EFFECT OF CALCINATION TEMPERATURE OF THE KAOLIN AND MOLAR Na₂O/SiO₂ ACTIVATOR RATIO ON PHYSICAL AND MICROSTRUCTURAL PROPERTIES OF METAKAOLIN BASED GEOPOLYMERS

M. A. Soleimani, R. Naghizadeh*, A. R. Mirhabibi and F. Golestanifard

* *rnaghizadeh@iust.ac.ir*

School of Materials Science and Engineering, Iran University of Science and Technology, Tehran, Iran.

Abstract: Metakaolinite-based geopolymer has been synthesized at about 25 °C from metakaolin which has been calcined in different temperatures (600-900 °C) and different Na₂O/SiO₂ ratio activator (0.3-1.1). Compressive strength and microstructure of cement pastes after 7-28 days curing at ambient temperature were measured. Compressive strength tests on the samples showed that the sample made with calcined kaolin at 700 °C and molar ratio of 0.6 has highest average compressive strength of 32 MPa after 28 days of curing. Evaluation of infrared spectroscopy (FTIR) and microstructure showed that geopolymer cement developed and new molecular structure established.

Keywords: Geopolymer, Metakaolin, Compressive strength, Activator

1. INTRODUCTION

Concrete is the most widely used construction material in the world. Ordinary Portland cement (OPC) has been traditionally used as the binding agent for concrete. The worldwide consumption of concrete is estimated to increase due to the increase of infrastructures especially in countries such as India and China. The amount of carbon dioxide released during the manufacturing process of OPC is in the order of 1 ton per each ton production of OPC. Globally, the OPC production contributes about 7% of the world's carbon dioxide. This is adding about 1.6 billion tons of carbon dioxide into the atmosphere [1]. Since it has now become a priority to control the trend of global warming by reducing the carbon dioxide emission, it is appropriate to search for alternative low-emission binding agents. The geopolymeric binder based on proper raw materials which is also known as inorganic polymer is one of such alternative materials. The geopolymer cement obtain from mixing of some aluminosilicate sources such as metakaolin and fly ash with alkali silicate solutions [2]. With usage of proper materials, the emission of carbon dioxide will be reduce in comparison with Portland cement production.

A geopolymer can be defined as the material that results from the geosynthesis of polymeric aluminosilicates and alkali-silicates; yielding a three-dimensional polymeric framework of linked SiO_4 and AlO_4 tetrahedral. An aluminosilicate material such as kaolinite can be dissolved in an alkali-silicate solution to form a rock hard brittle ceramic. Using the proper chemistry, one can attain a high strength material that can set as little as a few hours at room temperature [3,4]. Structural characterization of geopolymers reveals that these materials have amorphous or semi-crystalline structure. The geopolymer structure consists of cross-linked SiO_4 and AlO_4 tetrahedral that the negative charge on Al^{+3} sites in IV-fold coordination is compensated with alkali ions such as Na^+ and K^+.
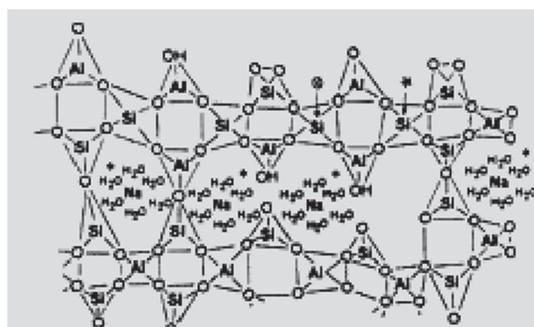

Fig. 1. Proposed geopolymer structure [5].

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A structural model proposed by Barbosa et al [5], is shown in Fig. 1.

Geopolymeric materials and cement blends can be used for a number of applications such as fire and acid resistant materials, immobilization of heavy metals, bonding of metal and ceramic surfaces, and various structural materials [3].

During the last few decades, fly ash, slag, kaolinite, mine tailings, etc. are used as raw materials to synthesize geopolymers. Among them kaolinite is the most common raw material due to its relatively purer components. In its raw form, kaolin can react and form a fully hardened geopolymer. However, metakaolin is often used due to increased reactivity over raw kaolinite. Metakaolin obtain from calcination or dehydroxylation of kaolin clay at 500-900 °C. This removes chemically bonded water and changes a large portion of the octahedral coordinated aluminum which is found in kaolin to four and five-fold configuration. Davidovits has shown that this type of coordination show greater reactivity during geopolymerization [6].

In this study, the effect of calcination temperature of kaolin clay and alkaline activator composition on the mechanical and microstructure of geopolymer cements were investigated. Strength development, X-ray diffraction, (XRD) Fourier transform infrared spectroscopy (FTIR) and scanning electron microscopy (SEM) techniques were utilized for characterizing obtained geopolymer cements.

2. EXPERIMENTAL

2. 1. Materials

Kaolin was used as the primary aluminosilicate source for geopolymerization, and was obtained from WBB Company in England under the brand name of kaolin CC31. Aqueous sodium silicate solution (SiO_2/Na_2O =2, solid =38.5 w.t %) and industrial grade NaOH pellets (99% purity) were used to prepare alkali activators system. Distilled water was used throughout all experiments. The chemical composition of the materials used to make the geopolymer cement are listed in Table 1.

Table 1. Chemical composition of the starting materials used.

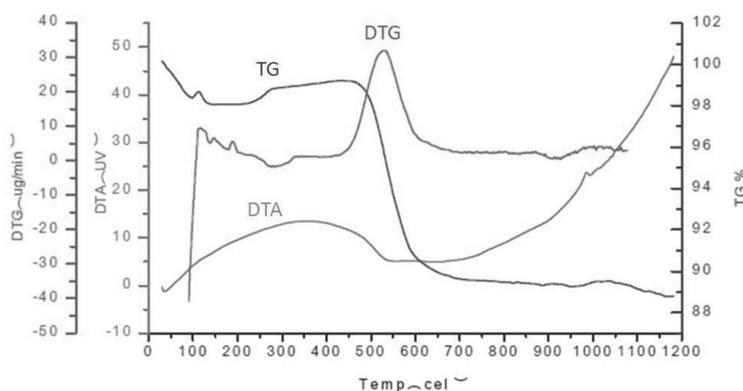| Material	H_2O	Al_2O_3	SiO_2	K_2O	Na_2O	Fe_2O_3	TiO_2	CaO	MgO	L.O.I
Kaolin	--	31.1	54.25	0.9	--	0.91	0.59	0.20	0.48	11.51
Sodium silicate$_{(aq)}$	61.4	--	25.5	--	13.1	--	--	--	--	--
NaOH(10M)$_{(aq)}$	76.2	--	--	--	23.74	--	--	--	--	--

Fig. 2. DTA, TG and DTG curves of CC31 kaolin.

Thermal behavior of the starting clay is shown in Figure 2. In DTA curve the broad endothermic peak at around 550°C along with intense loss weight in TG curve were attributed to dehydroxylation of kaolinite and formation of metakaolinite, at higher temperature metakaolinite alter to crystalline aluminosilicate such as Si-Al spinel and mullite. The small exothermic peak in DTA curve around 1000°C indicates crystallization of metakaolinite.

2. 2. Specimens Preparation for Mechanical Test

The calcination step was carried out at 600, 700, 800 and 900 ◦C for 24 hours. For preparation of the specimens, molar ratio Na_2O/Al_2O_3= 0.8 and mass ratio W/C = 0.53 for all specimens were used and molar ratios of the activator are selected as 0.35, 0.6, 0.85 and 1.1. Formation of different phases of geopolymer such as $Na_2Si_2Al_2O_8.(6-7)H_2O$ need above amount of water. Also water acts as ions transportation medium and provide required flow ability of geopolymer. For reaching to a proper structure, molecular chains and flowability, water to cement ratio were adopted equal to 0.53. NaOH and sodium silicate solutions are firstly mixed in a beaker and cooled down to room temperature, and then metakaolin powder was slowly added into the above pre-mix alkaline solution and further mixed for 5 minutes. After that, the fresh geopolymeric paste is rapidly poured into cubic steel mold of 50 mm by 50 mm by 50 mm. All samples vibrated for 2 min on the vibration table, and set at room temperature. In order to prevent the evaporation of mixing water and the carbonation of the surface, the specimens were covered by plastic film during the setting and hardening process. The mold is removed after hardening of the specimens. The demolded specimens cured at 22 °C in atmospheric pressure in a covered plastic film for 7, 14, 21 and 28 days. At least 3 specimens were made for each formula. Then compressive strength testing is performed and average value is served as the ultimate compressive strength.

2. 3. Sample Preparation for Microanalysis

The fragments of the selected formula were collected after compressive test. Some of them were used to conduct SEM-EDS analysis and the others are further finely crushed. Fragments are immersed in ethanol for 3 days to stop the further geopolymerization reactions, and subsequently oven-dried at 60 °C for 6 hours to remove the physically absorbed water. After this process, hardened geopolymeric paste fractions are further ground into very fine particles with an agate mortar.

2. 4. Method of Analysis

2. 4. 1. FTIR Analysis

Fourier transform infrared spectroscopy (FTIR) is performed on a SHIMADZU-FTS 8400 FTIR using KBr pellet techniques. The resolution and number of scans used in FTIR collection were 2.0 cm $^{-1}$ and 16, respectively.

2. 4. 2. XRD Analysis

X-ray powder diffraction is recorded on a Philips PW1800 spectrometer with the following testing parameters: 40 KV, 30 mA, Cu (Kα) Radiation. The XRD patterns obtained by a scanning rate of 1° per min from 2θ =5° to 60° and steps of 2θ = 0.04°.

2. 4. 3. SEM Analysis

VEGA\\TESCAN SEM is used to characterize the microstructure and chemical compositions of the reacted geopolymeric specimens. The following parameters are employed in this study: accelerating voltage of 15 kev, pressure and relative humidity in sample chamber of 4.2 Torr and R. H. 80 % respectively.

3. RESULTS AND DISCUSSION

3. 1. Compressive Strength

Fig. 3 shows the relationship between activator molar ratio, Na_2O/SiO_2, and the compressive strength of geopolymers at curing times of 7, 14, 21 and 28 days for different calcination temperature of kaolin. It can be seen in Fig. 3 that samples with curing time of 28 days have utmost of compressive strength and also with increasing calcination
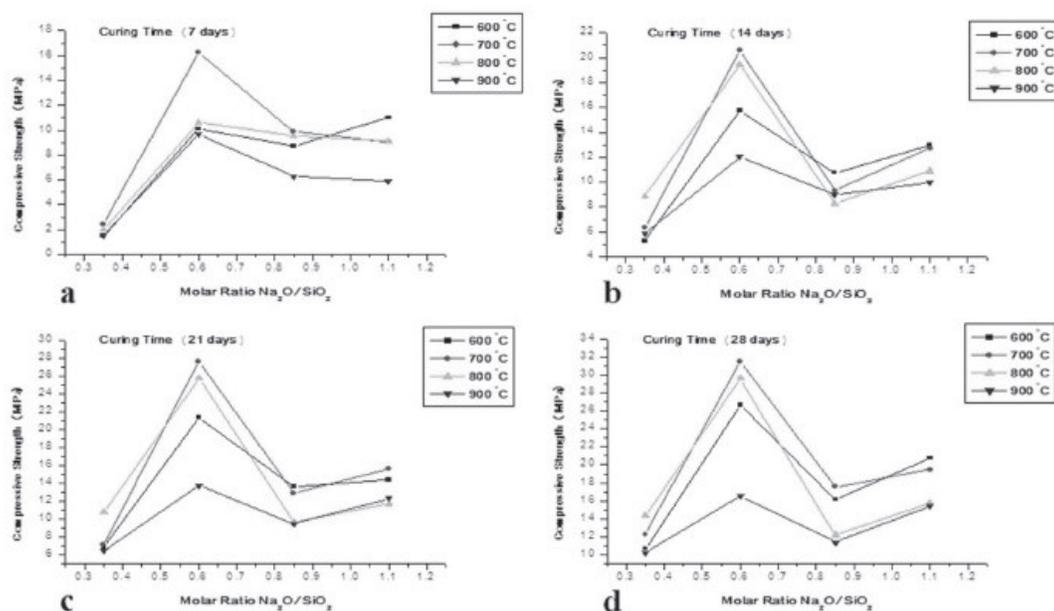
Fig. 3. Compressive Strength of geopolymer samples at curing time of: a) 7, b) 14, c) 21 and d) 28 days.

temperature from 600 °C to 700 °C compressive strength is increased. This increase in strength can be related to transformation Al(VI) coordination to IV and V-fold coordination. Further increasing of calcination temperature of kaolin from 700 °C to 800 °C and 900 °C caused compressive strength of the samples decreases because the amount of the Al(IV) coordination in comparison with Al(V) in metakaolinite structure is increased with high calcination temperatures. It seems that Al(V) coordination is very exothermic and accelerates geopolymerization process and setting while presence of Al(IV) coordination retarding the setting [6,7].

The effect of activator molar ratio, Na_2O/SiO_2, on compressive strength of the geopolymer samples can be divided into 3 steps (Fig.3-d). In first step, with increase of this ratio from 0.35 to 0.6, compressive strength is increased intensely. With more increase from 0.6 to 0.85 falling the compressive strength was observed and eventually in last step with increase of molar ratio from 0.85 to 1.1 compressive strength of samples increased slowly or remained almost constant. In first step with increasing molar ratio, Na_2O/SiO_2, solubility of metakaolin is increased and compressive strength will gain to maximum

amount of (32 MPa). In later step with further increasing of this ratio due to abortion of geopolymerization process and interruption in polymeric network, compressive strength of samples will be decreased [8,9]. Slow increasing of strength at 0.85-1.1 range of activator molar ratio, Na_2O/SiO_2, is probably related to development of sound samples with low microcracks in the surface of samples due to formation of very thin layer of dense geopolymer phase from migration of very small particle of metakaolinite to surface. It should be said that all of the four diagrams of the compressive strengths at different curing times are somewhat similar and effect of both parameters of molar ratio Na_2O/SiO_2 and calcination temperature is same on the compressive strength of samples at different curing times. The 28 days compressive strength of similar geopolymer cement pastes were 12-37 MPa and shows that obtained strengths at this study were appropriate [10].

3. 2. Infrared Spectroscopy Characterization

A selection of FTIR spectra of the kaolin and starting metakaolin in different calcination temperatures is shown in Fig. 4. The kaolin
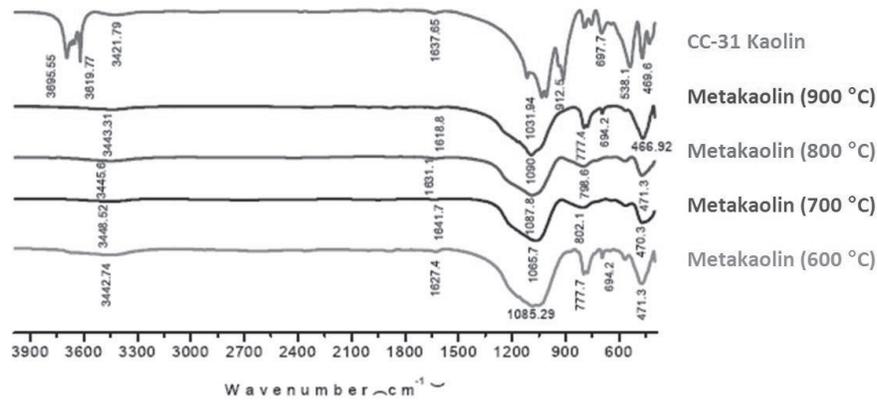
Fig. 4. FTIR spectra of the kaolin and metakaolin calcined at different temperatures.

(CC31) spectrum (Fig.4) is characterized by different vibration belong to Si-O, Al(VI)-O, Al(VI)-OH and Si-O-Al bonds. Two bands around 3600 cm^{-1} and one band at 912 cm^{-1} related to Al(VI)-OH and Al(VI)-O stretching vibration respectively. With calcination of kaolin these bands disappear and 4-coordination vibration of Al(IV)-O appear at around 780 cm^{-1} band. The broad bands at about 3420 cm^{-1} and 1640 cm^{-1} show adsorbed atmospheric water. The Si–O stretching vibration at 1031 cm^{-1}, Si–O–Al vibration at 810 cm^{-1} and Si–O bending vibration at about 470 cm^{-1} also present in kaolin IR spectrum. The shoulder near 912 cm^{-1} arises from the quartz impurity.

The band centered at 1032 cm^{-1} in the IR spectrum of kaolinite, corresponding to the Si–O-

Si or Si-O-Al bond became broad due to decreasing of crystallinity kaolinite structure during calcination and formation of metakaolin. Characteristic peak of kaolinite in 538 cm^{-1} due to Si-O-Al(VI) bond are reduced after calcination process and will disappear in 900 °C temperature. The broad bands in the region of 1640–3420 cm^{-1} are character of stretching and deformation vibrations of O-H and H–O–H groups from the weakly bound water molecules which are reduced in infrared spectra of metakaolins [9-11].

Fig. 5 shows FTIR spectra for different geopolymer cement contain metakaolin that calcined at 700 °C after 28 days curing with different activator ratio Na$_2$O/SiO$_2$. Geopolymer cement named as Mb-a that M denotes metakaolin based cement, b shows one hundredth
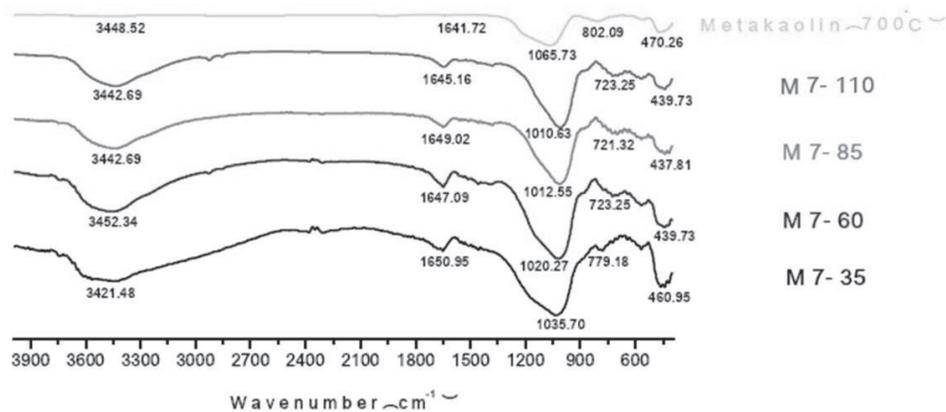

Fig. 5. FTIR spectra of the metakaolin calcined at 700 °C and geopolymer cements after 28 days curing with different molar ratio of Na$_2$O/SiO$_2$.

of calcination temperature and a shows hundred fold of Na_2O/SiO_2 molar ratio.

On the formation of the geopolymer, the following changes in the spectra are noticed:

a. The presence of the adsorbed water or weakly bond H_2O molecules at surface or cavities of geopolymer increases the intensity of the bands at about 3450 and 1650 cm^{-1}.

b. Major disruption of the Al environment is indicated by the loss of the Si–O–Al band at 810 cm^{-1} metakaolinite which is replaced by several weaker bands in the range 600–800 cm^{-1} in geopolymer.

c. The band centered at about 1088 cm^{-1} in the IR spectrum of calcined kaolin, corresponding to the Si–O asymmetric stretching in tetrahedral, is shifted to lower wavenumbers (about 1000 cm^{-1}) after polymerization reaction of geopolymer cement. The shift indicates a formation of new products which are different from calcined kaolin. The large shift towards lower wavenumbers might be attributed to the partial replacement of SiO_4 tetrahedral by AlO_4 tetrahedral, resulting in a change in the local chemical environment of Si–O bond. The intense but broadened feature of 1000 cm^{-1} band was indicative of the general disorder in the Si(Al)–O– network, reflecting the wide distribution of the SiQn(mAl) units in the geopolymer product

network [12-15].

3. 3. X-Ray Diffraction Characterization

Fig.6 shows the XRD patterns of CC-31 kaolin and those calcined at 600, 700, 800 °C and 900 °C for 24 h, respectively. The kaolin starting material shows the typical diffraction pattern of a well crystallized layer lattice mineral of kaolinite with quartz and muscovite impurities.

Patterns of 600, 700, 800 °C and 900 °C show that kaolinite peaks almost disappear and transfor to amorphous state. The distinctive peak at 12.3° of kaolinite disappeared in patterns of metakaolin indicating its destruction in (001) direction. Quartz phase present in the metakaolin as a crystalline state.

Fig.7a,b show the XRD patterns of geopolymer samples of different compositions. X-ray diffraction of the geopolymer samples show an amorphous structure that obtain from dissolution of metakaolinite particle in alkaline activator and then reconstruction of AlO_4 and SiO_4 species as gel structure [16-17]. Quartz and muscovite remain as a crystalline phases in the geopolymer cement. The similar large diffused halo peaks at about 2θ=20–40° further indicate that all geopolymers are mainly X-ray amorphous with lack of periodically repeating structure. But this doesn't confirm that there no nano-crystalline zeolite phases is formed due to the limited detectable scale amount by XRD. The alterations of calcination temperature and composition of
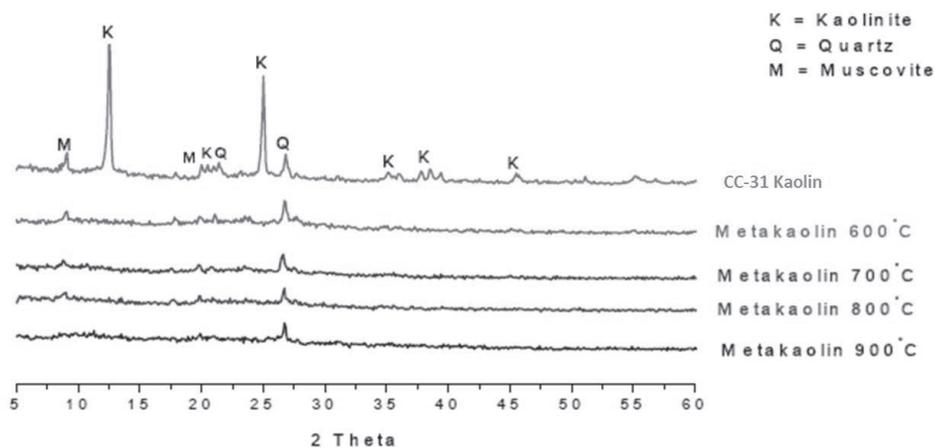

Fig. 6. XRD diffraction patterns of CC-31 kaolin at different calcination temperatures.
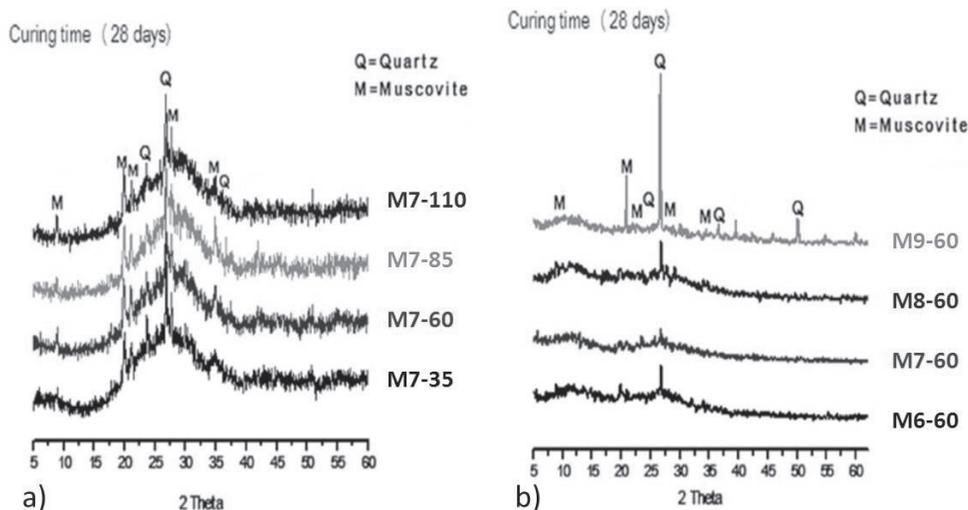
Fig. 7. XRD diffraction patterns of the geopolymer samples at curing time of 28 days a) for metakaolin 700°C in different composition of activators b) For 0.6 molar ratio of Na_2O/SiO_2 activator and different prepared metakaolins (600-900°C).

alkaline activator on the structure of amorph geopolymer cement didn't obviously show effect on the XRD patterns of geopolymer cements.

3. 4. SEM Analysis

SEM images of geopolymer samples with calcination temperature 700 °C metakaolin at different molar ratios 0.35, 0.6, 0.85 and 1.1 Na_2O/SiO_2 activator are presented in Fig. 8. As mentioned earlier, geopolymers are often mixtures of gel phase and remainder undissolved particles. Such mixtures can also be observed from the SEM images of geopolymer samples. Also, the presence of porosity and pores caused

by water evaporation and trapped air bubbles inside paste which will decrease the strength of cement samples is observed. Despite of having similar XRD diffraction pattern and IR spectra of geopolymer samples, their SEM images clearly show that these are very different in microstructure. As shown, the microstructure of M7-60 (Fig.8b), which exhibit the highest strengths was highly homogeneous. SEM images of the samples M7- 35 (Fig.8a), M7-85 (Fig.8c) and M7-110 (Fig.8d) clearly show the presence of high amounts of unreacted particles or microcracking which caused the decreased compressive strength.

With increasing activator molar ratio,

Table 2. SEM-EDX analysis of geopolymer cements.

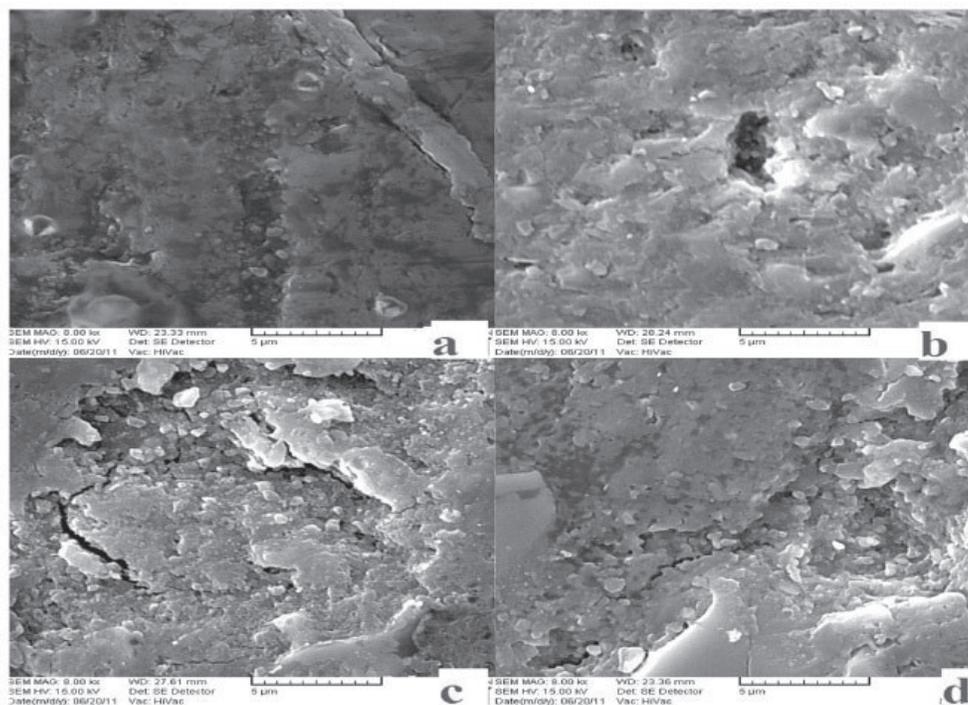| Element / Sample	Si	Al	O	Na
M7-35	49.01	9.52	27.22	9.92
M7-60	33.42	20.24	30.26	12.73
M7-85	30.28	20.46	13.99	22.48
M7-110	37.44	31.97	9.69	17.07

Fig. 8. SEM images of geopolymer samples: a) M7-35 , b) M7-60 , c) M7-85 and d) M7-110

Na_2O/SiO_2, dissolution of metakaolin is increased but for formation of gel structure of geopolymer, the rates of dissolution and gelation must be controlled. At higher molar ratio of Na_2O/SiO_2 due to high setting rate (low setting time) the mature and dense structure of gel can not be established, that decrease the compressive strength.

According to SEM- EDS of geopolymeric samples (Table II), it can be said that with increasing activator molar ratio, Na_2O/SiO_2, the molar ratio of $SiO2/Al_2O_3$ of geopolymer cement decreases and reach from 9 to 2.5 at molar ratio of 0.35 and 1.10 activator respectively. This shows that dissolution of metakaolinite particle increased and high amount of AlO_4 species enter to gel structure.

5. CONCLUSIONS

The following conclusions can be drawn from this study.

1. The compressive strength of geopolymer cement paste samples increases with increasing the calcination temperature of kaolin between 600 and 700 °C but decreases above 700°C. During calcination Al(VI) coordination transfer to four and five coordination and amorphous structure were obtained. The ratio of Al(IV) and Al(V) determine the trend of progressive properties. Presence of both of the Al(IV) and Al(V) is necessary for attainment of suitable compressive strength and setting time.

2. With increasing mortar ratio of Na_2O/SiO_2 activator up to 0.6, the strength increased and reaches to 32 MPa after 28 days of curing at ambient temperature. The rates of dissolution of metalaolinite particles and gelation of AlO_4 and SiO_4 species must be accurately selected until reach to complete formation of gel structure.

3. The microstructure trend of different geopolymers show that at optimum condition (0.6 activator molar ratio, Na_2O/SiO_2, and calcination temperature 700°C) homogeneous microstructure and microcrack free samples were obtained.

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