

## VARIABLE FACTORS CONTROLLING AMORPHOUS-ZEOLITE PHASE TRANSFORMATION IN METAKAOLIN BASED GEOPOLYMER

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### Abstract

Metakaolin based geopolymer binder was synthesized using variable factors such as  $\text{Na}_2\text{O}/\text{SiO}_2$ ,  $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$  and  $\text{H}_2\text{O}/\text{Na}_2\text{O}$  molar ratios as well as curing time. Metakaolin was used as an aluminosilicate source incorporating with strong alkali activators; sodium hydroxide solution to undergo polycondensation and hence a formation of hardened geopolymeric binder. This work was aimed to investigate the effect of  $\text{Na}_2\text{O}/\text{SiO}_2$ ,  $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$  and  $\text{H}_2\text{O}/\text{Na}_2\text{O}$  ratios, as well as curing time on phase transformation. The chemical composition, phase development and microstructure of reaction products were examined by X-ray fluorescence, X-ray diffraction analysis and scanning electron microscopy with respect to their final compressive strength. Increasing the molar ratios of  $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$  and  $\text{H}_2\text{O}/\text{Na}_2\text{O}$  tended to favour the transformation of amorphous gel to various types of crystalline zeolite. Sodalite (pseudo-phase zeolite) and zeolite belonging to the Faujasite group, as well as zeolite X and A were identified in these mixtures. Based on this study, systems that favoured the formation of zeolitic products tended to possess lower strengths.

**Keywords:** Geopolymer binder, Microstructure, Zeolite, Amorphous gel, Aluminosilicates

### 1 Introduction

Geopolymer or alkali polysialate is an entirely known material that could be used in a wide range of potential applications includes: fire resistant materials, thermal insulation, ceramic tiles, thermal shock refractories, cements and concretes, high-tech composites aircraft interior and automobile, radioactive and toxic waste containment, arts and decoration. These can be formed by mixing aluminosilicate materials such as silica fume, fly ash, rice husk ash, slag, waste glass, industrial wastes, kaolinite and metakaolin with strong alkali activators or solution [1-3]. The basic of geopolymerization process involve dissolution of solid aluminosilicate oxides in alkali hydroxide or alkali silicate solution, diffusion or transportation of the dissolved Si and Al complexes from the initial raw material, formation of a gel phase and finally hardening of the gel phase. The hydration products forming in the three-dimensional rigid network geopolymer are composed of variety structures, such as amorphous phase, semi-crystalline phase, as well as fully crystalline zeolite phase. A high content of amorphous geopolymeric gel resulted to the high compressive strength, while a formation of zeolite phase in geopolymer matrix produced lower strength [4-7].

The aim of this work was to investigate the effect of key parameters on the microstructures (phase transformation) and strength development of geopolymer pastes. Metakaolin was chosen as starting material since it was a good source of reactive  $\text{Al}_2\text{O}_3$  and  $\text{SiO}_2$  when activated with alkaline solution. The microstructure and compressive strength of the hardened pastes were evaluated as a function of molar ratios of  $\text{Na}_2\text{O}/\text{SiO}_2$ ,  $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$  and  $\text{H}_2\text{O}/\text{Na}_2\text{O}$ . The effect of curing time was also observed.

## 2 Experimental materials and methods

### Raw materials

Metakaolin and analytical Sodium hydroxide pellet (NaOH) were purchased from BASF (USA.) Limited and Sigma-Aldrich, respectively. Chemical compositions of metakaolin determined by X-ray fluorescence spectrometer was listed in **Table 1**. Noted that, the  $\text{SiO}_2/\text{Al}_2\text{O}_3$  molar ratio of used metakaolin was 1.96.

**Table 1** Chemical compositions of metakaolin (% w/w).

Compounds	$\text{SiO}_2$	$\text{Al}_2\text{O}_3$	CaO	$\text{Na}_2\text{O}$	$\text{SO}_3$	$\text{Fe}_2\text{O}_3$	$\text{K}_2\text{O}$	$\text{TiO}_2$	$\text{P}_2\text{O}_5$	LOI
Metakaolin	51.40	44.59	0.06	0.38	0.09	0.42	0.11	1.79	0.12	0.99

*L.O.I = Loss on ignition*

### Specimen preparation

In the synthesis of geopolymer, metakaolin was first dried in an oven at  $100^\circ\text{C}$  to remove free water before mixing. The sodium hydroxide activator was mixed with de-ionized water to obtain differences in  $\text{H}_2\text{O}/\text{Na}_2\text{O}$  molar ratios (7.5-27.5) and the solution was cooled down to room temperature prior to mix with metakaolin. To prepare specimens, metakaolin powders were mixed with the as-prepared sodium hydroxide solution for 3 min using mixing machine. Mass ratios of liquid activator and metakaolin were slightly adjusted in certain range to obtain different  $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$  molar ratios (0.6-2.4) [8-10]. Then, the fresh prepared geopolymer pastes were poured into cubic acrylic moulds with 25 x 25 x 25 mm. As-prepared samples were vibrated for 1 min to remove free bubble inside samples. All samples were cured in incubator at  $30^\circ\text{C}$  with more than 50% of humidity with a plastic sheet coverage during the setting and hardening process to avoid the evaporation of water. The samples were removed from the moulds after 24 hrs curing and further cured in incubator at  $30^\circ\text{C}$ , 50% of humidity for 1, 7, 28 and 90 days. Mix design compositions of each sample were listed in Table 2. The variation of  $\text{H}_2\text{O}/\text{Na}_2\text{O}$  molar ratios in this study was based on a workability of geopolymer paste [11, 12].

### Mechanical property and characterizations of geopolymer samples

Mechanical performance of the as-prepared samples was determined by measuring the compressive strength of the hardened pastes at 1, 7, 28 and 90 days. The loading rate of compressive machine was set at 5 mm/min with a maximum load of 100 kN. The fragment samples after strength test were collected and used for morphology and mineralogical compositions analysis. Before characterizations, the fracture samples were further finely crushed and then immersed in an absolute propanol to stop geopolymerization reaction. The samples were then dried in an oven at  $60^\circ\text{C}$  for 1 day. The fracture samples were examined using a cold-

field emission SEM (JEOL JSM-6335F). The dried pieces of sample were again finely crushed with an agate mortar, ground to pass through a 250 mesh of sieve size to obtain fine powder for mineralogical characterization. Mineralogical compositions of dried and fresh samples were examined using a Bruker AXS (D4 ENDEAVOR) and a Bruker (D8 ADVANCE) X-ray diffractometer (in-situ analysis), respectively, using Cu K $\alpha$  radiation.

**Table 2** Mixed design composition of geopolymer pastes with SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> of 1.96 at different ratios of Na<sub>2</sub>O/SiO<sub>2</sub>, Na<sub>2</sub>O/Al<sub>2</sub>O<sub>3</sub> and H<sub>2</sub>O/Na<sub>2</sub>O

Samples	Na <sub>2</sub> O/SiO <sub>2</sub>	Na <sub>2</sub> O/Al <sub>2</sub> O <sub>3</sub>	H <sub>2</sub> O/Na <sub>2</sub> O
		(mole ratio)	
NH064	0.31	0.60	20.0
NH065	0.31	0.60	22.5
NH066	0.31	0.60	25.0
NH067	0.31	0.60	27.5
NH102	0.51	1.00	12.5
NH103	0.51	1.00	15.0
NH104	0.51	1.00	17.5
NH105	0.51	1.00	20.0
NH162	0.82	1.60	7.5
NH163	0.82	1.60	10.0
NH164	0.82	1.60	12.5
NH166	0.82	1.60	20.0
NH242	1.22	2.40	7.5
NH243	1.22	2.40	10.0

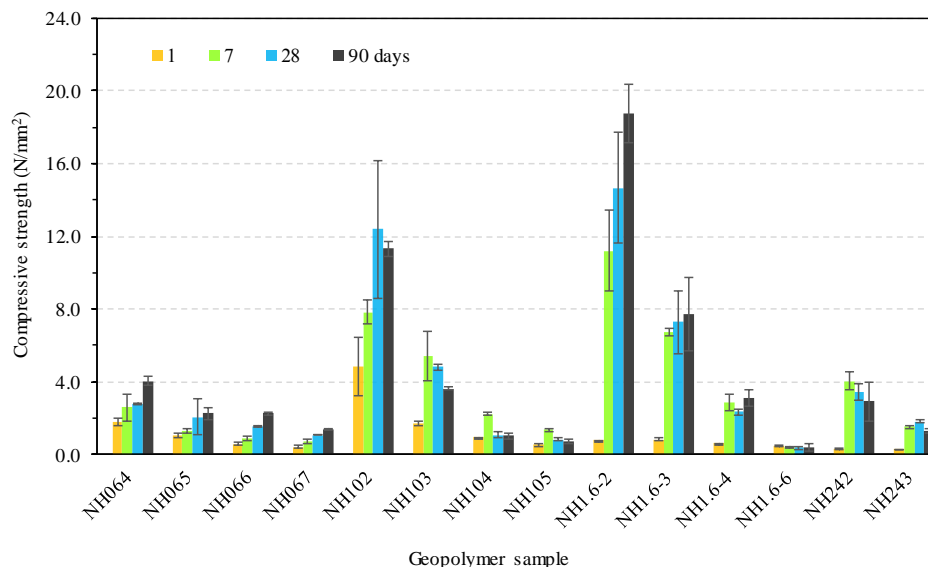
### 3 Results and discussion

#### Compressive strength test

The compressive strength of all geopolymer samples cured at 30°C as shown in **Fig. 1** increased with prolonging curing times from 1 to 28 days and then decreased at 90 days in samples. The better development of early-age strength of geopolymer at 1 day was obtained in sample using small ratio of H<sub>2</sub>O/Na<sub>2</sub>O. This suggested that the higher H<sub>2</sub>O content, the lower concentration of alkaline activator leading to the difficulty of silica and alumina breakdown from raw material resulting in insufficient SiO<sub>4</sub> and AlO<sub>4</sub> tetrahedral units to form geopolymeric gel [13]. In addition, the system that had higher H<sub>2</sub>O/Na<sub>2</sub>O, for example, at H<sub>2</sub>O/Na<sub>2</sub>O of 20 (NH166) favoured the formation of various zeolite products. These products possessed lower strength as the connectivity of binding phases was interrupted by the formation of particulate zeolites [14-16]. The highest early-age compressive strength was found in sample having ratios of Na<sub>2</sub>O/Al<sub>2</sub>O<sub>3</sub> = 1.0 and H<sub>2</sub>O/Na<sub>2</sub>O = 12.5. The improvement of compressive strength was gradually increased by increasing curing time and found to reach highest value at 90 days in sample having higher ratio of Na<sub>2</sub>O/Al<sub>2</sub>O<sub>3</sub> (1.6) and lower ratio of H<sub>2</sub>O/Na<sub>2</sub>O (7.5). However, sample having lower ratios of Na<sub>2</sub>O/Al<sub>2</sub>O<sub>3</sub> = 1.0, H<sub>2</sub>O/Na<sub>2</sub>O = 12.5 did not confirm to the

previous trend. The decline in both early and later-age of sample was obtained at the ratio of  $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3 = 2.4$ ,  $\text{H}_2\text{O}/\text{Na}_2\text{O} = 7.5\text{-}10.0$ . Based on this study, the ratio of  $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$  higher than 2.4 could not be performed since the concentration of alkaline precursor would become extremely high. Then the reprecipitation of white clear solid crystal was formed.

The results confirmed that the variable selection such as  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{Na}_2\text{O}$  and  $\text{H}_2\text{O}$  contents in the initial mixtures had a great impact on final property of geopolymer samples. The decreasing in compressive strength would be correlated to the microstructure transformation [17]. Characterization techniques such as XRD and SEM were used to identify microstructure of reaction products in geopolymer samples.

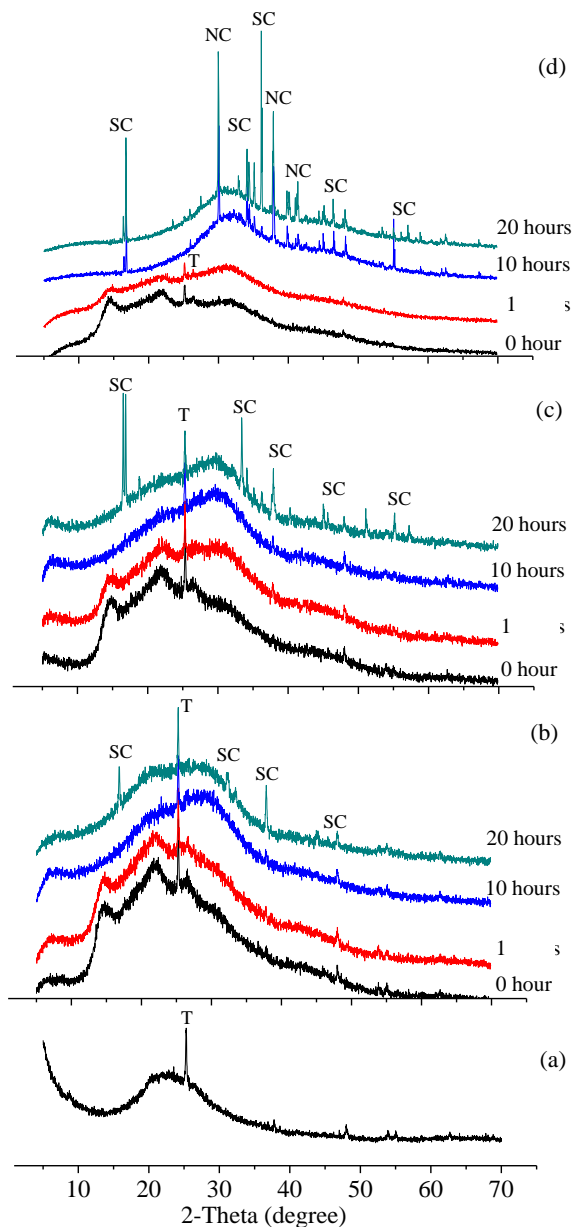


**Fig. 1** Compressive strength of geopolymer samples at different ratios of  $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$  and  $\text{H}_2\text{O}/\text{Na}_2\text{O}$  cured at  $30^\circ\text{C}$  for 1, 7, 28 and 28 days

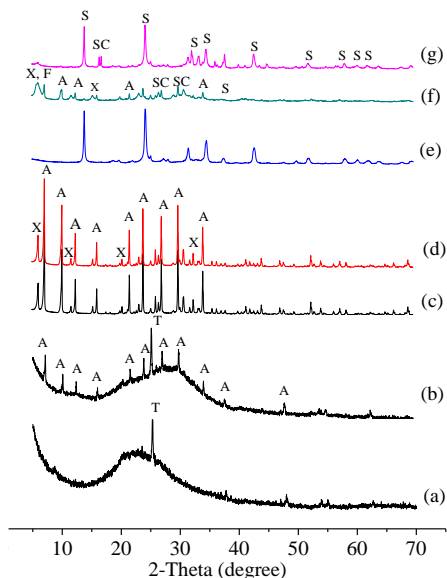
### Characterizations of geopolymer samples

**Fig. 2** shows in-situ XRD patterns of fresh geopolymer pastes of selected sample NH064 ( $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3 = 0.6$  and  $\text{H}_2\text{O}/\text{Na}_2\text{O} = 20$ ), NH102 ( $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3 = 1.0$  and  $\text{H}_2\text{O}/\text{Na}_2\text{O} = 12.5$ ) and NH243 ( $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3 = 2.4$  and  $\text{H}_2\text{O}/\text{Na}_2\text{O} = 10$ ). Three set of samples; minimum, medium and maximum ratio of  $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$  were observed. By increasing curing time, broad and low intensity appeared at 2-Theta of 30 degrees instead of 20 degrees, indicating the transformation of amorphous phase (metakaolin)-to-amorphous gel (geopolymer). In addition, phase transformation from geopolymeric gel to zeolite phase could also be occurred [18]. Sample using minimum ratio of  $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$  tended to have slower rate of phase transformation (metakaolin-geopolymeric-zeolite) as shown in **Fig. 2** (b) and **Fig. 3** (b), indicating non-preference to form geopolymer. The faster phase transformation was observed in sample having high ratio of  $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$  as presented in **Fig 2** (c) and (d). These could be suggested that the higher  $\text{Na}_2\text{O}$  content, the rising of pH in system resulting in better dissolution rate of  $\text{SiO}_4$  tetrahedral and  $\text{AlO}_6$  octahedral units in metakaolin to form geopolymeric gel [19-21]. The presence of amorphous gel supported the development of high compressive strength. Moreover,

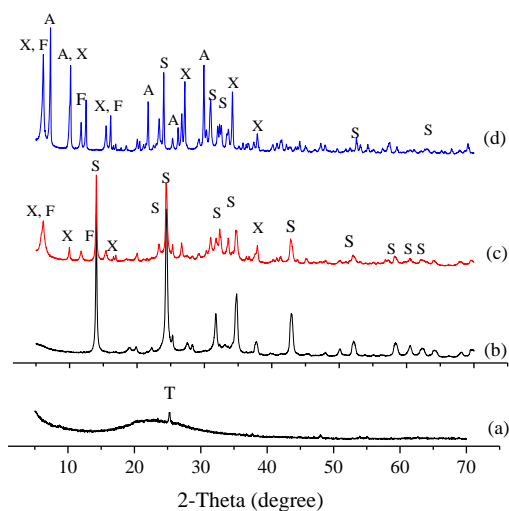
due to the real-time observation by in-situ XRD machine, the extra Na ion was found to form compounds with  $\text{CO}_2$  in atmosphere. Appearances of sodium bicarbonates,  $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$  and  $\text{Na}_2\text{CO}_3$  were found in all samples. The decline rate of geopolymerization reaction and the formation of sodium bicarbonates compounds resulted in the degradation of the compressive strength of geopolymer samples.



**Fig. 2** In-Situ XRD patterns of fresh geopolymer pastes with different ratios of  $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ ; (a) Metakaolin, (b) NH064, (c) NH102 and (d) NH243, performed at  $30^\circ\text{C}$  for 0-20 hours. T =  $\text{TiO}_2$  (Anatase), SC =  $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$ , NC =  $\text{Na}_2\text{CO}_3$

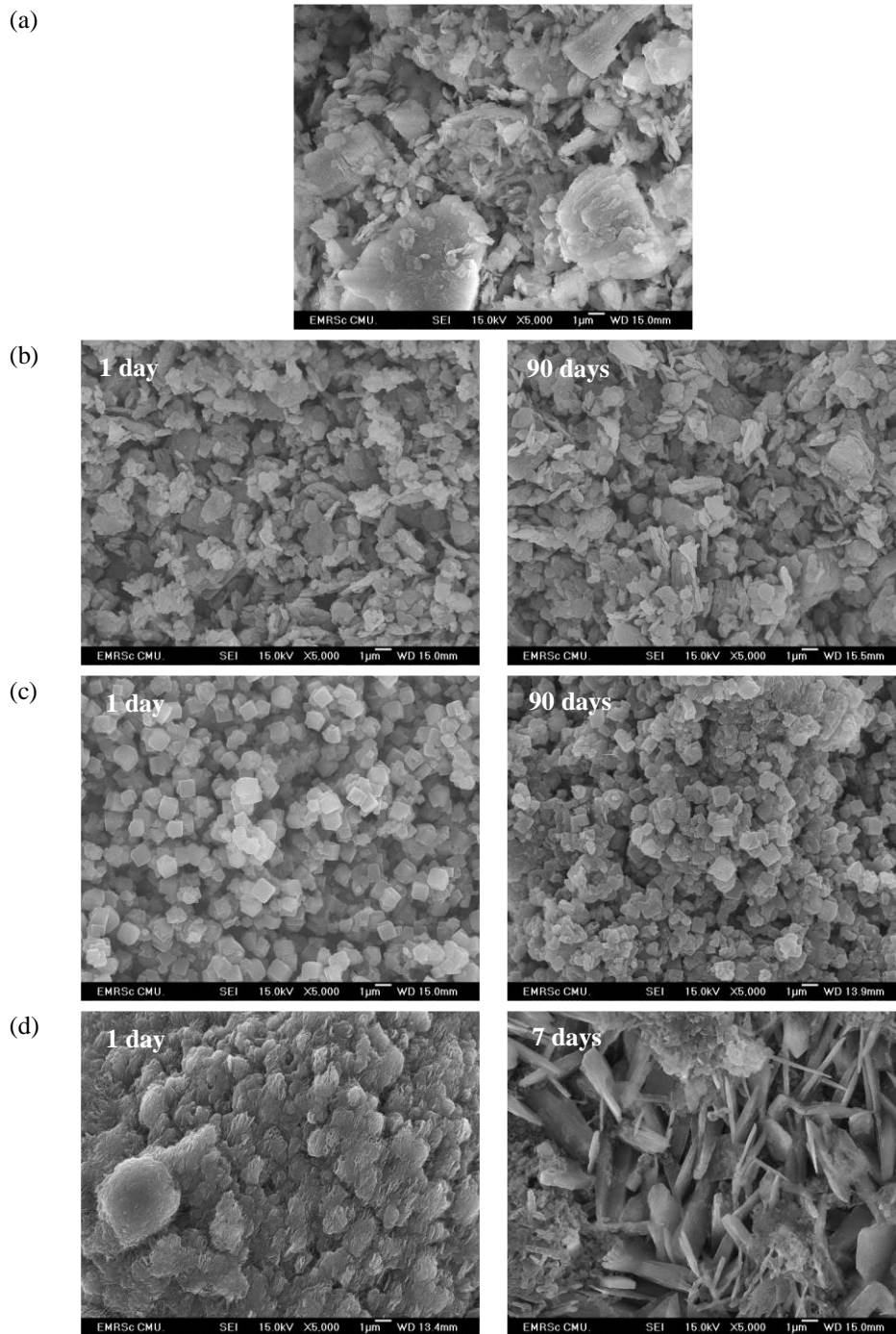


**Fig. 3** XRD patterns of fresh geopolymer pastes with different ratios of  $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$  and curing times; (a) Metakaolin, (b) NH064, 21 days, (c) NH102, 28 days, (d) NH102, 90 days, (e) NH162, 28 days, (f) NH162, 90 days and (g) NH243, 28 days. T =  $\text{TiO}_2$  (Anatase), SC =  $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$ , A = Zeolite A, X = Zeolite X, F = Faujasite, S = Sodalite



**Fig. 4** XRD patterns of geopolymer paste with  $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$  of 1.6 using different ratios of  $\text{H}_2\text{O}/\text{Na}_2\text{O}$ ; (a) Metakaolin, (b) 7.5, (c) 12.5 and (d) 20.0, curing at  $30^\circ\text{C}$  for 28 days. T =  $\text{TiO}_2$  (Anatase), A = Zeolite A, X = Zeolite X, F = Zeolite Faujasite, S = Sodalite

Degree of crystallinity increased with curing times in all samples as shown in **Fig. 3** and **Fig. 4**. The XRD patterns indicated that all geopolymer samples consisted of crystalline zeolite as a



**Fig. 5** SEM images of geopolymer samples with different ratios of  $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$  and  $\text{H}_2\text{O}/\text{Na}_2\text{O}$ ; (a) Metakaolin, (b) NH064, (c) NH102, (d) NH243 cured at  $30^\circ\text{C}$  with different curing times

majority together with small amounts of amorphous geopolymeric gel. The zeolites observed in these samples included sodalite (pseudo-phase zeolite) and zeolite belonging to the Faujasite group, type A and X. **Fig. 5** illustrates the SEM images of reaction products cured at different times. All above results confirmed that an increase in  $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$  and  $\text{H}_2\text{O}/\text{Na}_2\text{O}$  ratios promoted the transformation of amorphous gel to zeolite, resulted in lower compressive strength.

#### 4 Conclusion

Metakaolin based geopolymers with  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio of 1.96 and different ratios of  $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$  and  $\text{H}_2\text{O}/\text{Na}_2\text{O}$  were successfully formulated with sodium hydroxide solution. The formation of amorphous gel was obtained with increasing curing times, resulted in the improvement of compressive strength. The adjustment of initial molar ratios of  $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$  and  $\text{H}_2\text{O}/\text{Na}_2\text{O}$  was found to have significant effect on amorphous (metakaolin) to amorphous geopolymeric gel to zeolite phase transformation. Increasing the ratios of  $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$  and  $\text{H}_2\text{O}/\text{Na}_2\text{O}$  tended to favour the formation of amorphous gel and various types of zeolite. These could be identified as sodalite (pseudo-phase zeolite) and zeolite belonging to the Faujasite group, as well as zeolite X, and A. The systems that favoured the formation of zeolitic products tended to provide lower strength products.

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