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The South Kalimantan ilmenite leach is decomposed by NaOH using a hydrochloric acid solution

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ABSTRACT

Indonesia has an abundance of mineral resources. These natural resources' richness has not yet been fully exploited. Ilmenite is one of the minerals that has not been exploited efficiently as a precursor for $TiOSO_4$. Ilmenite, having the chemical formula $FeTiO_3$, is the raw material utilized to produce $TiOSO_4$ precursors. The sulfate and chloride routes can be used to extract ilmenite. The base breakdown will proceed through a leaching procedure utilizing HCl as a solvent to extract ilmenite chloride. The goal of this research is to examine the kinetic elements in order to develop effective and efficient response rate management. The optimal process parameters were determined by analyzing changes in HCl concentrations of 3M, 5M, 7M, 9M, and 12M. The measured temperature fluctuations in leaching varied from 70°C to 120°C. The leaching time was varied from 30, 60, 90, 120, 150, and 180 minutes. The South Kalimantan ilmenite leaching investigation found that decomposing NaOH efficiently created 14,530 ppm TiO_2 levels when 9M HCl was used for 90 minutes. A rise in leaching temperature, an increase in Ti content recovery, and a maximum temperature of 120°C Chemical reaction control, with an activation energy of 20 kJ/mol, serves as the rate controller throughout the ilmenite leaching process.

ABSTRAK

Indonesia adalah negara dengan sumber daya mineral yang berlimpah. Kekayaan sumber daya mineral tersebut hingga saat ini belum dapat dimanfaatkan secara maksimal. Ilmenit adalah salah satu mineral sebagai bahan pembuatan prekursor $TiOSO_4$ yang belum dimanfaatkan secara optimal. Bahan baku yang digunakan untuk pembuatan prekursor $TiOSO_4$ berupa ilmenit dengan rumus kimia $FeTiO_3$. Ekstraksi ilmenit dapat dilakukan melalui jalur sulfat dan klorida. Pada ekstrasi klorida ilmenit hasil dekomposisi basa akan melalui proses pelindian menggunakan HCl sebagai pelarut. Tujuan dari penelitian ini menganalisis aspek kinetika untuk mengetahui pengendali laju reaksi agar berlangsung efektif dan efisien. Analisis melalui variasi konsentrasi HCl 3M, 5M, 7M, 9M, dan 12M dilakukan untuk mengetahui parameter proses optimum. Variasi suhu pelindian yang diamati mulai dari 70°C hingga 120°C. Variasi waktu pelindian dianalisis mulai 30, 60, 90, 120, 150, hingga 180 menit. Hasil penelitian pelindian ilmenit Kalimantan Selatan terdekomposisi NaOH, efektif menghasilkan kadar TiO_2 14.530 ppm pada penggunaan HCl 9M selama 90 menit. peningkatan temperatur leaching, peningkatan perolehan kadar Ti dan maksimum pada 120°C. Sebagai pengendali laju selama proses pelindian ilmenit adalah chemical reaction control, dengan energi aktivasi 20 kJ/mol.

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1. Introduction

Ilmenite is a mineral spread in several areas in Indonesia, including West Kalimantan, South Kalimantan, and the Bangka Belitung Islands [1]. Ilmenite with the chemical formula $FeTiO_3$ is a TiO_2-producing compound [2, 3]. TiO_2 is very useful in life because of its function as an inert and suitable semiconductor. TiO_2 can absorb UV light maximally and has a high oxidation level so that TiO_2 has a maximum photocatalytic activity compared to other compounds such as SnO_2 and ZnO [4-5]. Nearly 95% of the world's ilmenite is utilized in the synthesis of TiO_2 [6]. TiO_2 can be divided into 3 phases, namely brookite, anatase, and rutile [7-8].

Utilization of TiO_2 in everyday life, among others, as a photocatalyst based on its semiconductor properties and as a white paint pigment [9–11]. Pyrometallurgical and hydrometallurgical methods can carry out the production of TiO_2 through the extraction process from $FeTiO_3$. For this research, hydrometallurgical and pyrometallurgical pathways will be used to produce higher purity TiO_2 so that it can be utilized optimally in various fields of life. Previous studies [12-13] have synthesized TiO_2 using ilmenite decomposed by NaOH base followed by leaching using H_2SO_4. However, this study did not discuss the kinetic aspect. Research [1] discusses the kinetic aspects of the alkaline decomposed ilmenite leaching process, but the reactant used is not NaOH but KOH.

In this study, we discuss the kinetic aspects of the acid leaching process of HCl in South Kalimantan ilmenite in the decomposition of NaOH base. The addition of acid concentration and leaching time is expected to accelerate the separation between TiO_2 and impurities, thereby increasing the recovery of TiO_2. In this study, an analysis of the leaching kinetics of acid-base ilmenite was carried out to determine the rate control so that the reaction was effective and efficient. The synthesis of TiO_2 is generally through the sulfate and chloride pathways. In this study, TiO_2 extraction through chloride by dissolving ilmenite using HCl solution will be carried out. The leaching is intended to separate the gangue from the valuable minerals.

Before the acid leaching process, an alkaline decomposition process is carried out to separate the impurities so that the following process can take place efficiently [12–14]. By knowing the magnitude or small value of the activation energy, it can be seen whether the process takes place efficiently or not. The ilmenite leaching process is close to the shrinking core model [15–17]. The selection of the shrink core model is because the ilmenite particles have a spherical and homogeneous shape, the reaction that occurs with dissolution that has a fluid phase, when leaching takes place, the thickness of the core layer will be constant [17]. The shrinking core model equation is divided into two, chemical reaction control and diffusion control. In Equations (1) and (2), two models of kinetic equations are used [18–20].

Equation with chemical reactions control:

$$1-(1-\alpha)^{\frac{1}{3}}=\frac{Mk_C C_A t}{dr}=k_1 t \quad (1)$$

Equation with rate controller diffusion control :

$$1+2(1-\alpha)-3(1-\alpha)^{\frac{2}{3}}=\frac{6\mu MDC_A t}{dr}=k_2 t \quad (2)$$

Where,

α	= reaction fraction with respect to time t (minutes)	r	= particle initial radius (m)
M	= molecular weight of the reactant solids (kg/mol)	d	= particle density (kg/m^3)
k_c	= rate constant first order (m/min)	μ	= stoichiometric coefficient
C_A	= concentration of leached solution	k_1 dan k_2	= average rate constant (m.min)
D	= diffusion coefficient (m^2/min)		

2. Research Methodology

Ilmenite sand originating from South Kalimantan was first characterized to determine the constituent elements using x-ray fluorescence (XRF), followed by characterization of the mineral phase using x-ray diffraction (XRD). After initial characterization, ilmenite sand was reduced in particle size using a disc mill. Before leaching, ilmenite went through a basic decomposition process with a ratio of ilmenite: NaOH at 5:6 wt%. The ilmenite base decomposition process took place in a muffle furnace at a temperature of 900^{0}C for 3 hours. The results of the base decomposition were followed by leaching using water at a temperature of 40^{0}C for 90 minutes with a sample: water ratio of 1:5% by weight. Frit from water leaching was followed by acid leaching using HCl solution. Variations in HCl concentration were carried out starting from 3M, 5M, 7M, 9M, and 12M. Variations in leaching temperature were analyzed at 70-120^{0}C with controlled leaching times ranging from 30, 60, 90, 120, 150, and 180 minutes. The characterization of the resulting TiO_2 levels was analyzed using inductively coupled plasma-optical emission spectrometry (ICP-OES) to determine the levels of Ti and Fe.

3. Results and Discussion

The ilmenite sample went through an initial characterization process using XRF, intending to know the levels of elements that make up the ilmenite sand of South Kalimantan. The results of the characterization using XRF can be seen in Table 1. Table 1 shows that the dominant element in South Kalimantan ilmenite is titanium with a content of 49.87%, iron as an impurity element is still relatively high at 30.64%. The sample also contains other impurities such as Al and Si. Further characterization using XRD to determine the mineral phase contained in ilmenite in South Kalimantan. Figure 1 shows the results of sample characterization using XRD. Following the results of XRF characterization that the majority of samples are Ti elements, the results of XRD characterization on ilmenite in South Kalimantan confirmed that the dominant sample is ilmenite ($FeTiO_3$).

3.1. Effect of HCl Concentration

Figure 2 shows an increase in the dissolved iron and titanium fractions when the concentration of 3M to 9M. Furthermore, there was a significant decrease in the concentration of 12M. From the graph, and it can be seen that the highest levels of titanium and dissolved iron were produced at the concentration of 9M HCl. The amount of dissolved titanium content is followed by the amount of dissolved iron content. The cause of the high levels of dissolved Fe is that there was no Fe separation process as an impurity so that during the acid leaching process, not only Ti dissolved but Fe also dissolved. Thus the optimum condition for leaching acid ilmenite is alkaline decomposition using the optimum HCl solution at a concentration of 9M.

Table 1. Chemical composition of ilmenite.

Element name	Percentage (%)
Titanium (Ti)	49,87
Iron (Fe)	30,64
Silicon (Si)	3,56
Aluminum (Al)	2,47

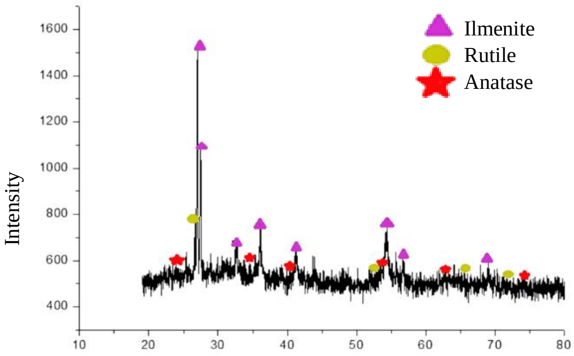

Figure 1. XRD characterization results on ilmenite in South Kalimantan

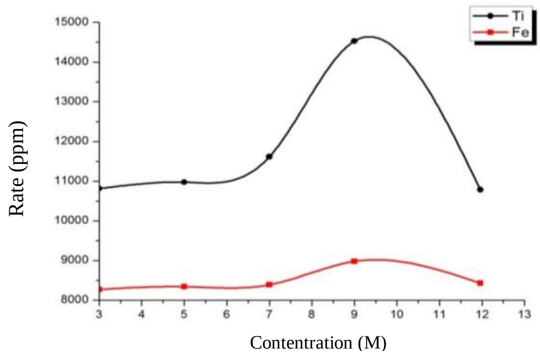

Figure 2. Effect of HCl concentration on the solubility of Ti and Fe

3.2. Effect of Leaching Temperature

In a leaching process, the temperature has an important role. Increasing the leaching temperature will speed up the reaction because an increase in temperature increases collisions between particles. The more collisions between particles, the leaching process will take place quickly, and the resulting product will increase. Figure 3 shows the effect of leaching temperature on the solubility of Ti and Fe. Figure 3 shows that in the temperature range of 70^0C-120^0C, there is a very significant increase in Ti and Fe levels. According to the Arrhenius equation for this type of endothermic reaction, the higher the reaction temperature more the resulting product will increase.

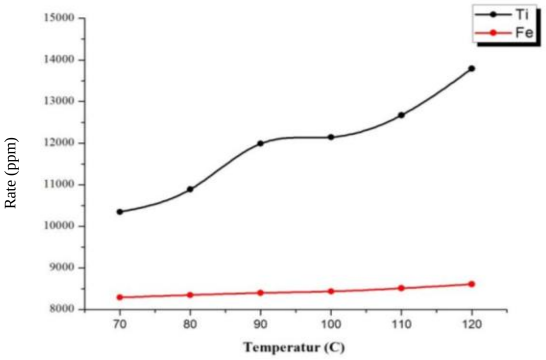

Figure 3. Effect of HCl leaching temperature on the solubility of Ti and Fe

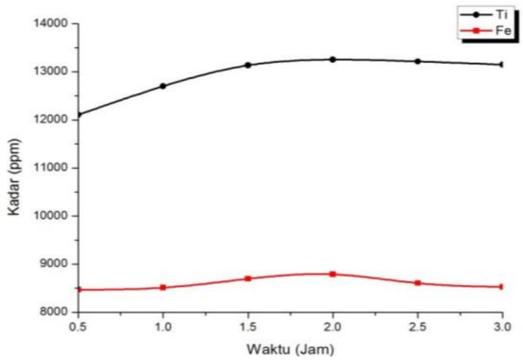

Figure 4. Effect of HCl leaching time on the solubility of Ti and Fe

3.3. Effect of Acid Leach Time on the Purity of Ti and Fe

Figure 4 shows that from 30 minutes to 90 minutes, there was an increase in the levels of Ti and Fe produced. However, from 90 minutes to 180 minutes, the levels of Ti and Fe tend not to experience significant changes. It is assumed that at 90 minutes of leaching time, the leaching process has reached saturation point. In a reaction, if the process reaches the saturation point, the process will no longer be optimal. Thus, the most effective time to perform acid leaching on alkaline decomposed ilmenite is 90 minutes.

3.4. Leaching Kinetics of Alkaline Decomposed Ilmenite

The ilmenite leaching process is close to the shrinking core model [15, 17]. The selection of the shrinking core model is assumed because the ilmenite particles have a spherical and homogeneous shape. The reaction that occurs is a reaction with a solvent that has a fluid phase. When the leaching process runs, the core layer thickness is constant [17]. The shrinking core model equation is divided into two, namely chemical reactions control and diffusion control. Equations (1) and (2) are approximate kinetic equations used to determine the rate control for the alkaline decomposed ilmenite leaching process. The method used to determine the process rate controller is a graph plotting method. By looking for the linearity of the existing graph, it will be known that the rate controller that plays a role in the process. Figure 5 shows a graph of the relationship between equation 1-$(1 - Xb)^{1/3}$ and the leaching time. Based on Equation (1) in Figure 5, several equations representing the chemical reaction control rate are shown. Table 2 shows the equation of each line and the value of R^2 in Figure 5.

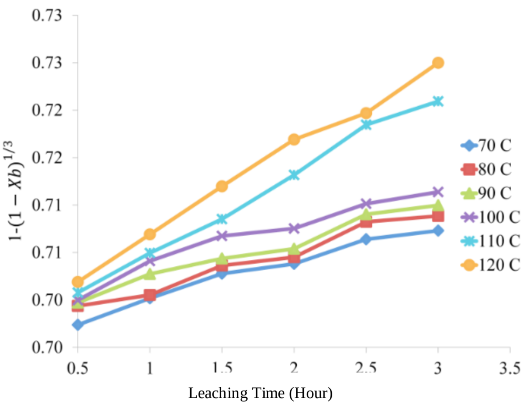

Figure 5. Relationship between 1-$(1 - Xb)^{1/3}$ and leaching time

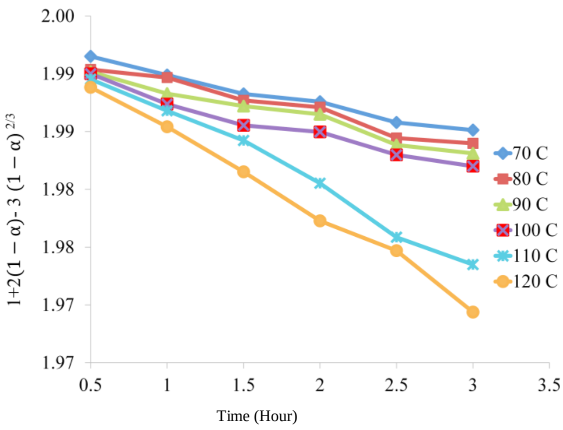

Figure 6. Relationship between 1+2$(1 - \alpha)$-3$(1 - \alpha)^{2/3}$ and leaching time

Table 2. Equation of line and value of R^2 based on chemical reaction control

Temperature	Linear equation	R^2
70^0C	$y = 0.004x + 0.696$	0.98
80^0C	$y = 0.0042x + 0.697$	0.98
90^0C	$y = 0.00423x + 0.6982$	0.97
100^0C	$y = 0.0043x + 0.6991$	0.97
110^0C	$y = 0.0083x + 0.6965$	0.99
120^0C	$y = -0.0091x + 0.6979$	0.99

Based on Equation (2), whereas the rate controller is diffusion control, Figure 6 shows a graph of the relationship between 1+2$(1 - \alpha)$-3$(1 - \alpha)^{2/3}$ to the leaching time. Equation (2) represents the rate controller for diffusion control. Table 3 shows the equation of the line and the value of R^2 in Figure 6.

Table 3. Equation of line and value of R^2 based on rate controller diffusion control

Temperature	Linear equation	R^2
70^0C	$y = -0.0026x + 1.9925$	0.98
80^0C	$y = -0.0028x + 1.992$	0.96
90^0C	$y = -0.0028x + 1.9914$	0.97
100^0C	$y = -0.0031x + 1.9909$	0.96
110^0C	$y = -0.0067x + 1.9934$	0.98
120^0C	$y = -0.0076x + 1.9929$	0.99

From Table 2 and Table 3, we can compare the average value of R^2 to find out which rate controller plays the most role in the leaching process. Table 2 shows the average value of R^2 of 0.98, while Table 3 shows the average value of R^2 of 0.97. Thus, the controlling rate of the leaching process is chemical reaction control with an average value of R^2 closer to 1. Equation (3) shows the calculation of the activation energy during the leaching process [21].

$$K = A.e^{-\frac{\varepsilon a}{RT}} \tag{3}$$

Where k is the rate constant, R is the ideal gas constant of 8.314 Joul/kelvin mol. A is the Arrhenius constant, Ea is the activation energy, and T is the leaching temperature. From Equation (3), a graph of the relationship between 1/T to ln k can be drawn, as shown in Figure 7, to obtain activation energy of 20 kJ/mol.

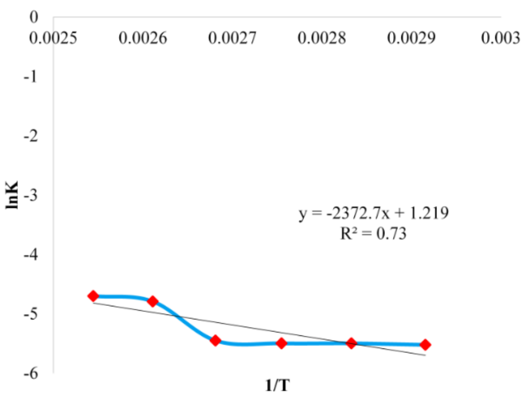

Figure 7. Graph of 1/T value and ln k

Base decomposition of ilmenite using NaOH is quite effective in producing TiO_2. It can be seen that the Ea value is not too high at 20 kJ/mol. According to previous researchers, base decomposition using NaOH is better than using Na_2CO_3 [12]. It was suspected that when the base decomposition process of ilmenite mixed with NaOH, the sodium titanate and sodium ferrite phases began to appear at a temperature of 500°C. Meanwhile, when using Na_2CO_3 at a temperature of 600°C-900°C for 4 hours, the sodium titanate and sodium ferrite phases begin to occur when the temperature is above 900°C [13]. Thus, NaOH is more efficiently used as a reactant in the base decomposition process in ilmenite. The results showed that the synthesis of TiO_2 by alkaline decomposition followed by leaching of 9M HCl produced TiO_2 of 14,530 ppm. TiO_2 levels are higher than previous studies using 3M H_2SO_4 resulted in TiO_2 of 4,784 ppm [12].

4. Conclusions

Extraction of ilmenite in South Kalimantan by alkaline decomposition at 900^0C for 3 hours, followed by leaching of 9M HCl for 90 minutes, produced TiO_2 levels of 14,530 ppm. The increase in leaching temperature is directly proportional to the increase in the recovery rate of Ti. The reaction rate controller for ilmenite mineral leaching in South Kalimantan is chemical reaction control with 20 kJ/mol activation energy.

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