



## GЕOPOLYMERIZATION OF METAKAOLIN USING RICE HUSK ASH AS SILICA SOURCE WITH NA-BASED ACTIVATOR

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### ABSTRACT

A study on alternative to Portland cement was carried out by applying geopolymerization process using metakaolin (MK) and rice husk ash (RHA). Metakaolin was produced through the calcinations of kaolin-processed clay at 700°C. Acid leached rice husk (RH) was incinerated at 700°C to produce rice husk ash (RHA), which acted as the silica source in the synthesis of geopolymer. Geopolymers (GP1-GP6) were produced by the alkaline activation (NaOH and Na<sub>2</sub>SiO<sub>3</sub>) of mixtures of metakaolin (MK) and rice husk ash (RHA) before curing them at 60°C. The parameters involved were Na<sub>2</sub>SiO<sub>3</sub>/NaOH ratio and metakaolin/silica ratio. The effects of SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio and solid/liquid ratio on the workability, brittleness, porosity and setting time of geopolymers were studied. The hardened geopolymer materials were sintered at temperature ranged from 600 to 1,000°C. Observations showed that the workability decreased when the alkali activator was doubled up, brittleness increased by increasing the SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio and at high solid/liquid ratio, the porosity decreased and eventually producing material that was less brittle. The optimum SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio was 3.18. Scanning Electron Microscope (SEM) micrographs and X-ray Diffraction (XRD) analysis showed the development of the geopolymer materials in the phase evolution in increasing temperature. At the highest temperature of sintering for GP1 (1,000°C), nepheline crystals were the main crystals formed with mullite as the minor crystals which started to develop. The presence of the crystalline phases can be further related to the mechanical strength of the geopolymer.

**Keywords:** ceramic, geopolymer, kaolin clay, rice husk

### INTRODUCTION

Geopolymers are amorphous to semi-crystalline three-dimensional aluminosilicate polymers, which were first introduced by Davidovits in 1978. Geopolymers can be obtained at slightly higher than room temperature through the synthesis of aluminosilicates as the raw materials via alkaline activation. Sources of these raw materials are industrial wastes, calcinated clays, natural minerals or several mixtures of the materials (Xu, 2001). The process of synthesizing geopolymers by utilizing solid waste and by-products is called geopolymerization (Khale and Chaudhary, 2007). Metakaolinite is one of the clay materials that are rich in Al source. The material can be produced by dehydroxylation of kaolin at the temperature of 450 to 980°C (MacKenzie *et al.*, 2008).

Metakaolin is widely used as mineral additives, therefore a good synthetic pozzolana. This is due to the highly disordered structure of metakaolin compared to kaolin that is crystalline in structure (Kakali *et al.*, 2001). Rice husk is the waste material abundantly available in the agricultural rice producing areas such as Kota Belud, Sabah. Pure silica can be produced by acid-leaching process of rice husk (Chen and Chang, 1991). A research done by Real *et al.* (1996) shows that rice husk ash is an alternative source of silica due to the production of pure silica (~99.5%). It has high specific surface area, fine particle size and high grade of amorphous form of silica.

The choice of alkali metal types that is used in geopolymerization depends on the types of raw materials being used and the application of the produced geopolymers (Komnitsas and Zaharaki, 2007). In this

study, NaOH and Na<sub>2</sub>SiO<sub>3</sub> were used as the alkali activator. It is studied by Poulesquen *et al.* (2011) that NaOH has better dissolution of the aluminosilicate source (metakaolin) than KOH. It has been observed by Bakharev (2005) who concluded that geopolymer activated by a mixture of NaOH and Na<sub>2</sub>SiO<sub>3</sub> yields higher strength.

The objectives of this study were (1) to prepare pure silica source from the local rice husks, (2) to prepare metakaolin from the kaolin clay, and (3) to synthesize geopolymer ceramic based on different ratios of Na<sub>2</sub>SiO<sub>3</sub> to NaOH and different ratios of clay and silica. In addition, this study also focused on analyzing the microstructures crystal phase evolution of the geopolymer ceramic using X-ray Diffraction and Scanning Electron Microscope.

### EXPERIMENTAL PROCEDURE

#### Metakaolinization

Metakaolin were prepared from processed kaolin clay from Sibelco Malaysia Sdn Bhd. The chemical composition of the starting material provided by the manufacturer is given in Table-1. The kaolin clay was subjected to heat treatment at 700°C in order to prepare the reactive metakaolin.



**Table-1.** Compositions of materials and their mass fractions (%) in kaolin processed clay.

Composition	Mass fraction (%)
Silicon Dioxide (SiO <sub>2</sub> )	49.60
Aluminium Oxide (Al <sub>2</sub> O <sub>3</sub> )	34.20
Titanium Dioxide (TiO <sub>2</sub> )	0.52
Iron Oxide (Fe <sub>2</sub> O <sub>3</sub> )	1.01
Calcium Oxide (CaO)	0.01
Magnesium Oxide (MgO)	0.55
Potassium Oxide (K <sub>2</sub> O)	1.80
Sodium Oxide (Na <sub>2</sub> O)	0.07
Loss on Ignition	12.10

### Rice husk preparation

The prepared rice husk ash was washed with distilled water and dried completely at 110°C for 24 h. It was then subjected to acid leaching. 2M HCl at its boiling point was carried out under constant stirring for 1 hour. The leached rice husk was subjected to incineration at 700°C. The incinerated rice husk ash was then characterized using XRD and FTIR.

### Geopolymerization

Geopolymer samples were prepared by mixing of the alkali activator containing NaOH and Na<sub>2</sub>SiO<sub>3</sub> solution manually with stoichiometric amounts of metakaolin, Al<sub>2</sub>Si<sub>2</sub>O<sub>5</sub>(OH)<sub>4</sub>. The mixing of metakaolin with alkali activator was conducted using overhead mixer with constant stirring for 5 min. Then, the rice husk ash, which acted as the silica source, was added in stoichiometric amount compared to the amounts of metakaolin clay used. The mix proportions of the geopolymer pastes are given in Table-2. The slurry reactive mixture of geopolymer produced was then placed in the cylindrical mould.

**Table-2.** Chemical Formula and Composition of various geopolymer (GP) samples.

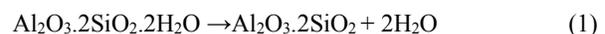
GP	Chemical formula	Na <sub>2</sub> SiO <sub>3</sub> : NaOH (by mol)	Na <sub>2</sub> SiO <sub>3</sub> : NaOH (wt)	Solid : Liquid (mol)	Solid : Liquid (wt)	MK : RHA (mol)	SiO <sub>2</sub> : Al <sub>2</sub> O <sub>3</sub> (wt)
1	Na <sub>2</sub> O.Al <sub>2</sub> O <sub>3</sub> .2.85SiO <sub>2</sub>	1:1	3.05	0.6	1.07	1 : 0.5	2.85
2	Na <sub>2</sub> O.1.25Al <sub>2</sub> O <sub>3</sub> .3.20SiO <sub>2</sub>	1:1	3.05	0.7	1.30	1.25 : 0.5	2.57
3	Na <sub>2</sub> O.Al <sub>2</sub> O <sub>3</sub> .3.245SiO <sub>2</sub>	1:1	3.05	0.8	1.19	1 : 1	3.24
4	1.33Na <sub>2</sub> O.Al <sub>2</sub> O <sub>3</sub> .3.18SiO <sub>2</sub>	2:1	6.10	0.6	1.25	1 : 0.5	3.18
5	1.07Na <sub>2</sub> O.Al <sub>2</sub> O <sub>3</sub> .2.84SiO <sub>2</sub>	2:1	6.10	0.7	1.52	1.25 : 0.5	2.84
6	1.33Na <sub>2</sub> O.Al <sub>2</sub> O <sub>3</sub> .3.58SiO <sub>2</sub>	2:1	6.10	0.8	1.40	1 : 1	3.58

Curing of the geopolymer paste was then carried out at the temperature of 80°C for 24 hours. The cured geopolymer was then undergone sintering to develop mechanical properties, as well as to study the phase evolution of the product of geopolymer ceramic. Sintering process of the geopolymer was carried out by 1 hour of soaking at 500, 600, 700 and 800, 900 and 1, 000°C respectively. The sintered samples were finally characterized using XRD and SEM.

XRD patterns were obtained with an X'Pert Pro PW3040 XRD machine using Co-K $\alpha$  radiation to determine the mineralogical composition of the raw materials and geopolymer components. The samples for SEM were fractured and carbon-coated. The SEM images were obtained using an EVO 10MA microscope to observe the microstructure evolution of the geopolymer ceramic products.

## RESULTS AND DISCUSSIONS

Metakaolin was successfully prepared based on thermal treatment at 700°C with 1 hour of soaking period. The thermal treatment of the clay removes water content from the mineral kaolinite (Al<sub>2</sub>O<sub>3</sub>.2SiO<sub>2</sub>.2H<sub>2</sub>O) through dehydroxylation, to produce the amorphous metakaolin (Al<sub>2</sub>O<sub>3</sub>.2SiO<sub>2</sub>). The dehydroxylation process can be summarized as in the equation below:



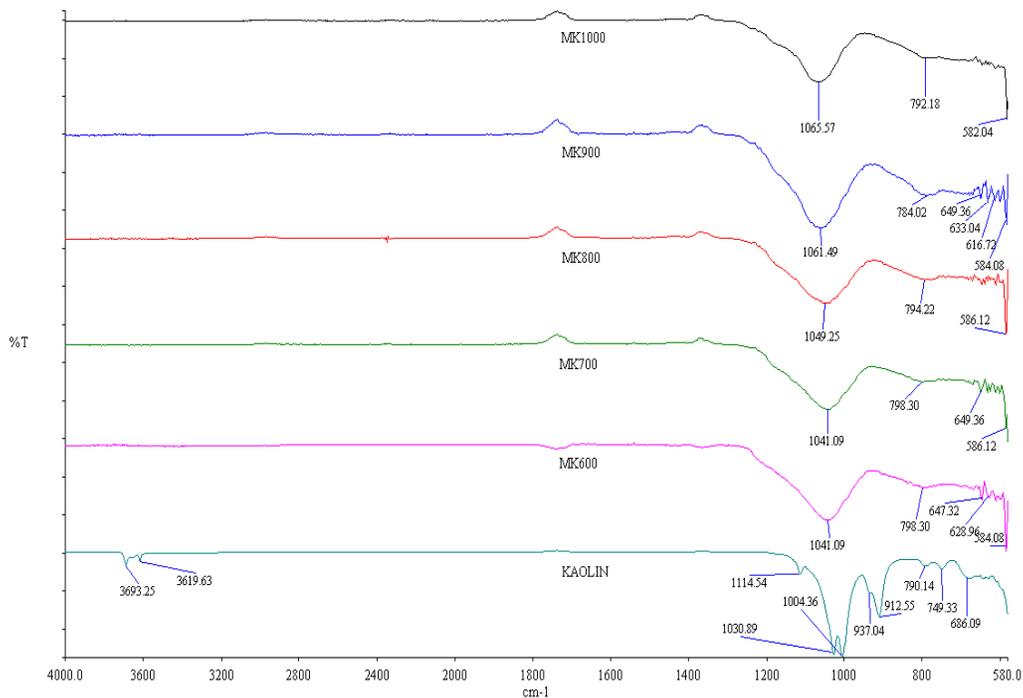
At the temperature of 700°C, the dehydroxylation process was at the maximum efficiency based upon the hydroxyl ions (OH<sup>-</sup>), which are strongly bonded to the aluminosilicate framework structure, were eliminated from the crystal structure (dehydroxylation), thus the overall structure loses its crystalline structure and become amorphous metakaolin (Ilic *et al.*, 2010). XRD and FTIR analyses also support this findings.



Figure-1 shows the IR spectra of kaolin. The kaolin showed the characteristic peaks at  $3693.5\text{ cm}^{-1}$  and  $3619.63\text{ cm}^{-1}$  corresponding to the OH- stretching vibrations. Bands at  $1114.54\text{ cm}^{-1}$ ,  $1030.89\text{ cm}^{-1}$  and  $1004.36\text{ cm}^{-1}$  were assigned to Si-O bonds in the  $\text{SiO}_4$  molecules (Granizo *et al.*, 2007) while bands at  $912.55\text{ cm}^{-1}$  and  $937.04\text{ cm}^{-1}$  that showed the Al-OH vibrations and bands at  $790.14\text{ cm}^{-1}$ ,  $749.33\text{ cm}^{-1}$  and  $686.09\text{ cm}^{-1}$  indicated Si-O stretching (Galan *et al.*, 1996).

IR spectra of the prepared metakaolin showed the absence of detectable Al-OH bands at  $912.55\text{ cm}^{-1}$  and the doublet at  $3693.5\text{ cm}^{-1}$  and  $3619.63\text{ cm}^{-1}$ , which

correspond to the OH- stretching vibrations and can be related with the changes from the octahedral coordination of  $\text{Al}^{3+}$  in kaolinite to tetrahedral coordination in metakaolinite (Cristobal *et al.*, 2010). The band of kaolin at  $1114.54\text{ cm}^{-1}$  shifted to a lower frequency, thus combined with the bands of Si-O to form a broad band at  $1041.09\text{ cm}^{-1}$ . There was a new significant bond that can be observed at approximately  $584.04\text{ cm}^{-1}$  to  $586.12\text{ cm}^{-1}$  in metakaolin. These correspond to the Si-O-Al bands, which shifted to higher frequency after the calcination process (Ilic *et al.*, 2010).

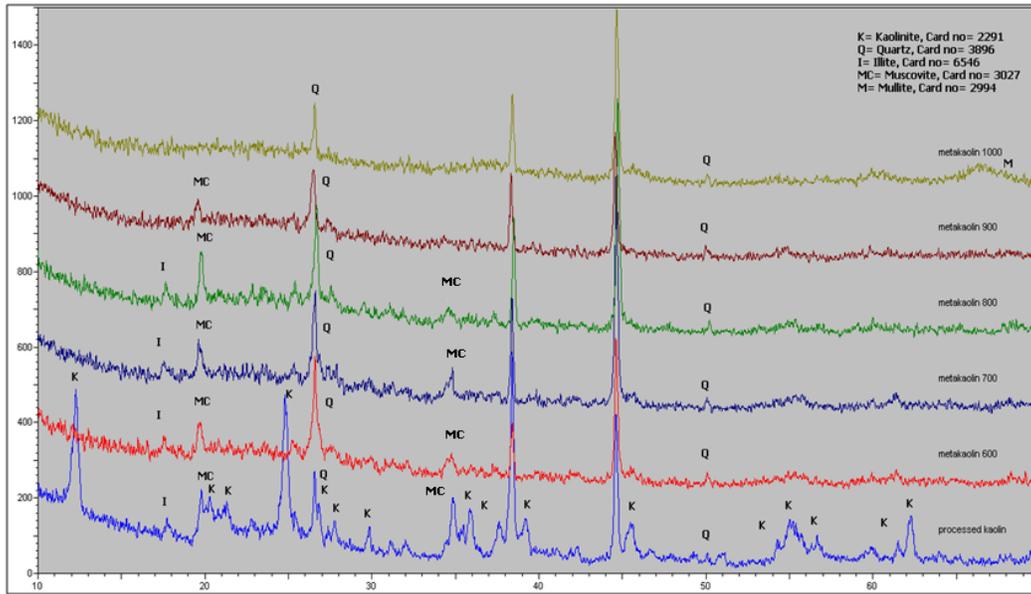


**Figure-1.** IR spectra of kaolin and metakaolin.

XRD diffractogram of pure kaolin clay showed major mineral constituents in the clay were kaolinite minerals ( $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ ) with the presence of quartz,  $\text{SiO}_2$  (Figure-2). After the thermal treatment of kaolin clay, the kaolinite peaks disappeared with presence of quartz ( $2\theta \sim 26.19$ ) remained unchanged. The broad reflection between  $10\text{-}35^\circ$  with relatively similar intensities was

assigned to metakaolinite which indicates it has amorphous structure (Komnitsas *et al.*, 2007).

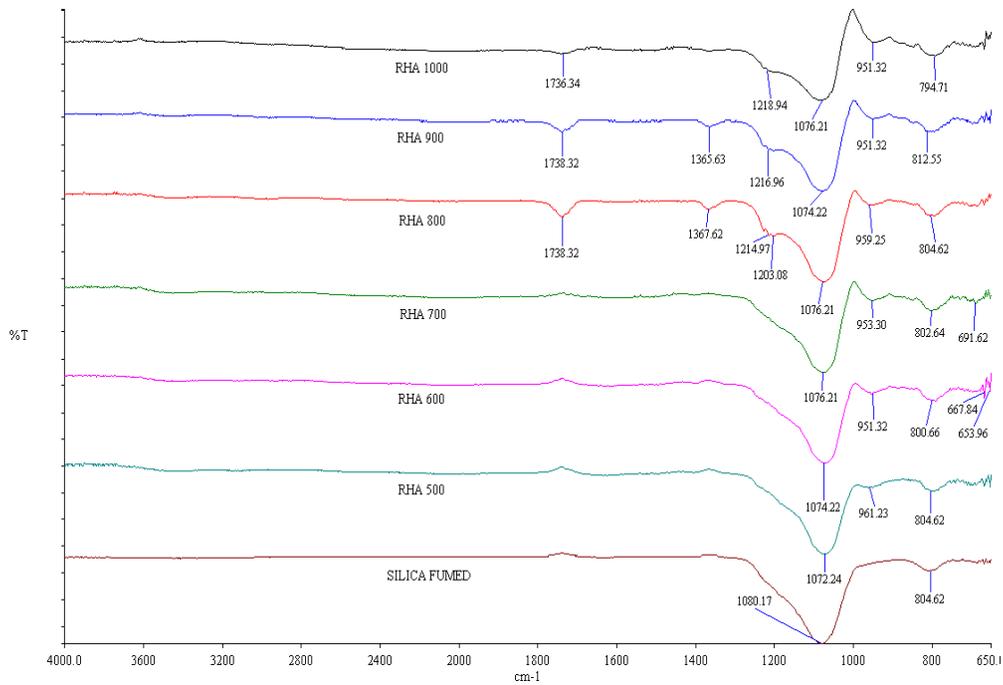
In addition, there were also two significant strong peaks at  $2\theta \sim 38.47$  and  $44.72$  where referred as aluminium, detected from the aluminium-based XRD sample holder.



**Figure-2.** X-ray diffractogram kaolin clay and metakaolin.

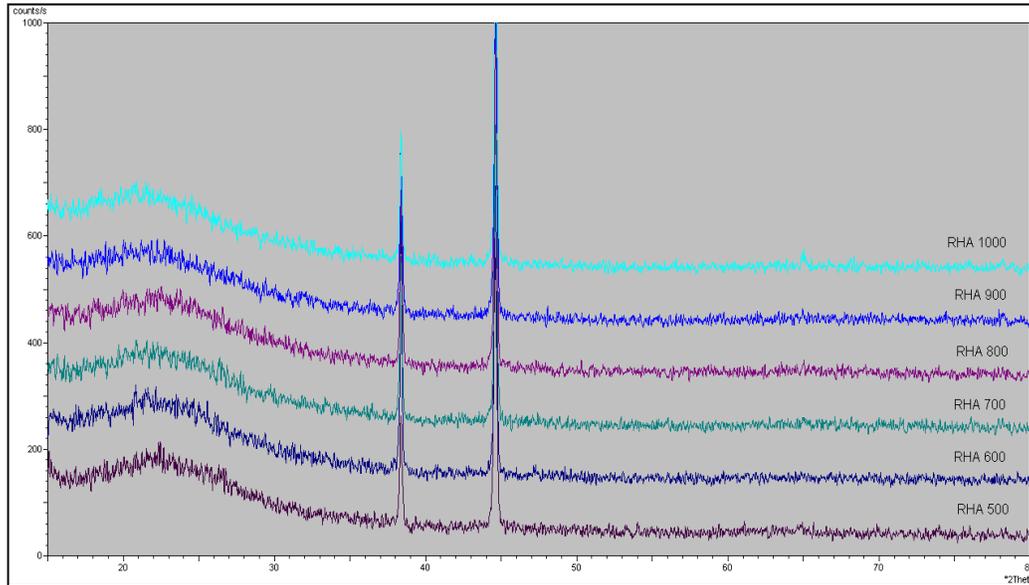
Rice Husk Ash (RHA) produced at 700°C showed intense broad characteristic peak for FTIR spectra at ~ 102.24 cm<sup>-1</sup>, with less intense broad peak at 804.62

cm<sup>-1</sup> indicating the presence of silica (Figure-3). Fumed silica was taken as the reference in the comparison of the rice husk ash.



**Figure-3.** IR spectra of leached RH and RHA produced at different incineration temperatures.

X-ray diffractogram (Figure-4) showed intense broad peak at the range of 2θ= 20-30 indicating the amorphous nature of silica.



**Figure-4.** X-ray diffractogram of RHA at different combustion temperatures.

### Geopolymerization

The geopolymerization of the mixtures of metakaolin (MK) and rice husk ash (RHA) with the alkali activators (NaOH and  $\text{Na}_2\text{SiO}_3$ ) occurred simultaneously, once all materials were mixed. As NaOH resulted in the dissolution of aluminosilicates sources (MK and RHA), while  $\text{Na}_2\text{SiO}_3$  acted as the binder. This study will only discuss on the workability, curing/setting time, brittleness and porosity of the geopolymers through the observations on the geopolymer paste produced.

### Effect of $\text{Na}_2\text{SiO}_3$ / NaOH ratios

The workability of the geopolymer products decreased when the ratio of  $\text{Na}_2\text{SiO}_3$ : NaOH was doubled up to 2:1. Less workable mixture was produced due to the difficulty in the compaction and molding process where excess silicate content hindered water evaporation and the formation of geopolymeric structure. The reduction in workability was based on the inhibition of the geopolymerization reaction due to the precipitation of Al-Si phase, which avoided contact between the reacting materials and the activation solution. GP4 and GP5 were still able to undergo polymerization after mixing and hardened after 1 day of curing. However, GP6 with most silicate content and the least polymeric gel, took longer curing time for it to become hardened.

### Effect of $\text{SiO}_2$ / $\text{Al}_2\text{O}_3$ ratios

For the 1:1 ratio of the activator content, GP1 and GP2 took less time to harden before curing, compared to GP3. For the 2:1 ratio, GP6 took longer hardening time compared to GP4 and GP5. The Si/Al ratio of the geopolymer products, which ranging from 2.57-3.58

affected the hardening and curing time of the geopolymer paste.

In this study, the brittleness of the geopolymers increased with increasing  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio. Ravindra and Somnath (2009) also stated that the increased of  $\text{SiO}_2$  content (decreasing  $\text{Al}_2\text{O}_3$ ) will increase the brittleness due to the higher degree of reactions that took place in the mixture. For GP3 and GP6, it can be suggested that the silica content was beyond the threshold level, which leads to reduction in reactivity, increase in brittleness and prolonged curing time. From this study, the optimum  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio is for GP4 with ratio of 3.18.

### Effect of Solid / Liquid ratios

The solid/liquid ratios from GP1 to GP6 are in the increasing range. GP1 and GP4 consist of the lowest solid/liquid ratio, thus, they composed of more activator content. This leads to higher viscosity and porosity of the mixtures. The viscosity of the mixture affects the porosity and brittleness of the mixture, as suggested by Kong *et al.* (2007).

Based on the three ratios,  $\text{Na}_2\text{SiO}_3/\text{NaOH}$ ,  $\text{SiO}_2/\text{Al}_2\text{O}_3$  and solid/liquid, it can be concluded that in general, the brittleness, porosity and curing/setting time of the geopolymer product increases from GP1 to GP6. On the other hand, the workability and loading of the geopolymeric mixtures decreases from GP to GP6.

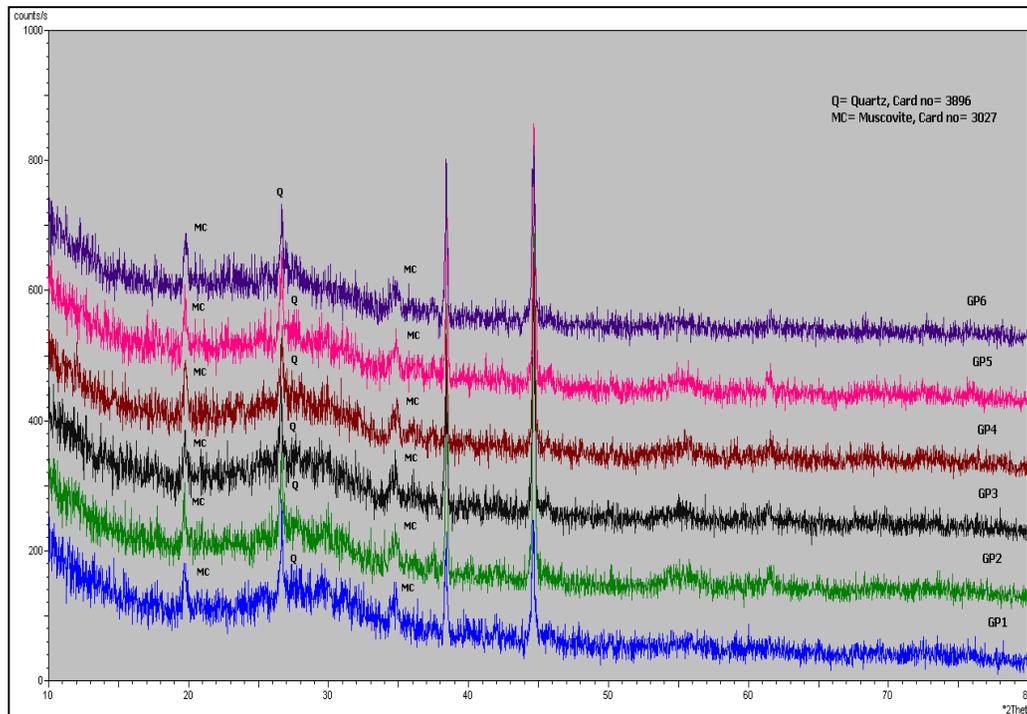
### Structural analysis of geopolymer

Figure-5 presents the XRD patterns of geopolymer produced (GP1 - GP6) at different compositions and various mixture proportions of starting materials after being cured at 60°C. After the alkali activation of metakaolin with the mixtures of NaOH and



NaSiO<sub>3</sub>, it can be observed at  $2\theta \sim 20-35$  that there was a broad peak in the XRD diffractograms of the synthesized geopolymeric materials (GP1-GP6). This hump represents typical amorphous characteristic of geopolymers (Zuhua *et al.*, 2009). These humps differed from the ones during metakaolinization, where the angle value of the humps shifted higher ( $2\theta \sim 15-25$ ) after geopolymerization. Liewet *al.* (2012) also found the same shifting and

suggested that there were occurrence of structural arrangement during geopolymerization. The quartz peak at  $2\theta \sim 16.78$  and muscovite at 19.91 and 34.72 were still present in the diffractogram, indicating that both minerals were not affected by geopolymer reactions. Besides quartz and muscovite, the aluminium peaks at  $2\theta \sim 38.47$  and 44.72 were present too.



**Figure-5.** XRD diffractogram of raw GP1-GP6 (before sintered).

### Phase evolution and microstructure

Each of GP1 to GP6 samples was subjected to thermal treatment at temperatures of 600°C to 1,000°C to study the formation of nepheline crystals from Na-based geopolymer. The colour of the geopolymer before sintering was slightly red. It can be observed that the resulting fired materials were whitish after the thermal treatment at 600°C to 800°C. At these temperatures, water was removed from the cured geopolymer materials. Above 800°C, there were colour changes for the geopolymers, where the colour became slightly reddish. Oxidation of the components in the geopolymer might cause the significant changes in colour. The development of microstructure and geopolymer phases after sintering was observed using X-ray Diffractometry (XRD) for the raw and sintered samples at 600°C, 800°C and 1000°C. Based on the XRD analysis, only the best and well-developed GP was further analyzed using Scanning Electron Microscope (SEM).

### X-ray Diffraction (XRD)

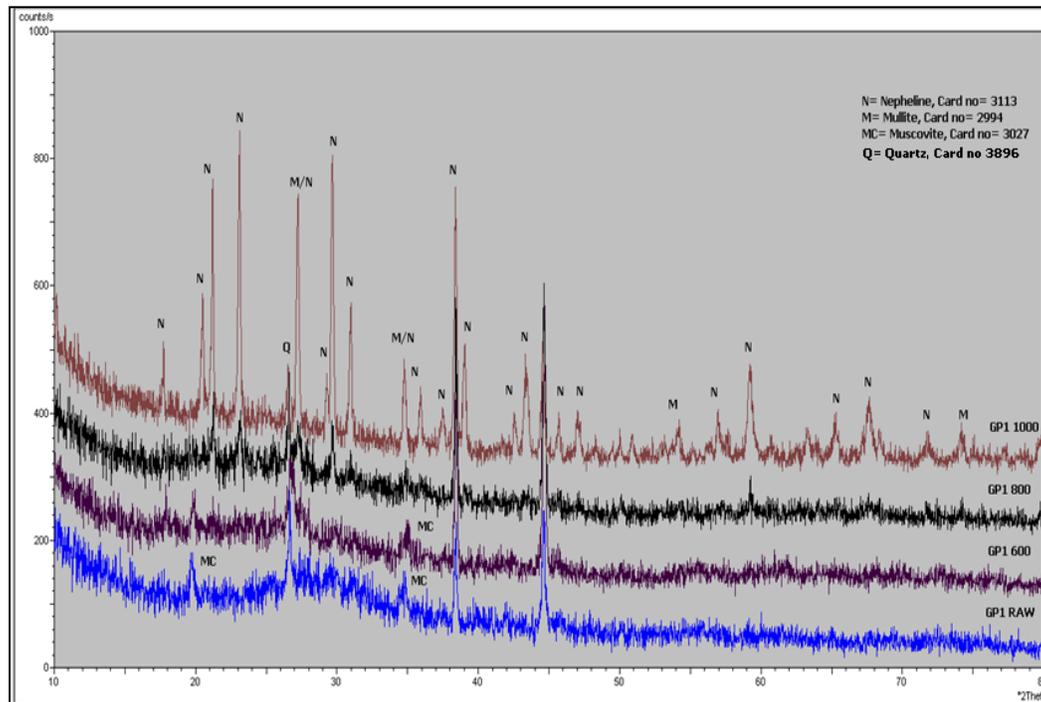
The XRD analysis was done on all of the GPs for the raw and sintered samples at 600°C, 800°C and 1000°C. Figure 6 shows the X-ray diffractogram of the GP1 geopolymer. As the temperature raised from 600°C to 800°C, there was no significant change in the diffractogram of the sintered geopolymer materials. The peaks of muscovite and quartz remained in the diffractogram. The intensity of the amorphous hump decreased as the temperatures raised. This supported the ideas that at higher temperatures, the amorphous material undergoes development to crystalline structure, and in this study, nepheline crystals were formed. From the GP1 diffractogram, it was found that crystalline nepheline started to form at the temperature above 800°C and was fully crystallized at 1,000°C.

The strongest peaks of nepheline crystals can be observed in GP1 at 1000°C. The nepheline peaks were less intense and fewer in GP2 to GP6. From the diffractogram in Figure-7, the nepheline crystals were not fully formed in GP5 and GP6. This might be due to the increasing of



the  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio. From the diffractograms, it was shown that the onset temperature of nepheline crystallization decreased with increasing  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio. Besides that, the extent of crystallization also decreased, as shown by fired GP 4, 5 and 6. From these findings, it can be concluded that the temperature of sintering for

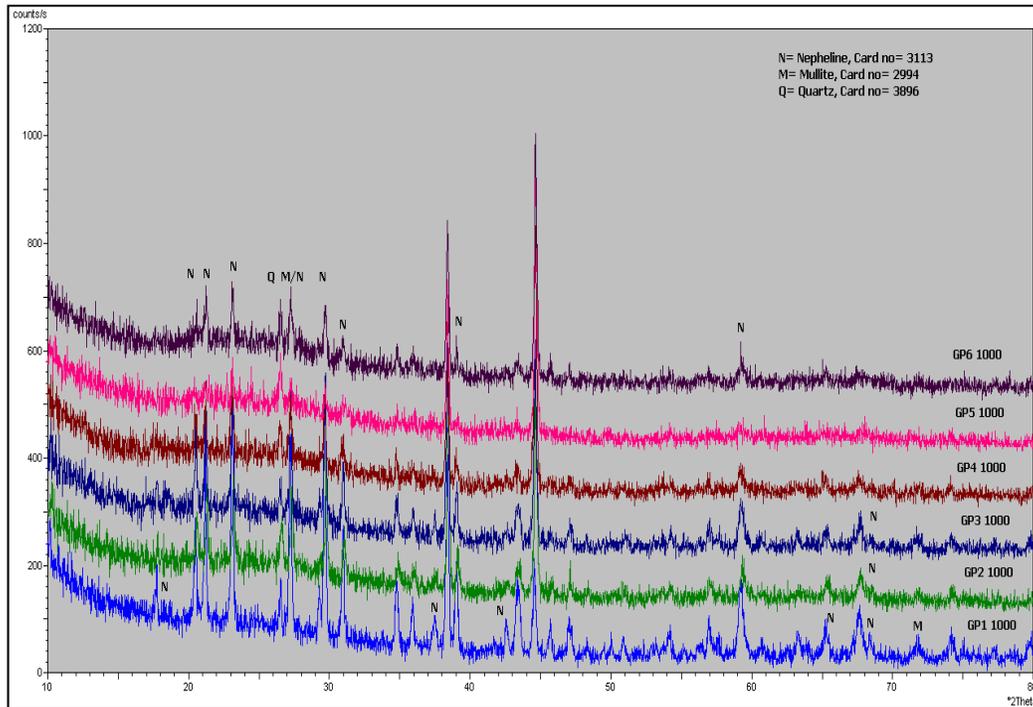
GP4, GP5 and GP6 was not sufficient in the evolution of nepheline crystals and temperature higher than 1,000°C is needed in order to obtain the nepheline crystals. Besides that, the excess of silicates in these mixtures hindered the crystal growth and retained its amorphous nature.



**Figure-6.** X-ray Diffractogram of GP1 at different temperature of sintering.

Besides nepheline crystals, in GP1 to GP3, a few mullite peaks were observed. The mullite peak in GP3 was less intense and overlapped with the nepheline peak at  $2\theta \sim 25.13$ . The mullite peaks in GP1 was more intense than GP2 and GP3. However, the mullite crystals were not fully developed as the intensity of the peaks was not as strong as the nepheline peaks. Gridi-Bennadji *et al.* (2009) also discovered similar outcomes. The formation of mullite can be associated with the disappearance of muscovite at temperature above 800°C. Mullite crystals

are formed by the transformation of muscovite in the geopolymer at high temperature. Figure-7 shows the X-ray analysis of all the GPs at 1,000°C. Quartz peak remained in all GPs up to 1,000°C. It can be clearly observed that there were differences in the formation of crystals due to the differences in the composition of the starting geopolymer. Based on Figure-7, GP1 was chosen to be analyzed using SEM to observe the microstructure of the evolution of nepheline crystals.



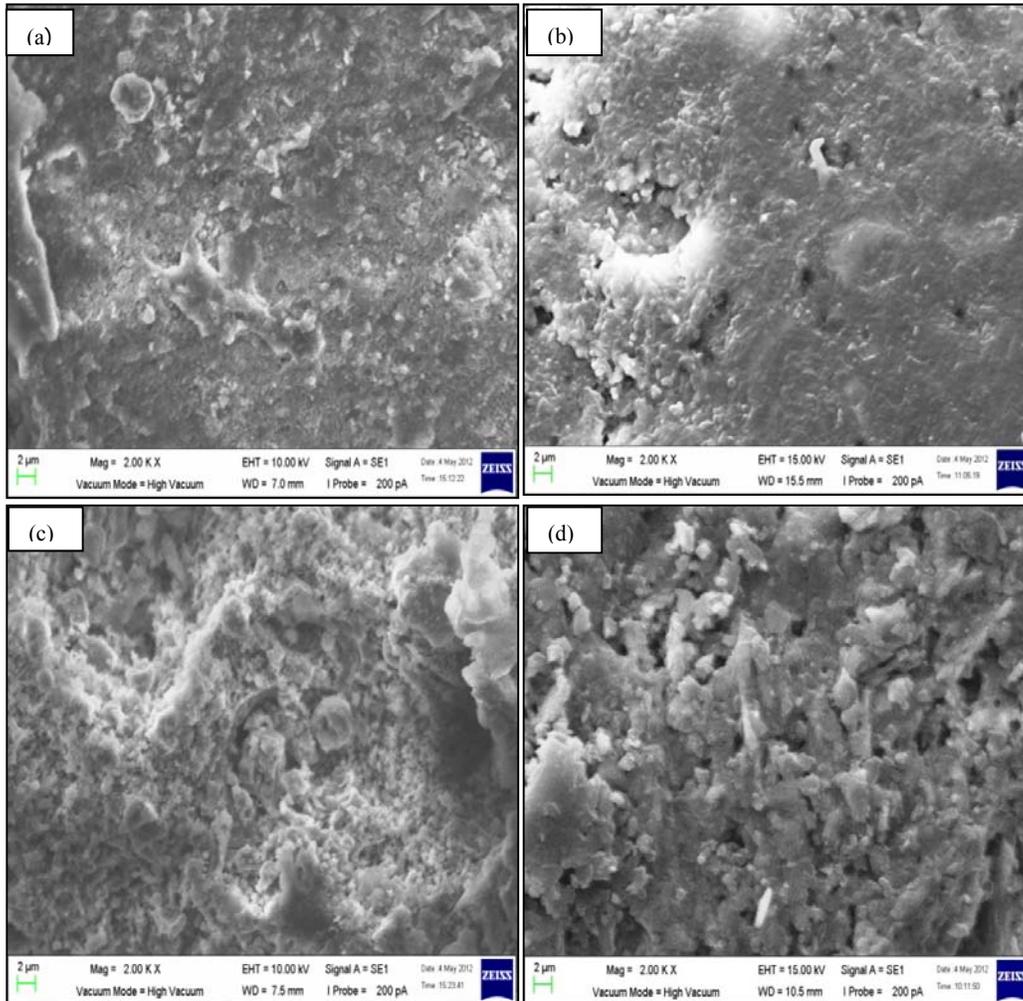
**Figure-7.** X-ray Diffractogram of GP1 to GP6 at different temperature of sintering.

### Scanning Electron Microscope (SEM)

In this study, the SEM analysis was conducted to study the phase evolution and microstructure of the synthesized Na-based geopolymer to produce nepheline crystal. Figure 8 displays SEM images of (a) the polished and etched raw GP1 sample, and after sintered at (b) 600°C, (c) 800°C, and (d) 1000°C.

Based on Figure-8, it can be seen that for the raw unsintered GP1, there was no development of crystal structure. At 600°C, some changes can be observed in the SEM micrograph, as indicated in Fig.8 (b). This indicated the starting of the changes in the geopolymer material to form nepheline. As the temperature rose up to 800°C,

it could be clearly observed that the crystals started to develop. At 1,000°C, the nepheline crystals were formed as discussed through XRD analysis. However, the nepheline crystals cannot be clearly identified in the microstructure. This might be due to the analysis on the surface was not suitable as there porosity was clearly observed in Figure-8(d). The large pores in the microstructure of the Na-geopolymer may be attributed to a high degree of gel polymerization as discussed in the effect of the  $\text{SiO}_2 / \text{Al}_2\text{O}_3$ . On the other hand, mullite crystals that were identified through XRD analysis were unable to be observed in the SEM micrographs.



**Figure-8.** SEM micrographs of (a) raw unsintered GP1, (b) GP1 at 600°C, (c) GP1 at 800°C and (d) GP1 at 1, 000°C.

## CONCLUSIONS

The starting materials were processed kaolin, rice husk ash with mixture of  $\text{Na}_2\text{SiO}_3$  and  $\text{NaOH}$  as the alkali activators. The best temperature to produce metakaolin from kaolin clay was 700°C, where crystalline kaolin decomposed to amorphous metakaolin. Silica source,  $\text{SiO}_2$  (RHA) was produced through incineration of HCl leached RH at the best temperature of 700°C.  $\text{Na}_2\text{SiO}_3/\text{NaOH}$ ,  $\text{SiO}_2/\text{Al}_2\text{O}_3$  and solid/liquid ratio have great effects on the workability, brittleness, porosity and setting time of the geopolymer product. Through the observations, the brittleness, porosity and curing/setting time of the geopolymer product increased from GP1 to GP6. On the other hand, the workability and loading of the geopolymeric mixtures decreased from GP to GP6. It was proven that optimum  $\text{SiO}_2/\text{Al}_2\text{O}_3$  was 3.18. Sintering of the geopolymer products will produce a potential geopolymer ceramic materials. SEM micrographs had proven that there was material development in the phase evolution in increasing temperature. XRD analysis had proven that at the highest sintering temperature (1, 000°C)

of GP1, nepheline crystals dominated the fired Na-based geopolymer with mullite and quartz as minor impurities.

Although the objectives of this study were successfully achieved, there are still limitations in this study. In future, further test on the dehydroxylation of kaolinite to metakaolin, as well as the incineration of rice husk can be analyzed using DTA to obtain a more accurate temperature to produce the starting materials for geopolymerization. Lack of certain parameters is limiting the justification in the concentration of alkali activator in the dissolution of starting materials. The mechanical strength and porosity measurement to study the effect of varying the ratios on the mechanical strength of the cement materials were unable to be conducted. In addition, further study should be performed on the phase evolution and microstructure of the geopolymer ceramic to study the crystal structure development by performing sintering steps at higher temperature and also by varying the compositions of the geopolymers.



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