

THE EFFECT OF TEMPERATURE, TIME OF CURING AND Na₂O/SiO₂ MOLAR RATIO ON MECHANICAL AND CHEMICAL PROPERTIES OF GEOPOLYMER CEMENT

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Abstract

The geopolymer cement is a suitable alternative material for Portland cement due to their environmental compatibility, low curing temperature, and high strength. In this research, Kaolin was used as a raw material for the construction of a geopolymer cement, while sodium hydroxide was an alkali hydroxide. Kaolin is calcined at 750 °C to obtain meta-kaolin. Geopolymer samples were prepared at various curing temperatures (25, 50, and 75 °C), different curing times (3, 7, 21, 28, and 60 days) and with different activator ratios (0.6-0.9). The thermal analysis of kaolin was done via DTA/TGA. Investigation on the geopolymer cement structure and phases were performed using X-ray diffraction (XRD), Fourier-transform infrared spectroscopy (FTIR), and magic angle spinning nuclear magnetic resonance (MAS-NMR). Also, the effects of temperature and time of curing and Na₂O/SiO₂ molar ratio were studied. The results showed that the maximum compressive strength was 115 MPa, which obtained at a molar ratio of Na₂O/SiO₂=0.9, a curing time of 60 days, and a curing temperature of 75°C. The microstructure of cement was studied using scanning electron microscopy (SEM).

Keywords: geopolymer; meta-kaolin; compressive strength; cement.

Introduction

Concrete is the most commonly used material in the building industry to build and develop the infrastructure. Therefore, the demand for concrete cement is increasing, so that the global consumption of concrete is the second after water consumption [1, 2]. The production rate of Portland cement is at approximately 3000 Mt/year [3], and about 13500 million tons of CO₂ are released in the atmosphere from this process worldwide. The main greenhouse gas is CO₂, which has an essential role in increasing global warming [4-6]. Due to the increasing temperature around the world, greenhouse gas emissions are an

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environmental issue, and the cement industry has an important role to play in their reduction [5, 7, 8].

On the other hand, concrete made from Portland cement, when placed in severe and unusual environmental conditions (acidic and corrosive environment), undergoes a compressive strength loss and starts degrading. Susceptibility to cracking and erosion are determining factors in reducing the structural behavior used concrete [9, 10]. Recently also *Martinović et al.* [11] investigated the synthesis of low cement concrete by ultrasonic measurements and image analysis.

In recent years, geopolymer materials have been considered as a substitute for concrete for their low density, easy synthesis, low processing temperature, low cost, high resistance to fire, environmental compatibility, and excellent thermal stability at high temperatures [12-15]. The development of geopolymer technology has provided a great opportunity for the growth and production of various types of geopolymer products [8]. Today, geopolymers have been introduced as a new category of three-dimensional aluminosilicate materials, as an excellent alternative for Portland cement. Geopolymers provide compressive strength and high corrosion resistance into Portland cement. Also, the temperature range of their production is much lower than conventional and traditional cement. The low temperature of the production of geopolymers will prevent the release of greenhouse gases such as CO₂ due to the cement furnaces and the contaminants. The geopolymer concrete technology produces five times less CO₂ compared to Portland cement [16-18]. In recent years, many attempts have been made to study and improve the properties of geopolymer cement. *Liu et al.* [19] investigated the nano-mechanical properties of the geopolymer/cement matrix in recycled aggregate concrete. *Ciccioli et al.* [20] used the rock materials for the industrial production of New Geopolymeric Cements. *Ahdaya et al.* [21] tested geopolymer cement performance in the presence of water-based drilling fluid. In this research work, after the geopolymer cement is produced, its mechanical and chemical properties were investigated. Also, the effect of curing temperature and Na₂O/SiO₂ ratio on mechanical properties and microstructure were studied.

Experimental procedure

Materials

Kaolin is a type of halloysite, and for this work was used as a source of aluminosilicates. The Kaolin we used is produced in New Zealand and had an average particle size of 5 microns. Sodium silicate (SiO₂/Na₂O=2, solid=38 w.t %) and Sodium hydroxide were acquired from Merck Company (purity of more than 98%) and were used as alkali activators. Distilled water was used throughout the experiments. The chemical composition of the starting material is given in Table 1.

Table 1. Chemical composition of the starting materials.

Material	H ₂ O	SiO ₂	Al ₂ O ₃	Na ₂ O	Fe ₂ O ₃	TiO ₂	Fe	Heavy metals	L.O.I
Kaolin	-	50.4	35.5	-	0.25	0.05	-	-	13.8
Sodium silicate(aq.)	61.42	25.5	-	13.08	-	-	0.005	0.005	-

Specimen Preparation of Geopolymer Cement

In order to prepare the geopolymer cement, kaolin was passed through a Sieve mesh 80. Meta-kaolin was obtained from the calcination of kaolin at 750°C for 24 hours because the dissolution rate of meta-kaolin is much higher than Kaolin due to the more reactive reaction of alkali solutions on amorphous aluminosilicates. For preparing the geopolymer specimens, molar ratios of SiO₂/Al₂O₃=1 and Na₂O/SiO₂=0.6, 0.7, 0.8, and 0.9 were considered. The alkaline activator solution containing the sodium hydroxide solution and sodium silicate was used to create a geopolymer network. In order to achieve the activation solution, according to Table 1, a mixture of sodium silicate solution and sodium hydroxide particles were placed under magnetic stirrer. Since the dissolution of sodium hydroxide is exothermic, it was cooled down to room temperature. After preparing the alkaline activator solution, it was added slowly and continuously to the meta-kaolin precursor to form the desired gel. In order to prepare alumina and silicate monomers, the mixture was stirred vigorously for 10 minutes to obtain a completely homogeneous pasty material. Adding water to the composition and synthesis of the geopolymer was conducted under vibration to prevent bubbles and porosity. Simultaneously adding water, the mixture was stirred. Finally, the mixture was shaken for 15 minutes to remove porosities. The homogeneous mixture was poured into a cubic mold (50 * 50 * 50 mm). The molds were insulated with plastic. It was vibrated for 15 minutes to exit the trapped air. After setting, the samples were removed from the mold and cured at 25, 50, and 75 °C in atmospheric pressure for 3, 7, 21, 28, and 60 days. The following formula aMKHb-c is used to name the samples, where (a) is curing time, (MKH) meta-kaolin, (b) is the 0.6 Na₂O/SiO₂ molar ratio, and (c) is curing temperature.

Characterization

X-ray diffraction patterns (XRD, PHILIPS-PW 1800) were used to identify the phases. Fourier transform infrared (FTIR, Thermo Nicolet, model Nexus 870) spectra were obtained in the wavenumber range of 400–4000 cm⁻¹. Differential thermal analysis (DTA, model Mettler, TGA/STTA 851) was accomplished on the halloysite kaolin. The compressive strength was carried out according to ASTM C39-96 standard. The morphology and microstructure of geopolymer Cement particles were characterized using a scanning electron microscopy (SEM, VEGA/TESCAN). For the MAS-NMR measurements, a BRUKER AVANCE 500 Nuclear Magnetic Resonance Spectroscopy (NMR) was used.

Results and discussion

The differential thermal analysis (DTA/TG) of kaolin is shown in Fig. 1. The absorbed water in pores, cavities, and surfaces is removed at temperatures below 200 °C. At around 200-450 °C, reorganization of the hexagonal layers of kaolin is carried out. In the DTA curve, the endothermic peak in a temperature range of 500-600 °C is related to the release of the hydroxyl groups of kaolin and the conversion of halloysite kaolin to meta-kaolin. While at the temperature of about 1000 °C, the recrystallization of meta-kaolin occurs, and the mullite is formed which is an exothermic reaction. With the formation of mullite, the reactivity and activity of meta-kaolin will decrease. Meta-kaolin is shown as 2SiO₂Al₂O₃ or Si₂O₅Al₂O₂ and is typically prepared at temperatures from 600 to 900 °C, but have reports indicated that the appropriate meta-kaolin for geopolymers is obtained at 700-750 °C [22,23].

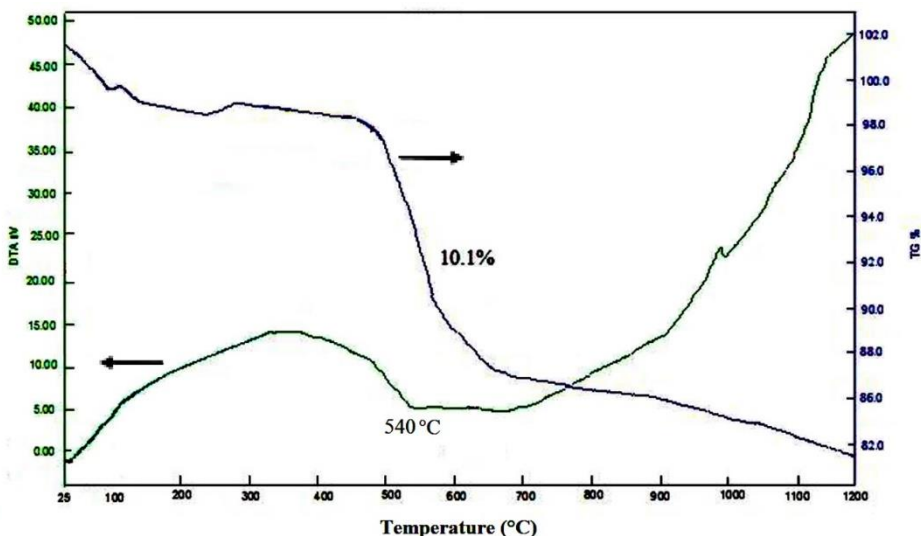


Fig. 1. DTA/TG curves of halloysite kaolin at a temperature range of 25-1200 °C.

Fig. 2 (a), (b), and (c) show the X-ray diffraction pattern of kaolin, meta-kaolin (kaolin after heat treatment at 750 °C for 24 hours) and geopolymer sample made with meta-kaolin during the curing time of 28 days (sample 28MKH9-75) respectively. As shown in Fig. 2 (a), the diffraction peaks marked in the X-ray diffraction pattern of halloysite kaolin are related to kaolinite, quartz, and calcite. In Fig. 2 (b), the kaolin peaks disappeared after the heat treatment at 750 °C for 24 hours, but the peaks of quartz and calcite impurities remained. Removing of peaks related to kaolin at $2\theta=12^\circ, 36^\circ$ after the calcination process, and the formation of meta-kaolin indicates the destruction of the kaolin network. Since the calcination process of kaolin is a diffusion process, it takes much time to exhaust hydroxyl units. In a short time, hydroxyl (OH) surface units are removed, but the process is not completely carried out. However, in the X-ray diffraction pattern of geopolymer samples, as shown in Fig. 2 (c), there is a large diffuse halo at $2\theta=20-40^\circ$ that is consistent with the diffraction pattern in other papers [5,10], indicating the formation of a new product with an amorphous structure without any regular repetitive structures [24]. Peaks in the diffraction pattern of geopolymer sample related to quartz and calcite minerals that it remains in the context of geopolymer after the geopolymerization reaction [5].

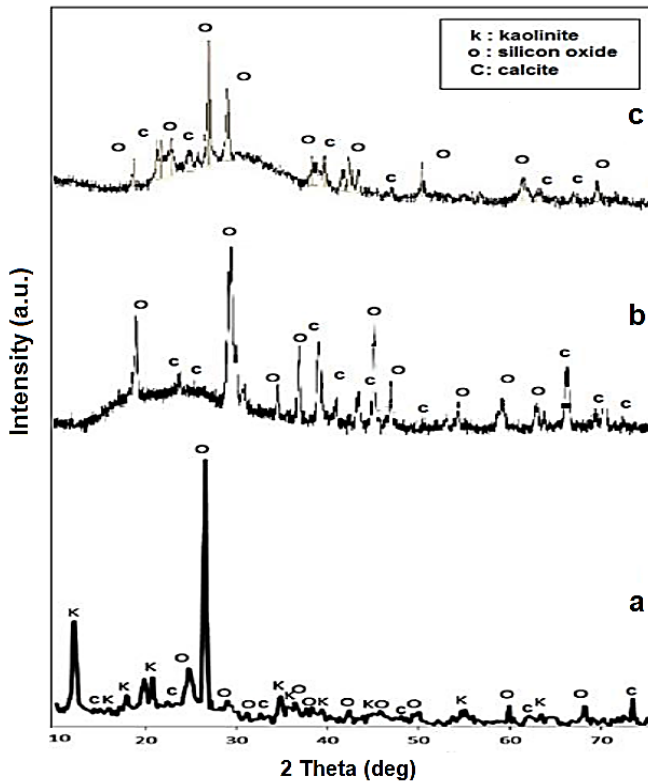


Fig. 2. X-ray diffraction pattern of a) kaolin, b) meta-kaolin, and c) geopolymer sample at the curing time of 28 days (sample 28MKH9-75).

The X-ray diffraction patterns of meta-kaolin powder and different geopolymers are shown in Fig. 3. As can be seen, the specimens have the same diffraction pattern, which includes a broad and amorphous hump at $W=20-40$. The X-ray diffraction patterns of geopolymer specimens show that amorphous structure results from the dissolution of meta-kaolinite particles in the alkali activator and then the regeneration of AlO_4 and SiO_4 species as a gel structure. The $\text{Na}_2\text{O}/\text{SiO}_2$ molar ratio and curing temperature do not affect the XRD patterns of the geopolymer cement [5].

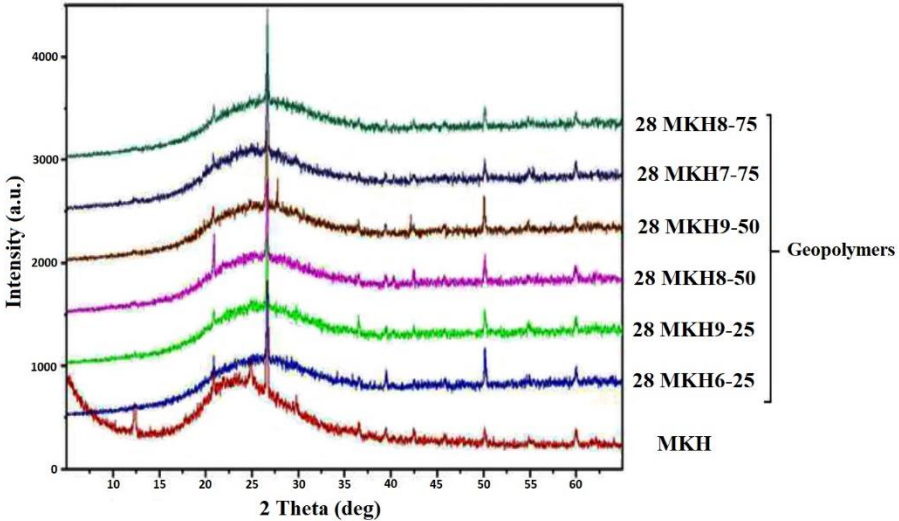
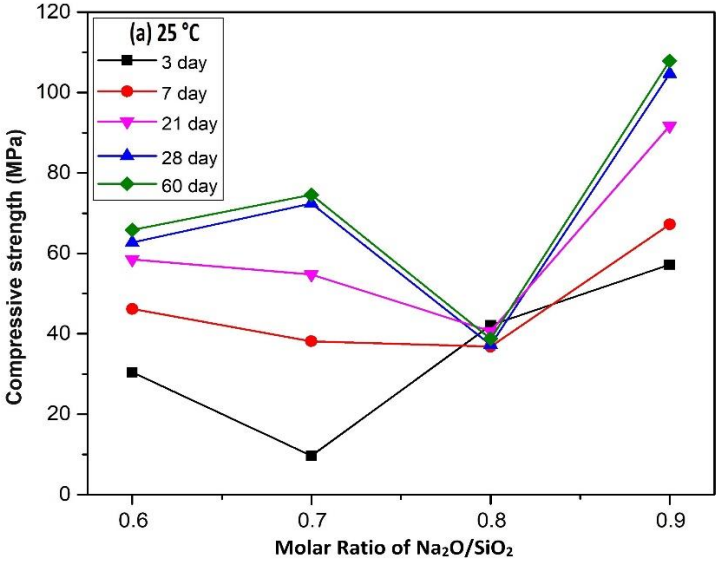
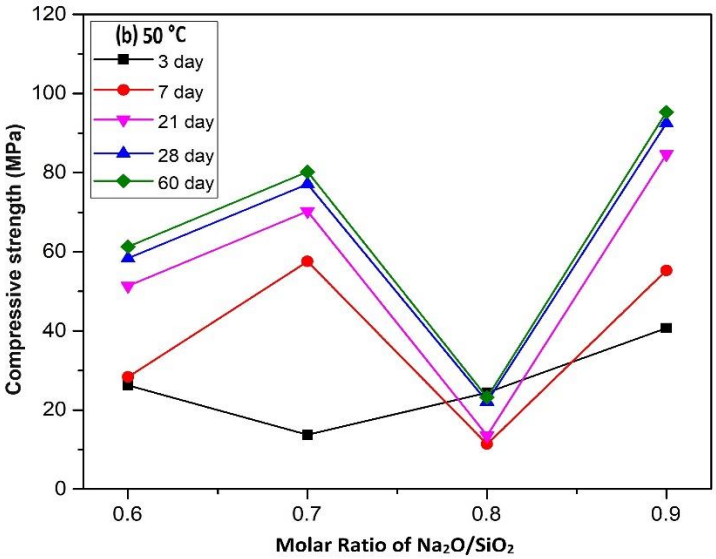


Fig. 3. X-ray diffraction patterns of meta-kaolin powder and some geopolymer samples.

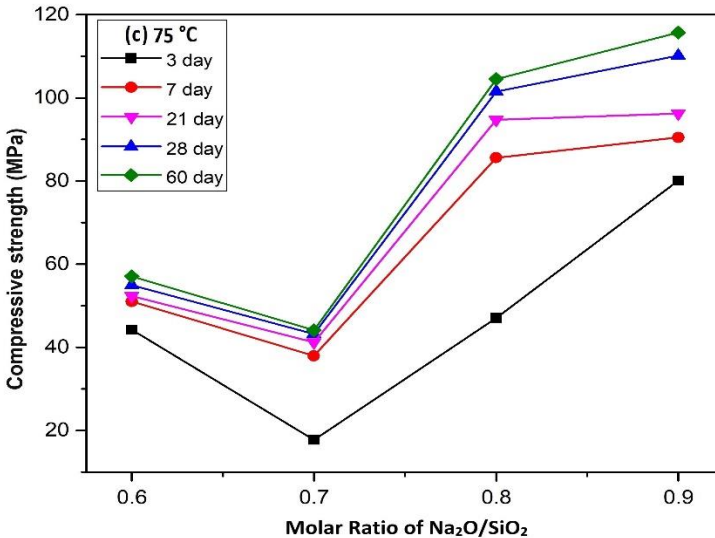
Fig. 4 shows the effect of $\text{Na}_2\text{O}/\text{SiO}_2$ molar ratio on compressive strength at curing of different temperature and time. In general, with increasing $\text{Na}_2\text{O}/\text{SiO}_2$ molar ratio, the alkali intensity of the medium increases, and consequently, the meta-kaolin solubility should increase in an alkali solution, which will improve compressive strength. On the other hand, with the increase of the $\text{Na}_2\text{O}/\text{SiO}_2$ molar ratio, some unreactive Na_2O will remain in the geopolymer network. This will prevent further the propagation of the polymer network and will create a breakdown that can reduce the strength of geopolymer specimens. In general, the curing process at a higher temperature will increase the speed of the process of geo-polymerization and increase compressive strength because it causes dehydration of gel phases or even crystallization of zeolites [23]. The results of the compressive strength of geopolymer samples at different curing times indicate that the use of curing temperature of 75°C and an activator solution with a molar ratio of $\text{Na}_2\text{O}/\text{SiO}_2=0.9$ (Fig. 4 (c)) would form samples with the highest compressive strength. Nevertheless, it should be noted that over-heating the curing process at higher temperatures will not only increase the strength but also reduce the compressive strength. In addition, it can be seen from Fig 4, that more increasing curing time after 28 day has no significant effect on compressive strength of geo-polymer samples.



(a)



(b)



(c)

Fig. 4. Effect of Na₂O/SiO₂ molar ratio on compressive strength of geopolymer samples at various curing temperatures and time.

Since XRD analysis is not suitable for investigation of the geopolymer structure due to the amorphous geopolymer, FTIR analysis was performed. Fig. 5 shows the FTIR spectrum of kaolin powder, meta-kaolin powder, and some geopolymer samples. For the halloysite kaolin spectrum, the peak at the wavelength of 1006 cm⁻¹ is associated with the asymmetric tensile vibration of the Si-O-Si or Si-O-Al bands. After thermal treatment and conversion to meta-kaolin, the peak has been transferred to 1087 cm⁻¹, indicating the weakening and breaking down of the mentioned bands. The peak that appears at 542 cm⁻¹ in the kaolin spectrum is related to the Si-O-Al band, which is lost due to heat treatment and the conversion of kaolin to meta-kaolin. The peak occurring at 912 cm⁻¹ in the kaolin spectrum is assigned to the tensile vibrations of Al-OH bands with 6-fold coordination. This peak is eliminated after the formation of meta-kaolin, and 6-fold units are converted into 4-fold Al units. It should be noted that the peaks at 3619 cm⁻¹ and 3696 cm⁻¹ in the kaolin spectrum belong to the kaolinite minerals, and it has been lost after the formation of meta-kaolin and is not observed in meta-kaolin spectrum [23, 25, 26].

As shown in Fig. 5, the peaks occurring at 1087 cm⁻¹ in the meta-kaolin spectrum were transferred to smaller wavelengths after the process of polymerization, which represents the formation of a new product. The Si-O-T (T= Al or Si) band has been displaced in all samples after the polymerization process. This phenomenon indicates a change in the microstructure during the geopolymer process, which led to the formation of a different product than meta-kaolin. This is consistent with the XRD spectrum. This large displacement towards lower wavelengths can be attributed to the substitution of the 4-fold AlO₄ units instead of the SiO₄ units, which causes changes in the chemical environment of the Si-O joints. As the Na₂O/SiO₂ molar ratio increases, this shift of peak will increase. The more of a shift there is toward smaller numbers, it represents a stronger

band formation, which could have a greater impact on the increase of compressive strength.

According to the results of FTIR geopolymer samples, during the polymerization reactions, the 4-fold units of AlO₄ and SiO₄ were released due to the attack of a highly alkaline solution from the surface of the meta-kaolin particles. After the dissolution process, a large number of these units enter the alkaline solution then after structural rearrangement begins the condensation polymerization reaction ultimately leads to the formation of a geopolymer product.

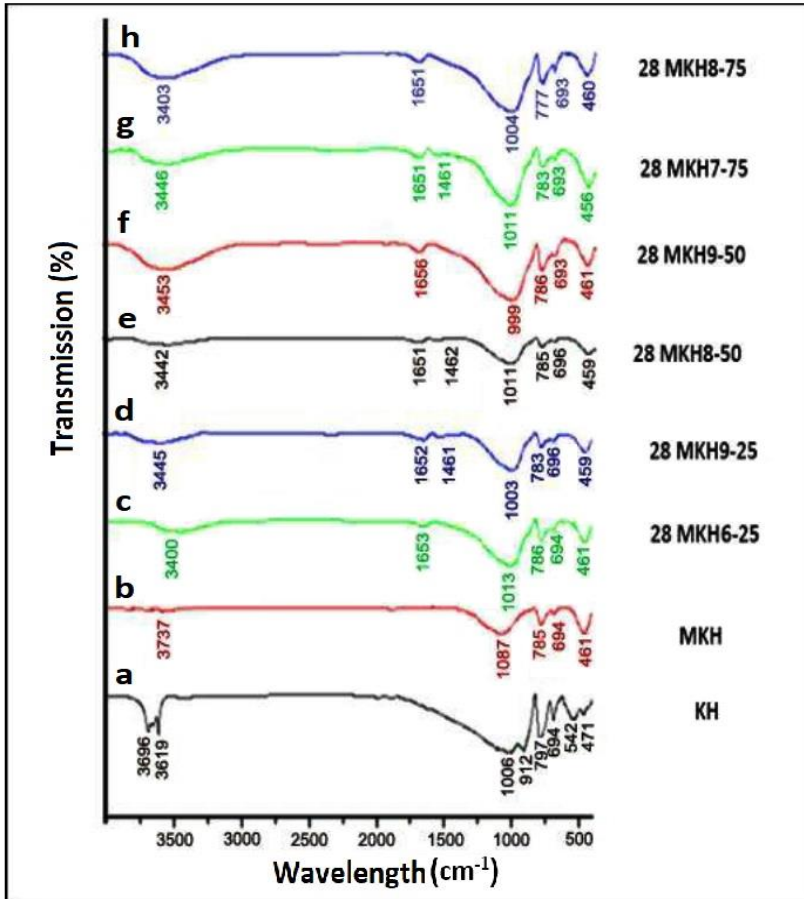


Fig. 5. FTIR spectra of a) kaolin powder, b) meta-kaolin powder and c-h) some geopolymer samples.

Fig. 6 and 7 show the MAS-NMR pattern of calcined material composition. In the pattern of ²⁷Al-MAS-NMR (Fig. 6), several peaks of Al are observed in various chemical displacements. After referring to the reference table, it was discovered that the chemical displacement peak of 56.5 ppm belonged to the 4-coordinated Al and other peaks in the chemical displacement of 1.8, 28.2, 66.3, and 78.9 ppm belong to the Al with the number

of neighborhoods 6 and 8. Therefore, there was Al with a number of different neighborhoods in this combination. However, since geopolymers are composed of AlO_4 and SiO_4 tetrahedrals, it is expected that after the polymerization process and the formation of geopolymers, only Al with four neighborhoods will be present. In Fig. 7. of the ^{29}Si -MAS-NMR pattern, three peaks assigned to in the chemical displacement of -68.2, -80.7, and -98.9 ppm. All of them are related to Na compounds such as Na_4SiO_4 and Na_2SiO_3 , and confirm the presence of silicon with the neighborhood of four in the raw material composition [27].

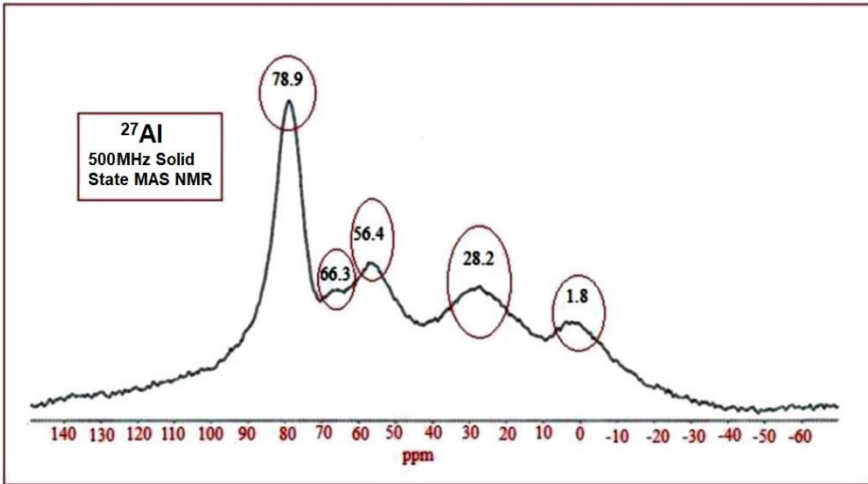


Fig. 6. ^{27}Al -MAS-NMR spectra of calcined material composition.

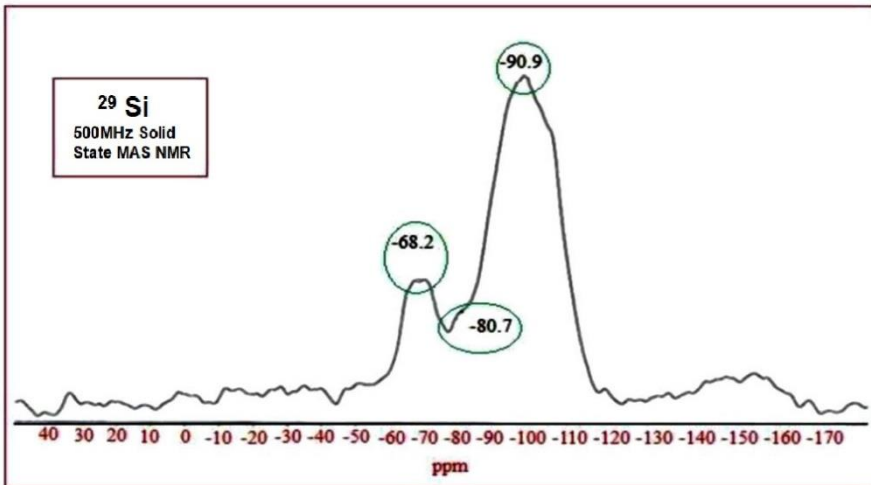


Fig. 7. ^{29}Si -MAS-NMR spectra of calcined material composition.

Fig. 8 shows the ^{27}Al -MAS-NMR spectra of a geopolymer sample after curing at a temperature of 75°C . Compared with Fig. 6, the only peak that is here is related to 4-

coordinated Al at a chemical displacement of 54.1 ppm, and peaks related to Al with other neighboring numbers have disappeared. Since the chemical displacement of this peak is very close to the chemical displacement of Al tetrahedral in geopolymers (55 ppm), it can be concluded that the polymerization process and geopolymer formation had been carried out [10]. According to Fig. 9, it is seen that in the ²⁹Si-MAS-NMR pattern, there is a broad peak in the range of -70 to -110 ppm, which reached -89 in the highest. Broad peaks are generally seen in zeolite gels before crystallization. The broad peak indicates that silicon and aluminum tetrahedral were not regularly oriented [10, 28].

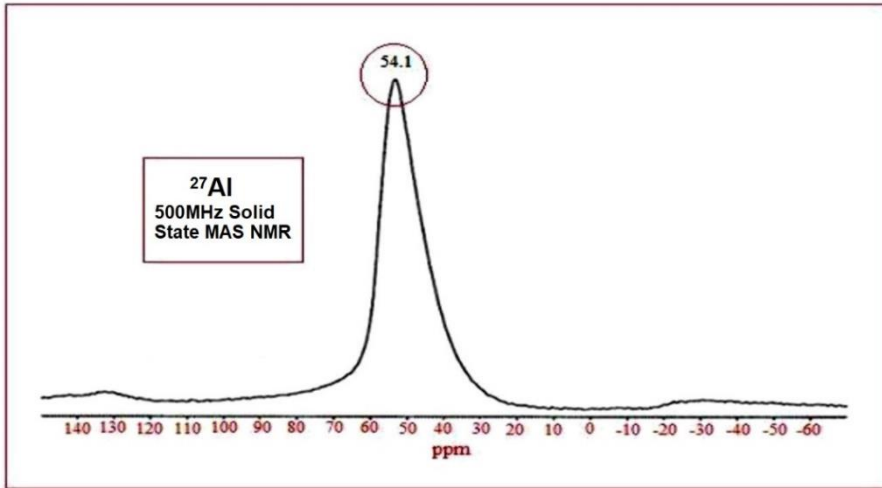


Fig. 8. ²⁷Al-MAS-NMR spectra of geopolymers.

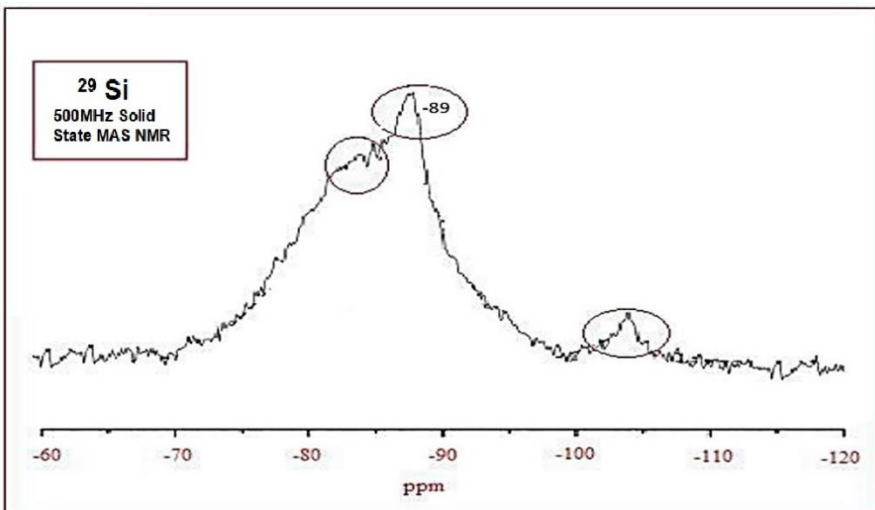
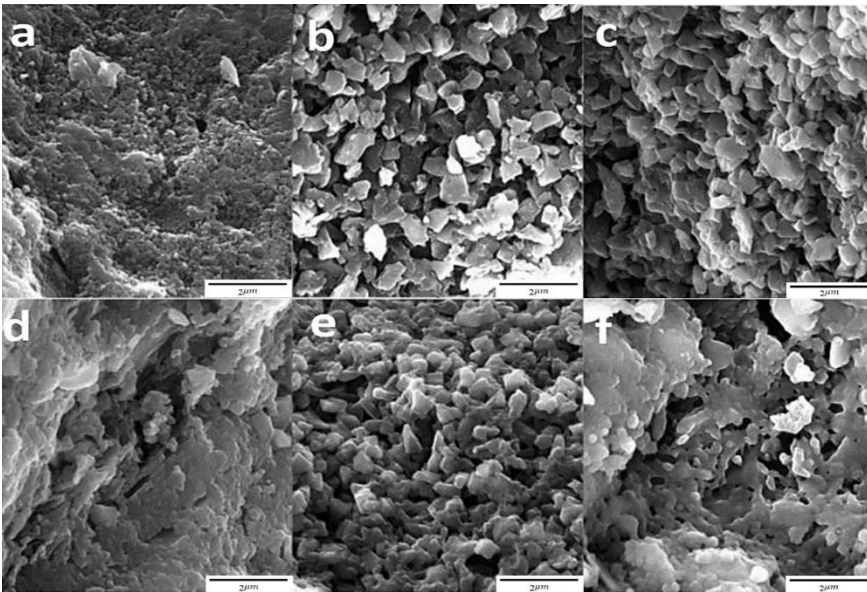


Fig. 9. ²⁹Si-MAS-NMR spectra of geopolymers.

The microstructure images of geopolymer cement samples are shown in Fig. 10. As we can see, in all samples, the geopolymer phase is well-formed. Generally, geopolymer cement is a composite material, which consists of composite materials that are formed from a gel phase with unreactive crystalline phases, despite the similarity spectra of the XRD and FTIR of cement samples, SEM images clearly indicate that they are very different in the microstructure. The presence of porosities due to evaporation of water and air bubbles enclosed in the cement paste is observed, which reduces their strength. Therefore, in order to achieve greater strength, the air bubble exit process is well done, and the amount of consumption water is also reduced [29]. By increasing the $\text{Na}_2\text{O}/\text{SiO}_2$ molar ratio, a significant change in the microstructure is observed, especially in terms of homogeneity [30].

The microstructural changes seen in different samples can be analyzed according to the Al role. In the geopolymers, the polymerization process and setting step depends on the amount of Al present in the system. In alkaline environments, the dissolution of Al is far greater than Si, so the probability of the reaction of the aluminate anions with the silicate components in the alkaline solution is higher. For this reason, the $\text{Na}_2\text{O}/\text{SiO}_2$ ratio and the presence of more silicate ions in the solution lead to an increase of Al to the polymer structure, the removal of more hydroxyl groups, and, consequently, a denser structure [22].

As shown in Fig. 10 (a), the 28MKH9-75 sample is more uniformity than other samples and has the highest compressive strength that matches the results. On the other hand, the 7MKH6-50 sample (Fig. 10 (f)) is very non-homogeneous and has the smallest amount of soluble silicate. The microstructure of this sample shows large and interconnected porosities, unreacted grains, and deposited particles.



*Fig. 10. SEM images of Specimens of geopolymers
a) 28MKH9-75, b) 28MKH8-50, c) 28MKH6-50,
d) 7MKH8-75, e) 7MKH8-50 and f) 7MKH6-50.*

Conclusion

The results of DTA showed that the conversion of kaolin to meta-kaolin occurs at a temperature range of 500-600 °C. Meta-kaolin suitable for geo-polymers was obtained at 750 °C. Geo-polymer samples were successfully prepared using meta-kaolin. The MAS-NMR pattern showed the chemical displacement of the peak of Al tetrahedral in geo-polymers, which confirmed the geo-polymerization process and the geopolymer formation.

The effects of Na₂O/SiO₂ molar ratios (0.6-0.9) on the geo-polymer samples (curing at 75 °C for 60 days) were examined. The compressive strength maximum was 115 MPa for a geopolymer sample obtained by curing at 75 °C for 60 days and with Na₂O/SiO₂ molar ratio of 0.9. The SEM images of different geopolymers show that at optimum conditions (curing at 75 °C for 28 days and with Na₂O/SiO₂ molar ratio of 0.8), the homogeneous microstructure is more uniform compare to other samples.

The results showed that the Na₂O/SiO₂ molar ratio and curing temperature do not affect XRD patterns of the geopolymer cement. The effects of curing temperature and the time on the compressive strength of the geopolymer samples were investigated.

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