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Formation of One-Part-Mixing Geopolymers and Geopolymer Ceramics from Geopolymer Powder

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Abstract

Geopolymer powder prepared through pre-curing and pulverization showed great potential to produce one-part-mixing geopolymers as well as high flexural strength geopolymer ceramics. The one-part-mixing geopolymers were prepared by mixing geopolymer powder with water while the geopolymer ceramics were prepared by powder metallurgy and sintering. The one-part-mixing geopolymers achieved a compressive strength of 10 MPa after 28 days with formation of geopolymer precipitates in conjunction with zeolite phases. Despite the lower strength, they remained stable and did

not disintegrate when immersed in water. Besides, the geopolymer ceramics exhibited high flexural strength (90 MPa) after sintering at 1200°C as result of nepheline formation.

1.0 Introduction

Geopolymers have become a potential alternative binder to ordinary Portland cement (OPC) in some applications due to its sustainability criteria of lower emission of greenhouse gases and low energy consumption [1]. Geopolymers are inorganic polymeric materials with three-dimensional Si-O-Al frameworks synthesized from aluminosilicates which dissolved in alkaline medium [2]. Apart from having excellent early and long-term mechanical strength, geopolymers also have low shrinkage value, low density, good immobilization of heavy metal and good fire and chemical resistance [3, 4]. This accounts for the suitability of geopolymers for applications as construction materials in building, refractory and wastewater treatment industries [5-8].

Geopolymers are formed through geopolymerization reaction involving the dissolution of aluminosilicate sources in highly alkaline medium releasing Si and Al species, diffusion, exchange and oligomerization between the dissolved species in aluminosilicates and alkaline solution with formation of small coagulated structures, gelation and lastly hardening to form hard solid [9-11]. The ordinary formation process of geopolymers was a two-part-mixing process, which involves preparation of alkali activator 1 day prior to mixing and the mixing of solid aluminosilicates with the prepared alkali activator. Due to the importance and growing demands of geopolymer technology, researchers are finding ways to produce geopolymers from a ready-mix precursor that can

2

directly mix with water just like OPC does, which is termed as the one-part-mixing geopolymer system [12]. There are few reasons whereby the one-part-mixing geopolymer system is essential. This is to avoid handling of a large quantity of highly corrosive solution as in the two-part-mixing geopolymer mix. Besides, the use of highly corrosive solution requires large storage as well as restricts the transportation of the solution for on-site applications. Hence, large-scale applications are limited.

Early study on one-part-mixing geopolymer mixture involved the calcination of aluminosilicates with solid alkali hydroxides or carbonates. Clinker was formed, pulverized into powder (one-part-mixing geopolymer precursor) and finally added with water to form one-part-mixing geopolymers. The calcination process involved transformation into Al-rich phase with hydroxides incorporated in the aluminosilicates matrix and formation of reactive functional groups. In particular, Kolousek *et al.* [13] calcined low-quality kaolin together with alkali hydroxides at 550°C for 4 hours, followed by pulverization and mixing water to produce one-part-mixing geopolymers. However, the one-part-mixing geopolymers exhibited extremely low compressive strength (< 1 MPa) after 7 days. Subsequently, Feng *et al.* [14] prepared one-part-mixing geopolymer precursor through the calcination of a mixture of albite, sodium hydroxide (NaOH) and sodium carbonate (Na_2CO_3). The produced one-part-mixing geopolymers had excellent compressive strength of > 40 MPa after 28 days. The final products contained amorphous geopolymer phases and crystalline zeolite phases. A similar study had been carried out by Ke *et al.* [15] using red mud and NaOH pellets. The one-part-mixing geopolymers attained a maximum compressive strength of 10 MPa after 28 days. These studies required the necessity of high-temperature calcination in order to obtain the

one-part-mixing geopolymer precursor. Another method of producing one-part-mixing geopolymers with no requirement of calcination was proposed by Hajimohammadi *et al.* [16]. One-part-mixing geopolymers were formed by direct mixing geothermal silica, solid sodium aluminate with water. Nevertheless, their study focused on the microstructural observation and the compressive strength of the one-part-mixing geopolymers was not discussed. Formation of geopolymer matrix and typical characteristic diffuse halo of geopolymer could be observed through SEM and XRD analyses, respectively. In addition, Nematollahi *et al.* [17] formed one-part-mixing geopolymers constituting low calcium fly ash, slag, hydrated lime with solid sodium silicate (Na_2SiO_3) and NaOH. The comparison of geopolymers formed through one-part and two-part mixing processes has found that the one-part-mixing geopolymers made from fly ash have moderate to high compressive strength of over 37 MPa after 28 days. The compressive strength was comparable to the two-part-mixing geopolymers (42.5 MPa after 28 days).

In the present study, the aluminosilicates and alkali activator were mixed to produce geopolymer paste which was pre-cured and then pulverized into geopolymer powder. The geopolymer powder was mixed with water directly to form one-part-mixing geopolymers. The adopted preparation method differed from those aforementioned above in order to study any possible formation methods of one-part-mixing geopolymers. The previous works have investigated the effect of NaOH concentration, metakaolin/activator and sodium silicate/sodium hydroxide ratios [18, 19] on the mechanical properties of the mixed geopolymer pastes. The geopolymer powder could be used as the ready-mixed precursor to form one-part-mixing geopolymers by just adding water. In this article, the

changes in physical properties and extent of strength increment were studied by varying the curing temperature and time.

Most importantly, geopolymer powder can be advantageously used to produce geopolymer ceramics. Sintering caused the formation of ceramics product due to the formation of crystalline phases. For as-cured monolithic geopolymers, direct high-temperature sintering caused excessive shrinkage and cracking and consequently lower the strength of the final products [20, 21]. Based on Xie *et al.* [22], the formation of geopolymer powder, powder metallurgy and lastly sintering could address the cracking issue which occurred in the as-cured geopolymers. They successfully produced leucite glass-ceramics from geopolymer powder based on potassium precursors. For sodium-based geopolymers, nepheline-predominated crystallites formed when sintered at elevated temperatures [23, 24]. Nepheline ceramics have hitherto been produced through sintering-crystallization, controlled devitrification and vitrification process of zeolites [25, 26], fly ash and slag [27] in the temperature range of 600 - 1200°C. In their study, the mechanical strength of the prepared nepheline ceramics was not studied. The production of nepheline ceramics using geopolymer powder has not been studied. Thus, this work investigated another choice method to produce nepheline ceramics from geopolymer.

To recap briefly, the physical and mechanical properties of one-part-mixing geopolymers and geopolymer ceramics prepared from sodium-based geopolymer powder were investigated in this work.

2.0 Experimental Work

2.1 Materials

Clay-based aluminosilicate source was used in this work. For the preparation of one-part-mixing geopolymers, metakaolin was used. Kaolin was subjected to thermal treatment at 800°C for 2 hours to obtain metakaolin. On the other hand, kaolin was utilised in the formation of geopolymer ceramics. The chemical composition of kaolin and metakaolin employed was determined using XRF analysis is tabulated in **Table 1**. The microstructures of kaolin and metakaolin particles are shown in **Figure 1**. It can be seen that both kaolin and metakaolin are plate-like and needle-like structures. However, the plate-like structure was more open in metakaolin [18, 28].

Table 1: Chemical composition of kaolin and metakaolin as determined by XRF analysis.

Compound	Mass (%)	
	Kaolin	Metakaolin
SiO_2	54.5	54.1
Al_2O_3	32.4	33.0
K_2O	5.58	5.67
TiO_2	1.33	1.34
Fe_2O_3	4.32	4.41
MnO_2	0.09	0.11
ZrO_2	0.08	0.09

Needle-
like
structure

Plate-
like
structure

Needle-
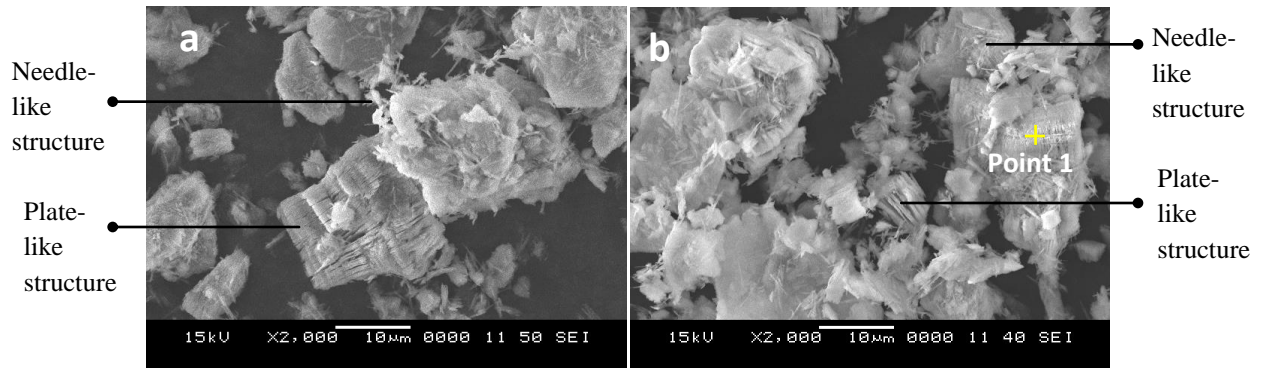like
structure

Plate-
like
structure

Figure 1: SEM image of (a) kaolin and (b) metakaolin (Point 1 – EDX Spot of metakaolin particle).

The activator solution was a mixture of sodium hydroxide (NaOH) solution and liquid sodium silicate (Na_2SiO_3). The NaOH pellet has purity of 99% while the liquid Na_2SiO_3 contains 30.1% SiO_2, 9.4% Na_2O and 60.5% H_2O and SiO_2/Na_2O modulus of 3.2. Based on Jansson *et al.* [29], the modulus of Na_2SiO_3 affected the pH, viscosity and the setting time of the geopolymer mixtures. Low modulus close to 1 led to precipitation of hydrous sodium metasilicate crystals [30]. Thus, higher modulus Na_2SiO_3 was chosen as it becomes more siliceous that provides more free Si species for geopolymer structure formation [31]. The NaOH stock solution was prepared and cooled down to room temperature before use. The activator solution was prepared 24 hours before mixing process.

To avoid confusion, the following terms are used in the present study:

i)   Fresh paste is the paste before pre-curing;

ii) Pre-cured geopolymers is the sample that has set after pre-curing;

iii) Fresh one-part-mixing geopolymer paste is the paste after the geopolymer powder was mixed with water;

7

iv) One-part-mixing geopolymer is the hardened geopolymer paste produced from the mixing of geopolymer powder and water;

v) Green body is the geopolymer ceramic before sintering; and

vi) Geopolymer ceramic is the sintered ceramics produced from the geopolymer powder.

2.2 Formation of Geopolymer Powder

The aluminosilicate source was mixed with the prepared activator solution until a homogeneous paste was achieved. The paste was moulded and pre-cured in the oven. Then, the pre-cured geopolymer was pulverized and sieved to produce geopolymer powder. The experimental procedure is illustrated in **Figure 2**.
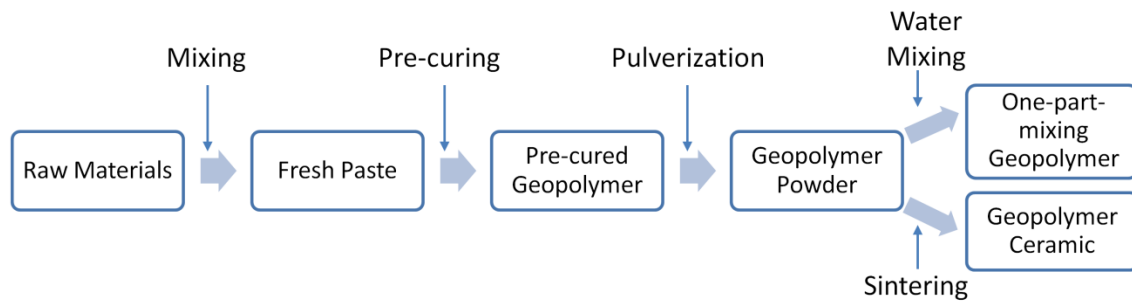
Figure 2: Steps to produce geopolymer powder, one-part-mixing geopolymer and geopolymer ceramic.

In order to produce metakaolin geopolymer powder, the metakaolin/activator and Na_2SiO_3/NaOH ratios were 0.8 and 0.2, respectively. The fresh paste was pre-cured at 80°C for 4 hours. These mixing ratios and pre-curing condition were selected based on

the previous experimental work [32] considering the viscosity of geopolymer mixtures and the highest compressive strength of the one-part-mixing geopolymers. Additionally, the pre-curing time was selected based on the setting time of the fresh paste. On the other hand, for kaolin geopolymer powder, the kaolin and activator solution were mixed at the ratio of 1 and the Na_2SiO_3/NaOH ratio was 0.24 based on previous work [33]. The corresponding fresh paste was pre-cured at 80°C for 24 hours. For kaolin fresh paste, the pre-curing time was longer because it requires longer setting time than metakaolin fresh paste.

2.3 Formation of Metakaolin One-Part-Mixing Geopolymers

One-part-mixing geopolymers were formed by mixing metakaolin geopolymer powder with 22% of mixing water. This meant that we are producing geopolymer powder which can be used to produce geopolymers again by just adding water just like the way of producing ordinary Portland cement (OPC) paste. The fresh one-part-mixing geopolymer paste was then cured in an oven at varying curing conditions (room temperature (RT, 29°C), 40°C, 60°C, 80°C and 100°C for 6, 12, 24, 48 and 72 hours). After the curing process, the one-part-mixing geopolymers were kept at room temperature until the day of testing. The details of mixtures for the formation of one-part-mixing geopolymers are given in **Table 2**.

Table 2: Details of mixtures for one-part-mixing geopolymers.

Mix No.	NaOH Molarity (M)	Metakaolin/ Activator Ratio	Na$_2$SiO$_3$/ NaOH ratio	Pre-curing Temperature (°C)	Time (hour)	Curing Temperature (°C)	Time (hour)
1	8	0.80	0.24	80	4	RT (29)	-
2 – 6	8	0.80	0.24	80	4	40	6, 12, 24, 48, 72
7 – 11	8	0.80	0.24	80	4	60	6, 12, 24, 48, 72
12 – 16	8	0.80	0.24	80	4	80	6, 12, 24, 48, 72
17 – 21	8	0.80	0.24	80	4	100	6, 12, 24, 48, 72

2.4 Formation of Kaolin Geopolymer Ceramics (KGC)

The KGC was prepared by powder metallurgy method. The kaolin geopolymer powder was compacted using a stainless steel die and pressed at 5 tonnes for 2 minutes using cold isostatic pressing. The green body was then sintered at varying sintering temperatures (900°C, 1000°C, 1100°C and 1200°C) in a furnace at heating rate of 5°C/min and soaking time of 3 hours to produce geopolymer ceramics. The range of sintering temperature was selected through trial-and-error and based on the temperature range used by previous researchers [25-27] in the formation of nepheline using different methods. The details of mixtures for the formation of KGC are tabulated in **Table 3**.

Table 3: Details of mixtures for KGC.

| Mix No. | NaOH Molarity (M) | Kaolin/ Activator Ratio | Na$_2$SiO$_3$/ NaOH Ratio | Pre-curing | | Sintering Temperature (°C) |
				Temperature (°C)	Time (hour)	
22	12	1.00	0.24	80	24	900
23	12	1.00	0.24	80	24	1000
24	12	1.00	0.24	80	24	1100
25	12	1.00	0.24	80	24	1200

2.5 Testing and Characterization

The setting time of fresh paste was measured by using Vicat apparatus as accordance to ASTM C191. The penetration of Vicat needle was recorded every 15 minutes until a penetration of 25 mm or less was obtained. By interpolation, initial setting time was determined. Final setting time was reached when the needle did not sink visibly into the paste. The density of samples was measured using AccuPyc II 1340 He Pycnometer. The water absorption of geopolymer ceramics was measured accordance to ASTM C373 and calculated using Equation 1.

$$\text{water absorption} = \frac{W_s - W_d}{W_d} \times 100\% \qquad (1)$$

Where W_s is the saturated weight after immersion in water and W_d is the dry weight before immersion in water. The compressive strength test was performed on the one-part-mixing geopolymers while flexural strength test was performed on the KGC. The specimen size was 50 mm × 50 mm × 50 mm for compressive strength test and 52 mm × 7 mm × 5 mm for flexural strength test. Both strength tests were carried out by using

11

Instron Machine series 5569 Mechanical Tester. Three specimens were tested for each parameter. The microstructural analysis was carried out using JSM-6460 LA model Scanning Electron Microscope (JEOL). The crystallographic analysis was performed using XRD-6000 Shimadzu X-ray diffractometer. The specimen for analysis was in powder form scanning from 10° to 80° 2θ at a scan rate of 2°/min and scan steps of 0.02° 2θ.

3.0 Results and Discussion

3.1 Metakaolin One-Part-Mixing Geopolymers

In this work, the fresh paste was pre-cured and then pulverized into geopolymer powder. The pre-curing process in oven promoted faster setting of fresh paste in order to obtain solidified geopolymers to proceed to the pulverizing process. **Figure 3** reveals the SEM images of geopolymer powder and the one-part-mixing geopolymers. Geopolymerization took place starting from the dissolution of metakaolin, formation of oligomers from the dissolved Si and Al species, gelation and hardening of gel to form geopolymers [9-11]. The geopolymerization reaction continued after hardening leading to rearrangement of the geopolymer matrix into three-dimensional networks together with the formation of zeolitic phases [34]. Thus, it was supposed that the pre-curing process begins from gelation towards the final set of fresh paste. This rendered the formation of initial geopolymer phases [35] and was considered as an initial step of geopolymerization reaction and the metakaolin had not fully reacted with the activator solution. Thus, the geopolymer powder had large amount of remnant particles of metakaolin (**Figure 3a**).

Only a small amount of geopolymer precipitation was seen in geopolymer powder indicated by the small globular-shaped particles [36].

In order to produce one-part-mixing geopolymers, the geopolymer powder was mixed with water and cured in oven. The geopolymerization reaction continued after the geopolymer powder was mixed with water. During the mixing of water with the geopolymer powder, water was important as a transportation and dissolution medium to allow for further geopolymerization reaction [37]. This was shown by more compact with spherical-shaped units, fewer voids and more intervening geopolymer matrix in one-part-mixing geopolymers (**Figure 3b-f**). The microstructure was almost similar to that for two-part-mixing geopolymers. As proposed in the previous work [38], the mixing water reacted with the excess Na content in the system forming NaOH that attacked the aluminosilicates in the geopolymer powder releasing dissolved species for polymerization to form rigid structure.

Curing temperature and time induced changes in the microstructure of one-part-mixing geopolymers. For room-temperature-cured one-part-mixing geopolymers (**Figure 3b**), large quantity of residual metakaolin particles was observed. Low-temperature curing led to the slower dissolution of MK and thus the geopolymerization process [35]. On the other hand, the one-part-mixing geopolymers cured at 60°C for 72 hours showed formation of geopolymer matrix packed in a unfastened manner after 1 day. Densification of structures could be clearly observed over age indicated by the thick intervening matrix (**Figure 3c – d**). As refer to the microstructure of one-part-mixing geopolymers cured at 80°C (**Figure 3e**) and 100°C (**Figure 3f**) for 72 hours, the structure was loosely-packed with large pores and residual metakaolin particles. The rapid polymerization and

13

transformation into hard geopolymer structures in conjunction with the moisture loss hindered the continual dissolution and structure formation and hence led to the production of a sparse matrix [9, 39].
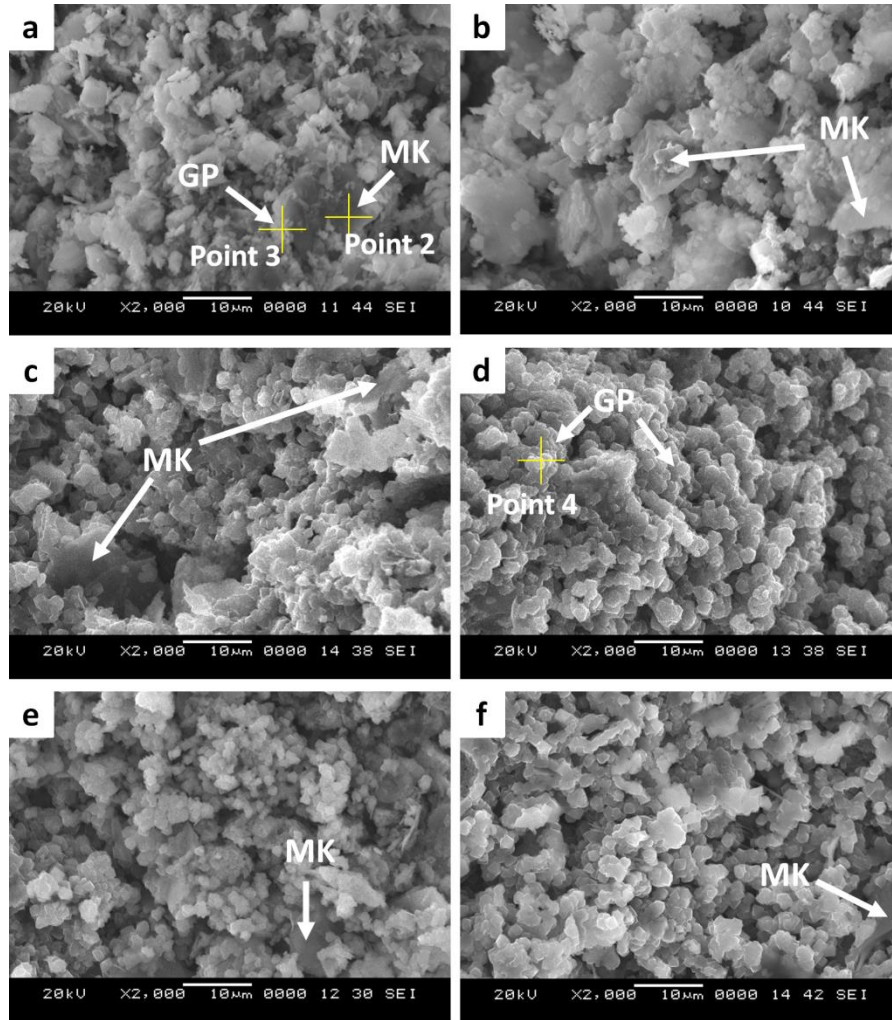

Figure 3: SEM micrographs of (a) geopolymer powder and one-part-mixing geopolymers cured at (b) RT (Mix 1) – 28 days; (c) 60°C – 72 hours (Mix 11) – 1 day; (d) 60°C – 72 hours (Mix 11) – 28 days; (e) 80°C – 72 hours (Mix 16) – 28 days; and (f) 100°C – 72 hours (Mix 21) – 28 days (MK – Remnant metakaolin particle, GP – Geopolymer precipitation, Point 2 – EDX spot of remnant metakaolin particles, Point 3 and Point 4 – EDX spots of geopolymer precipitation).

When the fresh one-part-mixing geopolymer paste was cured in oven at different temperatures, the setting time varied. **Table 4** presents the setting time of one-part-mixing geopolymer paste at varying curing regimes. Increasing curing temperature shortened the setting of one-part-mixing geopolymers. Heat accelerated and promoted the continual geopolymerization reaction. Room-temperature curing (Mix 1) had longer setting time whereby they reach to complete set after 20 hours. In overall, one-part-mixing geopolymer paste could be handled up to 79 minutes in temperature ranging from 40°C to 100°C. The similar observation has been reported by Tempest *et al.* [39] when optimizing the compositional mixing design and curing conditions of two-part-mixing geopolymers.

Table 4: Setting time of fresh one-part-mixing geopolymer paste at varying curing regimes.

Mix No.	Curing Temperature	Initial setting (minute)	Final Setting (minute)
1	RT (≈ 29°C)	923	1200
2	40 °C	637	795
7	60 °C	337	420
12	80 °C	165	255
17	100 °C	79	120

The bulk density of one-part-mixing geopolymers decreased with increasing curing temperature and longer heat exposure (**Table 5**). Ageing from 7 to 28 days reduced the bulk density due to the loss of moisture during the extended curing [35, 40].

The behaviour resembled the ordinary two-part-mixing geopolymers. However, the reduction was not significant. This was probably due to the formation of geopolymer structure that compensated the loss of moisture from the structure.

Table 5: Density values (g/cm^3) of one-part-mixing geopolymers at varying curing regimes.

Curing Time	Curing Temperature (°C)							
	40		60		80		100	
	Mix 2 – 6		Mix 7 – 11		Mix 12 – 16		Mix 17 – 21	
	7 days	28 days	7 days	28 days	7 days	28 days	7 days	28 days
6 hours	2.656	2.532	2.491	2.418	2.481	2.300	2.401	2.256
12 hours	2.623	2.311	2.454	2.312	2.322	2.298	2.358	2.194
24 hours	2.538	2.281	2.309	2.257	2.273	2.148	2.201	2.068
48 hours	2.481	2.188	2.298	2.258	2.268	2.128	2.168	2.026
72 hours	2.358	2.100	2.233	2.172	2.129	2.033	2.077	2.018

Room-temperature curing led to extremely low compressive strength in the one-part-mixing geopolymers (2.1 MPa after 28 days). At moderate curing temperatures (40°C and 60°C), the one-part-mixing geopolymers developed strength steadily at shorter curing time. Extending the curing time (> 24 hours) caused substantial strength increment at 40°C (**Figure 4a**). At 60°C, marginal increment in compressive strength with ageing was observed when cured from 12 hours to 48 hours. Instead, the compressive strength remained almost unchanged after 7 days (**Figure 4b**). Low temperature caused a delay in the beginning of setting and hindered the strength development while the supply of heat

during the curing process facilitated the rate of geopolymerization reaction as mentioned earlier.

Besides, at higher curing temperature (80°C and 100°C), the early compressive strength achieved was higher than that with lower curing temperature (40°C and 60°C). Higher curing temperature speeded up the chemical reaction that directly increases the mechanical properties of geopolymers [10, 41, 42]. Even so, the compressive strength deteriorated with longer curing time and the elevated temperature curing. Even though they gave higher early compressive strength, the strength did not develop further with ageing but in opposite, it decreased [43, 44]. The same behaviour was observed in two-part-mixing geopolymer system [35]. A substantial drop in compressive strength was noticeable for one-part-mixing geopolymers cured at 80°C for 72 hours (**Figure 4c**) and 100°C for 24 to 72 hours (**Figure 4d**). The key factor that caused a decline in strength at high-temperature curing was due to the rapid moisture loss at early of the curing process [45]. The compressive strength result was supported by the SEM images shown in **Figure 3**. Thus, the curing regimes play important role in determining the kinetics and degree of geopolymerization reaction as well as the development of the microstructure and consequently the strength of final products.

Just like ordinary two-part-mixing geopolymers [46], the compressive strength of one-part-mixing geopolymers generally improved with increasing curing temperature and time, particularly obvious at the lower curing temperature (40°C and 60°C) and it is recommended to cure at shorter curing time if high-temperature curing is chosen. As refer to **Figure 4**, at shorter curing time (< 48 hours), the strength increment was marginal. Yet, the strength increment at curing time of 72 hours was substantial, particularly in the case

of 60°C (**Figure 4b**). This implied that enough heat is acquired for the continuous geopolymerization reaction. Besides, the strength increment from 7 to 28 days was also small. The strength trend was well-agreed by Adam & Harianto [47] whereby most of the strength was achieved at early 7-day and only minimum increment up to longer ageing.

From the result, curing at 60°C for 72 hours was recommended as the optimum curing condition. Despite the lower compressive strength (2 − 10 MPa), they were resistance towards the water and did not disintegrate in water (result not shown here). Likewise, in the study by Peng *et al.* [48], some of the one-part-mixing geopolymers produced softened in the water. However, the compressive strength of one-part-mixing geopolymers obtained was higher than those obtained by Kolousek *et al.* [13] (< 1 MPa after 7 days) even for the room-temperature cured one-part-mixing geopolymer. Besides, the one-part-mixing geopolymers produced by Peng *et al.* [48] do not gain reasonable compressive strength even though they are cured at 80°C for 3 days. The compressive strength was also comparable to the compressive strength of one-part-mixing geopolymers obtained by Ke *et al.* [15] through the calcination of red mud and NaOH pellets.
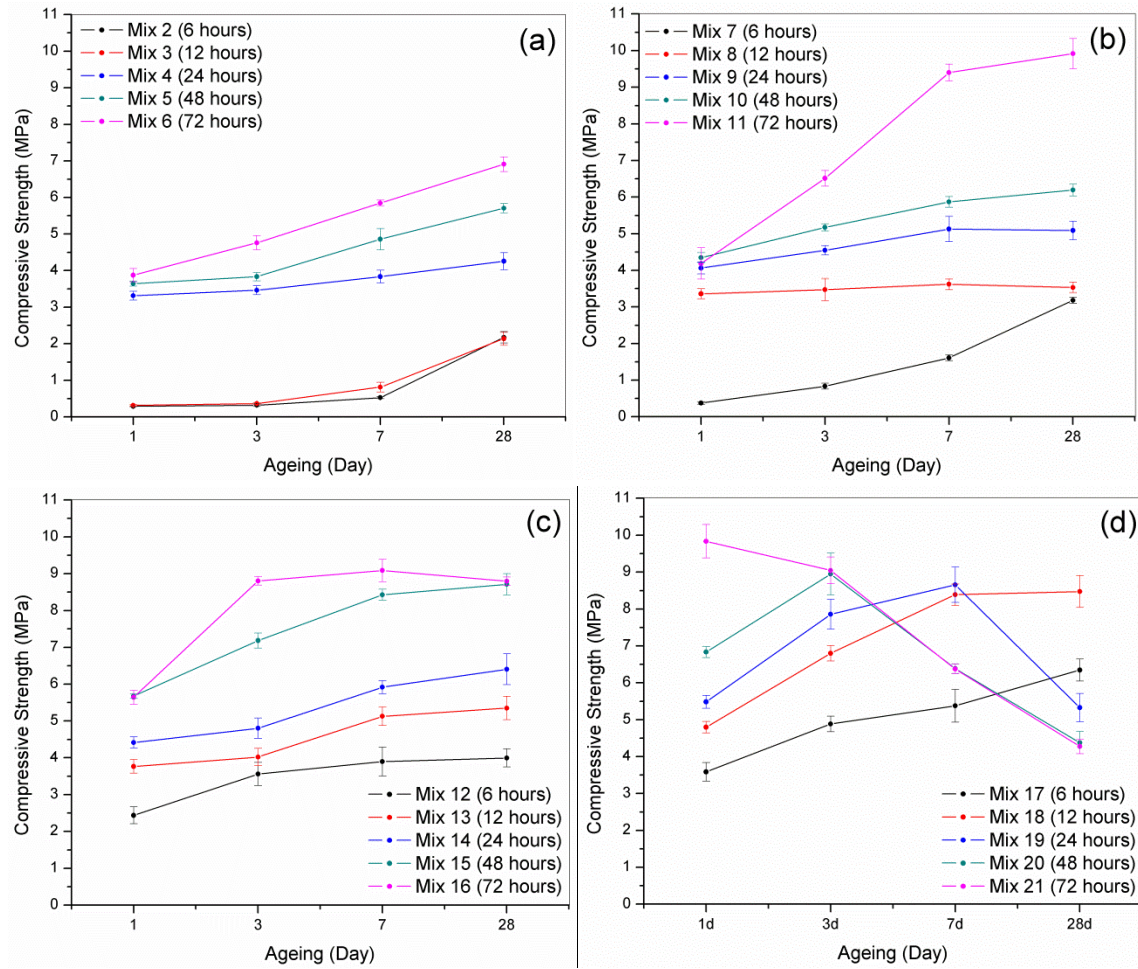
Figure 4: Compressive strength of one-part-mixing geopolymers cured at 40°C (a), 60°C (b), 80°C (c) and 100°C (d) for 6, 12, 24, 48 and 72 hours aged 1, 3 7 and 28 days.

The EDX analysis has been performed on metakaolin particles (Point 1 in **Figure 1b**), geopolymer powder (Points 2 and 3 in **Figure 3a**) and the resulting one-part-mixing geopolymers (Point 4 in **Figure 3d**). For geopolymer powder, the analysis was spotted at unreacted metakaolin (Point 2) and globular unit of geopolymers (Point 3). The Si/Al and Na/Al ratios are tabulated in **Table 6**. The Si/Al and Na/Al ratios of metakaolin (Point 1) were almost similar to that at Point 2 in geopolymer powder. The Si/Al ratio decreased while the Na/Al ratio increased from Point 2 to Point 3. This was resulted from the

19

incorporation of Al and Na in the geopolymer structure as the reaction progresses [49]. On the other hand, the Si/Al and Na/Al ratios increased from Point 3 to Point 4. This indicated the formation of more advanced geopolymer matrix. More Si, Al and Na were incorporated in the geopolymer network.

Table 6: The Al, Na and Si contents, Si/Al and Na/Al ratios in metakaolin, geopolymer powder and one-part-mixing geopolymers.

Elements	Metakaolin	Geopolymer Powder		One-part-mixing Geopolymer
	Point 1	Point 2	Point 3	Point 4
Al	19.99	19.20	19.48	18.14
Si	25.89	26.27	25.06	25.91
Na	0.74	1.52	3.30	4.04
Si/Al	1.30	1.37	1.29	1.43
Na/Al	0.04	0.08	0.17	0.22

Figure 5 presents the XRD diffractograms of metakaolin, geopolymer powder and the one-part-mixing geopolymers. As discussed in previous paper [50], metakaolin had semi-crystalline phases with diffuse halo at 15° - 35° 2θ mainly of kaolinite (K, ICDD# 29-1488). Trace amount of quartz (Q, ICDD# 46-1045) and alunite (A, ICDD# 86-2651) can be found in metakaolin. From metakaolin towards geopolymer powder and one-part-mixing geopolymers, the diffuse halo in metakaolin shifted to higher angles representing the typical characteristic of geopolymers, that is 20° - 40° 2θ [6]. Zeolites (Z)

crystalline peaks grew in geopolymer powder and one-part-mixing geopolymers. The zeolites found were zeolite Y (ICDD# 38-0238) and unnamed zeolite (ICDD# 44-0050).

As refer to the XRD pattern of one-part-mixing geopolymers, the transition of amorphous phase into crystalline zeolite peaks was multiplying with increasing ageing from 1 to 28 days. The reduction and increment of quartz peaks in the geopolymer powder and one-part-mixing geopolymers, respectively, was probably due to the overlapping with zeolite peaks. The occurrence of zeolite phases in one-part-mixing geopolymers and even in the two-part-mixing geopolymers was commonly observed [14, 48, 51]. The addition of more water provoked the formation of zeolites [52]. It was supposed that the formation of zeolite crystals in the geopolymers limits the development of compressive strength (**Figure 4b**). This was well-agreed by Palomo *et al.* [53] and Rowles *et al.* [54] as zeolites are highly porous and low strength. According to Sturm *et al.* [55], the reduction in the crystalline phases would definitely increase the mechanical strength of one-part-mixing geopolymers. This was achieved by using rice husk ash as the precursor materials.
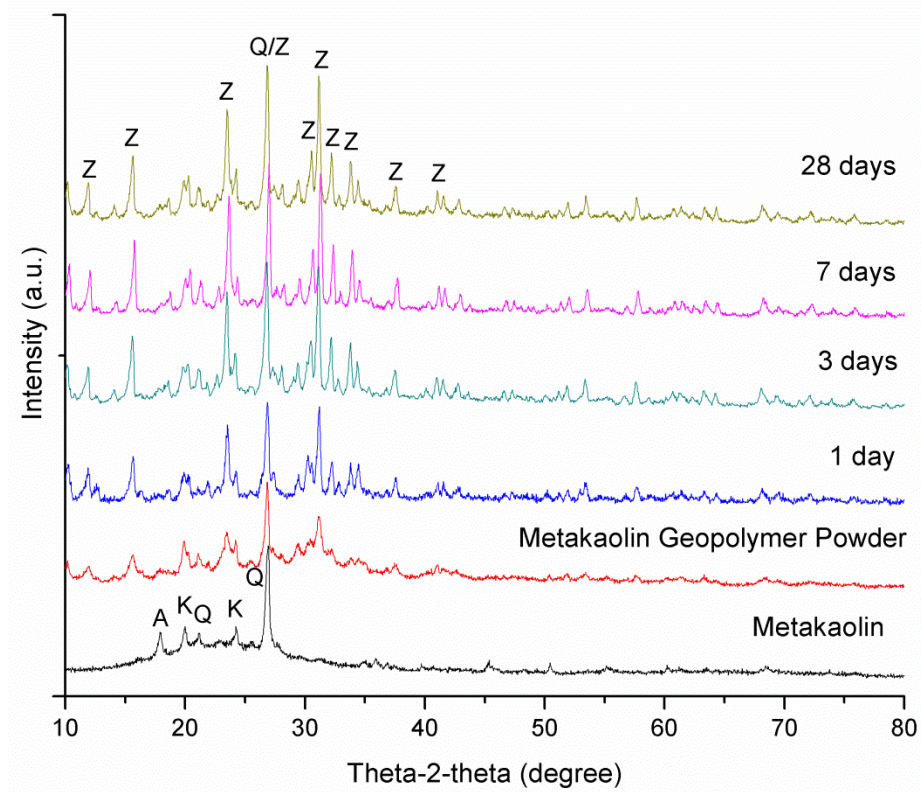
Figure 5: XRD diffractograms of metakaolin, geopolymer powder pre-cured at 80°C for 4 hours, and one-part-mixing geopolymers cured at 60°C for 3 days (Mix 11) after 1, 3, 7 and 28 days (K – kaolinite, A – alunite, Q – quartz and Z – zeolites).

3.2 Kaolin Geopolymer Ceramics (KGC)

In this work, the kaolin geopolymer powder was compressed using powder metallurgy method and the green body was sintered to produce ceramic products. **Figure 6** shows the visual appearance of KGC. The KGC surfaces became increasingly smooth and glassy with sintering temperature particularly for sample heated to 1200°C (Mix 25). The colour of the samples turned slightly lighter. The lightening of sample colours has been observed by Turkmen *et al.* [56] and Zhang *et al.* [57] for geopolymers based on slag and metakaolin-fly ash, respectively. It was supposed that the changing in colour is

due to the dehydration of moisture and phase transformation at elevated temperature. The sintering at 1300°C was overly high for KGC as it causes softening and melting (**Figure 6**). The KGC had no definite shape, which makes impossible for the measurement of flexural strength and its colour changed to brown.
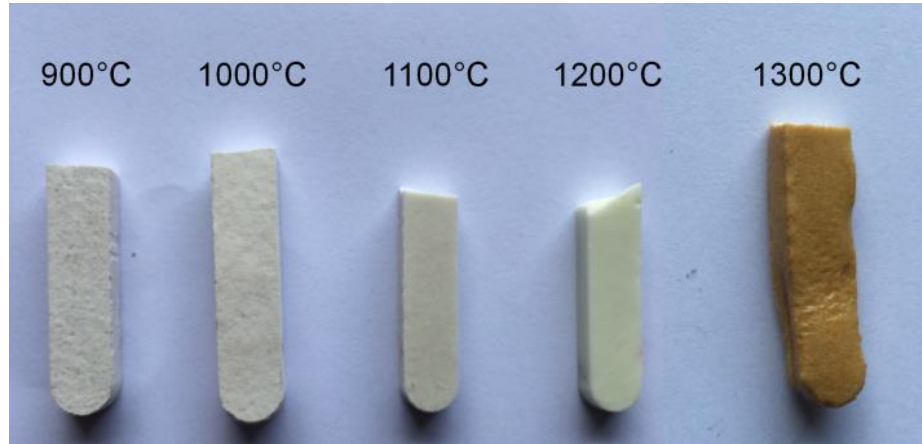

Figure 6: Visual appearance of KGC sintered at varying temperatures.

Figure 7 presents the density, water absorption and flexural strength of KGC with varying sintering temperatures. The density of KGC decreased slightly with increasing sintering temperatures. At the same time, the water absorption of KGC reduced with rising sintering temperature. It was believed that sintering causes the viscous flow of geopolymer matrix and transformation of crystalline phases leading to reduced water absorption [21]. The flexural strength of KGC was in the range of 35 – 90 MPa. The highest flexural strength (90 MPa) of KGC was achieved with sintering temperature of 1200°C (Mix 25). The increased flexure strength was due to the formation of crystalline nepheline in the sample due to sintering as shown in SEM images in **Figures 8** and evidenced by XRD diffractogram in **Figure 9**. Based on Kong *et al.* [58], it was caused

by the combination of polymerization and sintering. The statement was concurred by Sabbatini *et al.* [59], who stated that nepheline helps the enhancement of mechanical strength as the result of high amount of silicon-rich and polymerized species.
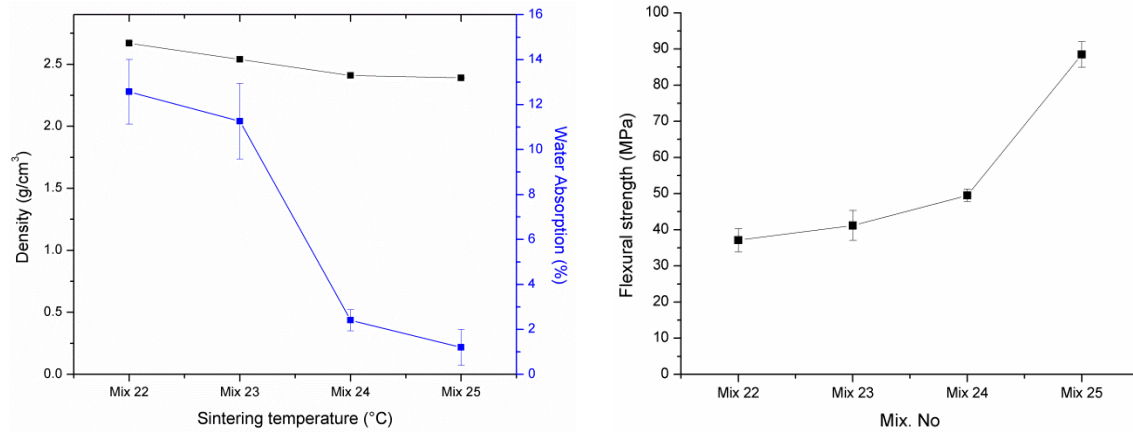

Figure 7: Density, water absorption and flexural strength of KGC with varying sintering temperatures.

The flexural strength was higher compared to the as-cured geopolymer mortars (10 – 20 MPa) sintered up to 1000°C [60]. At 1000°C, nepheline/quartz phases were formed in the geopolymer mortars. Increasing temperature up to 1100°C caused distortion of the sample. Additionally, Lemougna *et al.* [61] reported that high-temperature sintering does not significantly help to improve the mechanical strength in the case of as-cured red mud geopolymers. The flexural strength attained by KCG was substantially higher than as-cured geopolymers obtained by Rovnanik & Safrankova [62] when sintered up to 1000°C (1 MPa for metakaolin geopolymers and 4 MPa for fly ash geopolymers) even respectively containing predominant nepheline and albite crystalline phases. Meanwhile, the flexural strength was also greater than the nepheline ceramics (in

24

the range of 14 MPa to 71 MPa) produced using fast-firing process [27]. On the other hand, using the similar processing method (i.e. pulverizing and powder metallurgy followed by sintering), Xie *et al.* [22] obtained leucite ceramics with maximum flexural strength of 139 MPa at 1200°C.

Figure 8 reveals the SEM images of kaolin geopolymer ceramics prepared at varying sintering temperatures. Referring the images with smaller magnification (200x), the microstructure appeared rough at low sintering temperature (Mix 22 for 900°C and Mix 23 for 1000°C). Yet, with rising temperature (Mix 24 for 1100°C and Mix 25 for 1200°C), the microstructure became smooth and glassy. In addition, small pores could be seen distributed throughout the microstructure (**Figures 8a, b, c** and **d**) together with the transformation of amorphous and zeolite phases into nepheline crystalline ceramics. No cracking was observed in all the samples. This implied that the formation of kaolin geopolymer ceramics using kaolin geopolymer powder prevents cracking which usually occurs in as-cured geopolymers. This was also well-agreed by Xie *et al.* [22] as mentioned earlier. Direct heating as-cured geopolymers at elevated temperature caused severe cracking and deterioration of strength as a result of water vapour pressure developed in the pores [21, 60], as aforementioned. In the study by Kuenzel *et al.* [60], the as-cured geopolymers were heated and dried before sintering to avoid excessive shrinkage cracking.
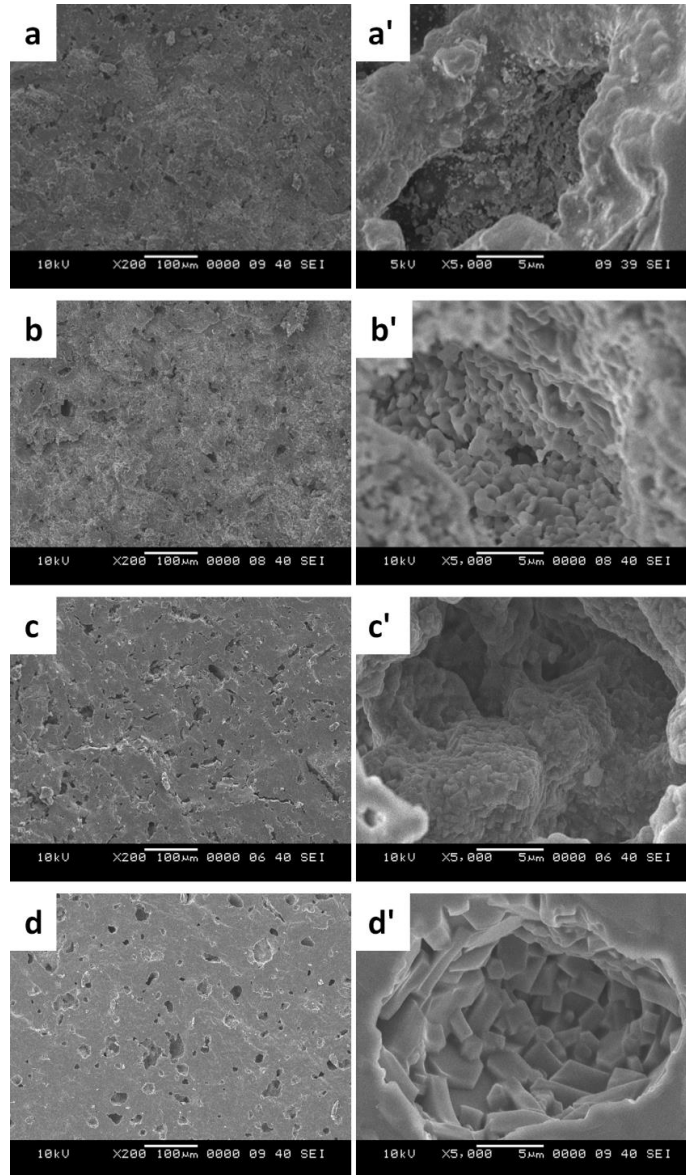
Figure 8: SEM images of KGC with magnification 200× (a, b, c and d) and 5000× (a', b', c' and d') for Mixes 22, 23 24 and 25.

The SEM images with larger magnification (5000x) showed no obvious crystallites formation at 900°C (Mix 22, **Figure 8a'**), but smooth geopolymer matrix. With rising sintering temperature, the crystallites formed embedded in the amorphous geopolymer matrix. Upon heating to 1200°C (Mix 25, **Figure 8d'**), hexagonal prism of

nepheline [27] could be clearly seen. The crystallites were bound together by the geopolymer matrix.

As refer to the XRD diffractograms in **Figure 9**, kaolin showed main diffraction peak of kaolinite (K, ICDD# 29-1488) with a strong peak at 24.9°2θ. Trace amount of quartz (Q, ICDD# 85-0798) and alunite (A, ICDD# 86-2651) could also be detected. The alkali activation of kaolin with activator solution caused the formation of amorphous diffuse halo centred at 30°2θ. This is the typical representative of geopolymers as aforementioned. The kaolinite peaks reduced intensity in geopolymer powder compared to raw kaolin. In addition, there was presence of zeolite phases (ICDD# 84-0698) in kaolin geopolymer powder as in the metakaolin geopolymer powder shown in **Figure 5**.
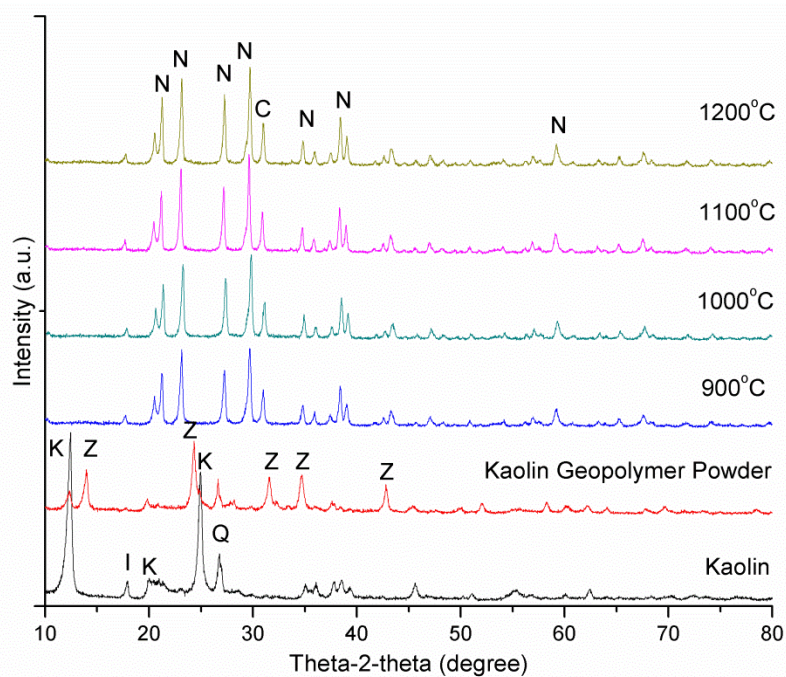

Figure 9: XRD diffractograms of kaolin, kaolin geopolymer powder and KGC sintered at varying temperatures (K – Kaolinite; A – Alunite; Q – Quartz; Z – Zeolite; C – Critoballite; and N – Nepheline).

Upon sintering, portion of the amorphous and zeolite phases transformed into crystalline nepheline (N, ICDD# 09-0338) diffraction peaks. The XRD result complied with the SEM images shown in **Figure 8**. Based on Markovic *et al.* [63], the structure of zeolites collapsed in temperature regions of 600 - 800°C due to the broken of Si-O-Si and Si-O-Al bonds. Nepheline crystals were the crystalline phases formed in sodium-based aluminosilicate [23, 61]. Commonly, leucite and kalsilite were formed in heat-treated potassium-based geopolymers [22, 64], while nepheline and albite were observed in heat-treated sodium-based geopolymers [23, 62].

4.0 Conclusion

In this paper, geopolymer powder has been successfully used to produce one-part-mixing geopolymers and geopolymer ceramics. From the present experimental data and analysis, the following conclusions can be drawn:

(a) The one-part-mixing geopolymers only exhibited maximum compressive strength of 10 MPa after 28 days. Continuous formation of geopolymer matrix was obvious after direct-mixing with water. It was supposed that the presence of zeolite crystallites due to the mixing with water reduced the compressive strength of the one-part-mixing geopolymers.

(b) Sintering the compressed geopolymer powder transformed the amorphous phases into nepheline phases without going through intermediate phases. The geopolymer ceramics possessed maximum flexural strength of 90 MPa at 1200°C. This method reduced the risk of cracking commonly occurring in as-cured geopolymers. However, it is recommended to lower the sintering temperature in

28

order to obtain nepheline geopolymer ceramics as the sintering temperature proposed in this work was high.

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