Primary study of KOH alkali fusion – nitric acid leaching process in extraction of West Kalimantan zircon concentrate

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Abstract. This paper aims to prepare the primary study of zirconia concentrate using KOH alkali fusion, nitric acid leaching and coprecipitation method. Alkali fusion with KOH was done with stoichiometric ratio ZrSiO$_4$/KOH of 1:1.5 at 700 °C and 180 min. Variation of water leaching temperature at 25 °C, 95 °C and concentration in nitric acid at 4M and 6M were investigated to determine the optimal parameter to form zirconia. Phase in raw material, residue of water leaching, and product of calcination were investigated by using XRD. High composition of zirconia at 52.12 % and silica 9.64 % in zircon concentrate corresponded to the intensity peak of XRD pattern. Alkali fusion with KOH changed the visual and microstructure into irregular and porous structure in the strong caustic environment. Temperature of water leaching at 25 °C was the optimal condition to produce the highest intensity peak of zirconate and the zirconia formation. Nitric acid at 4M was preferable to form the lower of silica gel formation and produce the highest zirconia.

Keywords: zircon concentrate, KOH alkali fusion, frit, nitric acid leaching, zirconia

1. Introduction
Zircon concentrate is the product of beneficiation process from zircon sand that still contains ilmenite, monazite, and xenotime. Zircon sand is a by-product of gold processing [1]. West Kalimantan is one area in Indonesia that potentially contains of 167 million tons of zircon mineral in various sub-districts [2]. West Kalimantan contains zirconia (ZrO$_2$) in zircon sand higher than other regions in Indonesia, such as Bangka Belitung and Central Kalimantan [3].

The process of zircon concentrate (ZrSiO$_4$) into zirconia was performed to produce refractory materials that have a high resistant in thermal shock [4]. An aggressive reaction condition is required to decompose the zirconia (ZrO$_2$) that bonded in stability with silica (SiO$_2$) [5]. Alkali fusion with NaOH, KOH, and Na$_2$CO$_3$ has been developed and resulted in the acquisition of high-grade zirconia [4–10]. Alkali fusion can be done with NaOH or KOH at the temperature of (600–900) °C [7]. Alkali fusion with KOH is more effective than KOH due to the change of Gibbs energy ($\Delta$G). Alkali fusion with KOH produces more negative value of Gibbs energy compared with NaOH at room temperature. Manual calculations of Gibbs energy change in alkali fusion with KOH produces a value at -85.57 kJ/mol and NaOH at -55.68 kJ/mol at room temperature. It shows that the alkali fusion reaction with KOH is more spontaneous than NaOH. Alkali fusion of zircon mineral with KOH is better than NaCO due to the required energy. Alkali fusion with Na$_2$CO$_3$ is carried out at the temperature up to 1000 °C which requires higher energy than with KOH and generates carbon dioxide (CO$_2$) as the fusion product which is dangerous to the environment [5].
The stoichiometric ratio between the zircon concentrate and solid alkali in fusion affects the acquisition of the zircon. The higher of solid alkali agent in alkali fusion shows an increase in the acquisition of zirconia [5]. The excess of stoichiometric ratio increases the decomposition of zircon concentrate \((\text{ZrSiO}_4)\) to form zirconate compound \((\text{K}_2\text{ZrO}_4)\) [5]. The formation of zirconate has occurred in the theoretical stoichiometric ratio zircon : KOH at 1:1 [8]. The temperature and time of alkali fusion process affect the zircon formation. The higher temperature and time of alkali fusion show an increase on percent acquisition of zircon that affect the zirconia formation as the final product [9].

Zirconia is able to produce up to 86 % purity through KOH alkali fusion – water leaching – chloride acid leaching [11]. The use of nitric acid \((\text{HNO}_3)\) as the leaching agent is one of the alternative parameters that can be applied to optimize the acquisition of zircon over 86 %. The effect of water leaching temperature and nitric acid concentration is a primary study of KOH alkali fusion – water leaching – nitric acid leaching – coprecipitation method which will be examined in this study to produce the highest intensity of zircon formation.

2. Experimental procedures

2.1. Decomposition of zircon concentrate in KOH

Alkali fusion with KOH used to decompose zircon concentrate was from West Kalimantan, Indonesia. Aggregate was put in the iron crucible after zircon concentrate \((100 \text{ g})\) evenly mixed with KOH \((183.8 \text{ g})\) in beaker glass. Zircon concentrate with size of below 200 mesh was used in alkali fusion process with stoichiometric ratio \(\text{ZrSiO}_4/\text{KOH}\) of 1:1.5, fusion temperature was 700 \(^\circ\text{C}\), and fusion time was 180 min. in muffle furnace. The microstructure of zircon concentrate with alkali fusion products (frit) were investigated to know the effect of decomposition to the crystalline structure.

2.2. Water leaching process

Frit that contains silica was leached by water with solid percent of 9.09 %. Water leaching process was done in 2000 mL beaker glass, stirred at 200 rpm of magnetic stirrer for 60 min. Variation of water leaching temperatures \((25 \text{ and } 95) \ ^\circ\text{C}\) was investigated to know the effect on zirconate formation in residue. Residue was separated from filtrate using filtration technique and dried in an oven at temperature 110 \(^\circ\text{C}\).

2.3. Nitric acid leaching process

The residue of water leaching was leached in 4M and 6M HNO\(_3\) at temperature of 70 \(^\circ\text{C}\) with a rotational speed of 250 rpm for 1 h. Variation of nitric acid concentrations was investigated to know the effect on zirconia formation as the final extraction process. Nitric acid leaching process was done in three-neck glass with reflux condenser to control the temperature and materials. Filtrate was separated with silica gel as residue using filtration.

2.4. Precipitation and calcination

Zirconyl oxynitrate as filtrate of nitric acid leaching was precipitated with ammonium hydroxide \((\text{NH}_4\text{OH})\) until reach the pH 7. Neutral condition (pH 7) was used to produce the highest crystal structure of zirconia formation [11]. Zirconyl oxynitrate was precipitated for 12 hours to produce a high grade of zirconia hydrate as residue. Zirconia hydrate was dried in an oven and calcined in muffle furnace at 800 \(^\circ\text{C}\) for 3 hours to produce high grade zirconia.

2.5. Instrumentations

Characterization with SEM JEOL JSM - 6390A was conducted to observe the change in microstructure in zircon concentrate and frit. XRF benchstop PANalytical Epsilon 1 was used to determine the chemical composition of West Kalimantan zircon concentrate. Compound and phase were identified using X-Ray Diffraction (XRD) Rigaku Miniflex 600 with CuK\(_\alpha\) radiation. Sampling preparation of XRD was done and interpreted using software Highscore Plus. Samples that investigated using XRD were raw material of West Kalimantan zircon concentrate, residue of water leaching, and product of calcination.

3. Results and discussion

3.1. Characteristics of West Kalimantan zircon concentrate
Table 1. Chemical composition of West Kalimantan zircon concentrate

| Compound | ZrO₂ | Na₂O | SiO₂ | MgO | CaO | TiO₂ | La₂O₃ | CeO₂ | Y₂O₃ | Pr₆O₁₁ | Al₂O₃ | K₂O |
|----------|------|------|------|-----|-----|------|-------|------|------|--------|-------|-----|
| % weight | 52.12| 24.18| 9.64 | 2.50| 1.33| 1.17 | 0.93  | 0.44 | 0.38 | 0.26   | 1.23  | 1.3 |

Figure 1 XRD pattern of West Kalimantan zircon concentrate

The chemical composition of West Kalimantan zircon concentrate using XRF identification contains dominant compound of zirconia (ZrO₂) about 52.12% based on table 1. High impurities (Na₂O, MgO, CaO, Al₂O₃, and K₂O) and rare earth oxides (La₂O₃, CeO₂, Y₂O₃, and Pr₆O₁₁) show that early zircon sand beneficiation process was ineffective. Rare earth oxides in zircon concentrate were monazite and xenotime minerals [3]. High composition of rare earth oxides in zircon concentrate was due to the ineffective separation in the beneficiation process.

XRD identification based on figure 1 shows that West Kalimantan zircon concentrate contains zircon in the form of zirconium silicate (ZrSiO₄) with reference code ICDD 01-075-1590, rutile (TiO₂) with reference code ICSD 98-006-9331, and silica (SiO₂) with reference code ICDD 01-083-2471. It was indicated by the highest intensity of zircon (ZrSiO₄). The main compound of zircon concentrate was zircon silicate (ZrSiO₄) [3].

Silica is a compound that sufficiently contained in West Kalimantan zircon concentrate which in accordance to the high silica peak intensity at 21.2° while rutile is a minor compound. Rutile as minor compound is shown by the lowest intensity of the diffraction pattern and chemical composition, in accordance to XRF data in table 1 which shows that the content of rutile in zircon concentrate is about 1.17%. The presence of rutile in zircon concentrate is occurred due to titanium (Ti) replaces some atoms of silicon (Si) and forms the TiO₂ octahedral structure [5].

3.2. Effect of KOH alkali fusion in the microstructure of frit

Visual aspect of zircon concentrate before and after alkali fusion presents the color change from brown to dark grey which shown by the strong caustic environment in figure 2. The visual structure changed into more porous and friable. Frit has a porous structure, high friability and caustic environment [4]. The formation of zircon concentrate microstructure in figure 3 presents some prismatic crystals of ZrSiO₄ which corresponds to highest intensity of diffraction data in figure 1. Prismatic crystals of zircon concentrate changed into irregular and porous structure as the alkali fusion process as shown by SEM micrograph in figure 3. Zircon particles reacted with molten KOH during alkali fusion as solid – liquid reaction. The solid – liquid reaction by molten KOH destroyed the zircon concentrate crystalline aspect [4].
3.3. Effect of water leaching temperature in zirconate formation

The residue of water leaching contains potassium zirconium silicate (K₂ZrSiO₄) with reference code ICDD 00-017-0282, potassium zirconium oxide (K₂ZrO₅) with reference code ICDD 00-020-0963, zirconium titanium oxide (ZrTiO₂) with reference code ICDD 00-007-0290, and dipotassium zirconate (K₂ZrO₃) with reference code ICDD 98-001-6264 according to figure 4. The formation of zirconate (K₂ZrO₅ and K₂ZrO₃) in water leaching residue shows the effectiveness of silicate (K₂SiO₃) dissolution in the alkali fusion product. This is consistent with solubility data which states that the potassium silicate is soluble in water [12].

The formation of potassium zircon silicate (K₂ZrSiO₆) as intermediate compound indicates that the water leaching process is not completely dissolved the silica. Silica can be dissolved as intermediate compound by high concentrate acid leaching [10]. The higher of water leaching temperature reduces the K₂ZrSiO₆ and K₂ZrO₃ compound. That was indicated by the lowering of some K₂ZrSiO₆ and K₂ZrO₃ diffraction peaks. Zirconate compound (K₂ZrO₃) was more soluble in water when the water leaching temperature increased. It was shown by the lowering of intensity peak of zirconate at 54.84°. Potassium zircon silicate (K₂ZrSiO₆) was more easily formed at room temperature of water leaching as indicated by the higher intensity XRD peaks at 19.22°, 31.4°, and 33.18°. The formation of K₂ZrSiO₆ as intermediate compound may be formed as the product of water leaching [13]. Zirconium silicate (ZrSiO₄) can be transformed into potassium zircon silicate (K₂ZrSiO₆, K₂ZrSiO₇, K₂ZrSiO₉, and K₂ZrSiO₁₁.H₂O) [13]. The potassium zircon silicate as intermediate compound occurred because the
zirconia structure in zirconate increasingly reacts with potassium silicate (K₂SiO₅) by the following equation [14]:

\[ \text{ZrO}_2 + \text{K}_2\text{SiO}_3 \rightarrow \text{K}_2\text{ZrSiO}_5 \]

3.4. Effect of water leaching temperature and nitric acid leaching concentration in the establishment of zirconia

Water leaching temperature and nitric acid concentration affect the zirconia formation as the final product of the extraction as shown in figure 5. The final product of zirconia extraction contains zirconia (ZrO₂) as the highest compound. The peak intensity of ZrO₂ (ICDD No. 01-088-1007) is a tetragonal phase compound with the dominant intensity of the XRD pattern. The higher of the water
leaching temperature and nitric acid concentration in acid leaching reduces the formation of zirconia significantly. That was indicated by the lowering of zirconia’s intensity peak at 30.48° and 50.38°.

Room temperature of water leaching process showed the best results to form zirconia. It showed that the increase of water leaching temperature formed a higher silica gel formation. Low acid concentration was preferable in nitric acid leaching to form a lower silica gel formation. It was shown that the intensity of SiO₂ and silica gel (ICDD No. 01-083-2466) at 30.48° increased with the increase of the nitric acid concentration. The increase of the silica gel was formed as the residue of an acid leaching process decreases the recovery of zirconia as final product [4].

4. Conclusions
Zirconia (ZrO₂) was obtained from the decomposition of West Kalimantan zircon concentrate by alkali fusion – nitric acid leaching process. High composition of zirconia (52.12 %) and silica (9.64 %) corresponded to the intensity of XRD pattern which showed the highest peak. Alkali fusion with KOH occurred by the solid – liquid reaction and changed the visual and microstructure into irregular and porous structure in the strong caustic environment. Temperature of 25 °C was the best water leaching temperature to produce the highest zirconate formation. The formation of zirconate (K₂ZrO₄ and K₃ZrO₄) at 25 °C water leaching temperature in residue was shown to be more effective to solute the silicate (K₂SiO₅) from alkali fusion product. The concentration of nitric acid leaching at 4M was preferable to be used to form the lower silica gel formation and produce the highest zirconia formation.

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