl⁻ ion, tests performed with the Cu²⁺ ion show ≈21.25% more copper extraction than tests performed with the addition of Fe³⁺ ion.

According to the Domic (2001), for systems using ferric as an oxidant, the mechanism of the process can be explained by the following reaction:



A negative value for the standard Gibbs free energy of reaction ($\Delta G_{25^\circ\text{C}}$) simply indicates that the reaction as written is thermodynamically possible at 25 °C under atmospheric pressure. This does not explain reaction kinetics or mechanism of the system. The values of $\Delta G_{25^\circ\text{C}}$ were calculated using Outotec's Chemical Reaction and Equilibrium software HSC (version 6.0).

In the study of Hirato et al. (1987) using Cu²⁺ (CuCl₂) as an oxidant, the redox potential was observed to increase when the Cl⁻ concentration increases (improvement of the copper extraction). This mechanism can be explained by the following equations:



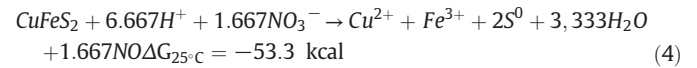
CuCl could be reoxidized with oxygen and acid to CuCl⁺. This was proposed by Herreros et al. (2006). The best result for copper extraction (≈37% Cu) in system B was corresponding to the test 10.

3.1.3. System C – effect of chloride on the HNO₃ and seawater leaching media

In system C (see Table 3), two sets of tests were performed to investigate the effect of Cl⁻ on chalcopyrite leaching using HNO₃ and seawater and/or pure water. Test number 11 was performed using 0.32 M HNO₃ (pH ≈ 0.5) prepared in either seawater or pure water. Test number 12 was the same as test 11 but with the addition of NaCl (0.16 M Cl⁻). Cumulative copper extractions are shown in Fig. 7 for these two experiments.

The nitrogen species, as nitrate and nitrite, is a strong oxidizing agent and their “catalytic” oxidant role in leaching of chalcopyrite at high temperature has been reported in the literature (Gok and Anderson, 2013; Sokić et al., 2009). Leaching of copper sulfide ores using the nitrogen species is known to accelerate the leaching kinetics and increase the total metal extraction (Anderson, 2003).

Fig. 7 (test 11) shows in general a low copper extraction, in both cases prepared in seawater and pure water, although the seawater-based acid leach shows better copper extraction (15.5%) than the pure water-based acid leach (5.5%). In leaching test 12, the increase in Cl⁻ concentration (addition of NaCl) increases the extraction rates of both pure water- and seawater-based leaches but the amount of copper leached by the nitric acid prepared in pure water (28.7%) was higher compared to the acid prepared in seawater (23.7%) (Fig. 7, test 12). This effect was the same as the effect observed in system A (tests 1 and 3), and system B (tests 5 and 6). Nitric acid, a powerful oxidant, helps to solubilize chalcopyrite as postulated by Prasad and Pandey (1998). This can be explained by Eq. (4):



Although the application of HNO₃ in the copper leaching process has some advantages such as being not corrosive on stainless steel equipment due to formation of oxide layer, however the nitrate-based leach solution presents other problems especially during subsequent solvent extraction stage (Watling, 2013). It should be noted that in most of the copper leaching processes at the industrial scale, using sulfuric acid has been given more priority due to the economical point of view.

3.2. Comparison of different acid leach systems

3.2.1. Effect of acid types

Cumulative copper extractions obtained using different acids were compared. Fig. 8 shows the comparison of the H₂SO₄ (system A – test 1), HCl (system B – test 5) and HNO₃ (system C – test 11), for both

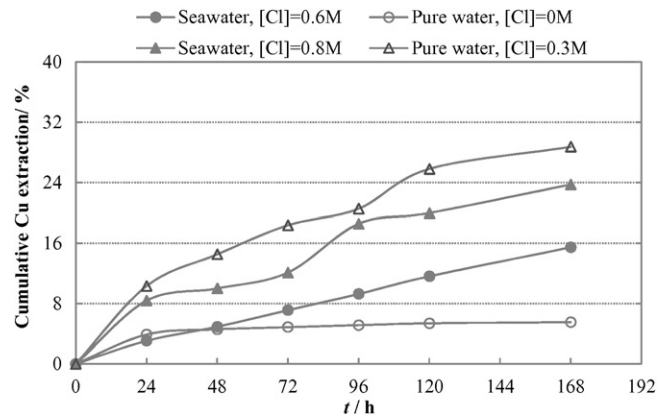


Fig. 7. Kinetic curves of HNO₃ system in seawater and pure water, test 11 (●) and kinetic curves of HNO₃ + NaCl system in seawater and pure water, test 12 (▲), [Cl⁻] added = 0.16 M (Test conditions for both systems: 7 days, 45 °C, 400 RPM, S/L = 100 g/L, P₈₀ of 62.5 μm, initial pH ≈ 0.5).

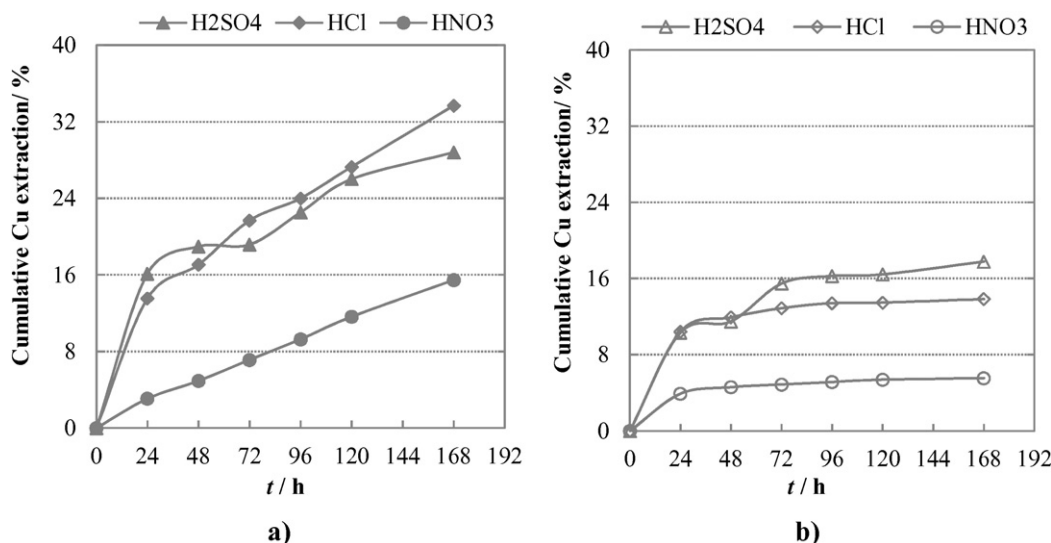


Fig. 8. Effect of different acids prepared in a) seawater; b) pure water (Test Conditions: System A – test 1, System B – test 5 and System C – test 11, 7 days, 45 °C, 400 RPM, S/L = 100 g/L, P_{80} of 62.5 μ m, initial pH \approx 0.5).

leach solutions, those prepared in seawater – (Fig. 8a) and those prepared in pure water (Fig. 8b).

As shown in Fig. 8a, b, the maximum copper extraction (33.7%) was obtained for system B – test 5, performed using HCl prepared in seawater. This was related to the presence of Cl^- ion, which increased the hydrogen ion activity (Puvvada et al., 2003; Dreisinger and Abed, 2002). Lower copper extraction was obtained in both seawater- and pure water-based acid leaches when HNO_3 was the leaching acid.

The effect of the H_2SO_4 concentration (0.32 M versus 1.0 M) was shown in Fig. 1 (system A – tests 1 and 2). In the seawater-based leach, the higher acid concentration does not necessarily equate to an increase in copper extraction. In the case of the pure water-based leach the higher copper extraction was achieved at lower acid concentration. Further investigation needs to be conducted to determine the optimum acid concentration and reason for this finding.

3.2.2. Effect of chloride (NaCl) addition

Cumulative copper extractions obtained using different acids and added NaCl were compared. Fig. 9a and b shows the comparison of system A – test 3, system B – test 6 and system C – test 12 using seawater-based and pure water-based leaches.

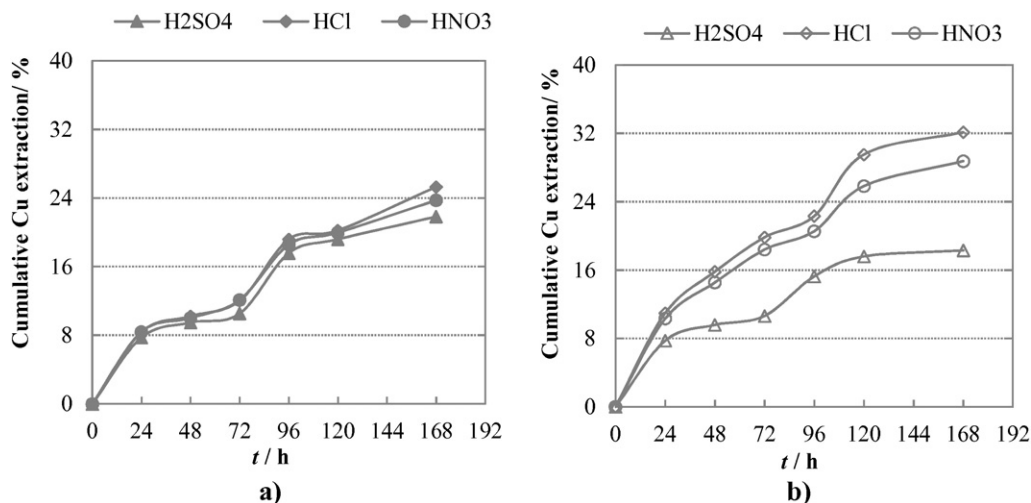


Fig. 9. Effect of different acids prepared in a) seawater; b) pure water, with addition of sodium chloride (test conditions: system A – test 3, system B – test 6 and system C – test 12, $[\text{Cl}^-]$ ion; NaCl = 0.16 M, 7 days, 45 °C, 400 RPM, S/L = 100 g/L, P_{80} of 62.5 μ m, initial pH \approx 0.5).

As shown in Fig. 9a, for all three different acids, in the presence of Cl^- ion, the seawater-based leach tests performed remarkably similarly. The kinetics curves for the system B - test 6 shows a maximum copper extraction of \approx 25.3% in 7 days. Relatively less copper was extracted when NaCl was added to the sulfuric and nitric acid systems.

In the case of pure water-based acid leaches (Fig. 9b), the best copper extraction was obtained from the HCl (system B – test 6, 32.1%). This is related to the presence of more Cl^- in the leach solution than in the other two leach solutions (tests 3 and 12). Comparing the copper extraction from tests 3 (18.3% Cu extraction) with 12 (28.7% Cu extraction) at the same Cl^- concentration (0.3 M Cl^-), the HNO_3 based leach performed slightly better than the test using H_2SO_4 . This finding is related to the stronger oxidation power of nitric acid.

3.2.3. Effect of the presence of added chloride and cupric ions

Cumulative copper extractions obtained using different acids in the presence of Cl^- and Cu^{2+} ions were compared. Fig. 10 shows the comparison of the extraction rates of the system A (H_2SO_4) – test 4 and system B (HCl) – test 9 using a seawater- and pure water-based acids.

In seawater-based acid leaches, the copper extraction in system A was 6% higher than system B. This figure increased to 10% when

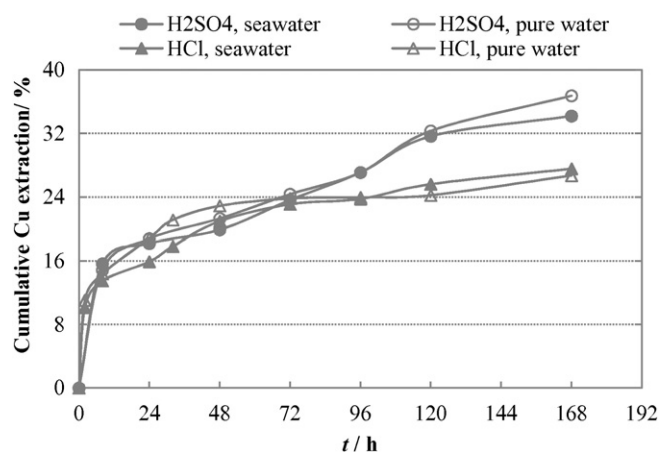


Fig. 10. Effect of different acids when added with chloride and cupric ions (test conditions: system A – test 4 and system B – test 9, $[Cu^{2+}] = 0.08$ M, $[Cl^-]$ added = 0.16 M, 7 days, 45 °C, 400 RPM, S/L = 100 g/L, P_{80} of 62.5 μ m, initial pH \approx 0.5).

extraction was done in acids prepared with pure water (see Table 3). Therefore, overall system A performed better than system B under the conditions studied in this work.

In system A – test 4, the higher the Cl^- concentration in the leaching solutions, the less copper extraction is obtained. This effect is tentatively related to the high ionic strength. However, in system B – test 9, the difference between copper leach rates was not much different among the high-chloride seawater-based leach (27.6% Cu) and the less chloride containing pure water based leach (26.7% Cu).

4. Conclusions

The arid climate in northern Chile has forced mining companies to seek out new water sources, and the only available new water source is seawater. In this study, the effect of seawater, containing approximately 18.8 g·L⁻¹ chloride ions, on chalcopyrite leaching was studied. Different types of acids including H₂SO₄, HCl and HNO₃ and oxidants (CuCl₂, FeCl₃) were prepared in chloride-rich seawater and tested against those prepared in pure water. The experimental studies showed the following:

- In the absence of oxidants and added sodium chloride, the leaching tests performed using seawater-based acid solution dissolved more copper than the pure water-based acid solutions. The addition of extra sodium chloride to the seawater-based acid declined the copper extraction. This was tentatively related to the increase in the ionic strength of the leach solution.
- In this study, the maximum copper extraction under the conditions studied was 37.7%, which was obtained from system B –test 10 leach, where HCl was prepared in seawater and contained cupric (Cu²⁺) as an oxidant. Copper extraction curves indicated that the extraction rates would improve if a longer leach time was given.
- Under the leaching tests condition in this study, the cupric chloride leaching of chalcopyrite effectively increases the copper extraction.
- Ferric chloride performed better only when NaCl was added to the system.
- The presence of added sodium chloride increased the copper extraction in system C where the acid is HNO₃.
- In the absence of oxidizing agents (Cu²⁺ and Fe³⁺), hydrochloric acid, prepared in seawater, extracted more copper than sulfuric and nitric acids.

Based on the results obtained in this work, we recommend further leach tests at higher temperatures and for extended leach times. It

would be useful the catalytic effects of other compounds to be investigated.

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