

## QUANTITATIVE LEACHING OF ZINC AND COPPER USING HCL FROM POLYMETALLIC SULPHIDE ORE OBTAINED FROM ZARARA HILL, NIGERIA

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### Abstract

*This is a study of the leaching and dissolution kinetics of zinc and copper from polymetallic sulphide ore obtained from Zarara Hill, Kaduna state, Nigeria. The elemental analysis ICP-OES showed that the ore contains iron (68440mg/kg), Zinc (27477mg/kg), Copper (26387mg/kg), lead (25130mg/kg) and Sulphur (33017mg/kg) as major elements. After leaching in different concentrations of HCl, the amount of zinc and copper dissolved increased meaningfully by an increase in HCl concentration from 0.5 to 9 M. The findings of this study demonstrate that increase in temperature is accompanied by an increase in the amount of zinc and copper that is leached from the roasted sulphide ore. From the plot of  $1 - 2/3X - (1 - X)^{2/3}$  versus leaching time for data displayed on the effect of HCl Concentration on zinc and copper dissolution, The slope of the straight-line graph ( $K_1$ ) was calculated, this means that the order of reaction concerning  $H^+$  ion concentration for zinc and copper dissolution is 0.53 and 0.67 respectively. Also, from the plot of  $1 - 2/3X - (1 - X)^{2/3}$  versus leaching time at different temperatures for the data presented on effect of temperature on zinc and copper dissolution by 9M HCl. The rate constants  $K_2$  were determined from the gradient of the straight lines in the various plots and were used to plot the Arrhenius plot where the activation energy was calculated to be 24.3 and 19.7kJmol<sup>-1</sup> for zinc and copper dissolution respectively.*

**Key Words:** Sulphide ore, Dissolution, Zinc, Copper, Leaching, HCl

### Introduction

Ores are complex by nature, despite the apparent simplicity of their chemical formula. Sulphide ores are the most complex of all mineral ores; for instance, chalcopyrite, a sulphide of Cu and Fe,

contains almost all the element in the periodic table that form sulphides (eg, Pb, Hg, As, Te, Se, Zn, Cd, Ni, Co, etc.). This makes the utilization of sulphide ores rather problematic (Gerald *et al.*, 2012). As these ores become more complex,

various technologies have emerged that have impact on their laboratory analysis, industrial, processes and uses. Some may involve pyrometallurgy in their utilization, some requiring hydrometallurgy, while others may need both processes, and even some eventually culminate in electrometallurgical route for the recovery and refining of the valuable metals and others of secondary value (Huai-Zhong *et al.*, 2010).

The hydrometallurgical method has remained the most prominent method in recovering many metals from their ores. The process typically entails extracting metal from ores by leaching into suitable solution, where it can be recovered using any other technique, including solvent extraction, precipitation, electro-winning and ion exchange. Various works were done on copper and lead leaching using different leaching solutions and with varying leaching conditions (Ajibola and Jimoh, 2014).

Sphalerite, a zinc sulfide, is the most abundant zinc-containing ore, its concentrate contains 60–62% zinc. Other zinc ores include smithsonite (zinc carbonate), hemimorphite (zinc silicate), wurtzite (another zinc sulfide) and so on.

The mineral chalcopyrite contains about 70% of the world's copper reserves. Currently, copper is extracted from high-grade chalcopyrite through smelting a high temperature process with undesirable

environmental side effects (Thomas, 2009). Other copper ores are chalcocite, covellite, bornite, malachite and many more.

The study focused on the leaching and dissolution kinetics of Cu and Zn present in Zarara hill sulphide ore using HCl, with the percentages recovered at different concentration of the acids and at the different time intervals been assessed. The leaching process of zinc and copper from the complex ore was described by the best kinetic model in this study, which examined the dissolution kinetics in accordance with shrinking core models.

## Methods

The polymetallic sulphide ore used for this research was collected from the geology department, Ahmadu Bello University, Zaria, Nigeria. The Zarara hill occupies an area lying between Latitudes 10°05'00" N – 10°52'00" N and Longitudes 8°33'00" E – 8°35'00" E.

It forms a prominent part of the peripheral ring dyke of the Banke Younger Granite ring complex. In Kaduna state, Nigeria, the Banke Younger Granite Ring Complex is accessible through the Jos – Saminaka – Kano, Pambegua – Ikara and Zaria – Dutsenwai – Anchau tarred roads. It is situated about 2 km northwest of Ririwai Complex, 15km north of the Kudaru Complex and 42km east of the Dutsenwai Complex.

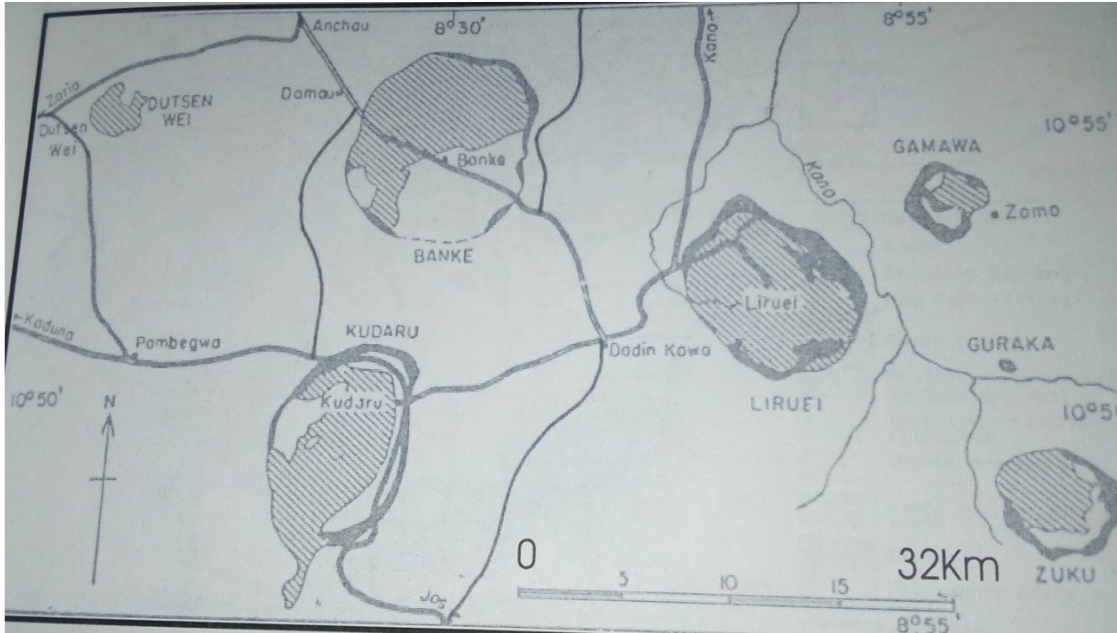
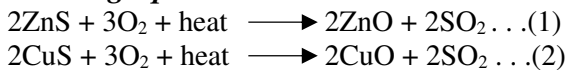


Fig. 1: Location of Zarara Hill (Banke Younger Granite Ring Complex)

Samples of the ore were crushed, ground and sieved to a size sufficiently fine to liberate the valuable minerals from one another using a crusher, ball mill and automatic sieve shaker respectively. The elemental analysis of the ore sample was carried out using ICP-OES (Perkin Elmer Avio 200, USA). The sieved ore was then roasted at 1000°C for 2 hours.

**Roasting equation**



**Leaching Procedure**

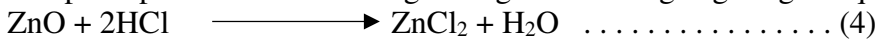
A 250ml glass reactor with a mechanical stirrer was used for the leaching experiment. The reactor was filled with 100ml of HCl (0.5 M – 12 M) which was heated to the desired temperature (Baba and Adekola, 2010). For every leaching experiment, the solution mixture was freshly prepared by

dissolving 10g/L of the sulphide ore in HCl at 28°C to 80°C by Aydogan *et al.* (2007a). The concentration that produced the greatest dissolution was subsequently used to optimize other leaching parameters including temperature and stirring speed. The activation energy,  $E_a$  was evaluated from the Arrhenius plots (A plot of  $\ln K$  versus  $1/T$  ( $K^{-1}$ )). In all cases, the amount of the zinc and copper dissolved was calculated using equation 2 below;

$$\alpha = \frac{\rho(M)}{w(M)\rho L} \dots \dots \dots (3)$$

Where  $\rho(M)$  is each of the concentration of the metal in leach liquor (g/L),  $w(M)$  is the mass fraction of each of the metals in the ore and  $\rho L$  is solid loading or solid–liquid ratio (g/L) (Baba *et al.*, 2014b).

The principal reaction occurring during the leaching is giving in equation 4 and 5



**Results and Discussion**

The result of the elemental analysis by ICP-OES in part per million (ppm) is presented in table 1 below;

Table 1: Elemental composition of the sulphide ore

Fe (mg/Kg)	Zn (mg/Kg)	Cu (mg/Kg)	Pb (mg/Kg)	S (mg/Kg)	Co (mg/Kg)	Ni (mg/Kg)	Mo (mg/Kg)	Cd (mg/Kg)
68440	27477	26387	25130	33017	24.54	13.4	833.7	21.6

The elemental composition of the Zarara Hill sulphide ore examined by the ICP-OES technique revealed that the ore contains Fe (68440mg/kg), Zn (27477mg/kg), Cu (26387mg/kg), Pb (25130mg/kg) and S (33017mg/kg) as major elements. With Co, Ni, Mo, Cd and so on, recorded at low to trace levels.

**Dissolution Kinetics Study**

The preliminary investigation on the search for suitable mineral acid for dissolution of zinc, copper revealed that HCl performed better than either HNO<sub>3</sub> or H<sub>2</sub>SO<sub>4</sub> in terms metals dissolution, this was also reported by Baba and Adekola (2011).

The dissolution kinetic study of the sulphide ore was limited to its dissolution in HCl which gives the highest percentage

dissolution of the metals in different concentrations of the HCl.

**Effect of Stirring Rate**

Table 2 shows the effect of stirring rate on sulphide ore dissolution in HCl 9M. The results revealed that the ore dissolution depends largely on the stirring rate of 0–720rpm. The dissolution increased from 59% (at 0rpm) to 83.8% at 450rpm for zinc and 64% (at 0rpm) to 78.6% at 450rpm for copper but above 450 rpm, the dissolution decreases, therefore, the stirring rate no longer influences solid dissolution. Hence, the optimal speed was attained at 450rpm and was used for further experiments. Similar results of this nature are available in the literature (Olanipekun, 2000; Baba and Adekola, 2012).

Table 2: Effect of Stirring Rate on Zinc Copper and Lead Dissolution in HCl 9 M

Stirring rate per minute	Percentage of zinc dissolved	Percentage of copper dissolved
0	59	64
90	66.6	67.4
180	72.8	70.5
270	77.8	73.4
360	81.5	76
450	83.8	78.6
540	82.8	77.3
630	80.9	76.1
720	80.2	75.7

**Influence of HCl Concentration**

Figures 2 and 3 represent the result of HCl concentration on zinc and copper dissolution respectively at a stirring speed

of 450 rpm, a temperature of 55°C using a particle size of -112 + 63µm and within 120 minutes.

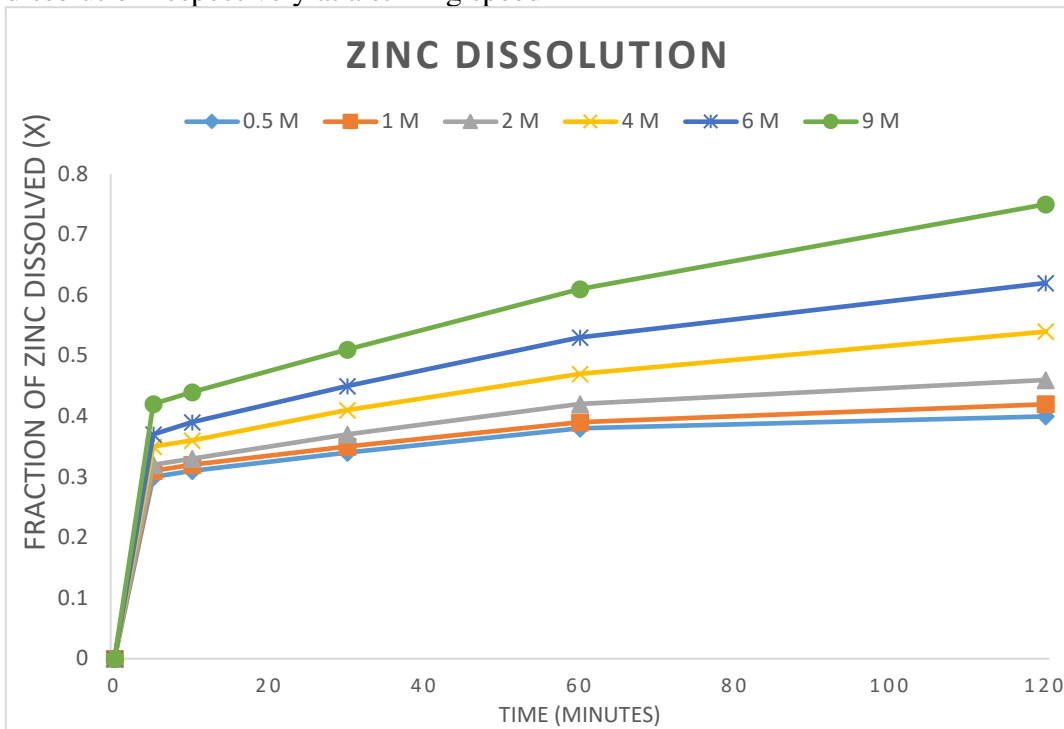


Fig. 2: Influence of HCl Concentration on Zinc Dissolution

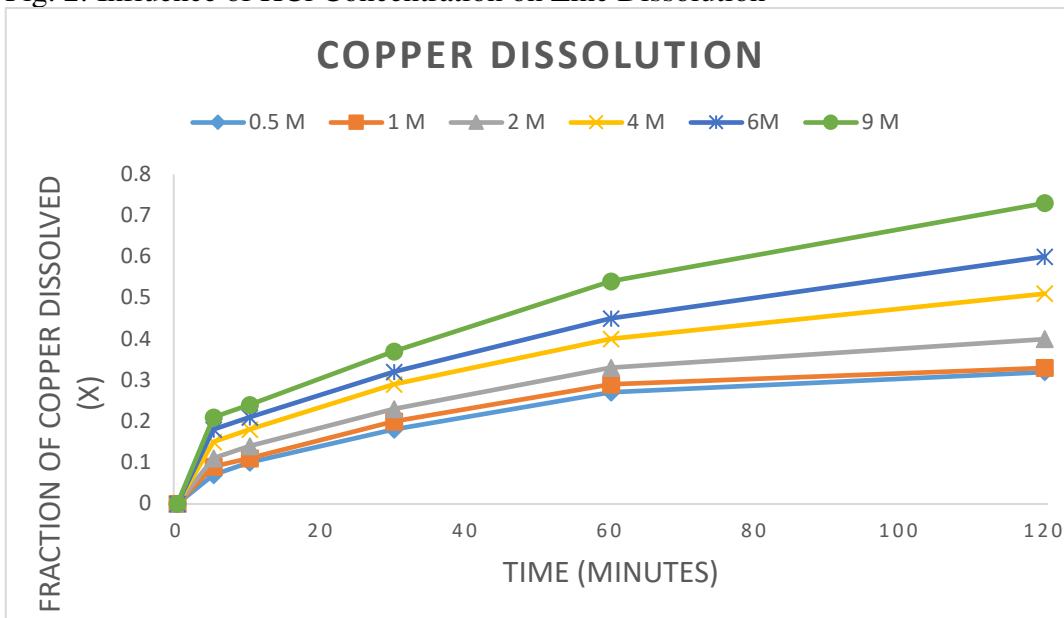


Fig. 3: Influence of HCl Concentration on Copper Dissolution

It is apparent from the two figures that dissolution increases with increase in HCl concentrations and increase in dissolution time from 5 to 120minutes. At the end of 2 hours about 75% zinc and 72% copper were dissolved in 9 M HCl. Therefore, 9M HCl solutions was used for further investigations. Baba and Adekola (2012) reported that the fraction of galena dissolved increases with increasing HCl concentration. It appears that the effect

was very mild when the acid concentration was increased from 8.06 to 12M.

**Effect of Temperature**

The effect of temperature on zinc, copper and lead dissolution from the polymetallic sulphide ore has been studied over the temperature range of 30 - 80°C, 9M HCl solution at a stirring rate of 450rpm using solid/liquid ratio of 10g/L. These results are illustrated in figure 4 and 5 for effect of temperature on zinc and copper dissolution respectively.

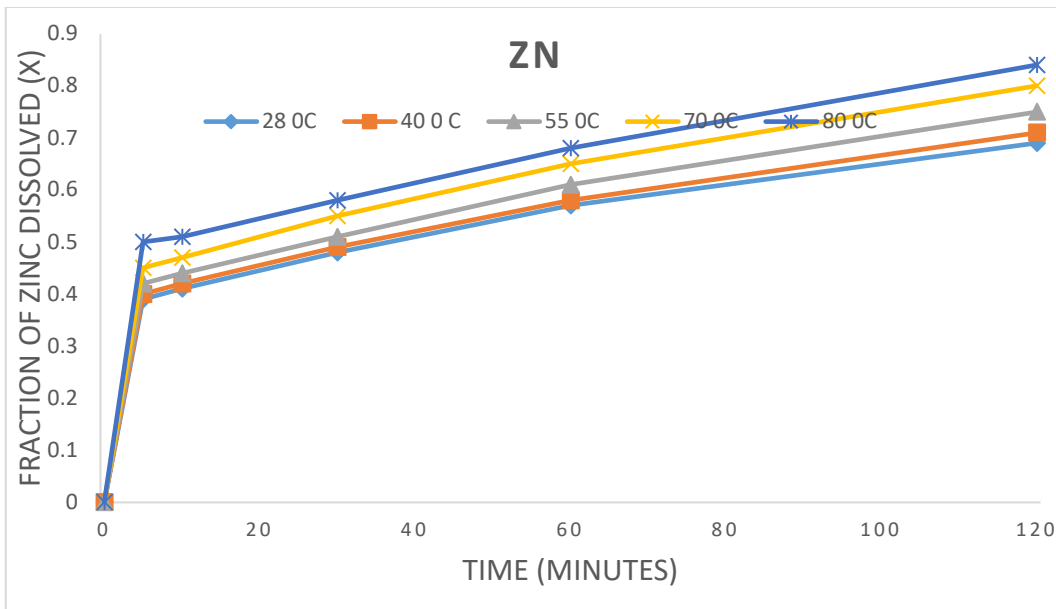


Fig. 4: Influence of Temperature on Zinc Dissolution by 9M HCl

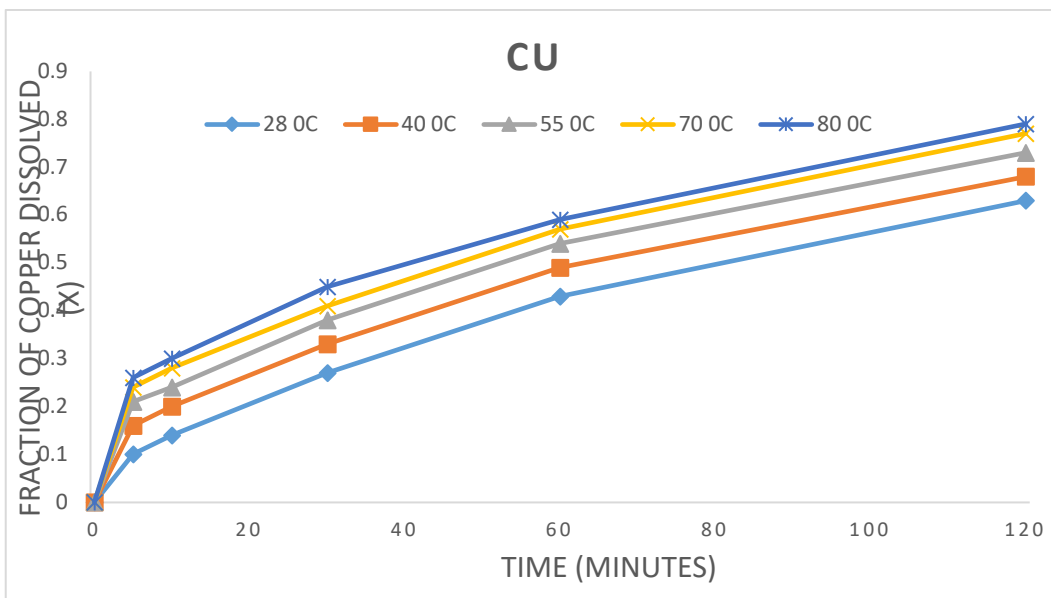


Fig. 5: Influence of Temperature on Copper Dissolution by 9 M HCl

From literature, increase in temperature brings about increase in zinc and copper dissolution in hydrochloric acid. This particular investigation was limited to 80 °C because of significant loss of acid solution due to evaporation (Baba and Adekola, 2010).

**Dissolution Kinetics Model**

For this analysis, three shrinking core models were tested for better understanding of the dissolution of zinc and copper in HCl media. The kinetic models as previously utilized by some authors such as Aydogan *et al.* (2007a,b), Baba and Adekola (2010) Baba and Adekola (2012), is as follows

$$1 - (1 - X)^{1/3} = \frac{K_0 M_s C_A}{\rho_s a r_0} = K_2 t \dots\dots\dots (6)$$

$$\left(1 - \frac{2}{3}X\right) - (1 - X)^{2/3} = \frac{2M_s D C_A}{\rho_s a r_0^2} = K_3 t \dots\dots\dots (7)$$

$$\left(1 - \frac{2}{3}X\right) - (1 - X)^{2/3} + \frac{1}{b} \left(1 - (1 - X)^{1/3}\right) = K_4 t \dots\dots\dots (8)$$

Equation 6 can be applied to a chemical reaction controlled process at the interface while Equation 7 is applied to diffusion-controlled process through the product layer and Equation 8 is a mixed controlled process (a combination of surface reaction and diffusion controlled process). Data were found only to fit the relation in Equation 7 with a perfect correlation. The analysis of the plots of other kinetic curves, however, did not give a perfect straight line. Hence, the linearization of Figure 2, 3, 4 and 5, by Equation 7 was

made. Due to this, the relation:  $1 - (2/3)X - (1 - X)^{2/3} = k_3 t$ , gave an average correlation coefficient of 0.9952 and 0.9541 and this is presented in Fig. 7 and 11 for zinc and copper dissolutions respectively.

The Arrhenius equation was used to determine the Activation Energy,  $E_a$

$$K = A e^{-E_a/RT} \dots\dots(9)$$

Where K is the rate constant, A is a constant related to the geometry needed, T is temperature in Kelvin (K) and R is the gas constant ( $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ ),

$$\ln K = \frac{-Ea}{R} \left(\frac{1}{T}\right) + \ln A \quad \dots\dots(10)$$

A straight line graph of lnK versus the inverse of the temperature (1/T) is plotted.

The value of the slope (m) is equal to  $-\frac{Ea}{R}$  and R is a constant ( $8.314\text{Jmol}^{-1}\text{K}^{-1}$ ).

**Zinc Dissolution Kinetic Model**

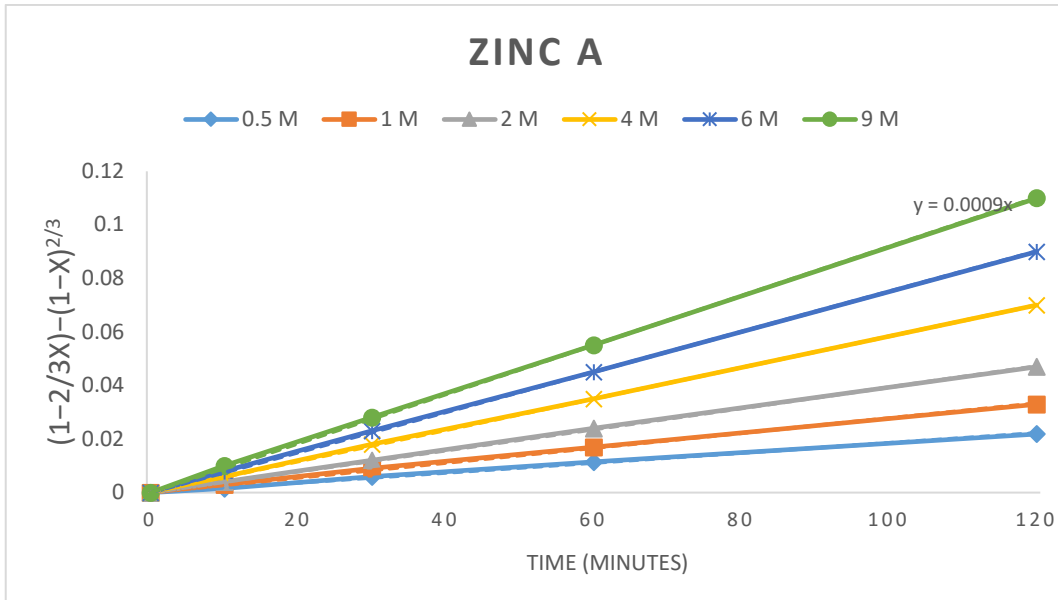


Fig. 6: Plot of  $1 - (2/3)X - (1 - X)^{2/3} = kt$  Versus Leaching Time at Various HCl

**Concentrations for Data on the Influence of HCl Concentration on Zinc Dissolution**

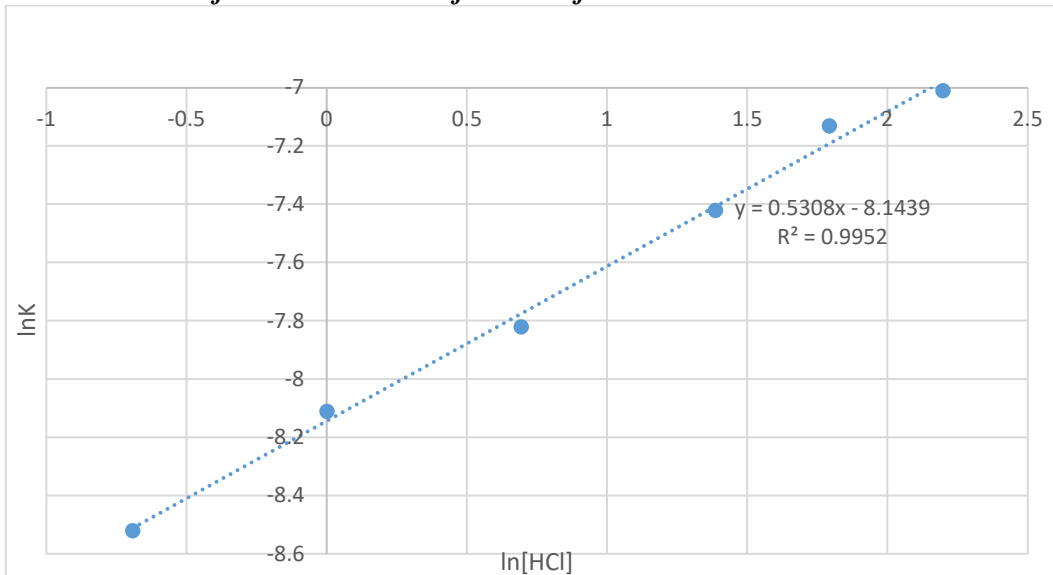


Fig. 7: Plot of  $\ln k_1$  Versus  $\ln [HCl]$  for Zinc Dissolution



The experimental rate constant  $k_1$  for zinc dissolution in HCl was calculated from figure 6 above using the slope of the straight line at different concentrations of HCl. The plot of  $\ln k_1$  against  $\ln [\text{HCl}]$  is illustrated in Fig. 7, with a slope of 0.53. This shows that the order of reaction for zinc dissolution with respect to  $\text{H}^+$  ion

concentration is 0.53 with correlation coefficient of 0.9952.

Additionally, equation 7 was used to linearize the data in figure 3 as shown in figure 8, and it allowed for the calculation of the apparent rate constant  $k_2$  using the slopes of the straight lines.

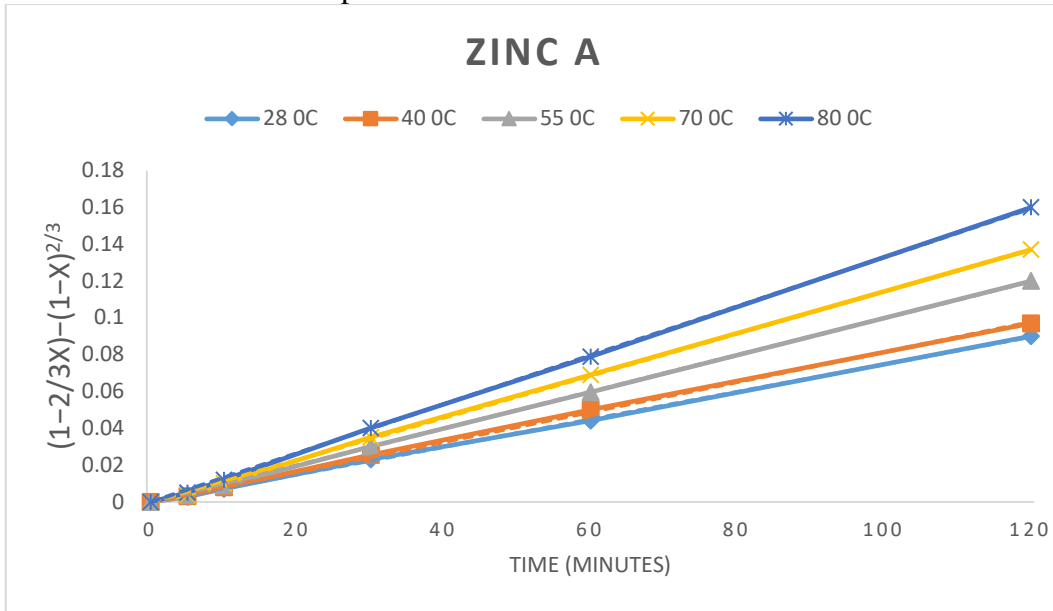


Fig. 8: Plot of  $1 - (2/3)X - (1 - X)^{2/3}$  Versus Leaching Time at Different Temperatures, for the Data Presented on the Influence of Temperature on Zinc Dissolution by 9 M HCl

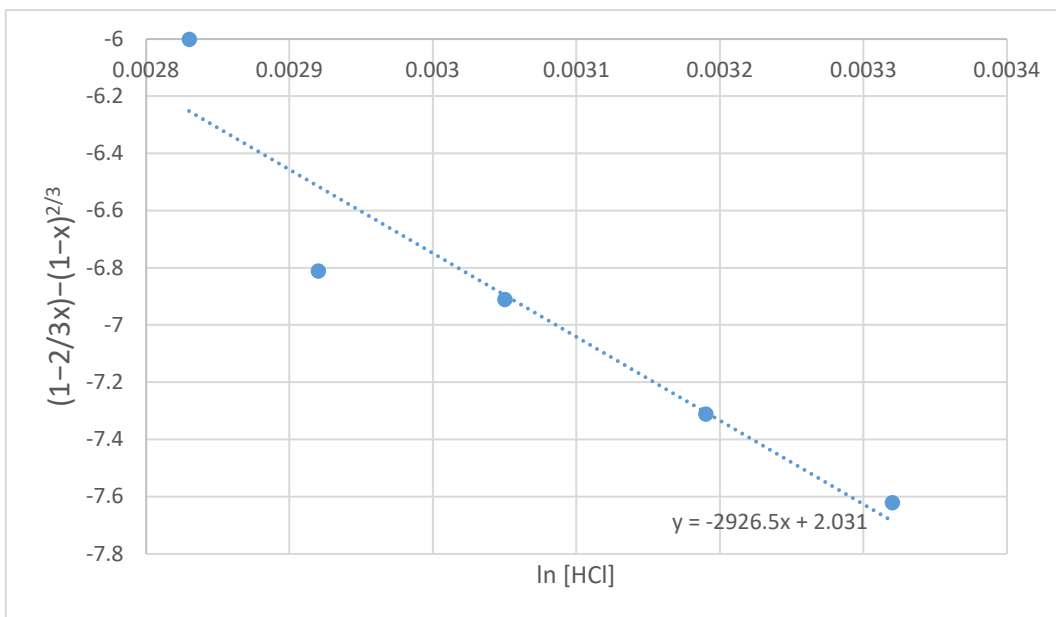


Fig. 9: Plot of  $\ln K_2$  Versus  $1/T$  ( $K^{-1}$ ) for Zinc Dissolution

From the rate constant derived from the slopes in Figure 7 and inverse of temperature ( $1/T$ ), the Arrhenius plot in Figure 9 was drawn from which gives a slope of -2926.5 and the activation energy for zinc dissolution was calculated to be 24.3 kJ/mol which supports the proposed diffusion controlled mechanism.

The dissolution data indicated that the shrinking core model is appropriate, and as result, the dissolution leaching procedure was carried out in accordance with the diffusion control mechanism with

surface chemical reaction serving as the rate controlling step.

**Copper Dissolution Kinetic Model**

The experimental rate constant  $k_1$  for copper dissolution was calculated from the slope of the straight line at different HCl concentrations as presented in figure 9 and the plot of  $\ln k_1$  against  $\ln[HCl]$  is shown in Figure 10 with a slope of 0.67. This demonstrated that the order of reaction for zinc dissolution with respect to  $H^+$  ion concentration is 0.67 with correlation coefficient of 0.9541.

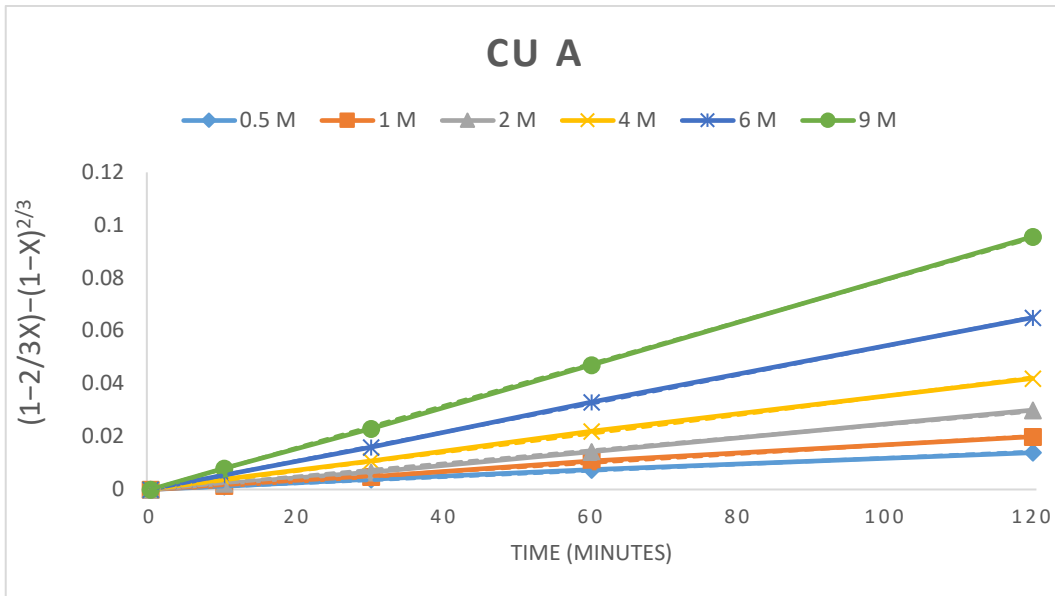


Fig. 10: Plot of  $1 - (2/3)X - (1 - X)^{2/3} = kt$  Versus Leaching Time at Various HCl Concentrations for Data Presented on the Influence of HCl Concentration on Copper Dissolution

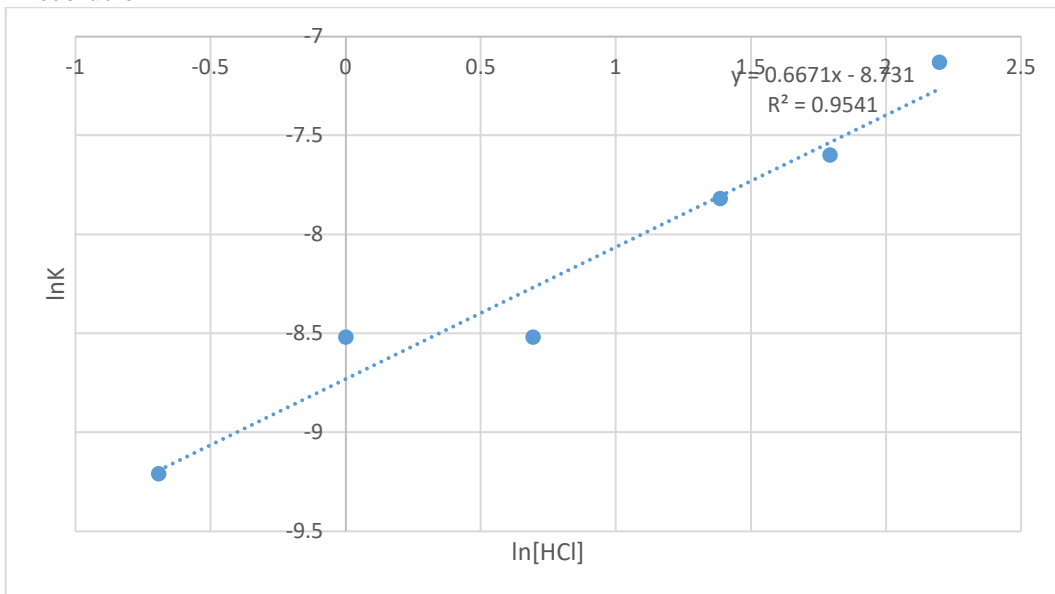


Fig. 11: Plot of  $\ln k_1$  Versus  $\ln [HCl]$  for Copper Dissolution

Additionally, equation 7 was used to linearize the data in Figure 3 regarding the influence of Temperature on Copper Dissolution by 9M HCl. This is

demonstrated in Figure 11, where the apparent rate constants,  $k_2$  was calculated from the slopes of the straight lines.

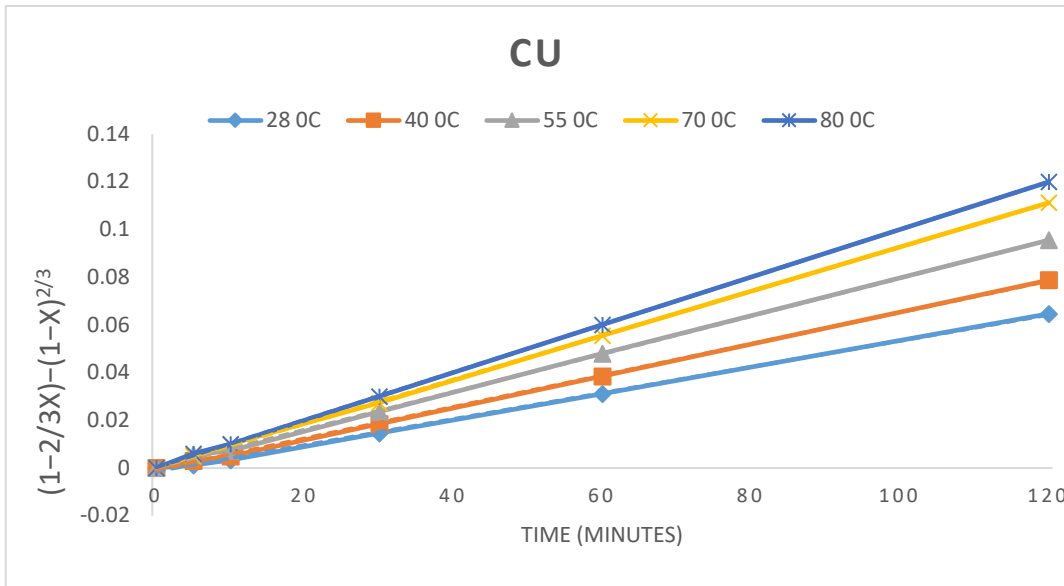


Fig. 11: Plot of  $1 - (2/3)X - (1 - X)^{2/3}$  Versus Leaching Time at Different Temperatures, for the Data Presented on the Influence of Temperature on Copper Dissolution by 9M HCl

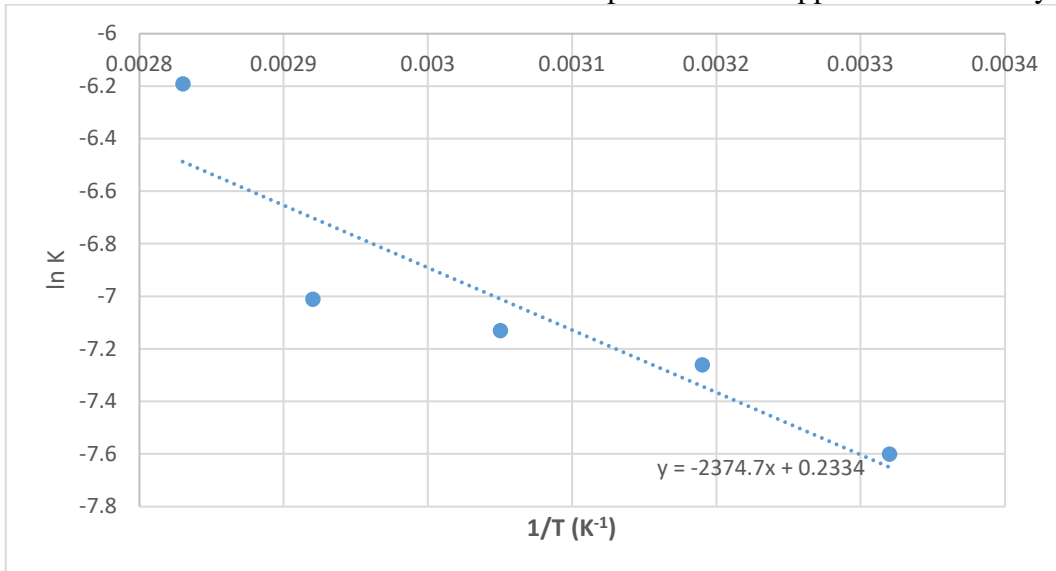


Fig. 12: Plot of  $\ln K_2$  Versus  $1/T$  (K<sup>-1</sup>) for Copper Dissolution

The rate constants from the slopes in Figure 11 and inverse of temperature ( $1/T$ ) was used to plot the Arrhenius diagram in Figure 12 for copper dissolution from which the activation energy of 19.7kJ/mol was calculated. these supported the proposed diffusion controlled mechanism.

The dissolution data indicated that the shrinking core model is appropriate, so the dissolution leaching proceeded according to the diffusion control mechanism with surface chemical reaction serving as the rate controlling step. A study on quantitative leaching of a Nigerian chalcopyrite ore by nitric acid by Baba *et*

al. (2014) found that the reaction rate is controlled by diffusion of copper through the porous product layer with the reaction order with respect to HNO<sub>3</sub> concentration found to be 0.51 and the activation energy E<sub>a</sub> to be 29.93kJ/mol.

### Conclusion

The optimal stirring rate was reached at 450 rpm and was used for further analysis because the effect of stirring rate on zinc and copper dissolution in 9 M HCl shows that stirring rate no longer affect solid dissolution above 450 rpm.

Additionally, it was found that increasing the concentration of HCl from 0.5 to 9M significantly increased the rate at which zinc and copper dissolves. The rate of zinc and copper dissolution was analyzed over the range of 28°C to 80°C, in 9M HCl, and a stirring speed of 450 rpm as seen in figure 3 and 4. The results indicated that increase in temperature is accompanied by an increase in the concentration of zinc and copper removed from the roasted sulphide ore.

From the plot of  $1 - 2/3X - (1 - X)^{2/3}$  versus leaching time for data presented on the influence of HCl Concentration on zinc and copper dissolution, the slopes gave the experimental rate constants, K<sub>1</sub>, these values were used to plot a graph of ln K<sub>1</sub> against ln [HCl] for both zinc and copper. The slope of the straight-line graph was calculated to be 0.53 and 0.67, this revealed that the order of reaction concerning H<sup>+</sup> ion concentration for zinc and copper dissolution is 0.53 and 0.67 respectively. Also, from the plot of  $1 - 2/3X - (1 - X)^{2/3}$  versus leaching time at different temperatures for the data presented on the influence of temperature on zinc and copper dissolution by 9 M HCl. The slope of the straight line gave the

apparent rate constants K<sub>2</sub> and were used to plot the Arrhenius plot and the activation energy was calculated to be 24.3 and 19.7kJmol<sup>-1</sup> for zinc and copper dissolution respectively.

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