JKPK (JURNAL KIMIA DAN PENDIDIKAN KIMIA), Vol. 6, No. 3, 2021
Chemistry Education Study Program, Universitas Sebelas Maret
https://jurnal.uns.ac.id/jkpk

Hal. 317-325
ISSN 2503-4146
ISSN 2503-4154 (online)

XRF AND XRD INVESTIGATION FOR THE RESULTS OF THE EXTRACTION OF MUD VOLCANO FROM NAPAN VILLAGE INTO SILICA

Marianna Caryna Kono, Yohana Ivana Kedang, Regina Seran, and Matius Stefanus Batu*

Department of Chemistry, Agriculture Faculty, University of Timor
Jln. El Tari - Km. 09, Sasi, Kefamenanu, East Nusa Tenggara 85613, Indonesia

* correspondence, tel/fax : +6281333220429, email: steve_b79@unimor.ac.id

Received: September 13, 2021 Accepted: December 6, 2021 Online Published: December 23, 2021
DOI : 10.20961/jkpk.v6i3.55022

ABSTRACT

Silica powder was obtained from the mud volcano of Napan Village following the co-precipitation method. This research aimed to determine the phase changes that occur in calcined silica with various temperatures. This research was carried out in three stages, there are the preparation of a mud volcano using the pre-treatment method, extraction of silica with sodium hydroxy solution, and calcination of silica with temperature variations. By analysis of XRF and XRD results, the mud volcano samples showed a high percentage of SiO_2 minerals. The results of silica characterization using XRD showed that uncalcined and calcined silica at 600^oC had an amorphous structure with broading peaks. Tridymite and cristobalite phases were detected in calcined silica at 800^oC and 1000^oC. Calcined silica at a temperature of 1000^oC transformed the tridymite phase to cristobalite with a decrease in the intensity of the tridymite phase while the cristobalite phase increased.

***Keyword**: Calcination, Co-precipitation, Mud Volcano, Silica*

INTRODUCTION

Silica as one of the main materials in the industrial sector needs to be developed and increased its availability. Silica dioxide is a natural mineral that has been used in daily life, such as the main ingredient in the industry of glass, building materials (cement, concrete, ceramics), paper, textiles, electronic devices and paints [1,2]. Generally, silica can be found in rice husks [3], volcanic ash [4], sand [5], mud [6], etc.

One of the natural potentials currently attracting attention is a mud volcano in Napan Village that has not been explored and utilized. The mud volcano of Napan Village has existed since 2007 and occurs naturally. Therefore, it is very difficult to stop the activities other than the end of the mudflow. So, this can have a bad impact on the surrounding area [7].

Research using the mud volcano of Napan village has not been widely reported. Research from Naikofi [8] reported in a geological science study and analysis results using XRD showed that the mineral composition that dominates this mud is quartz (SiO_2). Research conducted by Gelyaman [7] characterized mud volcanoes with two different treatments, there are

without heating and with heating. The results showed that the most dominant percentage of mineral composition was silica dioxide at 52.00% followed by iron oxide and aluminum oxide as well as other minerals, but these two results did not produce silica with a high enough purity level.

The level of silica purity is an effort that needs to be made to increase the percentage by weight. This can be done by separating silica from other minerals that become impurities in a material. Based on previous researchers, there are several methods of synthesizing silica from natural materials, including sol-gel at a temperature of 600^{o}C [3], alkaline fusion at 550^{o}C [9], co-precipitation only at 80^{o}C [10]. Therefore, the co-precipitation method is more energy efficient so it is relatively easy to do. This method has advantages when compared to other conventional methods, there are having a high level of purity, simple deposition process, relatively fast time, simple equipment and relatively low cost [11].

Generally, co-precipitation silica can be either amorphous or crystalline. Silica crystallinity can be increased by calcining [12]. Silica has a quart phase with a hexagonal structure at a temperature of 600^{o}C, while at a temperature of 700^{o}C and 800^{o}C the silica has a quart and cristobalite phase [12]. Micro silica synthesized from the beach sand of Bancar, Tuban, East Java by calcination at temperatures of 800^{o}C and 1000^{o}C produces quart phase, while the quart and low cristobalite phase produced at temperature of 1200^{o}C [13].

Based on the description above, this study will be preparing the mud volcano using the pre-treatment method. Mud volcano powder will be characterized using X-Ray Fluorescence (XRF) and X-Ray Diffraction (XRD) instruments as initial analyses to identify silica mineral content in mud volcano samples. Silica extraction was carried out using the co-precipitation method with various calcination temperatures and characterized using XRD to see the phase transformations that occur in calcined silica. The data can become an alternative utilizing mud volcano in Napan village as a silica resource.

METHODS

1. Materials

The chemicals used include Sodium hydroxide (NaOH), chloride acid (HCl), aquadest and mud volcano obtained from Napan village in the District of North Central Timor, Province of East Nusa Tenggara, Indonesia.

2. Procedure

a. Preparation of Mud Volcano

12 grams of mud volcano were washed with 60 mL of 3 mol/L HCl using a hot plate stirrer at 60^{o}C for 2 hours. The results obtained were filtered using filter paper. The residue was washed with distilled water until the pH was neutral and dried in an oven at 70^{o}C for 24 hours. Furthermore, it was mashed using a mortar and calcined using a furnace at a temperature of 900^{o}C for 1 hour. The pure mud volcano powder produced was filtered through a 100 mesh sieve and characterized using XRF and XRD.

b. Extraction of Silica

10 grams of mud volcano powder was added to 60 mL of 7 mol/L NaOH solution and heated in a closed 250 mL Erlenmeyer flask. The mixture was stirred using a magnetic stirrer at 70^{o}C for 1 hour. Then, the solution mixture was filtered through filter paper. The filtrate was titrated with 2 mol/L HCl gradually until it reached pH 7 and allowed to stand for a maximum of 24 hours. The silica gel formed was washed with warm distilled water at least 5 times to remove the NaCl content from the silica gel. Furthermore, the silica gel precipitate was dried in an oven at 80^{o}C for 24 hours and then calcined with a temperature variation of 600^{o}C, 800^{o}C, and 1000^{o}C for 3 hours. The calcined silica powder was characterized using XRD.

RESULTS AND DISCUSSION

1. Mud volcano preparation

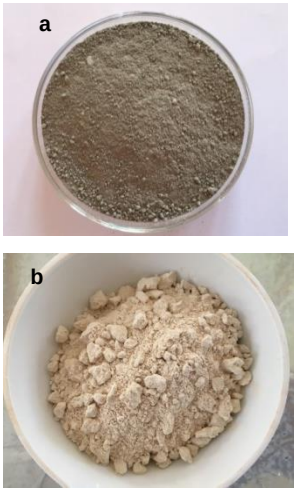

Figure 1. Mud volcano powder (a) Before preparation (b) Preparation result

Mud volcano preparation is carried out using a pretreatment method in which the mud volcano is separated from its impurities by washing with 3 M HCl solution. This method does not affect the crystalline or amorphous structure of the silica, but can affect the chemical composition of the mud volcano [14].

The colour change in the mud sample (Figure 1) is caused by the dissolved impurities contained in the sample, which are also wasted in the filtrate when the washing process is carried out using HCl [1].

a. XRF analysis

Table 1. XRF data on mineral composition in mud volcano of Napan village

Minerals	Samples Composition Persentage (%)	
	Before preparation	After preparation
Al_2O_3	16	17.8
SiO_2	53.8	69.1
K_2O	4.95	6.29
CaO	3.12	-
TiO_2	1.83	2.23
V_2O_5	0.062	0.073
Cr_2O_3	0.069	0.051
MnO	0.19	0.025
Fe_2O_3	18.9	4.15

The XRF data are presented in Table 1. The results show the mud volcano sample contains several minerals with the most dominant percentages, there are SiO_2, Al_2O_3, and Fe_2O_3. The acid and thermal treatment are efficient, resulting in a material with a high reduction in CaO, SrO, BaO, EuO_3, Cr_2O_3, MnO, Fe_2O_3, NiO, CuO, ZnO, Rb_2O and Yb_2O_3 content. HCl solution serves to purify a substance from impurities by dissolving the metal and non-metal content of a material [1,15]. In addition, the calcination process can also increase the percentage of silica minerals. These results are in accordance with research conducted by Ulfindrayani [16].

The Lapindo mud washing process reduces the levels of metals such as Fe_2O_3, CaO, V_2O_5 and MnO and increases the percentage of silica minerals.

b. XRD analysis

The XRD diffractogram of the mud volcano sample is shown in Figure 2. The diffractogram obtained was matched with the AMCSD (*American Mineralogist Crystal Structure Database*). Overall, the diffractogram shows the mud volcano sample contains the majority of compounds in the amorphous phase. This result resembles the diffractogram data from the Lapindo Sidoardjo mud which is a similar eruption to the mud volcano of Napan village [16]. The diffractogram shows the highest absorption peak of 2θ = 26.62° – 26.63° with a d-spacing of 3.34 Å according to the database AMCSD Number 0004267. This absorption shows the quartz SiO_2 compound and its the most dominant mineral in the mud volcano based on the composition percentage is 53.8% before preparation and 69.1% after preparation.

Other minerals found in the mud volcano sample are kaolinite which appears at the absorption peak of 2θ = 12.49° with a d-spacing of 7.086 Å. The 2θ absorption peak that appears at 22.03 and 27.90° indicates the presence of cristobalite minerals [17]. Another absorption of the mineral cristobalite appears at 36.54°; 68.32°; 73.42°, and 81.45°. According to the database AMCSD Number 0010761, gibbsite mineral appears at 45.80° with a d-spacing of 1.98 Å for both samples.

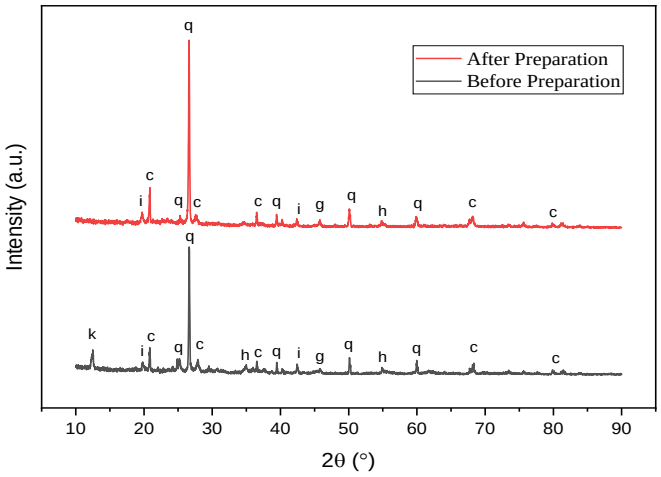

Figure 2. XRD diffractogram of mud volcano sample

The absorption peak which shows the mineral hematite appears at 54.89° with a d-spacing of 1.67 for both samples. The mineral alumina corundum was also detected in the sample of the mud volcano before preparation at 34.94° with a d-spacing of 2.56 Å. Illite minerals were detected at the peaks of 19.82° and 42.45° with d-spacing of 4.478 and 2.129 Å.

Based on XRD data, the mineral content in the mud volcano of Napan Village consists of quartz, kaolinite, cristobalite,

hematite, alumina, and illite. The mineral that has the largest content is the mineral quartz. Therefore, the mud volcano of Napan village can be used as a source of silica as suggested by previous researchers.

2. Silica extraction

The extraction process is carried out using sodium hydroxide (NaOH) as solvent. NaOH is used in this study because silica can react with bases, especially strong bases such as hydroxy alkali. The reaction mechanism that occurs is [18] :

$$SiO_{2(s)} + 2NaOH_{(aq)} \rightarrow Na_2SiO_{3(aq)} + H_2O_{(aq)}$$

The addition of HCl solution as a strong acid aims to exchange Na^+ and H^+ ions. The result is solid in the form of a gel which will then separate the particles of silica bound to water molecules, namely silica hydrosol or silicic acid (H_2SiO_3). The reaction mechanism that occurs is [18] :

$$Na_2SiO_{3(aq)} + 2HCl_{(aq)} \rightarrow H_2SiO_{3(s)} + 2NaCl_{(aq)}$$

The process of washing the precipitate with warm distilled water aims to remove excess acid and NaCl salt content during the reaction. Meanwhile, the sediment drying process resulted in a dehydration process of silica hydrosol so that silica gel would be produced. The reaction mechanism that occurs is [19] :

$$H_2SiO_{3(s)} \rightarrow SiO_{2(s)} + H_2O_{(aq)}$$

The extracted silica shows a broad peak at 2θ = 20-30^o and the result is presented in Figure 3. The broad peak confirms the formation of amorphous silica. The diffraction pattern of the extracted silica powder appears at sharp peaks, including 2θ = 20.115^o; 2θ = 21.322^o; and 2θ = 22,339^o. Silica gel from volcanic ash has an amorphous phase with the peak detected at 2θ = 22.6563^o [20].

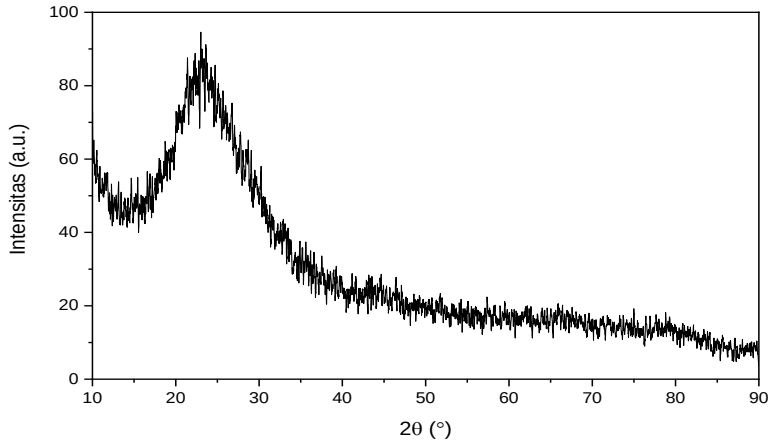

Figure 3. XRD diffractogram of extracted silica

Table 2. The yield of calcined silica

No	Silica calcined temperature (^{o}C)	Initial mass of silica (gr)	Mass of calcined silica (gr)	Yield of calcined silica (%)
1.	600	2,50	1,86	74,54
2.	800	2,50	1,76	70,4
3.	1000	2,50	1,57	62,8

Calcined silica content at a temperature of 600ºC to 1000ºC was decreased as shown in Table 2. When the calcination of temperature was increased along with the yield of silica decreased. Its because there has been a transformation of the amorphous phase into a crystal which can be seen from the XRD characterization results [21].

a. Characterization of calcined Silica by XRD

A Comparison of the diffraction pattern of silica samples is shown in Figure 4. The structure of calcined silica was change, because by the large of energy that can make a random structure changes to regularity. Silica calcined at 600ºC has an amorphous structure with a steeper absorption pattern when compared to silica without calcination. This is due to the lack of holding time in the calcination process. The diffraction pattern shows a shift in absorption to a smaller peak with a broading peak between 2θ = 17-27º. The maximum absorption peak appears at 2θ = 21.704º. Silica gel with broad peaks in the range of 2θ = 20-22º indicates silica with an amorphous phase [22].

The calcined silica samples at 800ºC and 1000ºC shows a phase change into crystals which were indicated by the presence of sharp peaks. The formation of this diffraction pattern is due to the scattering of atoms in the hkl plane in the crystal [12].

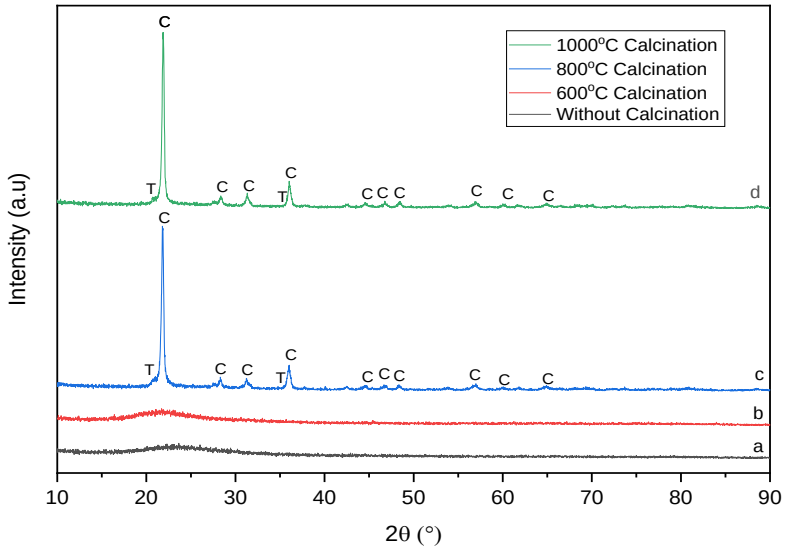

Figure 4. Silica diffraction pattern (a) without calcination (b) 600ºC calcination, (c) 800ºC calcination and (d) 1000ºC calcination

The sharp peak at 2θ = 21º indicates the calcined silica has a low cristobalite structure with an intensity of 100%. This study indicates that the silica phase conforms to the AMCSD Number 0010752. The crystal structure formed is tetragonal with Miller index [11] and has α = β = γ = 90º. Silica calcined at a temperature of 800ºC produces silica- cristobalite with a tetragonal structure at an angle of 21.923º with FWHM 0.1574 [12]. The observation indicates calcined silica at 800ºC and 1000ºC has tridymite (T) and cristobalite (C) phases. The intensity of the cristobalite phase in calcined silica at 1000ºC

increased along with the decrease in the intensity of the tridymite phase. A study from Deshmukh [23] shows that at a calcination temperature of 1000^{o}C, silica extraction from rice husks obtained a crystal phase, which was identified as tridymite and cristobalite. The transformation of α Quartz to β Quartz occurs at 573^{o}C. Quartz is converted to cristobalite at 870^{o}C and it converts to tridymite at 1.470^{o}C [23].

The position of the absorption peak and the width of the peak in each pattern shows a significant difference. To determine the peak position and peak width of the silica XRD results, it can be seen in the calculation of the full width at half maximum peak (FWHM) using Origin software. The results of the calculation of the peak width of the XRD pattern of silica samples in this study are summarized in Table 3 below:

Table 3. Width and peak position of the XRD pattern of silica samples

No	Sample type	Top position	Peak width
1.	Silica without calcination	23.673	20.52
2.	Calcined silica 600^{o}C	21.704	18.72
3.	Calcined silica 800^{o}C	21.829	1.44
4.	Calcined silica 1000^{o}C	21.894	1.09

The peak width value of the silica samples decreased significantly so that the phase of each sample analyzed could be identified. The smaller the peak width, the closer the crystal phase of the silica sample will be [24]. The results of the analysis showed that the un-calcined silica sample and the calcined silica sample at a temperature of 600 ^{o}C had not yet formed a crystalline phase but were still in the form of an amorphous phase due to the lack of holding time during the calcination process. On the other hand, synthesised silica nanoparticles had a quartz phase at a temperature of 600 ^{o}C with a calcination holding time of 5 hours [12].

Calcined silica samples at temperatures of 800 ^{o}C and 1000 ^{o}C have formed a crystalline phase which is characterized by smaller peak widths and narrow diffraction peaks. This result is in accordance with the research conducted by Latif [13] which produced silica with cristobalite phase at 1000 ^{o}C with a holding time of 4 hours. This calcination temperature resulted in the XRD pattern being at an angle of about 21^o with a narrow peak width.

CONCLUSION

Based on the research, it can be concluded that uncalcined silica and calcined silica at 600^{o}C had an amorphous structure with broad peaks. Silica calcined at temperatures of 800^{o}C and 1000^{o}C shows a structural change into a crystal. Silica calcined at 800^{o}C and 1000^{o}C has tridymite and cristobalite phases. The phase transformation from tridymite to cristobalite occurred in calcined silica at 1000^{o}C which was caused by the reduced intensity of the tridymite phase while the intensity of the cristobalite phase increased.

REFERENCES

[1] Ferlyasari, M. Anas, & Erniwati. "Efek Variasi Temperatur Sintering Sebelum Leaching Terhadap Kandungan Silika yang Diekstrak dari Lumpur Teluk Kendari Menggunakan XRF (X-Ray

Fluorescence)". *Jurnal Penelitian Pendidikan Fisika*, vol. 5, no. 4, pp. 339–345. 2020.
DOI: 10.36709/jipfi.v5i4.14756

[2] F. Meyori, R. Elvia, & I. N. Candra. "Sintesis dan Karakterisasi Xerogel Hasil Kopresipitasi dari Pasir Pantai Panjang Bengkulu". *Jurnal Pendidikan dan Ilmu Kimia*, vol. 2, no. 1, pp. 46–51. 2018.
DOI: 10.33369/atp.v2i1.4646

[3] V. H. Le, C. N. H. Thuc, & H. H. Thuc, "Synthesis Of Silica Nanoparticles From Vietnamese Rice Husk By Sol–Gel Method". *Nanoscale Research Letters*, vol. *8*, no. 1, pp. 58. 2013.
DOI: 10.1186/1556-276X-8-58

[4] Maulida, M. Ginting, & H. Wici, "Ekstraksi Abu Vulkanik Gunung Sinabung untuk Menghasilkan Silika Ge"l. *Jurnal Teknik Kimia USU,* vol. *6*, no. 3, pp. 41–46, 2017.
DOI: c10.32734/jtk.v6i3.1588

[5] L. Silvia, & M. Zainuri. "Analisis Silika (SiO_2) Hasil Kopresipitasi Berbasis Bahan Alam menggunakan Uji XRF dan XRD". *Jurnal Fisika dan Aplikasinya*, vol. 16, no. 1, pp. 12–17, 2020.
DOI: 10.12962/j24604682.v16i1.5322

[6] D. E. Humarli, M. Anas, & V. H. R. Mongkito. "Efek Variasi Temperatur Kalsinasi Terhadap Kandungan Senyawa Silika dari Lumpur Teluk Kendari dengan Menggunakan X-Ray Flourescence (XRF)". *Jurnal Penelitian Pendidikan Fisika ,* vol. 5, no. 4, pp. 346–350. 2020.
DOI: 10.36709/jipfi.v5i4.14803

[7] G. D. Gelyaman, & E. Edi. "Karakterisasi Komposisi Mineral Mud Vulcano Desa Napan Kawasan Perbatasan Republik Indonesia-Replubic Democratic Timor Leste dan Potensi Pemanfaatannya". *Jurnal Chimica et Natura Acta*, vol. 8, no. 2, pp. 58–67. 2020.
DOI : 10.24198/cna.v8.n2.29514

[8] M. I. R. Naikofi, B. Widjaja, & P. Rahardjo. "Studi Reologi Mudvolcano di Desa Napan Pulau Timor dengan Flow Box Test". *1st National Conference on Civil Engineering*. 2017.

[9] H. Mori. "Extraction of Silicon Dioxide from Waste Colored Glasses by Alkali Fusion Using Sodium Hydroxide". *Journal of the Ceramic Society of Japan.* vol. 111 no. 6, pp. 376-31. 2003.
DOI: 10.2109/jcersj.111.376

[10] S. Hadi, Munasir, and Triwikantoro. "Sintesis Silika Berbasis Pasir Alam Bancar menggunakan Metode Kopresipitasi". *Jurnal Fisika dan Aplikasinya*, vol. *7*, no. 2: 110202, 2011,
DOI: 10.12962/j24604682.v7i2.902

[11] R. Hayati, & Astuti, "Sintesis Nanopartikel Silika dari Pasir Pantai Purus Padang Sumatera Barat dengan Metode Kopresipitasi". *Jurnal Fisika Unand ,* vol. 4, no. 3, pp. 282–287, 2017,
DOI: 10.25077/jfu.4.3.%25p.2015

[12] T. Y. Rozi & A. Astuti, "Pengaruh Temperatur Kalsinasi pada Sintesis Nanopartikel Silika Pantai Purus Kota Padang". *Jurnal Fisika Unand,* vol. *5*, no. 4, pp. 351–356, 2016,
DOI: 10.25077/jfu.5.4.351-356.2016

[13] C. Latif, Triwikantoro, & Munasir. "Pengaruh Variasi Temperatur Kalsinasi pada Struktur Silika". *Jurnal Sains dan Seni Pomits,* vol.3, no. 1, pp 4–7, 2014.

[14] G. G. Kaya, E. Yilmaz, & H. Deveci, "A Novel Silica Xerogel Synthesized From Volcanic Tuff As An Adsorbent For High-Efficient Removal Of Methylene Blue: Parameter Optimization Using Taguchi Experimental Design". *Journal Of Chemical Technology And Biotechnology*, vol. *94*, no. 8, pp. 2729–2737, 2019,
DOI: 10.1002/jctb.6089

[15] D. Setyaningrum, E. B. Susatyo, & M. Alauhdin, "Sintesis Membran Kitosan-Silika Abu Sekam Padi untuk Filtrasi Ion Cd^{2+} dan Cu^{2+}". *Indonesian Journal Of Chemical Science*, vol. *3*, no. 1, pp. 2252–6951, 2014.

[16] I. F. Ulfindrayani, N. Fanani, Q. A'yuni, N. Ikhlas, B. L. Gaol, & D. Lestari,

"Pengaruh Perbedaan Preparasi Lumpur Lapindo terhadap Kandungan Senyawanya". *Prosiding Seminar Nasional Teknologi dan Sains (SNasTekS)*, vol. 1, no. 1, pp. 235–240, 2019.

[17] M. Sirappa, & A. Sastiono, "Analisis Mineral Lempung Tanah Regosol Lombok dengan Menggunakan Sinar X dalam Kaitannya dengan Penentuan Sifat dan Cara Pengelolaan Tanah". *Jurnal Ilmu Tanah dan Lingkungan*, vol. *3*, no. 2, pp. 1–6, 2002.

[18] Heriyanti, W. M. Sari, Sutrisno & R. Asyhar, "Analisis Kandungan Slikon (Si) pada Batubara PT. Tambang Bukit Tambi Provinsi Jambi". *Journal of the Indonesian Society of Integrated Chemistry*, vol. 11, no. 2, pp. 57–63, 2019, DOI: 10.22437/jisic.v11i2.7761

[19] A. F. Adziimaa, D. D. Risanti & J. Mawarni, "Sintesis Natrium Silikat dari Lumpur Lapindo sebagai Inhibitor Korosi". *Jurnal Teknik ITS*, vol. 2, no. 2, pp. 384–389, 2013, DOI: 10.12962/j23373539.v2i2.3533

[20] N. P. S. N. Utari, I. W. Sudiarta, & P. Suarya, "Sintesis dan Karakterisasi Silika Gel dari Abu Vulkanik Gunung Agung melalui Teknik Sol-Gel". *Journal Of Chemistry*, vol. 14, no. 1, pp. 30–36, 2020. DOI: 10.24843/JCHEM.2020.v14.i01.p06

[21] R. Zheng, Z. Ren, H. Gao, A. Zhang, & Z. Bian, "Effects Of Calcination On Silica Phase Transition In Diatomite". *Journal Of Alloys And Compounds*, *757*, pp. 364–371, 2018, DOI:10.1016/j.jallcom.2018.05.010

[22] U. Kalapathy, A. Proctor, & J. Shultz, "A Simple Method For Production Of Pure Silica From Rice Hull Ash". *Journal Of Fuel And Energy Abstracts*, vol. 42, no. 1, pp. 45, 2001, DOI:10.1016/S0960-8524(99)00127-3

[23] P. Deshmukh, J. Bhatt, D. Peshwe, & S. Pathak, "Determination of silica activity index and XRD, SEM and EDS studies of amorphous SiO_2 extracted from rice Husk Ash". *Transactions of the Indian Institute of Metals*, vol. 65, no. 1, pp. 63-70, 2012, DOI: 10.1007/s12666-011-0071-z

[24] N. Sari, T. A. Fadlly, & M. Maulinda, "Pengaruh Waktu Milling terhadap Sifat Desorpsi Material Penyimpanan Hidrogen MgH_2-Ni melalui Teknik Mechanical Alloying". *Journal of Serambi Engineering*, vol. 6, no. 3, 2021.