Synthesis of Zirconium Oxychloride and Zirconia Low TENORM by Zircon Sand from Landak West Kalimantan

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Abstract. In order to enhance the added value of zircon minerals (ZrSiO$_4$) derived from tailing gold mining in Mandor, Landak, West Kalimantan; the hydrometallurgical process is needed to obtain zirconium products such as zirconium oxychloride (ZrOCl$_2$.8H$_2$O) and zirconia (ZrO$_2$). Zirconium products that are sold must meet the requirement of Technologically Enhanced Naturally Occurring Radioactive Material (TENORM) or (ThO$_2$ + U$_3$O$_8$) is below 500 ppm. The purpose of this research was to process zircon sand with TENORM content 1784 ppm to be ZrOCl$_2$.8H$_2$O and ZrO$_2$ low TENORM. Zircon sand processing has been carried out through melting zircon sand with NaOH to bind Zr became Na$_2$ZrO$_3$ and Si as the impurities to become Na$_2$SiO$_3$, water leaching to separate Na$_2$ZrO$_3$ from Na$_2$SiO$_3$ and other impurities, acid leaching (HCl) to convert Na$_2$ZrO$_3$ to be zirconium oxychloride low Si (ZOC-1) then ZOC-1 to be zirconium sulfate base (ZBS), ZBS then being deposited to be ZrO(OH)$_2$, ZrO(OH)$_2$ converted to be zirconium oxychloride low TENORM (ZOC-2), ZOC-2 then being crystallized to be ZrOCl$_2$.8H$_2$O and calcinated to be zirconia. The results showed that zircon sand from Mandor, Landak, West Kalimantan could be synthesized into ZrOCl$_2$.8H$_2$O with NORM 1.2586 ppm and zirconia with NORM = 3.5511 ppm, both products have met the industrial-grade requirement.

1. Introduction

Zirconium is widely found in nature, including in the form of zircon sand (ZrSiO$_4$) and baddeleyite (ZrO$_2$). In Indonesia zircon sand is widely obtained as solid tailings from the beneficiation process in the separation of the mineral cassiterite from other minerals such as quartz, ilmenite, rutile, zircon, monazite, and xenotime found on the island of Bangka or scattered as sedimentary deposits that follow the spread of alluvium and swamp deposits swamps in the area of West Kalimantan and Central Kalimantan [1,2]. Until the last few years, the potential of zircon in Indonesia has not been processed and utilized optimally, but only sold as raw material (zircon sand) to several countries such as China. In accordance with Minerva Law number 4 of 2009 concerning Mineral and Coal Mining and Regulation of the Minister of Energy and Mineral Resources (ESDM) of the Republic of Indonesia Number 25 of 2018 concerning Mineral and Coal Mining Businesses [3], it is necessary to have a domestic industry that can processing local minerals into several semi-finished products and finished products so as to stimulate and increase industrial and economic growth in the country. These semi-processed products have many market opportunities as raw materials for the downstream industry that are already running and developing.

In general, zircon, mineral concentrations are formed as reflux in alluvium and are often associated with other minerals such as quartz, ilmenite, rutile, monazite and xenotime. According to article 2
paragraph (2), a. in Government Regulation number 23/2010 mentions that monazites include radioactive minerals [4]. Thus naturally zircon sand contains natural radioactive material called Technologically Enhanced Naturally Occurring Radioactive Materials (TENORM) such as ThO$_2$ and U$_3$O$_8$. In general, the TENORM content in some commercial zirconium products must be < 500 ppm [5]. Whereas if the amount of nuclear material (ThO$_2$ and U$_3$O$_8$) exceeds 2 (two) tons as stated in the Head of BAPETEN Regulation number 09 of 2009 concerning Interventions on Exposures Originating in TENORM in chapter II article 7 paragraph (1) a., Then the factory authority zircon processing is required to take remedial actions against TENORM that are generated [6].

The purpose of this research is the synthesis of zirconium products such as zirconium oxychloride (ZrOCl$_2$·8H$_2$O) and zirconia (ZrO$_2$) containing low TENORM from zircon sand from the Mandor, Landak, West Kalimantan.

2. Material and Methods

2.1. Material

The material used as raw material is zircon ore from Mandor District, Landak Regency, West Kalimantan. While the additional ingredients used are technical NaOH, water, technical HCl, (NH$_4$)$_2$SO$_4$, and NH$_4$OH.

2.2. Equipment

The equipment used is preparation equipment such as ball mills, vibratory sieves, technical scales; equipment for increasing zircon sand content such as shake tables and magnetic separators; equipment for the hydrometallurgical process consisting of furnaces, crystallizers, three-neck flasks, hot plates, glassware; equipment for analysis of raw materials and products resulting from the hydrometallurgical process consisting of sequential X-Ray Fluorescence spectrometer ADVANT XP Thermo ARL9900, Thermo 520 and Bruker S1 Turbo SD; Malvern Zeta Sizer Series for Particle Size Analyzer (PSA); X-Ray Diffraction (XRD) PANalytical X'Pert PRO PW3040/x0; alpha counter brand Technical Atomic and beta counter brand ORTEC.

2.3. Experimental Procedure

2.3.1. Increased ZrO$_2$ Contents in Zircon Sand

Increasing ZrO$_2$ contents in zircon sand is done by beneficiation, namely the separation of impurities minerals such as quartz, ilmenite, rutile, pyrite, monazite, and xenotime from zircon sand based on differences in specific gravity using shaking tables and differences in magnetic properties using a magnetic separator conducted at the Research Center and Development of Mineral and Coal Technology (P3Tekmira) Bandung.
2.3.2. Hydrometallurgical Process for Synthesis of Zirconium Oxychloride and Zirconia

The treatment of zircon concentrate is hydrometallurgically carried out through several stages of the process as follows: smelting zircon concentrate with NaOH to Na₂ZrO₃ and Na₂SiO₃, water leaching to separate Na₂ZrO₃ from Na₂SiO₃, residual NaOH and some other impurities, acid leaching to obtain ZrOCl₂ with low silicate content or ZOC-1, precipitation of zirconium sulfate base (ZBS), precipitation of ZrO(OH)₂ or ZOH, ZOH conversion to ZrOCl₂ with low TENORM levels or ZOC-2, ZOC-2 crystallization to ZrOCl₂·8H₂O, drying, and calcination of ZrOCl₂·8H₂O becomes ZrO₂ with low TENORM levels as shown in Figure 2.

Figure 1. Quantitative flow diagram of increasing contents of ZrO₂ in zircon ore
Some reactions process the processing of zircon concentrate to zirconium oxychloride and zirconia such as:

1. The reaction of the zircon melting process [7, 8, 9]
   \[
   \text{ZrSiO}_4 + 2\text{NaOH} \rightarrow \text{Na}_2\text{ZrSiO}_5 + \text{H}_2\text{O} \tag{1}
   \]
   \[
   \text{ZrSiO}_4 + 4\text{NaOH} \rightarrow \text{Na}_2\text{SiO}_3 + \text{Na}_2\text{ZrO}_3 + 2\text{H}_2\text{O} \tag{2}
   \]
   \[
   \text{ZrSiO}_4 + 6\text{NaOH} \rightarrow \text{Na}_4\text{ZrO}_3 + \text{Na}_2\text{SiO}_4 + 3\text{H}_2\text{O} \tag{3}
   \]

2. The reaction of the water leach process [7, 8]
   \[
   \text{Na}_2\text{SiO}_3 + 2\text{H}_2\text{O} \rightarrow \text{H}_2\text{SiO}_3 + 2\text{NaOH} \tag{4}
   \]
   \[
   \text{Na}_2\text{ZrO}_3 + 2\text{H}_2\text{O} \rightarrow \text{ZrO(OH)}_2 + 2\text{NaOH} \tag{5}
   \]

3. The reaction of the acid leach process [9]
   \[
   \text{Na}_2\text{ZrO}_3 + 4\text{HCl} + 6\text{H}_2\text{O} \rightarrow \text{ZrOCl}_2.8\text{H}_2\text{O} + 2\text{NaCl} \tag{6}
   \]
   \[
   \text{Na}_2\text{SiO}_3 + 2\text{HCl} + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SiO}_4 + 2\text{NaCl} \tag{7}
   \]
   \[
   \text{Na}_2\text{ZrSiO}_5 + 4\text{HCl} \rightarrow \text{ZrOCl}_2 + \text{SiO}_2 + 2\text{NaCl} + 2\text{H}_2\text{O} \tag{8}
   \]

4. The reaction of the ZBS precipitation process [10]
   \[
   5\text{ZrOCl}_2.8\text{H}_2\text{O}+2(\text{NH}_4)_2\text{SO}_4+3\text{H}_2\text{O} \leftrightarrow \text{Zr}_5\text{O}_8(\text{SO}_4)_2.15\text{H}_2\text{O}+25\text{H}_2\text{O}+4\text{NH}_4\text{Cl}+6\text{HCl} \tag{9}
   \]

**Figure 2.** The zircon concentrate processing flow chart becomes ZrOCl$_2$.8H$_2$O and ZrO$_2$.
5. The reaction of the ZOH precipitation process [11]

$$\text{Zr}_5\text{O}_8(\text{SO}_4)_2\cdot15\text{H}_2\text{O} + \text{NH}_4\text{OH} \rightarrow 5\text{ZrO(OH)}_2 + 2(\text{NH}_4)_2\text{SO}_4 + 12\text{H}_2\text{O}$$  \hspace{1cm} (10)

6. The reaction of the ZOH leaching process [12]

$$\text{ZrO(OH)}_2 + \text{H}_2\text{O} \rightarrow \text{Zr(OH)}_4$$  \hspace{1cm} (11)

7. The reaction of the ZOC conversion [12]

$$\text{Zr(OH)}_4 + 2\text{HCl} \rightarrow \text{ZrOCl}_2 + 3\text{H}_2\text{O}$$  \hspace{1cm} (12)

8. Reaction of the ZOC calcination process [12]

$$\text{ZrOCl}_2\cdot8\text{H}_2\text{O} + 0.5\text{O}_2 \rightarrow \text{ZrO}_2 + 8\text{H}_2\text{O} + \text{Cl}_2$$  \hspace{1cm} (13)

3. Results and Discussion

3.1. Characterization of Zircon Ore and Zircon Concentrate

Raw material analysis is performed to see zircon ore and zircon concentrate characteristics including chemical and mineralogical composition analysis. Chemical composition analysis was carried out using XRF at the Geological Survey Centre in Bandung which aims to see zirconium oxide and other oxide compounds.

| Compound | Content, % | Compound | Content, % |
|----------|------------|----------|------------|
| ZrO$_2$  | 38.46      | Cr$_2$O$_3$ | 1.04       |
| SiO$_2$  | 22.23      | MnO       | 1.00       |
| Fe$_2$O$_3$ | 10.11    | CeO$_2$   | 0.575      |
| TiO$_2$  | 20.00      | P$_2$O$_5$ | 0.539      |
| Al$_2$O$_3$ | 0.912    | La$_2$O$_3$ | 0.292      |
| ThO$_2$  | 0.11       | Nd$_2$O$_3$ | 0.199      |
| U$_3$O$_8$ | 0.0464    | Y$_2$O$_3$ | 0.161      |
| Na$_2$O  | 0.703      | V$_2$O$_5$ | 0.0798     |
| HfO$_2$  | 0.85       | Nb$_2$O$_5$ | 0.0271     |
| MgO      | 0.186      | ZnO       | 0.0161     |
| CaO      | 0.090      | CuO       | 0.0123     |
| S        | 2.23       |           |            |

Table 1 shows that in zircon ore from the Mandor Subdistrict, Landak District, West Kalimantan contains valuable elemental oxides such as ZrO$_2 = 38.46\%$, TiO$_2 = 20.0\%$, rare earth oxide (REO) = 1,227\%, TENORM (ThO$_2$ + U$_3$O$_8$) = 1564 ppm. The economic requirements for zircon sand can be hydrometallurgically processed into zirconium products if the ZrO$_2$ content in zircon ore is $\geq$ 60\% [13]. The content of TiO$_2 = 20.0\%$ and Fe$_2$O$_3 = 10.11\%$ represents that the zircon sand contains ilmenite mineral (FeTiO$_3$). Whereas the presence of rare earth oxide (REO), P$_2$O$_5$, and ThO$_2$ in the zircon sand represent that in the zircon sand contains monazite minerals (LREE, Th)PO$_4$ [14]. The REO content of 1,227\% in zircon ore consists of CeO$_2$, La$_2$O$_3$, Nd$_2$O$_3$, Y$_2$O$_3$. If the amount of REO contained in natural minerals is 0.5 - 2\% by weight, it is economically feasible to take it hydrometallurgically [15].

The homogeneity of zircon particle size of the zircon ore smelting process with NaOH under hot conditions will affect the reaction of solid-liquid between zircon particles and NaOH molecules that melt at their melting point. The results of the measurement of zircon ore particle size distribution using PSA are shown in Figure 3.
Figure 3. Zircon ore particle size distribution

Figure 3 shows that the zircon ore particle size distribution in Mandor Subdistrict, Landak Regency, West Kalimantan is relatively homogeneous in the particle size of -90 mesh (passing 90 mesh sieve size) around 78%.

The zircon ore beneficiation process uses a shaking table and magnetic separator conducted at P3Tekmira Bandung to produce zircon concentrate. After measuring the particle size distribution with PSA, it shows that there is an increase in the number of zircon concentrate particles with the size of -90 mesh to 90%.

Figure 4. The size distribution of zircon concentrate powder

The results of the analysis of chemical composition in zircon concentrate using XRF that have been carried out at the Geological Survey Center are shown in Table 2.
Table 2. Chemical composition in zircon concentrate

| Compound | Content, % | Compound | Content, % |
|----------|------------|----------|------------|
| ZrO$_2$  | 60.00      | K$_2$O   | 0.0233     |
| SiO$_2$  | 28.81      | S        | 1.34       |
| Fe$_2$O$_3$ | 1.38      | CuO      | 0.0106     |
| TiO$_2$  | 1.60       | V$_2$O$_5$ | 0.0238     |
| Al$_2$O$_3$ | 0.453    | Cr$_2$O$_3$ | 0.0215     |
| ThO$_2$  | 0.0940     | Y$_2$O$_3$ | 0.230      |
| U$_3$O$_8$ | 0.0844   | La$_2$O$_3$ | 0.0163     |
| Na$_2$O  | 1.12       | Yb$_2$O$_3$ | 0.0510     |
| HfO$_2$  | 0.855      | Sc$_2$O$_3$ | 0.0115     |
| MgO      | 0.0751     | Er$_2$O$_3$ | 0.0187     |
| CaO      | 0.0489     | Am$_2$O$_3$ | 0.0284     |
| MnO      | 0.0116     | MoO$_3$   | 0.305      |

The results of the XRD analysis of zircon concentrate (ZrSiO$_4$) that have been carried out at the Geological Survey Center are compared with ZrSiO$_4$ from other studies, as shown in Figure 5.

![XRD analysis of ZrSiO$_4$](image)

(a) The diffraction patterns of ZrSiO$_4$ raw material for the synthesis (b) ZrSiO$_4$ diffraction patterns from other experiments [16]

**Figure 5.** Comparison of ZrSiO$_4$ raw material diffraction patterns for synthesis (a) and ZrSiO$_4$ from other experiments (b)

3.2. **Synthesis Results**

Through several stages of the processing process of zircon concentrate hydrometallurgically, such as smelting, water leaching, and acid leaching, then produced ZrOCl$_2$·8H$_2$O with low silicate content or ZOC-1, waste in the form of gel and remaining zircon sand that is not melted. The XRD analysis of ZOC-1 was carried out at the Geological Survey Center with results as shown in Figure 6.
After obtaining ZOC-1 then continued hydrometallurgical processes such as precipitation of ZBS, precipitation of ZOH, conversion of ZOH, crystallization and drying to obtain ZrOCl$_2$·8H$_2$O containing low TENORM or ZOC-2: Comparison of XRD analysis results on ZOC-2 synthesis results with the ZOC made by E-Merck that has been carried out at the Geological Survey Center is shown in Figure 7.

Figure 6. Synthesized ZOC-1 diffraction patterns

Figure 7 shows that the results of the XRD analysis of ZOC-2 resulting from synthesis and ZOC made by E-Merck each gave a similar diffraction pattern.

To find out whether the synthesized ZOC-2 meets commercially available ZOC standards, the composition of the oxide compounds in the ZOC-2 synthesized is compared with the composition of the oxide compounds in the ZOC made by Allegheny Technologies Incorporated (ATI) as shown in Table 3.

Table 3. Comparative composition of zirconium oxychloride (ZOC-2) synthesized and ZOC manufactured by ATI

| Compound       | Content, % | Compound       | Content, % |
|----------------|------------|----------------|------------|
| (ZrO$_2$ + HfO$_2$) | 38.39      | (ZrO$_2$ + HfO$_2$) | Min. 35    |
| TiO$_2$        | 0.0033     | TiO$_2$        | Max. 0.002 |
| Fe$_2$O$_3$    | 0.0014     | Fe$_2$O$_3$    | Max. 0.005 |
Table 3 shows that when viewed from the chemical composition (oxide compounds), the quality of ZOC-2 synthesized is almost the same as ZOC made by ATI. This is indicated by the content (ZrO$_2$ + HfO$_2$) in the ZOC-2 synthesized that is higher than ZOC made by ATI, and the oxide impurity content in each sample does not provide a significant difference.

Furthermore, if the result of ZrOCl$_2$.8H$_2$O synthesis is low TENORM calcination process is carried out at 800 °C for 2 hours, then ZrO$_2$ is produced with a low TENORM content. The results of ZrO$_2$ synthesis with low TENORM content after being analyzed by XRD at the Geological Survey Center were then compared with ZrO$_2$ made by E-Merck and ZrO$_2$ from the results of other experiments shown in Figure 8.

![Synthesized ZrO$_2$ diffraction pattern](image1)

![ZrO$_2$ diffraction pattern made by E-Merck](image2)

![ZrO$_2$ diffraction patterns of other experiment](image3)

![ZrO$_2$ diffraction patterns of other experiment](image4)

Figure 8. Comparison of synthesized ZrO$_2$ diffraction patterns (a), ZrO$_2$ E-Merck products (b), ZrO$_2$ results of other experiments (c) and (d)

Figure 8 shows that from the XRD analysis of ZrO$_2$ synthesized, made by E-Merck, and from the results of other experiments have similar diffraction patterns.
To find out whether the synthesized ZrO$_2$ can meet commercially available ZrO$_2$ standards, the composition of the oxide compounds in the synthesized ZrO$_2$ is compared with the composition of the oxide compounds in Zirchem made by ZrO$_2$ as shown in Table 4.

Table 4. Comparative composition of zirconia synthesized and manufactured by Zirchem

| Component                              | Zirconia synthesized | Zirconia made by Zirchem [14] |
|----------------------------------------|----------------------|--------------------------------|
| (ZrO$_2$ + HfO$_2$)                    | 99.5524              | (ZrO$_2$ + HfO$_2$) 99.54%    |
| TiO$_2$                                | 0.0160               | TiO$_2$ < 0.01             |
| Fe$_2$O$_3$                            | 0.0083               | Fe$_2$O$_3$ < 0.02          |
| Na$_2$O                                | 0.0460               | Na$_2$O < 0.01             |
| SiO$_2$                                | 0.0062               | SiO$_2$ < 0.03             |
| Al$_2$O$_3$                            | 0.0008               |                                |
| MgO                                    | 0.0056               |                                |
| CaO                                    | 0.0277               |                                |
| ThO$_2$                                | 3.0440 ppm           |                                |
| U$_3$O$_8$                             | 0.5071 ppm           |                                |
| Cl                                     | 0.0442               |                                |

Table 4 shows that if the ZrO$_2$ composition of the synthesis results is compared with ZrO$_2$ made by Zirchem, then the ZrO$_2$ from the synthesis approaches ZrO$_2$ made by Zirchem. Thus the prototype of the synthesized ZrO$_2$ product has fulfilled the requirements of the Minister of Energy and Mineral Resources Regulation with (ZrO$_2$ + HfO$_2$) $\geq$ 99.0% [3].

Table 3 and Table 4 show that the TENORM levels in the ZOC-2 and ZrO$_2$ synthesized were 1.2586 ppm, and 3.5511 ppm which were significantly lower than the requirements of commercial zirconium products on the world market with TENORM levels must be < 500 ppm [5]. In the hydrometallurgical process with the steps shown in Figure 2, there was a significant reduction in the TENORM (U$_3$O$_8$ + ThO$_2$) level from 1784 ppm in zircon concentrate to 1.2586 ppm in ZOC-2 and 3.5511 ppm in ZrO$_2$.

Based on a review of the aspects of radiation safety to workers and the environment in the hydrometallurgical process, the radioactivity of raw materials, products, and waste generated using the alpha-beta counter. The results of measurements of weight or volume and radioactivity of raw materials, products, and waste are shown in Table 5.

Table 5. The amount and radioactivity of raw materials, products, and waste

| Component                              | Amount (weight or volume) | Total radioactivity $\beta\gamma$ (Bq/g) | Total radioactivity $\alpha$ (Bq/g) |
|----------------------------------------|---------------------------|------------------------------------------|-----------------------------------|
| The number of raw materials and products from the beneficiation process: |
| Zircon ore                             | 57 kg                     | 11.59 ± 0.91                             | 3.750 ± 0.82                      |
| Zircon concentrate                     | 18 kg                     | 8.41 ± 0.77                              | 2.550 ± 0.677                     |
| Tailing from beneficiation             | 34.6 kg                   | 7.51 ± 0.73                              | 3.487 ± 0.791                     |
| The amount of product and waste in the hydrometallurgical process using 500 g of zircon concentrate: Products: |
| Sodium zirconate                       | Not weighed               | 6.03 ± 0.66                              | 5.040 ± 0.952                     |
| ZOC-2                                  | 235 g                     | 0.072 ± 0.072                            | 0.270 ± 0.22                      |
| ZrO$_2$                                | 92 g                      | 0.084 ± 0.077                            | 0.050 ± 0.094                     |
| Waste:                                 |                           |                                          |                                   |
Table 5 shows that the highest reduction in TENORM levels in the hydrometallurgical process was in gel waste from the results of ZOC-1 centrifugation in the acid leaching process. Each 500 g zircon concentrate feed used for the hydrometallurgical process has generated 420 g of gel waste with a total beta / gamma radioactivity of 3.12 Bq/g and alpha radioactivity of 1.152 Bq/g. The total volume of wastewater is 43500 mL originating from the water leaching process, precipitation of ZBS, and precipitation of ZOH with very little alpha or beta/gamma radioactivity levels around 0.0012 - 0.031 Bq/g.

The results of alpha and beta radioactivity measurements on 34.6 kg of tailings from the beneficiation process were 3.487 Bq/g and 7.51 Bq/g, respectively. Requirements for the radioactivity of waste generated from mining activities must be managed if the waste contains TENORM with radioactivity ≥ 1 Bq/g [6]. Therefore, for wastewater arising from the synthesis of zirconium oxychloride and zirconia from zircon concentrate, it does not require TENORM management, but for tailings arising from the zircon sand beneficiation process, TENORM management is required as required in BAPETEN Regulation No. 9/2009 [6].

4. Conclusions

From the results of the experiment, it can be concluded that zircon sand from the Mandor, Landak, West Kalimantan with TENORM levels of 1784 ppm can be synthesized hydrometallurgically into ZrOCl₂.8H₂O with levels of TENORM = 1.2586 ppm and its chemical composition approaches ZOC made by ATI, zirconia with a TENORM level = 3.5511 ppm and its chemical composition approaches that of Zirchem.

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