Leaching of Copper Ores: Effects of Operating Variables

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ABSTRACT

Leaching of copper from a Jordanian copper ore has been studied using a stirred batch reactor with hydrochloric acid as the main lixiviant, under the following conditions: temperature 25 – 45 °C, acid concentration 0.05 – 0.2 N, particle size 462 – 1850 µm, stirring speed of 700 – 1000 rpm, and solid/liquid ratio of 1 – 4 g/L. It was found that the rate of leaching of copper ore with hydrochloric acid or sulfuric acid, increases with temperature and acid concentration, while it decreases with increasing particle size. At the same operating conditions, leaching with sulfuric acid gave slightly greater conversion than leaching with hydrochloric acid, particularly at operating conditions of high temperature, high acid concentration, and small ore particle sizes. A maximum copper dissolution of about 87 % can be recovered at a leaching temperature of 45 °C, 462 µm particle size, 0.2 N hydrochloric acid, 1.0 g/L solid to liquid ratio, and 1000 rpm stirring speed. Keeping all these operating parameters constant while decreasing the hydrochloric acid concentration to 0.05 N will decrease the copper dissolution to 83 %. On the other hand, decreasing the leaching temperature to 25 °C while keeping the other parameters fixed at 0.2 N, 1.0 g/L solid to liquid ratio, 1000 rpm stirring speed, and a particle size of 462 µm decreases the copper dissolution to 80 %.

Key words: Leaching, Copper Ore, Lixiviant, Particle Size, Surface Reaction, Pore Diffusion

1. INTRODUCTION

Materials are abundantly present and available in nature in the form of ores, which are extracted and undergoes different manufacturing process, one of these processes is leaching [1]. Leaching refers to the extraction of a soluble constituent from a solid by means of a solvent. The process may be employed either for the production of a concentrated solution of a valuable solid material, or in order to free an insoluble solid from a soluble material with which it is contaminated. There are many factors influencing the rate of leaching such as temperature, lixiviant concentration and type, particle size and agitation speed of the fluid-particles mixture [2-5].

Heterogeneous reactions between liquids and solids, play a major role in materials processing industries which encompass a broad range of operations, such as extractive metallurgy. The chemical interactions could involve simple single-step or multistep reactions with or without changes in the volume of the phases and heat effects. The particles themselves could be porous or nonporous or may become porous during the reaction. They may also change their size, and significant alterations in the structure might accompany the chemical reaction[6].

The basic steps when a solid particle reacts with a liquid species may include liquid-phase mass transfer, diffusion inside the pores, absorption of reactants, chemical reaction and desorption of products. Although these steps occur in succession, any one or more of these might be rate limiting [7].There are many variables affecting leaching processes. The first of these variables is the boundary layer around the solid particles, when a solid in contact with a liquid is covered by a stagnant film of liquid through which reactants have to diffuse before they reach the reaction location. This film is called the Nernst's boundary layer, its existence is due to two hydrodynamics factors [8]; the adhesion of the liquid to the surface and the viscosity of the liquid.

The second variable is the fluid velocity, when the process is film diffusion-controlled, for a stirred solid/liquid reaction system, increasing the stirring speed sometimes increases the rate of dissolution or reaction. And the thickness of the boundary layer decreases with increasing speed of stirring. In such case, the rate of reaction can be usually expressed as a function of speed. The rate of reaction, however, does not increase indefinitely with increasing speed of stirring because other factors such as the formation of air pockets in the liquid usually interfere. The third variable is the reaction temperature which plays an important rule because chemical reaction velocity constants are experimentally dependent on temperature according to Arrhenius equation [9, 10], also the pore diffusion coefficient depends on temperature according to Erying equation[11]. A diffusion-controlled process is characterized by being slightly dependent on temperature while chemically controlled process is strongly dependent on temperature [12].

Copper is considered as one of base metals in our daily life and has high economic importance. Over 80% of the primary copper production comes from pyro-metallurgical treatment of copper ores [13-15].In Jordan, copper ores were mined on

both sides of Wadi Araba since prehistoric times and continued with some interruptions until the early medieval period of history. After at least 2500 years of activity, mining appears to have ceased and the ancient sites were forgotten until almost the 20th century [16]. At the east side of Wadi Araba, the first systematic geological investigations began in 1961. The natural Resources Authority carried out, in collaboration with foreign companies, Bureau de Recherches Geologiques et Minieres (BRGM) [17] and Seltrust Engineering Limited (SEL)[18], a number of studies on the mineral deposits in Jordan. These studies have established the location of many large deposits of copper ores of various compositions. Mineralization in the area is limited to two sedimentary rock units. The first is white fine-Sandstone Unit (WFS), which contain a copper mineralization changing in intensity very rapidly within short distance. The second is dolomite-Limestone-Shale Unit (DLS), in which the manganese and iron-bearing copper minerals are mainly observed on top of and within the uppermost dolomite beds. The main copper minerals associated with the DLS unit are: malachite, chrysocolla, placheite, cuprite, tenorite, atacamite, crednerite (CuO, Mn_2O_3) and delafossite (Cu_2O, Fe_2O_3). Detailed geological surveys and exploration activities resulted in a total estimate of 60 million tons of copper ore reserves, with an average grade of 1.63 % [17].

There are many studies published in the literature on the leaching of non-Jordanian copper ores using various lixiviant. For example, Madsen et al. [19], developed a shrinking core model to describe the leaching of copper from sulfide ores using acidic ferric sulfate. Bryden [8], studied the leaching of copper from malachite using the ammonium sulfate solution and showed that the mixed kinetics model is suitable for their experimental data. Benner and Roman [20], derived a shrinking core model for the leaching of sandstone malachite ore with H_2SO_4. The reaction was controlled by the diffusion of hydrogen ions through the rock. Kuzmanvska et al. [21], applied the mixed kinetics model to the leaching, by percolation method, of low-grade chalcocite-covellite ore using sulfuric acid as lixiviant.Few studies have been done on the leachability of the Jordanian copper ores. The French group BRGM [17] and Seltrust Eng. Ltd. [18] carried out a study into the feasibility of exploiting the copper deposits in Wadi Araba. The study showed that the percentage of acid soluble copper, on the average, is about 70-80 % of the total copper content. A series of bench scale tests was carried out to determine the response of the various samples to sulfuric acid leaching [18]. The first series of tests investigated the vat leaching characteristic: three separate size ranges, -40 +20 mm, -20 +10 mm, and -10 +2.5 mm, were prepared with sulfuric acid solution. The results showed that, for the coarse size range, copper extraction did not exceed 50% in 32 hours. The conclusion attained was that it was unlikely in practice that high recoveries by percolation leaching would be obtained from the samples with highly carbonated gangue.A second series of agitation leaching tests was then carried out which investigated size of particles, acid strength and leaching time. The results showed that copper extraction ranging from 3.4 - 22.2 kg H_2SO_4/kg copper. Overall conclusions from the

agitation leaching tests were that average copper extractions of 75% would be realistic for the low carbonate samples but only about 50% for highly carbonated samples. Another series of alternative techniques was then studied in an attempt to improve on the copper extraction, including leaching with SO_2 and leaching with ammonia or sulfuric acid after reduction roast. The results showed that only leaching with SO_2 increased copper extraction significantly. This method, however, resulted in an uneconomical consumption of sulfur. The above studies on Jordanian copper ores did not present any mathematical models to describe the leaching process. Al-Sayyed [22], however, studied the leaching of copper from a Jordanian copper ore from Wadi Araba in a batch reactor using sulfuric acid solution. He found that the shrinking core model is suitable for fitting his experimental data.

There is scarcity of detailed information on the leachability of the Jordanian copper ores using different lixiviants. The objective of current article is to present the effect of the operating parameters on the leaching process of copper from a Jordanian copper ore, in a batch reactor using hydrochloric acid as the main lixiviant. For comparative purpose, however, some experiments were carried out using sulfuric acid solution. The kinetics and modelling of the leaching process will be presented and discussed in another article.

2. MATERIALS AND METHODS

2.1 Equipment

The experimental arrangement is shown in figure 1, and it consists of a 1-liter nominal capacity Pyrex glass rounded bottom flask with three necks carrying a thermometer, a stirrer, and a sampling device [23]. The stirrer, made of Teflon, consists of a 25 cm long shaft of 1 cm diameter with two 3×0.5×1 cm blades at its end. The stirrer passes through a glass tube which fits tightly into a rubber stopper, to separate the rotating shaft from it. The stirrer is driven by a variable speed electric motor, IKA-WERK type RW 20, and can give a maximum stirring speed of 1000 rpm without generating excessive vibrations and large temperature rise. The reactor temperature was maintained at the desired temperature within ± 0.5 °C using a stirred water bath, Techne model TU16A.
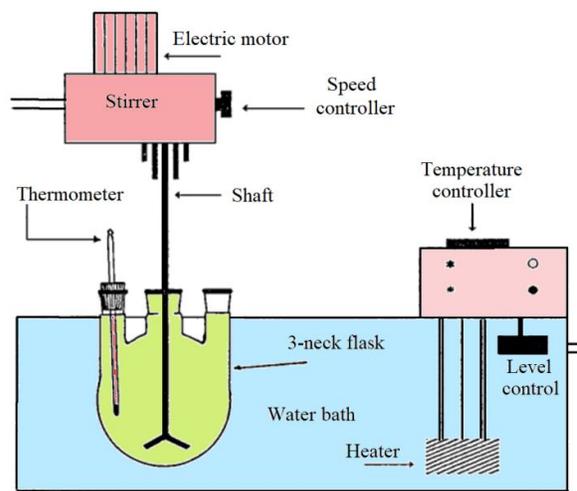
Figure 1: Experimental setup for copper ore leaching

2.2 Sampling Device

The sampling device, figure 2, is calibrated to deliver 5 mL solution, and has a fritted glass end for filtering the reaction solution. The fritted end stops particles greater than 42 μm from passing into the sampling pipette. The sampling device, when connected to a vacuum pump, Gerb. Becker type WB 71G4S, decreases the time needed for drawing off liquid samples from the reaction flask and allows obtaining five samples during the first two minutes of the reaction. By manipulated the 2-way and 3-way valves to appropriate positions, drawing off or delivery of the sample can be achieved easily [23].
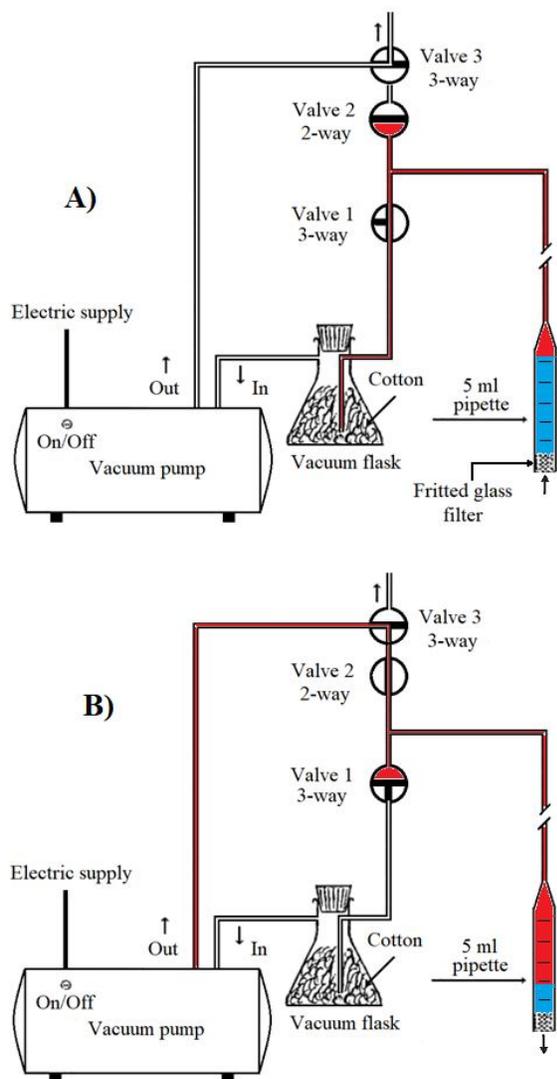
Figure 2: Sampling device arrangement; A) with valves arranged to draw off sample B) with valves to deliver sample

2.3 Materials Preparation

A copper ore sample has been supplied by the Natural Resources Authority-Jordan from different locations in Wadi Araba. The ore is whitish beige, medium hard, medium crystalline, and fractured dolomite with copper disseminations. Enough amounts of the ore was grounded using a jaw crusher, Retch model BBIA. The ground sample was then classified to different sizes using standard sieves and a shaker, manufactured by Pascall Engineering. Three sizes of each ore, -500 +425, -1200 +1000 and -2000 +1700 μm, were chosen for leaching studies. Using the definition of the arithmetic average [24]

$$D_{Pi} = \frac{D_{small} + D_{large}}{2}$$

The average particle sizes used in this study are 462, 1100 and 1850 μm, respectively. Samples from the chosen ore particles were then analyzed spectrophotometrically for copper and other elements. The method used for the analysis involved digestion of the particles in aqua regia ($HNO_3:H_2O:HCl$ with a volume ratio of 2:2:1), dilution with distilled water and analysis of the solution for the required elements. The analysis was performed using atomic absorption spectrophotometer, SP9 Pye Unicam type. Table 1 shows the average results of the replicate analysis for the copper ore used in the current study. The table also shows the densities of the ores particles.

Table 1: Average analysis of the copper ore used in the study

Particle size μm	Cu %	Mn %	Ca %	Fe %	Al %	Density g/cm³
462	4.06	0.601	0.235	0.136	0.364	2.55
1100	5.05	0.578	0.106	0.163	0.395	2.55
1850	8.36	0.47	0.082	0.203	0.503	2.57

2.4 Studied Variables

The experimental program was planned to study the effects of stirring speed, solid-to-liquid ratio, temperature, acid type and concentration, and particle size. To decrease the effect of the diffusion through the boundary layer, stirring speed was increased from a low value, 700 rpm, which is sufficient to suspend freely the largest particles, to a high value, 1000 rpm. Experiments were performed at three temperatures 25, 35 and 45 °C, which is a suitable range, because Wadi Araba is a hot region in Jordan, and its climatic conditions are generally of low rainfall, mild winters and hot summers . The temperature reaches 40 °C in summer, so, if a copper leaching plant is established in the Wadi Araba area, and since most leaching processes are done near climatic temperatures, the kinetics data obtained at the chosen temperature range will be useful in operating and designing the plant. Hydrochloric acid was used as the main lixiviant in this study. In addition, for comparative purposes, some experiments were done using sulfuric acid solution.

2.5 Experimental Procedure

For a given experiment, one liter of acid solution (hydrochloric or sulfuric acid) is prepared with the desired normality then poured into the reaction vessel. The water in the heating bath was heated and stirred until the desired constant temperature was attained. When the reaction solution

equilibrated at the desired temperature the solution in the reaction vessel was agitated, at the desired stirring speed. The sample of the ore of the required particle size, was accurately weighted, using Sartorius model 2007MP balance, and quantitatively transferred into the reactor, at the same time of pressing the start button of a stopwatch.

Samples from the reactor were removed at different predetermined times using sampling device. Each sample was poured into a marked flask, stoppered and kept for copper analysis by atomic absorption technique. From the copper ion content in the sample solution, as measured in ppm, the total copper ion content in the reaction solution was calculated taking into consideration the change in the volume of the reaction solution as successive samples were withdrawn. The total copper ion content in the reactor at any particular instant during the reaction, divided by the amount of copper in the ore, initially charged into the reactor, gave the copper dissolution percentage (X_{Cu}). In some experiments and for chosen sample solutions, analysis was done for other elements: Manganese Mn, Aluminum Al, Iron Fe and Calcium Ca. The results of these measurements will be used in the acid consumption calculation.

3. RESULTS AND DISCUSSIONS

Five variables and their effects on the rate of leaching of copper from its copper ores were taken into consideration, and are reported below.

3.1 Acid Consumption

During the analysis, some samples were analyzed for Cu, Mn, Ca, Fe, and Al, at different intervals of time. These results, Tables 2 and 3, were used to estimate HCl acid consumption, since calculations based on measuring the pH of the solution cannot be used because the variations in the pH of the solution are very small and are within the precision of the measuring instrument. An approximate acid consumption was determined from the concentration of different elements in the reaction solution. Some of the elements which are found in the copper ores are in the form of Cu^{+2}, Mn^{+4}, Ca^{+2}, Al^{+3}, and Fe^{+3}, so when these elements react with HCl to form the corresponding chlorides, each mole of Cu^{+2} or Ca^{+2} needs 2 moles of HCl, while one mole of Mn^{+4} needs 4 moles of HCl and each mole of either Al^{+3} or Fe^{+3} needs 3 moles of HCl. Thus using the conversion for each of the above mentioned elements, acid consumption needed to react with each element can be calculated according to the following equation:

$$HCl \ (g) \ needed \ = \frac{FC \times MO \times MYO \times SL \times Mwt \ HCl}{Mwt \ Y}$$

where: FC is the percentage dissolution of Y, MO is the mass of the ore in the reactor, MYO is the mass fraction of element Y in the ore, SL is acid to element Y mole ratio, and Mwt is the molecular weight.

Using the values presented in Table 1 and Table 2, a sample calculation for the acid consumption at 120 min reaction time under the reaction conditions indicated in Table 2 can be written as:

HCl needed for

$$Cu = \frac{0.7568 \times 1 \times 0.0406 \times 2 \times 35.5}{63.5} = 0.0343 \ g$$

$$Mn = \frac{0.0585 \times 1 \times 0.006 \times 4 \times 35.5}{54.9} = 9.09 \times 10^{-4} \ g$$

$$Ca = \frac{0.3267 \times 1 \times 0.00235 \times 2 \times 35.5}{40} = 1.36 \times 10^{-3} \ g$$

$$Fe = \frac{0.313 \times 1 \times 0.00136 \times 3 \times 35.5}{55.8} = 8.1 \times 10^{-4} \ g$$

$$Al = \frac{0.4955 \times 1 \times 0.00364 \times 3 \times 35.5}{27} = 7.11 \times 10^{-3} \ g$$

Total HCl consumed $= 0.0343 + 9.09 \times 10^{-4} + 1.36 \times 10^{-3} + 8.1 \times 10^{-4} + 7.11 \times 10^{-3} = 0.0458 \ g$

Two experiments were done to determine the acid consumption, Tables 2 and 3. During the maximum leaching time used in the present study, 2 hr, the acid consumption was about 0.09 g of HCl. This acid consumption, Table 3, occurred at the most severe reaction conditions, namely: 45 $^{\circ}$C and 0.2 N HCl. Knowing that the masses of the concentrated HCl of concentrations 0.05, 0.10, and 0.2 N charged into the reactor is 5.154, 10.307, and 20.614 g, respectively, it can be concluded that the percent of the acid consumed is very low and does not exceed 1 %. Accordingly the reaction environment around the solid particles in the reactor during the reaction time is almost uniform.

In their study, Lui et al. [25] used dilute sulfuric acid to recover copper from coper oxide ore by heap leaching. The results show that heaps of -40 mm ore leached for 68 days produced a copper leaching rate of up to 85.8% and the consumption of the dilute sulfuric acid was 24.2 kg per ton-ore. In another study, Araya et al.[26] reported dilute H_2SO_4 consumption of 122.6 kg/tone of copper ore, the ore was crushed and milled to a particle size below 150 μm in this study. Azmayandeh et al. [27] investigated the acid consumption in a heap leaching process to recover copper from low grade oxide-sulfide copper ore. The authors reported that a weak sulfuric acid consumption of up to 54 kg per ton of ore was needed to recover about 59 % of the copper exist in the ore.

Table 2 : Elements percentage dissolution at 45 °C, 1000 rpm, 1.0 g/L solid to liquid ratio, 0.05 N HCl, and 462 μm particles

Time (min)	X_{Cu} %	X_{Mn} %	X_{Ca} %	X_{Fe} %	X_{Al} %	Acid consumed (g)
15	50.82	2.07	18.29	8.43	19.94	0.028
40	68.76	3.6	25.2	17.28	30.99	0.0373
120	75.68	5.85	32.67	31.29	49.55	0.0458

Table 3 : Elements percentage dissolution at 45 °C, 1000 rpm, 1.0 g/L solid to liquid ratio, 0.2 N HCl, and 1850 μm particles

Time (min)	X_{Cu} %	X_{Mn} %	X_{Ca} %	X_{Fe} %	X_{Al} %	Acid consumed (g)
15	32.35	3.25	40.76	6.12	34.74	0.0395
40	53.04	4.6	45.85	20.19	48.4	0.0608
120	63.71	6.3	51.89	42.76	54.43	0.0871

3.2 Stirring Speed Effect

It is known that for particles of different sizes reacting under similar conditions, the importance of diffusion effects through the boundary layer film in controlling the overall rate of reaction is reduced as the particles of unchanging size are increased in size[9]. Accordingly the smallest particles were used in this investigation to determine the minimum stirring speed beyond which the effect of film boundary layer surrounding the ore particles can be neglected in determining the overall rate of leaching.

The effect of the impeller speed was studied, using particle size of 462 μm of ore No. 1, and under the experimental conditions: temperature of 25 °C, HCl concentration of 0.1 N and solid to liquid ration of 1.0 g/L. Stirring speed was varied from 700 to 1000 rpm and the results are shown in Figure 3.To check for a significant difference between conversions at different stirring speeds, a statistical test, Wilcoxon signed rank test [28], has been implemented. The average values of copperconversions at stirring speeds of 700, 900, and 1000 rpm, used in this analysis, are show in Table 4.
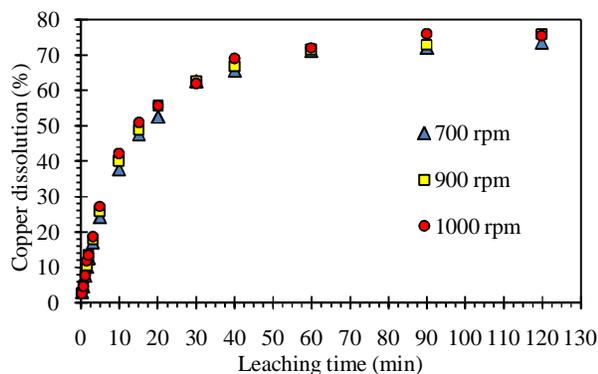
Figure 3 : Copper dissolution as a function of stirring speed at 25 °C; particle size 462 μm of ore; solid/liquid ratio 1.0 g/L and 0.1 N HCl.

Let Δ_1 be the difference between pairs of conversions at stirring speeds of 900 and 700 rpm, and Δ_2 be the difference between pairs at stirring speeds of 1000 and 900 rpm, as shown in Table 4. Now, Δ_1 and Δ_2 are ranked according to their absolute values, with the smallest rank given to smallest difference value. If there is no difference in the degree of conversion when stirring speed vary from 700 to 900 rpm or from 900 to 1000 rpm, the sum of the positive ranks should be nearly equal numerically to the sum of the negative ranks. The total sum of all ranks for n paired observations is given as [28]:

$$Sum\,of\,all\,ranks = 1 + 2 + \cdots + n = \frac{n(n + 1)}{2}$$

Now, for the $\Delta1$ sample:

$$Sum\,of\,all\,ranks = \frac{15(16)}{2} = 120$$

And, hence, the expected sum of either positive or negative signed ranks is 120/2 = 60.

The observed sum of negative ranks, Table 4, is $\sum|-ve\,ranks| = 2 + 3 = 5$ and the observed sum of positive ranks is $\sum|+ve\,ranks| = 4.5 + 4.5 + 7.5 + 7.5 + 12 + 13 + 11 + 15 + 1 + 10 + 6 + 9 + 14 = 115$

To check for a significant difference, the absolute value of the smaller sum of ranks, that is, 5 should be compared to the critical value of the smaller sum of signed ranks (R) given in Table VII [28]; this is for n = 15:

R = 25 at 5 % level of significance, R = 20 at 2 % level of significance, and R = 16 at 1 % level of significance

Since 5 < 16 < 20 < 26, the null hypothesis can be rejected, at the corresponding significance level, and we can infer that there is a difference in the degree of conversion when stirring speed is increased from 700 to 900 rpm.

For the Δ_2 sample:

$$Sum\,of\,all\,ranks = \frac{14(15)}{2} = 105$$

And, hence, the expected sum of either positive or negative signed ranks is 105/2 = 52.5.

From Table 4, $\sum|-ve\,ranks| = 3 + 4 + 8 + 7 = 22$ and the observed sum of positive ranks is $\sum|+ve\,ranks| = 10 + 1 + 6 + 9 + 11.5 + 11.5 + 2 + 13 + 5 + 4 = 83$

To check for a significant difference, the absolute value of the smaller sum of ranks, that is, 22 should be compared to the critical value of the smaller sum of signed ranks (R) given in Table VII [28]; this is for n = 14:

R = 21 at 5 % level of significance, R = 16 at 2 % level of significance, and R = 13 at 1 % level of significance

Since 22 > 21 > 16 > 13, the null hypothesis cannot be rejected at the indicated significance level, and we can infer that there is no significance difference in the degree of

conversion when stirring speed is increased from 900 to 1000 rpm.

Table 4 : Statistical analysis for stirring speed effect

P	X_1 at 700 rpm	X_2 at 900 rpm	X_3 at 1000 rpm	Δ_1 X_2-X_1	Δ_2 $X3$-X_2	Rank for Δ_1	Rank for Δ_2
1	2.99	2.76	2.58	-0.23	-0.18	-3	-3
2	4.65	4.6	4.6	-0.05	0	-2	-
3	7.58	7.89	7.62	0.31	-0.27	4.5	-4
4	10.12	10.43	11.89	0.31	1.46	4.5	10
5	12.47	13.32	13.34	0.85	0.02	7.5	1
6	17.14	17.99	18.6	0.85	0.61	7.5	6
7	24.1	25.85	27.3	1.75	1.45	12	9
8	37.77	40.05	42.03	2.28	1.98	13	11.5
9	47.66	48.88	50.86	1.22	1.98	11	11.5
10	52.57	55.55	55.6	2.98	0.05	15	2
11	62.52	62.53	61.88	0.01	-0.65	1	-8
12	65.6	66.65	68.99	1.05	2.34	10	13
13	71.16	71.52	72.09	0.36	0.57	6	5
14	72.01	72.89	75.86	0.88	2.97	9	14
15	73.54	75.95	75.32	2.41	-0.63	14	-7

From this analysis, it can be inferred that there is a significant difference in the degree of conversion when stirring speed is increased from 700 to 900 rpm, but increasing the stirring speed from 900 to 100 rpm does not produce a significant difference in the conversion, using the 5 % significance level. Based on the above findings and in order to eliminate, as much as possible, the influence of diffusion through the boundary layer in controlling the reaction rate, all subsequent leaching rate measurements were done using the high stirring speed of 1000 rpm.

3.3 Solid to Liquid Ratio Effect

Four runs were done to investigate the effect of solid to liquid ratio on leaching rate. These runs were conducted under the conditions: HCl concentration fixed at 0.1 N, temperature at 25 °C, stirring speed of 1000 rpm, and 462 μm particle size, the solid to liquid ratio varied from 1 g/L to 4 g/L. Figure 4 shows the results and it can be seen that increasing the solid to liquid ratio results in a decrease in the conversion. This reduction in the rate of leaching of copper may be attributed to one or both of the following reasons:

a) Increasing the solid to liquid ratio results in an increased acid consumption corresponding to a given fixed percentage recovery of copper. Thus, experiments conducted at a high solid to liquid ratio and fixed initial acid concentration are effectively conducted in a lower acid concentration environment, compared to experiments conducted at low solid to liquid ratio. This should results in lowering the leaching rate since as will be shown later, that decreasing the concentration of the

acid medium in which the reaction takes place, results in decreased rate of leaching.

b) For the same degree of conversion of copper and under the same experimental conditions, the concentration in the acid medium of the reacted gangue materials are increased as the solid to liquid ratio is increased, and may adversely influence the rate of recovery of copper. Such interfering effect of gangue material ions (Al^{3+}, Mg^{2+}, Fe^{2+} and Fe^{3+}) has been investigated and shown to affect the rate of leaching of copper ores with sulfuric acid [29].
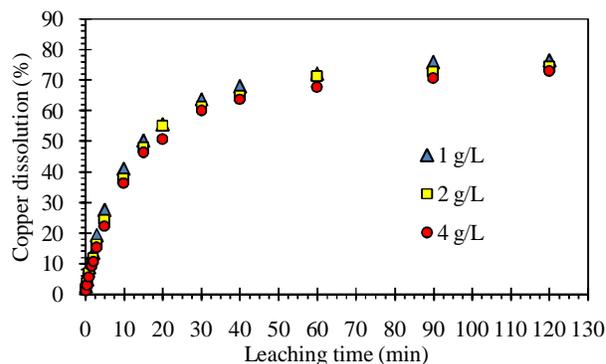
Figure 4: Copper dissolution as a function of S/L ratio at 25 °C, 100 rpm, 462 μm particle size, and 0.1 N HCl

In order to minimize the plausible undesirable by-products effect and to achieve one of the assumptions of the models under investigation, namely, that each solid particle issurrounded by a uniform and constant concentration of reagent at any instant [9],the majority of runs were conducted using 1.0 g/L solid to liquid ratio.

A solid to liquid ratio of 100 g/L was used by Lundstrom et al. [30] when they studied sulfuric acid leaching for capturing copper from copper rich convertor slag, a copper rich process solution with iron as the main impurity metal was obtained as a result of the leaching process. Yang et al. [31] reported a solid to liquid ratio of 1 to 10 g/mL to extract higher than 90 wt% of copper from spent printed circuit boards using sulfuric acid. Compared with the current study; most available studies in literature used sulfuric acid rather than hydrochloric acid and the concentration used was dilute or weak acid while in this study up to 0.2 N HCl is used.

3.4 Temperature and Hydrochloric Acid Concentration Effects

At various fixed temperatures the effect of increasing HCl concentration on the conversion were studied. Figures 5and 6 show the influence of HCl concentration (lowest and highest) on copper dissolution at 25, 35, and 45 °C, with 462 μm particle size. It is clearly seen that increasing the leaching temperature eliminates the effect of the HCl concentration and the percentage of copper dissolution almost approaches same values by the end of the leaching time. Figure 7 reveals that at a given temperature, increasing the concentration of HCl results in an increase in the percentage of copper dissolution

(X_{Cu}) especially at low temperatures, while at higher temperatures the % of copper dissolution is high even at low HCl concentration. For a fixed concentration of HCl, increasing the leaching temperature results in an increase in the % of copper dissolution (X_{Cu}) and this can be depicted clearly at low acid concentration. At higher temperatures and high acid concentration the % of copper dissolution values were almost close to each other by the end of the leaching time. So, temperature and concentration effects are complimentary.
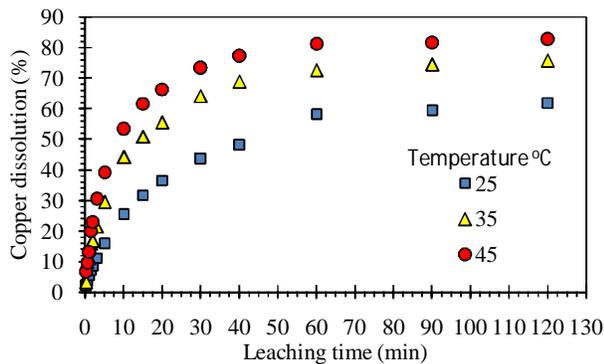
Figure 5 : Copper dissolution as a function of temperature at 0.05 N HCl, 1000 rpm, 1.0 g/L S/L ratio, and 462 μm particle size.
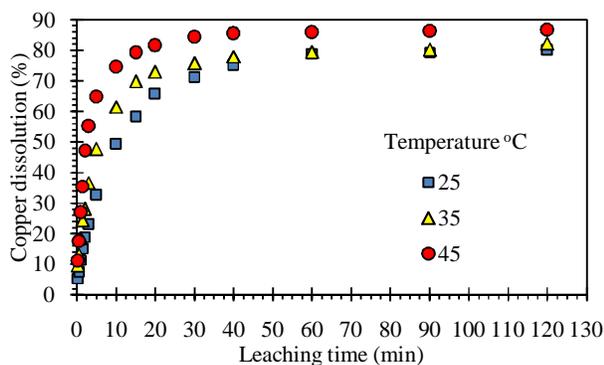
Figure 6 : Copper dissolution as a function of temperature at 0.2 N HCl, 1000 rpm, 1.0 g/L S/L ratio, and 462 μm particle size.
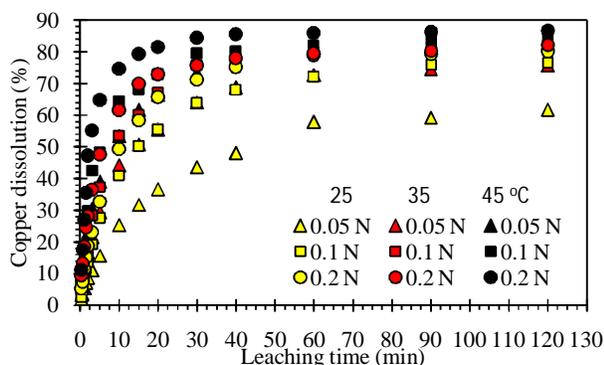
Figure 7 : Copper dissolution as a function of temperature and HCl concentration at 1000 rpm, 1.0 g/L S/L ratio, and 462 μm particle size.

In a recent study, Wang et al. [32] found that copper can be easily leached at ambient temperature from copper oxide minerals such as malachite and pseudo- malachite, only the bonded copper minerals were not leached at all at this temperature. Increasing temperature was favorable to the leaching of bonded copper minerals, and the dissolution of copper was mainly in isomorphism state at a temperature of 40 °C. The leaching rate of copper in the adsorbed state was significantly accelerated with an increase in temperature to 60 °C. And at 80 °C, the isomorphic copper was completely leached, but leaving 11.2% adsorbed copper un-leached. By the end of leaching time of 240 min, 1.0M NaNO3, 2.5M H2SO4, and S/L ratio=1:60, Nyamdelger et al. [33] found that copper dissolution was increased from 69.5% to 86.8% by raising the leaching temperature from 70°C to 90 °C.

3.5 Particle Size Effect

For a fixed weight of particles, the effective surface area available for reaction increases and the diffusion path decreases as the particles are ground to finer size, the reaction will be fast and the leaching time will be small, while, for large particles the reaction will be slow and the leaching time will be large. Thus, the conversion increases inversely with particle size. This effect is demonstrated dramatically in Figures 8 to 10, at various temperatures and HCl concentration. By the end of leaching time, copper dissolution was increased from 43% at 1850 mm to 80 % at 462 mm when the leaching temperature was 25 °C, i.e. increased by 86 % as shown in Figure 8. Figure 9, reveals that by increasing the reaction temperature to 45 °C, the difference in copper dissolution between 1850 and 462 μm are noticeable but much smaller than the difference at 25 °C for the same particle size, i.e. increased by about 36 %.
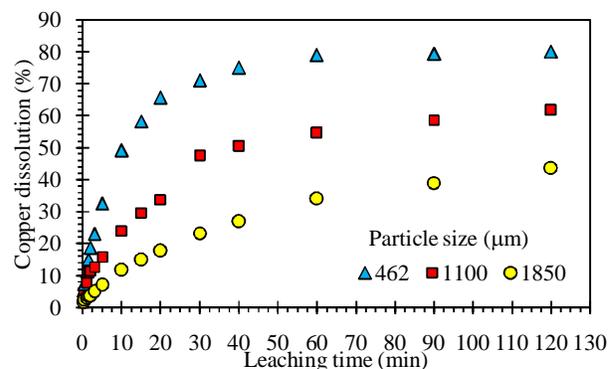
Figure 8: Copper dissolution as a function of reacted particle size at a temperature of 25 °C, 0.2 N HCl, 1000 rpm, and 1.0 g/L S/L ratio.
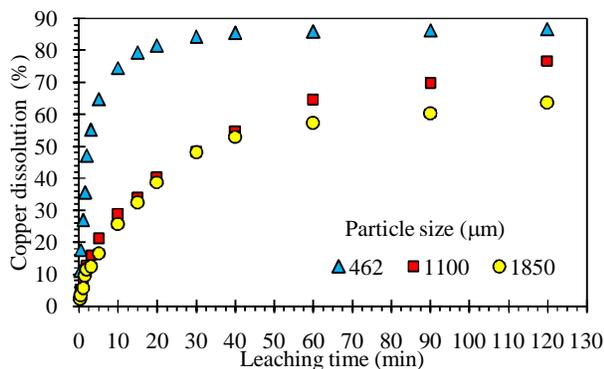
Figure 9 : Copper dissolution as a function of reacted particle size at a temperature of 45 °C, 0.2 N HCl, 1000 rpm, and 1.0 g/L S/L ratio.
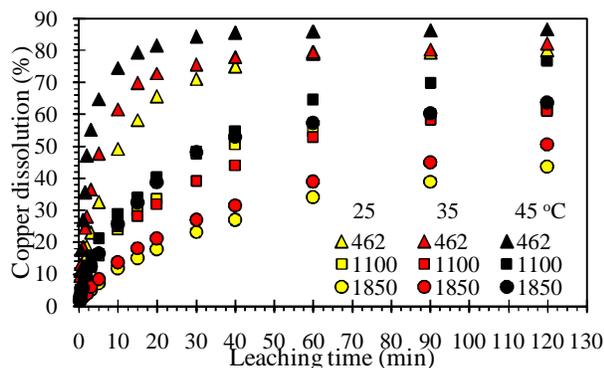
Figure 10 : Copper dissolution as a function of reacted particle size at different reaction temperatures and 0.2 N HCl, 1000 rpm, and 1.0 g/L S/L ratio.

Nyamdelger et al. [33] reported that that the copper dissolution rate is highly dependent on the particle size, when the same leaching conditions were applied the dissolved copper increased from 60.58 to 90.3 % by changing the particle size from +74 mm -25.4 mm. The effect of different particle sizes on the rate of the copper leaching was investigated by Zhou et al. [34]. The authors found that 89.27% of copper was extracted at 5-10 µm while only while only 57.08% was extracted at 15-25 µm.

3.6 Comparison between HCl and H₂SO₄ as a Lixiviant

Figures 11and 12 show a comparison between HCl and H_2SO_4 as leaching lixiviants. From these figures it is clearly seen that at the same operating conditions, H_2SO_4 gives slightly greater conversion than HCl at low temperature and low acid concentration. But the differences between the conversions become smaller as the temperature and acid concentration are increased and the ore particles become smaller. Cho et al. [35] investigated the influence of the acid type and concentration on the acid leaching process for Mongolian apatite-based ore containing rare-earth elements. Sulfuric, hydrochloric, and nitric acids were used in the study and it has been found that hydrochloric acid was the most effective leaching agent, leached more than 90% of rare-earth elements.
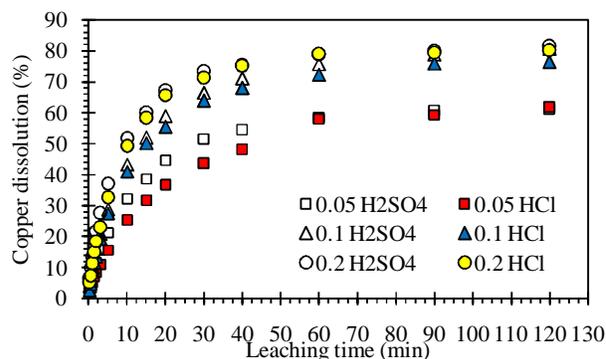
Figure 11: Comparison between HCl and H_2SO_4 as lixiviant at 25 °C, 462 µm particle size, 1.0 g/L S/L ratio, and 1000 rpm.
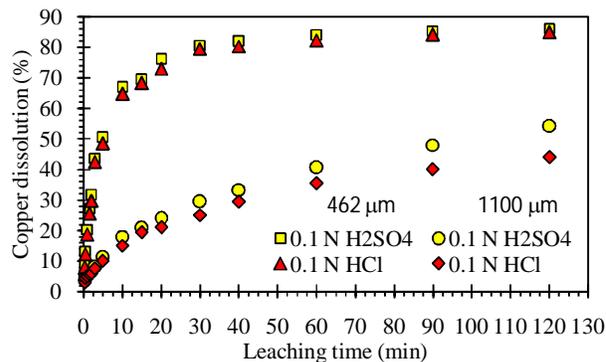
Figure 12 : Copper dissolution as a function oflixiviant and particle size at 45 °C, 1000 rpm, 1.0 g/L S/L ratio, and 462 µm particle size.

4. CONCLUSIONS

The rate of leaching of Jordanian copper ore using hydrochloric acid was found to increase with increasing temperature and acid concentration but decreases with increasing particle size. Stirring speed above 900 rpm had slight effect on the percentage of copper dissolution. And thus the diffusion through the liquid film surrounding the ore particles under the operating conditions used in the present study can be neglected.

With the present condition of the study, it was found that hydrochloric acid consumed during the leaching time of 2 hours and using solid to liquid ratio of 1 g/L does not exceed 1 % of the initial acid poured into the batch reactor. Also, it has been found that at similar operating conditions and at low temperature and acid concentration, sulfuric acid gave slightly greater conversion than hydrochloric acid, but the difference between the conversions become smaller as the temperature and acid concentration are increased.

A copper dissolution % of about 87 can be achieved at a leaching temperature of 45 °C, 0.2 N hydrochloric acid, 1.0 g/L solid to liquid ratio, 1000 rpm stirring speed, and 462 µm particle size, while a copper dissolution % of about 83 can be obtained by decreasing the normality of the acid to 0.05 and keeping all other operating parameters constant. Less than 10

% reduction in the copper dissolution was obtained by decreasing the leaching temperature to 25 ^{o}C while keeping the other operating parameters fixed at 0.2 N, 1.0 g/L solid to liquid ratio, 1000 rpm stirring speed, and a particle size of 462 μm.

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