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# The Leaching of Dolomitic-Copper Ore Using Sulphuric Acid Under Controlled Conditions

Felix W. Ntengwe*

*Copperbelt University, School of Technology, Chemical Engineering Department, 4662 Jambo Drive, Riverside, Kitwe, Zambia*

**Abstract:** The leaching of dolomitic-copper ore using sulphuric acid under controlled conditions was studied with a view to evaluating the economic value and the effect of ore pulverisation, particle size, temperature and pH on the recovery of copper from chalcopyrite. The samples were ground and mixed with water and sulphuric acid to form an acid soluble copper content of 4.07 %, 8.14 % total copper and 22 % solids. The leaching was carried in duration of 0-6 hours. The sulphuric acid was found to be effective in recovering copper from chalcopyrite with efficiencies of 72 to 93 % for 75 micron particle size and 65 to 84% for the 212 micron sieve size at different pulverising times. The kinetics of dolomitic ore showed the reaction with $H_2SO_4$ was second order with respect to chalcopyrite and first order with respect to dolomite and was consistent with the shrinking core model. The increase in temperature produced an increase in the recovery of copper from solids into the bulk solution. The leaching was favoured at low pH values ($1.8<pH<3$) than at high ones ($pH>3$). Profit levels for the reversed pH numbers, high to low (low to high pH), were higher than values for leaching from low to high pH numbers (high to low pH) particularly for acid sales. Since the economic evaluation showed positive profit levels for both acid and copper sales, the process was viable.

**Keywords:** Leaching; Sulphuric-acid; Dolomitic-ore; controlled-conditions; Economic-value, Mineral-processing; Hydrometallurgy.

## INTRODUCTION

The dissolution of metals from solid ore into liquid phase, a process called leaching, is aided by the concentration of reagents [1]. The most common reagent used in leaching of metals is sulphuric acid ($H_2SO_4$) [2]. Whereas other heavy metals are able to dissolve in $H_2SO_4$, copper (Cu) dissolves quicker in this acid than metals such as zinc, cobalt and iron because it is higher up in the electrochemical series.

Leaching can be controlled by a number of factors in order to optimize the usage of materials. The concentration of acid, particle distribution, temperature, pulverisation and leaching duration are some of the factors that can be used. The concentration of the acid determines the pH of the slurry to be leached. Increased level of acid can allow unwanted metals to dissolve and may be leached along with the desired metal. The particle distribution has the advantage of easy separation of the desired mineral from gangue, easy exposure of the mineral to chemical reaction and producing the desired surface area. A finer particle distribution produces a higher leach extraction [3]. The concentration of solids can affect leaching in two ways. High concentration can increase viscosity and cause blockage problems and reduce copper extraction rate due to lack of fluidity [4]. Low concentration can increase the overall slurry overflow rate and this can reduce the slurry residence time and hence reduce extraction rate [4]. The residence time for the slurry in the leaching reactor determines the overall leaching time. It depends on the flow rate and the concentration of solids in the slurry. Agitation leaching is suitable for high grade ores (40-70 % solids) and increases percolation of acid into solids at different agitation speeds [1, 5]. Buffle plates, in addition to agitators, may be used to maximize slurry mixing [6]. Compressed air leaching in pachuca tanks is the most common method for leaching copper ore [7-9]. Non-oxidative leaching of copper in the absence of oxygen has been studied elsewhere [10]. The temperature of the reaction has an effect on the rate of leaching according to Arrhenius Law [3].

Since the leaching of copper is dependent on effective liberation of sulphide ore from gangue, which includes carbonates of magnesium, calcium and other metals, the presence of such carbonates results in parallel reactions [11], [12] taking place simultaneously and hence introduces competition in the system for the acid reagent. The shrinking core model has been used elsewhere [13] to evaluate the kinetics of leaching process since the ground particles are assumed to be spherical [1]. In this study, the leaching process was assumed to follow the shrinking core model with parallel reactions of copper and dolomite. An evaluation of the effect of pulverising, temperature, pH and leaching time was carried out on both low and high-dolomitic copper ore in addition to the economic evaluation of the leaching process. In order to assess the economic value of leaching process, an evaluation of the level of acid usage and expected sales of copper leached was required. This was the best way to as-

*Address correspondence to this author at the Copperbelt University, School of Technology, Chemical Engineering Department, 4662 Jambo Drive, Riverside, Kitwe, Zambia; Fax: 260 212 228212;
Tel: 260 212 228212; E-mail: fntengwe@cbu.ac.zm

sessing the profitability of the process. The objectives of the study were to evaluate the leaching of low and high dolomitic-copper ore using $H_2SO_4$ as the leaching reagent. The specific objectives were; to establish the copper distribution in the percent passing samples, determine the effects of pulverizing time, temperature and pH on the leaching efficiency and to assess the economic value (viability) of the leaching process.

## KINETICS OF LEACHING DOLOMITIC ORE

Leaching reactions for the recovery of dolomitic copper are as shown in equations (1-3) for dissolution of chalcopyrite ($CuFeS_2$) in $H_2SO_4$ to produce the sulphates of copper ($CuSO_4$) and iron ($FeSO_4$) and water ($H_2O$) and the dissolution of dolomite ($CaMg(CO_3)_2$) into the same acid producing the sulphates of magnesium ($MgSO_4$) and calcium also known as gypsum ($CaSO_4.2H_2O$) and carbon dioxide ($CO_2$). The rate constants $k_1$, $k_2$, and $k_3$ ($s^{-1}$) are activation energy dependent. The dissolution of malachite ($CuCO_3.Cu(OH)_2$), azurite ($2CuCO_3.Cu(OH)_2$) covellite (CuS), chalcocite ($Cu_2S$), bornite ($Cu_5FeS_4$) and chrysocolla ($CuSiO_3$) produce the same types of sulphates of copper when leached in $H_2SO_4$ acid. It can be observed that $CuFeS_2$ requires 2 moles of $H_2SO_4$, which is 1 more than that required by each of $MgCO_3$ and $CaCO_3$.

$$CuFeS_2(s) + 2H_2SO_4(aq) + O_2(g) \xrightarrow{k_{CuSO_4}} CuSO_4(s) + FeSO_4(s) + 2S(s) + 2H_2O(l) \quad (1)$$

$$MgCO_3(s) + H_2SO_4(aq) \xrightarrow{k_{MgSO_4}} MgSO_4(s) + CO_2(g) + H_2O(l) \quad (2)$$

$$CaCO_3(s) + H_2SO_4(aq) \xrightarrow{k_{CaSO_4}} CaSO_4(s) + CO_2(g) + H_2O(l) \quad (3)$$

The leaching model for the above reactions is shown in Fig. (**1**), which is the shrinking core model [12]. Although the model has been used in studies conducted elsewhere, parallel reactivity of dolomitic-copper with sulphuric acid was not demonstrated [14]. A comparison of the effect of low and high dolomite on leaching of copper was not found in literature.

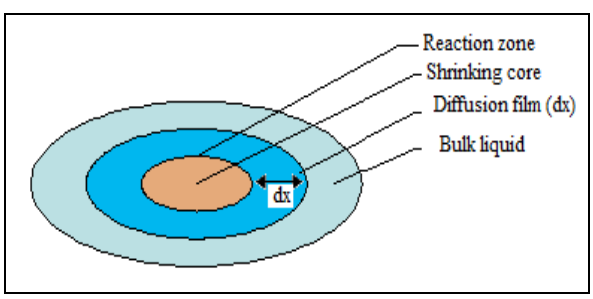


**Fig. (1).** The shrinking core model for the leaching of dolomitic-copper ore.

The ions from the acid migrate by diffusion from bulk solution through the film to the reaction zone where they react with chalcopyrite, calcium and magnesium carbonates. The products $CuSO_4$, $CaSO_4$ and $MgSO_4$ diffuse in opposite direction from the reaction zone, through the film (dx), to the bulk solution according to Ficks Laws [13].

The overall rate of reaction (r) for the system is dependent on the concentration of $H_2SO_4$ and the particle size of ore [11]. It is, also, dependent on the rates of formation of products and rate of diffusion as given by equations (4-5) where $k_{(CuSO4)}$ ($s^{-1}$), $k_{(CaSO4)}$ ($s^{-1}$) and $k_{(MgSO4)}$ ($s^{-1}$) are rate constants that are dependent on temperature and activation energy, $Q_A$ is the flux of ions reacting with the particles while the rates of reaction ($mols^{-1}$); $r_{(CuSO4)}$, $r_{(MgSO4)}$ and $r_{CaSO4}$) for individual reactions, which are dependent on temperature [12], are given by equations (6-8) where E (J/mol) is the activation energy, T (K) is the absolute temperature, $A_1$, $A_2$ and $A_3$ are the frequency factors while R (J/mol, K) is a constant, $[CuSO_4]$, $[CaSO_4]$, $[MgSO_4]$ and $[H_2SO_4]$ are the concentrations of copper, calcium and magnesium sulphates and sulphuric acid respectively.

$$-r_{(H_2SO_4)} = r_{(CuSO_4)} + r_{(CaSO_4)} + r_{(MgSO_4)} = \frac{dN_A}{dt} = 4\pi r^2 Q_A \quad (4)$$

$$-r_{(H_2SO_4)} = k_{(CuSO_4)}[H_2SO_4]^2 + k_{(CaSO_4)}[H_2SO_4] + k_{(MgSO_4)}[H_2SO_4] \quad (5)$$

$$r_{(CuSO_4)} = \left[A_1 \exp\left\{\frac{E_{(CuSO_4)}}{R}\right\}\left\{\frac{1}{T}\right\}\right][H_2SO_4]^2 \quad (6)$$

$$r_{(CaSO_4)} = \left[A_2 \exp\left\{\frac{E_{(CaSO_4)}}{R}\right\}\left\{\frac{1}{T}\right\}\right][H_2SO_4] \quad (7)$$

$$r_{(MgSO_4)} = \left[A_3 \exp\left\{\frac{E_{(MgSO_4)}}{R}\right\}\left\{\frac{1}{T}\right\}\right][H_2SO_4] \quad (8)$$

Since the activation energies of $CaSO_4$ and $MgSO_4$ would be larger than that of $CuSO_4$, the contribution of $MgSO_4$ and $CaSO_4$ to compete for the reactant would be low. However, a significant contribution would come from the combined effect of both $MgSO_4$ and $CaSO_4$, which can be reduced by carrying out leaching at increased temperature or increased concentration of acid in order to increase the selectivity of copper sulphate.

## MATERIALS AND METHODS

### Materials

The materials used were concentrated $H_2SO_4$ (98 w/w%) for adjusting pH, distilled water for topping up the level of volumes, starch and methyl orange indicators for indicating the end-points of reactions during titration, nitric acid and hydrochloric acid for digesting the ore samples, potassium iodide, ammonium di-fluoride and sodium thiosulphate for the determination of copper by titration and leach solution containing 3.5 g/l $H_2SO_4$ for leaching purposes.

### Methods

#### *Sampling and Preparation*

A 900 $cm^2$ net was covered on top of heaped Lonshi ore and samples were collected from each square in order to form a composite sample. A 20 kg of the composite sample, containing 4.07 % AsCu and 8.14 % total copper was riffled

and then dried in the oven at 110°C for 12 hrs before crushing in the laboratory Jaw crusher. 12 kg of this sample was pulverised for 20 s before packing it into 1000 g samples using plastic-sample bags.

### *Copper Distribution*

In order to determine the copper distribution in the feed, 200 g of the ore sample was weighed on a balance and pulverised for different times in a pulverizer (TS 1000 Siebec) before subjecting it to wet sieving using 38μm sieve in order to remove the particles with diameter less than this size (-38 μm). After drying in the oven at 110°C, the sample was dry sieved in a bank of sieves (38, 53, 75, 106, 150, 212, 425 and 1180 μm) with the largest aperture sieve (1180 μm) on top and the smallest aperture sieve (38 μm) at the bottom. The bank of sieves was shaken for 30 minutes by a sieve shaker to allow the particles to collect at each sieve. Each size fraction was weighed and the acid soluble copper (ASCu) and copper distribution was determined using the titration method.

During the titration method, a mixture of 10 ml of aqueous solution and distilled water was mixed and then 4 ml of 100% ammonium hydrogen di-fluoride solution and 5 ml of potassium iodide were added and shaken before titrating with sodium thiosulphate, using burette, to brown-pale-yellow colour. The titration continued, after adding 2 ml of starch solution, to milky-white colour end-point. The concentration of copper was determined by multiplying the volume from the burette by the concentration factor of sodium thiosulphate.

In order to determine the AsCu, 2g of ore was weighed and digested in 10 ml nitric and 10 ml hydrochloric acids and 1:1 $H_2SO_4$ mixture on a hot plate to dryness at 250 °C. The residue was then dissolved in 10 ml nitric acid and diluted to 250 ml volume. The concentration of copper in digested sample and raffinate, which was the aqueous layer from the bottom of the second stage of solvent extraction plant, was determined using the atomic absorption spectrophotometer (AAS) method where 5 ml of sample was added to distilled water to make up to 250 ml. The sample was aspirated in the ASS and the reading was used to determine the concentration of copper using equation (9) where F is the dilution factor and W is the weight of the sample. This method is good for ores with 1% Cu while the titration method is good for Cu concentrations above 10 g/L both in the feed and leached product. The same equation was used to evaluate the AsCu in the leached residue (cake) collected during filtration. The leaching efficiency (Eff%) was determined using equation (10) where LAsCu (g) is the leached acid-soluble copper and RAsCu (g) is the residue acid-soluble copper.

$$\%AsCu = \frac{[AAS\ reading]xFx100}{Wx10^6} \tag{9}$$

$$Eff\ \% = \frac{\left[LAsCu - RAsCu\right]}{LAsCu} x100 \tag{10}$$

### *Effect of pH on Leaching of Copper*

Four 500 g samples of low-dolomitic ore were weighed and placed in a leach vessel. To each sample was added 1023 ml of raffinate containing 0.13 g/L copper, 12 ml of new raffinate acid containing 3.8 g/L $H_2SO_4$, 750 ml of process water giving the final volume of the sample to be 1945 ml with 22 % solids giving a density of about 1250 g/L. The leaching tests were carried out at pH ranges 1.4-1.8, 1.8-2.2, 2.2-2.6 and 2.6-3.0. The leaching tests were also carried out on another set of four 500 g samples in reverse order of pH, i.e., 3.0-2.6, 2.6-2.2, 2.2-1.8, and 1.8-1.4 in order to determine the effect of different pH values on the leaching of copper ore. The adjustment of pH was achieved by dosing $H_2SO_4$ (98%w/w) from a graduated burette above the leaching vessel while, at the same time, the pH was monitored using a pH meter. The ratio of tonne acid (tAc) to tonne copper (tCu) was obtained from equation (12) where V (ml) is the volume of new acid used, C is its concentration and LCu (g) is the copper leached.

$$\frac{tAc}{tCu} = \frac{CV}{LCu} \tag{11}$$

### *Effect of Ore-Particle Size on Leaching*

The effect of particle size on leaching of copper was studied by crushing 2000 g of each of the four ore samples in Jaw crusher and then 500 g of each of the same samples was pulverized for different times (Table **1**) in order to determine the percent passing sieve size 75 μm. A 500 g of each of the % passing size 75 μm at each pulverizing period was leached at desired stirring speed (400 rpm) for 6 hours with raffinate containing $H_2SO_4$ (3.8 g/L) and 0.04 g/L copper.

A similar study was conducted on seven 500 g samples passing sieve size 212 μm. Different pulverizing times and different amounts of raffinate and process water were used but the same amount of sample size and pH was maintained (Table **2**). The leaching period for each test was also maintained at 6 hours.

### *Effect of Temperature on Leaching*

The effect of temperature on the leaching of Cu was studied at temperatures from 25 to 50 °C using a thermostat controlled water bath. In order to ensure uniform temperature of the leaching pulp, Heidhoff stirrer was set at 400 rpm to give adequate stirring and to homogenize the pH at 1.8 levels, which was maintained by the addition, dropwise, of 98 % $H_2SO_4$ using 50 ml burette.

### *Effect of High Dolomite on Leaching of Copper*

The effect of dolomite was studied using 2 kg high-dolomite ore with 4.07 % AsCu. The leach tests were carried out for 6 hours on both high and low-dolomite ores at pH 1.8 and pH 2.6 in order to determine the effect on the leaching of copper at the desired temperature and to assess the viability of the process by evaluating miscellaneous costs and costs associated with the use of the acid and then comparing them to the income that would be realised from acid and copper sales.

## Data Analysis

The data was analysed in excel using exploration method in order to establish the underlying trends of data that would establish the relationship between the dependent and independent variables [15, 16].

**Table 1. Leach Test Specification for Ore Passing Sieve Size of 75 µm**

| Parameter | Units | Trials | | | |
|---|---|---|---|---|---|
| | | 1 | 2 | 3 | 4 |
| Pulverizing time | s | 0 | 30 | 60 | 90 |
| pH | - | 1.8 | 1.8 | 1.8 | 1.8 |
| Weight of sample | g | 500 | 500 | 500 | 500 |
| % Passing 75 µm | % | 58 | 68 | 71 | 78 |
| Raffinate Cu | g/L | 0.04 | 0.04 | 0.04 | 0.04 |
| Raffinate $H_2SO_4$ | g/L | 3.8 | 3.8 | 3.8 | 3.8 |

**Table 2. Leach Test Specification for Ore Passing Sieve Size of 212 µm**

| Parameter | Units | Trials | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | 1 | 2 | 3 | 4 | 5 | 6 | 7 |
| Pulverizing time | s | 0 | 5 | 10 | 15 | 20 | 25 | 30 |
| pH | - | 1.8 | 1.8 | 1.8 | 1.8 | 1.8 | 1.8 | 1.8 |
| Weight of sample | g | 500 | 500 | 500 | 500 | 500 | 500 | 500 |
| % Passing 212 µm | % | 60 | 73 | 75 | 79 | 80 | 82 | 86 |
| Raffinate | ml | 1023 | 1023 | 1023 | 1023 | 1023 | 1023 | 1023 |
| Process water | ml | 750 | 750 | 750 | 750 | 750 | 750 | 750 |

## RESULTS

### Kinetics of Leaching

The chemical reactions between the ore and sulphuric acid were, as shown in the kinetics section, between $CuFeS_2$ and $H_2SO_4$ and dolomite with $H_2SO_4$. The dolomite reactions were split into two reactions; magnesium carbonate with the acid and calcium carbonate with the acid. The standard Gibbs free energy for the reaction of acid with $CuFeS_2$ was higher (-407 $kJmol^{-1}$) than that for the reaction with $MgCO_3$ (-42 $kJmol^{-1}$) which was lower than that for the reaction with $CaCO_3$ (-69 $kJmol^{-1}$). The rate constants for the reactions, calculated from equation (12) where β ($JK^{-1}$) is Boltzmann constant and h (Js) is Planks constant, were found to be $8.25x10^{83}$ $s^{-1}$ for the reaction of acid with $CuFeS_2$, $1.4x10^{20}$ $s^{-1}$ for the reaction with $MgCO_3$ and $7.1x10^{24}$ $s^{-1}$ for the reaction with $CaSO_4$ at standard temperature (298 K) and pressure (101325 $Nm^{-2}$). These values suggest that the reactions were spontaneous due to negative free energy of reaction. The results mean, also, that the reaction of $CuFeS_2$ with acid was faster when compared to individual reactions of $MgCO_3$ and $CaCO_3$ with acid. The reactions of $MgCO_3$ and $CaCO_3$ thus required more acid in order to increase the rate of reaction. The factors pH, as a measure of concentration of acid, and particle size of ore were contributors to the speed of reaction.

$$k = \beta Th^{-1} e^{-\Delta G / RT} \quad (12)$$

### Effect of Sieve Size on Ore Distribution

The effect of sieve size on the percent of ore passing showed that the smaller the size the lower the percent passing (%Passing) and the larger the size the larger the ore passing through the sieve. However, the tests for copper (%Cu) revealed low values of Cu (<5 % Cu) for sieve sizes above 53 µm and high Cu (>5 % Cu) for sieve sizes below this number and sieve sizes 425 and 1180 µm (Fig. **2**). It was also observed that as the percentage passing increased the percentage retained (%Retained) decreased.

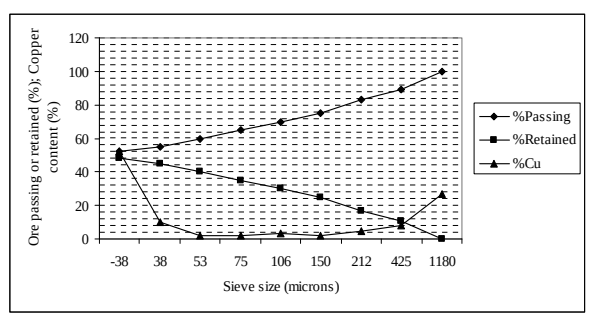


**Fig. (2).** The effect of sieve size on the percent passing and copper content.

### Effect of Pulverizing on Leaching Efficiency

Pulverization of ore homogenizes the pulp so that exposure of the ore to the acid is enhanced. This is one of the ways in which the leaching efficiency can be improved. The results in Fig. (**3**) indicate that when the leaching of copper (Lcu) from ore passing (%Pass) sieve size 75 µm increased from 12 g/L to 24 g/L, the leaching efficiency (Eff %) increased from 72 to 93 % with the increase in pulverizing time. Therefore, the pulverization of the ore improved the efficiency. When the %Pass of particles increased from 56-74%, the Eff% increased to 93%. It means that the surface area for chemical reaction increased and more molecules had access to the reactant. This is one reason why a high percentage of copper was leached from ore.

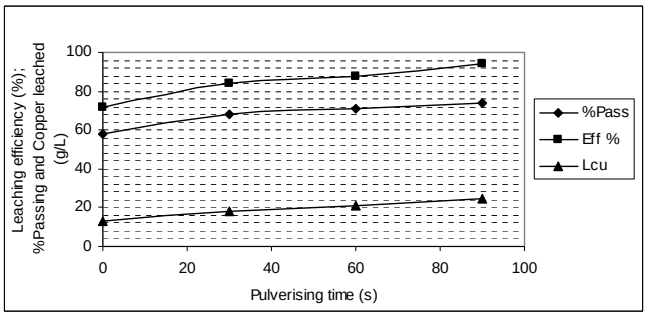


**Fig. (3).** The effect of pulverizing time on leaching of ore passing sieve size 75 µm.

The %Pass in sieve size 75 µm produced an increase in the Lcu from 9 g/L concentration at 0 seconds to 25 g/L concentration in 30 seconds representing an increase of 178 %. Similarly, the Eff % increased from 65 to 84% representing and increase of 19% (Fig. **4**). However, the Eff % was higher for the 75 µm than the 212 µm sieve sizes at zero time of pulverisation (72%; 65%).

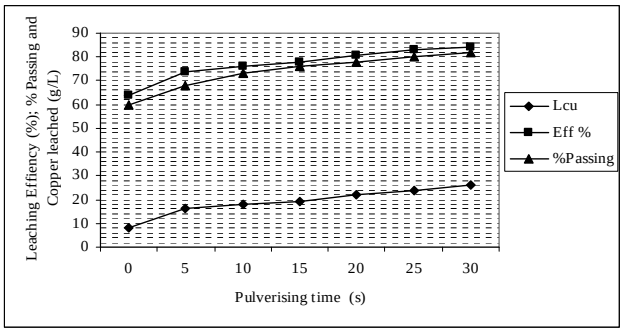


**Fig. (4).** The effect of pulverizing time on leaching of ore passing sieve size 212 µm.

### Effect of Temperature on Leaching Efficiency

The general effect of temperature on the leaching Eff % was that when the temperature increased, the leaching Eff % increased (Fig. **5**). At specific pH, the increase in temperature produced an increase in leaching Eff %. At pH1.8 the increase in temperature from 25-60 $^{o}$C produced an increase in Eff % of 20 % while the increase for the same temperature rise at pH 3.0 produced an increase in Eff % of 10 %, which was lower than that at pH 1.8.

The increase in Eff % at pH 2.2 and pH 2.6 was 20 % and 14 % respectively for the same temperature increase. This means that the Lcu was faster at pH 2.2 than at pH 2.6. Therefore the leaching favoured high pH (pH <2.6) than low pH (pH >2.6) at a particular temperature. The leaching Eff % was lower than those obtained at 25$^{o}$C. At 0 $^{o}$C and temperatures up to 4 $^{o}$C, the transport of copper into the bulk solution was hindered by the solidification of the system and hence little copper was leached resulting in low values of Eff % at these temperatures.

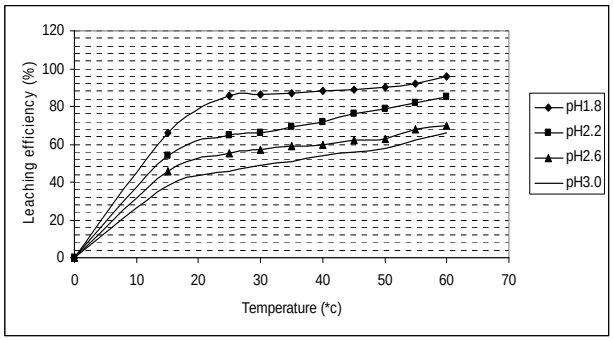


**Fig. (5).** The effect of temperature on leaching efficiency.

### Effect of pH on Leaching Efficiency

The results in Fig. (**6**) show that the leaching of copper (CuL) decreased as the pH number increased. The leaching Eff (%) decreased as the pH decreased also i.e. as the pH number increased. The decrease in pH was due to the decrease in the acid added (Aused) to the sample. This means that the CuL of ore was effective at high pH (low pH number) than at low pH (high pH number) since the drop in Eff (%) was from 89 to 70 %. This represents 19 % drop in the leaching Eff (%). Therefore the pH range of 1.4-2.0 favoured CuL at a particular leaching temperature as the Eff (%) was highest in this pH range.

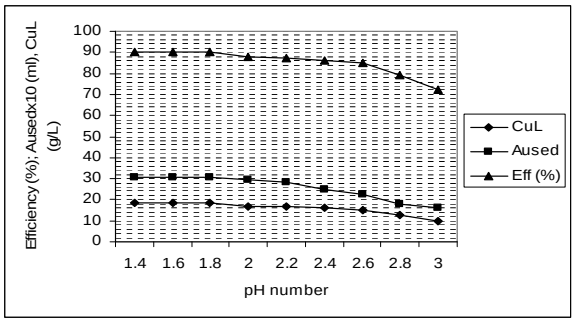


**Fig. (6).** The effect of pH on leaching efficiency.

When the leaching pH was reversed from pH 3 to pH 1.4, the results in Fig. (**7**) gave a similar effect of pH on the leaching Eff (%) of copper. The pH range 2 to 1.4 produced the highest values of Eff (%) than that of pH 3 to pH 2.2. An increase in pH from pH 3 to 1.4 increased the Eff (%) from 85 to 91 % representing an increase of 6 %. Leaching in the reverse order, i.e., from low to high pH, produced a lower increase in Eff (%) than that produced in the decreasing order, i.e., from high to low pH. However, leaching in the reverse order of pH produced higher leaching Eff (%) than those in the decreasing order of pH. This was one of the ways to improving the recovery of copper although additives

may also improve the Eff (%) [1, 17-21] but introduces the cost element. In general, the leaching Eff (%) was in the same range with the lowest at 70 and 85 % for the decreasing and increasing pH respectively while the highest values were 89 and 91 % respectively.

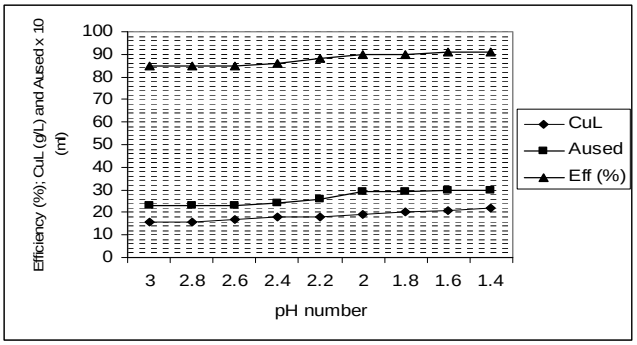


**Fig. (7).** The effect of reversed pH on the leaching efficiency.

### Effect of Time on Leaching Efficiency

The increase in leaching duration produced an increase in the leaching Eff (%) (Fig. **8**). At zero time, the leaching was assumed to be zero. The values obtained at 1-hour interval exceeded the previous values reaching the highest leaching Eff (%) at an interval of 6 hours. An increase in duration of 4 hours produced an increase in Eff (%) of 18, 19, 13 and 15% at pH 1.8, 2.2, 2.6 and 3.0 respectively.

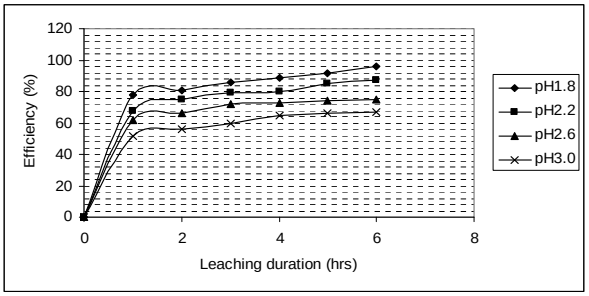


**Fig. (8).** The effect of leaching duration on the leaching efficiency.

### Economic Evaluation of Leaching

The economic evaluation of the leaching of ore containing high-dolomite ore was based on the materials (Table **3**) where tonne acid (tAc), tonne acid per tonne copper (tAc/tCu), cost of acid per tonne copper (cAc/tCu), miscellaneous costs (Misc. cost), profit levels of acid (Ac) and copper (Cu) are shown. The profit levels determined the viability of the process. The profit values for copper and acid sales ranged from 4300-4500 $/ton and 1400-3200 $/ton copper respectively at pH 1.8. The profit decreased as the acid production decreased or acid usage decreased. The profit levels for different pH ranges are shown in Table **4**. The profit levels ranged from 1700-350 $/ton for pH ranges 1.4-1.8 to 2.6-3.0 while the values for the reversed pH 1.8-1.4 to pH 3.0-2.6 were 1600-700 $/ton for acid sales. The profit levels for copper sales were 4300-4700 $/ton copper. Despite the decrease in profits with the decrease in acid production, the profit levels were reasonable to provide sustainable operation of the leaching process.

## DISCUSSION

The grinding of ore releases the $CuFeS_2$, $CaSO_4$ and $MgSO_4$ in the dolomitic ore and hence the level of copper is uniform in the ground ore but distributed differently in samples passing through each sieve. Grinding of dolomitic ore releases the gangue that contributes to the occurrence of parallel reactions in the leaching reactor. However the smaller the sizes of ore the larger the surface area for the reaction and the rate of reaction would increase and hence the yield. This study has shown a high percentage of copper in the samples that passed through sieve sizes 53 microns and below while larger sieve sizes produced lower values of copper. The increase in copper content in the samples passing in sieve sizes 212 and 1180 microns could be due to ineffective grindability. Most importantly is the finding that the Eff (%) increased with the decrease in particle size. The rate of leaching was directly proportional to the decrease in particle size [22]. The Eff (%) for the particles passing sieve size 75 microns were higher (70-96 %) when compared to those of the larger pored sieve of 212 microns (60-85 %). This is the advantage of reducing the size of particles of the ore before

**Table 3. Cost of 6-Hour Test Leaching at pH 1.8**

| Test No | Fraction size (µm) | Eff (%) | tAc/tCu | tAc | cAc/tCu ($) | Misc.cost ($/tCu) | Total cost ($/tCu) | Profit-Cu sales ($/t) | Ac sales ($/tCu) | Profit-Ac sales ($/t) |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 53 | 87.5 | 15.0 | 787 | 1620 | 551 | 2171 | 4442 | 5037 | 2866 |
| 2 | 75 | 88.3 | 15.6 | 828 | 1685 | 551 | 2236 | 4377 | 5299 | 3063 |
| 3 | 106 | 89.0 | 15.7 | 841 | 1696 | 551 | 2247 | 4370 | 5382 | 3135 |
| 4 | 150 | 86.5 | 15.2 | 796 | 1642 | 551 | 2193 | 4420 | 5094 | 2901 |
| 5 | 212 | 82.5 | 14.0 | 711 | 1512 | 551 | 2063 | 4550 | 4550 | 2487 |
| **6** | 425 | 80.3 | 16.0 | 575 | 1728 | 551 | 2279 | 4334 | 3680 | 1401 |

Cost of producing acid=108$/ton; Copper selling price=6,613$/ton; Price of acid=6.4$/ton.

**Table 4. Cost of 6-Hour Leach Test at Different pH Ranges**

| Test No | pH | Eff (%) | tAc/tCu | tAc | cAc/tCu ($) | Misc. cost ($/t) | Total cost ($/t) | Ac sales ($/t) | Profit-Ac sale ($/t) | Profit-Cu sale ($/t) |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 1.4-1.8 | 90 | 15.9 | 613 | 1717 | 551 | 2268 | 3923 | 1655 | 4345 |
| | 1.8-1.4 | 91 | 17.4 | 625 | 1879 | 551 | 2430 | 4000 | 1570 | 4183 |
| 2 | 1.8-2.2 | 87 | 16.8 | 565 | 1814 | 551 | 2365 | 3616 | 1251 | 4248 |
| | 2.2-1.8 | 90 | 17.7 | 588 | 1912 | 551 | 2463 | 3763 | 1300 | 4150 |
| 3 | 2.2-2.6 | 85 | 17.0 | 557 | 1836 | 551 | 2387 | 3565 | 1178 | 4226 |
| | 2.6-2.2 | 86 | 16.6 | 483 | 1793 | 551 | 2344 | 3091 | 747 | 4269 |
| 4 | 2.6-3.0 | 79 | 13.0 | 364 | 1404 | 551 | 1955 | 2330 | 375 | 4658 |
| | 3.0-2.6 | 85 | 12.9 | 453 | 1393 | 551 | 1944 | 2899 | 955 | 4669 |
| Control test | 1.6-2.0 | 92 | 15.0 | 656 | 0 | 0 | 0 | 0 | 0 | 0 |
| | | | | | 1620 | 551 | 2171 | 4198 | 2027 | 4442 |

Cost of producing acid=108$/tonne; Copper selling price=6,613$/ton; Price of acid=6.4$/tonne.

leaching commences. In a study by Alubambi *et al.* (2006) [23], the leaching Eff (%) was found to increase with the decrease in particle size. This is in agreement with the findings of this study.

Pulverisation of the ore was found to increase the recovery of copper in sulphuric acid. Studies elsewhere have shown that continuous stirring increased the recovery of copper but increasing speed reduced it [19, 21]. Stirring maintains uniform level of the concentration of the copper and increases the exposure of particles to sulphuric acid. Similarly, pulverising homogenizes the ore and therefore increases exposure of particles to the acid. This is what resulted in the increase of the recovery of copper by sulphuric acid.

The increase of temperature by 35 $^{o}$C produced an increase in efficiency of 20 % at constant pH of 1.8. However, when the pH reduced by almost half, from pH 1.8 to pH 3, the increase in efficiency was 10 %, which was 50 % of the increase at pH 1.8. This shows the dependence of leaching on the concentration of the acid. In another study, metal bioleaching from a low-grade, black-schist ore containing pyrrhotite, pyrite, pentlandite, chalcopyrite and other mineral sulfides, increased with decreasing pH [24]. The concentration of the acid is high at pH 1.8 than that at pH 3. Therefore the leaching of dolomitic-copper ore would be favoured at pH values <2.2.

The general trend of the effect of temperature on the leaching of dolomitic ore was that the increase in temperature produced an increase in the recovery of copper from solids into the bulk solution. This trend was consistent for different pH values. The results were, also, consistent with Arrhenius Law [3]. Other studies have alluded to this fact [1, 25]. Increasing temperature, and decreasing pH and particle size positively influence the extraction of cadmium and copper from the ore [14, 26].

The effect of time on leaching of dolomitic copper produced positive results. The Eff (%) reached 53, 60, 68, and 78 % for pH values of 3, 2.6, 2.2, 1.8 respectively in one hour. Similarly, the Eff (%) reached 67, 75, 90 and 98 % for the same pH values respectively in six hours. As can be observed, the 6-hour Eff (%) were higher than the 1-hour Eff (%) and therefore more copper was leached in 6 hours than in 1 hour at the desired pH values though it has been reported than Eff (%) as high as 90 % are attained within 30 minutes in conventional leaching [27]. Therefore, leaching or extraction of copper from dolomitic ore, like other copper ores, increases with time. The kinetics of dolomitic ore shows that the reaction with $H_2SO_4$ was second order with respect to chalcopyrite and first order with respect to dolomite.

The economic evaluation of dolomitic-copper leaching was found to be profitable though there was an increased usage of gangue acid due to the presence of dolomite. The presence of dolomite in ore is disadvantageous because it increases the consumption of acid for leaching and can make the process unsustainable. A sustainable process is that which gives positive balance (profit) between costs and sales [28, 29]. Reversing the pH of the leaching process, by arranging reactors in series, the profit margins can greatly be improved. The results of this study have produced higher levels of profit when high pH was used; i. e., pH from 1.8-2.2.2 particularly for acid sales. The profit levels did not change significantly despite reversing the pH. However leaching from low to high pH would be more favourable than from high to low pH. This would allow more of metal to be leached before the solution passes through the reactors and prevent excess metal leftover in solution.

## CONCLUSIONS

The kinetics of dolomitic ore showed that the reaction with $H_2SO_4$ was second order with respect to chalcopyrite

and first order with respect to dolomite and was consistent with the shrinking core model. The increase in temperature produced an increase in the recovery of copper from solids into the bulk solution. The leaching of dolomitic-copper ore was favoured at low pH values (1.8<pH<3) than high ones (pH >3). The increase in pulverisation time increased the recovery of copper by sulphuric acid. The Eff (%) increased with the decrease in particle size. The profit levels decreased as the acid production decreased. Profit levels based on copper sales were higher than those based on the acid sales. The profit levels based on variable pH; high to low pH (pH 1.8-2.2), were higher than values for leaching from low to high pH (pH 3.0-2.6). The presence of dolomite increased the cost of leaching as it took up acid that could have been used for leaching copper.

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