

PROPERTIES AND POTENTIAL OF LAO KHAM VARISCITE'S APPLICATION IN CHEMICALLY BONDED PHOSPHATE CEMENT

* Watcharagon Wongkamjan¹ and Thanawat Jumepaeng²

¹Faculty of Liberal Arts and Science, Roi Et Rajabhat University, Thailand

²Faculty of Sports and Health Science, Thailand National Sports University Udon Thani Campus, Thailand

*Corresponding Author, Received: 14 May 2020, Revised: 12 July 2020, Accepted: 20 July 2020

ABSTRACT: This study aimed to investigate properties and applications of Lao Kham Variscite, LKV, variscite at Lao Kham village Roi Et province Thailand. The sample properties were investigated using microscopic characteristics analysis with digital stereomicroscope, Petrographic analysis with thin-section analysis, chemical compositions, and mineral analysis. The applications of LKV in chemical cement were also investigated using setting time and compressive strength. The results indicated that the randomly selected sample was itself a composite with several crystalline in microstructure characterization most of all were silica oxide (SiO₂) and some part of Variscite (Al(PO₄)(H₂O)₂) clearly the sample needed to be screened for more composition of Variscite before continuing the experiment. It was also found that calcination affected the mineral state of LKV, all samples that had calcined were not found in Variscite, but the mineral composition changed to Aluminum Phosphate (AlPO₄) and non-calcined sample (LKV NOR) found no formation when mixed with 3M NaOH solution while LKV600 had the fastest setting time and compressive strength compared with the reference cement. In the summary LKV 600 was the most reactive and has the potential to be developed for use as Chemically Bonded Phosphate Cement (CBPC).

Keywords: Variscite, Chemically Bonded Phosphate Cement, Petrographic, Aluminum Phosphate, Geopolymer

1. INTRODUCTION

Aluminum phosphate is an aluminum compound found in natural minerals, including angelite, coeruleolactite, evansite, lucinite, metavariscite, sterretite, variscite, vashegyite, wavellite, and zepharovicht. According to a recent study, these minerals can be used as an additive in cement by mixing them with calcium sulfate and sodium silicate solutions as concrete, flux for ceramics, dental cements, waterproofing, and catalyst in organic synthesis [1,2].

Chemically Bonded Cement/Ceramics (CBCs) have been widely applied, especially in radiation protection systems, solid nuclear waste coagulation and encapsulation, active structures in high-temperature composites and medical applications, especially chemically bonded phosphate cement/ceramics. CBPCs, which are ceramic materials that have complete mechanical properties from chemical reactions at low temperatures (below 300 degrees Celsius), instead of normal ceramic properties at high temperatures. Practically, this material has both cements and ceramics qualities. The original CBCs were primarily studied and researched in dentistry [3] and since 1970, magnesium phosphate ceramics had been used in

construction materials for construction work, started by the Brookhaven National Laboratory (BNL) in the United States as well as many studies in Calcium Phosphate Compounds (CPC) which was developed to use as cement material [4,5]. After that, aluminum phosphate (found in the target local material source) has also been applied to CBPCs as well [6].

According to a study of Japakasetr, 1982 [7]; Sheldon, 1984 [8] the phosphate group of aluminum phosphate was found "Variscite" (Al(PO₄)(H₂O)₂) at Lao Kham Village, Si Kaeo Sub-District, Mueang Roi Et District. However, there are no studies that would lead to guidelines for use of industrial raw material. Guidelines for the development of Variscite at Lao Kham Village or Lao Kham's Variscite; LKV, in material and application, are necessary for further development in this study. This work aims to apply LKV for Chemically Bonded Phosphate Cement (CBPC).

2. MATERIALS AND METHODS

2.1 Sample Preparation

The material is a mineral composed aluminum phosphate found at the Lao Kham Village Roi Et

Thailand which was a mineral that is likely to be the secondary mineral of the phosphate group of aluminum phosphate, namely "Variscite" ($\text{Al}(\text{PO}_4)(\text{H}_2\text{O})_2$) [8]. Two groups of samples were collected, collected as a random sample from rocks containing the mineral. Also a screen sample was collected, which was extracted the mineral from a streak in the original rock. In the screen sample group, the sample would be calcined by heat to determine the effect of the temperature, including, non-calcining sample (LKV NOR), sample calcined at 400, 600, 800 and 1,000 °C (LKV400, LKV600, LKV 800 and LKV1000 respectively). Type I Portland cement, according to ASTM C150-07 [9] was used for a reference cement in this study.

2.2 Microscope Analysis

The cold mount method was used for preparing the mounted sample and polished section. This is a method for preparing brittle parts and may cause breakage when polishing the surface by applying the sample in the mold. Then epoxy was applied and set at room temperature for 24 hours. The sample was removed from the mold and polished until the surface was smooth which was indispensable as a prerequisite for the success of investigations using transmitted or reflected light microscopy [10].

2.3 Petrographic Analysis

Thin section petrography was carried out using an Olympus BX-41 imaging petrographic microscope equipped with plane and cross polarization illumination modes. The petrographic analysis was used to study the microstructure of the aggregates, to identify the constituent minerals, and to classify the aggregates. When placed between two polarizing filters set at right angles to each other, the optical properties of the minerals in the thin section alter the color and intensity of the light as seen by the viewer. As different minerals have different optical properties, most rock forming minerals can be easily identified [11].

2.4 Chemical Compositions and Mineral Analysis

The chemical compositions were analyzed with X-ray Fluorescence spectroscopy (XRF). XRF is a relatively effective quantitative technique to determine the elemental composition of any material, with trace element abundances at the ppm level. The mineral composition was analyzed with X-ray diffraction spectroscopy (XRD, Bruker AXS Model D8 Discover) for determining the

concentration of various minerals of material.

2.5 Initial Setting Time and Final Setting Time Testing

Initial setting time and final setting time testing of cement paste and LKV mixed with NaOH 3M were tested in this study with ASTM C 191: Time of setting of hydraulic cement by Vicat needle [12].

2.6 Compressive Strength

Compressive strength index (%) of cement paste and LKV mixing sample was tested by using an ELE EL24-9150 compressive test at the sample age of 14 and 28 days.

3. RESULTS AND DISCUSSION

3.1 Random Sample

The random sample, which was collected from rocks containing mineral is shown in Fig.1.



Fig.1 Random sample

3.1.1 Microscope analysis

In the polished section analyzed with a digital microscope, at magnifications of 15 times and 35 times, the rock sample has the white mineral line in the red-brown coarse particle of sandstone (Figs.2a and 2b). Variscite had a very fine grain particle size (fine-grained, unable to find the mineral grain size) compared to the particle size of the quartz crystals (the mineral grain size around 50-200 μm) in sandstone. Also iron oxide (Iron, Fe) was found distributed in the rock with the yellow to dark brown color particles.

3.1.2 Petrographic analysis

The result of Petrographic analysis, found that the nordstrandite and variscite microscopic texture, both of which consist of quartz mineral

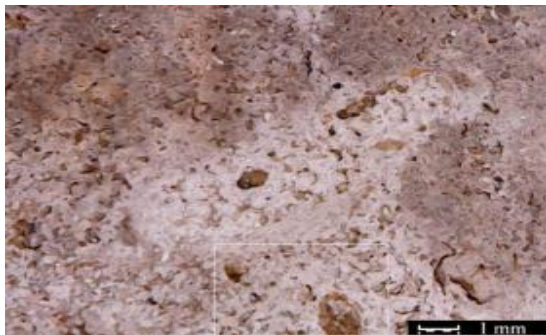
nordstrandite and Variscite ore are shown in Figs.3(a) and 3(b).

3.1.3 X-ray diffraction spectroscopy

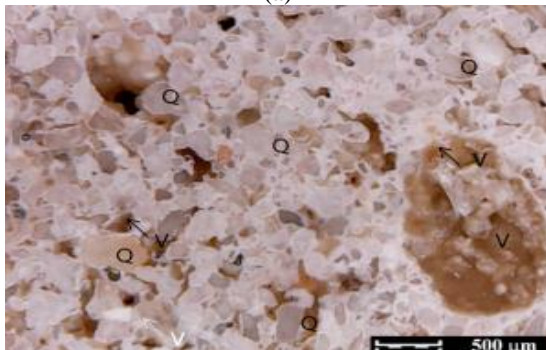
The XRD result shown in Table 1 found that the random sample consisting of quartz (SiO_2), mostly (81.0%) making the majority of the elements are sandstone, because the test samples were tested without the separation of the mineral. However 6.9 percent of variscite ($\text{Al}(\text{PO}_4)(\text{H}_2\text{O})_2$) was found in the sample.

3.1.4 X-ray Fluorescence spectroscopy

The XRF result shown in Table 2, it was found that most of the samples contained silica oxide (SiO_2) or Quartz (33.90%), followed by Phosphorus pentoxide (P_2O_5), with 13.95%.



(a)



(b)

Fig.2 Digital Microscope of Random Sample LKV (a) at 15X (b) at 35X (V: Variscite ($\text{AlPO}_4 \cdot 2\text{H}_2\text{O}$) Q: Quartz (SiO_2))

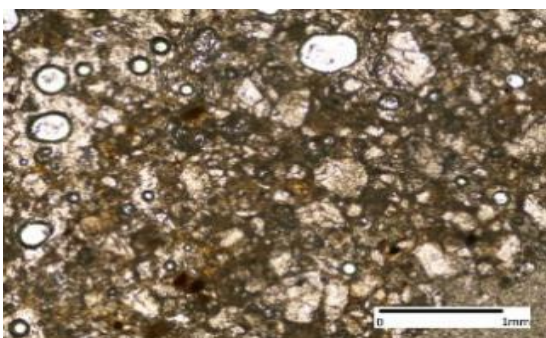
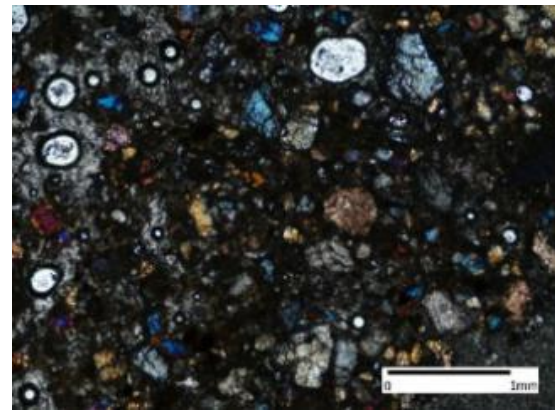


Fig.3 (a)



(b)

Fig.3 Thin section microscopy of Random Sample LKV (a) without using polarized light and (b) using polarized light

Table 1 X-ray diffraction of Random Sample LKV

Mineral	Formula	Concentration (wt%)
Quartz	SiO_2	81.0
Variscite	$\text{Al}(\text{PO}_4)(\text{H}_2\text{O})_2$	6.9
Nordstrandite	$\text{Al}(\text{OH})_3$	7.2
Bayerite, syn	$\text{Al}(\text{OH})_3$	4.8

Table 2 X-ray fluorescence of Random Sample LKV

Formula	Concentration (wt%)
SiO_2	33.90
P_2O_5	13.95
Na_2O	19.59
Fe_2O_3	11.44
Al_2O_3	10.11
CaO	4.73
MgO	5.48
K_2O	0.20
SrO	0.60
Total	100.00

3.2 Screening Sample

Based on the polished section test a white mineral, variscite, had a very fine grain size compared to the particle size of the sand which could be observed, as shown in Fig.4. Therefore, this study separated the mineral from the sandstone to be the main example in the study of the screening sample group, as shown in Fig.5. After that, ground samples passing 300 μm sieve were calcined at various temperatures of 400, 600, 800 and 1,000 degrees in the next study.

3.2.1 X-ray diffraction spectroscopy

The XRD result shown in Table 3 found that the survey sample consisted of the same amount of quartz (SiO₂)(46.12% - 56.72%). LKVNOR with Variscite (Al(PO₄)(H₂O)₂, 23.51%, which was significantly higher than the random sample.

While all the calcined samples were not found Variscite, but the mineral composition was changed to aluminum phosphate (AlPO₄) altogether. Aluminum phosphate hydrate (AlPO₄x (H₂O) was only found in LKV400. When the temperature rose above 600 degrees, some parts of aluminum phosphate hydrate had changed to aluminum phosphate (AlPO₄) which was composed of aluminum phosphate equal to 34.12%, 34.51% and 30.44% for LKV600 LKV800 and LKV1000 respectively.

According to previous study found at high temperature, variscite (Al(PO₄)(H₂O)₂ dehydrate to form berlinite (AlPO₄) which consists of a framework of alternating PO₄ tetrahedra and Al tetrahedral [13]. Also, some parts of phosphate (PO₄) appeared in calcium iron phosphate and calcium hydrogen iron phosphate for the samples that are calcined with temperatures up to 600 degrees while not found this mineral in the sample calcined at 400 degrees.



Fig.4 The mineral from the sandstone texture



Fig.5 White mineral obtained from sandstone extraction use as screening Sample

3.2.2 Setting time

Mixing of NaOH 3M with LKV was conducted to find the setting time. While 3M was the amount of NaOH estimated by the chemical equation balance by weight, to make the reaction even with AlPO₄ in LKV (average of 30% AlPO₄ in the sample and the mixture ratio of the solution and LKV was 0.35). It was found that the non-calcined LKVNOR was not set when being mixed with the 3M NaOH solution while the LKV600 had the fastest formation (initial setting time 15 minutes, and final setting time was 90 minutes). This indicated that the LKV 600 was most likely to react with the NaOH 3M solution, followed by LKV800, LKV1000, and LKV400 respectively. As shown in Fig.6, the setting time of LKV600 was faster than Portland cement according to ASTM (45-60 minutes for initial setting time) [14]. Another study of geopolymer found that the setting time varied from 120 to 870 min. at room temperature affecting variability depending on solution concentrations and the presence of mineral in geopolymer material. However, the setting time of geopolymer as well as at higher curing temperatures to setting at 28-58 min [15-19] at the room temperature LKV600 had significantly faster formations than another geopolymer.

Table 3 X-ray Diffractometer of Screening LKV Sample

Sample	Formula	LKVNOR	LKV400	LKV600	LKV800	LKV1000
Quartz	SiO ₂	46.12	48.51	52.6	55.81	56.72
Kaolinite	Al ₂ (Si ₂ O ₅)(OH) ₄	15.61	13.1	-	-	-
Variscite	AlPO ₄ (H ₂ O) ₂	23.51	-	-	-	-
Aluminum Phosphate	AlPO ₄	-	18.42	34.12	34.51	30.44
Aluminum Iron Phosphate	Al _{0.67} Fe _{0.33} (PO ₄)	-	8.6	-	-	-
Aluminum Phosphate Hydrate	AlPO ₄ x(H ₂ O)	-	6.24	-	-	-
Crandallite	CaAl ₃ (OH) ₆ (PO ₃ (O _{0.5} (OH) _{0.5})) ₂	5.43	5.12	-	-	-
Calcium Iron Phosphate	Ca ₉ Fe ₂ (PO ₄) ₁₄	2.56	-	6.91	7.37	8.23
Calcium Hydrogen Iron Phosphate	Ca ₉ FeH(PO ₄) ₇	6.77	-	6.37	2.31	4.61

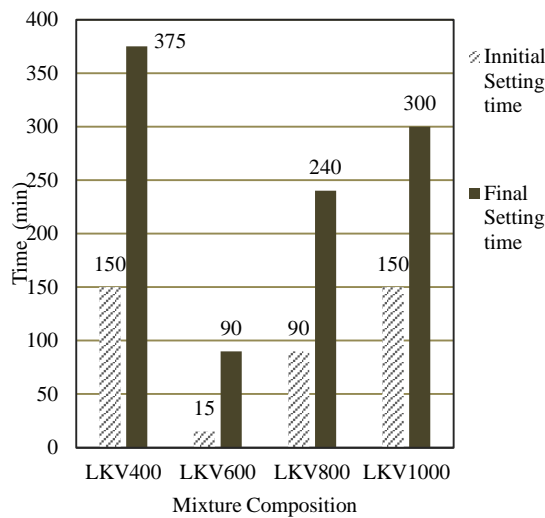


Fig.6 Setting time results of calcined LKV

3.2.3 Compressive strength

Compressive strength index (%) of cement paste and LKV mixing sample at the age of 14 and 28 days as shown in Fig.7 found that LKV600 had the highest compressive strength (24.5%) followed by LKV800 LKV1000 and LKV400 respectively (14.9%, 6.2%, and 3.3%). While LKVNOR, no formation was found so the compressive strength test was not possible. This corresponds to the previous setting time test results that LKV600 has the fastest formation. However, LKV600 has compressive strength only 24.5% with the reference cement, while when considering at 28 days this proportion tends to improve in LKV600 and LKV800 (26.4% and 16.6%). Another study found that many impressive characteristics of geopolymers had higher compressive strength and durability [20-23]. Many of them which were the studies in fly ash used as geopolymer found the different solutions at a ratio of mass between alkaline activator and fly ash. Curing temperatures affected compressive strength, the maximum compressive strength obtained at high concentration of alkaline and high temperature [24-27]. Therefore, the solution type and the appropriate concentration to optimize solution mixing LKV, it should be examined.

Furthermore, the cost of developed LKV for use as chemical cement must be investigated; however, it should consider calcined temperature (the major cost for cement produce) LKV clearly lower (600 degree) than cement (1,450 degree).

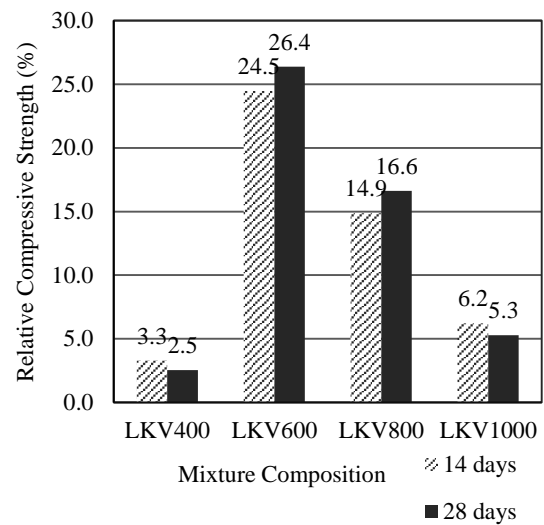


Fig.7 Compressive strength index (%) of cement paste and LKV mixing sample at the age of 14 days and 28 days.

4. CONCLUSIONS

1. LKV, which was a screen sample, had Variscite mineral of 23.5% which was much higher than the random sample.

2. Calcination affected the mineral state of LKV. All samples that had been calcined were not found Variscite, but the mineral composition changed to Aluminum Phosphate.

3. Non-calcined LKVNOR found no formation when mixed with 3M NaOH solution. While LKV600 had the fastest setting time when mixed with 3M NaOH solution. It indicated that LKV 600 was the most reactive with NaOH 3M.

4. The LKV600 had the highest compressive strength. However, when compared to the reference cement, LKV600 only received 24.5% of compressive strength when compared with the reference cement. There should be a study of the appropriate solution and concentration to optimize solution mixing LKV.

5. ACKNOWLEDGMENTS

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6. REFERENCES

[1] Kawasaki S., and Akiyama M., Unique Grout Material Composed of Calcium Phosphate

- Compounds, *International Journal of GEOMATE*, Vol. 4, No. 1, 2013, pp.429-435.
- [2] Pangdaeng S., Sata V., and Chindaprasirt P., Effect of Sodium Hydroxide Concentration and Sodium Silicate to Sodium Hydroxide Ratio on Properties of Calcined Kaolin-White Portland Cement Geopolymer, *International Journal of GEOMATE*, 14, Issue 46, 2018, pp.121-128.
- [3] Colorado H.A., Hiel C., Hahn T., and Yang J.M., Wollastonite-Based Chemically Bonded Phosphate Ceramic Composites, *Metal, Ceramic and Polymeric Composites for Various Uses*, 2011, pp.265-282.
- [4] Dilrukshi R.A.N., Watanabe J., and Kawasaki S., Strengthening of Sand Cemented With Calcium Phosphate Compounds Using Plant-Derived Urease, *International Journal of GEOMATE*, 11, Issue 25, 2016, pp.2461-2467.
- [5] Amarakoon G.G.N.N., Takefumi K., and Satoru Kawasaki S., Effect on Unconfined Compressive Strength of Sand Test Pieces Cemented with Calcium Phosphate Compound, *International Journal of GEOMATE*, Vol. 7, Issue 2, 2014, pp.1070-1075.
- [6] Wagh A.S., *Chemically Bonded Phosphate Ceramics*, 2016, pp.1-283.
- [7] Japakasetr T., *Phosphate in Thailand; Economic Geology Division, DMR, 1982*, p.7.
- [8] Sheldon R.P., 1984, *Phosphate Resource Assessment and Exploration in Thailand*, Thai Department of Mineral Resources, p52.
- [9] American Society for Testing and Materials. *Standard Specification for Portland Cement*, 2007, ASTM C150- 07.
- [10] Moreland G.G., *Preparation of Polished Thin Sections*, *American Mineralogist*, Vol. 53, Issue 6-5, 1968, pp.2070-2074.
- [11] Barber D.J., *Demountable polished extra-thin sections and their use in transmission electron microscopy*. *Mineralogical Magazine*, Vol. 44, 1981, pp.357-359.
- [12] American Society for Testing and Materials. *Time of Setting of Hydraulic Cement by Vicat needle*, 2018, ASTM C 191-18a.
- [13] Ng H.N., and Calvo C., X-ray study of the α - β transformation of berlinite (AlPO_4), *Canadian Journal of Physics*, Vol. 54, Issue 6, 1976, pp.638-647.
- [14] American Society for Testing and Materials. *Standard Specification for Portland Cement*, 2020, ASTM C 150-20.
- [15] Davidovits J., Comrie D.C., Paterson J.H., and Ritcey D.J., *Geopolymeric concretes for environmental protection*. *Concrete International*, Vol. 12, Issue 6, 1976, pp.30-39.
- [16] Giannopoulou I., Dimas D., Maragos I., and Panias D., Utilization of metallurgical solid wastes/by-products for development of inorganic polymeric construction materials. *Global NEST Journal*, 2009, Vol. 11, No 2, pp.127-136.
- [17] Vargas A.S.D., Dal Molin C.C., Vilela A.C.F., and da Silva F.J., The effects of $\text{Na}_2\text{O}/\text{SiO}_2$ molar ratio, curing temperature and age on compressive strength, morphology and microstructure of alkali-activated fly ash-based geopolymers. *Cement and Concrete Composites*, Vol. 33, 2011, pp.653-660.
- [18] Panias D., Giannopoulou I.P., and Perraki T., Effect of synthesis parameters on the mechanical properties of fly ash-based geopolymers. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, Vol. 301, 2007, pp.246-254.
- [19] Rattanasak U., and Chindaprasirt P., Influence of NaOH solution on the synthesis of fly ash geopolymer, *Minerals Engineering Journal*, Vol. 22, 2009, pp.1073-1078.
- [20] Hardjito D., and Rangan B.V., *Development and properties of low-calcium fly ash-based geopolymer concrete*, Research Report, Perth, Australia: Curtin University of Technology, 2005, p.94.
- [21] Duxson P., Fernandez-Jimenez A., Provis J.L., Lukey G.C., Palomo A., and Van Deventer J.S.J., *Geopolymer Technology: The Current State of the Art*, *Material Science*, Vol. 42, 2007, pp.2917-2933.
- [22] Pacheco-Torgal F., Castro-Gomes J., and Jalali S., *Alkali Activated Binders: A review, Part 1, Historical Background, Terminology, Reaction Mechanisms and Hydration Products*, *Construction and Building Materials*, Vol.22, 2008, pp.1305-1314.
- [23] Xu H., and Van Deventer J.S.J., The Geopolymerisation of Alumino Silicate Minerals, *International Journal of Mineral Processing*, Vol. 59, No.3, 2000, pp.247-226.
- [24] Hussain M., Varley R.J., Cheng Y.B., Mathys Z. and Simon G.P., *Synthesis and Thermal Behavior of Inorganic-Organic Hybrid Geopolymer Composites*. *Journal of Applied Polymer Science*, Vol. 96, 2005, pp.112-121.
- [25] Van Jaarsveld J.G.S., Van Deventer J.S.J., and Lukey G.C., The Effect of Composition and Temperature on the Properties of Fly Ash And Kaolinite-Based Geopolymers, *Chemical Engineering Journal*, 89, No. 1-3, 2002, pp.63-73.
- [26] Tabassum R.K., and Khadwal A., Effect of Sodium Hydroxide Concentration on Various Properties of Geopolymer Concrete, *International Journal of Engineering and Technical Research*, 3, No.10, 2015, pp.28-32.
- [27] Hamidi R.M., Man Z., and Azizli K.A., Concentration of NaOH and the Effect on the Properties of Fly Ash Based Geopolymer, 4th International Conference on Process

Engineering and Advanced Materials, Procedia
Engineering 148, 2016, pp.189-193.

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