Leaching of low-grade chalcopyrite ore using Persian Gulf water

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Abstract
Water supply is becoming an increasingly important aspect of hydrometallurgical operations due to the water deficiency in arid regions. The consumption of fresh water in heap leaching of copper ores can be significantly reduced by adoption of the processes that can incorporate the salt water. In this research, the incorporation of the sulfate-chloride solutions in treatment of low-grade chalcopyrite ores at ambient temperature were investigated. Bottle roll leaching tests were performed to study the adoption of seawater at Sarcheshmeh copper mine. In this regard, the effect of the chloride ions on the dissolution behavior of copper, iron, manganese, and magnesium was studied. Results were shown that increasing the chloride concentrate can increase the dissolution of copper and reduce the acid consumption. Increasing the chloride concentration from 0 to 40 g/L, was shown to improve the recovery of copper from 10 to 20%. The dissolution rate of other impurities was however improved, consequently.

Keywords: Persian Gulf water, seawater, bottle roll test, low-grade chalcopyrite ore

Introduction
Chalcopyrite ($CuFeS_2$) is the most abundant primary copper ore. Currently, copper extraction from chalcopyrite is mainly done through pyrometallurgical routes[1]. However, due to the high operational cost and emission of sulfur dioxide with simultaneous copper-grade decay, the extraction of copper by hydrometallurgical processes is increasing[2]. Hydrometallurgical processing of copper usually consists of three main stages: leaching, solvent extraction, and electrowinning. Leaching with sulfuric acid is a conventional method for the dissolution of copper ores[1], but the dissolution rate of chalcopyrite is much slower as compared to leaching of copper secondary sulfides and oxides. Therefore, the economic acceleration of this dissolution is desirable.
Water scarce is a significant issue in hydrometallurgical processing, which prompts mining companies to search for alternative water sources[3]. Moreover, several countries around the world are suffering from water shortage and scarcity. Iran, similar to the most Middle-Eastern countries, is experiencing a serious water crisis. The dramatic water issues of Iran is rooted in rapid population growth, inefficient agriculture sector, mismanagement, and inappropriate remedies. Seawater is a looked-for alternate to freshwater. Therefore, the use of seawater in mineral processing and hydrometallurgical processes is increasing[4]. Seawater, on average, contains about 20 g/L chloride ions in the form of different chloride salts[5]. Chloride is one of

the additives that can greatly improve the dissolution rate of chalcopyrite[6, 7]. Thus, seawater can be used as an alternative to freshwater and also as an improver for leaching of chalcopyrite. A major portion of Iranian copper mines is located in the arid and semi-arid central south of Iran. In order to meet the water demand of the existing plants, there have been developing plans to transmit Persian Gulf water to the consumption sites. Currently, before transmission of the Persian Gulf water to the determined destination, the water is treated for desalination in order to remove the salts components, especially chloride.

Chalcopyrite dissolution is known to have slow kinetics. The slow kinetics is attributed to the formation of the non-porous passive layer of sulfur on the outside layer of the chalcopyrite particles, which inhibits further dissolution of copper. The presence of the chloride ions in the copper leaching solution can affect the morphology and porosity of the generated elemental sulfur on the surface of the chalcopyrite particles. The leach residues resulted from leaching with the sulfate-chloride solution are generally more porous and have a larger microporous area and volume compared to the residues obtained by leaching with only sulfate solution[8].

The presence of chloride ions in the solution can change the aqueous species of copper, and chloro-complexes of copper can be formed. Apart from changing the morphology of the elemental sulfur, a redox couple of cupric (Cu^{2+}) to cuprous (Cu^{+}) (as chloride complexes) can also affect the dissolution of chalcopyrite. Because of the greater stability of chloro-complexes of Cu^{+} compared with Cu^{2+}, dissolution of chalcopyrite can happen[7].

There has been a vast amount of published work on effect of the chloride ions on the dissolution behavior of chalcopyrite. It has been shown that along with chloride concentration, temperature of the solution plays a vital role in the dissolution of the chalcopyrite. In the approximate temperature of 90 ^{o}C, increasing chloride concentration above 0.5 M has little impact on the leaching of chalcopyrite[6, 7, 9]. Due to suitable chloride concentration (>0.5 M) in the Persian Gulf water, its application for leaching of chalcopyrite can be propitious. However, concentration of the impurities, especially chloride, in the pregnant leach solution will be increased. Contamination of the chloride in the electrolyte adversely affects the electrowinning of copper; therefore, removal or controlling chloride concentration before electrowinning, during solvent extraction stage is essential. Most of the previous works have investigated the effect of chloride ions on the dissolution of chalcopyrite in the laboratory scale. Bottle roll leach is a dynamic type of leaching test which is performed to simulate the results obtained from leaching in an agitated tank at an industrial scale. Thus, the present work has been carried out to evaluate the effect of the chloride ions and other impurities on the bottle roll leach of copper from low-grade chalcopyrite in order to obtain a proper perspective on the use of seawater on leaching of chalcopyrite at a larger scale.

Experimental

Materials

The low-grade chalcopyrite used in this research was received in a pulverized condition (particle size below 38 μm) from Sarcheshmeh mine, Iran. To determine the chemical composition of the mineral, a representative sample was first digested in aqua regia, and then copper, iron, manganese, and magnesium content of the ore were analyzed using atomic absorption spectroscopy AAS (Agilent 200 series, United States). The results are represented in Table 1.

Table 1. Chemical composition of the ore

Element	Cu	Fe	Mg	Mn
Amount %	0.32	15.45	0.75	1.82

The chemicals used in this research were all analytical grade. Sulfuric acid (>95 pure) and sodium chloride (>99 pure) were purchased from Merck, Germany.

Bottle Roll Tests

Bottle roll tests were conducted in the 2.5-liter bottles. Overall, four leaching tests were designed to evaluate the effect of the chloride ions on the dissolution of copper and other impurities from chalcopyrite. The main variable in the leaching tests was chloride concentration. The effects of the chloride on four different levels of 0, 10, 20, and 40 g/L were studied. The chloride concentration was adjusted by adding the required amount of sodium chloride to the distilled water. The constant leaching conditions in all experiments are reported in Table 2.

Table 2. Constant leaching parameters

Constant leaching conditions	
Solid weight (gr)	150
Solution Volume (ml)	700
RPM	90
T (ºC)	25
H_2SO_4 concentration (g/L)	6
pH	1
Time (days)	4

A set of new tests were designed to investigate the application of Persian Gulf water for leaching of chalcopyrite. The leaching conditions of the newly designed tests were as same as the previous tests; however, instead of distilled water, seawater was used. The effect of seawater on leaching of chalcopyrite was studied on two different levels of chloride concentration: 20 and 40 g/L. The chemical composition of the Persian Gulf water sample is shown in Table 3. The solution containing 40 g/L chloride was prepared by evaporation of a specific volume of the seawater to the half.

Table 3. Chemical composition of Persian Gulf water, concentrations are in ppm

Al	As	Bi	Ca	Cl	Cu	Fe
0.20	0.10	0.15	426	21400	0.50	<0.1
K	Mg	Mn	Na	P	Pb	S
420	1484	<0.1	11900	1	0.1	991

pH and Eh of the solutions were measured three times per day (overall 12 times). To measure the Eh, an Ag/AgCl reference electrode (3 M KCl) was used. After pH and Eh measurement, the pH of the solutions was brought down to 1 by sulfuric acid (95 v/v%). After pH adjustment, the amount of the added acid was measured to estimate the acid consumption per tonne of ore. After four days, the copper, iron, manganese, and magnesium content of the leach solution were analyzed by AAS.

Results and discussion

The effect of the chloride concentration on the leaching of copper is presented in Figure 1. As it is evident, by increasing the concentration of the chloride, the recovery of copper has increased. In the absence of chloride ions in the solution, the copper recovery after a four-day period was only about 10%, but, as the chloride concentration increased up to 40 g/L, leaching yield of copper doubled over the same period.

The same trend was observed about dissolution behavior of iron, manganese, and magnesium. Increasing chloride concentration resulted in the higher dissolution of these elements. The effect of chloride concentration on the recovery of Fe, Mg, and Mn are shown in Figures 2, 3, and 4. Some previous researches have reported that the presence of sodium ions during leaching could result in the precipitation of Fe^{3+} as natrojarosite, which inhibits the dissolution of chalcopyrite[5, 9]. Thus, the lower recovery of copper and iron can be expected. However, in the present work, the use of low potential (<400 mV vs Ag/AgCl 3M KCl) and pH (<2) have hindered the formation of natrojarosite[11].

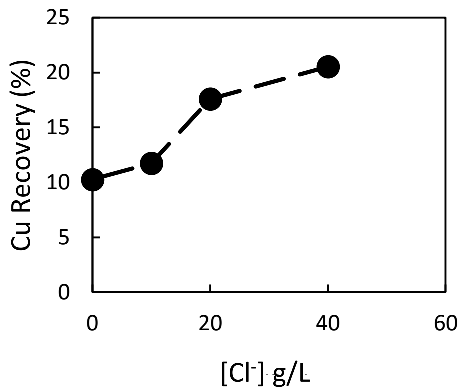

Figure 1. Effect of chloride concentration on copper recovery after 4 days at T=25 ºC and pH=1.

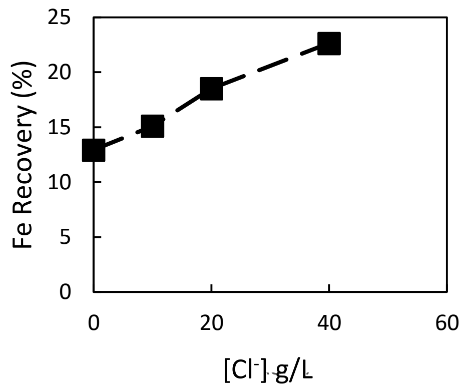

Figure 2. Effect of chloride concentration on Fe recovery after 4 days at T=25 ºC and pH=1

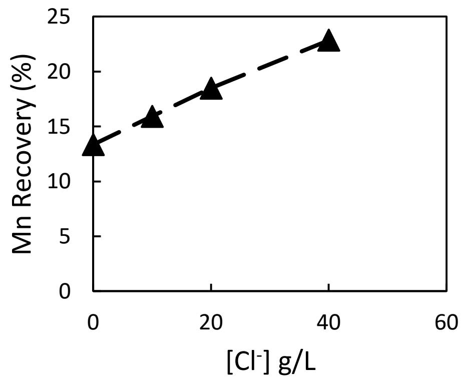

Figure 3. Effect of chloride concentration on Mn recovery after 4 days at T=25 ºC and pH=1

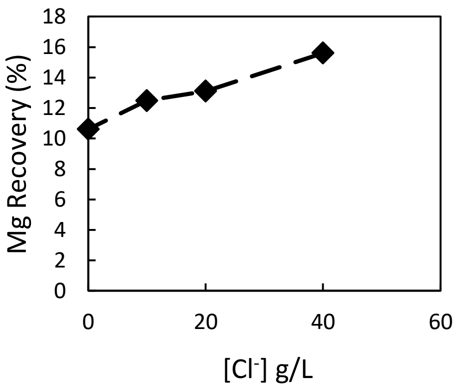

Figure 4. Effect of chloride concentration on Mg recovery after 4 days at T=25 ºC and pH=1

Acid consumption

In order to estimate the effect of the chloride ions on acid consumption, after pH adjustments, the amount of the added acid to the solution was measured. The pH in all the experiments set to be 1. The presence of the chloride ions in the solution resulted in a lower initial pH of the solution, which significantly decreased the acid consumption. Figure 5 compares the acid consumption estimation per one tonne of the used ore. Increasing chloride concentration significantly decreased the acid consumption since a lesser amount of sulfuric acid for pH adjustment was required. Presence of the chloride ions in the solution results in a higher hydrogen ion activity.

Figure 6 shows the required potential for different reactions in the system. The thermodynamic data are obtained from HSC software (version 6, Outokompo research) The stated potential can be affected by different factors such as pH, temperature, and concentration of the species.

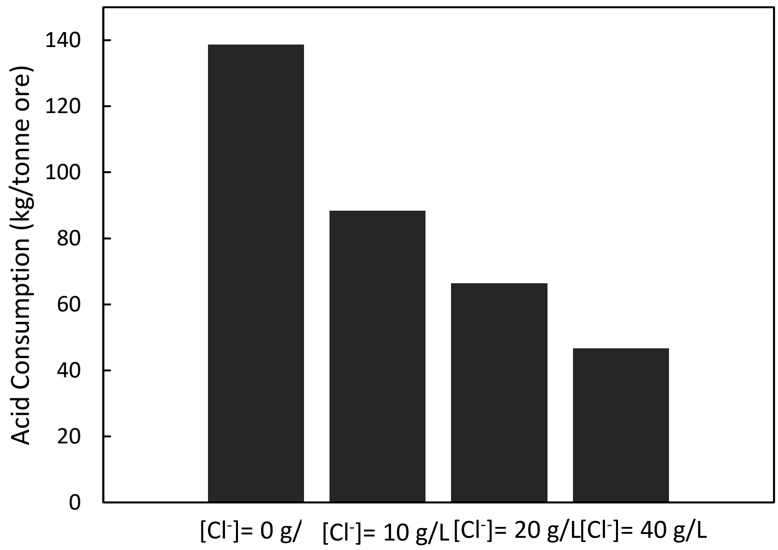

Figure 5. Effect of the chloride concentration on acid consumption

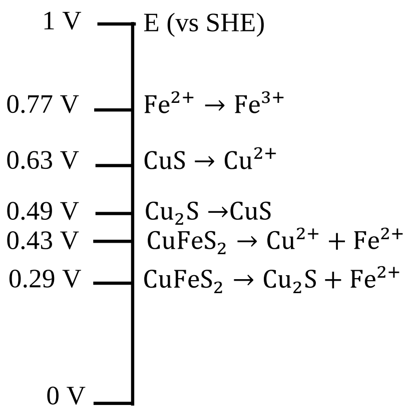

Figure 6. Required potential for dissolution of some copper species.

Application of Persion Gulf water

For comprehensiveness of the research, leaching tests in the presence of the chloride were repeated; however, in the new tests, instead of the addition of sodium chloride to distilled water, for adjustment of the chloride concentration, a real sample of the Persian Gulf water was used. The obtained results are shown in Figures 7 and 8. Recoveries of the Cu, Fe, Mn, and Mg were all lower in seawater compared to the distilled water. This could mainly be due to the presence of the other impurities. However, the recovery of the Cu was not much different, which can provide another indication for the successful industrial application of seawater for leaching of chalcopyrite.

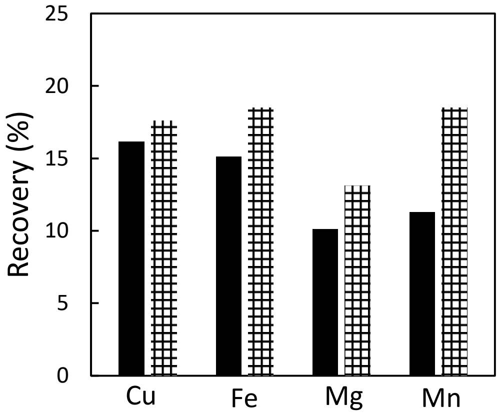

Figure 7. Effect of the water quality on recovery of Cu, Fe, Mg, and Mn in the presence of 20 g/L of chloride ions. Seawater, Distilled water + 20 g/L of chloride ions

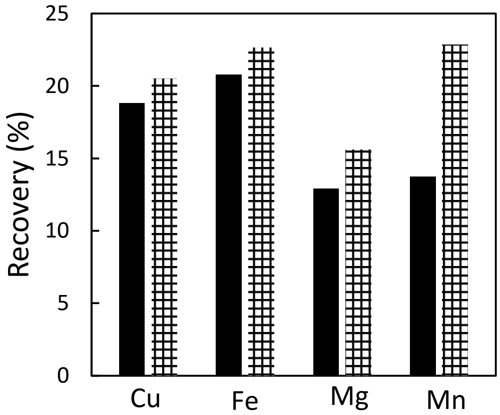

Figure 8. Effect of the water quality on recovery of Cu, Fe, Mg, and Mn in the presence of 40 g/L of chloride ions. Concentrated seawater, h Distilled water + 40 g/L of chloride ions

Conclusions

A mixed chloride-sulfate bottle roll leach process was applied to evaluate the effect of the chloride concentration on the dissolution behavior of low-grade chalcopyrite. The result showed that increasing chloride concentration positively affects the dissolution rate of copper. However, the dissolution of other impurities was also improved. Moreover, using chloride-sulfate leach solutions resulted in lower acid consumption.

Acknowledgements

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