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# The kinetic study of limonitic low grade nickel ore leaching using hydrochloric acid

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**Abstract.** The leaching kinetic ore from Pomalaa (Southeast Sulawesi, Indonesia) using hydrochloric acid solution was investigated in a batch reactor. Variables studied were temperature, pH and particle size. To evaluate the kinetic parameters, the experimental data were fitted with a shrinking core model of a constant particle size. The experimental data fit very well with the proposed model and the overall rate is controlled by dissolution rate of nickel through product layer. The activation energy ( $E_{De}$ ) for the dissolution of nickel is 22.5 kJ/mol. The maximum nickel recovery is 41.5% at pH 1, reaction temperature of 90°C, particle size of -200 mesh, solid to liquid ratio at 0.2 (w/w) and stirring speed of 400 rpm for 240 minutes.

## 1. Introduction

Nickel is one of strategic metals in many industrial and metallurgical applications. The use of nickel in the preparation of stainless steel and non-ferrous alloys is necessary because it can improve the impact strength, corrosion resistance and other electrical, heat and magnetic properties [1-3]. Nickel reserves in the world are mostly dominated by laterite ores (72%). However, the world's nickel production, around 54% of it, is resulted from nickel sulphide ores [4]. Indonesia is one of the countries that has an abundant amount of laterite ore reserves with the total amount of 15% of total world laterite ore reserves [5]. Around 70% of the total lateritic Ni reserves worldwide are limonitic laterites, which are rich in Fe but low in Mg [6,7]. The dominant mineral in most laterites is goethite (FeOOH) [1,9].

Hydrometallurgical processes are the main methods applied for the extraction of Ni from limonitic ores. Two existing hydrometallurgical processing currently used are Caron process and high pressure acid leaching (HPAL) [10,11]. The Caron process involves three steps which are drying, calcination and ammonia leaching, while HPAL needs high pressure and temperature within autoclaves. Due to such as high capital expenditure and energy consumption make these two processes less attractive. Therefore, McDonald and Whittington [12], Basturkcu et al. [13] and Wanta et al. [14] studied an atmospheric leaching method to extract Ni from limonitic ores.

One of the recent development in the extraction of nickel from laterite ores in atmospheric pressure is due to leachant which can be regenerated, such as hydrochloric acid. An atmospheric leaching has been performed by a few researchers such as Rice [15], Agacayak et al. [16] and Astuti et al. [17].

In this present study, the kinetic leaching of a limonitic ore using hydrochloric acid solvent was investigated. Variables investigated were temperature, pH, and ore particle size.



## 2. Materials and Methods

### 2.1. Materials

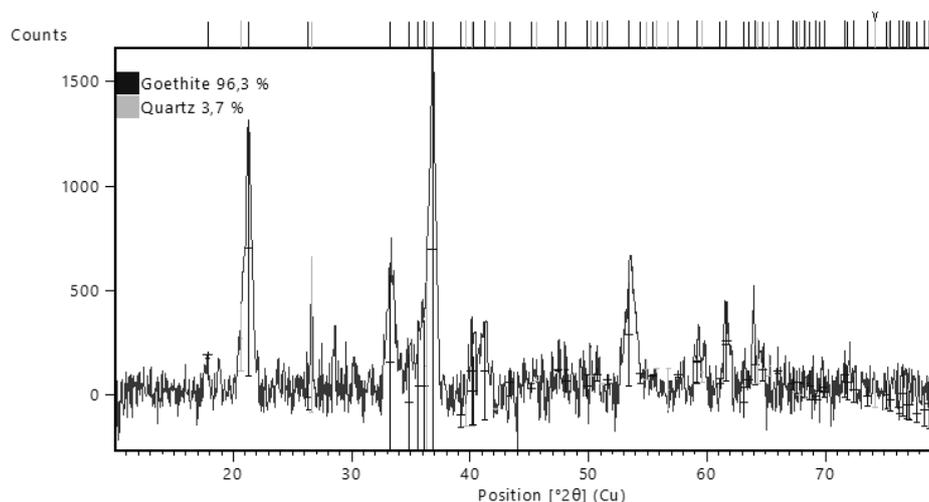
Nickel laterite was limonite type and mined from Pomalaa, Southeast Sulawesi Province, Indonesia. The chemical components of the samples were identified using X-ray fluorescence (XRF; PANalytical Epsilon 3XLE). The nickel content of the sample was 2.65% (Table 1).

The mineral phases of the raw ore samples were identified by X-ray diffraction (XRD; X'Pert 3 Powder, PANalytical) using Cu K $\alpha$  radiation, at an accelerating voltage and applied current of 40 kV and 40 mA, respectively, in the 2 $\theta$  range 5° to 80°. The result of XRD analysis is shown in Figure 1. It shows that goethite is the main minerals in limonite ore from Pomalaa. XRD test results further strengthen the results of XRF testing where iron is a component that dominates the sample.

As for the leachant reagent, hydrochloric acid (Merck) was used and deionized water was used for all the analytical preparations.

**Table 1.** Chemical analysis of the laterite ore sample

Component	Fe	Ni	Si	Al	Cr	Mn	Mg	LOI (Lost on Ignition)
Content wt.%	80.637	2.651	5.148	4.953	2.512	1.374	1.286	1.439



**Figure 1.** XRD pattern of the laterite ore sample

### 2.2. Experimental design

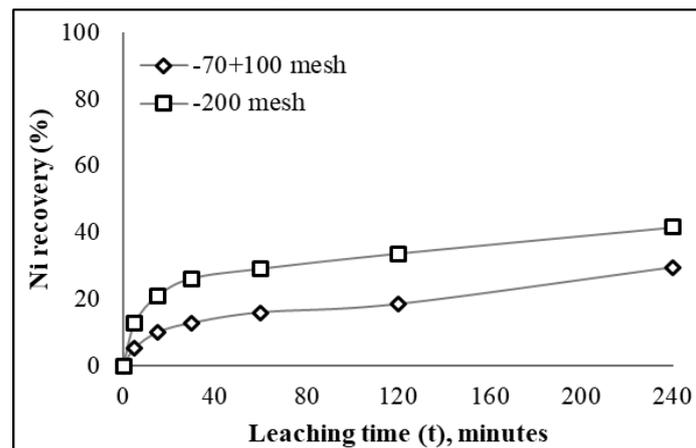
The experiments were carried out in a 500 mL three-neck flask reactor equipped with stirrer, temperature control unit and condenser. Three hundred milliliters (300 mL) of hydrochloric acid solution (pH = 1 or 2) was poured into the tree-neck flask and heated using a waterbath to a desired temperature (30°C, 60°C or 90°C). Sixty grams (60 gr) of nickel laterite sample (particle size : -70 + 100 mesh or -200 mesh) was then put into the reactor. The stirrer speed was set constant at 400 rpm during the leaching process. Each run of the leaching process was performed for 4 hours. Samples of the leach suspension were drawn at predetermined intervals and then the solid phase was separated from the liquid phase using a centrifuge at 1,000 rpm for 10 minutes. Then, the element in the liquid phase was analysed using the atomic absorption spectrometer (AAS).

## 3. Results and discussion

### 3.1. Leaching studies

### 3.1.1. Effect of particle size

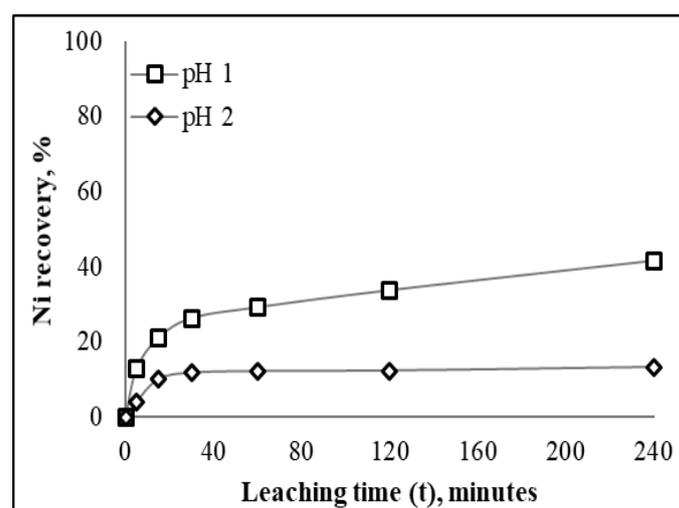
Effect of particle size on nickel recovery is shown in Figure 2. It can be seen from Figure 2 that nickel recovery increases with decreasing particle size. For the first 30 minutes, nickel recovery increases rapidly, followed by insignificant change due to the attained equilibrium condition. For particle size of -200 mesh nickel recovery is about twice that of -70+100 mesh. This phenomenon is caused by the increase of surface area in the smaller particle sizes per unit weight. This condition will surely enhance the mass transfer process of leaching [18,19].



**Figure 2.** Effect of particle size on the nickel recovery (pH = 1; stirring speed = 400 rpm; temperature = 90°C and solid/liquid ratio = 0.2 w/w)

### 3.1.2. Effect of pH

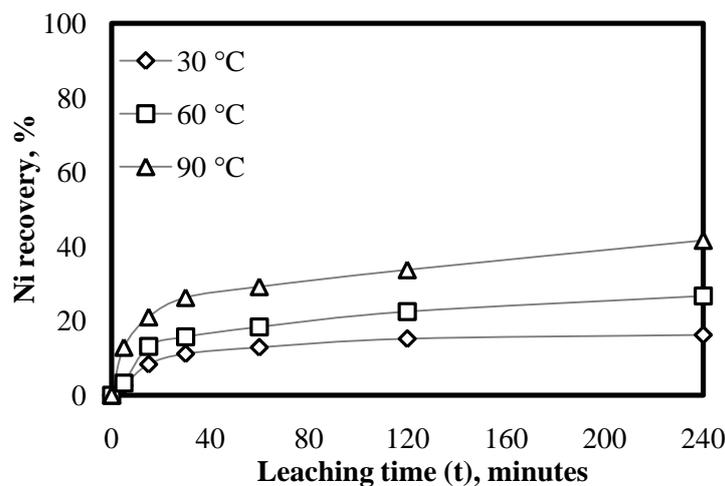
The effect of hydrochloric acid pH on nickel extraction is shown in Figure 3. Figure 3 exhibits that nickel recovery increases with decreasing pH. At pH 1, nickel recovery is about 3 to 4 times that at pH 2. pH will increase the affinity of nickel in the ore so that nickel recovery decreases with increasing pH. This is in accordance with experimental results conducted by Yan et al. [20]. Nickel recovery increases at the first 30 minute and starts to show insignificant increase due to approaching its equilibrium.



**Figure 3.** Effect of hydrochloric acid pH on the nickel recovery (particle size = -200 mesh; stirring speed = 400 rpm; temperature = 90°C and solid/liquid ratio = 0.2 w/w)

### 3.1.3. Effect of temperature

The leaching temperature also plays a significant role in metal extraction. Figure 4 shows the effect of leaching temperature on nickel recovery. Nickel recovery increases very significantly from the beginning to 15 minutes and then increasing slowly, because it is reaching the equilibrium condition. It can be seen from Figure 4 that nickel recovery increases with the increase of temperature. The optimum nickel recovery obtained is approximately 40% leaching temperature of 90°C for 4 hours. This is caused by the increase of both rate of chemical reaction and rate of diffusion at higher leaching temperature [21].



**Figure 4.** Effect of temperature on the nickel recovery (particle size = -200 mesh; pH = 1; stirring speed = 400 rpm and solid/liquid ratio = 0.2 w/w)

## 3.2. Kinetic model analysis

### 3.2.1. The selection of kinetic model

Nickel extraction from limonite ore can be represented by the general reaction of  $aA(aq) + bB(s) \rightarrow$  products. In a heterogenous reaction system, the reaction rate can be controlled by one or a combination of the following steps :diffusion through the fluid film, diffusion through the ash (or solid product) layer on the particle surface or the chemical reaction at the surface of reacted particles [24]. Several studies, like the studies conducted by Wei et al. [22], Agacayak et al. [19] and Parhi et al. [23] used shrinking core model to describe the physical phenomenon of the leaching process. In this study, the diffusion through film layer is assumed not to control the process because of high speed of stirring and high concentration of hydrochloric acid applied in the experiment. Therefore, diffusion through the ash layer and chemical reaction models were further investigated in this work.

For diffusion through the product layer, the correlation between  $t$  and  $x$  is calculated using Equation (1) and  $D_e$  is calculated using Equation (2) [24].

$$\frac{t}{\tau} = 1 - 3(1 - x)^{\frac{2}{3}} + 2(1 - x) \quad (1)$$

$$\tau = \frac{\rho_B R^2}{6bD_e C_{Al}} \quad (2)$$

While for the reaction controlling regime, the correlation between  $t$  and  $x$  calculated using Equation (3) and  $k_s$  is calculated using Equation (4) [24].

$$\frac{t}{\tau} = 1 - (1 - x)^{\frac{1}{3}} \quad (3)$$

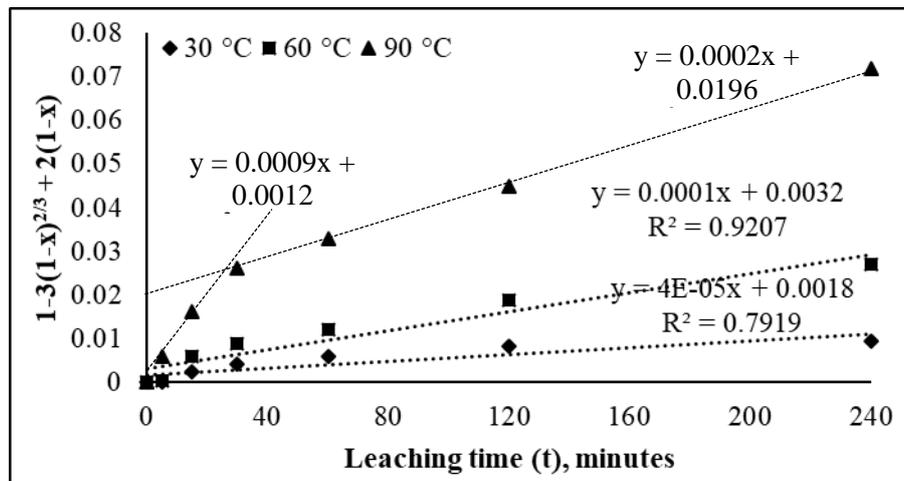
$$\tau = \frac{\rho_B}{k_s C_{Al}} \quad (4)$$

Where  $x$  is fraction of nickel leached,  $t$  is the reaction time,  $\tau$  is the overall time to reach unreacted core at the radius = 0,  $\rho_B$  is the density of the ore,  $R$  is the radius of the solid particle at  $t = 0$ ,  $b$  is the stoichiometric coefficient of the solid reactant,  $D_e$  is the diffusion coefficient in the porous product layer,  $C_{Al}$  is the concentration of A in the bulk of solution,  $k_s$  is the chemical kinetic constant. Equations (1), (2), (3) and (4) are applied to evaluate the kinetic parameters that contain in Equations (2) and (4). The calculated parameters are shown in Table 2.

**Table 2.**  $D_e$ ,  $k_s$  and correlation coefficients for different temperatures

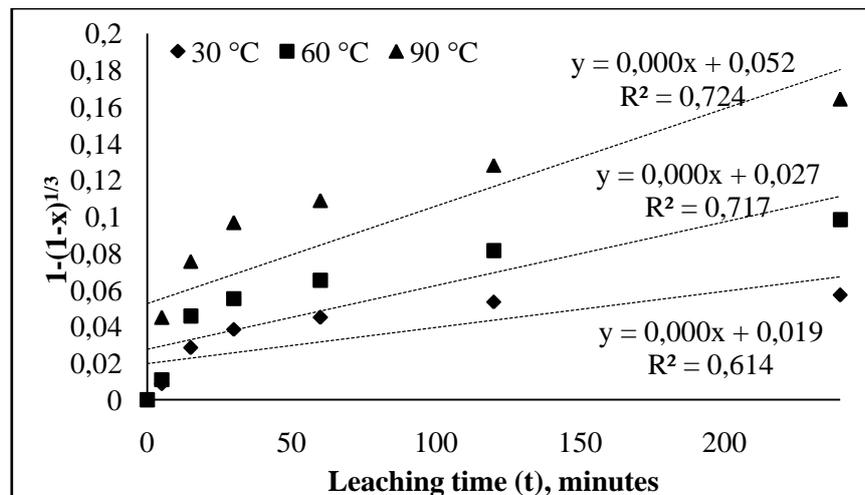
Temperature (°C)	Apparent rate constants for Ni		Correlation coefficients ( $R^2$ )	
	$D_e$ (cm <sup>2</sup> /min)	$k_s$ (/min)	Diffusion Through Product Layer	Chemical Reaction
30	$7.32 \times 10^{-8}$	$4.48 \times 10^{-2}$	0.79	0.61
60	$1.83 \times 10^{-7}$	$6.72 \times 10^{-2}$	0.92	0.72
90	$1.65 \times 10^{-6}$	$1.12 \times 10^{-1}$	0.98	0.72
	$0.36 \times 10^{-6}$		1	

From Table 2, it can be seen that the results indicate that the recovery of Ni is controlled by diffusion in the porous product layer.  $1-3(1-x)^{2/3}+2(1-x)$  versus  $t$  plotting will give a straight line with a slope of  $1/\tau$ , as depicted in Figure 5. By knowing the value of  $\tau$ , the value of  $D_e$  can be evaluated using Equation (2). At experimental temperature of 90°C, the data shows two regions that give two different values of slopes. It means that there are two different values of  $D_e$ . This is subjected to the internal structure changes of the ore. Around 30 minute starting from the beginning of experimental, the changing of pore size would be very fast. This is indicated by the changing value of  $D_e$ . The higher the slope, the higher the  $D_e$  is. In general, the experimental results are in good agreement with the results reported by Agacayak et al. [19], Wei et al. [22] and Parhi et al. [23]. The decreasing rate of diffusion in the product layer may be due to the smaller porosity. That is resulted by the formed products are still remained in the ash layer [25].



**Figure 5.**  $1 - 3(1 - x)^{\frac{2}{3}} + 2(1 - x)$  vs time for leaching of nickel from limonite ore at different temperature

To evaluate whether the chemical reaction phenomenon control the system, plotting  $1 - (1 - x)^{1/3}$  versus t should give a straight line with a slope of  $1/\tau$ . Figure 6 shows that experimental data do not fit the model related to the chemical reaction control.



**Figure 6.**  $1 - (1 - x)^{1/3}$  vs time for leaching of nickel from limonite ore at different temperature

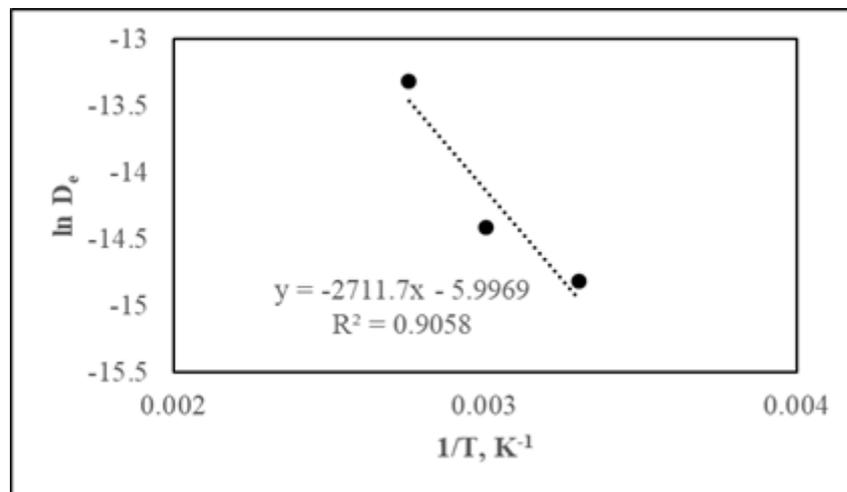
3.2.2. *Calculation of diffusion activation energy.* The diffusion activation energy can be expressed in accordance with Equation (5).

$$D_e = A \exp\left(-\frac{E_{D_e}}{RT}\right) \tag{5}$$

Equation (5) can be linearized as follows:

$$\ln D_e = \ln A - \frac{E_{D_e}}{RT} \tag{6}$$

Plotting  $\ln D_e$  versus  $1/T$  gives a straight line with a slope of  $(-E/R)$ , as exhibited in Figure 7. The slope in Figure 7 is  $-2.7117$ . Therefore the values of  $E/R = 2.7117$ , so that  $E = 2.7117 (8.413 \text{ kJ/mol.K}) = 22.5 \text{ kJ/mol}$ . This value is so closed to Wei, et al. [22] result. Table 3 shows the activation energy results researchers and this study.



**Figure 7.** In  $D_e$  versus  $1/T$

**Table 3.** The study activation energy

Researchers	Activation Energy, kJ/mol	Rate controlled by
Wei et al. [22]	23.279	Diffusion through product layer
Agacayak and Zedef [19]	68.66	Diffusion through product layer
Parhi et al. [23]	17	Diffusion through product layer
This study	22.5	Diffusion through product layer

#### 4. Conclusions

The leaching kinetic of Ni from low grade limonite ore was affected by pH, particle size and temperature. The lower pH and the smaller particle size, the higher the nickel recovery is. On the other hand, when the temperature decreases, nickel recovery is decreasing. Optimum nickel recovery is obtained at pH1, temperature of 90°C and particle size of -200 mesh, in which the recovery of nickel is 41.5%.

Shrinking core is the most appropriate model to describe the kinetic of nickel leaching from low grade limonite ore using of hydrochloric acid solution. The kinetic analysis shows that the nickel dissolution from low grade limonite ore is controlled by diffusion through product layer. The activation diffusion energy for conducted temperature in this study in between 30°C-90°C is 22.5 kJ/mol.

#### Acknowledgements

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