THE EFFECT OF PH AND CALCINATION TEMPERATURE ON THE ZrO₂ PHASE FORMATION FROM NATURAL ZIRCON SAND OF KERENG PANGI

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ABSTRACT

In this research ZrO₂ has been synthesized from Kereng Pangi zircon sand in Central Kalimantan through alkali fusion-coprecipitation method. Firstly, zircon sand (ZrSiO₄) was purified to reduce impurities by magnetic separation, cleaned using an ultrasonic cleaner, soaked/leached with HCl 2 M for 12 hours and leached with HCl at 60 °C for 3 hours. Secondly, alkali fusion was done with KOH as an alkali. This product was then washed by water and dried before leached with HCl 30% at 90 °C for 30 minutes to precipitate and separate Silica from Zircon. ZrO₂ filtrate (ZrOCl₂) precipitated with NH₄OH at pH 4, pH 7, and pH 10 forms Zr(OH)₄ gel. Zr(OH)₂ gel was dried and characterized by DTA-TGA, which was then followed by calcination based on DTA TGA results at temperature ranges of 350 °C - 700 °C to produce ZrO₂. XRD results show that single tetragonal phase of ZrO₂ is formed in all variations of pH precipitation and calcination temperature. An analysis using MAUD software show that crystal size reduces as the increase in precipitation of pH. The crystal size results are 110 nm, 66 nm and 48 nm at pH 4, pH 7 dan pH 10 at 700 °C, respectively. Moreover, XRF results show that ZrO₂ with purity is at around 95.8 % at pH 4 and 96.3 % at pH 7 and pH 10.

Keywords: Alkali Fusion; Coprecipitation; Phase; pH; Crystal Size.

Introduction

Indonesia is very wealthy in natural resources, one of which is mineral. However, the utilization of mineral is still limited to the raw materials, which makes the added value very small compared to the condition where the raw materials are processed into pure or alloy materials, which are ready to enter the industrialization. This potential is then realized by the government which later issued a regulation prohibiting the export of raw materials of deep mining minerals and imposing that they must be processed first in the country.

One type of minerals that has not been explored is zircon (Zr), whose form in zirconia (ZrO₂) is abundant in Sumatera and Bangka Island. Research on zirconia (ZrO₂) coming from natural resources has been widely carried out, but the number is still minimal compared to the number of research on technical or commercial zircon from companies. Based on the results of XRF, the zircon (Zr) content in Central Kalimantan especially in Kereng Pangi area reaches 70%, which is greater than the average of other zircon sand which reaches only around 60%.¹ Thus, is very potential to be explored considering that zirconia (ZrO₂) has many advantages including the electrical and thermal conductivity as well as very low thermal expansion, the high melting point, high hardness and toughness, and better

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performance than other types of ceramics. Moreover, zirconia (ZrO₂) is widely used in numerous areas from the electronics world, automotive, oxygen sensors, fuel cell coatings to extreme applications such as nuclear reactor furnace coatings.

The synthesis process for extracting zirconia from natural zircon sand is greatly influenced by the synthesis method and heat treatment carried out, so most of the research has focused on these two aspects. Variations and trials against parameters of both aspects are widely used to get the best results. One of the methods that is widely developed is alkaline fusion-coprecipitation. This method requires a temperature that is not too high, and the process is simple, so it supports the aspects of efficiency and effectiveness if applied in the industrialization. The alkaline fusion-coprecipitation method consists of two main components, which are zircon sand melting with alkaline materials leaching which also consists of two stages, namely water leaching and acid leaching, followed by coprecipitation. In the coprecipitation process, the effect of pH and precipitation calcination temperature which is formed from natural material has not been widely reported when compared to the effect formed from technical materials.²

The synthesis process of ZrO₂ with alkali fusion method using alkaline NaOH materials has been reported to be carried out by BATAN. In addition, a combination of NaOH and KOH from natural zircon sand of Bangladesh has also been conducted by Biswas. However, alkali fusion method with alkaline KOH has never been reported before. Therefore, this research will fill this gap and focus on the synthesis process of ZrO₂ from natural zircon sand of Kereng Pangi with alkaline KOH.³

Zirconia (ZrO₂) is a polymorphic material with 3 different phases, namely monoclinic (<1170 °C), tetragonal (1170 °C – 2340 °C) and cubic (> 2340 °C). This phase change becomes a problem in applications with a high temperature range, so many studies have been carried out to obtain the phases in a stable form over their stable temperature range. Research on the behavior of ZrO₂ phase change (transformation) is intensively carried out to obtain stable phase of ZrO₂ that supports its application. One technique that has been widely developed is by doping ZrO₂ with divalent or trivalent cations like Mg²⁺,Ca²⁺, Y³⁺,Sc³⁺ to obtain a stable phase at room and high temperatures.⁴ This present research focusing on natural zircon sand with pH and calcinations has never been done before.

**Methods**

Natural zircon sand from Kereng Pangi of Central Kalimantan analyzed by XRF and XRD to observe the elemental content of Zircon and its compound form in the form of ZrSiO₄ followed by a magnetic separation process to reduce magnetic impurities. Moreover, the reduction of the size of zircon sand was carried out until a size of 100 mesh was obtained, and then is was washed using an ultrasonic cleaner to clean the surface of the particles.

The melting process was later carried out with a mole ratio of zircon sand: KOH of 1: 4 at a temperature of 700 °C for 3 hours. The result of smelting namely “frit” was then continued to be washed using aqua dest 3 times for one hour of steering at a rotating speed of 160 rpm to remove any unreacted KOH residues. Following this, the melted product was dried and then leached with 10% HCl for one hour at a stearer speed of 160 rpm with a ratio of 1 gram of frit to 30 ml of 10% HCl. the solution was filtered to take the filtrate. The filtrate was later precipitated with NH₄OH at pH 4, 7 and 10 overnights. In the stage that follows, the precipitation was dried and then tested for DTA TGA to determine the temperature of calcination. Eventually, the results of calcination were tested by XRD and XRF to determine the characteristics of the sample.
Figure 1. Flow Chart of Zircon Sand (ZrSiO$_4$) Purification

Figure 2. Flowchart of the Synthesis of ZrO$_2$ from Zircon Sand (ZrSiO$_4$)
Results and Discussion

The results of XRD and XRF for natural zircon sand of Kereng Pangi as an initial identification of the elements contain an indication of their potential feasibility for the extraction process. From the XRF results in Table 1, it is shown that zircon (Zr) content is quite large, reaching 70% in the form of ZrSiO₄ in nature. The results of the synthesis of Zirconia (ZrO₂) of 86% were later be analyzed for the effect of pH and temperature calcination.

Smelting with alkaline materials for KOH produces different results from NaOH. Specifically, in the alkaline NaOH material, the same conditions including the temperature of 700 °C (for 3 hours) and the comparison between 1: 4 mole ratio are able to break the ZrO₂ and SiO₂ bonds in the ZrSiO₄ compound by reaction:

\[
\text{ZrSiO}_4 + 4 \text{NaOH} \rightarrow \text{Na}_2\text{ZrO}_3 + \text{Na}_2\text{SiO}_3 + 2\text{H}_2\text{O}
\]

\[
\text{ZrSiO}_4 + 2 \text{KOH} \rightarrow \text{K}_2\text{ZrSiO}_5 + \text{H}_2\text{O}
\]

NaOH is able to break down ZrO₂ and SiO₂ while KOH is not able to break it down, but it reacts to form K₂ZrSiO₅ which is more reactive with HCl.⁵

| Element | Weight Percent (%) | A   | B   | C   | D   | E   |
|---------|--------------------|-----|-----|-----|-----|-----|
| Zr      |                    | 70.40 | 90.90 | 95.20 | 95.30 | 95.80 |
| Ti      |                    | 19.40 | 3.59 | 1.29 | 1.30 | 0.54 |
| Fe      |                    | 6.34 | 0.27 | 0.099 | 0.077 | 0.09 |
| Hf      |                    | 1.23 | 1.27 | 1.41 | 1.36 | 1.42 |
| Si      |                    | 0.50 | 2.99 | 1.00 | 1.00 | 0.84 |

Table 1 Data on XRF results at each purification stage (A) initial conditions, (B) after magnetic Separation (C) leaching with HCl at 600 °C for 3 Hours (D) leaching with HCl at 600 °C for 6 Hours, and (D) ZrSiO₄ purification results by the factory

From Table 1, it is shown that the magnetic separation process is very good for reducing magnetic impurities, especially Fe impurity elements. In addition, the zircon sand has a lighter color than the color before the magnetic separation, which is dark due to the presence of impurities which contain a lot of Fe and Ti. Then, the zircon sand was washed with an ultrasonic cleaner to clean the surface and dried.

The Zr(OH)₄ powder from the synthesis results was analysed by DTA-TGA to determine thermal characteristics and calcination temperature in forming the zirconia phase. The DTA-TGA result process was carried out with a rise in temperature of 100 °C / minute. The DTA-TGA results are shown in Figure 3.
temperatures of around 650 °C, 707 °C and 750 °C. The TGA graph at pH 4 falls at a temperature of 834.5 °C, so it is possible that mass overflow occurs because of the use of Zr(OH)$_4$ mass that is too large.

![Figure 3](image)

**Figure 3.** Results of DTA-TGA of Zr(OH)$_4$ synthesized from natural zircon sand of Kereng Pangi (a) DTA (b) TGA.

Based on the results of DTA-TGA analysed, calcinations were carried out at temperature variations of 550 °C, 600 °C, 650 °C and 700 °C with a holding time for 3 hours. The XRD results are shown in Figure 4.

XRD analysis results for all depositional pH show that the higher calcination temperature, the higher the degree of crystallinity of ZrO$_2$, specifically in the increase in crystal size formed. The crystal size of ZrO$_2$ is also influenced by pH precipitation; with an increase of pH precipitation, it makes crystal size smaller. The size of crystallinity and the largest number of crystalline fields are formed at
acidic depositional pH and vice versa, while
the smallest crystal size is formed at alkaline
depositional pH.

ZrO$_2$ resulting from alkaline deposition
(pH 10) still has an amorphous structure at a
temperature of 550 °C, while at acidic and
neutral pH, tetragonal ZrO$_2$ crystals have
been formed, indicating that the

\[
\text{crystallization process at pH 10 is much}
\text{slower than the crystallization process at}
\]

other pH. This difference is possible because
the deposition process at pH 10 is much

\[
\text{faster than that other pH, so it produces more}
\text{random gel structure than the acidic and}
\]

neutral pH gel structure do, which makes it

\[
\text{more difficult to form crystals. Zr(OH)$_4$ gel}
\text{at depositional pH 10 is dispersive and soft,}
\]

characterized by water filtering which is
easier to penetrate the gel. In this present
study, there are 5 crystal fields identified,
namely (011), (110), (020), (121) and (202).

\[
\text{Figure 4. XRD results of synthesis of ZrO$_2$}
\text{from natural zircon sand of Kereng Pangi for}
\]

precipitation at pH 10.

\[
\text{Figure 5. XRD results of synthesis of ZrO$_2$ from}
\text{natural zircon sand of Kereng Pangi at (a) neutral}
\text{depositional pH (pH 7) and (b) acidic depositional pH (pH 4)}
\]
The same condition also occurs at pH 7, but the number of crystalline fields formed is more at than pH 10 with 7 crystal fields, namely (011), (002), (110), (020), (112), (013), (121). Moreover, (202) is also possible because the precipitation rate at neutral pH is not as fast as at pH 10, so the Zr(OH)₄ regularity is better than the regularity at pH 10 are.

XRD results also show the crystallinity of ZrO₂ at acidic pH (pH 4) is higher than that at neutral (pH 7) and alkaline (pH 10). This is because at pH 4 the precipitation rate is very slow compared to the rate at other pH as it takes about 12 hours (overnight). The result is the structure of Zr(OH)₄ gel which is formed more regularly, marked by a clumpy gel condition due to a coagulation process in the gel, whit forms a stronger bond, marked with water on the gel. Thus, it is more difficult to penetrate the gel and filter paper compared to pH 7 and 10. Therefore, pH 4 is much easier to form crystal structures than pH 7 and 10.

The number of crystalline fields formed is at most 8 crystal planes, namely (011), (002), (110), (112), (020), (013), (121 ) and (202). When compared with the commercial ZrO₂ Aldric product, Figure 5. shows that commercial ZrO₂ consists of two phases, namely the tetragonal and monoclinic phases. The monoclinic phase has appeared, so only the recalcination process is needed. Furthermore, the transformation process will occur from a tetragonal to monoclinic phase and at the end, one monoclinic stable phase will be obtained.³

The XRD results analysis combined with MAUD calculation result at a temperature of 550 ºC, which indicates that pH 4 has a crystal size greater than pH 7 and pH 10 do. The exothermic peak of pH 10 at 688 ºC (DTA-TGA figure) has a high exothermic peak only due to the total crystallization process. Meanwhile, the exothermic peak of pH 7 at 655 ºC and pH 4 at 589 ºC is smaller due to not only the crystallization process but also the evaporation process, which is marked by the process of decreasing mass on the TGA graph at around that temperature.

Garvie reported that the maximum crystal size of tetragonal ZrO₂ phase before transforming into the monoclinic phase is 30 nm. However, the ZrO₂ synthesized from natural zircon sand of Kereng Pangi produces a tetragonal phase that can survive even though the crystal size is more than 30 nm. Moreover, the impurity factor inhibits tetragonal to monoclinic phase transformation process. The tetragonal phase is formed to be a metastable phase because it is susceptible to temperature, pressure, crystal size and depositional pH which can withstand the temperature and crystal size ranges of commercial technical precursors.
that have been reported by previous researchers. 

### Table 2. Results of the calculation of the crystal size of ZrO₂ synthesized using MAUD software

| Calcination Temperature | pH 4 | pH 7 | pH 10 |
|-------------------------|------|------|-------|
| 550°C                   | 101  | 44   | 8     |
| 600°C                   | 102  | 47   | 42    |
| 650°C                   | 104  | 54   | 47    |
| 700°C                   | 110  | 66   | 48    |

### Table 3. PSA results of synthesized ZrO₂ from natural zircon sand of Kereng Pangi

| Calcination Temperature | pH 4 | pH 7 | pH 10 |
|-------------------------|------|------|-------|
| 550°C                   | 255  | 301  | 227   |
| 600°C                   | 238  | 243  | 261   |
| 650°C                   | 251  | 248  | 262   |
| 700°C                   | 292  | 261  | 264   |

The results of PSA analysis show that the particle size is getting bigger with the increasing temperature. The relationship between particle size and pH settling is still very different from the relationship between pH and crystal size as a result of MAUD software analysis. Particles are a combination of several crystals, and the relative particle size increases with the increasing temperature. However, for the comparison of particle size with pH, a relationship cannot be drawn, in contrast to MAUD analysis showing that a higher pH precipitation results in a smaller crystal size. This is possible because of the large agglomeration of zirconia samples due to a lack of deposition time or the type of dispersant in the form of soap to disperse the ZrO₂ particles, so it is less effective at dispersing the ZrO₂ trenches. The smaller particle size tendency for agglomeration to occur is greater because it has a larger active outer surface. The atoms on this surface have an incomplete coordination site (dangling bond), so the surface atoms will fill each other with the empty coordination site to form agglomerations.

The results of XRF analysis in Table 4. show that ZrO₂ levels at pH 4 are around 98.5%, slightly smaller than those at pH 7 and pH 10 at around 96.3%. This is possible because the mass of Zr(OH)₄ or ZrO₂ is less, so the percentage decreases slightly. This happens because at pH of acidic precipitation, the quantity of OH⁻ ions from the addition of NH₄OH is less than that in neutral or alkaline conditions. The presence of H⁺ ions in acidic conditions also reduces the rate of precipitation process because H⁺ ions also bind OH⁻ ions to form water thereby reducing the concentration of OH⁻ ions to precipitate Zr⁴⁺ from ZrOCl₂ to form Zr(OH)₄. On the contrary, in neutral or alkaline conditions, H⁺ ions as a measure of acidic pH do not exist, and the abundant OH⁻ ion concentration makes OH⁻ bonds at each corner of the Zr⁴⁺ ions bind...
perfectly to OH\(^-\) and precipitate at a fast precipitation rate.\(^6\)

The amount of OH\(^-\) ion concentration greatly affects the quantity of Zr\(^{4+}\) deposition in the form of Zr(OH)\(_4\) gel. The result is that the mass of Zr(OH)\(_4\) and ZrO\(_2\) at alkaline pH (pH 10) is greater than that in the the neutral and acidic pH. The mass of Zr(OH)\(_4\) is directly proportional to the mass of ZrO\(_2\) with a mass reduction of 20-30% after the calcination process. The mass of ZrO\(_2\) resulting from pH 4 is relatively smaller, so the concentration decreases compared to the mass of impurities and vice versa. This is the reason why the ZrO\(_2\) level at the pH of the depositional pH (pH 4) is relatively smaller than that at the neutral pH (pH 7) and alkaline (pH 10).

The purity level of synthesized ZrO\(_2\) is known through XRF analysis as shown in Table 4. The results of XRF analysis show that ZrO\(_2\) can only be produced with an average purity level of 96%. The lowest ZrO\(_2\) level at pH 4 is possible because at pH 4 the concentration of NH\(_4\)OH as a precipitant is less than at pH 7 and pH 10, so the ZrO\(_2\) concentration is less than that at pH 7 and pH 10. Another reason is that the distribution of impurities in Zircon sand is not possible. To be uniform.

**Table 4.** XRF results of synthesized ZrO\(_2\) from natural zircon sand of Kereng Pangi

| Element | Weight percent (%) |
|---------|-------------------|
|         | pH 4 | pH 7 | pH 10 |
| ZrO\(_2\) | 95.80 | 96.30 | 96.30 |
| HfO\(_2\) | 1.56 | 1.41 | 1.46 |
| TiO\(_2\) | 2.09 | 1.71 | 1.51 |
| Fe\(_2\)O\(_3\) | 0.12 | 0.10 | 0.08 |
| SiO\(_2\) | - | - | - |

**Conclusion**

From the research that has been done, it can be concluded that the synthesis of ZrO\(_2\) from Kereng Pangi natural zircon sand using alkali fusion-coprecipitation method with alkali KOH has been successfully carried out. The results show that ZrO\(_2\) level under acidic depositional pH conditions (pH 4) is 95.8%, while in neutral pH (pH 7) and alkaline (pH 10), the pH condition is 96.3%. The increase of pH precipitation has an effect in reducing crystal size of ZrO\(_2\) formed with the largest crystal size at the calcination temperature of 700\(^\circ\)C, namely acidic depositional pH (pH 4) 110 nm, neutral depositional pH (pH 7) 66 nm and alkaline deposition pH (pH 10) 48 nm. The effect of pH precipitation variations in acidic (pH 4), neutral (pH 7) and alkaline (pH 10) conditions with a calcination temperature ranging of 550 \(^\circ\)C to 700 \(^\circ\)C has not yet formed a ZrO\(_2\) monoclinic phase. The ZrO\(_2\) phase formed is a tetragonal single phase, which is stable up to the temperature of 700 \(^\circ\)C.

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