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KINETIC OF DISSOLUTION OF NICKEL LIMONITE CALCINE BY SULFURIC ACID SOLUTION

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Abstract

Currently, more than 60% of nickel processing is carried out using nickel sulfide as a raw material. Nonetheless, due to the depletion reserves of nickel sulphide, nickel laterite has drawn a lot of interest to be processed as raw material. Nickel laterite in Indonesia is generally found in low grades, with nickel concentration of <1.15%. One method of treating nickel limonite is leaching in a sulfuric acid solution. This study aims to determine the reaction rate in the leaching process of calcine nickel limonite and the effect of sulfuric acid concentration and leaching temperature on the percent nickel extraction. In this research, the limonite ore from Pomalaa, Southeast Sulawesi, Indonesia, which has undergone a reduction process, was used as raw material. This research was conducted by leaching method on nickel limonite calcine using sulfuric acid reagent with 0.2, 0.5, and 1 M concentration variation, temperature variations of 60, 70, and 90°C, stirring speed 500 rpm, and %S/L (w/w) 10%. In this leaching research, the activation energy obtained at a sulfuric acid concentration of 0.2, 0.5, and 1 M are 13,7379 kJ/mol, 19,7582 kJ/mol, 20,3161 kJ/mol, respectively. The leaching process of nickel limonite calcine was controlled by diffusion. The optimum nickel extraction percentage in this study was 97.45%, obtained at a concentration of 1 M sulfuric acid, temperature of 70 °C, and leaching time of 240 minutes.

Keywords: *Nickel limonite, calcine, leaching, kinetics, sulfuric acid*

1. INTRODUCTION

Indonesia is renowned for its abundant natural resources, particularly in the mining sector. Mining resources are non-renewable resources, one of which is minerals. Minerals serve as raw materials for the mining industry [1]. Nickel is one of the minerals found in Indonesia. Regions in Indonesia with nickel reserves include Papua, Sulawesi, and Maluku.

Nickel ore consists of nickel sulfides and nickel laterites [1]. Approximately 70% of nickel ore worldwide is categorized as nickel laterite [2]. However, more than 60% of nickel ore processing currently uses nickel sulfide as a raw material. Due to the decreasing reserves of nickel sulfide, the metallurgy industry is shifting towards processing nickel laterite as a raw material [3].

Nickel laterite ore consists of saprolite and limonite nickel ore. In Indonesia, the processing of nickel laterite ore is mainly focused on saprolite ore, which is aimed at producing ferronickel and nickel matte. Meanwhile, limonite ore, which contains less nickel compared to saprolite ore, is not widely utilized or processed commercially. Utilizing limonite nickel ore is necessary due to the decreasing supply of high-grade ore. Research is needed to

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increase the nickel content in limonite nickel ore [4].

There are two technological processes for processing limonite nickel ore: pyrometallurgy and hydrometallurgy. One pyrometallurgical process is selective reduction. Hydrometallurgy involves a leaching process. Both selective reduction and leaching processes aim to make the processing of limonite nickel ore commercially viable [5]. Selective reduction of limonite nickel ore can be done using coal as a reducing agent to convert metal oxides into their metallic form.

Selective reduction within the ore through reduction roasting is based on the affinities of iron and nickel towards oxygen. Iron typically remains in the form of an oxide after nickel has been converted to a metallic state due to its greater affinity. Reduction is the result of the presence of reducing gases such as H_2 (hydrogen) or CO (carbon dioxide) [6].

The iron present in lateritic ore, known as Fe_2O_3, must undergo multiple chemical steps in order to transform into metal :

$$2Fe_3O_4 + 2CO/2H_2 \rightarrow 6FeO + 2CO/2H_2O......(1)$$

$$2FeO+2CO/2H_2 \rightarrow 2Fe+2CO_2/2H_2O...............(2)$$

Meanwhile, the reaction of nickel oxide (NiO) to become metal occurs in only one stage, as follows:

$$2NiO + 2CO/2H_2 \rightarrow 2Ni + 2CO_2/2H_2O........(3)$$

The previous research [7] has identified the potential reactions that may occur during the leaching process of reduced limonite nickel ore employing sulfuric acid as a leaching agent. These reactions correspond to the Equation (4):

$$Ni+2Fe_3O_4+8H_2SO_4 \rightarrow Fe_2(SO_4)_3+NiSO_4+4FeSO_4+ 8H_2O.. (4)$$

The utilization of ammonia for leaching on calcine was initially pioneered by Caron in 1930 [8]. However, its effectiveness was found to be limited and it could only be employed under concentrated conditions. An alternative technique involving the use of chlorine gas was introduced for leaching. This material has a high level of reactivity and a moderate level of selectivity, nevertheless, it presents difficulties in handling due to its corrosive properties. An alternative option is the utilization of diluted sulfuric acid due to its convenient handling, notable selectivity, and reactivity.

The reactions in the sulfuric acid leaching process with the presence of oxygen are as follows:

$$Ni(Co)+H_2SO_4\frac{1}{2}O_2 \rightarrow Ni(Co)SO_4+H_2O.........(5)$$

Another advantage of this process is that it is not influenced by the excess reduction condition, allowing the dissolved iron to react with nickel with the following equation:

$$2Ni+2Fe^{2+}\frac{3}{2}{}_2 \rightarrow 2Ni^{2+}+Fe_2O_3..........................(6)$$

Previously, several studies were conducted using non-reduced limonite nickel ore to achieve high nickel extraction percentages. The leaching process conducted by Wahab [9] achieved the highest recovery percentage of 62.81% at a temperature of 90 °C, sulfuric acid concentration of 0.8 M, and leaching time of 90 minutes. Then, a study conducted by Tristiyan [10] obtained a nickel recovery of 96.754% using a sulfuric acid concentration of 1 M, a solids-to-liquid ratio of 2.5%, a temperature of 90 °C, and an agitation rate of 400 rpm for 480 minutes. In this study, calcine, which is the result of the reduction of limonite nickel ore from Pomalaa in Southeast Sulawesi Province, was used as the raw material. In this research, the calcine had undergone a reduction process at 1100 °C using 20% coal as the reducing agent. This research was conducted using the leaching method on the nickel limonite calcine, varying the sulfuric acid concentration and leaching temperature.

2. MATERIALS AND METHODS

2.1 Materials

In this research, the limonite ore from Pomalaa, Southeast Sulawesi, Indonesia, has undergone a reduction process at a temperature of 1100 °C, utilizing 20% coal as the reducing agent in order to produce calcine.

Table 1. Chemical composition of calcine by XRF

Element	wt.%
Fe_2O_3	45.29
SiO_2	45.43
Cr_2O_3	2.89
NiO	1.34
MnO_2	1.27
TiO_2	0.32
MgO	2.33
Others	1.14

The chemical composition result of the calcine of nickel limonite using XRF (x-ray fluorescence) technique is presented in Table 1. The results of the XRF characterization (dry base sampel) in Table 1 indicate that the limonite calcine primarily consists of iron (Fe), with a concentration of 45.29% as Fe_2O_3. The XRF data suggest that Ni is 1.05% (as NiO =1.34%) of the composition. In addition, the XRF analysis data indicates the existence of other elements, specifically Si, S, Mn, Cr, and Ti, with percentages of 39.18%, 8.59%, 0.98%, 2.23%, and 0.19%, respectively.

2.2 Methods

In this study, leaching experiments of calcine were conducted using sulfuric acid with varied concentrations (0.2, 0.5, and 1 M). The temperature was also varied at 60, 70, and 90 °C. The leaching experiments were performed at a solid/liquid ratio of 10% (w/w) and leaching durations ranging from 60 minutes to 240 minutes. Afterward, the solution was filtered to separate the pregnant leach solution (filtrate) and the residue. Then, the pregnant leach solution was analyzed using AAS (atomic absorption spectrometry) to measure dissolved nickel and iron concentrations.

This research was conducted to determine whether the leaching rate is controlled by chemical interface reactions or by diffusion through the fluid film. It also aims to understand the influence of sulfuric acid concentration and leaching temperature in the leaching process of the limonite calcine.

3. RESULT AND DISCUSSION

3.1 Characterization of Calcine Raw Material

XRD analysis is a useful method for identifying the degree of metallization in nickel limonite calcine. Figure 1 displays the composition of the nickel limonite calcine, which comprises several minerals such as quartz (SiO_2), trevorite (Fe_2NiO_4), clinoenstatite ($MgSiO_3$), and fayalite ($Fe_2(SiO_4)$).

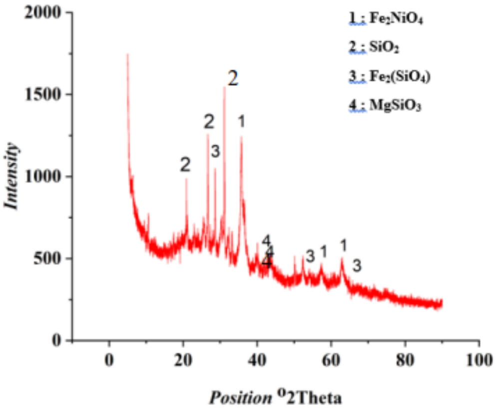


Figure 1. XRD diffractogram of calcine

The findings align with prior investigations conducted by Iwan [11] and Mayangsari [12]. [11] and Mayangsari [12]. Trevorite ($NiFe_2O_4$), quartz (SiO_2), and fayalite ($Fe_2(SiO_4)$) were formed at reduction temperatures of 800 and 900 °C, with identical compositions and distributions. At a temperature of 1000 °C, clinoenstatite ($MgSiO_3$) was produced by dehydroxylation process of lizardite.

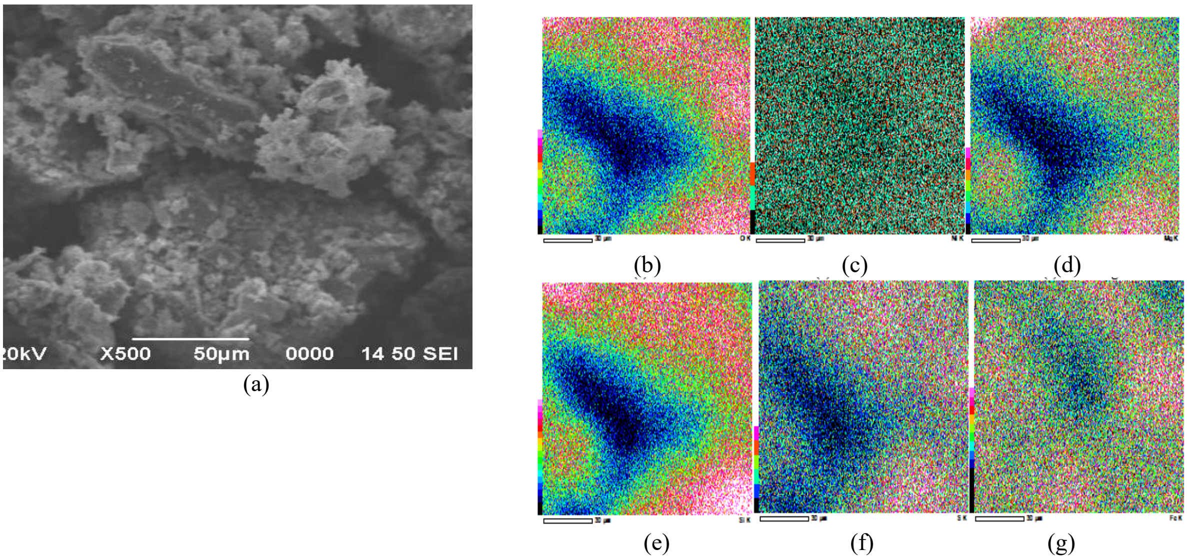


Figure 2. (a) SEM image of calcine at 500x magnification and EDS elemental mapping of (b) Oxygen, (c) Nickel, (d) Magnesium, (e) Silicon, (f) Sulphur, (g) Iron

The red-colored area in the SEM (scanning electron microscope) mapping data indicates a significant concentration of that particular element. Figure 2 illustrates that the composition predominantly comprises Fe, O, and Si, while nickel (Ni) is not the primary element. Moreover, it demonstrates that nickel establishes complex chemical bonds with iron and is surrounded by silicon and magnesium.

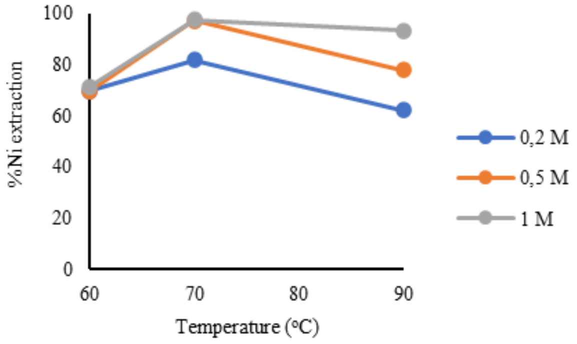


Figure 3. Influence of temperature on the percentage of nickel extraction at 240 minutes

3.2 The Effect of Temperature on the Percentage of Nickel Extraction

This study used a solid-to-liquid ratio (%S/L) of 10% (w/w) with an agitation speed of 500 rpm at three different temperatures: 60, 70, and 90 °C. Figure 3 shows the profile of nickel extraction as a function of temperature. In the leaching process, temperature is one of the factors that can significantly influence its outcome. Temperature plays a crucial role in affecting the rate at which the nickel leaching process occurs. There is a decrease in nickel extraction at a temperature of 90 °C due to a reduction in the dissolved oxygen content, causing the dissolution reaction as in equation 5 to slow down. This is characterized by a decrease in the solution potential by 50 mV. The decrease in dissolved oxygen content is related to the formation of water vapor bubbles that carry oxygen out of the solution.

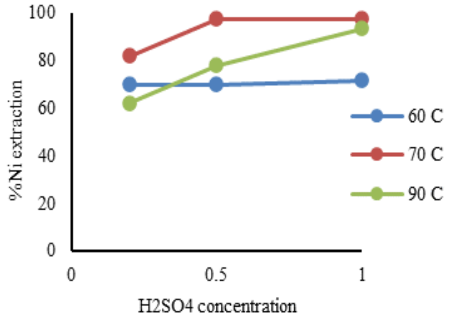
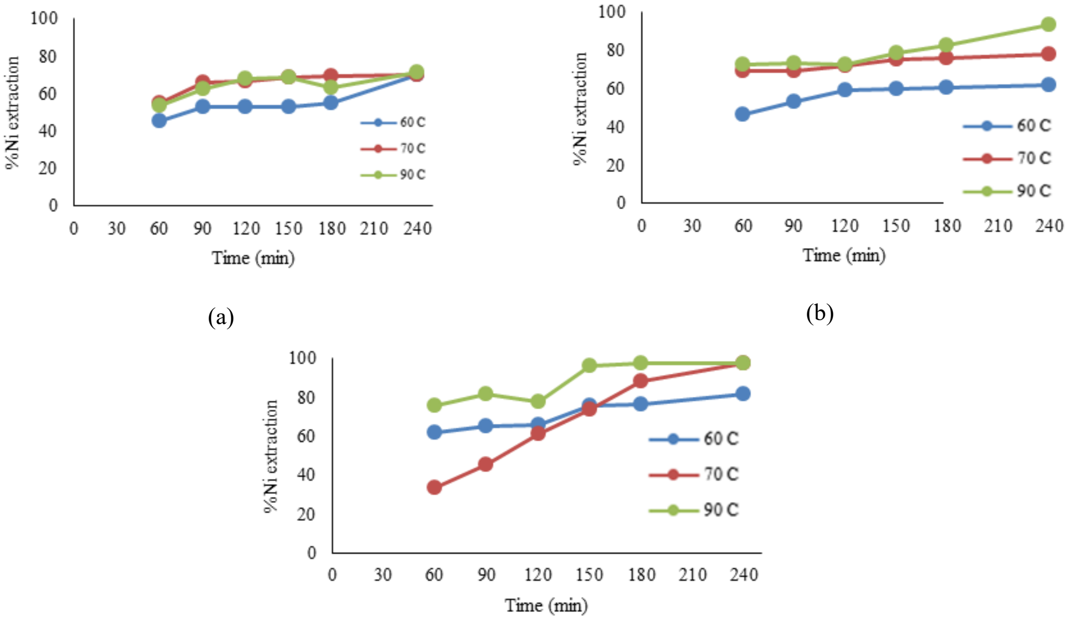


Figure 4. Influence of H_2SO_4 concentration on the percentage of nickel extraction at 240 minutes

3.3 The Effect of Acid Concentration on the Percentage of Nickel Extraction

In this investigation, a solid-to-liquid ratio (%S/L) of 10% (w/w) and an agitation speed of 500 rpm were employed with different sulfuric acid concentrations of 0.2, 0.5, and 1 M. Figure 4 illustrates that the percentage of nickel extracted increases with the increase of sulfuric acid concentration. This suggests that with an increased amount of sulfate ions used, the formation of $NiSO_4$ also increases.



(a)

(b)

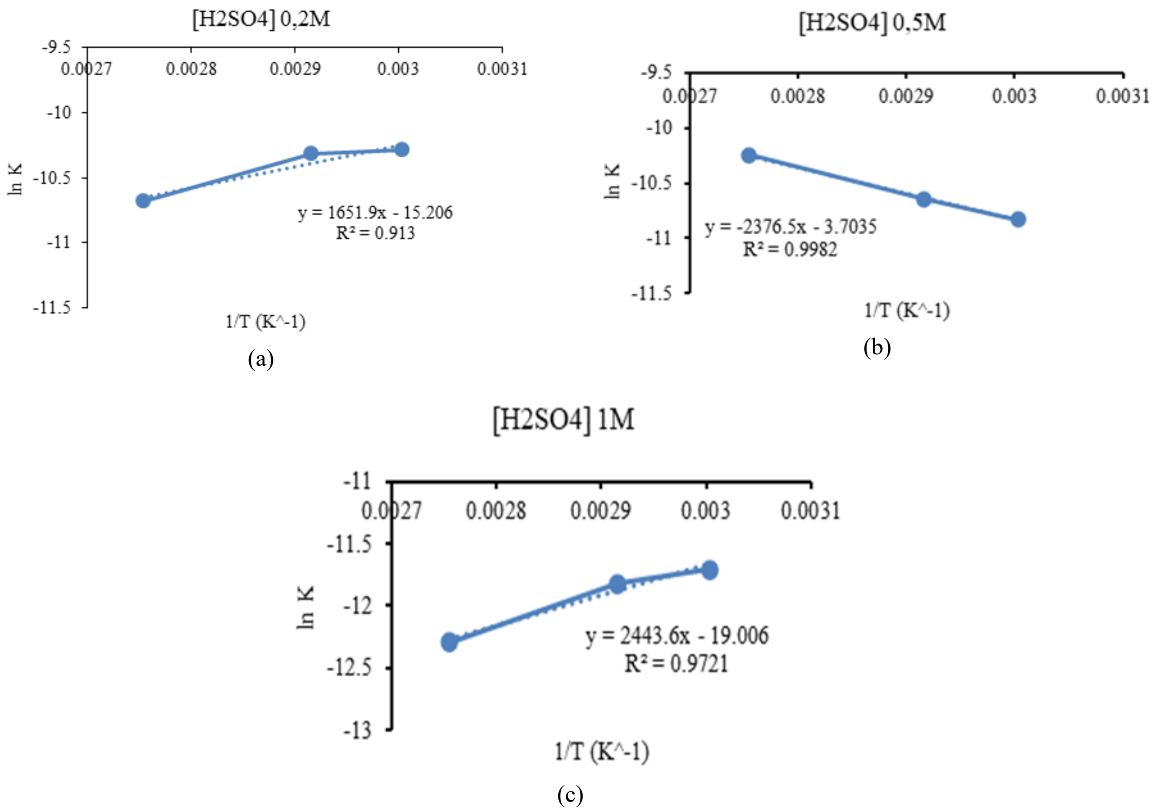
(c)

Figure 5. Relationship between time and percentage of nickel extraction at H_2SO_4 concentration (a) 0.2 M; (b) 0.5 M; (c) 1 M

The optimum percentage of nickel extraction was 97.45%, achieved at a concentration of 1 M H2SO4 and a temperature of 70 °C. The increase in the percentage of nickel extraction with higher H_2SO_4 concentration aligns with the findings of previous research [9], which also indicated that higher H_2SO_4 concentrations lead to significant nickel extraction percentages.

3.4 Effect of Leaching Time on Percentage of Nickel Extraction

The leaching processes are carried out at 60, 90, 120, 150, 180, and 240 minutes intervals. As observed in Fig. 5, the percentage of nickel extraction increases with longer leaching times. The highest percentage of nickel extraction in this investigation was reached after 240 minutes. These findings align with the results of previous research [9], which indicated that longer leaching times result in a higher amount of dissolved reactants.



(a)

(b)

(c)

Figure 6. Ln k vs (1/T) plot to calculate the activation energy of leaching at H_2SO_4 concentration of (a) 0.2 M, (b) 0.5 M, (c) 1 M

3.5 Kinetics of Nickel Limonite Calcine Leaching

The kinetic study on the leaching of nickel limonite calcine aims to determine the rate-controlling step of the reaction, whether it is controlled by chemical reactions (chemical controlled) or diffusion (diffusion controlled). In this research, the kinetic model employed is the SCM (shrinking core model). The SCM enables us to comprehend the rate-controlling step by analyzing the activation energy value. By identifying the rate-controlling step, we can determine the factors that influence the leaching process.

This study includes three different temperature variations: 60, 70, and 90 °C. The leaching processes at these three different temperatures are carried out at 60, 90, 120, 150, 180, and 240 minutes intervals. The variation of temperature and time intervals in leaching is conducted to determine the activation energy value for the leaching process. The mole fraction value, which can be used to determine the reaction kinetics, will be obtained during leaching. The following equation [13] describes the relationship between dissolution and leaching time (t), where k is the rate constant.

$$\left(1-\frac{2}{3}\alpha\right) - (1-\alpha)^{\frac{2}{3}} = kt \text{……………………..……..(7)}$$

k = Reaction rate coefficient
α = Fraction of reactant
t = Leaching time (second)

Equation 7 represents a *diffusion-controlled process*. In a diffusion-controlled process, the kinetic leaching process is characterized by the chemical reaction rate at the surface being significantly faster than the rate at which reactants diffuse to the surface of the concentrate.

$$1 - (1-\alpha)^{\frac{1}{3}} = kt \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(8)$$

On the other hand, a chemically-controlled process is the reverse of a diffusion-controlled process, as expressed in Equation 8. In a chemically-controlled process, the chemical reaction rate is substantially slower compared to the diffusion rate [14].

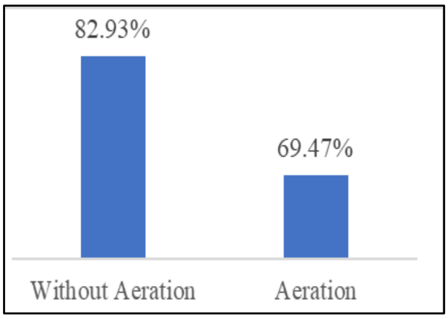


Figure 7. Effect of oxygen addition on the percentage of iron extraction

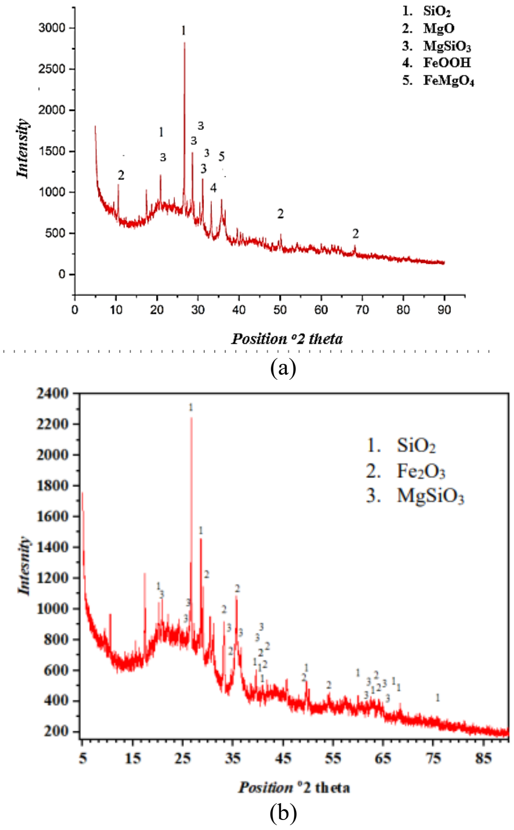
The rate-controlling step can also be determined by calculating the activation energy value for the leaching process. This is done by calculating the rate constant values and then plotting ln k against 1/T at various H_2SO_4 concentration (Fig. 6).

The activation energy values were obtained after performing calculations using the Arrhenius equation. The activation energy values obtained in this study at H_2SO_4 concentrations of 0.2, 0.5, and 1 M, respectively, are 13.7379 kJ/mol, 19.7582 kJ/mol, and 20.3161 kJ/mol.

The activation energy for a chemically regulated process is commonly greater than 42 kJ/mol [15]. This suggests that the leaching process of Pomalaa nickel limonite calcine is controlled by diffusion. Concentration of reactant is significant element in determining the rate of diffusion-controlled reactions, which can impact the flow of species across the medium.

3.6. The Effect of Oxygen Addition (Aeration) on the Percentage of Iron Extraction

Oxygen is added through the aeration method, which involves blowing external air at a flow rate of 1 liter per minute at room temperature. In the nickel leaching process, the addition of oxygen tends to decrease the percentage of iron extraction compared to leaching without oxygen. This experiment used a 0.5 M H_2SO_4 solution, a temperature of 70 °C, and a leaching time of 120 minutes to evaluate the effect of oxygen addition on the leaching process.



(a)

(b)

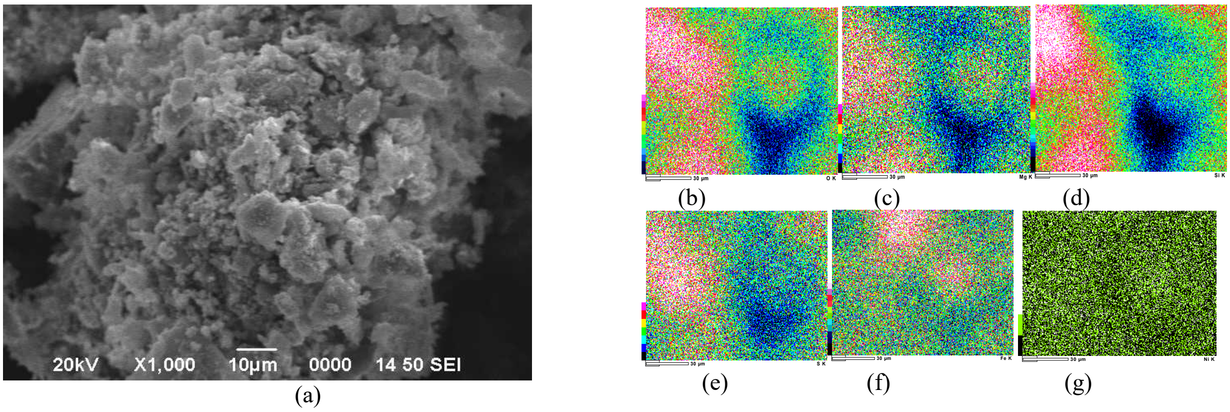
Figure 8. XRD diffractogram of residue from (a) leaching without aeration and (b) oxidative leaching

As can be seen in Fig.7, the percentage of iron extraction during oxidative leaching was 69.47%, while iron extraction without oxygen was 82.93%.

3.7. Residue Characterization from the Leaching Process

XRD analysis was conducted on the residue from the leaching process of calcined nickel limonite to assess the mineral composition of the residue. The XRD results in Fig. 8 reveal that the residue from oxidative leaching consists of Fe_2O_3, SiO_2, and $MgSiO_3$. This might be due to the fact that these substances are not soluble in the sulfuric acid leaching solution. On the other hand, the oxygen-free leaching residue has a greater concentration of minerals such as MgO, FeOOH, and $FeMgO_4$ that are insoluble during the calcined nickel limonite leaching process.

Figure 9, which shows elemental mapping at 1000x magnification, indicates very little distribution of nickel. The mapping results also exhibit a relatively high colour intensity for elements such as iron (Fe), oxygen (O), magnesium (Mg), and sulfur (S), indicating that these elements are more prevalent in the residue.



(a) (b) (c) (d) (e) (f) (g)

Figure 9. (a) SEM image of calcine at 500x magnification and EDS elemental mapping of (b) Oxygen, (c) Magnesium, (d) Silicon, (e) Sulphur, (f) Iron, (g) Nickel

4. CONCLUSION

This study used the shrinking core model to explain the nickel limonite calcine dissolution kinetics further. The results showed that the activation energies varied based on the concentration of H_2SO_4; these were 13.7379 kJ/mol, 19.7582 kJ/mol, and 20.3161 kJ/mol for concentrations of 0.2, 0.5, and 1 M, respectively. The research results indicate that the dissolution rate of nickel limonite calcine is controlled by the diffusion process (diffusion-controlled).

The H_2SO_4 concentration and leaching temperature affect the percentage of nickel extraction. The amount of iron extracted is also influenced by the oxygen used in the leaching process; adding oxygen lowers the iron extraction percentage. The optimal percentage of nickel extraction, reaching 97.45%, is achieved by using 1M H_2SO_4 concentration, a dissolution temperature of 70 °C, a dissolution time of 240 minutes, agitation speed at 500 rpm, and a solid-to-liquid ratio (S/L) of 10% (w/w).

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