Leaching kinetics of Sodium Zirconate in Hydrochloric Acid based on shrinking core models

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Abstract. The leaching kinetics of sodium zirconate in hydrochloric acid has been studied. Sodium zirconate was the result of melting zircon sand after separation from sodium silicate. The variables studied were temperature, contact time and the mole ratio of solvent to feed (R). These study aims are to determine the optimum conditions, the reaction rate controller and the reaction rate constant (k) and activation energy (Ea) for the leaching process of sodium zirconate (NaZrO3). This experiment performed by leaching the sodium zirconate in hydrochloric acid solution with various temperatures of 50 °C, 70 °C and 90 °C, the mole ratio of solvent to feed of 5, 7 and 9, and various contact time of 10 minutes to 50 minutes. The experimental data were analyzed according to the kinetic models for heterogeneous reaction processes by using shrinking core models. It was found that the leaching of sodium zirconate in hydrochloric acid solution is controlled by chemical reaction with the activation energy was -62.974 kJ/mol. The optimum conditions for the performed experiment in the leaching step were achieved at a temperature of 50 °C, the mol ratio of solvent to feed of 5 and contact time of 50 minutes with the conversion of sodium zirconate was 43.43% and the value of reaction rate constant was 0.0027 min⁻¹.

1. Introduction
Nuclear energy is an alternative energy that has a higher prospect than fossil energy and renewable energy. Various studies have been conducted to prepare the Nuclear Power Plant (NPP) construction in Indonesia. In line with the preparation of nuclear power plant construction in Indonesia, the plant's type that will be developed is the high-temperature reactor (HTR). This reactor has high energy efficiency and can also be used in industrial processes. HTR with coated particle fuel is a future reactor (generation IV) because it does not only has high efficiency but also releases any fission product into the environment. It has passive safety principles and negative reactivity [1]. Zirconium (Zr) is a strategic material for both the nuclear and non-nuclear industries. In the nuclear industry, zirconium in the form of ZrC (Zirconium Carbide) is used as a UO2 kernel coating material for High-Temperature Reactor (HTR) fuels. Zirconium Carbide (ZrC) is used as a substitute for SiC (Silicon Carbide) in the high-temperature reactor (HTR) nuclear fuel element. This is because ZrC has corrosion-resistant properties against nuclear fission. In addition, ZrC has a very high melting point of around 3450°C while SiC decomposes at temperatures above 1600°C so operating at temperatures above 1600°C will cause TRISO kernel fuel leakage [1]. In the non-nuclear industry, ZrO2 has many uses, including color stabilizers for paints or inks, ceramic coatings (coatings), for fuel cell cathodes, refractories, catalysts, construction materials, and electrolyte components [1,2]. Zirconium
Oxychloride Octahydrate is a soft white solid, tetragonal crystalline form consisting of tetramel, has a refractive index of 1.552, density 1.91 g/cm³, loses six water molecules at 150ºC, becomes anhydrous at 210ºC, decomposes at 400ºC, can dissolve in water, acidic solution, also soluble in alcohol and ether, and slightly soluble in hydrochloric acid. Zirconium dichloride oxide (ZrOCl₂·8H₂O), commonly called zirconium oxychloride (ZOC) is an important basic material in the production of other zirconium chemicals, especially for the production of zirconia and zirconium metals. At present, ZOC is widely used in various industries, such as textile dyeing, oil industry to stabilize oil, antiperspirants, water repellent, TiO₂ pigment coatings, base solvents, paint dryers. ZOC is also applied in the manufacture of ceramics, electronic devices, and nanomaterial technology [3,4]. Processing of zircon minerals begins with a physical process (beneficiation) followed by chemical purification. Beneficiation is a process of separation between minerals so that higher levels can be obtained. The composition and compounds which included in zircon minerals are vary depending on the origin of the zircon region obtained. The physical level increase is done by using a combination of shaking table equipment or rocking table, magnetic separator and high tension separator. Chemical purification can be done by a wet process or dry process method. The dry process method is performing by processing zircon sand at high temperature (1700 ºC) with chlorine gas and carbon reagent, while the wet method, begins with zircon sand smelting, leaching using water, leaching using acid, crystallization and dissolution. Sodium zirconate is formed as shown by Eq. 1 together with sodium silicate and all reaction products are then leached in water to dissolve the Na₂SiO₃ [4,5].

\[
\begin{align*}
\text{ZrSiO}_4 + 4\text{NaOH} & \rightarrow \text{Na}_2\text{ZrO}_3 + \text{Na}_2\text{SiO}_3 + 2\text{H}_2\text{O} \\
\text{Na}_2\text{ZrO}_3(s) + 4\text{HCl} (l) & \leftrightarrow \text{ZrOCl}_2(l) + 2\text{NaCl} (l) + 2 \text{H}_2\text{O}
\end{align*}
\]

2. Materials and methods

2.1. Materials
The main material used for the experiment was zircon sand from West Kalimantan. The other materials were distilled water, NaOH, NaF, Na₂CO₃, and HCl. In this experiment, the feed was done by melting zircon sand with NaOH in a weight ratio of 1:1.1 by using the furnace at 750-800 ºC for two hours. The process was resulting in a solid form mixed of Na₂ZrO₃ and Na₂SiO₃. The mixture of sodium zirconate and sodium silicate then leached by using water so that sodium silicate dissolves in water as much as possible.

2.2. Apparatus
The tools used were glass and measuring tools, analytical balance sheets, a set of reflux devices, heating with various rotation, magnetic stirrer, stopwatch, mercury thermometer, furnace M 1100, porcelain cup, buchner filter, whatmann filter paper and AAS.

2.3. Experimental procedure
In this experiment, 416 mL of 6 N hydrochloric acid was put into the reactor then the cooling system was run. The reactor and its contents were heated to a temperature close to the target of 50 ºC. For each experiment, 92.6 grams of sodium zirconate was put in a reactor and then magnetic stirring was run. Leaching is done with contact time variations of 10, 20, 30, 40, and 50 minutes. After the reaction time was completed, the suspension was immediately filtered to separate un-dissolved materials. The leached filtrate was analyzed for Zr levels using Atomic Absorption Spectroscopy (AAS). This procedure was repeated for different process conditions, namely the volume parameters of HCl as much as 583 mL and 750 mL and the reaction temperature of 70 ºC and 90 ºC.
2.4. Leaching kinetics study

Kinetics of the leaching process can be approximated by the shrinking core model or SCM abbreviated kinetics model. The use of shrinking core models for the analysis of leaching kinetics is based on the following assumptions [6,7]:

- Round particles
- During the process, the particles shrink uniformly, thus maintaining their spherical shape.
- In the absence of adequate information, the thickness of the layer around the core is assumed to be constant during the leaching process.
- The temperature remains constant throughout the process
- Other substances present in the bait have no significant effect on the kinetics

An illustration of the various mechanisms in the shrinking core model (SCM) is shown in Figure 1.

![Illustration of various mechanisms of leaching](image)

**Figure 1.** Illustration of various mechanisms of leaching [6]

Kinetics metallurgy is one of the factors the length of time or the speed of reaction of a reaction mechanism. Bases the determination of the reaction rate calculation is based on the data percent leached. Mechanical rate control equation is expressed as follows [8-12]:

Interfacial chemical reaction model:

\[
1 - (1 - X)^{\frac{1}{2}} = k_1 t
\]

Ash/product layer diffusion model:

\[
1 + 2(1 - X) - 3(1 - X)^{\frac{3}{2}} = k_2 t
\]

First-order pseudo-homogeneous model:

\[
-\ln(1-X) = k_3 t
\]

Where [X] is the conversion fraction of solid particle, \([k_1]\) is the apparent rate constant (min⁻¹) for the surface chemical reaction, \([k_2]\) is the rate constant (min⁻¹) for diffusion through the product layer, \([k_3]\) is the rate constant (min⁻¹) for first-order pseudo-homogeneous and \([t]\) is the reaction time.

The fractional conversion was determined by the formula [7,10]:

\[
X = \frac{Zf in leaching solution}{Zf in the feed}
\]

To predict the leaching reaction mechanisms controlling the rate of leaching, percent leaching substituted at equations 3, 4 and 5. The results obtained from the equation and the data obtained are then plotted a graph [7,8].

3. Results and Discussions

3.1. Effect of Temperature and Contact Time

Based on Uchenna’s research [10], the experimental results on the effect of leaching temperature on iron yield revealed that as leaching temperature increased, the amount of iron dissolved in the solution
increased and the highest yield was achieved at the highest temperature of 85 °C. Regina et al. [11] reported that the dissolution rate increases with an increase in temperature up to the highest temperature range employed (80 °C). The extraction was observed to reach 95% at 80 °C. Another researcher Alafara et al. [12] studied the dissolution kinetics and leaching of rutile ore in hydrochloric acid. They reported that the dissolution rates were greatly influenced by the hydrogen ion concentration, temperature, stirring speed and particle diameter.

Our study, the effects of temperature and contact time on the leaching process were studied at varying temperatures (50 °C, 70 °C and 90 °C) and at varying contact time (10, 20, 30, 40, and 50 minutes). The results are shown in Figure 2 – Figure 4.

Figure 2. Effect of temperature and contact time on the fractional conversion of sodium zirconate for mol ratio of solvent to feed of 9

Figure 3. Effect of temperature and contact time on the fractional conversion of sodium zirconate for mol ratio of solvent to feed of 7
In general, Figure 2, Figure 3, and Figure 4 show that the leaching rate increases with increasing contact time up to the highest contact time of 50 minutes. But the leaching rate decreases with increasing temperature up to the highest 90 °C temperature. This shows that the leaching of sodium zirconate in hydrochloric acid is an exothermic reaction so the effect of heat will be significant in shifting equilibrium.

Based on the pictures above (Figure 2, Figure 3, and Figure 4), it shows that sodium zirconate conversion increases with increasing contact time except in Figure 2 (time of 10 minutes, mole ratio of solvent to feed of 9, temperature of 70 °C) and Figure 3 (time of 30 minutes, mole ratio of solvent to feed of 7, temperature of 50 °C) fluctuating conversion is obtained. Based on the 9 variations above, the optimum operating conditions occurred at R = 5 and T = 50 °C with the conversion of 43.43%.

3.2. Kinetic analysis

The leaching of sodium zirconate using the solvent of hydrochloric acid was carried out at the mol ratio of solvent to feed of 5, 7 and 9, the temperature of 50, 70 and 90 °C. The leaching of sodium zirconate in hydrochloric acid is an exothermic reaction so the leachability of zirconium increases gradually by increasing contact time but the leaching rate decreases with increasing temperature. The optimum conditions for effective leaching of 43.43 % zirconium were contact time of 50 minutes, the mol ratio of solvent to feed of 5 and reaction temperature of 50 °C. The shrinking-core model is the most commonly used mathematical model to describe the heterogeneous reactions. The solid-liquid–gas-phase reactions like leaching; the rate of reaction is controlled by the following steps: solid or product layer diffusion and chemical reaction. One or more of these factors might control the rate of the reaction. In order to understand the leaching mechanism, Eq. (3), (4) and (5) models were used to describe this mechanism.
Figure 5. The plot of $1 - (1 - x)^{1/3}$ versus time for the temperature of 90 °C and different mol ratio of solvent to feed

Figure 6. The plot of $1 - (1 - x)^{1/3}$ versus time for the temperature of 70 °C and different mol ratio of solvent to feed
Figure 7. The plot of $1 - (1 - X)^k$ versus time for the temperature of 50°C and different mol ratio of solvent to feed.

Figure 8. The plot of $1 + 2(1 - X) - 3(1 - X)^k$ versus time for the temperature of 90°C and different mol ratio of solvent to feed.
Figure 9. The plot of \(1 + 2(1 - X) - 3(1 - X)^{3/2}\) versus time for the temperature of 70°C and different mol ratio of solvent to feed.

Figure 10. The plot of \(1 + 2(1 - X) - 3(1 - X)^{3/2}\) versus time for the temperature of 50°C and different mol ratio of solvent to feed.
Figure 11. The plot of $-\ln(1 - X)$ versus time for the temperature of 90°C and different mol ratio of solvent to feed

Figure 12. The plot of $-\ln(1 - X)$ versus time for the temperature of 70°C and different mol ratio of solvent to feed
Figure 13. The plot of $-\ln(1-X)$ versus time for the temperature of 50 °C and different mol ratio of solvent to feed

The relationship between reaction model and leaching time, at different temperature and difference mol ratio of solvent to feed are given in Figure 5 to Figure 13. The mean values of the reaction rate constants ($k$) were determined from the slopes of the straight line of the relation between the kinetic model and time. The best fit has $R^2$ of 1.0.

Table 1. Linear regression equations, apparent rate constant with their coefficient of determination ($R^2$) at different temperature and difference mol ratio of solvent to feed.

| The ratio of solvent to feed | Temperature (°C) | Chemical reaction model | Product layer diffusion model | First-order pseudo-homogeneous model |
|------------------------------|------------------|-------------------------|------------------------------|-----------------------------------|
| 9                            | 90               | $k_1 = 0.0008$          | $k_2 = 0.0004$               | $k_3 = 0.0024$                    |
|                              |                  | $R^2 = 0.8667$          | $R^2 = 0.7378$               | $R^2 = 0.8642$                    |
| 70                           |                  | $k_1 = 0.0014$          | $k_2 = 0.0007$               | $k_3 = 0.0045$                    |
|                              |                  | $R^2 = 0.3351$          | $R^2 = 0.3891$               | $R^2 = 0.341$                     |
| 50                           |                  | $k_1 = 0.0028$          | $k_2 = 0.0016$               | $k_3 = 0.0093$                    |
|                              |                  | $R^2 = 0.8415$          | $R^2 = 0.738$                | $R^2 = 0.8283$                    |
| 7                            | 90               | $k_1 = 0.0004$          | $k_2 = 0.0005$               | $k_3 = 0.0012$                    |
|                              |                  | $R^2 = 0.8219$          | $R^2 = 0.7161$               | $R^2 = 0.8202$                    |
| 70                           |                  | $k_1 = 0.0006$          | $k_2 = 0.0001$               | $k_3 = 0.0018$                    |
|                              |                  | $R^2 = 0.9636$          | $R^2 = 0.9398$               | $R^2 = 0.9628$                    |
| 50                           |                  | $k_1 = 0.0001$          | $k_2 = 0.0001$               | $k_3 = 0.0012$                    |
|                              |                  | $R^2 = 0.262$           | $R^2 = 0.262$                | $R^2 = 0.2364$                    |
| 5                            | 90               | $k_1 = 0.0002$          | $k_2 = 1E-05$                | $k_3 = 0.0006$                    |
|                              |                  | $R^2 = 0.7784$          | $R^2 = 0.6954$               | $R^2 = 0.7776$                    |
| 70                           |                  | $k_1 = 0.0011$          | $k_2 = 0.0004$               | $k_3 = 0.0035$                    |
Based on Table 1, the best regression coefficient value ($R^2$) at the temperature of 90°C, the mol ratio of solvent to feed of 9, 7 and 5 respectively is 0.8667 on the mechanism of the chemical reaction; 0.8219 on the mechanism of the chemical reaction and 0.7784 on the chemical reaction control mechanism. The same is the best regression coefficient at the temperature of 50°C, the mol ratio of solvent to feed of 9, 7 and 5 respectively is 0.8415 on the mechanism of the chemical reaction; 0.262 on the mechanism of the chemical reaction and 0.6117 on the chemical reaction control mechanism. It can be inferred that the predominant leaching mechanism of zirconium from sodium zirconate using the solvent of hydrochloric acid is chemical reaction controlled only.

![Figure 14](image)

**Figure 14.** The plot of ln $k$ against reciprocal of absolute temperature (K)$^{-1}$

From the obtained data, the logarithmic values of these reaction rate constants [ln $k$] were plotted against the reciprocal of the absolute reduction temperature according to the Arrhenius equation as shown in Figure 14. Determining the value of activation energy ($E_a$) in the leaching process using water in accordance with the Arrhenius graph, the line equation $y = 7574.5x - 29.215$ or ln $k = 7574.5 (1/T) - 29.215$ where the regression coefficient ($R^2$) = 0.9562. The apparent activation energy ($E_a$) was calculated from the slope of the straight line obtained which is 7574.5 for the model that is controlled by chemical reactions. Therefore, the slope of the graph ln $k$ vs. 1/T is equal to $E_a / R$ (ideal gas constant 8.314 J/mol K). After calculation, the activation energy value ($E_a$) is -62,974.393 J/Mol or -62.974 kJ/Mol.

4. **Conclusion**

A shrinking core model was developed for leaching of zirconium from a sodium zirconate. It was shown that increasing the mol ratio of solvent to feed and contact time increased zirconium yield while a decrease in temperature increase zirconium yield. The leaching of sodium zirconate in the hydrochloric acid solution is an exothermic reaction. The leaching process followed the chemical reactions controlled process model. The kinetic equation is given by $1 - (1-X)^{1/3} = k, t$ with the activation energy is -62,974 kJ/mol. The optimum conditions for effective leaching of 43.43% of the zirconium were found to be the temperature of 50°C, the mol ratio of solvent to feed of 5 and contact time of 50 minutes with the value of reaction rate constant is 0.0027 min$^{-1}$.
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