Correlation between initial $\text{SiO}_2/\text{Al}_2\text{O}_3$, $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$, $\text{Na}_2\text{O}/\text{SiO}_2$ and $\text{H}_2\text{O}/\text{Na}_2\text{O}$ ratios on phase and microstructure of reaction products of metakaolin-rice husk ash geopolymer

K. Juengsuwattananon^a, F. Winnefeld^b, P. Chindaprasirt^c, K. Pimraksa^{a,d,*}

^aDepartment of Industrial Chemistry, Faculty of Science, Chiang Mai University, 50200, Thailand

^bEmpa, Swiss Federal Laboratories for Materials Science and Technology, Überlandstrasse 129, CH-8600 Dübendorf, Switzerland

^cSustainable Infrastructure Research and Development Center, Department of Civil Engineering, Faculty of Engineering, Khon Kaen University, 40002, Thailand

^dCenter of Excellence in Materials Science and Technology, Faculty of Science, Chiang Mai University, 50200, Thailand

Abstract

Phase evolution and microstructure development of metakaolin-rice husk ash geopolymer have been investigated. The initial molar ratios of $\text{SiO}_2/\text{Al}_2\text{O}_3$ were designed in the range of 2.0-7.0 with $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ ratios of 0.6-1.6, $\text{Na}_2\text{O}/\text{SiO}_2$ of 0.20-0.72 and $\text{H}_2\text{O}/\text{Na}_2\text{O}$ of 10.0-20.0. The specimens were cured at 30°C for 1-90 days prior to characterization of phase and microstructure as well as mechanical properties. The designed molar ratios were found to correlate with phase and microstructure of reaction products related to their compressive properties. Various zeolite types (sodalite, zeolite A, zeolite Y, zeolite X and faujasite) were prominently observed in samples containing low initial molar ratios of $\text{SiO}_2/\text{Al}_2\text{O}_3$ (2.0-2.5) with $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3 \geq 1.0$ and $\text{H}_2\text{O}/\text{Na}_2\text{O}$ in the range of 10.0-20.0. These low $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios provided low strength geopolymer. Formation of geopolymeric structures was established in samples containing higher initial molar ratio of $\text{SiO}_2/\text{Al}_2\text{O}_3$ (3.0-4.0) with $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ ratio of 1.0 and $\text{H}_2\text{O}/\text{Na}_2\text{O}$ ratios in the range of 10.0-15.0. The highest strength was achieved when initial molar ratios of $\text{SiO}_2/\text{Al}_2\text{O}_3$, $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ and $\text{H}_2\text{O}/\text{Na}_2\text{O}$ were 4.0, 1.0 and 10.0, respectively. When the initial molar ratios of $\text{SiO}_2/\text{Al}_2\text{O}_3$ increased to 6.0-7.0 with $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ ratios of 1.0-1.6 and $\text{H}_2\text{O}/\text{Na}_2\text{O}$ ratios of 10.0-15.0, sodium bicarbonate compounds and unreacted raw materials were observed within the geopolymeric structures. Correlation of phase structures of reaction products with different starting chemical compositions were evaluated and revealed in a ternary composition diagram.

Keywords: metakaolin; rice husk ash; geopolymerization; geopolymer; zeolites

*Corresponding author: Tel: 66-5394-3401 Fax: 66-5389-2262 email: kedsarin.p@cmu.ac.th

This document is the accepted manuscript version of the following article: 1
Juengsuwattananon, K., Winnefeld, F., Chindaprasirt, P., & Pimraksa, K. (2019). Correlation between initial $\text{SiO}_2/\text{Al}_2\text{O}_3$, $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$, $\text{Na}_2\text{O}/\text{SiO}_2$ and $\text{H}_2\text{O}/\text{Na}_2\text{O}$ ratios on phase and microstructure of reaction products of metakaolin-rice husk ash geopolymer. *Construction and Building Materials*, 226, 406-417. <https://doi.org/10.1016/j.conbuildmat.2019.07.146>
This manuscript version is made available under the CC-BY-NC-ND 4.0 license <http://creativecommons.org/licenses/by-nc-nd/4.0/>

Introduction

Geopolymer is an alkali-aluminosilicate material with excellent physical and chemical properties. Alkali earth elements such as Ca^{2+} and Mg^{2+} can be partly located in the geopolymer structure. This material is used in a wide range of potential applications such as mortars and concretes, art and decorating materials, ceramic tiles, thermal insulating materials, fire resistant materials and high-tech composites. Several studies on the synthesis method, their properties and applications have been reported in the literature [1-3]. Geopolymer is made by blending reactive aluminate, silicate and aluminosilicate materials such as silica fume, rice husk ash, waste glass, fly ash, slag and metakaolin with strong alkaline activators. Sodium (or potassium) hydroxide and sodium (or potassium) silicate or their combinations are normally used as alkaline activators [4, 5]. In many cases, alkaline hydroxide can be used without alkali silicates depending on the reactivity of starting materials [6-9]. Metakaolin (MK) is often used as the sources of reactive SiO_2 and Al_2O_3 . The mechanism of geopolymerization to produce geopolymer is related to dissolution–hydrolysis and hydrolysis–polycondensation processes as suggested in many previous studies [1, 2]. An activation with alkaline solution leads to the dissolution of Si and Al from the alumino-silicate starting materials, followed by the orientation, polycondensation, and then the formation of a three-dimensional rigid network. The cross-linking of $[\text{SiO}_4]$ and $[\text{AlO}_4]$ tetrahedra is linked by sharing oxygen atoms whereas the negative charge of Al in IV-fold coordination is balanced with cationic species such as Na^+ , K^+ and Ca^{2+} . Based on a polymeric model of Davidovits [1, 2], the geopolymerization that involved dissolution, hydrolysis, condensation and generation of 3D networks could be expressed as [10, 11-13]:

The generation of three-dimensional rigid networks composes of a variety of structures, such as amorphous phase (geopolymeric gel), semi-crystalline phases, as well as crystalline zeolites depending on the used chemical compositions. Many research works reported the correlation of reactive SiO_2 and Al_2O_3 in each starting raw material, synthesis condition, as well as curing time and temperature with the characteristics of geopolymerization products. The system having low initial molar ratio of $\text{SiO}_2/\text{Al}_2\text{O}_3$ (~ 2) favors the condensation of poly(sialate) structures (PS, atomic ratio of $\text{Si}/\text{Al} = 1$). Increasing the initial molar ratio of $\text{SiO}_2/\text{Al}_2\text{O}_3$ promotes formations of silicate and aluminate species (from hydrolysis) and structures of poly(sialate-siloxo) (PSS, atomic ratio of $\text{Si}/\text{Al} = 2$), poly(sialate-disiloxo) (PSDS, atomic ratio of $\text{Si}/\text{Al} = 3$), and poly(sialate-multisiloxo) (PSMS, atomic ratio of $\text{Si}/\text{Al} > 3$) [12-14, 16].

The influences of the molar ratios of $\text{SiO}_2/\text{Al}_2\text{O}_3$ and $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ affect microstructure and compressive strength of geopolymer binders [11-13]. High strength and durability can be achieved in systems having initial molar ratios of $\text{SiO}_2/\text{Al}_2\text{O}_3$ around 3.5-4.5, $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ in the range of 0.8-1.6, $\text{Na}_2\text{O}/\text{SiO}_2$ of 0.2-0.48 and $\text{H}_2\text{O}/\text{Na}_2\text{O}$ ratios of 10-25. It is worth noting here that these parameters work with highly reactive starting materials such as MK and nano-silica and -alumina [17]. This is due to the fully dissolved capacity of those materials that can provide the final geopolymeric structure with the same molar ratios as initial starting mix. $\text{H}_2\text{O}/\text{Na}_2\text{O}$ ratio is one of the key parameters to allow a development of polycondensation. When $\text{H}_2\text{O}/\text{Na}_2\text{O}$ ratio was higher than 25, sample with $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of 3.3 and $\text{Na}_2\text{O}/\text{SiO}_2$ ratio of 0.25 did not undergo polycondensation leading to an unset material [18].

Although reaction kinetics of MK activated by sodium silicate/sodium hydroxide solutions has already been discussed in literature [11, 13], only a few investigations with the use of a high molar ratio of $\text{SiO}_2/\text{Al}_2\text{O}_3$ have been carried out [15-19]. High SiO_2 content in MK together with sodium silicate slurry can cause high viscosity and inadequate flowability that limits the application. This work, therefore, aimed to study the relation of geopolymeric microstructures and their mechanical properties in the wide range of initial $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratios. The main SiO_2 and Al_2O_3 sources used in this study came from MK. Rice husk ash (RHA) was also used as a source of additional reactive SiO_2 . Various characterization techniques (X-ray Diffraction (XRD), Scanning electron microscopy and Energy dispersive spectroscopy) (SEM&EDX) and Fourier transform infrared spectroscopy (FTIR) were used

to evaluate the microstructure and phase assemblage of the reaction products as a function of molar ratios of $\text{SiO}_2/\text{Al}_2\text{O}_3$, $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$, $\text{Na}_2\text{O}/\text{SiO}_2$, $\text{H}_2\text{O}/\text{Na}_2\text{O}$ and curing time [20-24]. The correlation of the mix design of initial compositions of raw mix with the resulting phase compositions and microstructure of geopolymer was determined and revealed in a ternary composition diagram. Thus this work could add one step further to understand and estimate the geopolymer properties in relation to its compositions.

2. Experimental

2.1 Starting materials

Starting materials to supply SiO_2 and Al_2O_3 were MK and RHA. MK was purchased from BASF (USA) Limited. RHA was prepared by burning rice husk (obtained from northern Thailand) at 700°C and 30 minutes of soaking time in a gas kiln under oxidization atmosphere. The ash was then ground in a ball mill for 24 hours to obtain a median particle size of $9.44\ \mu\text{m}$ (d50). Chemical compositions of the starting materials determined by X-ray fluorescence spectroscopy are listed in Table 1. The initial $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio of used metakaolin was 1.96. Sodium hydroxide pellets and sodium silicate solution were purchased from Sigma-Aldrich and Thai Silicate Chemical Company Limited, respectively.

2.2 Mix design and specimen preparation The initial molar ratios of $\text{SiO}_2/\text{Al}_2\text{O}_3$, $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$, $\text{Na}_2\text{O}/\text{SiO}_2$ and $\text{H}_2\text{O}/\text{Na}_2\text{O}$ were varied from 2.0-7.0, 0.6-1.6, 0.20-0.72 and 10.0-20.0, respectively. All mix design compositions of samples are shown in Table 2. The chemical mixtures were calculated according to theoretical formulation values to generate different types of geopolymer; PS, PSS, PSDS and PSMS [25]. MK and RHA were dried in an electric oven at 110°C to remove excess water prior to mixing with alkaline solution. Sample series were categorized into 2 main parts. The first part was “NH series” standing for the conditions without sodium silicate as alkaline activator and RHA. The second part was “NS series” standing for the conditions with sodium hydroxide and sodium silicate as alkaline activator. RHA was also used to increase the molar ratio of $\text{SiO}_2/\text{Al}_2\text{O}_3$ in NS series. To obtain different molar ratios of $\text{SiO}_2/\text{Al}_2\text{O}_3$ (~ 2.0 -7.0) and $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ (0.6-1.6), proportions of alkaline activator and MK-RHA powders were calculated based on the chemical compositions of each starting material. The combination of sodium hydroxide and sodium silicate solutions as alkaline activator was adjusted with de-ionized water to obtain different $\text{H}_2\text{O}/\text{Na}_2\text{O}$ molar ratios in the range of 10.0-20.0. The

prepared alkaline activator was cooled down to room temperature prior to mixing with MK and RHA. To produce geopolymer specimens in NH series, MK was mixed with NaOH solution for 3 min. Without sodium silicate solution and RHA, $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio of this series was kept constant at 1.96. For NS series, MK and RHA were homogeneously mixed before adding the alkaline activator. The NS series with $\text{SiO}_2/\text{Al}_2\text{O}_3$ in the range of 2.5-3.5 was made by the combination of MK and alkaline activator ($\text{NaOH} + \text{Na}_2\text{SiO}_3$). The higher $\text{SiO}_2/\text{Al}_2\text{O}_3$ range of 4.0-7.0 was obtained by adding additional RHA. After mixing, the pastes were casted into acrylic cubic molds with 25 mm x 25 mm x 25 mm and vibrated for 1 min. All specimens were covered with plastic sheet and cured in a moist chamber at 30°C for 1-90 days.

2.3 Measurement and characterization

The compressive strength of hardened geopolymer pastes at various curing times were measured. The loading rate for compressive measurement was set at 5.0 and 0.68 mm/min with a maximum load of 100 kN. The fragments of samples after strength test were used for further investigations. Isopropanol was used to stop geopolymerization reaction in samples. This was followed by rinsing with diethyl ether (ACS reagent, $\geq 98.0\%$) to remove the isopropanol. The samples were then dried in an electric oven at 50°C for 24 hr [25-27]. After drying, they were cut into small-flat pieces and ground to fine powders for SEM&EDS and XRD, respectively.

Fine powders were sieved through a 250-mesh for an investigation of mineralogical compositions using X-ray diffractometers with Co $K\alpha$ (PANalytical) and Cu $K\alpha$ radiation (Bruker D4 Endeavor). Samples prepared using NaOH activator (NH series) were analyzed using Cu $K\alpha$ radiation, while those prepared using sodium hydroxide/sodium silicate activator (NS series) was analyzed using Co $K\alpha$ radiation. Data from PANalytical X-ray diffractometer was collected over an angular range of 5-90° with 0.017° 2 θ step size and scan rate of 0.708°/min, resulting in a total measurement time of about 2 hours. For Bruker D4 Endeavor X-ray diffractometer, the data was collected over an angular range of 5-70° with 0.02° 2 θ step size and scan rate of 5.42°/min, resulting in a total measurement time of about 12 minutes.

Sample preparation procedures for SEM&EDS analysis were divided into the following two types: fractured samples (qualitative analysis) and polished surface samples (quantitative chemical compositions analysis-EDS). To examine the fractured sample, small piece of the specimen was adhered to aluminum stub with a piece of double-sided conducting tape and then dried at 50°C for two hours. Before analysis, the gold layer was sputtered onto the surface of the sample for 30 seconds to avoid a charging effect. A cold-field emission SEM (JEOL JSM-6335F) was used to study the morphology of the reaction products of the fractured surface.

For polished surface sample, a piece of geopolymer sample was first mounted in an epoxy resin and then cured at room temperature for 24 hours. The cured specimen was roughly polished to obtain a flat surface using 240, 600, 1200, 2400, and 4,000 grit of SiC sandpapers. Then, specimens were finely polished on a lap wheel with 1 and 0.3 micrometer alumina colloidal suspensions. After each polishing step, the specimens were cleaned with alcohol, dried, and coated with carbon for 1 minute to provide a conductive surface for SEM imaging. Finely polished samples were analyzed using scanning electron microscopy (Philips XL30 ESEM FEG) interfaced to an energy dispersive X-ray spectrometer (EDS) to obtain quantitative chemical compositions of reaction products. 45-65 points of each sample were collected to calculate Si/Al and Na/Al atomic ratios.

Fourier transform infrared spectroscopy was performed with the attenuated total reflection (ATR) sampling technique for measuring the absorption spectra of the set geopolymer samples. With ATR-FTIR, opaque samples can be detected without destruction of samples. The spectra obtained from ATR-FTIR is a collection of evanescent waves, which are transmitted through the internal reflection of a high refractive index ART crystal. The absorbance spectra of the set geopolymer samples were collected at 4,000–600 cm^{-1} .

3. Results and discussion

3.1 Characterization and mechanical properties of geopolymer samples

3.1.1 Phase structure investigation using XRD

Phase and microstructure developments of geopolymer samples as summarized in Table 2 were determined using several techniques; XRD, SEM, and ATR-FTIR. XRD patterns of the formulated samples cured at 30°C for 1-90 days are presented in Fig. 1. MK and RHA as

starting materials showed broad peak around 25° and 27° of 2-Theta (CoK α radiation) reflecting the amorphous nature of both materials. TiO₂ and quartz were also detected as minorities in both MK and RHA. In general, the developments of phase and microstructure of geopolymer samples were gradually changed over time. With an increase in curing time, reaction products of hardened samples were gradually developed either in forms of porous (zeolite phases) and tightly packed structures (amorphous geopolymeric gel), depending on the synthesis conditions as shown in Fig. 1. Fig. 1 (a), (b) and (c) presented XRD patterns of samples using different SiO₂/Al₂O₃ molar ratios of 2.5, 3.0, and 4.0, with constant ratios of Na₂O/Al₂O₃ (1.0) and H₂O/Na₂O (10.0). With prolong curing times from 1 to 90 days, broad peaks of starting materials (MK and RHA) were gradually shifted from 25° to around 34° of 2-Theta (CoK α) indicating the formation of geopolymeric gel. Only inert titania (TiO₂) which was present in starting MK was detected. Geopolymer samples containing SiO₂/Al₂O₃ ratios of 3.0 and 4.0 in NS3010A and NS4010A showed only amorphous gel structures as shown in Fig. 1(b) and (c). While geopolymer samples with lower SiO₂/Al₂O₃ molar ratio (2.5) and the same Na₂O/Al₂O₃ and H₂O/Na₂O ratios was more sensitive to form zeolite A as shown in Fig. 1 (a). With different batch of preparation, different phase could be obtained in sample with SiO₂/Al₂O₃ of 2.5. Zeolite A was formed in batch 1 at only 1 day while batch 2 could undergo geopolymerization. As known, geopolymerization generally undergoes through dissolution–hydrolysis and hydrolysis–polycondensation. Once alkaline solution is introduced to the system of aluminosilicate and silicate starting materials, the disordered Si–O–Si and Al–O–Si starting materials can be dissolved into small units and afterwards transformed into a colloidal phase dispersed in alkaline solution media. When silicate and aluminate tetrahedral molecules are sufficiently created, reconstruction of coagulated structures occurred with a release of water (polycondensation). Dissolved silicate species were very crucial factor to start polycondensation reaction [1, 28-31]. With the lowest SiO₂/Al₂O₃ molar ratio (2.0), the crystalline sodalite, zeolite type-A and faujasite were detected as majority in samples having the similar Na₂O/Al₂O₃ (1.0) and H₂O/Na₂O (10) as shown in Fig.1 (m). SiO₂/Al₂O₃ of 2.0 with MK as starting material could be prepared with no sodium silicate. As a matter of fact, the low SiO₂/Al₂O₃ molar ratio was about to reach chemical structure of zeolitic materials as demonstrated in Fig. 1(n) and (o) [32-34]. At this SiO₂/Al₂O₃ ratio, the silicate (SiO₄) and aluminate (AlO₄) species were linked together to form zeolite structure rather than amorphous geopolymer because Na⁺ ions could be more largely involved in zeolite structures for charge balancing. Therefore, for MK without sodium

silicate solution, samples tended to undergo crystallization rather than geopolymerization [29-31]. However, phase transformation to generate geopolymeric gel in system having higher initial $\text{SiO}_2/\text{Al}_2\text{O}_3$ (~ 4.0) with limited Na_2O content was hindered due to the difficulty of raw material dissolubility as shown in Fig. 1(c) demonstrating the amorphous phases of unreacted raw materials within the geopolymer structure. The flowability of some samples evaluated as viscosity are shown in Table 3. The viscosity of slurry with higher $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio was larger than that with lower $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio. The increase in viscosity corresponded to an increase in a degree of geopolymerization when $\text{SiO}_2/\text{Al}_2\text{O}_3$ increased from 2.0 to 4.0. Higher $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio (5.0-7.0) provided the lower degree of geopolymerization.

Na_2O and H_2O were also included as influential parameters that affected the dissolution and hydrolysis reaction in geopolymerization process. The presence of Na_2O in alkaline solution caused the breaking down of Si and Al from raw materials (dissolution) resulting in formation of oligomeric silicate and aluminate species (hydrolysis). These oligomeric silicates then condensed with $\text{Al}(\text{OH})_4^-$, creating networks of various kinds of structures [11-14]. Na_2O localized nearby aluminate species in geopolymeric structure for charge balancing. H_2O bonded well with Na_2O via ion-dipole interaction. XRD patterns in Fig. 1 (h), (i), (k), (m), (n) and (o) are for the ratios of $\text{SiO}_2/\text{Al}_2\text{O}_3$ from 2.0-5.0, $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ from 1.2 to 1.4, $\text{Na}_2\text{O}/\text{SiO}_2$ from 0.28-0.72 and $\text{H}_2\text{O}/\text{Na}_2\text{O}$ from 10.0-12.5 of systems with and without sodium silicate. Better dissolubility of Si and Al from raw materials using higher contents of Na_2O was obtained in samples of NS3014A, NS4014A and NS5014A as shown in Fig. 1(k), (h) and (i), respectively. Shifting position of broad peak of amorphous starting materials from 25° to 34° (2-Theta) was observed, showing higher content of geopolymeric gel phase compared to those of lower Na_2O content in samples NS3010A and NS4010A (Fig. 1 (b) and (c)). It was noticeable that sample NS5010A ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 5.0$, $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3 = 1.0$, $\text{Na}_2\text{O}/\text{SiO}_2 = 0.20$, $\text{H}_2\text{O}/\text{Na}_2\text{O} = 10.0$) showed very high viscosity, and increasing Na_2O in sample of NS5014A ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 5.0$, $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3 = 1.4$, $\text{Na}_2\text{O}/\text{SiO}_2 = 0.28$, $\text{H}_2\text{O}/\text{Na}_2\text{O} = 10.0$) was to adjust flowability and increase dissolubility of Si and Al in raw materials. It was worth noting here that for the sample with medium $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio (NS4014A) ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 4.0$, $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3 = 1.4$, $\text{Na}_2\text{O}/\text{SiO}_2 = 0.35$, $\text{H}_2\text{O}/\text{Na}_2\text{O} = 10.0$), no crystalline phase was observed overtime. With lower $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio (NS3014A) and prolongation of curing times to 90 days ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 3.0$ and $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3 = 1.4$), crystalline zeolite-Y was formed as a major phase. This was probably due to the excess Na_2O left over from

geopolymerization thus creating zeolitization. With high Na_2O content and the lowest $\text{SiO}_2/\text{Al}_2\text{O}_3$ (2.0) ($\text{Na}_2\text{O}/\text{Al}_2\text{O}_3 = 1.2\text{-}1.4$, $\text{Na}_2\text{O}/\text{SiO}_2 = 0.61\text{-}0.72$ and $\text{H}_2\text{O}/\text{Na}_2\text{O} = 10.0$) as shown in Fig. 1 (n) and (o), crystalline zeolitic materials such as sodalite, zeolite-A and faujasite could be observed as majorities.

Water (H_2O) was used to mainly support hydrolysis reaction and to adjust workability for the synthesis of geopolymer binder. In this study, the initial molar ratios of $\text{H}_2\text{O}/\text{Na}_2\text{O}$ were kept between 10.0-20.0 to achieve good workability for casting and to maintain the geopolymerization. With higher than 25.0, the sample did not get set [18]. As shown in Table 3, sample with $\text{H}_2\text{O}/\text{Na}_2\text{O}$ of 25.0 contained very low viscosity when compared to that with $\text{H}_2\text{O}/\text{Na}_2\text{O}$ ratio of 15.0. Comparison of results of samples using constant initial $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ ratio (1.0) with different $\text{SiO}_2/\text{Al}_2\text{O}_3$ and $\text{H}_2\text{O}/\text{Na}_2\text{O}$ ratios were observed. For samples having low initial ratio of $\text{SiO}_2/\text{Al}_2\text{O}_3$ (2.5) and medium ratio of $\text{H}_2\text{O}/\text{Na}_2\text{O}$ (12.5), the presence of zeolite-A was detected in all ages of curing (1-90 days), as shown in Fig. 1(d). Contrary trend was observed in samples with medium $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios of 3.0 and 4.0 and medium level of $\text{H}_2\text{O}/\text{Na}_2\text{O}$ ratios of 12.5 and 15.0 as shown in Fig. 1(e) and (f), respectively. There was no zeolite formation. Samples having similar $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios (3.0 and 4.0) but lower ratio of $\text{H}_2\text{O}/\text{Na}_2\text{O}$ (10.0) also presented the formation of geopolymeric gel as a major reaction product with no zeolitic formation.

It was worth noting here that changing both $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ and $\text{H}_2\text{O}/\text{Na}_2\text{O}$ ratios dramatically displayed an impact on the formation of different phase structures in reaction products. Formulation of geopolymer samples prepared with low $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ and the highest $\text{H}_2\text{O}/\text{Na}_2\text{O}$ content was revealed in Fig. 1(g), belonging to sample of NS3006D ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 3.0$, $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3 = 0.6$, $\text{Na}_2\text{O}/\text{SiO}_2 = 0.20$, $\text{H}_2\text{O}/\text{Na}_2\text{O} = 20.0$). It showed amorphous phase of unreacted raw materials due to insufficient alkalinity for dissolution. However, this sample showed no zeolite phase at $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of 3.0, although the water content was quite high. Samples with high $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ and low level of $\text{H}_2\text{O}/\text{Na}_2\text{O}$ were prepared as samples of NS3016B ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 3.0$, $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3 = 1.6$, $\text{Na}_2\text{O}/\text{SiO}_2 = 0.53$, $\text{H}_2\text{O}/\text{Na}_2\text{O} = 12.5$) and of NS3014A ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 3.0$, $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3 = 1.4$, $\text{Na}_2\text{O}/\text{SiO}_2 = 0.47$, $\text{H}_2\text{O}/\text{Na}_2\text{O} = 10.0$) which was elaborated in Fig. 1(j) and (k), respectively. The particulate zeolite types Y and faujasite were observed in these samples at all curing times (1 and 90 days). These results agreed with our previous works (using only NaOH as activation), which using molar ratio of

$\text{SiO}_2/\text{Al}_2\text{O}_3 = 2.0$ in range of $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ ratio = 0.6-2.4, $\text{Na}_2\text{O}/\text{SiO}_2 = 0.31$ -1.22 and $\text{H}_2\text{O}/\text{Na}_2\text{O} = 7.5$ -27.5 [6, 7] as demonstrated in Fig. 1 (m), (n) and (o). We repeated the experiments for comparison in this work. Every water content provided a precipitation of zeolitic materials in NH series. Other authors suggested that high water content accelerated rate of hydrolysis reaction in system having high content of Na_2O , leading to a construction of long-range order structure (crystalline phase) in reaction product of geopolymer [29, 30].

3.2.2 Microstructure investigation using SEM&EDS

SEM image of MK is shown in Fig. 2(a) displaying lumps of clay particles in various sizes. Lumps of platy particles still appeared in MK starting materials. Zeolite-A as majority was observed in fractured specimen prepared from non-sodium silicate system as shown in Fig. 2 (b). Its particle size was approximately 0.5-1.0 μm . Geopolymeric phase could also be observed as minority. The morphology of sample using low $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of 2.0 with $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ of 1.0 and $\text{H}_2\text{O}/\text{Na}_2\text{O}$ of 12.5 as shown in Fig. 2(b) displayed cubic structure of zeolite-A corresponding to XRD result as shown in Fig. 1 (m). Sample using $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of 3.0 with high $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ ratio of 1.6 and $\text{H}_2\text{O}/\text{Na}_2\text{O}$ of 12.5 as shown in Fig. 2(c) contained faujasite particles as a majority which agreed with XRD pattern as shown in Fig. 1(j)). These evidences were used as a guidance to distinguish between the crystalline structure of zeolite and amorphous phases of raw material and geopolymer gel in polished samples as demonstrated in the following results.

Morphologies of polished geopolymer samples with different initial molar ratios of $\text{SiO}_2/\text{Al}_2\text{O}_3$, $\text{H}_2\text{O}/\text{Na}_2\text{O}$ and $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ curing at 30°C for 7, 28 days are shown in Fig. 3. EDX analysis of each phase in reaction products as atomic ratio (Na/Al vs. Si/Al) were determined and presented in Fig. 4. Identification of reaction products after geopolymerization could be obtained from these photomicrographs. The results revealed that zeolitic phase and unreacted raw materials were imbedded in geopolymer gel matrix. Formations of zeolite-A in samples of NH2010B, NS2510A and NS3014A as shown in Fig. 3 (a), (b) and (e), respectively, and remaining of unreacted raw materials in samples of NS3006D and NS4010C as shown in Fig. 3 (c) and (g), respectively, resulted in the porous structures within geopolymeric matrix. The presence of submicron size zeolites in samples of NH2010B and NS2510A as shown in Fig. 3 (a) and (b) agreed with XRD-patterns as shown in Fig. 1 (m) and (a), respectively. Formations of amorphous geopolymeric phases

corresponded to the dense structures could be perceived in samples of NS3010A, NS4010A, NS4014A and NS5014A as shown in Fig. 3 (d), (f), (h) and (i), respectively. The remaining of unreacted MK was still found in these samples. An appearance of non-binding structure such as zeolite (porous material) and unreacted material typically decreased compressive strength of geopolymer sample as reported in many previous studies [35, 36]. However, the presence of zeolitic material in geopolymeric matrix can be a promising combination for various applications, for example, waste adsorption and stabilization.

Single EDX spots were applied to cover a wide area of geopolymer samples to quantify element compositions of final reaction products. Atomic ratio of Na/Al versus Si/Al obtained from reaction products were plotted to evaluate geopolymer structures as a function of initial mixed design compositions as shown in Fig. 4. To interpret the relation, initial molar and atomic ratios of raw mixes as given in Table 2 were compared with the atomic ratios of geopolymerization products analyzed using XRD and EDX. From these results, they could determine the type of geopolymeric networks (PS, PSS, PSDS, PSMS) and phase structures (amorphous or crystalline) of the reaction products [37, 38].

Assumption of phase development could be derived from the plot of EDX analysis; fast and slow rates of reaction in dissolution and polycondensation stages. Samples having atomic ratio rising along y-axis were found to undergo fast reaction. Atomic ratio of Si/Al in initial raw materials and reaction products was equal in samples with low Si/Al ratios about 1.0-1.25 (NH2010B and NS2510A) denoting a desirable capability of Al^{3+} substitution in silicate tetrahedral networks to generate polysialate structure (PS). Samples having this low initial Si/Al ratio, and Na/Al ratio of 1.0 preferred to form zeolite as a majority examined by XRD and SEM together with geopolymeric gel as a minority [13].

Gradually increasing of atomic Si/Al ratio in reaction products was observed along x-axis corresponded to slow reaction rate of dissolution and polycondensation stages. Formations of networks of PSS, PSDS, PSMS corresponding to Si/Al ratios of 2, 3, and >3, respectively with Na/Al of 1.0 were observed in samples using higher initial atomic ratios of Si/Al of 1.5-3.0, Na/Al in the range of 0.6-1.0 and Na/Si of 0.33-0.67. Samples having atomic Na/Al ratios in the range of 0.6-1.0 tended to contain unreacted raw materials together with geopolymeric phase. For example, samples of NS3006D and NS4010C showed larger hump

peaks of MK as confirmed in Fig. 1 (g) and (f) than other samples. Previous work suggested that dilution of alkaline activator concentration (low initial Na_2O and high H_2O contents) reduced the dissolution rate of active silicate from raw materials leading to the hindrance of crosslink formation of silicate and aluminate oligomers [19, 29]. Supplement of active silicate species improved the dissolution of raw materials (moderate contents of Na_2O and H_2O) in samples of NS3010A and NS4010A leading to the formation of complex crosslink structures. Amount of geopolymeric phase found in sample of NS3010A (Si/Al of 1.5) with PSS framework was smaller than sample of NS4010A (Si/Al of 2.0) with the same Na/Al ratio. The EDX plot of sample having Si/Al ratio of 2.0 mostly presented PSDS structure together with small amount of PSMS structure. As known well, the formation of geopolymer gel with high complex framework was related to the improvement in mechanical and physical properties [16]. It was worth noting here that a slight increase in H/Na ratio from 10.0 to 15.0 in starting mix affected the Na/Al ratios in reaction products. For example, samples of NS4010A and NS4010C although using the same Na/Al ratio from the beginning (Si/Al = 2.0, Na/Al = 1.0, Na/Si = 0.5). Sample having low H/Na ratio showed higher Na/Al ratio in reaction product than sample having high H/Na, indicating the greater polycondensation of low H/Na condition that consequently generated geopolymeric structure with more complex crosslink.

EDX plots agreed well with XRD analysis in that an increase in initial Na_2O content supported the dissolution rate of raw materials. All samples having Si/Al ratios of 1.5 (NS3014A), 2.0 (NS4014A), and 2.5 (NS5014A) with the same Na/Al ratio of 1.4 showed rapid reaction rate as a function of increasing atomic Na/Al ratio from 1.0 to 1.4 (along y-axis). It was also found that initial atomic ratios of starting materials conformed to the reaction products. The high probability was found in samples having Si/Al ratios of 1.5 and 2.0 with PSS structure while sample having Si/Al ratio of 2.5 presented the formation of PSDS structure. High Na_2O content could promote rate of reaction and support the ability of Al^{3+} substitution in silicate networks. However, the excess Na ion could interact with CO_2 at ambient temperature forming sodium bicarbonate compound. A small amount of the carbonate compound could not be observed by XRD analysis. Therefore, the presence of carbonate compound was confirmed using FTIR as shown in Fig.5.

3.2.3 Microstructure investigation using FTIR

Fig. 5 showed the ATR-FTIR spectra analysis of geopolymer pastes with different initial molar ratios of $\text{SiO}_2/\text{Al}_2\text{O}_3$, $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$, $\text{Na}_2\text{O}/\text{SiO}_2$ and $\text{H}_2\text{O}/\text{Na}_2\text{O}$ cured at 30°C for 28 and 90 days. FTIR spectra of MK and RHA as starting materials were approximately $1060\text{--}1064\text{ cm}^{-1}$. The shift to lower wave number of two main bands of the starting materials were examined according to phase development in geopolymer binder. When the transformation from starting materials into geopolymeric structures took place, strong and broad peak in the region of $1060\text{ to }1064\text{ cm}^{-1}$ associated with asymmetric Si-O-Si and Si-O-T stretching in RHA and MK were shifted to around $953\text{--}994\text{ cm}^{-1}$, showing the incorporation of aluminum in geopolymer structure, when T was defined as Si or Al. Weak bands at 796 cm^{-1} belonging to symmetric Si-O-Si stretching in RHA [22, 23, 25, 39] and at 800 cm^{-1} belonging to O-Al-O bending vibration in MK disappeared, implying the destruction of Si and Al from raw materials [23, 40]. Instead, the formation of bands at $695\text{ and }697\text{ cm}^{-1}$ were detected, denoting as symmetric stretching vibration of Si-O-Si in geopolymer structure [30]. Other spectra were observed at $3350\text{--}3500\text{ cm}^{-1}$ and $1640\text{--}1655\text{ cm}^{-1}$ describing as stretching and bending vibration of water molecules, respectively which were from geopolymerization [24, 28, 30-32]. The FTIR spectra complied with the EDX results. It was worth noting here that the mix design compositions of $\text{SiO}_2/\text{Al}_2\text{O}_3$, $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$, $\text{Na}_2\text{O}/\text{SiO}_2$ and $\text{H}_2\text{O}/\text{Na}_2\text{O}$ in starting materials altered the geopolymerization kinetics and phase structures of geopolymer binder. Based on FTIR results in this study, samples containing high initial ratio of $\text{SiO}_2/\text{Al}_2\text{O}_3$ (3.0-4.0) with theoretical ratio of $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ (1.0), $\text{Na}_2\text{O}/\text{SiO}_2$ (0.25-0.33) and $\text{H}_2\text{O}/\text{Na}_2\text{O}$ (10.0-15.0) showed the declination in rate of geopolymerization. The formation of stable geopolymeric phase was achieved in samples having slow rate of reaction (NS3010A, NS4010A and NS4010C). The observed geopolymeric binders showed no evidence of zeolite formation over time. Furthermore, unreacted raw materials were found to remain in samples using initial low ratios of $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ (0.6) and $\text{Na}_2\text{O}/\text{SiO}_2$ (0.20) and high ratio of $\text{H}_2\text{O}/\text{Na}_2\text{O}$ (20.0). The appearance of unreacted raw materials at wavenumber of 780 cm^{-1} was prominently observed in sample having $\text{SiO}_2/\text{Al}_2\text{O}_3$ of 3.0, $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ of 0.6 and $\text{H}_2\text{O}/\text{Na}_2\text{O}$ of 20.0 as shown in Fig. 5 (a). The small peaks at 788 cm^{-1} belonging to MK and RHA were detected from deconvolution of FTIR bands of $796\text{ and }800\text{ cm}^{-1}$, and did not show in this section. In addition, the rapid rate of reaction was obtained in samples using both low and high ratios of $\text{SiO}_2/\text{Al}_2\text{O}_3$ (2.0-4.0) with specific ratios of $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ (more than 1.0-1.6), $\text{Na}_2\text{O}/\text{SiO}_2$ (0.25-0.72) and $\text{H}_2\text{O}/\text{Na}_2\text{O}$ in the range of 10.0-15.0. As mentioned in

XRD result, some of samples containing high initial ratios of $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ and $\text{Na}_2\text{O}/\text{SiO}_2$ with $\text{H}_2\text{O}/\text{Na}_2\text{O}$ ratios of 10.0-12.5 showed the formation of crystalline zeolite, instead of geopolymeric phase. Samples having $\text{SiO}_2/\text{Al}_2\text{O}_3$ of 2.0 (without sodium silicate solution) cured at 28 days and $\text{SiO}_2/\text{Al}_2\text{O}_3$ of 3.0 (with sodium silicate solution) cured at very long term (90 days) as demonstrated in Fig. 5 (g) and (j) showed zeolitic structures at 741 and 747, and 673 cm^{-1} , respectively [30, 33, 41-43]. In contrast, samples having very high initial ratio of $\text{SiO}_2/\text{Al}_2\text{O}_3$ (5.0-7.0) necessarily required $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ ratio higher than 1.0 and moderate $\text{H}_2\text{O}/\text{Na}_2\text{O}$ ratio in the range of 10.0-15.0 to support dissolubility of Si and Al from starting materials. Therefore, the reaction underwent very slowly. For example, sample of NS7014C as shown in Fig. 5 (c) with $\text{SiO}_2/\text{Al}_2\text{O}_3$ of 7.0, $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ of 1.4 and $\text{Na}_2\text{O}/\text{SiO}_2$ of 0.20 and $\text{H}_2\text{O}/\text{Na}_2\text{O}$ of 15.0, obviously contained deconvoluted peak of unreacted raw material as a main phase at 780 cm^{-1} . The result of FTIR analysis indicated that the rate of reaction of the prepared specimens with different compositions were given in descending order as follows; NS2010B (963 cm^{-1}) > NS2510A, NS3014A (967 cm^{-1}) > NS4014A (971 cm^{-1}) > NS3010A, NS4010A (974 cm^{-1}) > NS4010C (975 cm^{-1}) > NS5014A (978 cm^{-1}) > NS7014A (987 cm^{-1}) > NS3006D (994 cm^{-1}).

> The reaction rate to obtain stable geopolymeric phase was medium, not too fast and too slow. Moreover, FTIR spectra revealed the formation of sodium bicarbonate compounds in all samples. Enlargement of FTIR spectra at wavenumbers of 1390 and 1450 denoting C-O stretching vibration of carbonate compounds were identified and compared in samples of NS4010A, NS5014A, NS2510A, NS3014A and NS4014A as shown in Fig. 5 (e), (f), (h), (i), and (k), respectively. Strong FTIR peak of sodium carbonate compound was clearly found in sample containing initial ratio of $\text{SiO}_2/\text{Al}_2\text{O}_3$ of 3.0 with high ratios of $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ (1.4) and $\text{Na}_2\text{O}/\text{SiO}_2$ (0.47), and low ratio of $\text{H}_2\text{O}/\text{Na}_2\text{O}$ (10.0) cured at 28 days. Sample having higher initial ratio of $\text{SiO}_2/\text{Al}_2\text{O}_3$ (4.0-5.0) that required high $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ and $\text{Na}_2\text{O}/\text{SiO}_2$ to promote dissolubility of Si and Al in raw materials, contained small amount of Na ions as shown in Fig 5 (f) and (k).

3.2.4 Ternary diagram of Na_2O - SiO_2 - Al_2O_3

Fig. 6 demonstrated the chemical compositions (in wt.%) of each geopolymer sample in ternary diagram of Na_2O - SiO_2 - Al_2O_3 . As mentioned before, the mix design composition of MK and MK-RHA based geopolymers were formulated to create different types of geopolymeric materials; PS, PSS, PSDS and PSMS. This diagram was derived on a basis of

using highly reactive aluminosilicate or silicate starting materials such MK and RHA. Relation of microstructures (phase transformation) of geopolymer have been found to rely strongly on variable components; molar ratios of $\text{SiO}_2/\text{Al}_2\text{O}_3$, $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$, $\text{Na}_2\text{O}/\text{SiO}_2$ and $\text{H}_2\text{O}/\text{Na}_2\text{O}$ in initial mix compositions. The summary of each sample cured at 30 °C for 1-90 days could be drawn here. It could be concluded that pure geopolymeric phase was obtained when the initial molar ratios of $\text{SiO}_2/\text{Al}_2\text{O}_3$ and $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ were in the range of 3.0-4.0 and 1.0, respectively. When $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios were in the range of 4.5-6.0, the flowability of mix was hindered with the formation of geopolymeric phase. Geopolymeric phase plus zeolitic material as minority were obtained when $\text{SiO}_2/\text{Al}_2\text{O}_3$ and $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ ratios were in the ranges of 2.5-4.0 and 1.2-1.6, respectively. With the rising of $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios to 4.0-7.0 and $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ ratio of 1.4-1.6, unreacted raw materials together with geopolymeric phase were mainly found. In addition, sodium bicarbonate was left behind due to the excess alkali species. With $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of 2.0 (without sodium silicate) and $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ ratios of 1.0-1.4, zeolitic material was formed as majority incorporating with geopolymeric phase. The formation of zeolite type theoretically agreed with the various kinds of zeolites (sodalite, zeolite A, zeolite Y, zeolite X and faujasite) as depicted in the ternary diagram.

3.2.5 Compressive strength of geopolymer samples

As mentioned previously, the geopolymerization reaction typically underwent the dissolution-hydrolysis and hydrolysis-polycondensation. After these reactions, the specimens became set, hardened and densified overtime with generation of various reaction products; binding phases as geopolymeric phase (providing high strength) and non-binding phases viz. zeolitic phase, unreacted raw materials and sodium bicarbonate (providing low strength) [32, 33]. Fig. 7 presented the compressive strength of geopolymer samples prepared at different mix compositions cured at 30°C for 1-90 days. The correlation of strength development and phase structures was investigated as a function of variable molar ratios of $\text{SiO}_2/\text{Al}_2\text{O}_3$, $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$, $\text{Na}_2\text{O}/\text{SiO}_2$ and $\text{H}_2\text{O}/\text{Na}_2\text{O}$ in starting materials. The result showed an increase in compressive strength conforming to the creation of amorphous geopolymeric phase with prolonged curing time from 1-28 days. The development of compressive strength continued and gradually increased at 90 days of curing time in most samples. It was worth noting here that sample of NS3014A ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 3.0$, $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3 = 1.4$, $\text{Na}_2\text{O}/\text{SiO}_2 = 0.47$ and $\text{H}_2\text{O}/\text{Na}_2\text{O} = 10.0$) obviously showed a declination in strength from 40.4 to 18.2 N/mm² at curing times of 28 to 90 days. This declination correlated with phase transformation from

geopolymeric phase to zeolite in long term. Referred to XRD, SEM-EDX and FTIR results in this study, a use of high initial ratio of $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ and $\text{Na}_2\text{O}/\text{SiO}_2$ favored phase transformation from geopolymeric phase to zeolite phase. Moreover, a significant change in bulk density of NS3014A occurred with a drop from 1.61 g/cm^3 at 28-day curing to 1.58 g/cm^3 after 90-day curing. The bulk density of geopolymer samples were also collected and summarized in Table 2.

Based on this study, two different trends could be drawn from the plot of compressive strength. Samples of NS3006D, NS7014C, NH2010B, NS6016B, NS4010C and NS3014A were classified as low strength geopolymers and samples of NS4014A, NS2510A, NS5014A, NS3010A and NS4010A represented high strength geopolymer. The 28-day strength was comparable to other work using MK as starting material [44]. A use of low ratio of $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ (0.6) that was less than theoretical value (1.0) and high demand of water ($\text{H}_2\text{O}/\text{Na}_2\text{O} = 20.0$) in sample of NS3006D with $\text{SiO}_2/\text{Al}_2\text{O}_3$ of 3.0 resulted in the lowest strength sample due to the remain of unreacted raw materials as major phase. A use of high initial molar ratio of $\text{SiO}_2/\text{Al}_2\text{O}_3$ (4.0) with theoretical value of $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ about 1.0 together with low water content ($\text{H}_2\text{O}/\text{Na}_2\text{O}$ of 10.0) mostly generated geopolymeric phase as a reaction product with the highest strength, as seen in sample of NS4010A (EDX-plot in Fig. 4, $\text{Si}/\text{Al} = 2.0$, $\text{Na}/\text{Al} = 0.2\text{-}1.0$). A decrease in initial molar ratio of $\text{SiO}_2/\text{Al}_2\text{O}_3$ to 2.5-3.0 with constant $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ about 1.0 and $\text{H}_2\text{O}/\text{Na}_2\text{O}$ of 10.0 resulted in the lower strength samples (sample of NS2510A, NS3010A). It is suggested that polycondensation reaction would be hindered by the lower content of silicate species. Sample with the lowest initial $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of 2.0 in sample of NS2010B ($\text{Na}_2\text{O}/\text{Al}_2\text{O}_3 = 1.0$ and $\text{H}_2\text{O}/\text{Na}_2\text{O} = 12.5$) showed no progression in development of both early and later-age strength, since its structure mostly contained particulate structures of crystalline zeolites [32, 33]. Moreover, a use of higher initial molar ratio of $\text{SiO}_2/\text{Al}_2\text{O}_3$ (> 4.0) in the range of 4.5-6.0 (or more) such as samples of NS4510A, NS5010A and NS6010A (Table 2) apparently provided very high viscosity that hindered the workability. Modification of the mix design compositions with increasing either molar ratios of $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ (> 1.0) or $\text{H}_2\text{O}/\text{Na}_2\text{O}$ (> 10.0) promoted dissolution rate and improved workability. The improvement in workability belonged to samples of NS4014A, NS4514A, NS5014A ($\text{Na}_2\text{O}/\text{Al}_2\text{O}_3 = 1.4$ and $\text{H}_2\text{O}/\text{Na}_2\text{O} = 10.0$), and NS6016B ($\text{Na}_2\text{O}/\text{Al}_2\text{O}_3 = 1.6$ and $\text{H}_2\text{O}/\text{Na}_2\text{O} = 12.5$) and NS7014C ($\text{Na}_2\text{O}/\text{Al}_2\text{O}_3 = 1.4$ and $\text{H}_2\text{O}/\text{Na}_2\text{O} = 15.0$) which were adjusted with the increasing in molar ratio of $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ and

either low or high $\text{H}_2\text{O}/\text{Na}_2\text{O}$. However, a use of higher molar ratio of $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ and $\text{H}_2\text{O}/\text{Na}_2\text{O}$ resulted in the lower strength sample. Sample of NS4014A with high $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ (1.4) and low $\text{H}_2\text{O}/\text{Na}_2\text{O}$ (10.0) showed lower compressive strength than sample using $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ ratio of 1.0 and $\text{H}_2\text{O}/\text{Na}_2\text{O}$ of 10.0 (sample of NS4010A). Both samples used the same $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio at 4.0. Previous research suggested that the silicate network of tetrahedral anions of $[\text{SiO}_4]^{4-}$ and $[\text{AlO}_4]^{5-}$ was linked by sharing oxygen atom, then Na^+ ions compensated the negative charge of Al^{3+} . Therefore, the proper Na/Al ratio in the ordinary structure of silicate structure should be approximately 1.0. When negative charge at aluminum position was surrounded with the excess of Na^+ ions ($\text{Na}/\text{Al} > 1.0$), the bond strength in silicate network could be weakened that finally caused the deduction of strength in geopolymer sample [45].

In addition, samples of NS5014A, NS6016B and NS7014C with higher initial molar ratios of $\text{SiO}_2/\text{Al}_2\text{O}_3$ (5.0-7.0) and $\text{H}_2\text{O}/\text{Na}_2\text{O}$ (12.5-15.0) but excess Na^+ ions ($\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ of 1.4-1.6) also showed a decline in compressive strength. This was due to the reduction of dissolution rate as clearly seen in the FTIR result of NS7014C sample (Fig. 5C). The microstructure obtained in this sample contained unreacted raw materials as a majority. The results suggested that high ratio of $\text{SiO}_2/\text{Al}_2\text{O}_3$ (5.0-7.0) required high ratio of $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ (> 1.6) to support dissolution of starting materials. However, in real application this ratio is not recommended since concentration of the alkaline precursor would become very high. Precipitation of white solid crystals could be formed in this case. System having extremely high amount of Na_2O could favor the formation of sodium bicarbonate compounds that hence the deterioration in the structure of geopolymer sample [7]. The improvement of workability by increasing $\text{H}_2\text{O}/\text{Na}_2\text{O}$ ratio was also observed in sample of NS4010C ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 4.0$, $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3 = 1.0$, $\text{H}_2\text{O}/\text{Na}_2\text{O} = 15.0$) [46] but the compressive strength was quite low as a result of dilution effect by adding more water in the system. High water content resulted in the reduction in pH of the system (dilution) and affected the reaction rate [29]. Liquid to binder and water/solid ratio were engineering concerns in practical use rather than $\text{H}_2\text{O}/\text{Na}_2\text{O}$ ratio. The effects of liquid/solid, water/solid and $\text{H}_2\text{O}/\text{Na}_2\text{O}$ ratio on compressive strength were, therefore, observed as shown in Table 4. Compressive strength likely decreased with increases in liquid/solid, water/solid and $\text{H}_2\text{O}/\text{Na}_2\text{O}$ ratio. Sample with $\text{SiO}_2/\text{Al}_2\text{O}_3$ of 4.0 showed the highest compressive strength at 1.04, 0.62 and 10.0 of liquid/solid, water/solid

and $\text{H}_2\text{O}/\text{Na}_2\text{O}$ ratios, respectively. The lower values hindered the workability of sample preparation and strength measurement could not be performed.

4. Conclusion

In summary, the mix design of MK and MK-RHA based geopolymer were formulated to create different types of geopolymeric materials; PS, PSS, PSDS and PSMS. Sodium silicate and RHA was introduced as active SiO_2 sources together with MK to prepare geopolymer samples. Relation of microstructures (phase transformation) and strength development of geopolymer have been found to rely on variable components; the molar ratios of $\text{SiO}_2/\text{Al}_2\text{O}_3$, $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$, $\text{Na}_2\text{O}/\text{SiO}_2$ and $\text{H}_2\text{O}/\text{Na}_2\text{O}$ in initial mix compositions, as well as curing time (1-90 days). The following trends could be drawn from this study;

- Particulate zeolites (PS structure) typically known as non-binding phase was prominently formed in geopolymeric samples having low initial molar ratio of $\text{SiO}_2/\text{Al}_2\text{O}_3$ (2.0-3.0) with $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3 \geq 1.0$ and $\text{H}_2\text{O}/\text{Na}_2\text{O}$ in the range of 10.0-12.5. Depending on the ratios of used $\text{SiO}_2/\text{Al}_2\text{O}_3$, $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ and $\text{H}_2\text{O}/\text{Na}_2\text{O}$, various types of zeolites such as zeolite type A, X, Y, faujasite and sodalite (pseudo-phase zeolite) were formed with geopolymeric phase.

- Amorphous geopolymeric phase was formed in samples having higher initial molar ratio of $\text{SiO}_2/\text{Al}_2\text{O}_3$ (3.0-4.0) with theoretical values of $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ (1.0), $\text{Na}_2\text{O}/\text{SiO}_2$ ratio of 0.25-0.33 and $\text{H}_2\text{O}/\text{Na}_2\text{O}$ in the range of 10.0-15.0. The highest strength was obtained with ratio of $\text{SiO}_2/\text{Al}_2\text{O}_3$ about 4.0, $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ ratio of 1.0, $\text{Na}_2\text{O}/\text{SiO}_2$ ratio of 0.25 and $\text{H}_2\text{O}/\text{Na}_2\text{O}$ of 10.0 with the formation of PSS (main part), PSDS and PSMS structures.

- Unreacted raw materials were observed as a composite with amorphous geopolymeric phase in sample having extremely high initial molar ratio of $\text{SiO}_2/\text{Al}_2\text{O}_3$ in the range of 6.0-7.0 with $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ ratio in the range of 1.0-1.6, $\text{Na}_2\text{O}/\text{SiO}_2$ ratio of 0.17-0.27 and $\text{H}_2\text{O}/\text{Na}_2\text{O}$ ratio of 10.0-15.0. Higher $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ of greater than 1.6, $\text{Na}_2\text{O}/\text{SiO}_2 > 0.27$ and $\text{H}_2\text{O}/\text{Na}_2\text{O}$ ratio around 10.0-15.0 could be used to promote the dissolution rate, but practically the high concentration of Na_2O in activator could also cause a problem from the reprecipitation of white solid powder. In addition, sample containing high $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ and $\text{Na}_2\text{O}/\text{SiO}_2$ ratios also showed the formation of sodium bicarbonate compounds as a minor reaction product.

Acknowledgement

The authors gratefully acknowledge the technical staffs at Swiss Federal Laboratories for the Materials Science and Technology (EMPA) for the assistance on characterization of samples. This research was financially supported by Chiang Mai University, the Thailand Research Fund (TRF) through the Research and Researchers for Industries (RRI), [Grant No. PHD56I0027).], and TRF under TRF Distinguished Research Professor [Grant No. DPG6180002 TRF].

References

- [1] J. Davidovits, Geopolymer chemistry and applications, 4th edition. Saint-Quentin, France: Institut Géopolymère, 2015.
- [2] J. Davidovits, Geopolymer chemistry and applications, 3th edition. Saint-Quentin, France: Institut Géopolymère, 2011.
- [3] K. J. D. Mackenzie, M. Welter, Geopolymer (aluminosilicate) composites: synthesis, properties and applications, *Advances in Ceramic Matrix Composites*, Woodhead Publishing, (2014) 445–470.
- [4] J. L. Provis, J. S. J. Van Deventer, Geopolymers: Structure, processing, properties and industrial applications, Woodhead Publishing, (2009) 50-71.
- [5] H. Xu, J. S.J. Van Deventer, Geopolymerization of multiple minerals, *Miner. Eng.* 15 (2002) 1131–1139.
- [6] K. Juengsuwattananon, K. Pimraksa, Variable factors controlling amorphous-zeolite phase transformation in metakaolin based geopolymer, *Acta Metall. Slovaca*. 23 (2017) 378-386.
- [7] K. Juengsuwattananon, K. Pimraksa, Effect of curing conditions on strength and microstructure of metakaolin based geopolymer with different $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ and $\text{H}_2\text{O}/\text{Na}_2\text{O}$ molar ratios, The First Materials Research Society of Thailand International Conference, October 31 – November 3, (2017) 334-341.

- [8] Z. Zhanga, H. Wanga, J. L. Provis, F. Bullena, A. Reidec, Y. Zhua, Quantitative kinetic and structural analysis of geopolymers: Part 1. The activation of metakaolin with sodium hydroxide, *Thermochim. Act.* 539 (2012) 23–33.
- [9] F. Pacheco-Torgal, J. Castro-Gomes, S. Jalali, Alkali-activated binders: A review. Part 2. About materials and binders manufacture, *Constr. Build. Mater.* 22 (2008) 1315–1322.
- [10] A. C. Lopes, P. Martins, S. Lancers-Mendez, Aluminosilicate and aluminosilicate-based polymer composites: Present status, applications and future trends, *Prog. Surf. Sci.* 89 (2014) 239–277.
- [11] P. De Silva, K. Sagoe-Crenstil, V. Sirivivatnanon, Kinetics of geopolymerization: Role of Al_2O_3 and SiO_2 , *Cem. Concr. Res.* 37 (2007) 512–518.
- [12] D. Khale, R. Chaudhary, Mechanism of geopolymerization and factors influencing its development: a review, *J. Mater. Sci.* 42 (2007) 729–746.
- [13] P. De Silva, K. Sagoe-Crenstil, Medium-term phase stability of Na_2O – Al_2O_3 – SiO_2 – H_2O geopolymer systems, *Cem. Concr. Res.* 38 (2008) 870–876.
- [14] M. Schmücker, K. J. D. MacKenzie, Microstructure of sodium polysialate siloxo geopolymer, *Ceram. Int.* 31 (2005) 433–437.
- [15] A. Fernández-Jiménez, A. Palomo, Composition and microstructure of alkali activated fly ash binder: Effect of the activator, *Cem. Concr. Res.* 35 (2005) 1984–1992.
- [16] P. Duxson, J. L. Provis, G. C. Lukey, S. W. Mallicoat, W. M. Kriven, J. S. J. van Deventer, Understanding the relationship between geopolymer composition, microstructure and mechanical properties, *Colloid. Surf. Physicochem. Eng. Asp.* 269 (2005) 47–58.
- [17] S. Greiser, G.J.G. Gluth, P. Sturm, C. Jaeger, $^{29}\text{Si}\{^{27}\text{Al}\}$, $^{27}\text{Al}\{^{29}\text{Si}\}$ and $^{27}\text{Al}\{^1\text{H}\}$ double-resonance NMR spectroscopy study of cementitious sodium aluminosilicate gels (geopolymers) and gel-zeolite composites, *RSC Adv.* 8 (2018) 40164–40171.
- [18] V.F.F. Barbosa, K.J.D. Mackenzie, C. Thaumaturgo, Synthesis and characterization of materials based on inorganic polymers of alumina and silica: sodium polysialate polymers, *Int. Inorg. Mat.* 2 (2000) 309–317.

- [19] R. A. Fletcher, K. J. D. MacKenzie, C. L. Nicholson, S. Shimada, The composition range of aluminosilicate geopolymers, *J. Eur. Ceram. Soc.* 25 (2005) 1471–1477.
- [20] S. E. Arshad, S. M. Aripitri, E. S. M. Zainuddin, Geopolymerization of metakaolin using rice husk ash as silica source with Na-based activator, *ARPN J. Earth Sci.* 4 (2015) 23–33.
- [21] A. Autef, E. Joussein, A. Poulesquen, G. Gasgnier, S. Pronier, I. Sobrados, J. Sanz, S. Rossignol., Influence of metakaolin purities on potassium geopolymer formulation: The existence of several networks, *J. Colloid. Interf. Sci.* 408 (2013) 43–53.
- [22] T. R. Barbosa, E. L. Foletto, G. L. Dotto, S. L. Jahn, Preparation of mesoporous geopolymer using metakaolin and rice husk ash as synthesis precursors and its use as potential adsorbent to remove organic dye from aqueous solutions, *Ceram. Int.* 44 (2018) 416–423.
- [23] P. Sturm, G. J. G. Gluth, H. J. H. Brouwers, H.C. Kühne, Synthesizing one-part geopolymers from rice husk ash, *Constr. Build. Mater.* 124 (2016) 961–966.
- [24] I. Ozer, S. Soyer-Uzun, Relations between the structural characteristics and compressive strength in metakaolin based geopolymers with different molar Si/Al ratios, *Ceram. Int.* 41 (2015) 10192–10198.
- [25] Z. Yunsheng, S. Wei, L. Zongjin, Composition design and microstructural characterization of calcined kaolin-based geopolymer cement, *Appl. Clay Sci.* 47 (2010) 271–275.
- [26] F. Winnefeld, A. Schöler and B. Lothenbach, A Practical guide to microstructural analysis of cementitious materials, Chapter I: Sample preparation, Taylor and Francis Group, LLC (2016) 1–36.
- [27] M. Ben Haha, G. Le Saout, B. Lothenbach, F. Winnefeld, The hydration mechanisms of alkali activated slag systems (AAS) with different MgO content, Cementing a sustainable future (Proceeding), 13th international congress on the chemistry of cement (XIII ICCC 2011), July 3–8, (2011) 7 pp.

- [28] C.Y. Heah, H. Kamarudin, A.M. Mustafa Al Bakri, M. Bnhussain, M. Luqman, I. Khairul Nizar, C.M. Ruzaidi, Y.M. Liew, Study on solids-to-liquid and alkaline activator ratios on kaolin-based geopolymers, *Constr. Build. Mater.* 35 (2012) 912–922.
- [29] Z. Zuhua, Y. Xiao, Z. Huajun, C. Yue, Role of water in the synthesis of calcined kaolin-based geopolymer, *Appl. Clay Sci.* 43 (2009) 18–223.
- [30] A. Buchwald, H.-D. Zellmann, C. Kaps, Condensation of aluminosilicate gels—model system for geopolymer binders, *J. Non-Cryst. Solid.* 357 (2011) 1376–1382.
- [31] A. Koleżyński, M. Król, M. Żychowicz, The structure of geopolymers – Theoretical studies, *J. Mol. Struct.* 1163 (2018) 465–471.
- [32] C. A. Rees, J. L. Provis, G. C. Lukey, J. S. J. van Deventer, The mechanism of geopolymer gel formation investigated through seeded nucleation, *Colloid. Surf. Physicochem. Eng. Asp.* 318 (2008) 97–105.
- [33] A. Currao, Understanding Zeolite Frameworks, Department of Chemistry and Biochemistry University of Bern, 1-65.
- [34] H. van Bekkum, E. M. Flanigen, J. C. Jansen, Eds., Appendix I zeolite structures, in *Stud. in Surf. Sci. Catal.* 58 (1991) 727–734.
- [35] M. Criado, A. Fernández-Jiménez, A. G. de la Torre, M. A. G. Aranda, A. Palomo, An XRD study of the effect of the $\text{SiO}_2/\text{Na}_2\text{O}$ ratio on the alkali activation of fly ash, *Cem. Concr. Res.* 37 (2007) 671–679.
- [36] M. C. Bignozzi, S. Manzi, M. E. Natali, W. D. A. Rickard, A. van Riessen, Room temperature alkali activation of fly ash: The effect of $\text{Na}_2\text{O}/\text{SiO}_2$ ratio, *Constr. Build. Mater.* 69 (2014) 262–270.
- [37] J. L. Provis, J. S. J. van Deventer, Direct measurement of the kinetics of geopolymerisation by in-situ energy dispersive X-ray diffractometry, *J. Mater. Sci.* 42 (2007) 2974–2981.
- [38] J. L. Provis, J. S. J. van Deventer, Geopolymerisation kinetics. 1. In situ energy-dispersive X-ray diffractometry, *Chem. Eng. Sci.* 62 (2007) 2309–2317.

- [39] P. Rovnaník, Effect of curing temperature on the development of hard structure of metakaolin-based geopolymer, *Constr. Build. Mater.* 24 (2010) 1176–1183.
- [40] P. N. Lemougna, K. J. D. MacKenzie, U. F. C. Melo, Synthesis and thermal properties of inorganic polymers (geopolymers) for structural and refractory applications from volcanic ash, *Ceram. Int.* 37 (2011) 3011–3018.
- [41] W. Pichor, W. Mozgawa, M. Krol, A. Adamczyk, Synthesis of the zeolites on the lightweight aluminosilicate fillers, *Mater. Res. Bull.* 49 (2014) 210–215.
- [42] T. Hu, W. Gao, X. Liu, Y. Zhang, C. Meng, Synthesis of zeolites Na-A and Na-X from tablet compressed and calcinated coal fly ash, *R. Soc. Open Sci.* 4 (2017) 1-11.
- [43] W. Lutz, Zeolite Y: Synthesis, Modification, and Properties—A Case Revisited, *Adv. Mater. Sci. Eng.* 2014 (2014) 1-20.
- [44] D. Pereira, F. Silva, A. Porto, V.S. Candido, A. Silva, F. Filho, S.N. Monteiro, Comparative analysis between properties and microstructures of geopolymeric concrete and Portland concrete, *J. Mater. Res. Technol.* 7 (2018) 606-611.
- [45] J.W. Phair, J.S.J. Van Deventer, Effect of the silicate activator pH on the microstructural characteristics of waste-based geopolymers, *Int. J. Miner. Proc.* 66 (2002) 121– 143.
- [46] N.R. Rakhimova, R.Z. Rakhimov, Reaction products, structure and properties of alkali-activated metakaolin cements incorporated with supplementary materials-a review, *J. Mater Res. Technol.* (2018), Article in press.

Captions of Tables

Table 1 Chemical compositions of starting materials (%w/w).

Table 2 Initial mixed design compositions of geopolymer pastes with different oxide molar and atomic ratios of $\text{SiO}_2/\text{Al}_2\text{O}_3$ (Si/Al), $\text{Na}_2\text{O}/\text{SiO}_2$ (Na/Si), $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ (Na/Al) and $\text{H}_2\text{O}/\text{Na}_2\text{O}$ (H/Na) cured at 30°C for 1-90 days.

Table 3 Viscosity of samples prepared using different $\text{SiO}_2/\text{Al}_2\text{O}_3$ and $\text{H}_2\text{O}/\text{Na}_2\text{O}$ ratios.

Table 4 Effects of liquid/solid, water/solid and $\text{H}_2\text{O}/\text{Na}_2\text{O}$ on compressive strength.

Captions of Figures

Figure 1 XRD patterns of geopolymer pastes with different ratios of $\text{SiO}_2/\text{Al}_2\text{O}_3$, $\text{H}_2\text{O}/\text{Na}_2\text{O}$ and $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ cured at 30°C for 1-90 days; (a) NS2510A, (b) NS3010A, (c) NS4010A, (d) NS2510B, (e) NS3010B, (f) NS4010C, (g) NS3006D, (h) NS4014A, (i) NS5014A, (j) NS3016B, (k) NS3014A, (m) NH2010B, (n) NH2012A, (o) NH2014A; T = TiO_2 (Anatase), A = Zeolite A, X = Zeolite X, Y = Zeolite Y, F = Faujasite, S = Sodalite, Na = Sodium hydroxide.

Figure 2 Scanning electron microscope of metakaolin starting material (a) and geopolymer pastes (fractured samples) containing zeolite prepared at $\text{SiO}_2/\text{Al}_2\text{O}_3$ of 2.0, $\text{H}_2\text{O}/\text{Na}_2\text{O}$ of 12.5 and $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ of 1.0 (b) and $\text{SiO}_2/\text{Al}_2\text{O}_3$ of 3.0, $\text{H}_2\text{O}/\text{Na}_2\text{O}$ of 12.5 and $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ of 1.6 (c), cured at 30°C for 1 day.

Figure 3 Scanning electron microscope of geopolymer pastes with different ratios of $\text{SiO}_2/\text{Al}_2\text{O}_3$, $\text{H}_2\text{O}/\text{Na}_2\text{O}$ and $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ cured at 30°C for 7 and 28 days.

Figure 4 Atomic ratios of Si/Al and Na/Al in geopolymer pastes with different initial molar ratios of $\text{SiO}_2/\text{Al}_2\text{O}_3$, $\text{H}_2\text{O}/\text{Na}_2\text{O}$ and $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ cured at 30°C for 7 and 28 days; Noted: the quantitative chemical compositions were obtained from E-SEM interfaced to an energy dispersive X-ray spectrometer (EDS), MK = Metakaolin, ZS, ZA, ZX, ZF = Sodalite, Zeolite type A, X, Faujasite, respectively.

Figure 5 ATR-FTIR spectra analysis of geopolymer pastes with different ratios of $\text{SiO}_2/\text{Al}_2\text{O}_3$, $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$, $\text{Na}_2\text{O}/\text{SiO}_2$ and $\text{H}_2\text{O}/\text{Na}_2\text{O}$ curing at 30°C for 28, 90 days; MK = metakaolin, RHA = rice husk ash, (a) NS3006D, (b) NS4010C, (c) NC7014C, (d) NS3010A, (e) NS4010A, (f) NS5014A, (g) NH2010B, (h) NS2510A, (i) NS3014A-28 days, (j) NS3014A-90 days, (k) NS4014A.

Figure 6 Ternary mixed design composition of geopolymer pastes with different ratios of $\text{SiO}_2/\text{Al}_2\text{O}_3$, $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$, $\text{Na}_2\text{O}/\text{SiO}_2$ cured at 30°C for 1-90 days; each of formula was mixed with various $\text{H}_2\text{O}/\text{Na}_2\text{O}$ ratios.

Figure 7 Compressive strength of geopolymer samples obtaining at different ratios of $\text{SiO}_2/\text{Al}_2\text{O}_3$, $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$, $\text{Na}_2\text{O}/\text{SiO}_2$ and $\text{H}_2\text{O}/\text{Na}_2\text{O}$.

Table 1 Chemical compositions of starting materials (%w/w).

Materials	SiO ₂	Al ₂ O ₃	CaO	Na ₂ O	SO ₃	Fe ₂ O ₃	K ₂ O	TiO ₂	P ₂ O ₅	LOI
Metakaolin	51.40	44.59	0.06	0.38	0.09	0.42	0.11	1.79	0.12	1.04
Rice husk ash	94.59	0.15	0.46	-	0.32	0.07	2.21	-	0.75	1.45
Sodium silicate (dry matter)	68.30	0.39	0.08	30.84	-	0.09	0.07	0.06	-	0.16

LOI = Loss on ignition

Table 2 Initial mixed design compositions of geopolymer pastes with different oxide molar and atomic ratios of $\text{SiO}_2/\text{Al}_2\text{O}_3$ (Si/Al), $\text{Na}_2\text{O}/\text{SiO}_2$ (Na/Si), $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ (Na/Al) and $\text{H}_2\text{O}/\text{Na}_2\text{O}$ curing at 30°C for 1-90 days.

Samples	SiO ₂ / Al ₂ O ₃ , (Si/Al)	Na ₂ O/ SiO ₂ , (Na/Si)	Na ₂ O/Al ₂ O ₃ , (Na/Al)*	H ₂ O/Na ₂ O (H/Na)*		Bulk density at 30°C for 1, 28, 90 days
	Oxide molar ratio, (atomic ratio)					g/ cm ³
NH2010B	1.96, (1.00)	0.51, (1.00)	1.0	N/A,	12.5	(1.58, 1.56, 1.31)
NH2012A	1.96, (1.00)	0.61, (1.20)	1.2	10.0,	N/A	(1.63, 1.61, 1.49)
NH2014A	1.96, (1.00)	0.72, (1.20)	1.4	10.0,	N/A	(1.63, 1.55, N/A)
NS2510A, B	2.5, (1.25)	0.40, (0.80)	1.0	10.0,	12.5	(1.69, 1.70, 1.66) ^A , (1.59, 1.56, 1.59) ^B
NS2512A, B	2.5, (1.25)	0.48, (0.96)	1.2	10.0,	12.5	(1.64, 1.65, 1.65) ^A , (1.55, 1.54, 1.54) ^B
NS2514B	2.5, (1.25)	0.56, (1.10)	1.4	N/A,	12.5	(1.54, 1.54, 1.54) ^B
NS3006D	3.0, (1.50)	0.20, (0.40)	0.6	N/A,	20.0	(1.56, 1.52, 1.56)
NS3010A, B	3.0, (1.50)	0.33, (0.67)	1.0	10.0,	12.5	(1.67, 1.67, 1.66) ^A , (1.58, 1.58, 1.61) ^B
NS3012A, B	3.0, (1.50)	0.40, (0.80)	1.2	10.0,	12.5	(1.57, N/A, 1.62) ^A , (1.49, N/A, 1.56) ^B
NS3014A, B	3.0, (1.50)	0.47, (0.93)	1.4	10.0,	12.5	(1.61, 1.61, 1.58) ^A , (1.50, 1.53, 1.54) ^B
NS3016A, B	3.0, (1.50)	0.53, (1.10)	1.6	10.0,	12.5	(1.58, 1.56, 1.59) ^A , (1.52, 1.53, 1.52) ^B
NS3510A	3.5, (1.75)	0.29, (0.57)	1.0	10.0,	N/A	(1.70, 1.66, 1.68)
NS4010A, C	4.0, (2.00)	0.25, (0.50)	1.0	10.0,	15.0	(1.72, 1.69, 1.69) ^A , (1.55, 1.55, 1.58) ^C
NS4014A	4.0, (2.00)	0.35, (0.70)	1.4	10.0,	N/A	(1.64, 1.65, 1.66)
NS4016A	4.0, (2.00)	0.39, (0.80)	1.6	10.0,	N/A	(1.61, 1.62, 1.60)
NS4510A [#]	4.5, (2.25)	0.22, (0.44)	1.0	10.0,	N/A	-
NS4514A	4.5, (2.25)	0.31, (0.62)	1.4	10.0,	N/A	(1.69, 1.65, 1.67)
NS5010A [#]	5.0, (2.50)	0.20, (0.40)	1.0	10.0,	N/A	-
NS5014A	5.0, (2.50)	0.28, (0.56)	1.4	10.0,	N/A	(1.69, 1.70, 1.69)
NS6010A [#] , B [#]	6.0, (3.00)	0.17, (0.33)	1.0	10.0,	12.5	-
NS6014A [#]	6.0, (3.00)	0.27, (0.47)	1.4	10.0,	N/A	-
NS6016A [#] , B	6.0, (3.00)	0.27, (0.53)	1.6	10.0,	12.5	(1.59, 1.61, 1.61) ^B
NS7014A [#] , C	7.0, (3.50)	0.20, (0.40)	1.4	10.0,	15.0	(1.60, 1.60, 1.59) ^C

A is defined as using $\text{H}_2\text{O}/\text{Na}_2\text{O} = 10.0$, $B = 12.5$ and $C = 15.0$, $D = 20.0$

*# = poor workability, N/A = not applicable, * = oxide molar ratio equal to atomic ratio.*

Table 3 Viscosity of samples prepared using different $\text{SiO}_2/\text{Al}_2\text{O}_3$ and $\text{H}_2\text{O}/\text{Na}_2\text{O}$ ratios.

Samples	$\text{SiO}_2/\text{Al}_2\text{O}_3$	$\text{Na}_2\text{O}/\text{SiO}_2$	$\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$	$\text{H}_2\text{O}/\text{Na}_2\text{O}$	Viscosity (Cp)
NH2010C	2.0	0.51	1.0	15.0	3527
NH2010E	2.0	0.51	1.0	25.0	163
NS5010C	5.0	0.20	1.0	15.0	6240
NS5010E	5.0	0.20	1.0	25.0	240
NS5014C	5.0	0.28	1.4	15.0	845

Table 4 Effects of liquid/solid, water/solid and H₂O/Na₂O on compressive strength.

<i>Samples</i>	<i>Liquid/Solid</i>	<i>Water/Solid</i>	<i>H₂O/Na₂O</i>	<i>Compressive strength at 28 days (N/mm²)</i>
NH2010B	1.25	0.98	12.5	3.8
NH2012A	1.27	0.94	10.0	19.7
NH2014A	1.48	1.10	10.0	13.7
NS2510A, B	1.20, 1.40	0.79, 0.98	10.0, 12.5	57.5, 11.5
NS2512A, B	1.41, 1.65	0.94, 1.18	10.0, 12.5	15.5, 9.8
NS2514B	1.90	1.38	12.5	6.7
NS3006D	1.38	0.95	20.0	4.9
NS3010A, B	1.33, 1.52	0.78, 0.98	10.0, 12.5	60.6, 21.8
NS3012A, B	1.54, 1.78	0.94, 1.18	10.0, 12.5	51.5, 31.2
NS3014A, B	1.75, 2.02	1.10, 1.38	10.0, 12.5	35.0, 14.3
NS3016A, B	1.96, 2.27	1.26, 1.57	10.0, 12.5	11.0, 6.3
NS3510A	1.46	0.79	10.0	64.1
NS4010A, C	1.04, 1.35	0.62, 0.92	10.0, 15.0	78.9, 29.8
NS4014A	1.37	0.86	10.0	57.4
NS4016A	1.54	0.99	10.0	31.2
NS4510A [#]	0.94	0.56	10.0	poor
NS4514A	1.24	0.78	10.0	workability 59.9
NS5010A [#]	0.85	0.51	10.0	poor
NS5014A	1.13	0.71	10.0	workability 62.9
NS6010A [#] , B [#]	0.83	0.54	10.0, 12.5	poor workability
NS6014A [#]	0.96	0.60	10.0	poor workability
NS6016A [#] , B	1.07, 1.24	0.69, 0.86	10.0, 12.5	18.6
NS7014A [#] , C	0.83, 1.09	0.52, 0.78	10.0, 15.0	9.3

A is defined as using H₂O/Na₂O = 10.0, B = 12.5 and C = 15.0, D = 20.0

= poor workability (no strength measurement)

Figure1 XRD patterns of geopolymer pastes with different ratios of $\text{SiO}_2/\text{Al}_2\text{O}_3$, $\text{H}_2\text{O}/\text{Na}_2\text{O}$ and $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ curing at 30°C for 1-90 days; (a) NS2510A, (b) NS3010A, (c) NS4010A, (d) NS2510B, (e) NS3010B, (f) NS4010C, (g) NS3006D, (h) NS4014A, (i) NS5014A, (j)

NS3016B, (k) NS3014A, (m) NH2010B, (n) NH2012A, (o) NH2014A; T = TiO₂ (Anatase), A = Zeolite A, X = Zeolite X, Y = Zeolite Y, F = Faujasite, S = Sodalite, Na = Sodium hydroxide.

Figure 2 Scanning electron microscope of metakaolin starting material (a) and geopolymer pastes (fractured samples) containing zeolite prepared at $\text{SiO}_2/\text{Al}_2\text{O}_3$ of 2.0, $\text{H}_2\text{O}/\text{Na}_2\text{O}$ of 12.5 and $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ of 1.0 (b) and $\text{SiO}_2/\text{Al}_2\text{O}_3$ of 3.0, $\text{H}_2\text{O}/\text{Na}_2\text{O}$ of 12.5 and $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ of 1.6 (c), cured at 30°C for 1 day.

Figure 3 Scanning electron microscope of geopolymer pastes with different ratios of $\text{SiO}_2/\text{Al}_2\text{O}_3$, $\text{H}_2\text{O}/\text{Na}_2\text{O}$ and $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ curing at 30°C for 7 and 28 days.

Figure 4 Atomic ratios of Si/Al and Na/Al in geopolymer pastes with different initial molar ratios of $\text{SiO}_2/\text{Al}_2\text{O}_3$, $\text{H}_2\text{O}/\text{Na}_2\text{O}$ and $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ curing at 30°C for 7 and 28 days; Noted: the quantitative chemical compositions were obtained from E-SEM interfaced to an energy dispersive X-ray spectrometer (EDS), MK = Metakaolin, ZS, ZA, ZX, ZF = Sodalite, Zeolite type A, X, Faujasite, respectively.

Figure 5 ATR-FTIR spectra analysis of geopolymer pastes with different ratios of $\text{SiO}_2/\text{Al}_2\text{O}_3$, $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$, $\text{Na}_2\text{O}/\text{SiO}_2$ and $\text{H}_2\text{O}/\text{Na}_2\text{O}$ curing at 30°C for 28, 90 days; MK = metakaolin, RHA = rice husk ash, (a) NS3006D, (b) NS4010C, (c) NC7014C, (d) NS3010A, (e) NS4010A, (f) NS5014A, (g) NH2010B, (h) NS2510A, (i) NS3014A-28 days, (j) NS3014A-90 days, (k) NS4014A.

MK = Metakaolin, ZS, ZA, ZY, ZX, ZF = Sodalite, Zeolite type A, Y, X, Faujasite

Figure 6 Ternary mixed design composition of geopolymer pastes with different ratios of $\text{SiO}_2/\text{Al}_2\text{O}_3$, $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$, $\text{Na}_2\text{O}/\text{SiO}_2$ cured at 30°C for 1-90 days; each of formula was mixed with various $\text{H}_2\text{O}/\text{Na}_2\text{O}$ ratios.

Figure 7 Compressive strength of geopolymer samples obtaining at different ratios of $\text{SiO}_2/\text{Al}_2\text{O}_3$, $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$, $\text{Na}_2\text{O}/\text{SiO}_2$ and $\text{H}_2\text{O}/\text{Na}_2\text{O}$.