Volume 16 No. 2
July 2024
ISSN : 2085 – 1669
e-ISSN : 2460 – 0288
Website : jurnal.umj.ac.id/index.php/jurtek
Email : jurnalteknologi@umj.ac.id

Jurnal Teknologi
UNIVERSITAS MUHAMMADIYAH JAKARTA

Effect of Mass Composition on Nano Zircon Synthesize from Local Zircon Sand Using Soda-Precipitation-Calcination-Caustic Fusion Method

Alvika Meta Sari[1*], Anwar Ilmar Ramadhan[2], Istianto Budhi Rahardja[3], Efrizon Umar[4], Anastasia Yudistirani[5], Akmal Imam Faisal[6], Fikriyansyah[7], Wan Hamzah Azmi[8]

[1,5,6,7]*Department of Chemical Engineering Study Program, Faculty of Engineering, Universitas Muhammadiyah Jakarta, Jl. Cempaka Putih Tengah 27, DKI Jakarta 10510, Indonesia*
[2]*Department of Mechanical Engineering Study Program, Faculty of Engineering, Universitas Muhammadiyah Jakarta, Jl. Cempaka Putih Tengah 27, DKI Jakarta 10510, Indonesia*
[3]*Department of Mechanical Engineering Study Program, Faculty of Engineering, Institut Teknologi PLN, Jl. Lingkar Luar Barat RT 01 RW 01, Duri Kosambi, Cengkareng, Jakarta Barat, DKI Jakarta 11750, Indonesia*
[4]*National Research and Innovation Agency, Jl. Tamansari No. 71, Bandung 40132, Indonesia*
[8]*Faculty of Mechanical and Automotive Engineering Technology, Universiti Malaysia Pahang Al-Sultan Abdullah, 26600 Pahang, Malaysia*

*Corresponding author email: alvika.metasari@umj.ac.id

Jurnal Teknologi use only:
Received 24 January 2024; Revised 23 March 2024; Accepted 26 June 2024

ABSTRACT

Zircon sand has the major component of ZrO_2 with impurities SiO_2, Fe_2O_2, and TiO_2. Zircon sand can be synthesized using various methods, such as caustic fusion method. This research purposed to determine the effect of the mass composition of NaOH on fusion process of zircon sand and to find the optimal mass ration of NaOH on yield and characteristics of nano zircon produced. This research was conducted using caustic fusion and precipitation process to obtain the mass ration of NaOH in best zircon sand fusion (melting) process. The nano zircon obtained was analyzed its size using SEM and chemical composition using FTIR. The result show that the correlation between NaOH ration and yield following the equation $y = 0.42x^2-2.532x+3.908$ and $R^2 =0.9696$. It showed that the higher NaOH composition will reduce the size of nano zircon. The optimum NaOH ratio is 1 : 3.6 with size od 41.983 nm and yield 1.84% which in white, odorless and powder texture. The FTIR spectrum showed the presence of the $-Zr-O_2$ functional groups at wave numbers 600 – 700 cm^{-1}.

Keywords: Calcination, fusi caustic soda, nano zircon, NaOh, precipitation, zircon sand.

Introduction

Zircon sand, which is found in several regions in Indonesia, contains zirconia as its main ingredient [1]. Where zircon is found in waste or leftovers from the process of separating cassiterite minerals from other minerals or scattered as sedimentary deposits [2]. Zirconia ($ZzrO_2$) or called zirconium oxide is a form of zircon compound in powder form with white crystals, which has the properties of not reacting easily, being resistant to high temperatures, resisting corrosion and thermal

DOI: https://dx.doi.org/10.24853/jurtek.16.2.169-178

ISSN : 2085 – 1669
e-ISSN : 2460 – 0288

shock [3]. Zirconia is included in the group of strong transition metals; its properties resemble titanium because it is resistant to corrosion [4]. The properties of zirconia depend on the combination of metal elements in the formation of oxide compounds, so zirconia also has different characteristics and applications.

Zirconia is a metal oxide compound of zircon which can be used variously, namely as a raw material for ceramics, as molding sand, and as the main ingredient for refractory bricks [5]. Apart from that, zircon can be applied to electrical components and electronic equipment, heat transfer applications [6], biomedical materials and applications because of its biocompatible properties [4], as an adsorbent [7] and application as a raw material for nuclear reactor coatings because of its high temperature resistance, non-corrosive and low neutron absorption [8]. Where the largest consumption of zircon is for the ceramic industry, where more than half of the world's zircon sand production is consumed by China, as the number 1 ceramic producing country in the world [9].

Even though Indonesia has zirconium reserves of 5.119 million tons [10], it cannot be exported directly in accordance with Minister of Energy and Mineral Resources Regulation No. 8 of 2015 must first be processed into other products for export purposes [11]. This regulation is an opportunity for investment in zircon processing because the added value of zircon will increase if it is processed into a high-value processed product compared to the raw material zircon sand and the current utilization of zircon sand is not optimal.

The challenge in processing zircon sand is the purity level of zircon. The development of research in the processing of zirconium and the manufacture of its derivative products quite rapid. Various synthetic routes have been used to synthesize metal oxide nanoparticles and metal oxide. Technically, the methods differ in assembling all these synthesis pathways. Zirconia can be synthesized using sol-gel method, hydrothermal, laser ablation method, wire, explosion process, hybrid transparent coating, chemical polymerization and coprecipitation method [12]. The four main methods for synthesizing zirconia nanoparticles can be seen in Figure 1 below.

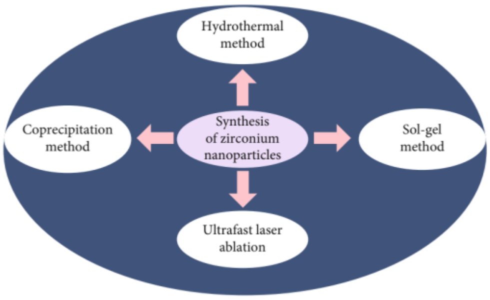


Figure 1. The main method of synthesis of zirconia nanoparticles [4].

The sol-gel method has advantages over other methods because it is easy and cheap. Apart from that, this process conducts at low temperature. The result obtained are purer, the particle size is more uniform and faster [13However, in the sol-gel process, there is relatively large shrinkage during the gel formation and drying process, large pores and still residues in the form of hydroxyl and other organic compounds [4].

The other method is hydrothermal, which is relatively short, simple due the fast-heating process. The product is tetragonal crystalline solid [14]. The resulting nano zirconia can be applied in the fields of optics, medicine, electronics and energy. However, the nanoparticles produced have less particle size distribution and less controlled composition [4].

The next process is precipitation. The advantages of this process is easy, the tools used are simple, the deposition process is easy using precursors and can be applied economically on a commercial scale [7]. However, due to the formation of nanoparticles during the deposition process, their size is difficult to control. So, this method needs to be modified by adding more steps.

The modification process can be applied is using caustic fusion method which is a leaching process. Yustanti et al [15] extracted zircon from East Kalimantan using a KOH solution and nitric acid. The composition of $ZrSiO_2$/KOH used is 1: 1.5 at a temperature of 700°C for 180 minutes to produce 52.12%

zircon. This result in an irregular microstructure due to alkaline conditions. To anticipate the weakness of the precipitation process, caustic fusion is used to extract zircon before the nano zircon formation process using the caustic precipitation method [16]. So in this research, modification of the nano zircon synthesis process from zircon sand using the caustic soda fusion method to purify ZrO_2. Followed by precipitation for the formation of zircon nanoparticles and powder formation using the calcination method.

Methods

Materials

The materials used in this research were zircon sand from Kalimantan, All chemicals were of analytical grade and used without furthur purification: 17.5% (w/w) NaOH; 5 M HCl, Aquadest and ammonia. The main equipment used were magnetic stirrer and hotplate for the synthesis process, centrifuge for purification and oven for the calcination process. The nano particles was analyzed identify the chemical compound using FTIR and the size using SEM.

Ekstraction of zircon using Caustic Fusion Method

Zircon were obtained via caustic fusion method from zircon sand. The zircon sand were prepared using varied mass composition (mass of zircon sand : NaOH) of 1:1, 1: 1.8, 1:2, 1:3, and 1:3.6. Then they were mixed and crushed around 2 minutes using grinding machine. After grinding, it was sieved using 100 mesh filter for 15 minutes. The mixture was put into nickel cup until ¾ full. Then it was baked in furnace of 400 °C for 1 hour. One it was cooled, removed and grinded until smooth.

Leaching process

The leaching process is used to increase the zircon oxide content of zircon mineral from zircon sand. A total of 50 grams of EFB was added to the heated residue, weighed 10 grams then leached using 100 ml of 5 M HCl solution (1:10). It was reheated using 1 hotplate at 150 °C for 30 minutes, while stirring using a stirred stick. Store the heated solution in an acid chamber overnight until it formed sediment and the texture changes to jelly-like. After one night and the texture changes into jelly-like, then added 100 ml of 5 M HCl, heated using hotplate for 10 minutes while stirring using a stirrer. Then it was stored in the acid chamber for one night.

Synthesis of nano zircon by Precipitation Method

Nano zircon was synthesized by precipitation method. The liquid was filtered using filter paper (Wathman 42). The 100 ml filtrate was mixed with 100 ml of distilled water and heated using hotplate for 30 minutes at 150 °C. Then it was washed using 100 ml of distilled water at least 6 times, then store the solution in the acid room for one night until settles. Discard sone of the sediment water until residue and a small amount of precipitate remain.

Calcination process

The solid phase formation was conducted by calcination process. The precipitate is burned at a temperature of 200 °C until the residue looks dry or cracked. Put the combustion results was calculate yield analyzed the FTIR and SEM.

Results and Discussions

Organoleptic Observation

Organoleptic observations of the resulting nano zircon are presented in Table 1 below.

Table 1. Organoleptic characteristics of nano zircon

Mass composition variation	Form	Odor	Color	Figure
1:1	granule	No	white	
1:1.8	granule	No	white	

ISSN : 2085 – 1669
e-ISSN : 2460 – 0288

1:2	granule	No	white	
1:3	granule	No	white	
1:3.6	granule	No	white	

From **Table 1**, it can be seen that the nano zircon produced is white, odorless and in granular or powder form.

The influence of the composition of zircon sand melting and NaOH on the yield of nano zircon

The mass composition was varied to obtain the best yield percentage in this research. The compositions varied of 1:1, 1:1.8, 1:2, 1:3, and 1:3.6 as shown in **Table 2**.

Table 2. Yield percentage results

Mass composition variation	Product mass (gr)	Yield (%)
1:1	0.87	1.74
1:1.8	0.3	0.6
1:2	0.1	0.2
1:3	0.14	0.28
1:3.6	0.92	1.84

From table 2 can be seen that nano zircon will be formed in this process, the zirconium mineral will decompose and water will be formed by the hydrolysis reaction [8]. The yield percentage was calculated by equation (1) [17].

$$yield = \frac{nano\ zircon\ massa}{raw\ material\ mass} x100 \quad (1)$$

The mass of each zircon sand used was 50 grams. The results obtained are presented in **Figure 1**.

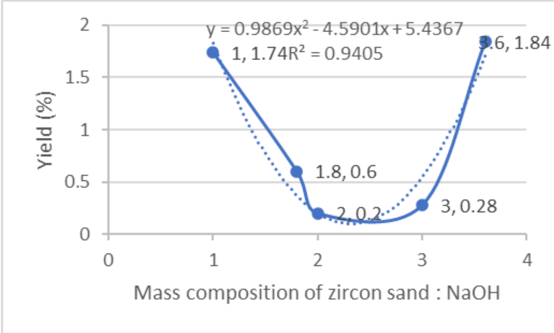


Figure 1. Plots of Mass composition of zircon sand: NaOH vs nano zircon Yield (%)

It can be seen from **Figure 1**, the yield obtained experienced a sharp decline at the composition of 1:1.8 and 1:2. Meanwhile, the yield increased at 1:3 and 1:3.6 composition. This is due to several factors that cause the yield to increase and decline, possibility caused by the samples not to be filtered at filtration process, the stirrer rotation was not consistently makes the sample not completely dissolved and the heating temperature is also inconsistent. It was higher than other research, using mass composition 1: 8, the yield obtained was 0.54% [18].

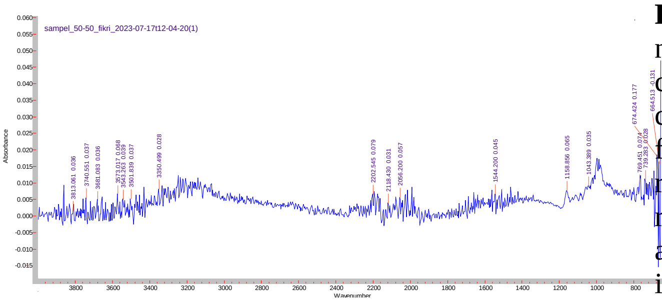
In **Figure 1**, it was showed that mass composition has a polynomial effect of nano zircon yield. The polynomial regression equation is obtained presented equation (2).

$$y = 0.9896x^2 - 4.5901x + 5.4367 \quad (2)$$

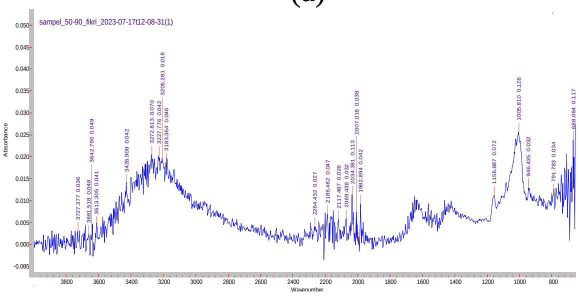
This is because statistical testing uses polynomial regression analysis so that the slope of the regression coefficient is negative and positive. It means that the increasing in composition variation will cause a decrease in yield of 4.5901 and quadratically an increase of 0.9869. Which the lowest yield was 0.2% at composition of 1:2. At that point, the magnitude of the decrease in yield are the same as the increase respectively. Yield will increase further after passing the smallest composition 1:1.2, where the coefficient of determination (R square) in the graph is R^2=0.9405. The rooting result is a correlation between the dependent variable and the independent variable [19]. Because the correlation coefficient of the interaction between mass composition and nano zircon yield almost to 1, which means the relationship between the two variables is very close and related. The results of this research show that the best nano zircon yield percentage was obtained at a composition variation of 1:3.6 of 1.84% yield.

The Effect of composition on the FTIR analysis of nano zircon

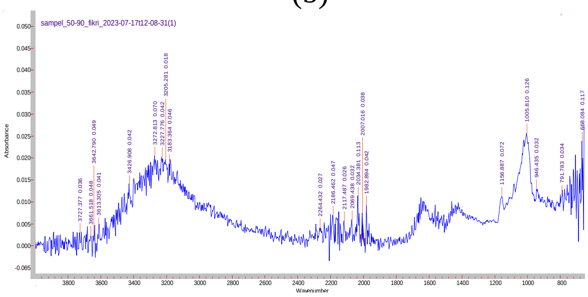
In this research, the FTIR analyzed was conducted to determine the functional groups of nano zircons from zircon sand. The result can be seen in **Figure 2** for different composition.



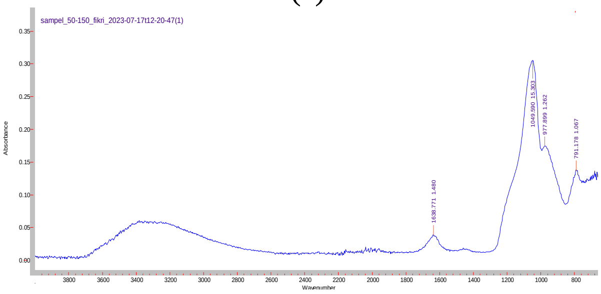
(a)



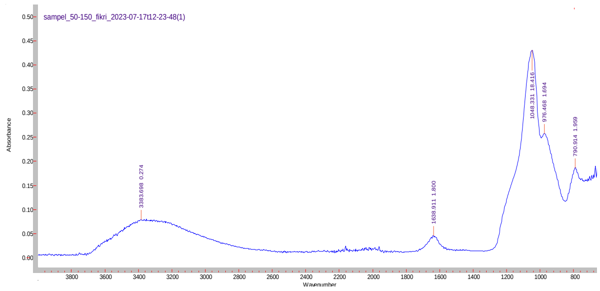
(b)



(c)



(d)



(e)

Figure 2. FTIR result of Mass composition of zircon sand : NaOH of 1:1 (a), 1:1.3 (b), 1:2 (c), 1:3 (d) and 1:3.6 (e)

Figure 2 shows the infrared absorption area of nano zircon from zircon sand after process of caustic soda fusion, leaching, precipitation and calcination. The first treatment, caustic soda fusion, using 17.5% NaOH, resulting the reduction of hydrogen bonds due to the reaction with sodium hydroxide. The result of alkali treatment presented of -OH groups, indicate the peak absorption area between wave numbers 3336.12 cm^{-1} and 3550.16 cm^{-1}. The main functional group in pure zircon is 600 – 700 cm^{-1}. Compare the result with zircon sand in Figure 3 [18], many groups have been lost during the synthesis process. It means that nano zircon is purer than zircon sand.

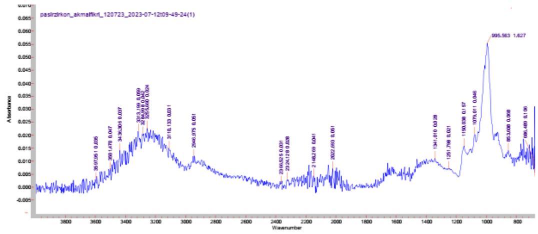


Figure 3. FTIR result of Mass composition of zircon sand : NaOH of 1:8 [18]

The Effect of composition on the size of nano zircon

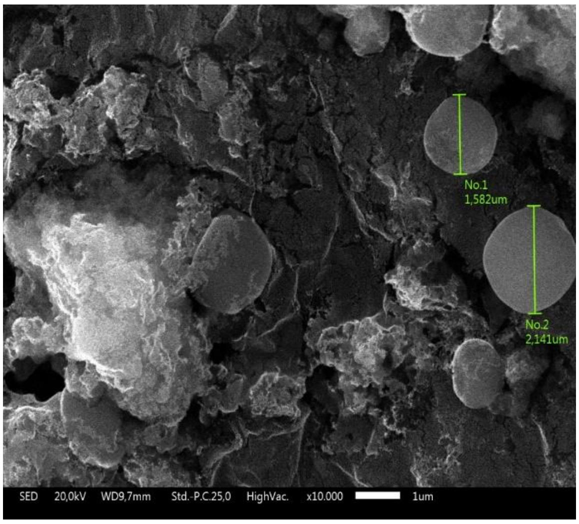
The nano zircon was analyzed by SEM (Scanning Electron Microscope) at BRIN Bandung to find out the size. The results of SEM analysis are presented in **Figure 4**.

Based on **Figure 4 (a)**, SEM analysis of nano zircon at mass composition of 1:1 show that the size of nano zircon is 1582 nm with a magnification of 10.000 times, which is still in micron range. The higher composition of 1:1.8

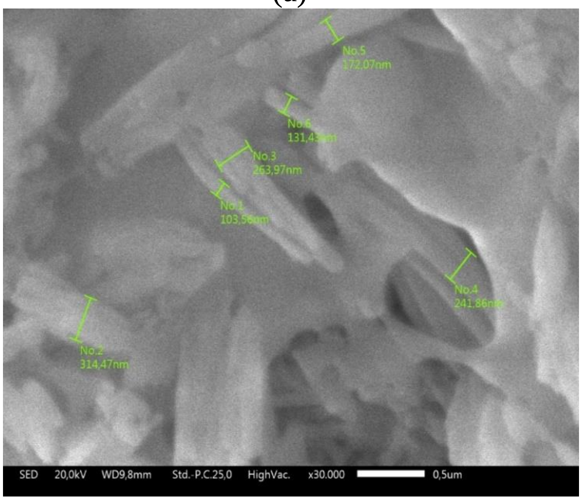
ISSN : 2085 – 1669
e-ISSN : 2460 – 0288

shows that the size of nano zircon obtained is decreasing, 103.56 nm with magnification of 30.000 times as shown in **Figure 4 (b)**. In this is going to get reduce in size for mass composition of 1:2 with size of 73.753 nm with magnification of 30.000 times as seen in **Figure 4 (c)**.

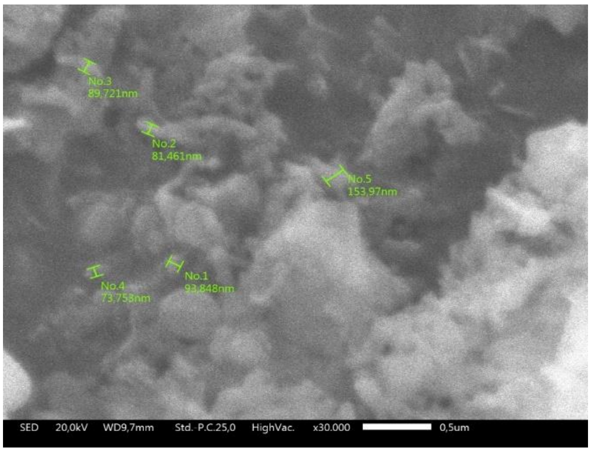
It can be seen in **Figure 4 (d) and (e)**, the size of nano zircon is getting smaller with increasing NaOH composition of 1:3 and 1.3.6 respectively. The size of nano zircons of mass composition 1:3 shows the size of 56.857 nm with magnification of 30.000 times. From **Figure 4 (e)** the highest variation of NaOH composition (1:3.6) showed the smallest size of 41.983 nm with magnification of 30.000. The regression analysis presented in **Figure 5**.



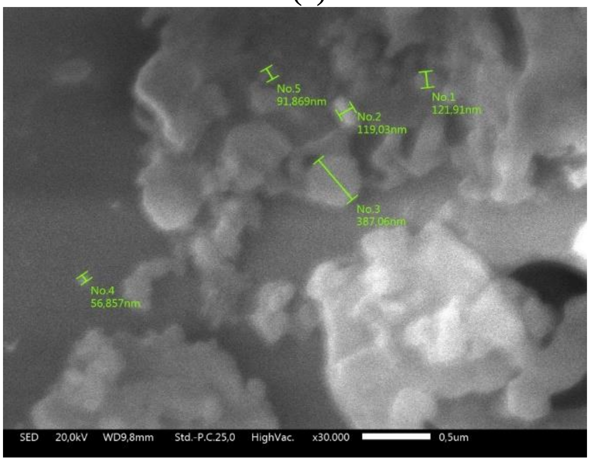
(a)



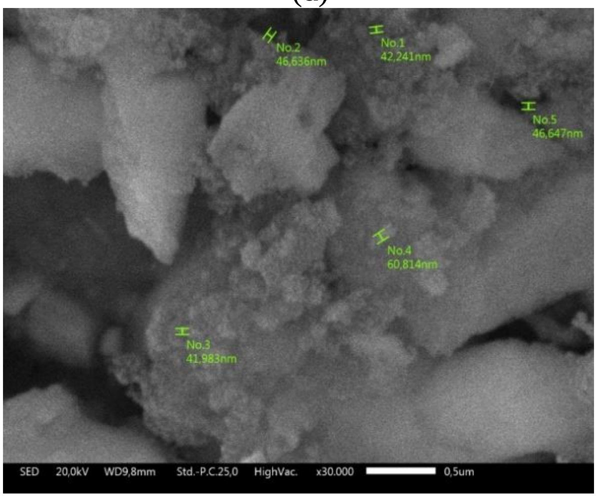
(b)



(c)



(d)



(e)

Figure 4. SEM result of Mass composition of zircon sand : NaOH of 1:1 (a), 1:1.3 (b), 1:2 (c), 1:3 (d) and 1:3.6 (e)

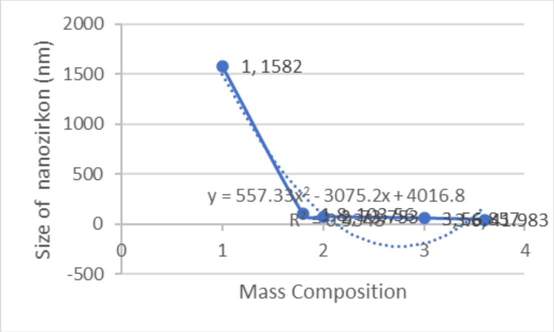


Figure 5. Regression analysis of nano zircon size

In previous research, using the same method, but with different composition ratio of zircon sand and NaOH 1:1.1 at temperature of 500 °C. The result using low fusion temperatures but high calcination (500 – 700 °C), obtained the same structural form, amorphous with a shape similar to commercial zirconia at a temperature of 600 °C.

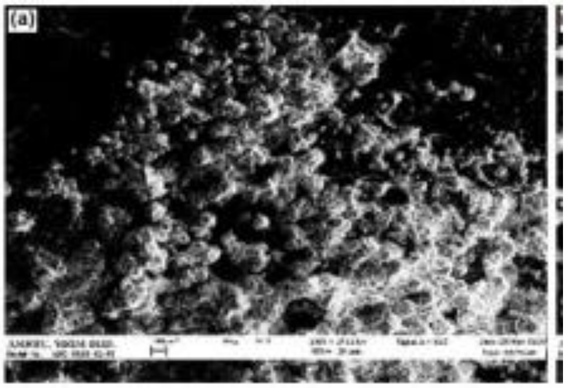


Figure 6. SEM result of Mass composition of zircon sand : NaOH of 1:1 at 500 °C [16]

Apriyani et al [20] found that zirconia was crystalline with a cubic structure with a size of < 10 µm at a final calcination temperature of 800 °C for 5 hours. From this it can be seen that the results of this research which was carried out at a lower calcination temperature produced a smaller size than the final higher calcination temperature, however an amorphous structure was obtained. It can be seen from Figure 4 that agglomeration occurs between nano zircon particles where agglomeration can be reduced by increasing the final calcination temperature [20], while Rahmawati suggest using grinding to overcome agglomeration [21].

Conclusions

Zircon sand from Indonesia local material can be used as raw material of nano zircon by a combination method of caustic soda fusion, leaching, precipitation and final calcination. The higher mass composition ratio of NaOH showed the smaller size of nano zircon. The optimum NaOH composition was 1:3.6 which resulting the size of nano zircon of 41.983 nm at fusion temperature of 400 °C for 60 minutes and calcination temperature of 200 C

Acknowledgment

The author would like to thank the support from LPPM UMJ, National Research and Innovation Agency, and LPDP for funding and Chemical Engineering Study Program, Faculty of Engineering, Universitas Muhammadiyah Jakarta for laboratory facilities.

Funding

This research was funded by the 2023 internal research grant scheme with Research contract number: 80/R-UMJ/VII/2023, and the National Research and Innovation Agency for supporting and LPDP for funding this research through contract number 82/II.7/HK/2022.

Author Contributions

AMS, EU, WHA: Conceptualization, method, writing, analyses, supervision, review, AIR: editing review, IBR: methodology, EU: methodology, analyses, AY: drafting, AIF: experiment, data experiment, F: experiment, data experiment.

Conflicts of Interest

The authors declare no conflict of interest in this paper.

References

[1] Y. Dahlan, N. Saleh and Pramusanto, "Pembuatan Zirkonia Semi Stabil dari Psir Zirkon Kalimantan Tengah dengan Menggunakan Bahan Penstabil Campuran CaO dan MgO," *Jurnal Teknologi Mineral dan Batubara*, vol. 06, no. 03 : 146 - 155, 2010.

[2] H. Poernomo, Sajima and N. D. Pusporini, "Synthesis of zirconium oxychloride and zirconia low TENORM

ISSN : 2085 – 1669
e-ISSN : 2460 – 0288

by zircon sand from Landak West Kalimantan," in *International Conference on Nuclear Capacity Building, Education, Research and Applications (I-Concern19)*, Yogyakarta, 2020.

[3] A. Sommers, Q. Wang, X. Han, C. TJoen, Y. Park and A. Jacobi, "Ceramics and ceramic matrix composites for heat exchangers in advanced thermal sytems-A review.," *Appl. Therm. Eng.,* vol. 30, no. 11-12 : 1277 - 1291, 2010.

[4] H. M. Arshad, A. Shahzad, S. Shahid, S. Ali, A. Rauf, S. Sharif, M. I. Ullah, M. Ali and H. I. Ahmad, "Synthesis and Biomedical Applications of Zirconium Nanoparticles: Advanced Leaps and Bounds in the Recent Past," *BioMed Research International,* vol. 2022, no. 1 : 1 - 9, 2022.

[5] R. A. Fauzan, "Sintesis serbuk zirkon menggunakan variasi jenis dan konsentrasi larutan NaOH dan KOH," Institut Teknologi Sepuluh November, Surabaya, 2018.

[6] A. K. Putri, M. R. Kirom, Abrar and D. G. Syarif, "INTESIS ZrO2 NANOPARTIKEL DARI PASIR ZIRKON UNTUK APLIKASI PADA MODEL RADIATOR," *e-Proceeding of Engineering,* vol. 3, no. 2 : 2062 - 2069, 2016.

[7] T. Athifah, Abrar and D. G. Syarif, "Sintesis Nanopartikel Zro2 Dari Pasir Zirkon Dengan Metode Presipitasi Untuk Adsorben Metilen Biru," in *e-Proceeding of Engineering*, Bandung, 2021.

[8] S. R. Susilowati, S. Pribadi, A. Sartono and D. P. Swasti, "Peningkatan kadar zirkonium oksida dari pasir mineral zirkon dengan cara pelindihan," *Pengelolaan Instalasi Nuklir,* vol. 13, no. 24, pp. :1-10, 2020.

[9] R. Suseno, "Analisis Prospek Pasir Zirkon Indonesia di Pasar DUnia," *Jurnal Teknologi Mineral dan Batubara,* vol. 11, no. 1: 61 - 77, 2015.

[10] C. M. Yasin, W. Ferlianta, A. I. Wardhana, Y. Ramanda, A. Praditya, A. Asdriargo, I. Arif , R. Djamaluddin and S. S. Herdadi, "Peluang Investasi Zirkon Indonesia," Direktur Jendral Mineral dan Batubara - Kementrian ESDM, Jakarta, 2021.

[11] Republik Indonesia, "Perubahan atas Peraturan Menteri ESDM No.1 Tahun 2014 tentang Peningkatan Nilai Tambah Mineral Melalui Kegiatan Pengolahan dan Pemurnian Mineral Dalam Negeri, Peraturan Menteri ESDM No. 8 Tahun 2015," Jakarta.

[12] M. Hisbergues, S. Vendeville and P. Vendeville, "Zirconia: established facts and perspective for a biometerial in dental implantology.," *Journal of Biomedical Materials Research Part B: Applaied Biometerials,* vol. 88B, no. 2: 519-529, 2009.

[13] A. Hardian, F. I. Hasnah, D. G. Syarif and S. Budiman, "Sintesis dan Karakterisasi Nanopartikel ZrO2 dengan Metode Sol-Gel Menggunakan Amilum Sebagai Capping Agent untuk Aplikasi Nanofluida," in *Prosiding Seminar Nasional dan Teknologi Nuklir*, Bandung, 2017.

[14] C. Reddy, B. Babu, I. Reddy and J. Shim, "Synthesis and characterization of pure tetragonal ZrO2 Nanoparticles with Enhanced Photocatalytic Activity," *Ceramic International*, vol. 4, no. 6 : 6940 - 6948, 2018.

[15] E. Yustanti, F. A. F. Ode and E. Sulistiyono, "Primary study of KOH alkali fusion - nitric acid leaching process in extraction of West Kalimantan zircon concnetrate," in *IOP Co.f Series : Materials Science and Engineering. 763 (2020). 012065*, 2020.

[16] I. Subuki, M. F. Mohsin, M. H. Ismail and F. M. Fadzil, "Study of the Synthesis of Zirconia Powder from Zircon Sand," *Indones J. Chem.*, vol. 20, no. 4 : 782 - 790, 2020.

[17] T. Y. Hendrawati, E. Umar, A. I. Ramadhan, A. M. Sari, M. Salsabila, R. Suryani, Firmansyah and I. B. Rahardja, "Sintesis dan Karakterisasi Nanoselulosa serbuk dari tandan kosong kelapa sawit menggunakan ultrasonikasi," *Jurnal Teknologi*, vol. 15, no. 1 : 159 - 165, 2022.

[18] Sari, A.M, Umar, E. Prajitno, D.H, Fitriana, R., Ramadhan, A.I., Firmansyah, Rahardja, I.B, Faisal, A.I, and Fikriyansyah. 2023. Sintesa Nano zirkon dari pasir zirkon lokal dengan metode fusi kaustik soda-presipitasi-kalsinasi. Jurnal Teknologi Vol 15 No. 2 : 189 – 197.

[19] Paiman, Teknik Analisis Korelasi dan Regresi Ilmu-Ilmu Pertanian, Yogyakarta: UPY Press, 2019.

[20] K. Apriyani, I. Permadani, D. G. Syarif, S. Soepriyanto and F. Rahmawati, "Electrical conductivity of zirconia and yttrium-doped zirconia from Indonesia local zirkon as prospective material for fuel cell," in *IOP Conf. Series : Materials Science and Engineering*, 2016.

[21] F. Rahmawati, B. Prijamboedi, S. Soepriyanto and Ismunandar, "SOFC composite electrolyte based on LSGM-8282 and zirconia or doped zirconia from zircon concentrate," *International Journal of Minerals, Metalurgy, and Materials*, vol. 19, no. 9 : 863 - 871, 2012.

ISSN : 2085 – 1669
e-ISSN : 2460 – 0288