



Chalcopyrite Leaching in Ammonia-Ammonium Chloride Solutions: Insight into the Dissolution Kinetic Studies

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Abstract: The hydrometallurgical method for processing chalcopyrite ore has gained enormous attention due to the environmental problems emanated by the conventional pyrometallurgical route. Here, hydrometallurgy is considered an alternative that may be more of low-cost and environmentally friendly. Thus, alkaline leaching has been considered an effective, efficient, and acceptable leachant for chalcopyrite ore dissolution. The dissolution behaviour of copper from low-grade chalcopyrite mineral was examined in an ammonia-ammonium chloride media. However, the influence of experimental conditions including alkali concentration, reaction temperature, and particle size was considered. At optimized leaching conditions (0.4 mol/L NH₃-NH₄Cl; 75 °C; 43 μm), 81.1% dissolution efficiency was achieved within 120 minutes. The dissolution mechanism with estimated activation energy (*E_a*) of 29.95 kJ/mol is by the proposed diffusion control mechanism. Hence, the dissolution rate was affirmed by analyzing the raw ore and un-leached residue using XRD and SEM-EDS analyses for possible industrial utilities.

Keywords: Chalcopyrite, leaching, dissolution kinetics, activation energy, ammonia-ammonium chloride

1. Introduction

As the global copper supply appreciably increases, so does the need for treating and processing low-grade copper mineral ores. The dissolution of low-grade sulphide minerals including chalcopyrite has gained enormous attention as a result of the downfall of high-grade copper ore reserves [1-3]. Chalcopyrite (CuFeS₂) has been reported to be the most viable copper ores in the world today [4]. Conventionally, chalcopyrite ore were being processed by smelting process. However, due to the high-energy intensive coupled with the evolution of sulphur dioxide (SO₂) gases associated with the process, it is worthwhile noting that new technological advancements capable of minimizing the drawbacks are being proposed [5,6].

Although more than 70% of copper was obtained via pyrometallurgical routes such as roasting, smelting, calcining, etc, much consideration has been given to hydrometallurgical methods [7]. The latter has been considered to be of low-cost and eco-friendly than the former, most especially when the metal of interest (copper) present in the ore was of low-grade [8,9].

Presently, approximately 18% of global copper production emanated from hydrometallurgy [10]. The process involves leaching, solvent extraction, and electrolytic precipitation. However, these routes can be classified based on the leachant type including sulfate, chloride, ammonia, and nitrate, among others [11]. Out of the aforesaid reagents, it has been reported that ammonium chloride dissolution has distinct properties, high dissolution, low-cost coupled with ease of copper recovery by solvent extraction [12].

The utilization of ammonia and ammonium salts as a leachant in the processing and extraction of copper from chalcopyrite ore has become an efficient and effective method of acidic leaching as a result of lowering the problems of acid consumption, ease of regeneration by evaporation, among others [13].

Therefore, the current study examined the leaching rate of a chalcopyrite ore in combined ammonia-ammonium chloride media.

2. Materials and Method

2.1 Materials

The chalcopyrite sample was obtained from Wase, located in Plateau State, Nigeria. The sample was taken selectively, crushed, and sieved into four different particle diameters 45, 75, 90, and 125 μm , respectively. Distilled water was used in all experiments.

2.2 Leaching Procedure

The leaching investigations were performed in a beaker equipped with a mechanical stirrer, a thermometer to control the reaction temperature, and the glass leach reactor was equilibrated to a temperature of 25 - 75°C at a constant stirring rate. The $\text{NH}_3\text{-NH}_4\text{Cl}$ concentration was varied from 0.05 – 0.5 mol/L; whilst the particle size diameters were 45, 75, 90, and 125 μm , respectively. Determination of copper ion and other associated gangues in the pregnant solution was determined at different leaching times by atomic absorption spectrophotometer (AAS) [14 – 17]. However, selected leach residues obtained at optimal conditions (0.4 mol/L $\text{NH}_3\text{-NH}_4\text{Cl}$, 75°C, 45 μm , 2 hours) were critically analyzed using scanning electron microscopy in conjunction with energy dispersive spectroscopy (SEM-EDS) to confirm the morphology of the product layers on the ore surface. Material purity in the residues was identified by a powdered X-ray diffractometer (XRD).

3. Results and Discussion

3.1 Ore Analysis

The analysis of the chalcopyrite ore investigated using MINI PAL 4 spectrometer with particle sizes 45 μm gave Fe_2O_3 (63.49%), Al_2O_3 (2.10%), CuO (11.30%), MnO (7.95%), SO_3 (8.60%), and SiO_2 (0.23%), respectively. As detected by EDS, other oxides that occurred in trace amounts include 0.47 wt.% CaO , 0.20 wt.% Na_2O , 0.10 wt.% MgO , and 0.06 wt.% K_2O . However, the XRD pattern revealed that *chalcopyrite* ($\text{Cu}_{4.00}\text{Fe}_{4.00}\text{S}_{8.00}$: 96-900-7573) and *siderite* ($\text{Fe}_{6.00}\text{C}_{6.00}\text{O}_{18.00}$: 96-900-0099) were the dominant mineral phases in the ore. Hence, the morphology of the raw chalcopyrite ore shows a cloudy *cum* agglomerated surface as summarized in Fig. 1 [18].

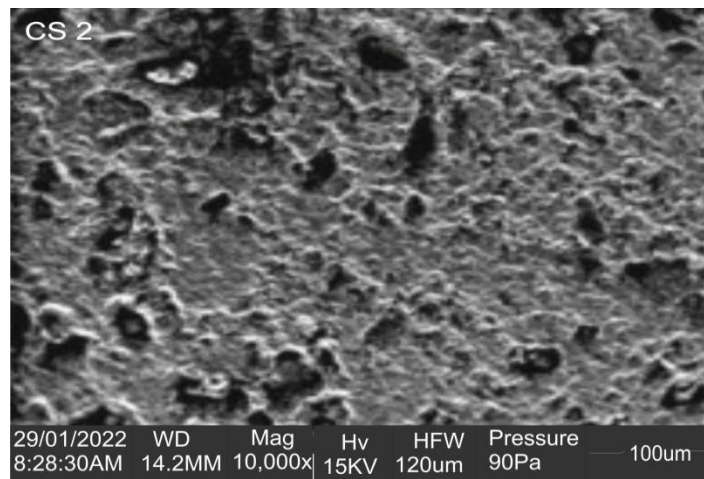


Fig. 1 - SEM micrograph of the raw chalcopyrite ore

3.2 Leaching Investigation

(a) Investigation Influence of Ammonia-Ammonium Chloride Concentration

The influence of ammonia-ammonium chloride ($\text{NH}_3\text{-NH}_4\text{Cl}$) concentration on ore dissolution shows appreciable copper extraction with increasing leachant concentration summarized in Fig. 2.

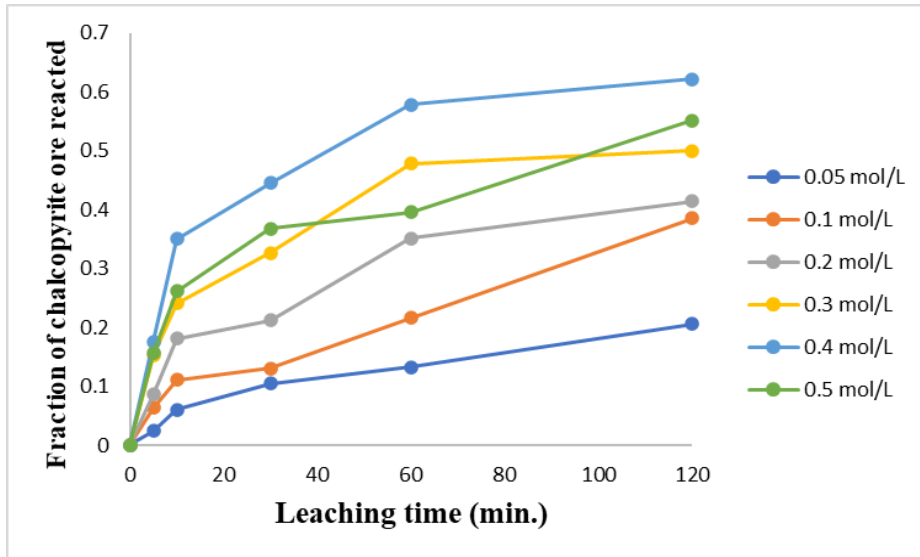


Fig. 2 - Influence of [NH₃-NH₄Cl] on ore dissolution at different leaching time. Conditions: [NH₃-NH₄Cl] = 0.05 – 0.5 mol/L, Reaction temperature = 55°C, Particle diameter = 45 μm

The chalcopyrite ore dissolved after 120 minutes at 55°C using 0.05 mol/L and 0.4 mol/L NH₃-NH₄Cl was 18.5% and 62.1%, respectively. However, it was affirmed that no appreciable difference with increasing the NH₃-NH₄Cl concentration from 0.4 mol/L to 0.5 mol/L was recorded; hence, 0.4 mol/L was chosen for further studies. Hence, the oxidative power of Cl⁻ ion increased with the increase of solution basicity, and thus contributed to copper dissolution [15,19].

(b) Influence of Reaction Temperature

The influence of reaction temperature on copper dissolution, under the experimental conditions: 0.4 mol/L NH₃-NH₄Cl, 25 – 75°C, 45 μm, and 120 minutes as shown in Fig. 3.

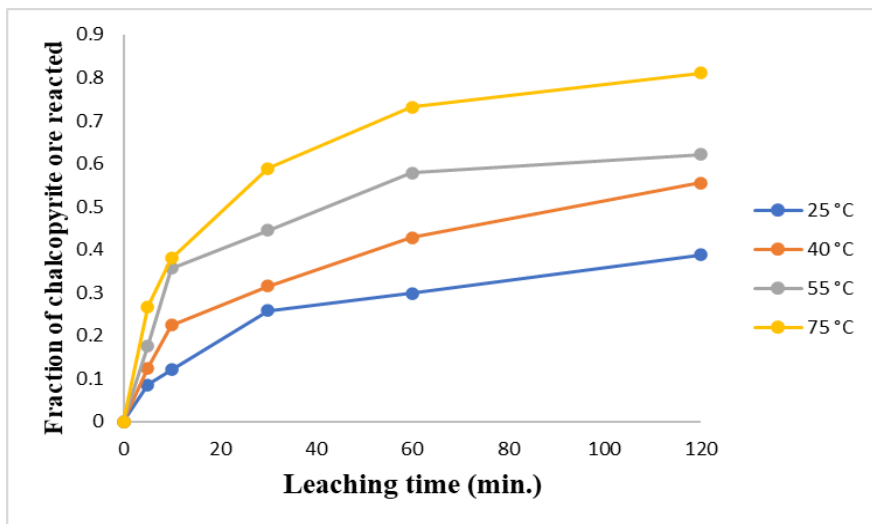


Fig. 3 - Influence of reaction temperature on chalcopyrite ore dissolution. Conditions: [NH₃-NH₄Cl] = 0.4 mol/L, Reaction temperature = 75°C, particle diameter = 45 μm

The reaction temperature has a great effect on ore dissolution rate. As projected, copper extraction increases with increasing reaction temperature. At 25°C, 32.4% copper was extracted after 120 minutes, and thus increased to 55.7% at 55°C. The maximum extraction (81.1%) at 75°C was recorded after 120 minutes. It was concluded that the rate of copper extracted into the solution was highly temperature dependent [20]. However, a slight decrease in the dissolution at the final stage of leaching was signified and could be due to the oxidative loss of the ammonia at higher temperatures [21].

(c) Influence of Particle Size

The influence of particle diameter on the dissolution rate was tested for four different size diameters (125, 90, 75, and 45 μm) at 75°C, in solutions containing 0.4 mol/L NH₃-NH₄Cl. The results depicted in Fig. 4 clearly shown that copper extraction greatly increased with a decrease in particle fraction.

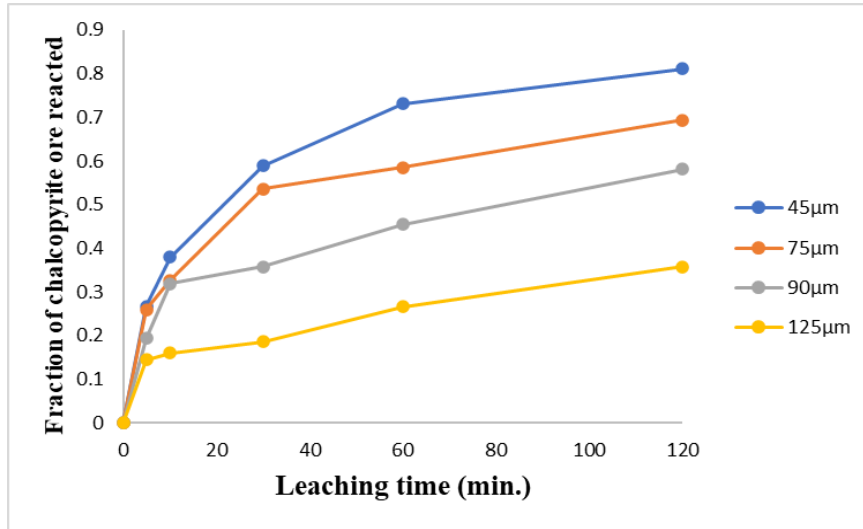


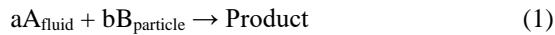
Fig. 4 - Influence of particle size on chalcopyrite ore dissolution. Conditions: [NH₃-NH₄Cl] = 0.4 mol/L, temperature = 75°C

Furthermore, copper dissolution reached 35.7, 58.1, 69.3, and 81.1% after 120 minutes of leaching for 125, 90, 75, and 45 μm particle fractions, respectively. It is obvious that least particle diameter gave a larger surface area between ore and leachant [22,23].

3.3 Discussion

(a) Kinetic Test

Dissolution of chalcopyrite ore can be explained by a shrinking core model (SCM) as summarized by the stoichiometry [24]:



The rate of chalcopyrite ore dissolution was fitted against shrinking core models through chemical and diffusion control reaction mechanisms. If the process obeyed a chemical controlled, the equation of the SCM can be given as [25]:

$$1 - (1 - \alpha)^{1/3} = kt \tag{2}$$

Also, if it is controlled by diffusion, the equation of the SCM can be expressed as Equation 3, where α = reaction fraction, k = rate constants, t = reaction time [26]:

$$1 - \frac{2}{3}\alpha - (1 - \alpha)^{2/3} = kt \tag{3}$$

From Equations (2) and (3), when the process is chemical control via product layer, the graph of $1 - (1 - \alpha)^{1/3}$ against time is a straight line with a correlation coefficient (R^2) of 0.986, and similarly, if the mechanism is diffusion controlled, the graph of $1 - 2/3\alpha - (1 - \alpha)^{2/3}$ versus time is also as a R^2 of 0.675. Hence, the results of the fitting test concerning NH₃-NH₄Cl leaching showed that the data fitted perfectly into Equation (3), as represented in Fig. 5.

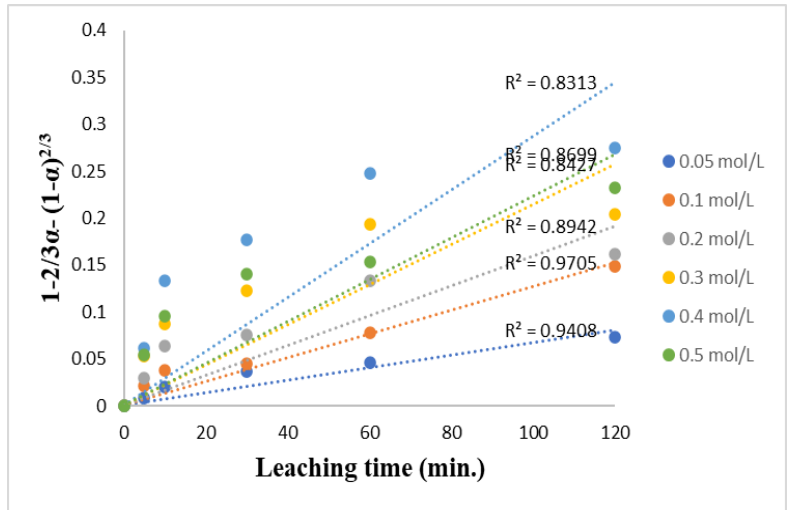


Fig. 5 - The plot of SCM against leaching time

However, experimental rate constant (*k*) was estimated from the gradient of Fig. 5, and results represented were used to make a plot of $\ln k$ versus $\ln [\text{NH}_3\text{-NH}_4\text{Cl}]$ as summarized.

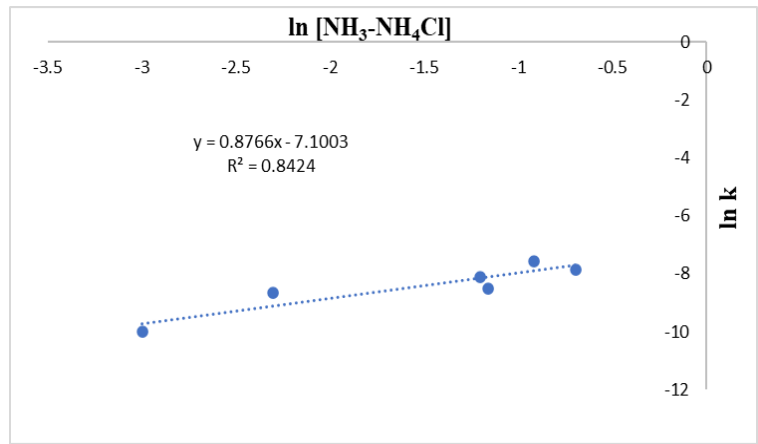


Fig. 6 - The plot of $\ln k$ as a function $\ln [\text{NH}_3\text{-NH}_4\text{Cl}]$

The slope of the straight lines graph estimated from the result in Fig. 6 was calculated to be 0.876 with a correlation coefficient of 0.842. This result indicates reaction order assumed to be first-order with respect to NH_4^+ ion. Again, the model Equation (3) was used to process the reaction temperature data (Fig. 7).

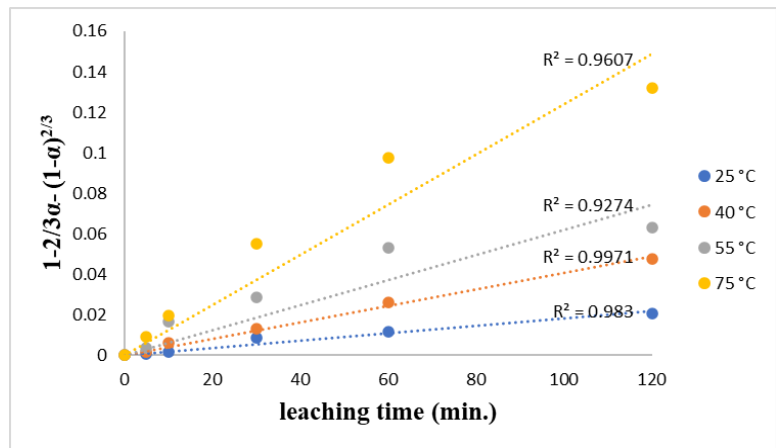


Fig. 7 - The plot of SCM against contact time at different temperatures

The rate constant, *k*, was obtained from the slopes of the straight line and was employed to make the plot of Arrhenius relation in Fig. 8.

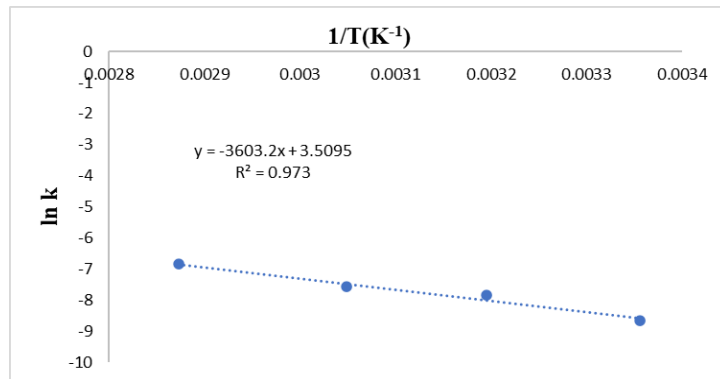


Fig. 8 - The plot of ln k against 1/T

From the slope of the straight lines in Fig. 8, activation energy was estimated to be 29.95 kJ/mol. This value suggests the rate mechanism occurs through a diffusion-controlled mechanism [27,28].

(b) Residual Mineralogical Characterization

The XRD data of the un-leached residue obtained at optimal conditions (0.4 mol/L NH₃-NH₄Cl, 75 °C, 45 μm, 120 min.) consisted of *albite* (Na_{2.00}Al_{2.00}Si_{6.00}O_{16.00}: 96-900-1634), *calcite* (Ca_{5.62}C_{6.00}O_{18.00}: 96-900-1298), *siderite* (Fe_{6.00}C_{6.00}O_{18.00}: 96-900-0099), and *quartz* (Si_{6.00}O_{6.00}: 96-500-0036) as the dominant phases as depicted in Fig. 9. Although, the presence of calcite in the trace phase couldn't be accounted for as a result of low intensity.

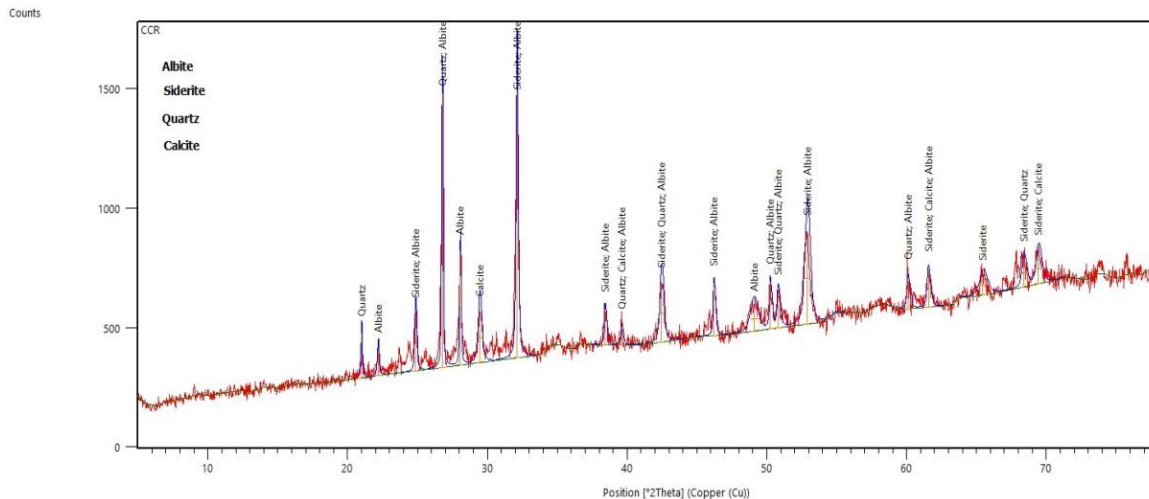


Fig. 9 - X-ray diffraction spectrum of the residual product

The SEM-EDS images of the residual product exhibit a sponge-like structure covering the surface of the mineral. The morphologies of the residual product are porous cum corrosive and the mineral surface is apparently passivating, which is in accordance with high dissolution obtained with the EDS yielding C (3.24%), O (20.50%), Al (9.10%), Cu (0.25%), and Si (59.72%), respectively as shown in Fig. 10.

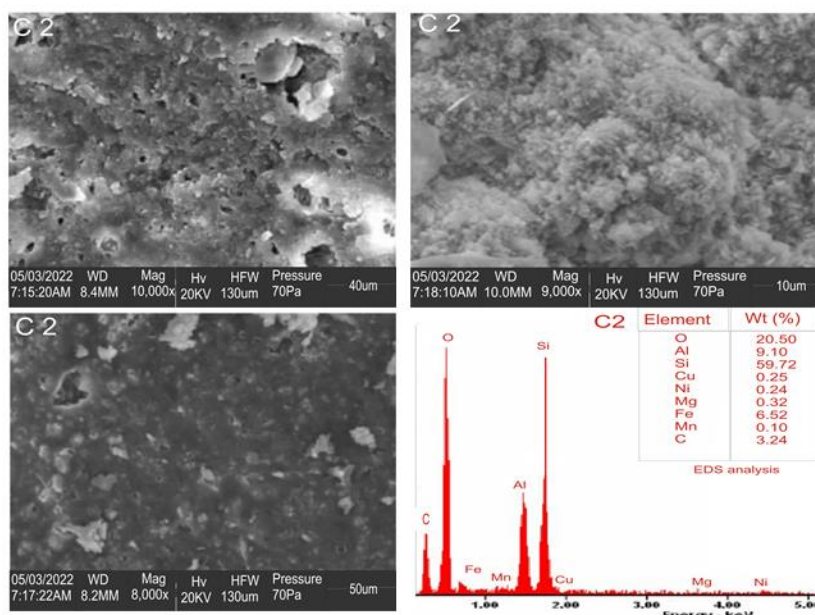


Fig. 10 - SEM-EDS micrographs of chalcopyrite leach residue by $\text{NH}_3\text{-NH}_4\text{Cl}$

4. Conclusion

Here, the chalcopyrite ore in ammonia-ammonium chloride solution has been systematically investigated by the hydrometallurgy technique. It was observed that the extent of ore dissolution appreciably increased with increasing ammonia-ammonium chloride and temperature and with a decrease in particle diameter. The best experimental conditions were determined as 0.4 mol/L $\text{NH}_3\text{-NH}_4\text{Cl}$ and 70°C . With a particle size of $45\ \mu\text{m}$, 81.1% copper dissolution efficiency was recorded after 120 minutes. However, dissolution rate is conforming by diffusion control with the calculated activation energy of $29.95\ \text{kJmol}^{-1}$ and the reaction order with was 0.876.

Conflict of Interest

The authors declare that there are no conflicts of interest.

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