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Effects of Roasting and Galvanic Action on the Recovery of Copper from Chalcopyrite

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Abstract: *Chalcopyrite ($CuFeS_2$) is the primary source of global copper supply, yet its extraction remains challenging due to passivation layers that form during the leaching process. This study investigated the combined effects of oxidative roasting and galvanic coupling with manganese dioxide (MnO_2) on copper recovery from a chalcopyrite concentrate with a head grade of 26.26% Cu. Samples of the concentrate were roasted at temperatures of 400°C, 600°C, and 900°C for one hour, the leaching of the roasted samples using a 0.03M sulfuric acid with and without MnO_2, at temperature ranges from 25°C to 55° for 8 hours. XRF, XRD, and SEM-EDS were used to analyse the phase transformations of the concentrate throughout the whole roasting process. Results showed that unroasted chalcopyrite yielded only 15% copper recovery with sulfuric acid alone but improved to above 60% with the addition of MnO_2. Roasting at 600°C produced the best results, achieving a recovery of 85% with only sulfuric acid and exceeded 90% when combined with MnO_2, reaching 95%. However, roasting at 900°C reduced copper recovery to 60%. Kinetic analysis revealed that the leaching process follows a diffusion-controlled shrinking core model with low activation energy. Overall, this study revealed that for effective copper recovery, and approach of combining both roasting and galvanic coupling is the best approach.*

Keywords: *Chalcopyrite, Roasting, Galvanic Action, Leaching Kinetics*

1. Introduction

Copper is an important metal used in modern industries such as construction, power generation, and electronics. Of all the copper minerals, chalcopyrite ($CuFeS_2$) is the copper mineral that provides about 70% of the world's copper supply [1-4]. In metallurgy, chalcopyrite is mainly subjected to pyrometallurgical methods like roasting after flotation. Roasting is a process in which sulfide ores are heated in the presence of oxygen to remove sulfur and other impurities as gases, leaving behind a more easily processed material. This method is meant to convert the chalcopyrite ore into an oxide for the leaching process to be performed with ease. However, this process releases large amounts of sulfur dioxide (SO_2), which harms the environment and has led to stricter global pollution regulations. Because of this, researchers have investigated alternative ways to extract copper, particularly hydrometallurgical and pyro-hydrometallurgical methods, which are more environmentally friendly and cost-effective [5-7].

The hydrometallurgical discipline has methods that can process low-grade copper ores while producing less SO_2 pollution. One of those methods is leaching. This method is a chemical process whereby an acid solvent is used to dissolve metals of value from their ores while simultaneously leaving behind the valueless material. The mineral chalcopyrite is an extremely difficult mineral to dissolve using standard leaching practices because of its tendency to form passivation layers. Passivation is the formation of surface layers during the leaching process of chalcopyrite, and these layers can hinder the dissolution of copper from the chalcopyrite mineral. The surface layers formed are elemental sulfur (S),

jarosite ($KFe_3 (SO_4)_2 (OH)_6$), and copper polysulfides (CuxS). Passivation is influenced by multiple factors such as temperature, pH, and redox potential [8].

Galvanic action, another factor in the leaching process. Galvanic action happens when two different minerals or metals come in contact within a solution, which then creates an electrochemical reaction that accelerates the dissolution of the desired metal. Pre-treatment methods such as roasting have been considered to reduce the passivation of chalcopyrite during the leaching process [9]. The use of different roasting temperatures, use of manganese dioxide as a galvanic couple, and low solution potentials have also been included.

Overcoming Passivation

Leaching at high temperatures, low solution potentials and galvanic coupling with manganese dioxide have been found to reduce the passivation of the chalcopyrite mineral. The oxidation of chalcopyrite is controlled at low redox potentials, which reduces the production of elemental sulphur and jarosite, which can form a passivating layer. Rather, the dissolution occurs through the direct electron transfer, which facilitates the extraction of copper [10]. The kinetics of chalcopyrite dissolution are improved by higher temperatures, which also increase reaction rates and decrease the persistence of intermediate passivation products. Pyrite acts as a galvanic couple with chalcopyrite, facilitating electron transfer. This galvanic interaction enhances iron dissolution from chalcopyrite, reduces the formation of iron-based passivation layers by preventing iron accumulation on the surface [11, 12].

2. Methodology

2.1. Chalcopyrite Sample Preparation

The chalcopyrite concentrate used in this experiment was received at a particle size of -75 µm. Before the roasting process, the concentrate was homogenized using a spinning riffler to ensure uniformity and representativeness.

A portion of the concentrate, 15 g for chemical analysis and 15 g for mineralogical analysis and surface structure analysis, was set aside for detailed analysis. Chemical analysis was performed using X-ray fluorescence spectrometry, mineralogical analysis was conducted using X-ray diffraction, and scanning electron microscopy (SEM) was used to analyse the surface structure of the chalcopyrite concentrate.

The chalcopyrite concentrate was roasted in a muffle furnace at temperatures of 400°C, 600°C, and 900°C for 1 hour. After the roasting process, the roasted concentrates were allowed to cool at room temperature and crushed to break up any agglomerates that had formed. The cooled roasted concentrates were then sieved to obtain a particle size range of -75 µm for the leaching step. Characterization was conducted on the roasted concentrates. The concentrates were analysed using XRF to determine compositional changes, XRD to identify phase transformations, and SEM to examine surface structural alterations from the roasting process.

The leaching of the roasted chalcopyrite was conducted in two processes: the first involved leaching using only a sulfuric acid solution, and the second involved galvanic-assisted leaching with manganese dioxide (MnO2).

2.2. Preparation of Manganese dioxide fines

The manganese dioxide (MnO_2) used in this experiment was received as a fine concentrate with a particle size of less than 75 µm. The received sample was sieved to ensure uniform particle size distribution of -75 µm. For the galvanic leaching process, the MnO2 to chalcopyrite ratio was optimized at 4:1 (w/w) based on previous studies and electrochemical considerations.

2.3. Leaching of Roasted Chalcopyrite concentrate with and without a galvanic couple

The leaching process was conducted in two ways. The first leaching process was leaching the roasted concentrate with only sulfuric acid, and the second leaching process was conducted on the roasted chalcopyrite using a galvanic-assisted process with manganese dioxide (MnO_2) to enhance copper dissolution. MnO_2 was introduced as an oxidant to facilitate the electrochemical oxidation of Cu(I) and

Fe(II) species.

Sulfuric acid with a purity of 98% was used as the leaching agent and prepared at a concentration of 0,03 M. 2,5 g of the roasted chalcopyrite were introduced into the leaching vessel. The solid-to-liquid (S/L) ratio that was used is 1:40 to provide sufficient solution volume to promote metal dissolution.

The leaching reaction was carried out at an agitation speed of 300 rpm using a magnetic stirrer to enhance mass transfer and prevent particle settling. To control reaction kinetics, temperatures of 25°C, 35°C, 45°C, and 55°C were used. The leaching process was conducted on hot plates in beakers of 250mL. Temperature played a critical role in the dissolution process, affecting both the reaction rate and solubility of metal ions in solution.

The leaching duration was varied between 2, 4, 6, and 8 hours to assess the kinetics of copper dissolution and identify the optimal reaction time. At specific time intervals, leachate samples were withdrawn, filtered, and analysed to track the progress of copper recovery. The filtered solutions were analysed for copper concentration using atomic absorption spectroscopy (AAS), allowing for precise quantification of leaching efficiency.

Throughout the leaching process, the pH of the leach solution was carefully monitored and maintained at 1.5 using a calibrated pH meter. Adjustments to pH were made via dropwise addition of sulfuric acid to maintain optimal acidity and ensure consistent reaction kinetics throughout the processh.

3. Results and Discussion

3.1. XRF

The XRF results show clear changes in the composition of the chalcopyrite concentrate as the roasting temperature increased. The unroasted concentrate contained 32.88% CuO and 27.82% Fe_2O_3 which indicates that this chalcopyrite concentrate has high contents of copper and iron. When roasted at 400°C and 600°C, CuO and Fe_2O_3 content increased slightly suggesting initial oxidation of sulfides. At 900°C, Fe_2O_3 had a sharp increase 43.10% while the CuO decreased to 29.92% showing that excessive roasting favors iron enrichment and partial copper volatilization or conversion into other phases. At the same time, the SO_3 content decreased from an initial amount of 19.80% to 12.97%, confirming the removal of sulfur as SO_2 gas. These changes in composition confirm progressive oxidation and desulfurization with rising roasting temperature, which is consistent with earlier reports [13].

3.2. XRD

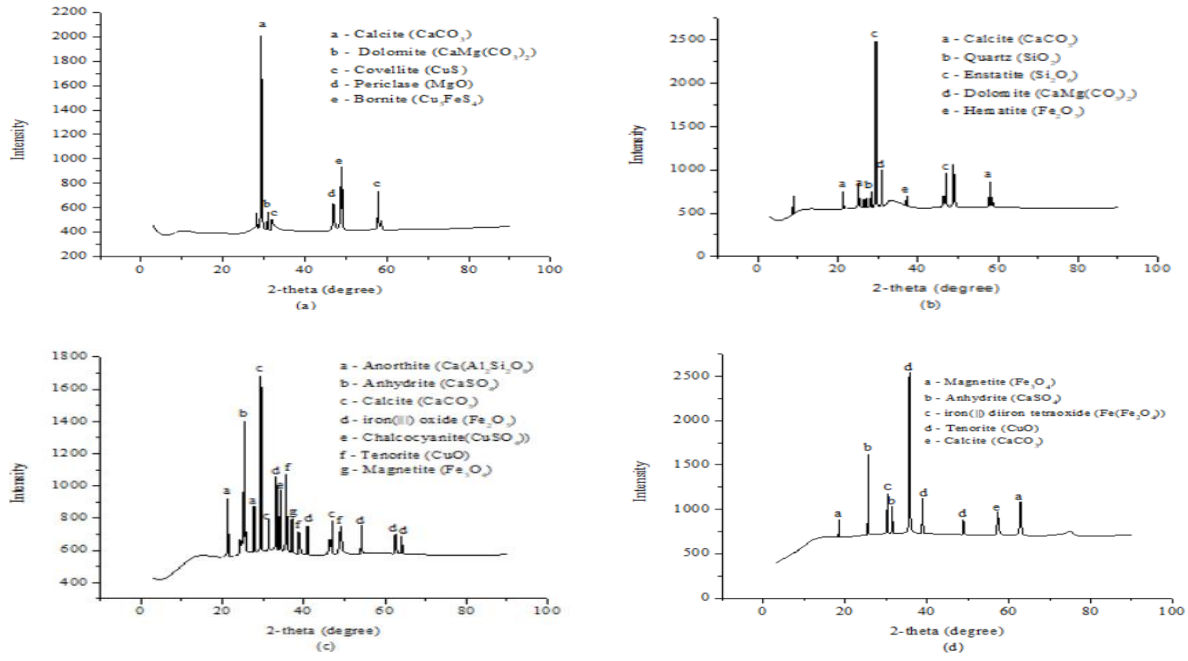

Fig. 1: XRD graphs of the chalcopyrite concentrate

Figure 1 shows XRD graphs of different chalcopyrite concentrates. Graph (a) is for an unroasted

chalcopyrite concentrate. Graph (b) is for a chalcopyrite concentrate roasted at 400°C. Graph (c) is for a chalcopyrite concentrate roasted at 600°C. Graph (d) is for a chalcopyrite concentrate roasted at 900°C. The XRD patterns show the phase evolution of the chalcopyrite concentrate with increasing roasting temperatures.

The unroasted sample (a) primarily consists of calcite ($CaCO_3$), dolomite ($CaMg(CO_3)_2$), covellite (CuS), periclase (MgO), and bornite ($Cu_5 FeS_4$), indicating the dominance of sulfide and carbonate minerals. At 400°C (b), new peaks of quartz (SiO_2), enstatite (SiO_3), and hematite ($Fe_2 O_3$) appear, suggesting the onset of sulfide oxidation and carbonate decomposition. Further roasting at 600°C (c) results in the formation of anorthite ($CaAl_2 Si_2 O_8$), chalcocyanite ($CuSO_4$), tenorite (CuO), and magnetite ($Fe_3 O_4$), confirming significant oxidation and phase transformation. At 900°C (d), the dominant phases are magnetite, anhydrite ($CaSO_4$), hematite, and calcite, showing complete oxidation of sulphides and stabilization of oxide and sulphate phases at high temperature.

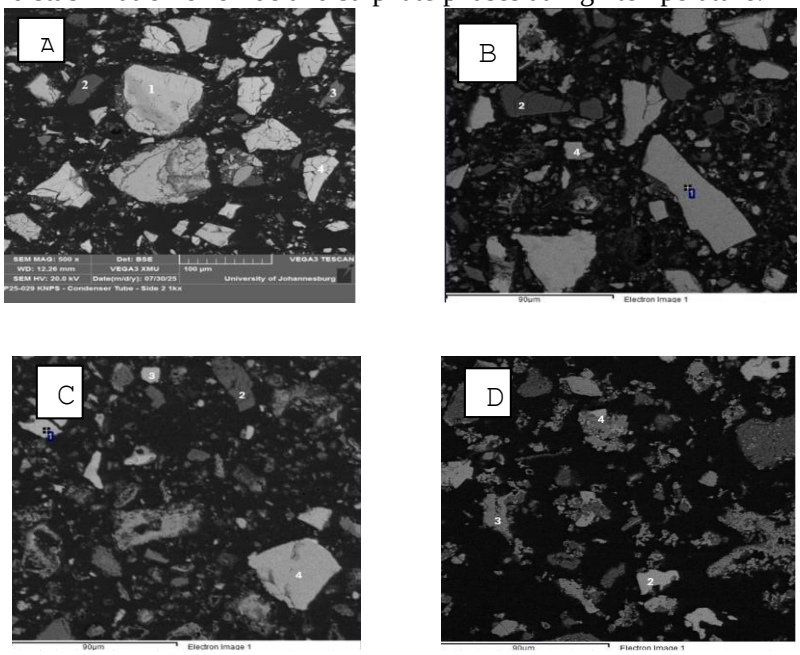

Fig. 1: SEM-EDS of the unroasted chalcopyrite concentrate and at different roasting temperatures

Figure 2 shows the EDS of the unroasted chalcopyrite and at different roasting temperatures. Picture A is the unroasted chalcopyrite concentrate, picture B, C, and D are for the concentrates roasted at 400°C, 600°C, and 900°C respectively. The SEM-EDS results confirmed the morphological evolution of the chalcopyrite concentrate with temperature. The unroasted surface appeared to be sulfur rich, with clear Cu-Fe-S associations. After roasting at 400°C and 600°C, the oxygen peaks increased and the sulfur decreased, showing oxidation. At 900°C, surfaces showed dominations of oxygen and Cu, with reduced S intensity, indicating oxidation of the concentrate. The morphological changes attained at moderate roasting temperatures improve the acid accessibility, enhancing subsequent leaching.

3.3. Leaching results

The different chalcopyrite concentrates of mass 2.5 g were leached under various conditions to obtain a pregnant liquor. The produced pregnant liquors were assessed for dissolution concentrations, and these were used to formulate the recoveries. The recoveries were used to assess the effect of roasting and the addition of a galvanic couple on the roasted concentrates.

3.4. Effects of Manganese dioxide on unroasted chalcopyrite

The effect of manganese dioxide (MnO_2) was investigated on the unroasted chalcopyrite concentrate at varying temperatures and varying times. Figure 6 gives the information about the recoveries obtained from leaching an unroasted chalcopyrite concentrate with and without MnO_2.

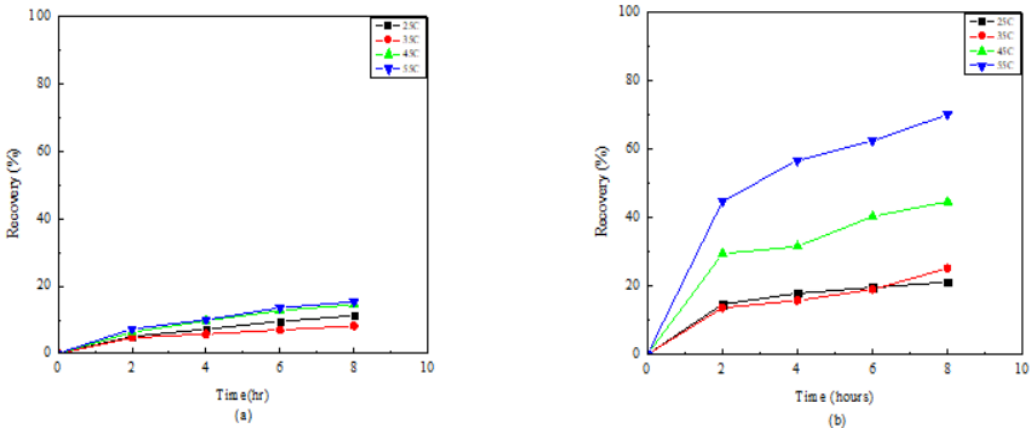

Fig. 2: Copper recovery on unroasted chalcopyrite

Figure 3 shows the copper recovery graphs obtained at different leaching temperatures. Graph (a) represents the copper recovery obtained from the unroasted concentrate using sulfuric acid and graph (b) represents the copper recovery obtained from the unroasted concentrate with the addition of MnO_2 as a galvanic couple. Graph (a) shows that leaching an unroasted chalcopyrite concentrate with only sulfuric acid results in very low copper recovery recoveries, with 15% recovery being the highest recovery obtained from this experiment after 8 hours, with temperature having a little impact. The reaction rate of this leaching process remains slow throughout the whole, indicating that passivation layers formed and limited the copper dissolution and diffusion through the product layer. Graph (b) shows that the addition of MnO_2 significantly improves the copper recovery, reaching a recovery of 70%. The initial leaching rate increases sharply, this is especially true at higher leaching temperatures, suggesting that the addition of MnO_2 as a galvanic couple accelerates the redox reaction and electron transfer between the chalcopyrite concentrate and MnO_2. These findings are consistent with literature, which report that $CuFeS_2$/ MnO_2 galvanic couples achieve higher recoveries due to their favourable electrochemical potential difference and reduced activation energy compared to chalcopyrite alone [14].

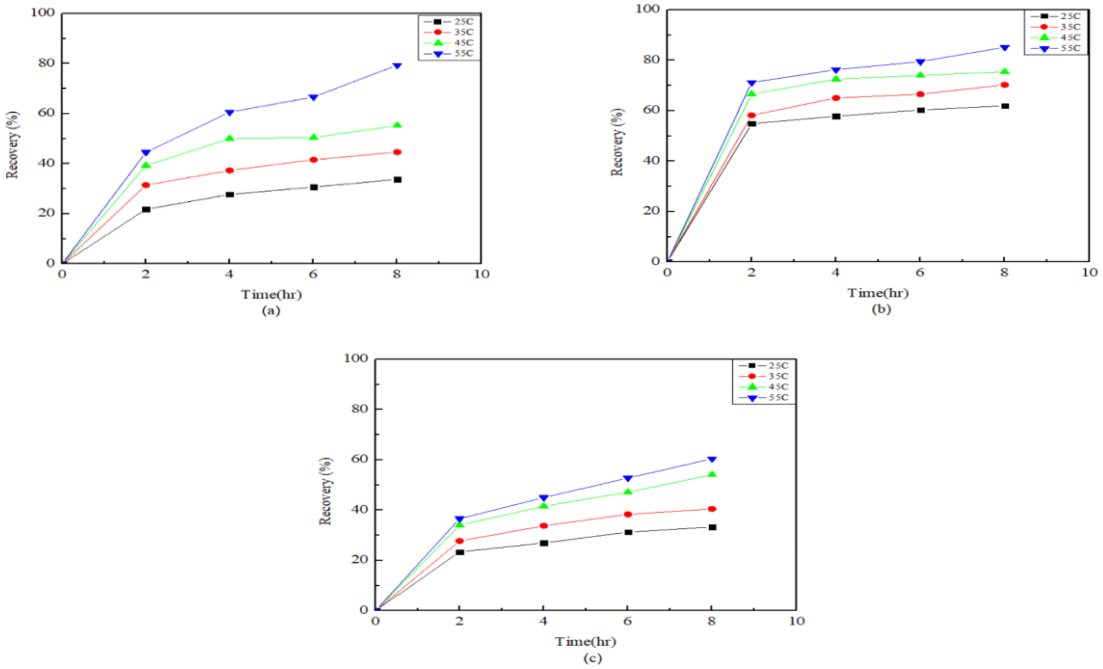

Fig. 3: Copper recovery for the chalcopyrite roasted at different temperatures

Figure 4 shows the copper recovery results obtained from copper concentrates that were roasted at different temperatures. Graph (a) shows the copper recovery obtained from the concentrate that was

roasted at 400°C. This graph shows an improvement in copper recovery when compared to the unroasted samples, with its optimum copper recovery being 79% at the leaching temperature of 55°C. The leaching rate showed a rapid initial dissolution rate in the first 2 hours, then rate slows down for the rest of the leaching process. Graph (b) is the copper recovery from concentrate roasted at 600°C. This graph presents the highest overall recovery, with rapid dissolution within the first 2 hours and the highest recovery reaching 85% at a higher leaching temperature for a longer leaching time. Similar to the results obtained from the sample roasted at 400°C, this leaching system had a rapid initial copper dissolution rate for the first two hours, then gradually became slower suggesting improved dissolution through the porous oxide layer. However, graph (c) had the lowest copper recovery, reaching a highest recovery of 60%. The reaction rate was initially fast for the first two hours then gradually slowed down for the rest of the leaching process. The results obtained from the samples roasted at 400°C and 600°C showed an increased recovery rate when compared to leaching the unroasted sample with only sulfuric acid and with the addition of MnO_2.

3.5. Effects of Galvanic Coupling on Roasted Chalcopyrite

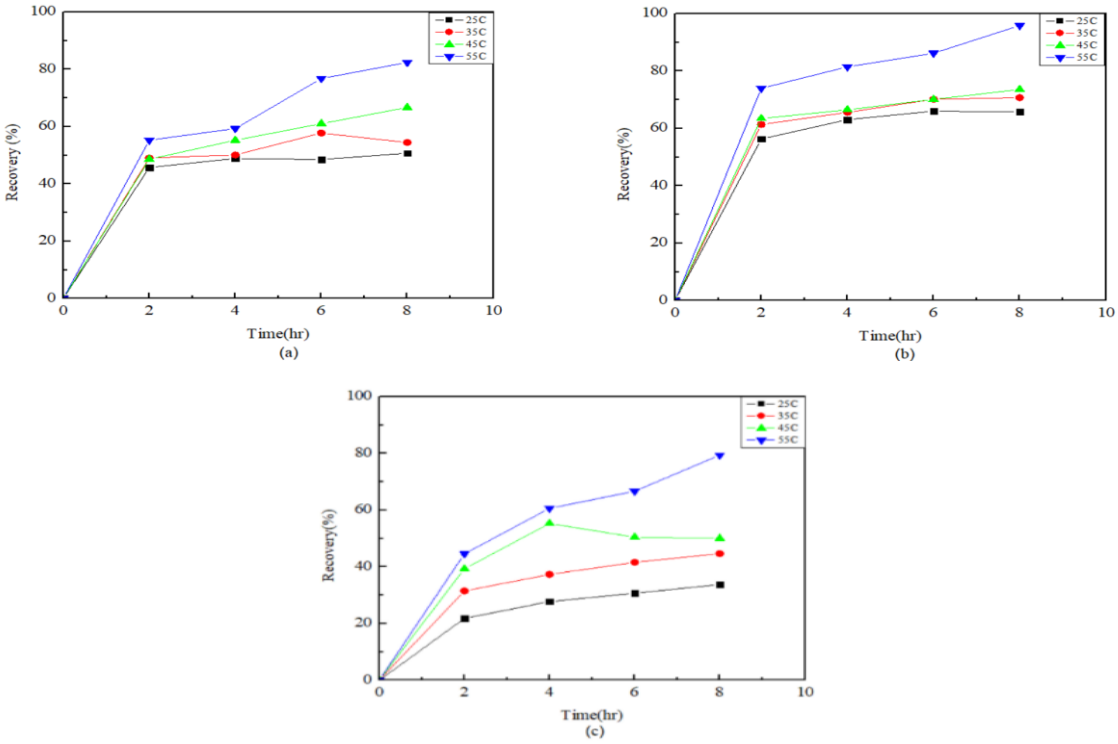

Fig.4: Copper recovery for the chalcopyrite roasted at different temperatures with MnO_2

Figure 5 shows the copper recovery obtained from copper concentrates that were roasted at different temperatures combined with MnO_2. Graph (a) represent the recoveries obtained from roasting at a temperature of 400°C and combining that roasted sample with MnO_2. Graph (b) and (c) represents the recoveries obtained from concentrates roasted at 600°C and 900°C combined with MnO_2. At 400°C + MnO_2 recoveries exceeded 70% reaching 82%, while 600°C + MnO_2 gave the best recoveries reaching a recovery of 95%. At 900°C + MnO_2 recoveries drop to 79%, however this recovery was better than the recovery obtained when leaching the concentrate roasted at 900°C with only sulfuric acid. The 400°C + MnO_2 and 600°C + MnO_2 graphs indicate fast copper dissolution within the first two hours and slowed down gradually for the rest of their respective processes. The rate trend for the 900°C + MnO_2 process was steady but slower, flattening after 4 hours, suggesting that over-roasting caused sintering and the formation of compact oxide layers. Overall, 600°C roasting with MnO_2 provides the most effective copper dissolution.

3.6. Leaching Model

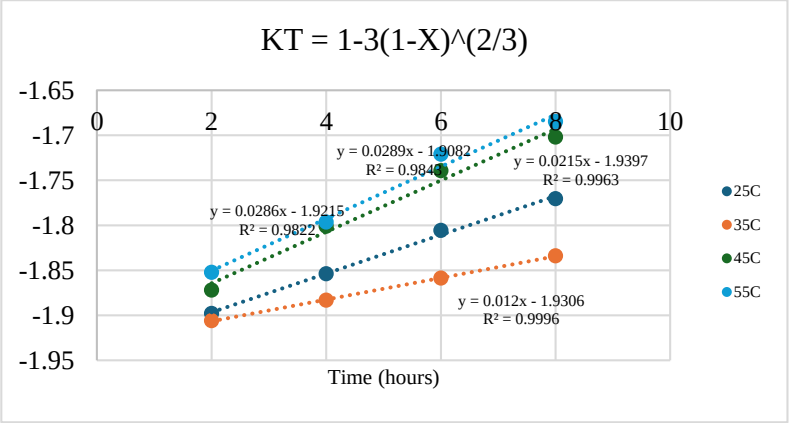

Fig. 5: Effect of leaching temperature on a chalcopyrite concentrate (diffusion-controlled)

Figure 6 applies the diffusion-controlled shrinking core model (KT = 1-3(1-X)2/3) to study the copper leaching kinetics, showing that higher temperatures improve diffusion through the product layer. The slopes show that 55°C and 45°C had the fastest copper diffusion rates, while the 35°C is the slowest. The high R^2 values confirm that process is well described by the diffusion-controlled model. This means that the rate-limiting step was not the chemical reaction but rather the diffusion of copper ions through the porous product layer.

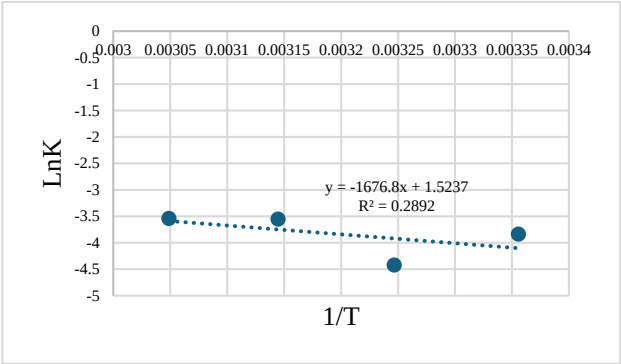

Fig. 6: Arrhenius Plot of Ln(k) against 1/T

The Arrhenius plot in Figure 7 shows the relationship between LnK and 1/T for copper dissolution. The slope of -1676.8 indicates a low activation energy, suggesting that the reaction can occur with minimal energy input and proceed even at lower temperatures. The calculated activation energy was 14 KJ.mol-1. However, the low R^2 value shows a weak correlation, implying that temperature has a limited effect. Instead the reaction was largely governed by mass transfer and diffusion phenomena through the product layer.

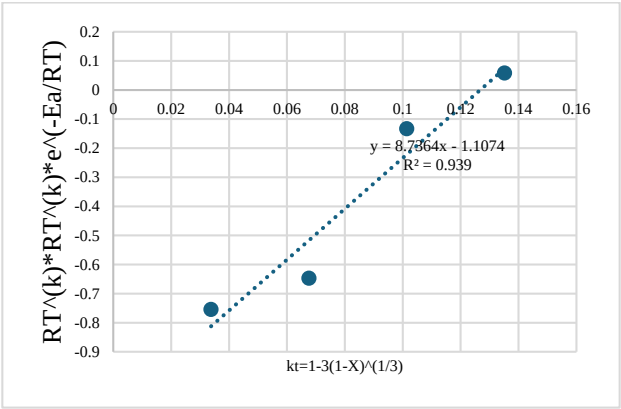

Fig. 8: Parity plot of experimental vs theoretical values correlation

Figure 8 shows a strong linear relationship (R^2 = 0.939) between the kinetic parameter kt = 1-3(1-X)1/3 and the normalized reaction rate term RTk*RTk*e-Ea/RT, with the equation y = 8.364x – 1.1074. The positive slope indicates a direct proportional relationship, and the high R^2 value demonstrates that the kinetic model accurately represents the experimental data, with approximately 94% of the variance explained by this linear fit. These findings confirm that the copper dissolution from roasted chalcopyrite in this experiment is controlled by diffusion through the product layer rather than by the surface chemical reactions.

4. Conclusion

This study aimed to investigate the effects of roasting and galvanic coupling with Manganese dioxide (MnO_2) on copper recovery from a chalcopyrite concentrate under different operational parameters including roasting temperature, leaching time, and leaching temperature. The copper head grade of the unroasted chalcopyrite concentrate was determined to be 26.26% using X-ray fluorescence spectrometry. The results showed that leaching the unroasted sample with only sulfuric acid yielded a recovery of less than 20%, but the addition of MnO_2 at the ratio of 1:4 improved the recovery to over 60% demonstrating the effectiveness of galvanic assistance in overcoming passivation. Roasting significantly enhance the leachability of the copper, achieving a recovery yield of 85% using only sulfuric acid and exceeded 90% with the addition of MnO_2. However roasting at 900°C reduced the copper recovery to around 60%, 79% with MnO_2.

Kinetic modelling revealed that the process follows a diffusion-controlled shrinking core model (R^2 = 0.939). With the Arrhenius analysis indicating low activation energy, suggesting that temperature and other factors like mass transfer influence the dissolution rates. Overall, this study revealed that for effective copper recovery, and approach of combining both roasting and galvanic coupling greatly improves copper recovery. It is recommended to maintain galvanic coupling with MnO_2 throughout the leaching process to prevent passivation and maintain reaction rates. Future work should focus on optimizing the roasting time and temperature to maximize copper recovery. Studies should also stick to either galvanic coupling or roasting the concentrate because combining the two methods can prove to be costly.

5. Acknowledgment

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