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Kinetics study of leaching ore nickel laterite using hydrochloric acid in atmosphere pressure

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ABSTRACT Leaching of nickel laterite ore at atmospheric pressure is a leaching method that can be operated at >100^{0}C temperatures in an atmospheric pressure, which is applicable to a low-grade laterite ore. This research aimed to study the effect of temperature, acid concentration, and leaching time on nickel extraction percentage and the leaching kinetics. Hydrochloric acid (HCl) was used as a leaching agent and several variables were applied, i.e., temperature (80^{0}C, 90^{0}C, 100^{0}C), HCl concentration (5 M, 6 M, 7 M), and leaching duration (120 minutes, 150 minutes, 180 minutes) to investigate their effect on nickel extraction percentage. In addition, the kinetics of the leaching process was studied using a Shrinking Core Model. The results showed that the percentage of nickel extraction increased with increasing temperature, HCl concentration, and leaching time. The lowest percentage of nickel extraction of 51.29% was obtained when 80^{0}C, five molar HCl, and 120 minutes leaching duration were applied. In contrast, the highest percentage of nickel extraction of 97.22% was obtained at 100^{0}C, seven molar HCl, and 180 minutes of leaching time. The kinetics study results show that diffusion through the unreacted solid product layer controls the nickel leaching rate.

INTRODUCTION

Nickel is a nonferrous metal widely used in the manufacture of stainless steel and steel alloys, electroplating, and catalysts in the hydrogenation process in the oil chemical industry (Wang *et al.*, 2017; Hosseini *et al.*, 2017). It occurs in nature as nickel sulfide (40%) and laterite nickel (60%) which formed from the leaching of ultramafic rocks (Rice, 2016). The depletion of nickel sulfide reserves and high nickel sulfide mining costs have made laterite nickel ore a primary source of nickel (Liu & Lee, 2015). There are two types of laterite nickel ore, namely limonite and saprolite. The limonites contain higher iron oxide but lower nickel and magnesium content than saprolite (Safitri *et al.*, 2018).

Generally, nickel extraction from laterite nickel ore can be carried out through pyrometallurgical and hydrometallurgical processes (Kursunoglu *et al.*, 2018). The extraction of low-grade laterite nickel ore using the pyrometallurgical process is challenging (Sudibyo *et al.*, 2018). However, hydrometallurgical processes using heap leaching (HL), high-pressure acid leaching (HPAL), and atmospheric acid leaching (AL) are able to extract nickel from laterite nickel ore (Mubarok & Yunita, 2015). HL method is widely applied to process copper, uranium, and gold. This method is quite a low investment and operating cost. However, this method has a low Ni and Co recovery compared to the leaching method inside the gaping reactor (Stopic & Friedrich, 2016). In addition, this method is prolonged because the acid needs to be sprayed on top of the pile before slowly descending to the bottom (Mystrioti *et al.*, 2018). HPAL method is applied to process low-grade nickel ore, but this method has relatively high investment and operating costs (Wang *et al.*, 2012; Miettinen *et al.*, 2019). AL method can be applied to process laterite nickel ore. This method has several advantages, i.e., low cost, accessible equipment, and low maintenance costs (Önal & Topkaya, 2014). It can be used as an alternative to the HPAL method (Wang *et al.*, 2018).

The laterite nickel ore leaching using the AL method in hydrochloric acid media has been studied by several researchers (Astuti *et al.*, 2016; Li *et al.*, 2018, 2020; Mystrioti *et al.*, 2018; Permana *et al.*, 2020; Top *et al.*, 2020). Li *et al.*'s (2019) in their research on the kinetic of laterite nickel ore leaching in the hydrochloric acid solution, have obtained a maximum nickel extraction of up to 92.3% under leaching conditions of hydrochloric acid concentration eight molars, temperature 80^{0}C, and 2 hours leaching time. This study applied an improved temperature and the leaching duration to increase the nickel extraction percentage. In addition, this study also investigates kinetics of the leaching process to determine the controlling factors and optimize the conditions (Ma *et al.*, 2017; MacCarthy *et al.*, 2016; Thubakgale *et al.*, 2013) and predicts the minerals' behavior in the solution (Luo *et al.*, 2017).

METHOD

Nickel ore samples from the Konawe Regency of Southeast Sulawesi Province were used for this study. The samples were crushed using mortar and pestle, then sieved to get a 200 mesh grain size sample. The chemical composition was analyzed using the X-Ray Fluorescence (XRF) Axios FAST.

Samples that have been refined and analyzed for their chemical composition are leached using hydrochloric acid. This study investigated three parameters: temperature, HCl concentration, and leaching duration, the variables of each parameter are presented in Table 1.

Table 1. Leaching parameters

No.	Parameters	Unit	Variables
1	Temperature	^{0}C	80, 90, 100
2	HCl concentration	molar	5, 6, 7
3	Leaching duration	minutes	120, 150, 180

The leaching process was started by pouring 20 grams nickel ore sample and 100 mL HCl 5 molar solution into a triple neck reactor. The mixture was heated up to 80^{0}C temperature, and the leaching solution was extracted after 120, 150, and 180 minutes. The exact process was repeated using 6 and 7 molars HCl concentrations and temperatures of 90^{0}C and 100^{0}C. Schematic series of the leaching reactor after Mohammadreza *et al.* (2014) is shown in Figure 1.

The nickel concentration of the leaching solution was analyzed using the PerkinElmer Atomic Absorption Spectrophotometer (AAS) instrument. The percentage of nickel extraction was calculated using equation (1) (Kursunoglu & Kaya, 2016). The leaching kinetics was then determined using the shrinking core model.

$$\text{Nickel extraction (\%)} = \frac{\text{Ni content in the leaching solution}}{\text{Ni content in the ore}} \times 100\% \quad (1)$$

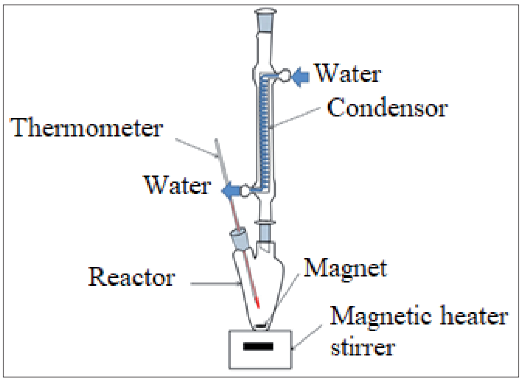


Figure 1. Schematic circuit of leaching reactor

RESULTS AND DISCUSSIONS

Composition of nickel laterite ore

The chemical composition of nickel laterite ore was determined using X-Ray Fluorescence (XRF) to identify the elements concentration of the samples. The result is presented in Table 2.

Table 2. Composition of Nickel Laterite Ore

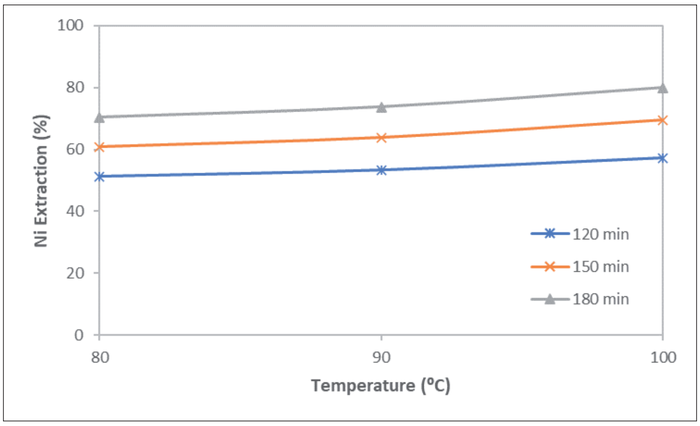
Element	Concentration (%)
Fe	9.403
Si	8.077
Ni	1.021
Al	1.159
Ca	0.968
Cr	0.340
Mn	0.175
Co	0.063
S	0.042
P	0.022
V	0.011
Sb	0.035
Cd	0.022
Zn	0.0094

The XRF analysis result shows that iron is the dominant element with a concentration of 9.403% (Table 2). On the contrary, zinc occurs in the lowest concentration of 0.0094%. Nickel concentration in the sample is relatively low about 1.021%. Based on the nickel concentration, the nickel laterite ore sample was classified into limonite type with <1.5% Ni.

Effect of temperature on nickel extraction

Temperature is one of the parameters that affect nickel ore extraction. In this study, temperature variables of 80^{0}C, 90^{0}C, and 100^{0}C were applied in the experiment to investigate the temperature effect on the nickel extraction percentage. A graph of the temperature relationship to the nickel extraction percentage is presented in Figure 2.

The relationship between temperature and nickel extraction percentage can be explained as the higher the leaching temperature, the higher the percent of nickel extraction. This tendency occurs in hydrochloric acid concentrations of five, six, and seven molars. Higher temperature causes an increase in kinetic energy between the molecules, increases the collision between the molecules, and ultimately causes an increase in the reaction product (Wanta *et al.*, 2018). The relationship between temperature to reaction rate follows the Arrhenius equation, $\ln k = \ln A - \frac{E_a}{RT}$, where k is the reaction rate constant, A is the frequency factor, and Ea is the activation energy (Li *et al.*, 2019).



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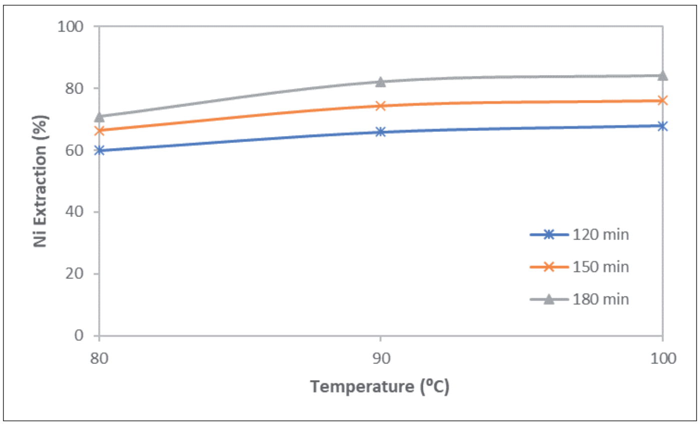

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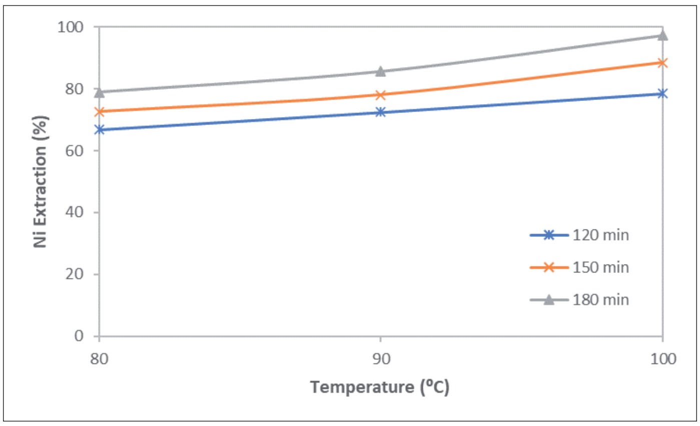

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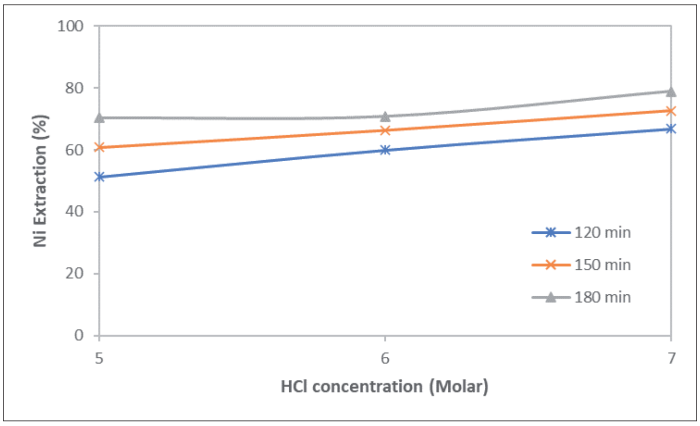
Figure 2. Effect of leaching temperature on nickel extraction at (a) 5 molar HCl, (b) 6 molar HCl, (c) 7 molar HCl

Effect of hydrochloric acid concentration on nickel extraction percentage

Similar to temperature, acid concentration also affects the nickel extraction percentage. Leaching experiments were carried out using three variables of hydrochloric acid concentration, which are five, six, and seven molars. The effect of hydrochloric acid concentration on the nickel extraction percentage is presented in Figure 3.



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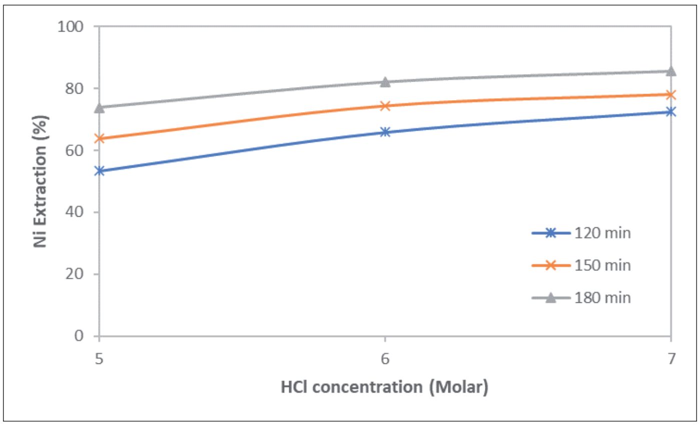

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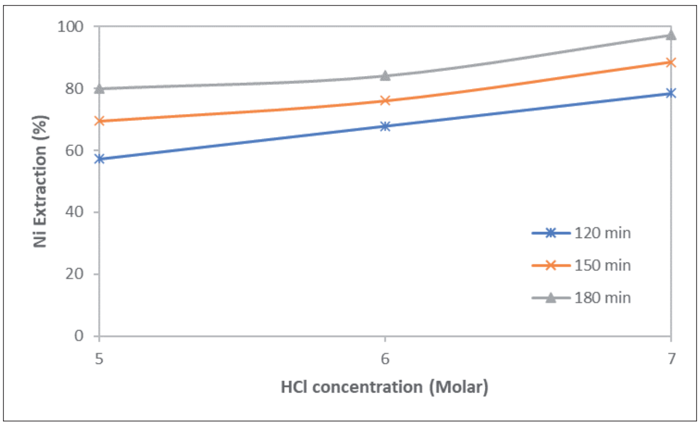

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Figure 3. Effect of hydrochloric acid concentration on nickel extraction percent at (a) 80^{0}C, (b) 90^{0}C, and (c) 100^{0}C

The increase in acid concentrations leads to an increase in nickel extraction percentage (Figure 3). The increase in acid concentration means an increase in hydrogen ions (H^+) activity, which ultimately increases nickel concentration in the solution. Based on Le Chatelier's principle, when the acid concentration increases (the concentration of H^+ ions increases), then the reaction of the acid with the nickel present in the laterite nickel ore will shift to the right (reaction product) (Hosseini et al., 2017).

Effect of leaching duration on nickel extraction percentage

In addition to temperature and acid concentration, the influence of leaching duration was also studied. The effect of the leaching duration on the nickel extraction percentage is presented in Figure 4.

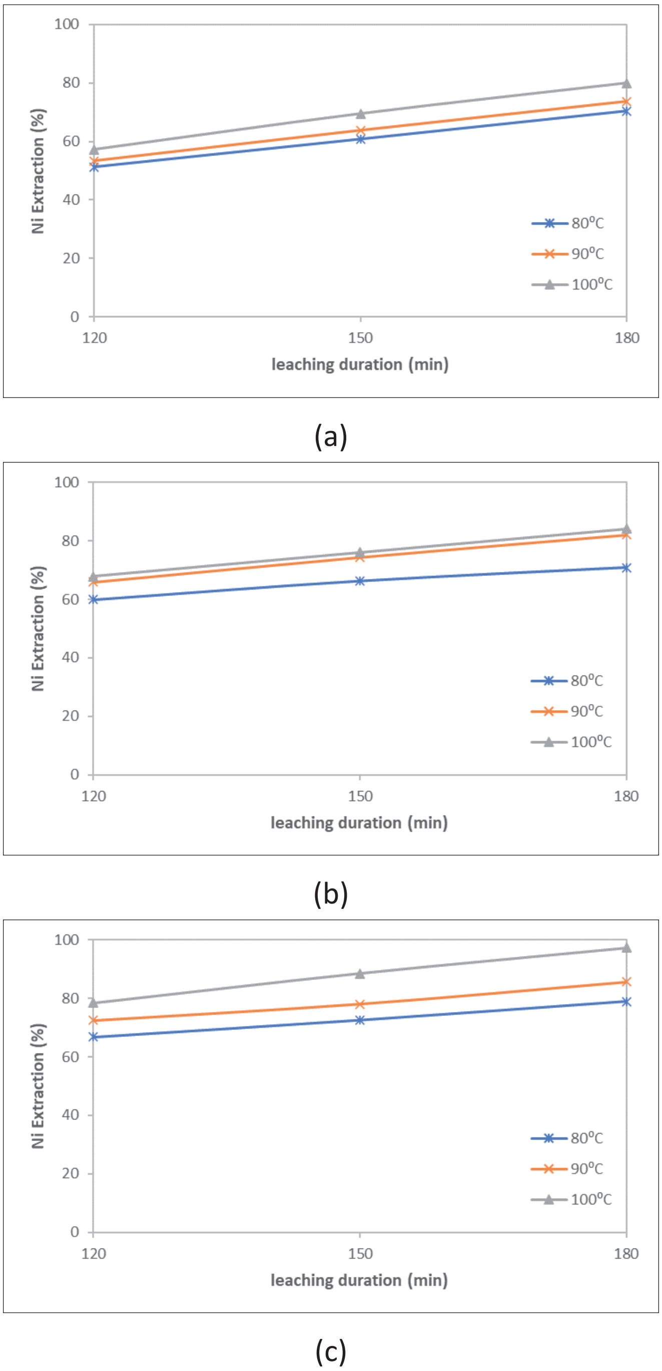


Figure 4. Effect of leaching duration on the nickel extraction percentage at (a) 5 molar HCl, (b) 6 molar HCl, (c) 7 molar HCl

Leaching experiments were carried out for three leaching duration of 120 minutes, 150 minutes, and 180 minutes to investigate the effect of leaching duration on the nickel extraction percentage. The result shows that the longer the leaching duration, the higher the percentage of nickel extraction (Figure 4). The longer the leaching duration means longer contact time between hydrochloric acid and nickel laterite ore samples, which results in more products. The highest percentage of nickel extraction (97.22%) was obtained after 180 minutes of leaching duration, in eight molars HCl concentration and at 100^0C temperature.

Leaching kinetics

The kinetics of the leaching process of oxide minerals depends on the activity of the protons in the solution (Kursunoglu & Kaya, 2016). The kinetic study was carried out using a shrinking core model, in which the mathematical equation follows the equation from Astuti *et al.* (2015), Mubarok & Fathoni (2016), Wanta *et al.* (2018), and Xiao *et al.* (2020):

a. *Diffusion through the fluid film layer*

$$K_f.t = x \tag{2}$$

b. *Diffusion through the unreacted solid product layer*

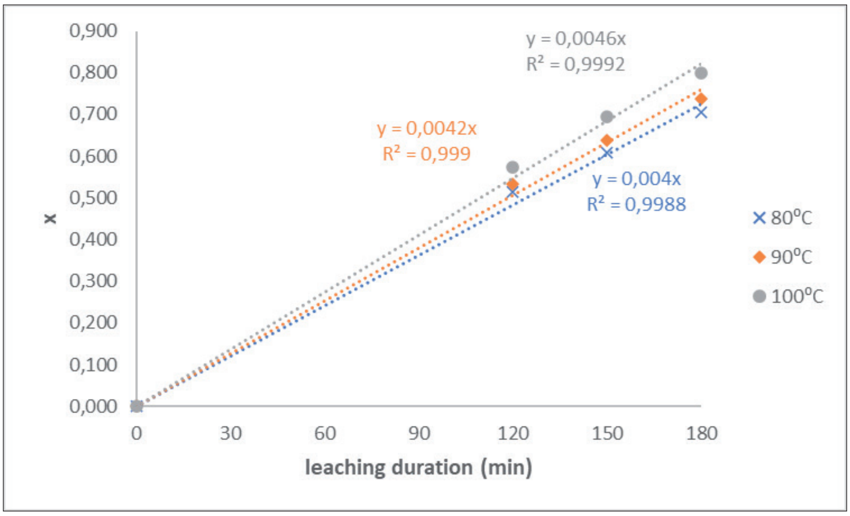
$$K_d.t = 1 - 3(1 - x)^{0,67} + 2(1 - x) \tag{3}$$

c. *Chemical reaction*

$$K_r.t = 1 - (1 - x)^{0,33} \tag{4}$$

where x is the recovering value of nickel, t represents the leaching duration, K_f, K_d, and K_r are each constant of the rate reaction of leaching for diffusion through fluid film layer, diffusion through unreacted solid product layer, and chemical reaction.

The rate control of the leaching process is determined from the rate constants of each model according to equations (2), (3), and (4). The linearity of the regression curve is determined from the value of R^2 of the regression curve that is closest to 1. Linear regression curves for diffusion through the fluid film layer, diffusion through the unreacted solid product layer, and chemical reactions are presented in Figure 5, Figure 6, and Figure 7 respectively.



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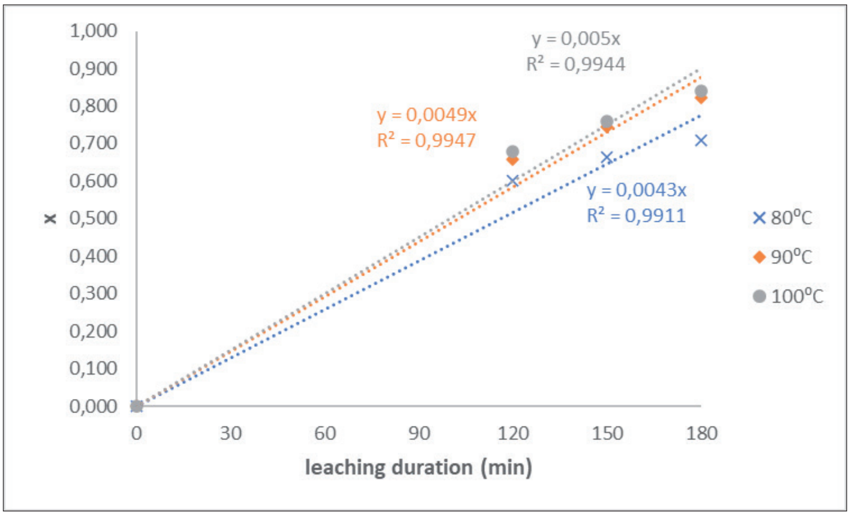

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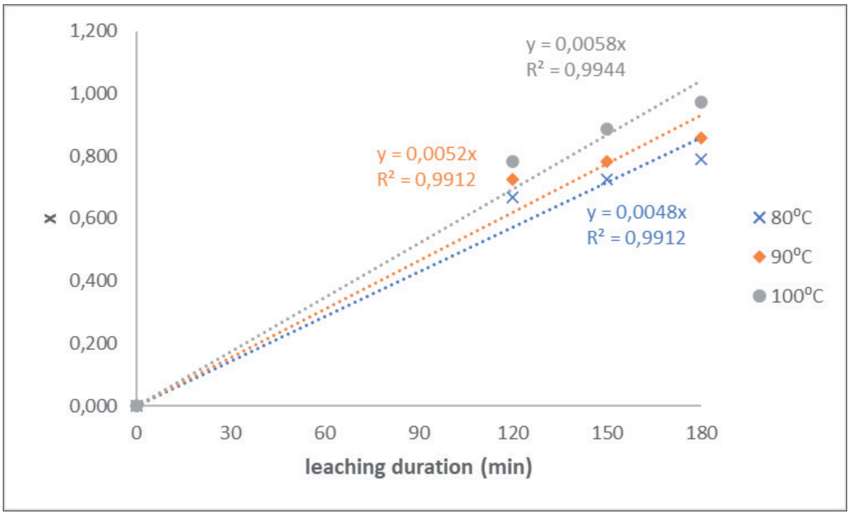

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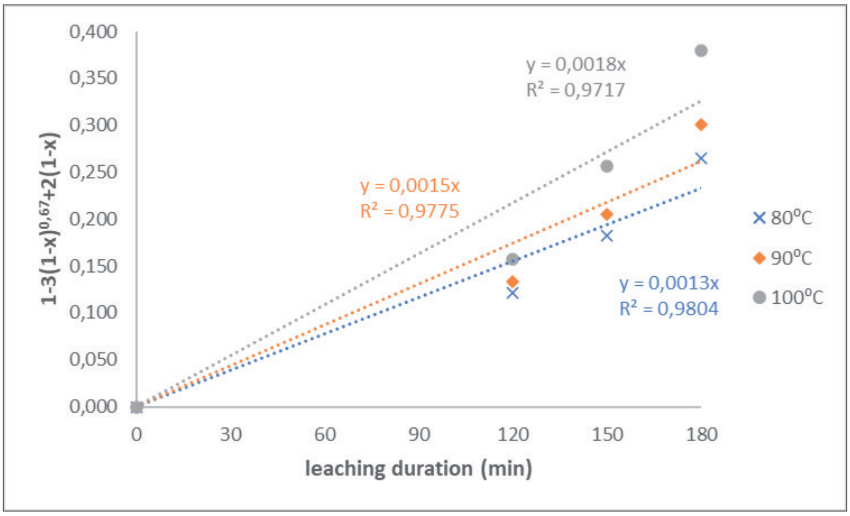
Figure 5. Linear fit results of leaching on the shrinking core model for diffusion through the fluid film layer in (a) 5 molar HCl, (b) 6 molar HCl, (c) 7 molar HCl



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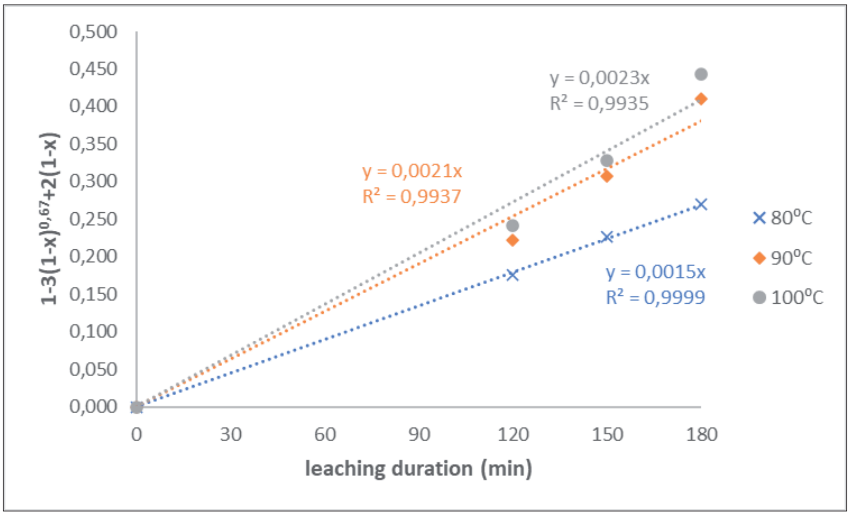

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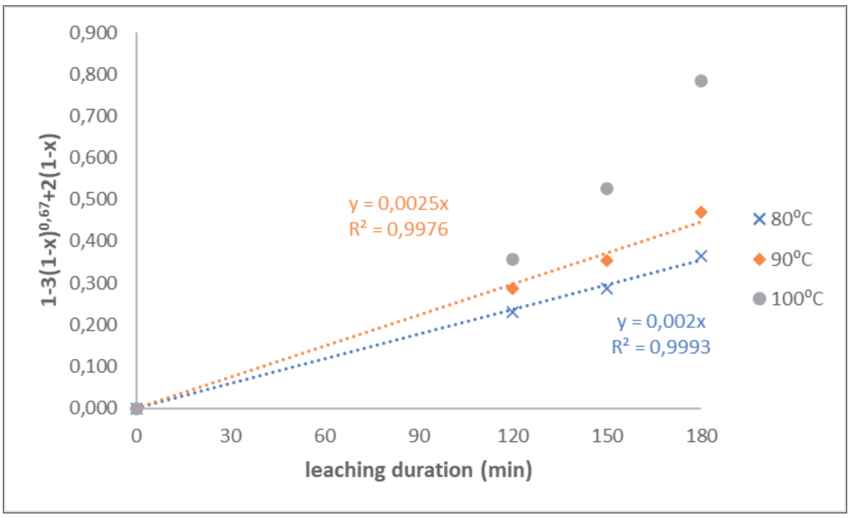

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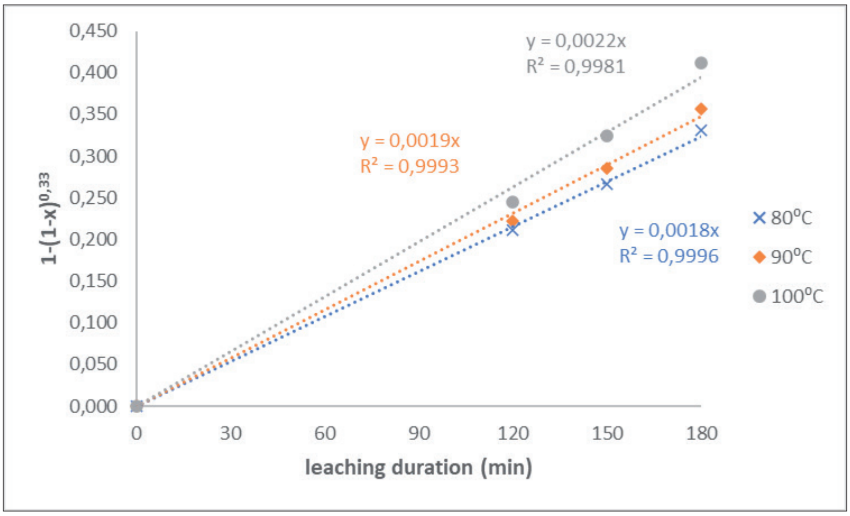
Figure 6. Linear fit results of leaching on the shrinking core model for diffusion through the unreacted solid product layer in (a) 5 molar HCl, (b) 6 molar HCl, (c) 7 molar HCl



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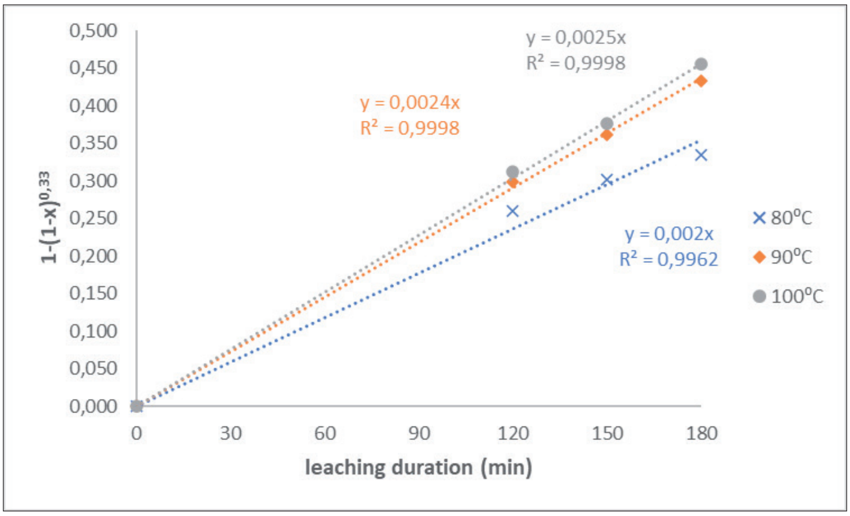

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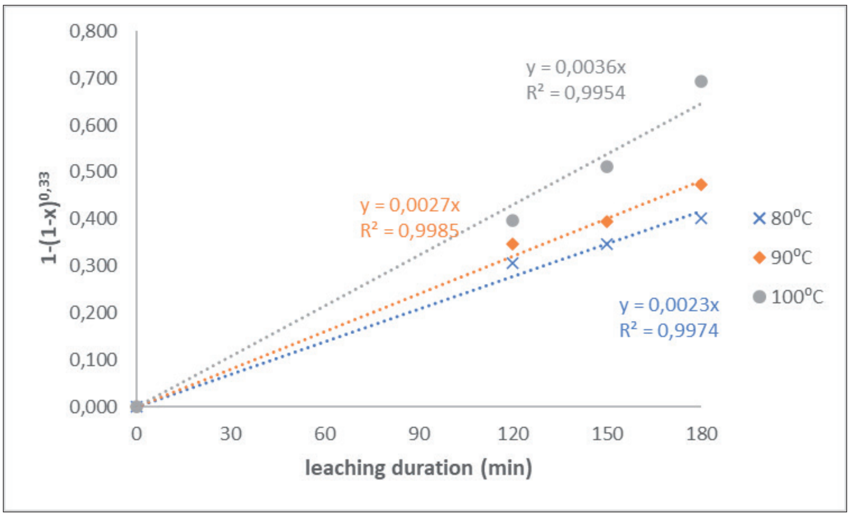

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Figure 7. Linear fit results of leaching on shrinking core models for chemical reactions in (a) 5 molar HCl, (b) 6 molar HCl, (c) 7 molar HCl

The linear regression curves in Figures 5 to 7 mostly show a linear line indicated by an R^2 value of 0.99. However, there is a graph that does not represent linear lines because the nickel extraction percentage significantly increases at 180 minutes of leaching duration. The reaction rate constant for each rate controller was obtained from these linear regression curves. The constant values of the reaction rates at each process rate controller for every HCl concentration and temperatures variables are presented in Table 3.

Table 3. The constant value of each model's reaction rate on variations in HCl concentration and temperature

Concentration of HCl (molar)	Temperature (^{0}C)	Constants of the rate reaction		
		Diffusion through the fluid film layer	**Diffusion through the unreacted solid product layer**	**Chemical reaction**
5	80	0.004	0.0013	0.0018
	90	0.0042	0.0015	0.0019
	100	0.0046	0.0018	0.0022
6	80	0.0043	0.0015	0.002
	90	0.0049	0.0021	0.0024
	100	0.005	0.0023	0.0025
7	80	0.0048	0.002	0.0023
	90	0.0052	0.0025	0.0027
	100	0.0058	0.0038	0.0036

The reaction rate constant is used to determine the process rate controller. The process rate controller is the one that has the smallest rate constant value. The data presented in Table 3 shows that the constant value of the reaction rate for diffusion through the solid product layer does not react at all temperatures and has a constant value that smaller than the other controllers. It suggests that the kinetics of the nickel laterite ore leaching reaction using hydrochloric acid follows a kinetic model that is controlled by diffusion through the unreacted solid product layer. The layer of solid products is formed because there are minerals that are undissolved or reaction products that settled back (Mubarok & Fathoni, 2016). These results are in line with Li *et al.* (2019) who suggested that the kinetics of leaching laterite nickel ore using hydrochloric acid is following a kinetic model controlled by diffusion through the unreacted solid product layer.

CONCLUSION

The percentage of nickel extraction is influenced by the leaching variables, namely temperature, HCl concentration, and leaching duration. The result from this study suggests that an increase in the leaching variables led to an increase in the nickel extraction percentage. The highest nickel extraction percentage of 97.22% was obtained at a temperature of 100^{0}C, HCl concentration of 7 molars, and a leaching duration of 180 minutes. The kinetics of laterite nickel ore leaching reactions using hydrochloric acid follows the kinetic models which are controlled by diffusion through layers of non-reacting solid products.

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