

## Synthesis of Low TENORM Zirconium Sulfate from $ZrO(OH)_2$ with Sulfuric Acid

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**Abstract:** Zirconium sulfate (ZS) has become one of the alternative chemical compounds for substituting traditional tannery substances using chromium(III) which was not environmentally friendly. The purpose of this research was to synthesize ZS from  $ZrO(OH)_2$  using  $H_2SO_4$  with low Technologically Naturally Occurring Radioactive Material (TENORM) content. This ZS synthesis process shortened the old processing flow at which plenty of chemical reactors were used. The results showed that with 300 mg of feed, 600 mL of 95%  $H_2SO_4$ , at a temperature of 250 °C, the contact time of 150 min, the obtained conversion was 77.76%. Furthermore, in this 95% acid leaching reactor, the  $SiO_2$  content was still 2.79% and it was not TENORM free yet, but the FTIR and XRD images were in accordance with BDH standards. Moreover, the quenching process results had been free of  $SiO_2$  and TENORM content, but they still contained 1.48%  $HfO_2$ . The surface of the TEM images from the quenching results had been in the form of elongated and transparent crystals. The result of the economic feasibility analysis showed that the new ZS synthesis process was more economical or profitable when it was compared to the old ZS synthesis process, with a BCR value of 1.258.

**Keywords:** TENORM; acid leaching; quenching process; FTIR; XRD; XRF; TEM; BCR

### ■ INTRODUCTION

Green chemistry has appeared as an area of research interest for environmental chemists. This has encouraged many researchers to create environmentally friendly methods, particularly in the tannery field [1]. Tannery products are the largest export commodities from Indonesia, but the traditional tannery products still use chromium(III). This may threaten the export of tannery products where they will not be accepted as an export commodity since it is less environmentally friendly and does not meet the current regulations that prioritize eco-labeling [1-2]. To address this problem, several researchers have developed the tanning of leather using zirconium sulfate (ZS) substances instead of chromium(III) [1-3]. Therefore, research on the synthesis of ZS compounds as new tannery substances is very interesting while simultaneously addressing the ideals of green chemistry.

In this report, the researchers will synthesize ZS from  $ZrO(OH)_2$  using  $H_2SO_4$ , which is also naturally low

in Technologically Naturally Occurring Radioactive Material (TENORM). Based on the regulation of the head of Bapeten number 9 in 2009 on the intervention of radiation exposure from TENORM, the level of contamination from the products derived from zirconium minerals, such as zirconium sulfate, is not more than 1 Bq/cm<sup>2</sup> or 1 Bq/g of product which is equivalent to 500 ppm [4]. The purpose of this study was to shorten the process flow in the previous synthesis of ZS which was carried out through the old zirconium oxychloride (ZOC) process [5-7]. The old flow process contained many chemical reactors, which would be less economical from the commercial point of view. Both new and old ZS synthetic flow diagrams were compared in Fig. 1.

There are differences in the quenching process in the old and new ZS synthetic process, as seen in Fig. 1. In the old process, the quenching was repeated only twice leading to the sole formation of  $Na_2ZrO_3$ , while in the new process, the quenching process was carried out

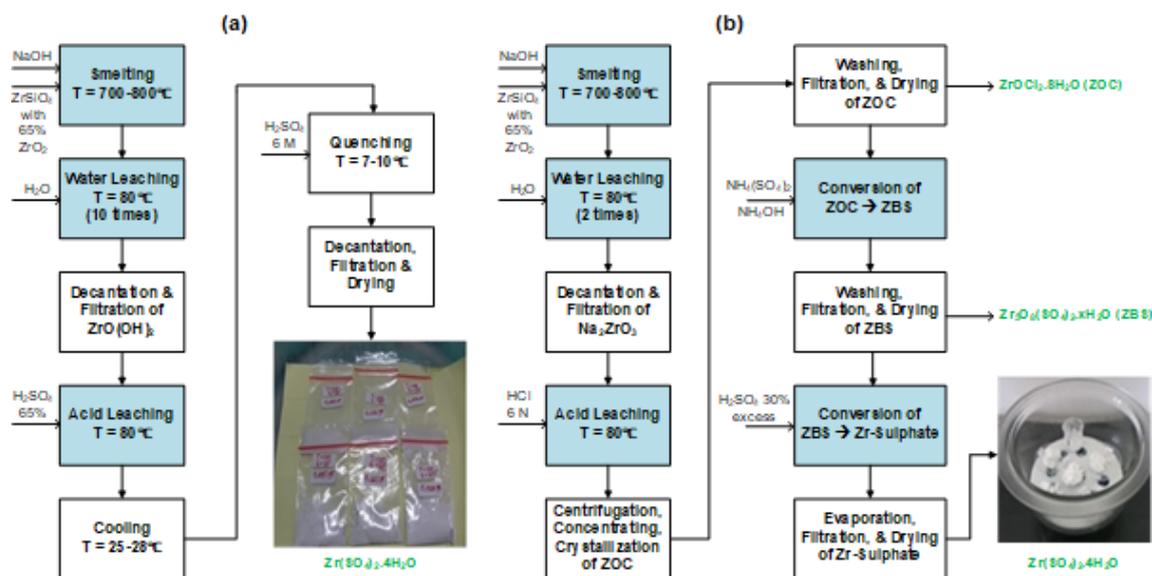


Fig 1. ZS synthesis based on (a) new and (b) old process flow diagram

Table 1. Major oxides (%) in  $ZrO(OH)_2$  feed

| SiO <sub>2</sub> | P <sub>2</sub> O <sub>5</sub> | SO <sub>3</sub> | TiO <sub>2</sub> | Fe <sub>2</sub> O <sub>3</sub> | Y <sub>2</sub> O <sub>3</sub> | ZrO <sub>2</sub> | SnO <sub>2</sub> | HfO <sub>2</sub> | ThO <sub>2</sub> | U <sub>2</sub> O <sub>8</sub> |
|------------------|-------------------------------|-----------------|------------------|--------------------------------|-------------------------------|------------------|------------------|------------------|------------------|-------------------------------|
| 4.167            | 2.142                         | n.d.            | 0.648            | 0.326                          | 0.272                         | 88.021           | 0.618            | 2.588            | 0.0519           | 0.0651                        |

10 times so that sodium zirconate ( $Na_2ZrO_3$ ) would be hydrolyzed to  $ZrO(OH)_2$ . According to Beyer et al., zirconium sulfate could be synthesized from the hydrolysis of sodium zirconate, which was then reacted with 85% sulfuric acid, and the basis of this ZS synthesis was from a simple chemical reaction in an acid leaching reactor as follow [6,8],



With the ultimate goal to commercialize the ZS products, we report, herein the elimination of the TENORM content ( $U_3O_8$  and  $ThO_2$ ) apart from conducting the economic feasibility analysis. To qualitatively and quantitatively produce the ZS products, a comparison of major oxide concentrations between the feed, the product, and the standard of BDH was carried out. Meanwhile, the final product would be characterized by XRF, FTIR, XRD, and TEM.

## EXPERIMENTAL SECTION

### Materials

The materials used were  $ZrO(OH)_2$  feed from the water leaching process [5]. Table 1 shows the results of the major oxide analysis of  $ZrO(OH)_2$  feed with XRF. KBr

salts,  $H_2SO_4$  95% was obtained from E-Merck. The distilled water was locally prepared by PSTA-BATAN laboratory.  $Zr(SO_4)_2$  standard was purchased from BDH Reagents and Chemicals.

### Instrumentation

The equipment used in this study included a unit of acid leaching reactors in the form of a three-neck flask (with a capacity of 1 L, equipped with stirrer, temperature regulator and vertical cooling), drying ovens, 4-digit sartorius scales, Fourier Transform Infrared spectrometer (FTIR, ALPHA II MODULE ATR ZnSe), X-Ray Diffractometer (XRD, PANanalytical Aeris type DY844 equipped with 161039 databases) and X-ray Fluorescence spectrometer (XRF, Malvern PANanalytical type High-Performance ED-XRF Epsilon 4), and Transmission Electron Microscope (TEM, JEOL JEM-1400).

### Procedure

#### Acid leaching reactor calibration

The calibration of the acid leaching reactor was done in a 1 L three-neck flask equipped with a heating mantle, temperature controller, and an adjustable stirrer

with a maximum speed of up to 30 rpm. As much as 400 mL of 95%  $\text{H}_2\text{SO}_4$  was introduced into the reactor, and then heated with constant stirring at 15 rpm at the 200 °C for 120 min. The process was repeated with temperature variations at 250 °C and 300 °C, then repeated with addition 300 g of feed at 250 °C. Then, the change of the temperature was recorded every 5 min, and the rate of temperature change every 5 min (°C/min) was calculated with the following equation.

$$\text{Rate}\left(\frac{^{\circ}\text{C}}{\text{min}}\right) = \left(\frac{T_n - T_1}{W_n - W_1}\right) \quad (2)$$

where  $T_n$  is the temperature at the time of  $n^{\text{th}}$  (°C),  $T_1$  is the initial temperature (°C),  $W_n$  is the time to reach temperature  $T_n$ , and  $W_1$  is the initial time.

#### Optimization of acid leaching reactor

Into the acid leaching reactor, 300 g of feed and 600 mL  $\text{H}_2\text{SO}_4$  (95%) were introduced. The mixture was heated to 200 °C with constant stirring at 15 rpm for 120 min. After the temperature reaching 200 °C, the reaction was left for 60 min; then, the temperature controller was turned off and the mixture was allowed to stand to  $\pm 30$  °C. Then, 300 mL of distilled water was added into the acid leaching reactor. It was then reheated up to a temperature of 100 °C, with a stirring speed of 15 rpm for 60 min. Next, the reaction was allowed to cool to  $\pm 30$  °C. The mixture was separated into the filtrate (water phase) and residue (paste). As much as 100 g of paste was dried in the oven at 110 °C, and the dried paste was analyzed with XRF. Similar procedure was then repeated using  $\text{H}_2\text{SO}_4$  (65%). The conversion was calculated with Eq. 3.

$$\text{Conversion (\%)} = \frac{\text{Zr}(\text{SO}_4) \text{ formed(g)}}{\text{ZrO}(\text{OH})_2 \text{ in feed(g)}} \times 100\% \quad (3)$$

#### Quenching process

As much as 500 mL of paste was sampled from the acid leaching reactor, pipetted dropwise into 2 pieces of beaker glass, where the first beaker (outer) already contained liquid ice and the second beaker (inner) contained 6 M of  $\text{H}_2\text{SO}_4$  solution. After the quenching process completed, the  $\text{H}_2\text{SO}_4$  solution was separated with the formed ZS solid. To remove the remaining  $\text{H}_2\text{SO}_4$ , the ZS solid was washed with 0.01 M  $\text{H}_2\text{SO}_4$ . Then, the ZS solid was dried in the oven at 110 °C for 2–3 h. Next, the obtained white ZS solid was crushed and sieved at 100 mesh and sampled 50 g to be analyzed with XRF, XRD, and FTIR.

## RESULTS AND DISCUSSION

### Acid Leaching Reactor Calibration

Based on Fig. 1(a) on the new process of ZS synthesis, the main indicator of success lies in the operational process of the acid leaching reactor and the quenching. Therefore, we performed the calibration followed by taking a closer look at the performance of the acid leaching reactor. The results of the acid leaching reactor calibration can be seen in Fig. 2. At the 200 °C calibration point using  $\text{H}_2\text{SO}_4$  95%, the maximum heating rate 2.28 °C/min was obtained at the temperature of 203 °C. At 200 °C of the calibration condition, it was proven that the temperature drop rate curve was shorter. When the calibration was done at 300 °C, the maximum rate was achieved at 3.3 °C/min.

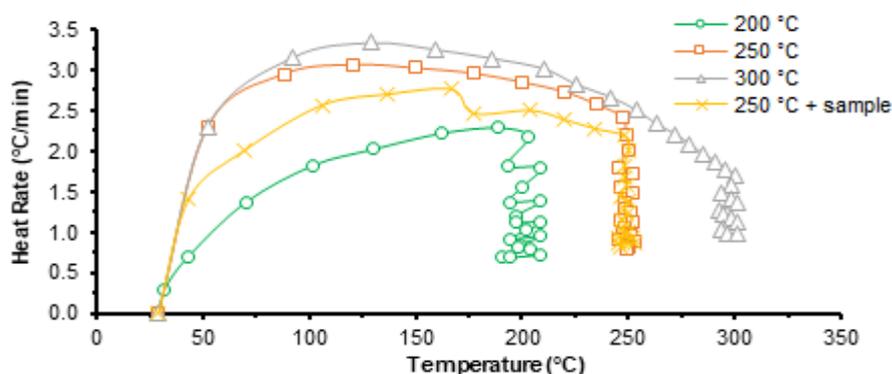


Fig 2. Curve between temperature vs. heat rate on the calibration of the acid leaching reactor

However, the rate curve at 300 °C was longer than that at 200 °C. Therefore, the shorter temperature curve rate was calibrated at 200 °C.

Furthermore, for the calibration at 250 °C, the maximum rate was achieved is at 3.08 °C/min, with a fairly long temperature curve. Based on Levenspiel [9], the length of the temperature rate curve will ensure that the chemical reaction goes would proceed to the side of product. Thus, the calibration was continued at the temperature of 250 °C, in which the feed as much as 300 g was added and hereinafter referred to as calibration 250 °C (+) feed. The results showed that the calibration of 250 °C (+) feeds gave quite long temperature rate curve but lower than 250 °C without feeding. Therefore, the operation of the temporary sulfate leaching reactor was carried out at the optimum temperature condition of 250 °C (+) feed, where the temperature rate curve was quite long.

### Optimization of Acid Leaching Reactor

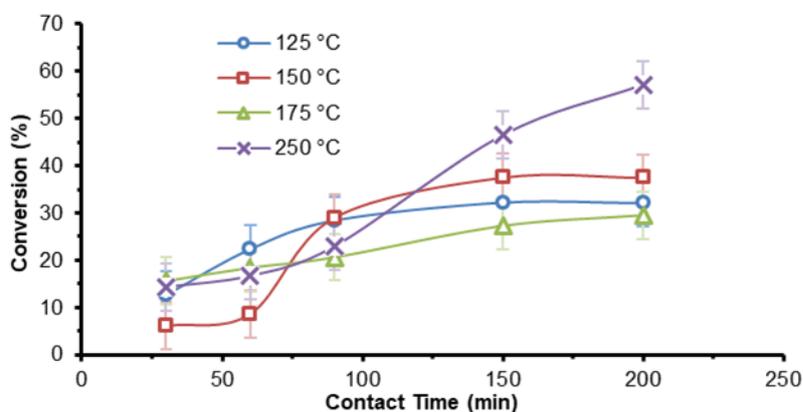
With the optimum temperature at the calibration at 250 °C (+) feed, we performed the synthesis of ZS with various temperatures and contact times. The optimization of the acid leaching process was then done using 65% of sulfuric acid solution (Fig. 3). It can be seen from Fig. 3 that the highest conversion of ZS synthesis (57.2%) was achieved at 250 °C with a contact time of 200 min. The results turned out to be in accordance with the calibration temperature of the acid leaching reactor in Fig. 2, where the temperature curve at the temperature calibration under 200 °C was not long enough leading to the low

conversion (Fig. 2). The results showed that the optimization conditions were in accordance with the reports by Beyer et al. [8] and Houchin et al. [10] on the production of zirconium sulfate tetrahydrate (ZS).

The acid leaching process was carried out using 95% of H<sub>2</sub>SO<sub>4</sub> solution with the same amount feed of 300 g. Based of Fig. 4, the best conversion of 77.76% was obtained at a temperature of 250 °C with a time of 150 min. The results of this experiment are not contrary to the results in Fig. 2 and 3. Based on Fig. 2 and 3, we know that the acid leaching operating conditions carried out under 200 °C are less stable and the reaction is less than perfect. In Fig. 4, it has been confirmed that the optimization of acid leaching should be carried out at 250 °C for 150 min to obtain high conversion. The optimized conditions were in line reports by Beyer et al. [8] and Houchin et al. [10] on the production of zirconium sulfate tetrahydrate (ZS).

The optimal acid leaching reactor operation (Fig. 2, 3, and 4) was taken at the temperature of 250 °C (+) feed for 150 min. Then, each product was analyzed using XRF to determine the contents of major oxides. The content was then compared with feed and BDH standards (Fig 5).

Fig. 5(a) showed the concentration of SiO<sub>2</sub>, SO<sub>3</sub>, and ZrO<sub>2</sub> in the feed, acid leaching process using 65% and 95% H<sub>2</sub>SO<sub>4</sub> solution as well as BDH standard. The results showed that the concentration of SiO<sub>2</sub> in the acid leaching reactor operation using 65% of H<sub>2</sub>SO<sub>4</sub> solution was relatively the same with that in the feed due to the low



**Fig 3.** Relationship between conversion (%) and contact time as the function of temperature using 65% of H<sub>2</sub>SO<sub>4</sub> solution

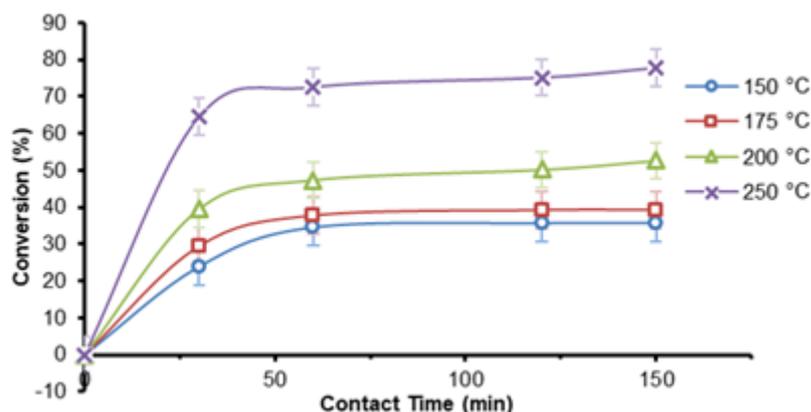


Fig 4. Relationship between conversion (%) and contact time as the function of temperature using 95% of  $H_2SO_4$  solution

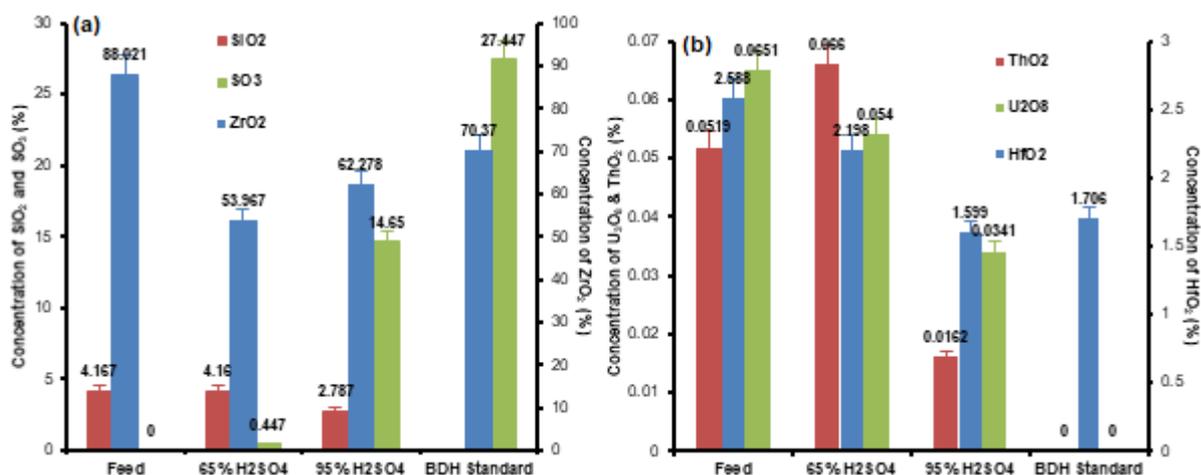


Fig 5. Concentration (%) of major oxides (a)  $SiO_2$ ,  $SO_3$ ,  $ZrO_2$  and (b)  $ThO_2$ ,  $U_2O_8$ ,  $HfO_2$ , after the acid leaching process

solubility of  $SiO_2$  in 65% of  $H_2SO_4$  solution. Comparing to the previous condition, a decrease on  $SiO_2$  concentration (from 4.16% to 2.78%) was observed in the reactor operation using 95% of  $H_2SO_4$  solution. However, when compared to ZS from BDH standard, the concentration of  $SiO_2$  has reached 0.00%.

The concentration of  $SO_3$  is equivalent to that of  $SO_4^{2-}$ , which is bound as ZS compound. As displayed in Fig. 5(a), the concentration of  $SO_3$  in the feed, in the leaching reactor operation using 65% and 95% of  $H_2SO_4$  solution were 0%, 0.45% and 14.65, respectively. It indicated the ZS formation is more optimal in the operation using 95% of  $H_2SO_4$  solution. However, when compared to the BDH standard, the concentration has reached 27.45%.

It could be seen from Fig. 5(a) that the concentration

of  $ZrO_2$  bound as  $ZrO(OH)_2$  in the feed was 88.02%. An insignificant increase of  $ZrO_2$  concentration was observed in acid leaching reactor operations, from 53.97% (using 65% of  $H_2SO_4$ ) to 66.28% (using 95% of  $H_2SO_4$ ). However, when compared to BDH standards, the concentration of  $ZrO_2$  has reached 70.37%, which still small.

As depicted in Fig. 5(b), the concentration of  $ThO_2$  in the feed was 0.0529%. The concentration was slightly increased to 0.066% in the 65% acid leaching reactor. While the concentration of  $ThO_2$  in the 95% acid leaching reactor has dropped to 0.0162%, this oxide was not detected in the BDH standard. The concentration of  $U_3O_8$  in the feed was 0.651% and has dropped to 0.054% (in the 65% acid leaching reactor) and 0.0341% (in the 95% acid leaching reactor). Similar with  $ThO_2$ ,  $U_3O_8$  was

not detected in the BDH standard. Likewise, the  $\text{HfO}_2$  concentration in the feed (2.588%) slightly decreased to 2.198% (in the 65% acid leaching reactor) and 1.599% (in the 95% acid leaching reactor). When compared with the BDH standard, the value was smaller.

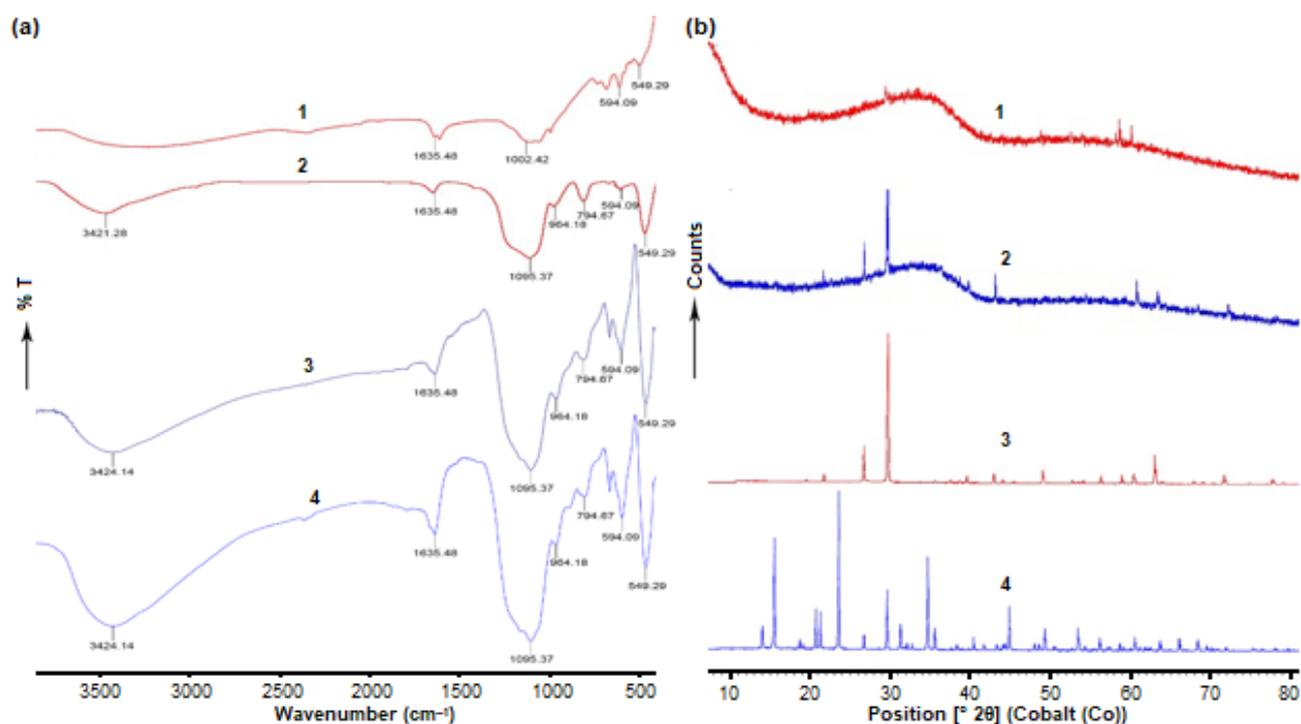
From Fig. 5, it can be concluded that the concentration of  $\text{H}_2\text{SO}_4$  affected the concentration of oxides contained in the feed. The addition of  $\text{H}_2\text{SO}_4$  concentration could reduce the concentration of oxide impurity, namely  $\text{SiO}_2$ ,  $\text{ThO}_2$ ,  $\text{U}_2\text{O}_8$ , and  $\text{HfO}_2$ . As expected, the addition of  $\text{H}_2\text{SO}_4$  concentration increased the concentration of both  $\text{ZrO}_2$  and  $\text{SO}_3$ .

The FTIR spectrum of the feed (Fig. 6(a), no. 1) showed the absence of band at  $3424\text{ cm}^{-1}$  belong to the hydroxyl group bound to water molecules, indicating that the feed state was quite dry. The band at  $1635\text{ cm}^{-1}$  appeared as the asymmetric stretching of the hydroxyl group in the  $\text{ZrO}(\text{OH})_2$  molecule [11]. However, the appearance of the band at  $1635.64\text{ cm}^{-1}$  in FTIR spectrum of the product reactor 65% (no. 2), reactor 95% (no. 3), and BDH standard (no. 4), is a sign of the  $\text{H}_3\text{O}^+$  compounds, which is the asymmetric OH stretching of  $\text{H}_2\text{O}$  adsorption by

sulfate ion compounds with models  $(\text{SO}_3)_{\text{ads}}$  [11-12]. It turned out that  $\text{H}_2\text{O}$  adsorption was supported by the appearance of bands at  $3424\text{ cm}^{-1}$  representing the hydroxyl group (Fig. 6(a), no. 2, 3 and 4).

The presence of the  $\text{H}_3\text{O}^+$  was strengthened by the appearance of band at  $964\text{ cm}^{-1}$  from  $\text{SO}_3$  sulfite ion. Furthermore, the band at  $1095\text{ cm}^{-1}$  represented sulfate species  $(\text{SO}_4^{2-})_{\text{ads}}$  that played an important role in the formation of zirconium sulfate compounds [13]. These peaks have been observed in the FTIR spectra (Fig. 6(a), no. 2, 3 and 4) but for feed (no. 1), the band  $1002.42\text{ cm}^{-1}$  may be an impurity (see Table 1). Furthermore, the appearance of the bands at  $794$ ,  $594$ , and  $549\text{ cm}^{-1}$  came from symmetry and asymmetry stretching of Zr-O bonding in the form of Zr-O-Zr and O-Zr-O [13-16].

Fig. 6(b) no. 1 was the XRD diffractogram of the feed) which still displayed the amorphous structure because the crystallization process was incomplete [17]. Furthermore, the intensity of peaks at  $2\theta = 28^\circ$  and  $30^\circ$  increased in the 65% and 95% acid leaching reactors (Fig. 6(b) no. 2 and 3), Then, the peaks at  $2\theta = 50.2^\circ$  and  $60.1^\circ$ , even with small intensity, had been seen in both 65% and



**Fig 6.** Comparison of (a) FTIR spectra and (b) XRD diffractogram: (1) feed, (2) the product of 65% reactor, (3) the product of 95% reactor, and (4) BDH standard

95% of the reactor product. The appearance of peaks at  $2\theta = 28^\circ, 30^\circ, 50.2^\circ,$  and  $60.1^\circ$ , was in a good agreement with the previous reports that showed there is a zirconium sulfate compound [17-21].

### Quenching Process

In addition to the acid leaching reactor, the quenching process will also determine the success of ZS synthesis Fig. 1(a). The quenching process is the process of settling the solution, which is quickly carried out and slowly added with 6 M of  $H_2SO_4$  solution at  $0.0-1.0^\circ C$ . The quenching process in ZS synthesis is carried out to remove or reduce the concentration of oxide impurities, particularly  $U_3O_8$  and  $ThO_2$ . The impurities of the TENORM nuclear in the ZS products such as  $U_3O_8$  and  $ThO_2$  are undesirable for commercial purposes, especially in leather tannery applications ( $< 500$  ppm).

Based on the XRF analysis (Fig. 7(a)), the concentration of  $SiO_2$  in the feed was 4.17%. While the concentration of  $SiO_2$  increased (26.03%) in the process without the quenching, the use of the quenching process might eliminate the impurity of  $SiO_2$ , as in the BDH standard. The concentration of  $ZrO_2$  in the feed was 88.02% and decreased to 57.11% without the quenching process. When the quenching process was applied, the concentration of  $ZrO_2$  increased to 68.88%, but was still lower than the BDH standard (70.37%). The results showed that the feed did not contain  $SO_3$ . Furthermore,

the concentration of  $SO_3$  increased to 8.30% when the process was carried out without the quenching. With the quenching process, the concentration of  $SO_3$  will dramatically increase to 40.95%, which was even higher than the BDH standard, which is 27.45%.

According to Fig. 7(b), it could be seen that the concentration of  $ThO_2$  was 0.052% in the feed and decrease to 0.020% when the synthesis was carried out without the quenching process. It should be noted that the quenching process might reduce the concentration of  $ThO_2$  to 0.0%. The same concentration was also found in the BDH standard. Then, the concentration of  $U_3O_8$  in the feed reached 0.0651% and decreased to 0.0371% when the synthesis was conducted without quenching. Similar with  $ThO_2$ ,  $U_3O_8$  was not detected in the quenching process and in the BDH standard, as well. It is interesting to note that the quenching process might reduce the concentration of  $HfO_2$  contained in the feed, from 2.59% to 1.48%. Although this process could reduce the concentration of  $HfO_2$ , the resulting ZS compound was not reached the nuclear grade.

TEM images of the ZS products (Fig. 8, focused on 200 nm) showed a real difference between the products obtained with or without the quenching process. It has been proven that after the quenching process, there were transparent crystals that have elongated, whereas, before the quenching process, the product was still in the form of

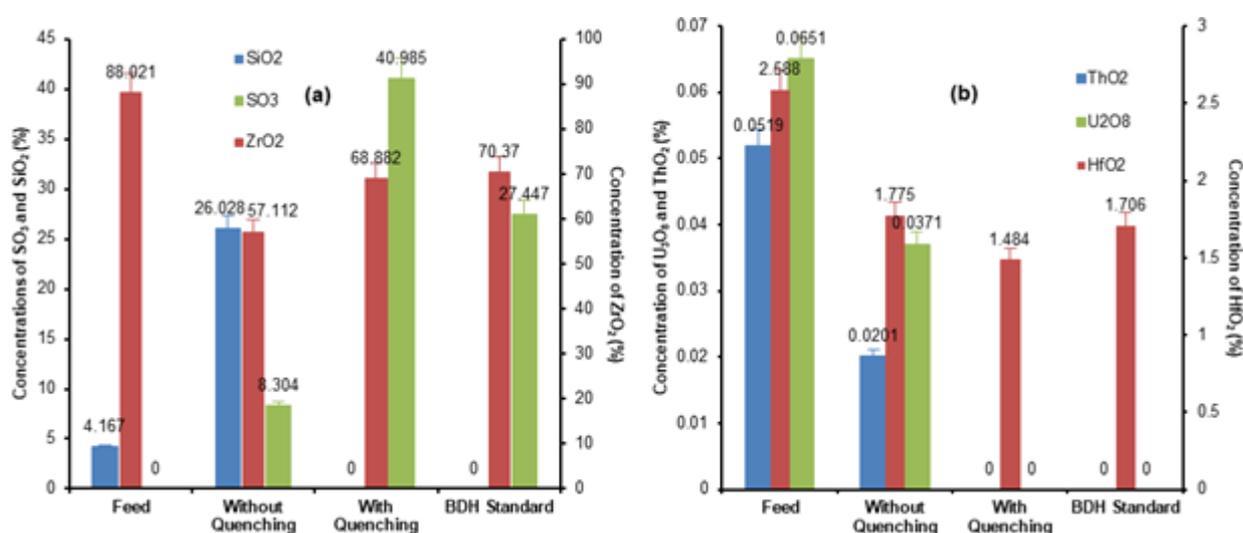


Fig 7. Concentration (%) of major oxides (a)  $SiO_2$ ,  $SO_3$ ,  $ZrO_2$  and (b)  $ThO_2$ ,  $U_2O_8$ ,  $HfO_2$ , after the quenching process

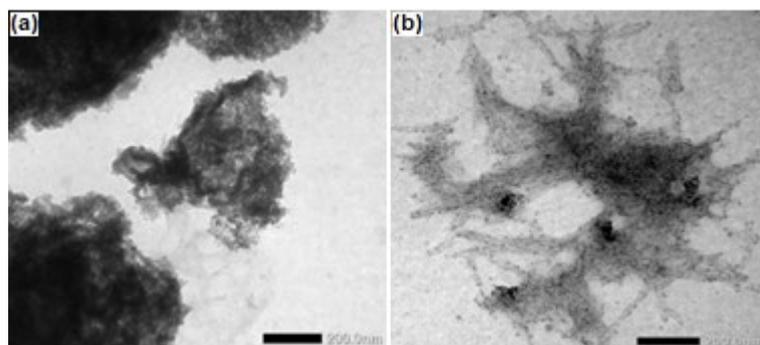


Fig 8. TEM images of ZS product (a) before and (b) after quenching process

particles clumps with a transparent agglomeration form [16-17].

### Economic Feasibility Analysis

In this paper, a simple economic feasibility analysis was carried out to compare the economic value of the chemical processes in managing zircon sand into zirconium sulfate products. The economic value of a chemical process can be seen from the value of the Benefit-Cost Ratio (BCR), which is a comparison between the benefits obtained against the costs required for the process [21-22]. The eligibility criteria for the process are considered to be economical if the value of BCR is more than 1, indicating that the profit gained is greater than the production costs incurred [23]. The production costs for the new and old synthesis process were calculated based on the type and amount of raw materials used, while the large profits derived from the total value of zirconium sulfate produced based on market prices. Based on calculations, the BCR value of the new process flow is 1.258 (more than 1), and the BCR value of the old process flow is 0.437. This value becomes the parameter showing that the new zirconium sulfate synthetic process is a financially feasible process to be developed and be considered for investment on a larger scale.

### CONCLUSION

The new ZS synthetic process has been able to replace the old process which required many chemical reactors. The new process was carried out in the acid leaching reactor and quenching reactor. The optimal results of the acid leaching reactor were obtained using 300 g of feed, 600 mL of 95% of  $H_2SO_4$  solution, at the

temperature of 250 °C, and the contact time of 150 min and gave the conversion of 77.76%. Furthermore, the acid leaching reactor with 95% of  $H_2SO_4$  solution still gave  $SiO_2$  content as much as 2.79% and was not free from TENORM. Even though the FTIR spectra of the product of 95% reactor were in accordance with the BDH standards, it turned out that the XRD diffractogram were only suitable at the  $2\theta = 30^\circ$  and  $28^\circ$ . Then, the ZS products in the quenching process were free from  $SiO_2$  and TENORM-free but still contained 1.48% of  $HfO_2$ . The TEM images from the quenching showed the surfaces of zirconium sulfate forming the elongated and transparent crystals. Based on the economic feasibility calculations, the new zirconium sulfate synthetic process was more profitable than the old one. This was proven by the BCR value (more than 1), indicating that it is financially feasible to be further developed to a larger scale.

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