Characterization of natural puya sand extract of Central Kalimantan by using X-Ray Diffraction

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Abstract. Start Zircon sand extraction in this study use natural sand material from Kereng Pangi village of Central Kalimantan, also known as Puya sand. There are only three ways to extract the Puya sand. The first is magnetic separation, the second is immersion in HCl, and the third is reaction with NaOH. In addition, sample of each extraction step is analyzed with X-Ray Diffraction (XRD). Then based on the quantitative analysis using XPert Highscore Plus software, the samples are identified mostly as zircon (ZrSiO₄) and silica (SiO₂). Moreover, after the immersion process with HCl, the silica compound goes down and the zircon compound climbs to 74%. In the reaction process with NaOH zircon compound content further to increase to 88%.

1. Introduction

Puya sand or commonly known as zircon sand is by-product from the processing of heavy mineral sand that commonly found in river and shore. It can also be acquired from the processing of rare earth minerals [1-2]. Zircon is the common accessory mineral in the majority of igneous and metamorphic rocks with Zr as an essential structural constituent [3]. Zircon minerals are mostly associated with some valuable minerals such as monasite, senotim, and ilmenite [4]. Pure Puya sand has density of 4.68 g/cm³ with varied colors like yellowish, pink, reddish, brownish, colorless, and sometimes green, blue or black [5-6].

Nowadays Zircon mineral in Indonesia can be discovered in many areas of Sumatra, Kalimantan, Sulawesi and Papua [4]. Its existence has been known for a long time as an alluvial sediment with tin sand and other mineral by-products at the waters of Bangka Belitung. In addition, Zircon is also present along the rivers in rural Kalimantan following the spread of gold alluvial sediment and swamp. In the Borneo island, the sediment containing Zircon are identified from the results of alluvium recycling to obtain gold and diamond [5].

The natural resources that become the object of this research is the Puya sand which is mined in Kereng Pangi area, as by-product of gold mining. Puya sand can be processed into zirconia as one of the ceramic material with toughness and strength as its advantages [7]. In general, zircon compound in nature is discovered zirconium silicate compound (ZrSiO₄) commonly referred as zircon hence it has to be purified first in order to gain zirconia.

Extraction is one of purification methods with magnetic separation, immersion with acid, and reacting with a strong base as the steps [8-9]. In this research, X-Ray Diffraction (XRD) is used to determine the crystallographic character and composition of Puya sand before and after the extraction process such as magnetic separation, immersion with acid and reaction with NaOH. Furthermore, it is
also used to know other details like the arrangement of various types of atoms in the crystal, the presence of defects, orientation, and crystal defects [7].

2. Research Method
The initial phase of this research is started with the preparation of the Puya sand samples from Kereng Pangi, Central Kalimantan. The Puya sand is watered with aquades to remove the initial visible impurities before drying. Prior to the treatment, Puya sand samples are analyzed first using XRD. The extraction process begins with a magnetic separation using a permanent magnet to separate the Fe element [8]. The sand is smoothed using the planetary milling ball for 2 hours to reduce the particle size. The powder is soaked with 2M HCl for 12 hours. The precipitate is watered with aquades until it reaches pH 7 and then is dried. Dry powder is reacted with 7M NaOH at a temperature of 300 °C until the sample is shoveled, thensettled to room temperature [9]. Moreover, aquades is added to the sample and stirred for 1 hour using magnetic bar and stirrer. Then it is filtered to obtain sediment and Na$_2$SiO$_3$ solution. The result of the precipitate is watered again with aquades until it reaches pH 7 and dried to produce Zircon powder subsequently characterized using XRD. XRD test aims to obtain the characteristics of crystallography and the composition of Puya sand. The XRD was setup at voltage of 40 kV with 35 mA in current. Angle shots start from 15-90 deg, a step size of 0.02 deg, time/step 0.5 s, and a scan speed of 0.04 deg/s. XRD data is analyzed using Highscore Plus software which is the commercial powder diffraction analysis software from PAN analytical [10].

3. Results and Discussion

3.1. Puya extraction process
Magnetic separation on the extraction process aims to reduce magnetic element that contained in Puya [8]. This process was done because Zircon (ZrSiO$_4$) is a non-magnetic mineral [11]. The following images of Puya sand before and after treatment are presented: XRD analysis of the composition of Puya sand

![Figure 1](image_url)  
**Figure 1.** Samples of Puya sand; (a) Puya sand (b) after magnetic separation (c) after milling process (d) after immersion in HCl (e) after reaction with NaOH.

Figure 1(a) shows the samples of Puya before treatment. While Figure 1(b) shows the samples of Puya after magnetic separation treatment. Based on Figure 1(a) and Figure 1(b) can be seen the difference of color between before and after the treatments. The color of sample before the magnetic separation is darker than after the magnetic separation. Elsner said that dark color is caused by the presence of impurities particles, especially compounds of magnetic element [6]. Figure 1(c) shows the samples after milling process. While Figure 1(d) and Figure 1(d) show the samples after the immersion treatment with
HCl and after thermal immersion treatment with NaOH, both of these samples resulted a white powder that was estimated as zircon

3.2. XRD analysis of the Composition of Natural Puya
One of important functionalities in Highscore Plus software is quantification of phases with partially known or unknown crystal structure. In this software, empirical structure factors are extracted via a Pawley or a LeBail fit and are used for HKL file fit (together with a pseudo-formula mass derived from the known concentration in the binary mixture) for further quantifications following the Rietveld formalism [10].

Figure 2 shows the results of XRD data that has been analyzed by using software Highscore Plus. The result shows that the Puya contains the composition of ZrSiO$_4$ 58% and SiO$_2$ 23% and CaSi$_2$ 19%. From the result can be seen that there is exist two main elements of Zr and Si. Elsner said that the sand which contains element of Zr and Si can be used as the basic material for zirconia production, with the main target being zircon (ZrSiO$_4$) [6] so that need extraction process to get Zr and Si with higher purity.

![Figure 2. XRD Result of Natural Puya.](image)

3.3. XRD Analysis of Puya Sand Composition after Magnetic

![Figure 3. XRD data Result of Puya Sand after Magnetic Separation.](image)

Magnetic Separation of the extraction process aims to separate the magnetic element from sample, especially Fe element. This process is done because zircon (ZrSiO$_4$) is a non-magnetic mineral so that can be separated with Fe element by utilizing magnetic field.
Figure 3 shows the results of XRD data Result of Puya Sand after Magnetic Separation that has been analyzed by using software Highscore Plus. The result shows that the sample contains the composition ZrSiO$_4$ 65% and SiO$_2$ 35%. The increase of zircon and silica content occurs due to the loss of impurities particles, especially the Fe containing compounds so that obtain zircon and silica sample with a better purity level.

3.4. XRD analysis of the Puya Sand composition after HCl Immersion

Before the HCl immersion process, the milling process was done to increase the particle's reactivity because with the small particle size the contact surface area of the reaction becomes larger making it easier in the dissolution process.

Figure 4 shows XRD data results after HCl immersion process that has been analyzed by using software X'Pert Highscore Plus. The result shows that there was an increase of zircon content from the previous treatment from 65% to 74% and silica decreased from 35% to 26%. The immersion process was using high concentration of HCl that aims to dissolve the impurities that can not be separated by magnetic separation, so that resulted the increase the purity of zircon. While the decrease of silica percentage caused by some non-framework of silica also dissolved due to HCl immersion process.

3.5. XRD analysis of the composition of the Puya Sand after NaOH Reaction

Figure 5 shows XRD data result after NaOH reaction that has been analyzed by using software Highscore Plus. The result shows that there was an increase of zircon content from the previous treatment from 74% to 88% and silica decreased from 26% to 12%. The decrease of silica percentage occurs because when the sample was dissolved in NaOH solution there was occurs demolition of chemical bond of SiO$_2$ due to reaction with NaOH solution so that it was formed the dissolved of sodium silicate (Na$_2$SiO$_3$) precursor, and then there was occurs the decrease of SiO$_2$ percentage in sample. Based on the extraction results, the purity of zircon after reaction with NaOH was quite high. So the sample can be synthesized into zirconia (ZrO$_2$).
Less purity of zircon obtained as a result of extraction because treatment with HCl and NaOH still leaves the Hf element whose forming phase that was not identified XRD. The presence of Hf elements in zircon powder was difficult to be identified because all of Zr compound contain Hafnium about 1-3%. Chemically, Zr and Hf have very similar properties that can not be separated by the extraction process in general [2,4,5].

3.6. Characteristic Crystallography of Puya Sand

Further analysis of the samples was performed with XRD to determine the crystallographic characteristics of the Puya sand before and after the extraction process. Based on the analysis of XRD data, most of the identified peaks were zircon (ZrSiO$_4$) with crystal parameters $a = b = 6.607$ Å and $c = 5.982$ Å and $\alpha = \beta = \gamma = 90^\circ$, with density 4.66 g/cm$^3$ and cell volume 261.13 µm$^3$ with crystal system is tetragonal, and silica having quartz structure (SiO$_2$) with crystal parameter $a = b = 4.913$ Å and $c = 5.404$ Å and $\alpha = \beta = 90^\circ$ and $\gamma = 120^\circ$, with density 4.66 g/cm$^3$ and cell volume 112.96 µm$^3$ with crystal system is hexagonal.

4. Conclusion

The characterization result of Puya using X-Ray Diffraction after extraction process, we can describe as follows: (1) After the final extraction process with NaOH, the content of zircon compound in the Puya sand is 88%, so that the sand extract can be processed into zirconia. (2) Most of the identified peaks were zircon compounds (ZrSiO$_4$) with crystal parameters $a = b \neq c$ and $\alpha = \beta = \gamma$ with crystal system is tetragonal, and silica having quartz structure (SiO$_2$) with crystal parameters $a = b \neq c$ and $\alpha = \beta \neq \gamma$ with crystal system is hexagonal.

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