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Research Article

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Effects of Sodium Silicate Solution to Properties of Geopolymer-based Materials Synthesized from Diatomaceous Earth

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Abstract Investigations on geopolymer-based materials are always interesting topics for researchers. Geopolymer is environmentally friendly material which has been potential applications for many different fields such as technical materials, building materials, insolation or refractories, and others. This study used diatomaceous earth or diatomite (DE) as a raw material for geopolymerization process to develop novel materials with high porosity. DE contains high alumino-silicate resources were mixed with sodium silicate solution for 20 minutes to obtain the geopolymer pastes. Sodium silicate solution was used as an alkaline activator which has been changed for concentration (percentage in weight) to evaluate its effects to properties of DE-based geopolymer materials. After 28 days cured at room conditions (30°C, 80% humididty), the geopolymer specimens were tested for engineering properties and microstructure. In which, the engineering properties included compressive strength (MPa), volumetric weight (kg/m^3), and water absorption (kg/m^3); and the microstructure was characterized for the DE-based geopolymer with the best engineering properties (highest strength, low volumetric weight and water absorption) using X ray diffraction (XRD) and scanning electron microscope (SEM). Results indicated that the DE-based materials are considered as lightweight materials with volumetric weight around 675kg/m^3; the values of compressive strength are in the range of 6.33 to 14.19 MPa; and water absorption is under 275.16 kg/m^3.

Keywords Lightweight Materials, Geopolymer, Diatomaceous Earth, Sodium Silicate Solution, Alkaline Activator, Engineering Properties

Introduction

Geopolymer, originally named as “soil cement”, is a kind of synthetic alumino-silicate material that is found to have several applications including as a material for high-performance composites, ceramics, as well as, as a replacement for Portland cement [1-4]. Geopolymer-based materials are capable of setting rapidly with high final compressive strength and they are highly resistant to chemical attack. Thus, it is predicted that this new material would be popularly applied as a sustainable construction material in the future [1].

Since the raw materials of geopolymer are mainly composed of aluminium oxide, silicon dioxide, and other oxides, its mechanical properties are influenced by the development of its microstructure. Geopolymerization is based on a chemical reaction between different alumino – silicate oxides (Al^{3+}) with silicates under highly alkaline conditions, yielding polymeric Si – O – Al – O bonds [5]. The thermal and chemical stability of these bonds are hypothesized to be determined by the nanostructure and molecular structure within the gel phase [1, 5]. In the raw materials, these oxides are believed to be in amorphous or semi – crystalline phases that participate in geopolymerization process whereas the crystalline phases do not take part in forming the geopolymers [1, 5-8].

DE is one kind of light – weight mineral materials formed million years ago by diatom algae groups. DE contains high silica (60 – 97%) in chemical composition with amorphous structure. There is a vast DE reserves available all over the world.The United States, China, and other countries have DE reserving sources about 250, 110 and 550 million tons respectively up to 2012 [9]. In another report, total DE reserves of the world are near 918.9 million tons estimated before 2006 [10].

Properties of diatomite are different for every region and depend on the forming processes as presented in above part. Outstanding characteristics of DE is high silica SiO2 (60—97%) with amorphous structure [11] and porosity over 80% and water absorption of nearly 100% [12]. Therefore, diatomite naturally is light-weight with grey or light yellow color. The material density varies between 0.25 – 0.5 ton/m^3 [13-14]. Chemical and mineral compositions of DE are complex because it contains many clay minerals in the sinking process such as silicon, sodium, boron, titanium, aluminium, iron, magnesium, potassium [11, 15].

The alkali silicates include sodium and potassium silicates, which have the greatest amount of industrial production as alkaline activators [1, 2]. Lithium silicate with low solubility as well as rubidium and cesium silicates is high costs and the limited industrial production. Therefore, these compounds are not used commonly in research and industry. The sodium and potassium silicates are produced from calcination of carbonate salts and silica and then dissolved in water with the desired ratios. This process also consumes the energy and emitted CO_2 but total energy consumption and CO_2 emission are much lower than Portland cement production [2, 16].

Among the alkali silicates, the sodium silicate solution or water glass solution has more advantages than potassium silicate solution. The sodium silicate solution is more commonly produced and used than the potassium silicate solution [2]. When the potassium silicate is dissolved in solution, formation of KOH causes higher standard enthalpy dissolution (around 60 kJ/mol) than dissolution of the sodium silicate (around 45 kJ/mol) [2, 17-18]. Therefore, the use of high concentration sodium silicate solution could increase the temperature of the geopolymer mixtures, which negatively affects the geopolymerization reactions as well as the hardening process of geopolymer products similarly to increase temperature of solution when used to high concentration of the alkali hydroxides [1,2].

There has been no study research on geopolymer using DE as a raw material and no evaluations for effects of alkaline activators to formation of the geopolymer-based materials. Especially in Vietnam, this is the first study which is carried out for production of DE-based geopolymer materials with using the different concentration of sodium silicate solution or water glass solution (WGS).

Materials and Methods

DE used in this study was from Lam Dong province, Viet Nam where has a large reserve of diatomite without solution for mining and using as a raw material for others industries. DE was ground in a ball miller for 4 hours and dried at 110^{o}C for 24 hours. DE powder had particle size distribution less than 90µm was used for synthesis of geopolymer-based materials. On the other hand, *sodium silicate solution or water glass solution (WGS) was a commercial product from Bien Hoa Chemical Factory, Dong Nai province, Viet Nam.*

Table 1: Mix proportions used in the design of experiments

Mixture (Sample)	Proportion of materials (%wt)	
	DE	WGS
Geo DE100	100	0
Geo DE95	95	5
Geo DE90	90	10
Geo DE85	85	15
Geo DE80	80	20
Geo DE75	75	25
Geo DE70	70	30
Geo DE65	65	35
Geo DE60	60	40

In this study, DE powder was mixed with WGS concentration from 0 to 40% (in weight of liquid powder per solid solution) using a laboratory cement mixer. Water was added to adjust the paste mixtures to appropriately plasticity enough for workability. Table 1 showed the mix proportions of DE and WGS for producing of DE-based geopolymer materials. The fresh pastes of the geopolymer were formed in standard cubic molds with size of 50mm and cured for 28 days at room conditions (30^oC, 80% humidity). Engineering properties of the geopolymer products were evaluated by testing for compressive strength (MPa), volumetric weight (kg/m^3), and water absorption (kg/m^3). From the experimental data, this paper conducts for evaluation on effects of WGS to engineering properties of the DE-based geopolymer materials. All of the tests for engineering properties were carried out according to ASTM C109/C109M [19] and ASTM C140 [20]. Moreover, the geopolymer sample with the highest strength and low water absorption and volumetric weight was characterized microstructure using XRD and SEM.

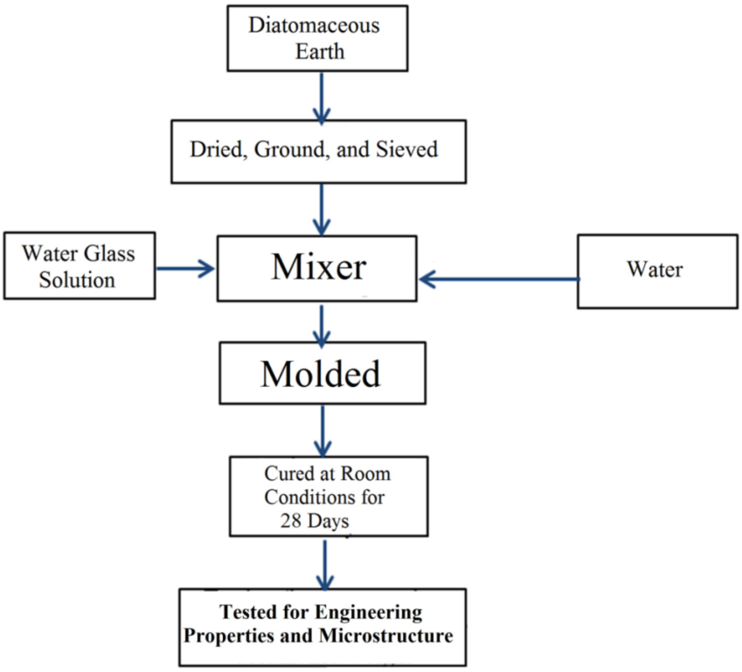

Figure 1: The flow of experimental process

Results and Discussion

Properties of Raw Materials

The raw materials of DE and WGS were tested for physic-chemical properties and the results as shown in Table2. In which DE has moisture content of 5.27%, bulk density of 0.68 g/cm^3, apparent density of 2.54 g/cm^3, mean particle size of 34µm, and LOI value at 8.49%. For the chemical composition using x ray fluorescence (XRF), DE *contains* 6.46% of Al_2O_3, 58.16% of SiO_2, 12.07% of Fe_2O_3, and others. Figure 2 shows XRD pattern of DE which is in amorphous phases of alumina and silica suitable for geopolymerization reactions at high alkaline condition. For mineral compositions, DE has quartz, halloysite, nontronite, and kaolinite. For the alkaline activator, this study used water glass or sodium silicate solution from Bien Hoa chemical factory which has 32% SiO_2, 12.5% Na_2O and 55% H_2O with a silica modulus of 2.5.

Table 2: Physico-chemical properties of DE and WGS

Physico-chemical properties	DE	WGS
Al_2O_3	16.46	-
SiO_2	58.16	32.00
Fe_2O_3	12.07	-
Na_2O	2.22	12.50
K_2O	0.56	-
Others	2.04	-
L.O.I	8.49	-
Moisture content (%)	5.27	55.50
Bulk density (g/cm^3)	0.68	-
Apparent density (g/cm^3)	2.54	-
Mean particle size (µm)	34	-

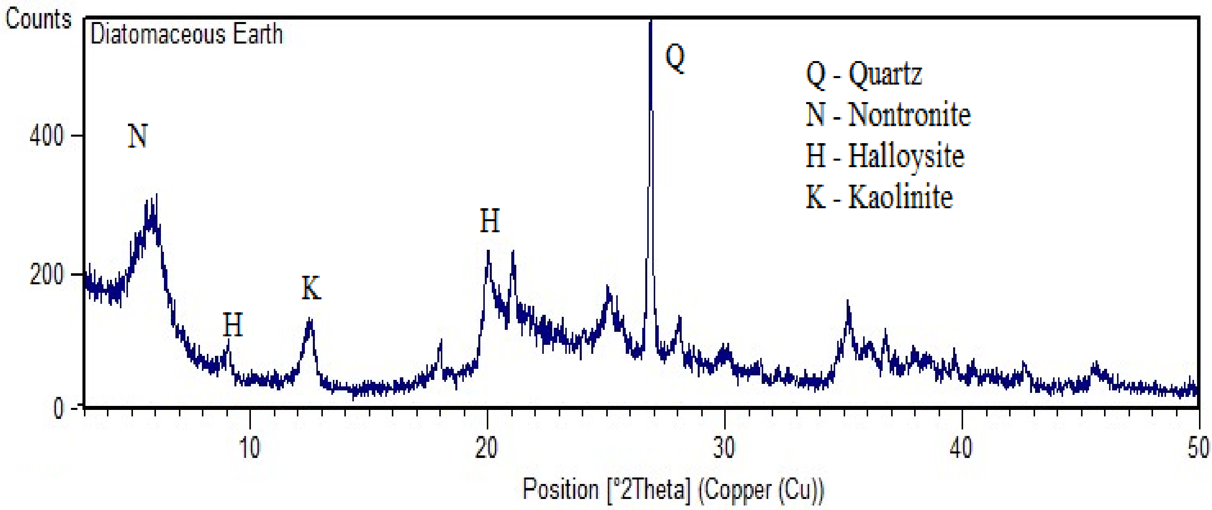

Figure 2: XRD patterns of DE

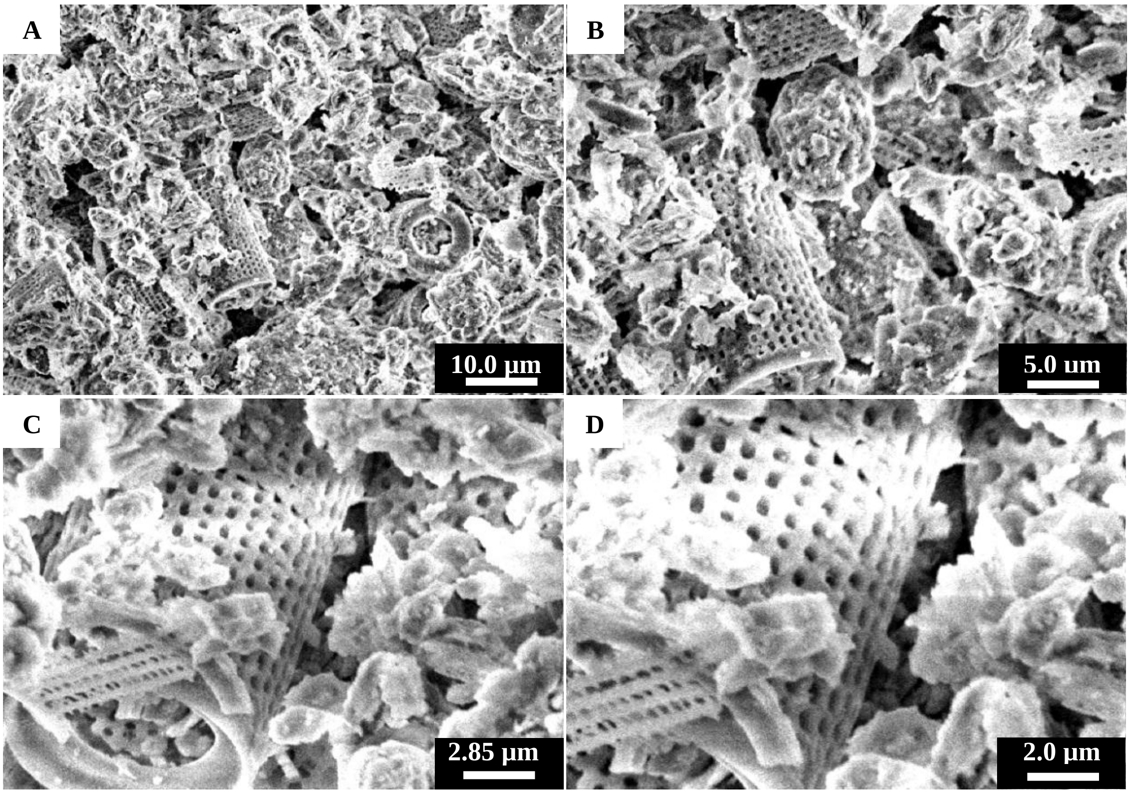

Figure 3: SEM of DE with magnification at 1000X (A), 2000X (B), 3500X (C), and 5000X (D)

Figure 3 shows SEM of DE contains opal ($SiO_2.xH_2O$) with micro pores. Figure 3D shows that the pore size of DE is under 1 µm. DE is a lightweight material with bulk density at 0.68 g/cm^3. These are consistent with the experimental results in Table 2. The porous microstructure of DE makes it a proper raw material to make lightweight geoplymer-based material with low thermal conductivity.

Effects of Alkaline Activator to Engineering Properties of Geopolymer Products

The values of volumetric weight for all DE-based geopolymer specimens are in range of 668 to 678 kg/m^3 which are less than the prescribed volumetric weight (1680 kg/m^3) for a lightweight concrete brick in ASTM C55-99 and ASTM C90-99a [21-22]. This property is inherited from the porous material of diatomite as described in term of 3.1. Moreover, the geopolymerization processes and the evaporation of water during the cured process were also produced micro-pores in the geopolymeric structures [1-2, 4-5].

Table 3: Engineering properties of geopolymer specimen

Samples	Volumetric weight (kg/m^3)	Compressive strength (MPa)	Water absorption (kg/m^3)
Geo DE100	678	0.13 (unformed when exposed in water)	-
Geo DE95	672	6.33	275.16
Geo DE90	668	8.19	254.15
Geo DE85	671	10.22	239.28
Geo DE80	673	12.16	194.33
Geo DE75	669	14.19	181.54
Geo DE70	670	13.27	215.32
Geo DE65	675	9.38 (Swelling solid with macro-cracks)	236.68
Geo DE60	669	7.03 (Swelling solid with macro-cracks)	267.08

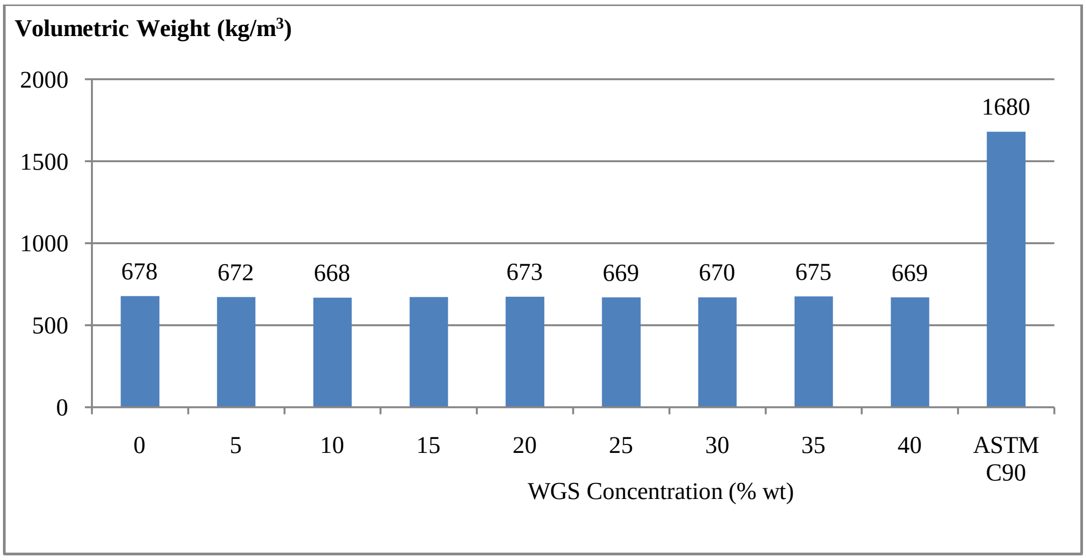

Figure 4: The lower values of volumetric weight compared with ASTM C90 for lightweight concrete brick.

Table 3 showed that the geopolymer sample of Geo DE100 without WGS or alkaline activator had no strength and it was failed in water (test of water absorption), because the activated alumino-silicate resources were impossible to react geopolymerization without alkaline condition. The DE-based geopolymer specimens with 35% - 40% WGS appeared phenomena of swell and macro-cracks. This is related an increase of temperature in high sodium geopolymer paste because of enthalpy of dissolution of the formed NaOH [1, 2]. High temperature in fresh geopolymer pastes may cause thermal stress that produce cracks in the sample. In fact, the DE-based geopolymer sample with 30%WGS was decreased compressive strength at 13.27 and increased water absorption at 215.32 kg/m^3. For WGS concentration from 5 to 25% (in weight), the geopolymer specimens increased significantly the compressive strength from 6.33 to 14.19 MPa and decreased steadily water absorption from 275.16 to 181.54 kg/m^3. These are effects of WGS concentration or alkaline activators to engineering properties of the geopolymer-based materials which are interested in investigations. Thus, the WGS concentration should be optimized around 25% to obtain the DE-based geopolymer products prescribed limit according to ASTM C55 or C90 [21-22] requirements for lightweight concrete brick materials.

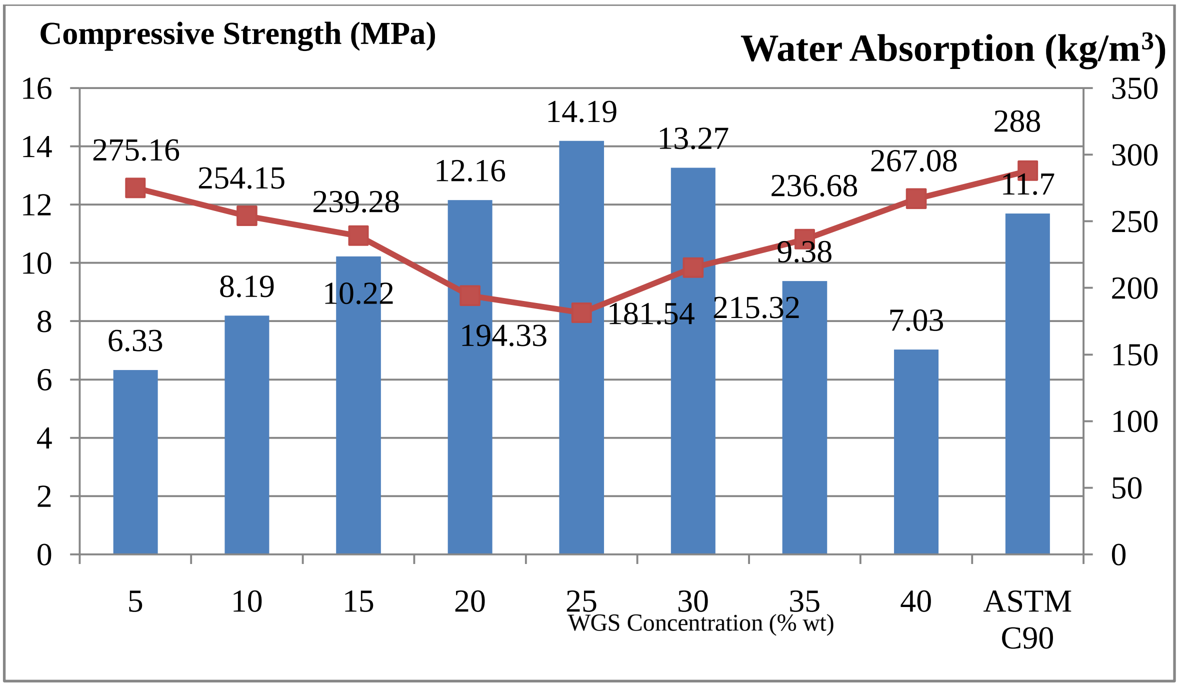

Figure 5: Relationship among WGS concentration (%, in weight) and engineering properties of DE-based geopolymer materials compared with lightweight concrete brick in ASTM C90.

Engineering Properties of Geopolymer Products

The DE-based geopolymer sample of Geo DE75 had the best engineering properties on low volumetric weight and water absorption (kg/m^3) and the highest compressive strength was carried out for analysis of microstructure using XRD and SEM.

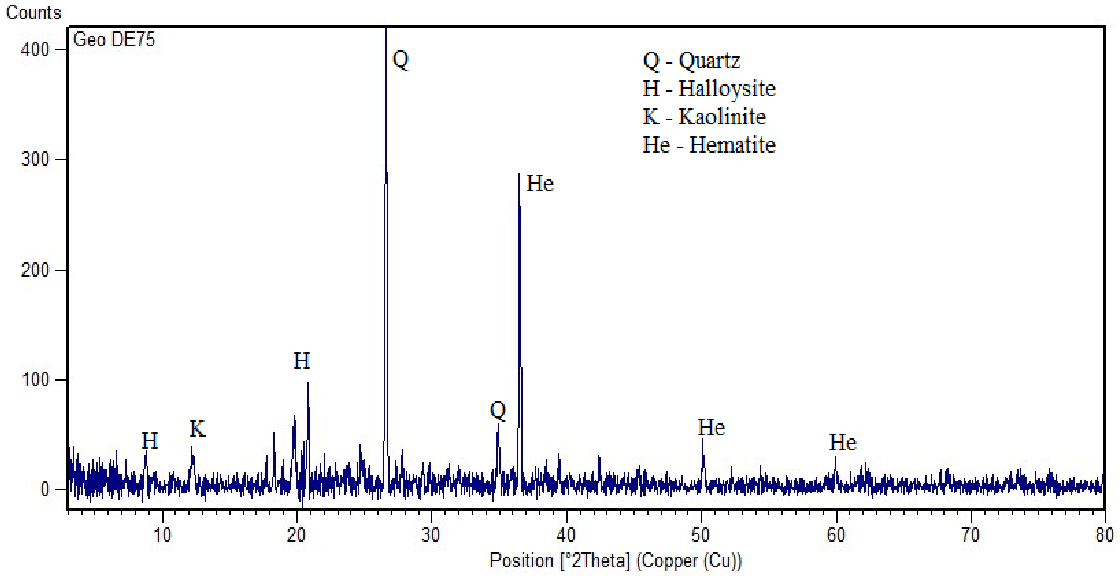

Figure 6: XRD pattern of the DE-based geopolymer material with 25% WGS

The XRD pattern of the DE-based geopolymer sample of Geo DE75 showed differences among structures of raw material (DE) and the geopolymer product. Many key peaks of clay minerals in DE (Fig. 2) were decreased intensity in the geopolymer (Fig. 6) such as nontronite, kaolinite, and halloysite. There was increase of intensity of peaks of hematite which are very low in DE. This is explained that the geopolymerization reactions were dissolved the alumino silicate to from alumino-slicate networks in amorphous phases. The crystal phases of quartz and hematite was dissolved with low concentration and continuously existence in the geopolymer in crystal structures. As a result, the crystal structures appeared in XRD pattern with high intensity among background of amorphous phases in the DE-based geopolymer material.

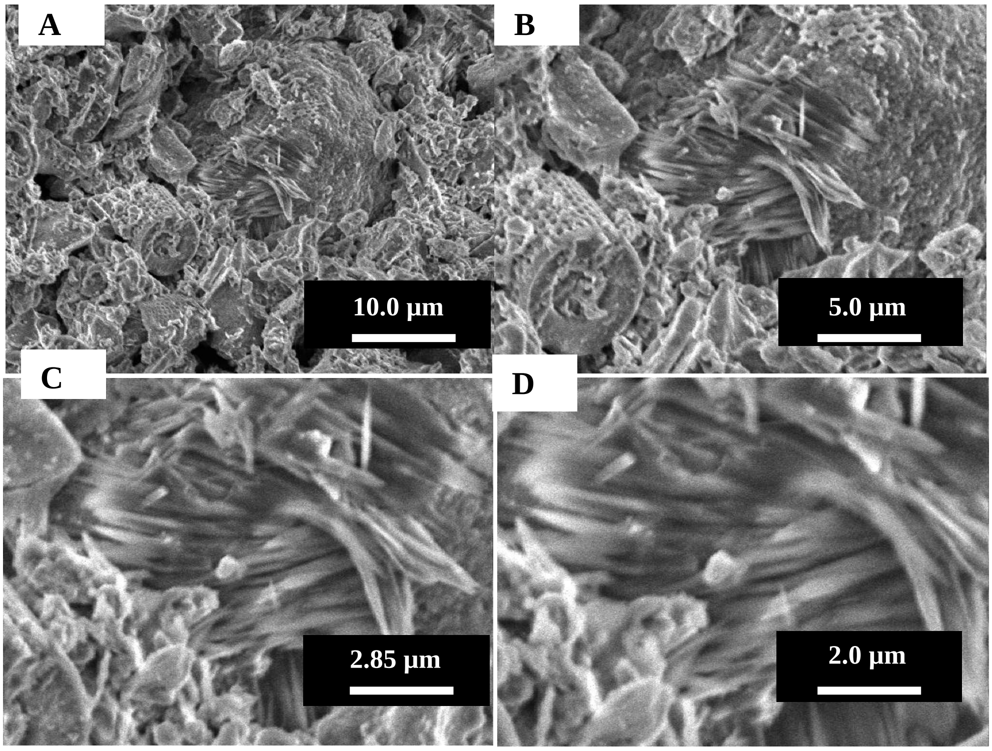

Figure 6: SEM of Geo DE75 with magnification at 1000X (A), 2000X (B), 3500X (C), and 5000X (D)

Microstructures of the DE-based geopolymer material (sample of Geo DE75) had change with appearance of new structure in rods as shown in Figure 6. The length of rods is around 10µm which promoted development of strength for the DE-based geopolymer material. The porous structures of silica have still existed with lower concentration than the raw material of DE. This is easy to realize in Fig. 6A and 6B. Thus, SEM images are explanation for the experimental data of volumetric weight and compressive strength in terms of 3.2.

Conclusions

Diatomaceous earth is one kind of mineral clays with a large reserve in Lam Dong province, Vietnam. The material has no solution for mining and applying for others field. This study utilized DE in combination with sodium silicate solution to synthesize e new lightweight material known as the geopolymer-based material. The DE-based geopolymer materials have engineering properties after cured at room conditions for 28 days responded to requirements of ASTM C55 and C90 for lightweight concrete brick. Effects of alkaline activator (WGS) concentration to formation of the DE-based geopolymer materials were also evaluated via the experimental data related to the engineering properties. In which WGS concentration should be in range of 20-30% in weight of liquid per solid. The DE-based geopolymer material with 75% DE and 25% WGS (in weight) has interesting microstructure with appearances of new phases in amorphous structures. The analytical results of XRD and SEM are also scientific evidences for explanation of the geopolymerization processes in this research.

References

[1]. Davidovits, J. (2011). *Geopolymer chemistry and application,*Institut Géopolymère, Paris, 3rd edition,1-33.

[2]. Provis, J. L. and van Deventer, J. S. J. (2014). *Alkali Activated Materials: State of the art report. RILEM-TC244 AAM,* Springer Dordrecht Heidelberg, New York, 1st edition, 1-100.

[3]. Promentilla, M. A. B., Nguyen, H. T., Pham, T. K., Hinode, H., Bacani, F. T., and Gallardo, S. M. (2016). Optimizing Ternary-blended Geopolymers with Multi-response Surface Analysis, *Waste biomass valorize*, **7**: 929-939.

[4]. Nguyen, H. T., Pham, T. K., and Abdullah, M. M. A. B. (2017). Lightweight Heat Resistant Geopolymer-based Materials Synthesized from Red Mud and Rice Husk Ash Using Sodium Silicate Solution as Alkaline Activator, *MATEC Web Conf.* 97: 011-019.

[5]. Xu,H. and van Deventer, J.S.J. (2000). The geopolymerisation of alumino-silicate minerals. *International journal of mineral processing*, 59: 247-266.

[6]. Nguyen, H. T., Pham, T. K. and Promentilla, M. A. B. (2018). Development of Geopolymer-Based Materials from Coal Bottom Ash and Rice Husk Ash with Sodium Silicate Solutions, *Lecture Notes in Civil Engineering*8: 402-410.

[7]. Bakharev, T. (2005). Resistance of geopolymer materials to acid attack, *Cement and Concrete Research*, 35: 658 – 670.

[8]. Kalaw, M. E. L., Culaba, A. B., Nguyen, H. T., Nguyen, K., Hinode, H., Kurniawan, W., Gallardo, S. M., Promentilla, M. A. B. (2015). Mechanical and thermal properties of geopolymers from mixtures of coal ash and rice hull ash using water glass solution as activator, *ASEAN Journal of Chemical Engineering*, 15: 57-65.

[9]. Crangle, R.D. Jr. (2012).*Diatomite [Advance Release],* U.S. Geological Survey Minerals Yearbook, New Yord, 1-85.

[10]. Klein,S.L. (2006).*Diatomite*, DNPM/RN, New Yord, 200-400.

[11]. Do, Q. M. and Nguyen, H. T. (2010). Prorous brick from Diatomite, *Journal of science and technology,* 76: 123-127.

[12]. Subramanyam B. and Roesli, R. (2000). *Chapter 12 – Inert Dusts*, Dept. of Grain Science and Industry, Kansas State University, 1-200.

[13]. Fields, P., Allen, Korunic, Z., McLaughlin, A., and Stathers, T. (2002). Standardized testing for diatomaceous earth. *Proceedings of the Eighth International Working Conference of Stored-Product Protection,* New York, 1-13.

[14]. Antonides, L. E. (1997). *Diatomite*, Published by the U.S. Bureau of Mines, New Yord, 5-48.

[15]. Fernandez, M. I., Woodward, B. W., and Strornberg,B. E. (1998). Effect of diatomaceous earth as an anthelmintic treatment on internal parasites and feedlot performance of beef steers, *Animal Science,* 66: 635-641.

[16]. Gartner, E. (2004). Industrially interesting approaches to “low-CO_2” cements, *Cem. Concr. Res.*, 34(9): 1489-1498.

[17]. Gurvich, L. V., Bergman, G. A., Gorokhov, L. N., Iorish, V. S., Leonidov, V. Y., Yungman, V. S. (1996). Thermodynamic properties of alkali metal hydroxides. Part 1. Lithium and sodium hydroxides, *J. Phys. Chem. Ref*., 25(4): 1211-1276.

[18]. Simonson, J. M., Mesmer, R. E., Rogers, P. S. Z. (1989). The enthalpy of dilution and apparent molar heat capacity of NaOH (aq) to 523 K and 40 MPa, *J. Chem. Thermodyn*, 21: 561-584.

[19]. ASTM C109/109M, Standard Test Method for Compressive Strength of Hydraulic Cement Mortars (Using 2-in. or [50-mm] Cube Specimens), American Society for Testing and Materials. Philadelphia June 2000. Sec.4, Volume 04.01.

[20]. ASTM C140 – 99b, Standard Test Methods for Sampling and Testing Concrete Masonry Units and Related Units, American Society for Testing and Materials. Philadelphia June 2000. Sec.4, Volume 04.05.

[21]. ASTM C55 – 99, Standard specification for concrete brick, American Society for Testing and Materials. Philadelphia June 2000. Sec.4, Volume 04.05.

[22]. ASTM C90 – 99a, Standard specification for loadbearing concrete masonry units, American Society for Testing and Materials. Philadelphia June 2000. Sec.4, Volume 04.05.