

## GEOHERMAL SILICA WASTE AS SUSTAINABLE AMORPHOUS SILICA SOURCE FOR THE SYNTHESIS OF SILICA XEROGELS

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### ABSTRACT

Silica waste from the geothermal plant in Dieng-Indonesia can be utilized as amorphous silica source regarding the high content of silica and high productivity in the plant. However, in the presence of metal oxides, a series of purification steps need to be carried out. This paper describes silica xerogels preparation via acid leaching and sol gel method. Sulfuric acid was chosen in acid leaching due to corrosivity and safety factors. In the beginning, FTIR spectrophotometry and BET-BJH of geothermal silica revealed characteristic functional groups and physisorption of amorphous silica. Response data were collected based on XRF data to obtain silica content at optimum sulfuric acid concentration. To ensure the optimum data, it was confirmed by using XRF at prior and post leaching. The result informed that acid leaching attained optimum at 25% of acid concentration with  $R^2 = 1$  releasing more than 98% of silica. Leached silica was introduced a sol-gel method by using NaOH 2 N with a ratio of SiO<sub>2</sub> to NaOH (1:6 (w/V)) followed 1 N of HCl addition. The product was aged for 18 h before washing and drying at 105 °C. The functional groups spectra such as hydroxyl (-OH), silanol (Si-OH), and siloxane (Si-O-Si) account for the molecular model that might be formed along with the polymerization process. Analysis of SEM and FTIR confirmed morphology, particle size, and disappearance of organic functional groups during the xerogel synthesis process from geothermal silica.

**Keywords:** Amorphous Silica, Geothermal Silica Waste, Silica Xerogel, Acid Leaching, Sol Gel.

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### INTRODUCTION

Silica dioxide (silica), SiO<sub>2</sub> can be found as minerals in the earth's layer with various structures. Silica is available naturally in bamboo leaves,<sup>1-2</sup> rice husks,<sup>3</sup> bagasse ash<sup>4-5</sup>, or manufactured as silica fume and sand.<sup>6</sup> The silica can be used as a material in catalysts, adsorbents, biosensors, and chemosensors<sup>7</sup>. Additionally, silica can appear as silica solid waste in piping equipment in geothermal power plants. The silica solid waste releases out as brine solution by dissolving the solid waste with acid solution. The brine solution goes through a landfill following natural drying surrounding geothermal plant<sup>8</sup>.

Previous studies were carried out to figure out how to prevent the formation of geothermal silica, such as the seeding method to reduce silica content.<sup>9</sup> Silica reacted with alkali can form metal silicates. At the current study, it was found that the silica sol could be extracted from this silicate metal solution via sol gel method.<sup>10,12</sup>

Silica acts as a source for a large number of silica-based products supporting chemical,<sup>13</sup> and other manufacturing industries.<sup>14</sup> Previous study reported utilization of silica with large specific surface area and array ordered hexagonal, i.e. as mesoporous silica.<sup>15</sup> Moreover, the development of nanotechnology also drives the demand for silica. Therefore, an effort to utilize silica waste can be considered. Unlike common silica sources, geothermal silica waste contains many kinds of metal oxides. Thus, a purification process is required to be carried out. One method of purifying silica can be carried out by acid leaching using sulfuric acid. Previous studies have been investigated the use of sulfuric acid to remove iron and aluminum content

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in silica sand up to 97.96% and 94.23%, respectively.<sup>16</sup> Furthermore, the acid can dissolve zinc and iron metals.<sup>17</sup> The sulfuric acid was chosen in this research in acid leaching. Though the acid is effective to reduce metals, while it has weaknesses such as high level of corrosivity and difficulty in metal recovery unsuitable to be applied on an industrial scale given that the leached metal can still be recovered, thereby preventing the potential for environmental pollution.<sup>18-20</sup> In this study, geothermal silica waste was investigated as a source of silica in xerogel synthesis with a combination of sulfuric acid leaching and sol-gel methods.

## EXPERIMENTAL

### Material

Silica waste was collected and procured from the geothermal plant in Dieng Indonesia. Sulfuric acid ( $\text{H}_2\text{SO}_4$  95-97%), hydrochloric acid (HCl 37%), and sodium hydroxide (NaOH 99%) were provided from Merck. All chemicals have been used without any further purification. Geothermal silica was first introduced drying at 105 °C: The dried geothermal silica was sized using milling and screened to obtain the homogeneous size.

### Methods

The silica xerogel synthesis process scheme can be seen in Fig.-1 adapting from other research.<sup>4</sup> Geothermal silica procured from the geothermal plant in Dieng was dried at 105 °C. The dried silica was sizing using milling for ten minutes and screening using Retsch AS 200 Vibratory Sieve Shaker releasing 325 mesh (45  $\mu\text{m}$ ) silica. The size reduction and sieving process were brought at the laboratory of the Integrated Service Unit (UPT), Diponegoro University, Indonesia.

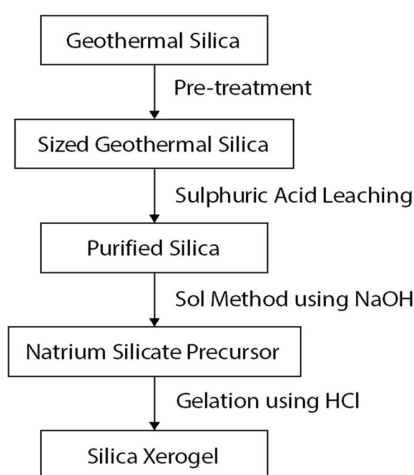


Fig.-1: Silica Xerogel Synthesis Process

Acid leaching treatment was conducted by pouring sulfuric acid to the dried geothermal silica at 100 °C for 105 minutes. The dried silica was immersed in the acid solution with weight/volume ratio of 1: 4.<sup>16</sup> Once a slurry was formed, it was vacuum filtered through filter paper, washed using demineralized water until neutral acidity (pH = 7) was reached, and finally dried at 105 °C until its weight was constant in a drying oven.

After the silica was leached, sodium hydroxide (NaOH 2 N) was added with a ratio of mass to volume ( $\text{SiO}_2$  to NaOH) at 1: 6 to form a sodium silicate solution ( $\text{Na}_2\text{SiO}_3$ ) at a temperature of 80 °C.<sup>21</sup> Hydrochloric acid (HCl) diluted 1 N was then added to the sodium silicate solution gradually until colloidal silica gel was formed under acidic condition and was left for 18 hours. The colloidal gel was washed with demineralized water to remove salt and impurities and was dried at 105 °C.

### General Procedure

The silica xerogel synthesis process consisted of geothermal silica pre-treatment, acid leaching, sol gel method via sodium hydroxide addition to leached geothermal silica, aging 18 h after mixing with hydrochloric acid, washing up to be neutral pH, then drying at 105 °C.

## Characterization

Silica and metal oxides content were analyzed using XRF Spectrophotometer (PANalytical Minipal 4). The surface area of the geothermal silica waste, as well as porosity, were detected by BET-BJH method (Quantachrome Instruments). Functional groups were analyzed using FTIR Spectrophotometer (Shimadzu IRPrestige 21), while particle topography and morphology were observed using SEM (FEI Inspect-S50).

## RESULTS AND DISCUSSION

Geothermal silica is classified as amorphous silica with mesoporous material. It existed in a series of strong diffraction peaks of XRD analysis in the range of  $20^\circ$  to  $25^\circ$ .<sup>22</sup> Moreover, silica from geothermal power plants solid phase also has an amorphous structure.<sup>23</sup> BET-BJH analysis was performed to analyze the porous material properties of the geothermal silica waste.

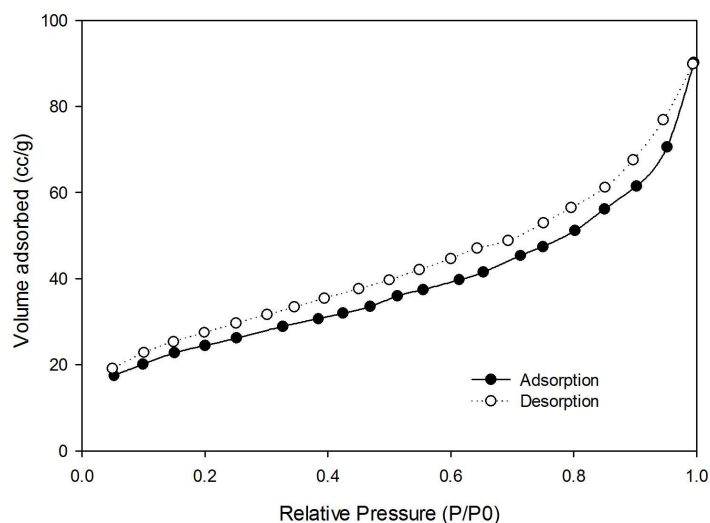


Fig.-2: Sorption Isotherms (BET) and BJH Plot of Amorphous Geothermal Silica

In Fig.-2, it visualizes a sorption isotherm with type IV. It was indicated that the geothermal silica involved as mesoporous material having amorphous silica. The specific surface was found at  $40.899 \text{ m}^2/\text{g}$  with a pore volume of  $0.113 \text{ cc/g}$  and a pore radius of  $19.831 \text{ \AA}$ . The amorphous structure of silica allows silica to form a polymeric structure having a hydroxyl group (-OH). This group forms a silanol group through a covalent bond with the Si element becoming Si-O-H. Based on FTIR analysis in Fig.-3, there is a strong -OH group signal in the spectra range of  $3,226\text{-}3,325 \text{ cm}^{-1}$ . The spectra of  $1,622 \text{ cm}^{-1}$  also show the presence of silanol groups in silica. The silanol group releases silica to be hydrophilic. The siloxane (Si-O-Si) group can be denoted as three spectra peaks at  $1,066 \text{ cm}^{-1}$ ,  $802 \text{ cm}^{-1}$ , and  $418 \text{ cm}^{-1}$ . Similar findings are also found in several studies.<sup>24-26</sup> Based on spectra analysis, the predicted geothermal silica form can be depicted in Fig.-4.

There are hydroxyl groups in silica with siloxane and silanol groups contained in the internal part of the silica.<sup>27</sup> Amorphous silica can be found in several silica sources such as rice husk,<sup>28</sup> wheat husk,<sup>29</sup> and bagasse ash.<sup>30</sup> However, it should be underlined that geothermal silica has a higher metal oxide content compared to silica from organic material sources. Without purification, metals can be remained in silica precursors such as sodium silicate ( $\text{Na}_2\text{SiO}_3$ ) and trapped in the structure of silica polymers as impurities decreasing the quality of the final product. The quality standard for sodium silicate requires at least 99% silica.<sup>14</sup> Therefore, due to the high content of metal oxide in the geothermal silica, it was conducted to improve the quality by leaching process with sulfuric acids. Silicon has an electronegativity like oxygen which does not allow them to form ionic bonds and covalent bonds are formed instead.<sup>31</sup> The effect of sulfuric acid concentrations was observed to obtain silica content as seen in Fig.-5.

This paper focuses to investigate empirically the optimum sulfuric acid concentration remaining high silica content and low metal oxides during acid leaching. The result was attained based on the value of R-squared closed to unity.

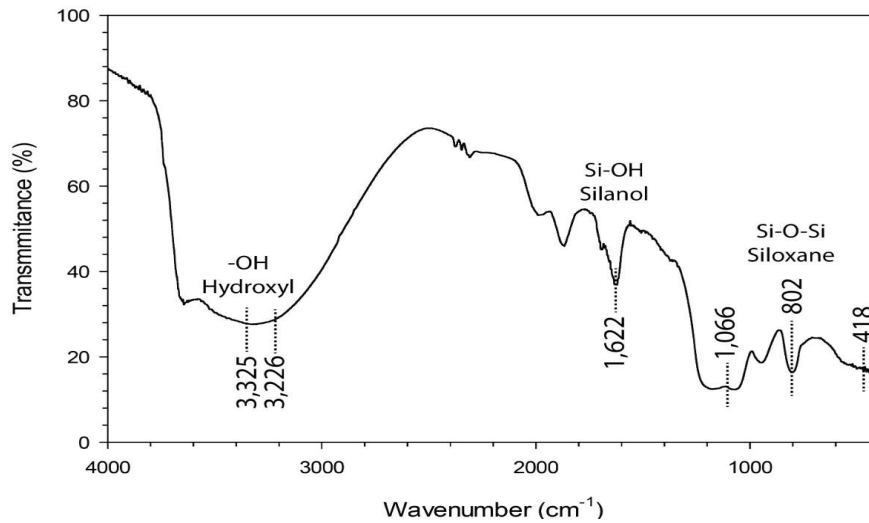


Fig.-3: Infrared Spectra of Geothermal Silica

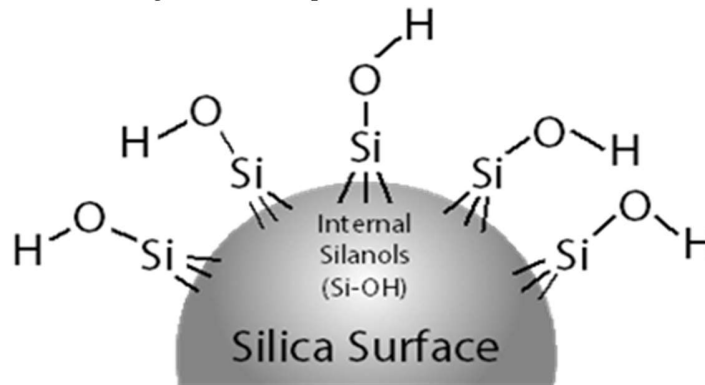


Fig.-4: Molecular Structure of Geothermal Silica

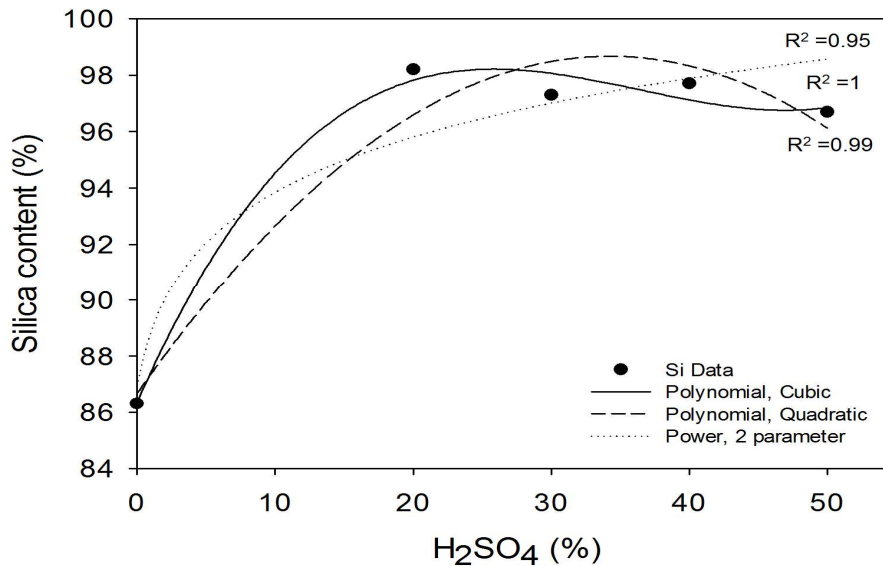
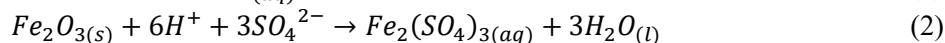


Fig.-5: Concentration of Sulfuric Acid Versus Silica Content

The leaching can generate higher silica content (>98%) and reduce metal oxides impurities at an acid concentration of around 25%. The reaction between H<sub>2</sub>SO<sub>4</sub> and metal oxides causes the breakdown of ionic bonds of metal molecules with oxygen. SO<sub>4</sub><sup>2-</sup> ions bind to metal elements to form metal sulfate compounds

while  $H^+$  ions bind to oxygen to form  $H_2O$ . A brief example of a reaction can occur to metal oxides such as Fe oxide in the following equation:



Self-inhibition effects occur as a result of the in-situ deposition of metal sulfate. At high concentrations of  $H_2SO_4$ . The self-inhibition model that describes the kinetics of leaching has been investigated.<sup>32</sup> The model states that there is resistance to mass transfer and diffusion rate both on the surface and pore. In the end, this metal sulfate precipitation layer acts as a kinetic barrier that causes a peak point in the leaching process itself. A similar phenomenon occurred in other studies.<sup>33-35</sup> All changes in the content of geothermal silica can be seen in Fig.-6. These figures described the reduction of impurities number including Fe oxide. Therefore, many kinds of impurities peak disappeared in Fig.-6(B).

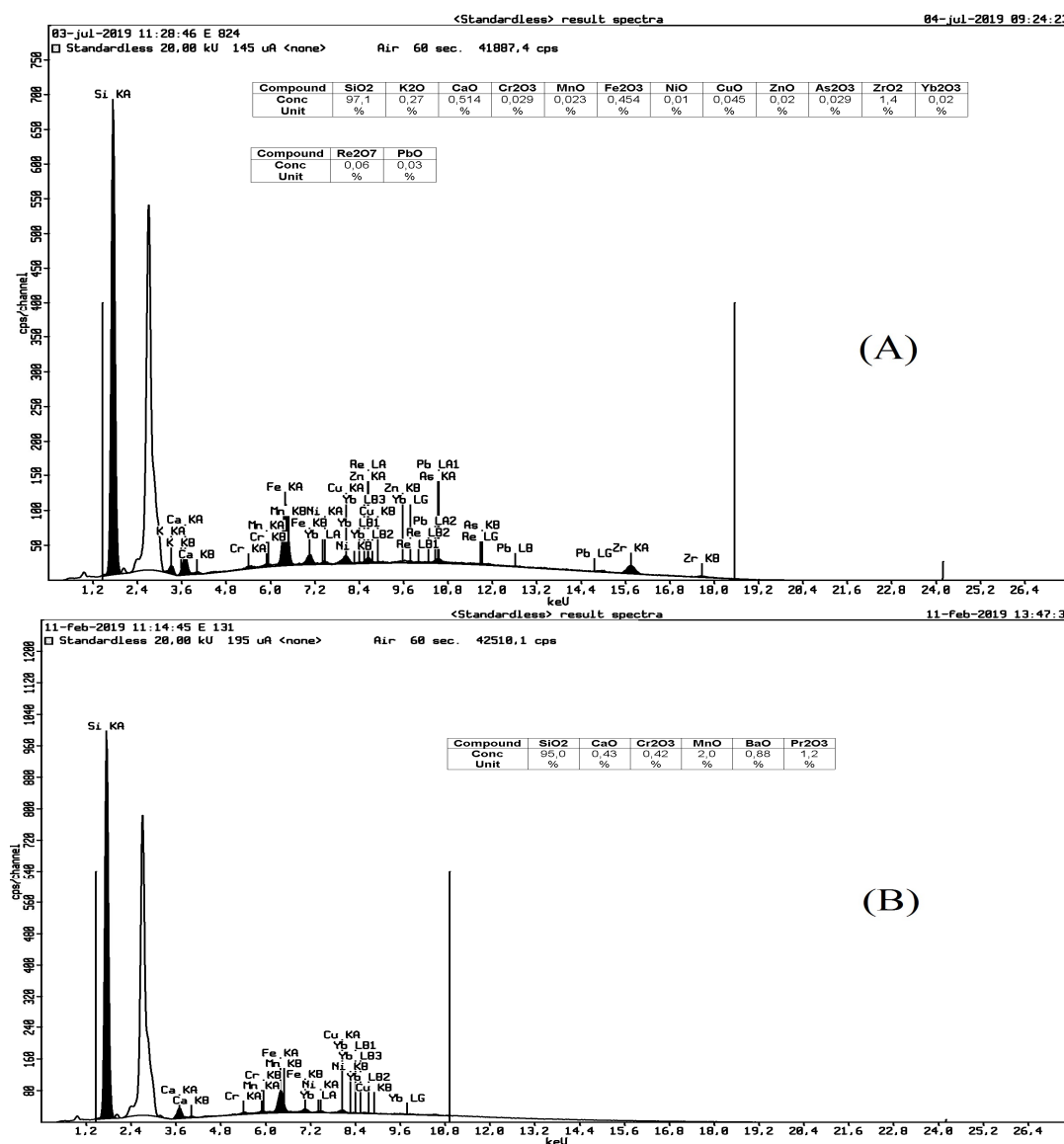


Fig.-6: XRF Spectra of Geothermal Silica: Before (A) and After (B) to Leaching Process

Synthesis of silica xerogel was carried out through the sol-gel stage by introducing leached silica and sodium hydroxide (NaOH) releasing a solution of sodium silicate ( $Na_2SiO_3$ ) precursor. Then, it can be replaced by the Si-OH silanol group into Si-ONa ionic bonds. In this manner,  $Na_2SiO_3$  can be further reacted

with water by hydrolysis to convert silicic acid ( $\text{Si}(\text{OH})_4$ ) through the addition of hydrochloric acid ( $\text{HCl}$ ). The condensation polymerization of  $\text{Si}(\text{OH})_4$  caused the formation of colloidal spherical silica with hydroxyl groups on its surface as depicted in Fig.-7 and the equation of (3) to (5). After washing and drying at ambient pressure, silica xerogel was obtained as the final product. Drying in supercritical conditions will produce silica aerogel instead.<sup>36</sup> However, several studies have succeeded in synthesizing aerogel under atmospheric condition.<sup>37-38</sup>

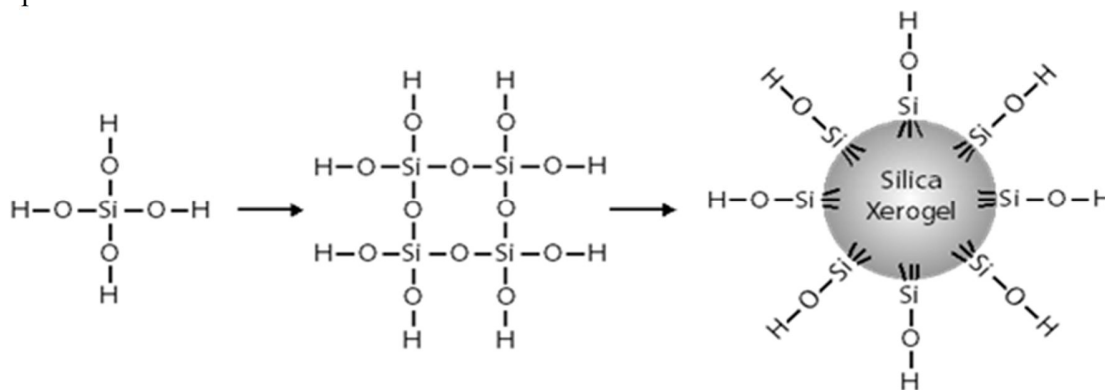
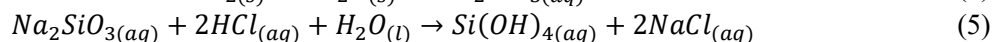
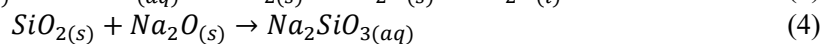
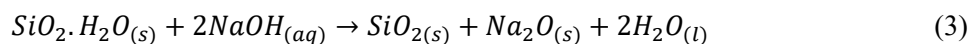


Fig.-7: Polymeric Condensation of Silica Xerogel



In Fig.-8, it characterizes certain peaks such as peaks of silanol and siloxane groups both from the geothermal silica and the silica xerogel. This result indicated the presence of functional group components are similar between geothermal silica and silica xerogel. However, the spectra also display the presence of a peak at  $1,867 \text{ cm}^{-1}$  that distinguishes geothermal silica from xerogel. It can be seen also this certain peak in Fig.-3. Some references indicated this functional group denoting as a carboxyl group ( $\text{C}=\text{O}$ ) or a group in organic components. It was expected an organic impurity remained in the geothermal silica.<sup>40</sup> Furthermore, it might the leaching stage can eliminate organic compounds contained in geothermal silica.

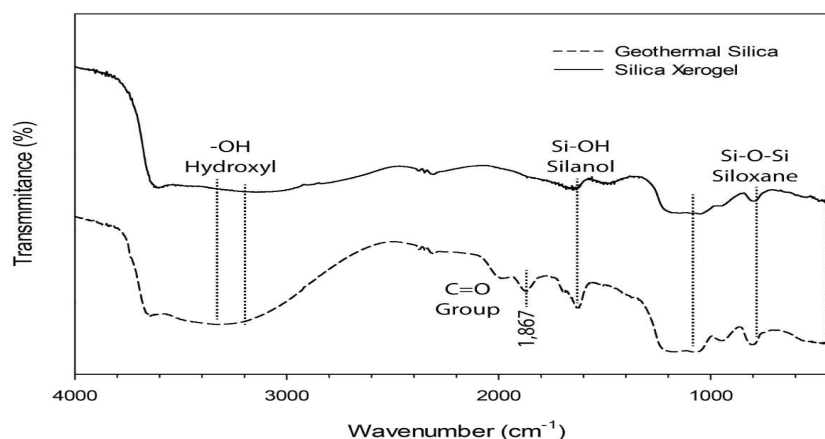


Fig.-8: FTIR Spectra of Geothermal Silica and Silica Xerogel

The condensation polymerization generates different morphology between the geothermal silica and the silica xerogel. It is reflected in Fig.-9 and Fig.-10. Several studies mentioned that the silica xerogel forms in nano-sized amorphous silica.<sup>41-43</sup> However, forward research might be considered to investigate characterization and more in-depth observations of the silica condensation stage.

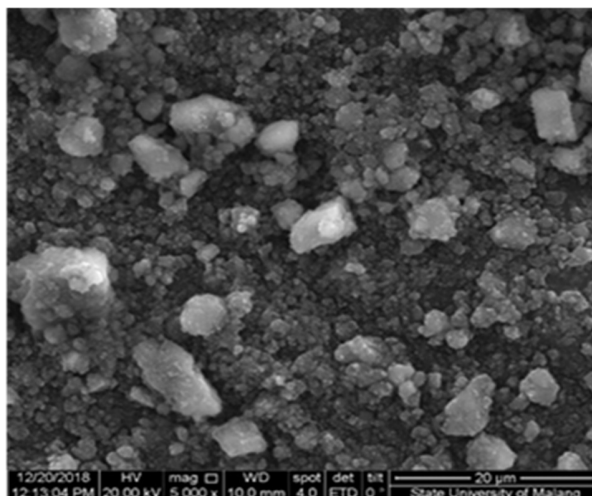


Fig.-9: Morphology of Geothermal Silica

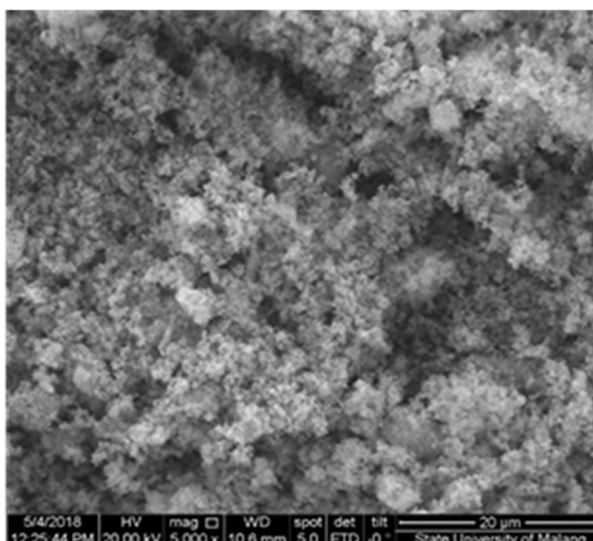


Fig.-10: Morphology of Geothermal Silica Xerogel

## CONCLUSION

Geothermal silica has a huge silica content as a source in silica xerogel preparation. However, the metal oxides impurities must be leached out through acid leaching by sulfuric acid. The leaching resulted in higher silica concentration at a sulfuric acid concentration of 25%. It was confirmed by XRF analysis releasing more than 98% of silica and reducing the number of metal oxides. Moreover, organic components in geothermal silica can be removed through acid leaching. The silica xerogel was obtained from the leached silica process through sol-gel method. The silica xerogel possessed a similar functional group of the geothermal silica, while the morphology and size of both silica were the difference.

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