Effect of Temperature and Activator Molar of Na_2O to SiO_2 in the Process of Synthesis and Microstructure of Cement Geopolymer

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ABSTRACT

Inorganic polymers were synthesized from dehydroxylated aluminosilicate clay (metakaolinite) condensed with sodium silicate in a highly alkaline environment. The thermal treatment of aluminosilicate materials causes changes in their structure with an increase in the amorphous phase. For that kind of structural change XRD analysis is not appropriate, so those changes are currently assessed by infrared emission spectra analysis (FTIR). The most characteristic FTIR band in the geopolymeric systems appears in the wavenumbers region 990-1090cm^{-1} and is attributed to the asymmetric stretching vibration of T-O-Si, where T denotes Si or Al. The shift of this peak towards lower wavenumbers indicates the dissolution of the amorphous aluminosilicate phase of the raw material and the formation of a new amorphous gel in which the backbone consists of polymeric chains with smaller length in relation to the ones of the raw material. The SEM result showed that geopolymer paste was formed from quartz remaining particles and gel. The remaining particle size was reduced by increase of the curing temperature and Na_2O/SiO_2 molar ratio. The results indicated that samples with adequate strength are created compact and crack-free areas.

1. Introduction

Geopolymers are a group of mineral polymers with mostly amorphous to semi-crystalline microstructure and are generally produced in atmosphere temperature or below 100°C by polymerization of monomers and aluminate oligomers as well as gel deposition in alkaline solutions [1, 2]. The major difference between geopolymers and Portland cement is that its mechanism does not occur by hydration, but with polymerization reaction in a short time, whereas hydration of cement usually continues until one month and is completed in a year [3]. Geopolymerisation is a reaction between chemical cations to produce aluminosilicate.

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The mechanism of geopolymerisation consists of solution, transmission and polymerization of precursor samples containing Al and Si.

Polymerization process includes a rapid chemical substitution reaction on Si-Al minerals under alkaline environment, the result of which is 3-D polymer rings made up of Si-O-Al [4, 5].

The structure of geopolymer can be expressed by the following formula:

$$M_n[-(SiO_2)_z - Al_2O_3]_n.wH_2O$$

Where, M is an alkaline cation, n is the degree of polycondensation, Z is 1, 2, 3 or more, and W is binding water amount.

In geopolymerisation process, $(Na^+,K^+,H_3O^+,Ca^{++},Ba^{++},NH_4^+)$ ions play the role of balancing electric and catalyzer charges [6].

2- Materials and methodology

Fig 1 shows an overview of the research method in the present study. Two major precursors are used in synthesis of geopolymer: a solid aluminosilicate and an alkaline silicate solution. In the present study metakaolin was used as aluminosilicate source material. The alkaline solution was prepared by solving sodium hydroxide in sodium silicate solution and distilled water in order to achieve specific concentrations of silicate and alkaline. For producing the gel, the alkaline activator solution was slowly poured on metakaolinite precursor. In order for aluminate and silicate monomers to be formed, this gel should be intensively stirred for at least 3 minutes. The stirring process continues until a completely homogeneous paste is obtained. The resulted homogeneous composition is poured into cubic wooden molds (50×50×50mm) before it is hardened. The curing was different in temperature and duration conditions. In the present study kaolin soil (Iran China Soil Co.) was used as primary aluminosilicate material for producing geopolymer cement. The faulty ZS is Zeus Kaolin. The characteristics of these soils are presented in the form of chemical composition and mineral analysis are given in table 1 and 2, respectively.

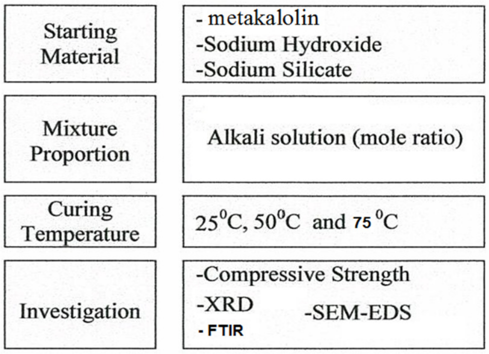


Fig.1. Overview of research methods

Table1. Chemical analysis of raw materials

L.O.I	Na_2O	K_2O	MgO	CaO	TiO_2	Fe_2O_3	Al_2O_3	SiO_2	Chemical analysis
4-5	0.25	0.2	0.3	2-3	0.04	0.3-0.5	9-12	81-79	ZS

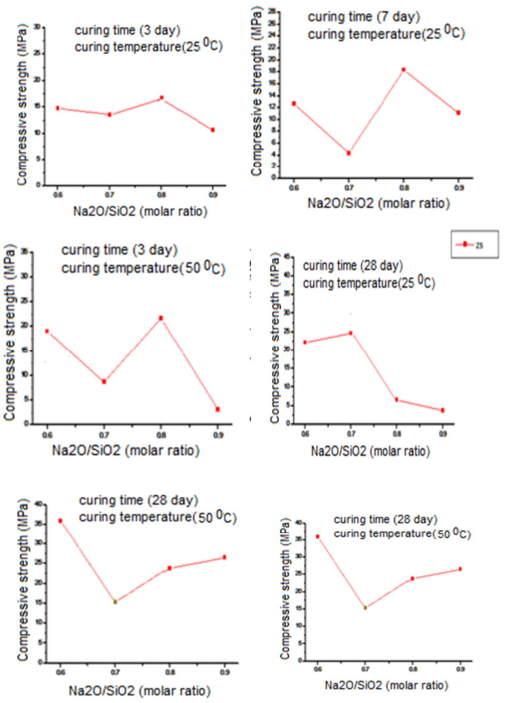
Table2. Analysis of mineral raw materials

Others	Free silica	Calcite	Kaolinite	Primary materials
2-4	67	5.4	25	ZS

3- Results and discussion

3-1- Compressive strength

Fig.2 shows compressive strength of geopolymer samples based on molar ration of Na_2O/SiO_2 in curing temperatures 25, 50 and 75°C and curing durations 3, 7 and 28 days. Generally, curing at higher temperatures increases the speed of geopolymerisation process as well as compressive strength but it should be noted that overdoing the curing process at higher temperatures or longer durations not only does not increase strength but will cause its decrease because it results in dehydration of gel phases or even formation of zeolite crystalline phases. Curing at higher temperatures (50°C) compared to room temperature increases compressive strength of geopolymer samples which is due to more complete accomplishment of geopolymerisation process. However, it should be added that heat treatment and increase of curing temperature decreased the strength of some samples which seems to be due to the rapid evaporation of the water in geopolymer samples and incomplete accomplishment of geopolymerisation process in these samples.



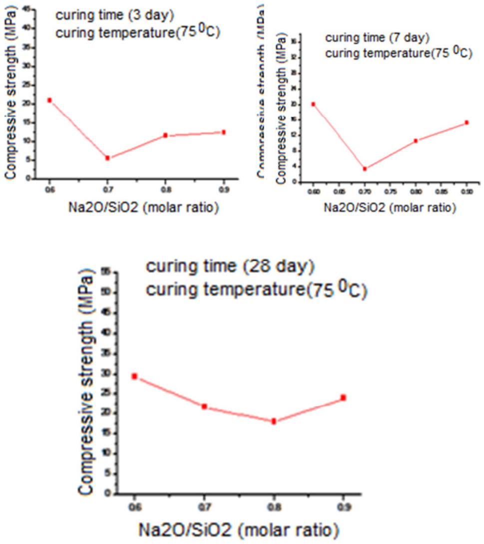


Fig.2. Compressive strength of geopolymer with metakaolin (ZS) with a molar ratio of activator in curing temperatures of 25, 50, 75°C and curing times of 3, 7 and 28 days

Regarding the effect of curing temperature on compressive strength of geopolymer samples in curing duration of 3 days and the primary strength of these samples it should be mentioned that in samples made from ZS metakaolin the strength of samples decreases in most cases. As can be seen in the above figure, in curing duration of 7 days, the variation of curing temperature has different effects on compressive strength of samples, so that for some samples using average curing temperature with a longer duration is more suitable and causes the increase of strength, but in some samples using temperature regime with high curing temperature and shorter duration has advantages for compressive strength. Also, for the samples with curing duration of 28 days and the final strength the effect of curing temperature on compressive strength does not follow a specific trend and acts differently for various samples. But generally speaking, increase of curing temperature results in better and more complete geopolymerisation process and helps the more complete formation of geopolymer network. However, it should be noted that applying high temperatures and longer durations not only does not show a positive effect but it also decreases the compressive strength. With respect to the effect of molar ratio of Na_2O/SiO_2 on compressive strength of geopolymer samples it can be claimed that with increase of this ratio many parameters will be effective on compressive strength of geopolymer samples. With increase of molar ratio of Na_2O/SiO_2 the intensity of alkalinity of the solution will increase; also, silicate and aluminate present in kaolin will be solved more, which is advantageous for compressive strength and will enhance it. On the other hand, however, Na_2O elements will not react and the formation of free alkalines and transportation of these elements into the geopolymer network will increase, too, which is unfavorable for strength and will decrease it. Therefore, these two parameters are always in conflict with each other in increase or decrease of strength.

It should be mentioned that in addition to the above parameters, with increase of Na_2O/SiO_2 molar ratio the amount of consumed kaolin (metakalolin) for producing geopolymer samples will increase and the amount of ratio of water content to cement (W/C) decreases. Therefore, with increase of Na_2O/SiO_2 ration, the strength of samples is expected to increase because the amount of consumed kaolin and hence the amount of kaolinite solved in alkaline solution have increased which are advantageous for compressive strength and more geopolymer gel will be formed.

On the other hand, the amount of consumed free silica present in kaolin will increase, too, which is sometimes valuable and some other times inconvenient. Thus, according to the above mentioned issues, it should be claimed that in the amount of consumed kaolin, too, two parameters are competing together: 1) the amount of kaolinite present in kaolin the decrease of which is advantageous for strength and will enhance it; 2) the amount of free silica present in kaolin which is sometimes of positive effect (as a filler), increasing the strength, and sometimes of negative effect (unreacted particles and disturbers of the network), decreasing compressive strength.

3-2- Results and analysis of FTIR

In order to come up with microscopic structure of geopolymer, XRD analysis is not convenient due to the amorphous property of geopolymers. To investigate the structure of geopolymer and make sure of the formation of geopolymer network FTIR analysis was performed.

Fig 3 shows the infrared spectrum (FTIR) of ZS Kaolin and ZS metakaolin and geopolymer samples constructed by SZ metakaolin in curing duration of 28 days, molar ratio of 0.6, 0.7 and 0.9 at 25, 50 and 75°C curing temperatures. As can be seen in this figure, in the spectrum of ZS kaolin, the peak present in wavenumber $1031 cm^{-1}$ which is resulted from asymmetric stretching vibration of Si-O-Si or Si-O-Al bonds has shifted to larger wavenumber $1089 cm^{-1}$ after heat treatment and changing into metakaolin, which shows the weakening and breaking of these bonds and formation of metakaolin.

The peak specifying the kaolinite mineral shows itself for kaolin ZS at wavenumber 537 cm^{-1} which is due to $Si\text{-}O\text{-}Al^{VI}$ bonds; this peak disappears due to heat treatment and the changing of kaolin to metakaolin and shows the increase of reactibility of metakaolin compared to the primary kaolin. The peak present at wavenumber 911 cm^{-1} in kaolin ZS spectrum has also been generated by strain vibrations of 6 co-ordinated Al-OH bonds; after the formation of metakaolin this peak disappears and hexahedral Al units change into fourfold and fivefold Al units. It should be mentioned that the peaks present in wavenumbers 3619 and 3696 cm^{-1} in kaolin ZS spectrum are also related to kaolinite mineral which have disappeared after metakaolin is formed and are not observed in the infrared spectrum of metakaolin. As can be seen in fig 3, the strong bound present in wavenumber 1089 cm^{-1} for FTIR of metakaolin (Si-O-T, T=Si or Al) shifts toward smaller wavenumbers after polymerization. This phenomenon (shift toward wavenumbers) means that during hydration process, the microstructure has undergone some alterations and has resulted in formation of a new product (geopolymer gel) which is different from metakaoline microstructure. This shift toward smaller wavenumbers can be assigned to the partial replacements of SiO_4 units by tetrahedral AlO_4 units which will cause changes in chemical environment of Si-O links. The peaks near 1000 cm^{-1} are related to geopolymer materials and symmetric strain of Al-O and Si-O, which shows that geopolymerisation reaction is taking place in many molecular structures of the materials. Moreover, the location of the major peaks near 1000 cm^{-1} shifts down toward smaller wavenumbers. This phenomenon proves that geopolymerisation reaction has been carried out and more silica has been replaced with aluminum.

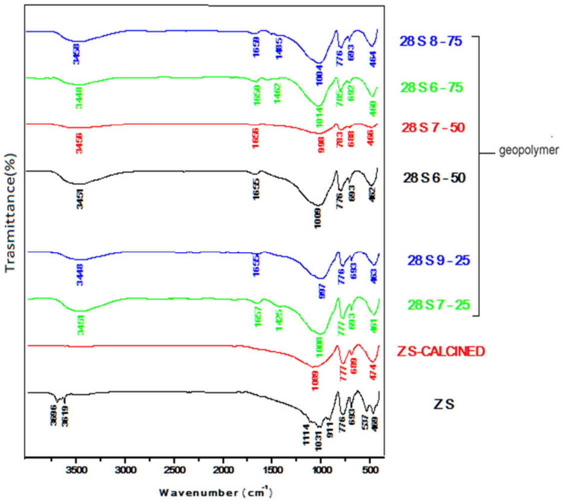


Fig.3. FTIR of ZS kaolin, ZS calcinated kaolin (zs metakaolin) and constructed geopolymeric samples in 28 days molar ratio was 0.6- 0.9 for Na_2O/SiO_2 and curing temperature was 25-75°C

As can be seen in fig 3, the peaks around wavenumbers 1650 and 3540 cm^{-1} for both samples 28 S 9-25 and 28 S 7-25 are related to the absorbed water in the structure of these geopolymer samples and are the result of vibrations of deformation and stretching vibrations of O-H and H-O-H sheets of water, respectively. For sample 28 S 7-25 the peak at wavenumber 1008cm^{-1} has more intensity compared to the peak at wavenumber 997cm^{-1} for sample 28 S 9-25, which shows the formation of more amount of geopolymer gel. The higher strength of this sample can be attributed to this issue. The increase of molar ratio of Na_2O/SiO_2 increases the amount of metakaolin consume for constructing geopolymer samples; as a result, the bulk ratio of W/C decreases and less water is presented to the system for geopolymerisation procedures and hence decrease of compressive strength is resulted. Of course, it should be noted that the shift (toward smaller wavenumbers) of the peak related to Si-O-Si bounds in sample 28 S 9-25 is greater compared to the sample 28 S 7-25 which is an evidence for the generation of stronger bonds; however, the strength of these samples is lower. In the figure it can be observed that the intensity of this peak in sample 28 S 7-50 has been reduced and less gel (geopolymer) phase has been formed and hence lower compressive strength is expected, which is confirmed with the obtained results. The intensity of the peak related to the absorbed water in sample 28 S 7-50 is much less than that of sample 28 S 6-50. It seems that with increase of molar ratio of Na_2O/SiO_2 and increase of curing temperature, not only the ratio W/C has decreased, but after completion of geopolymerisation processes, the water required for these processes has been evaporated and left the samples. From this figure it can also be observed that the shift of Si-O-Si or Si-O-Al peak toward smaller wavenumbers in sample 28 S 6-75 is less compared to sample 28 S 8-75, which shows the formation of weaker bonds; however, the strength of theses samples is relatively higher. It seems that the presence of free alkaline particles of Na_2O in sample 28 S 8-75 causes the incoherence of the network and decrease of strength.

3-3- Scanning electron microscopy (SEM)

As can be seen in fig 4, these samples are made up of two adjoining phases which can be identified by difference in the contrast in SEM images. Phase 1 is related to the continuous geopolymer matrix and phase 2 which is embedded in phase 1 and has caused its incompactness is related to unreacted silica or quartz particles.

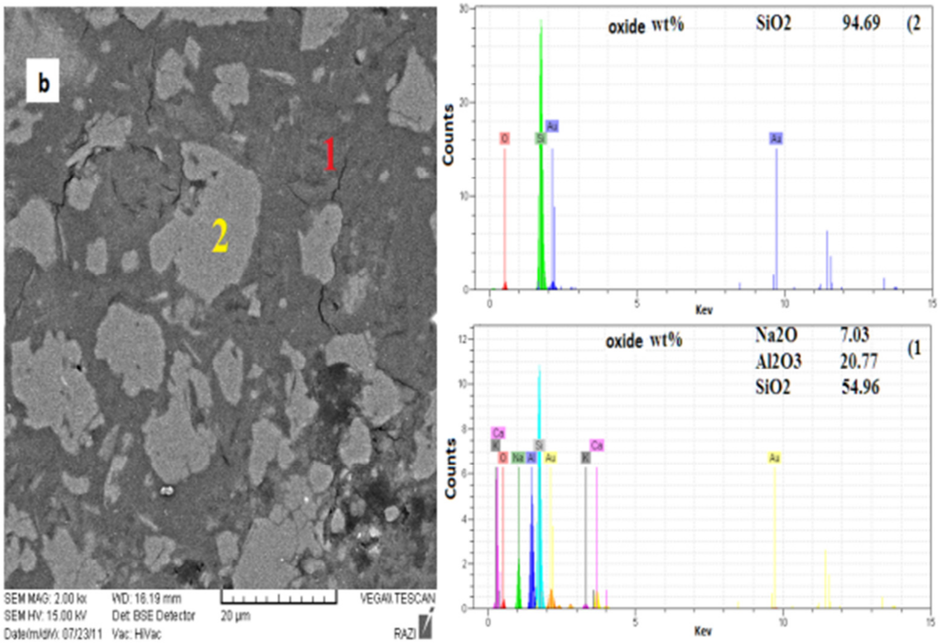


Fig.4. SEM micrograph of the samples a) 28 S 6 -50 and b) 7 S 6 -50 with EDAX analysis (magnification: 2000)

It seems that with the passage of time some SiO_2 particles of quartz phase have been dissolved and entered the primary phase (geopolymer matrix) which will make the secondary quartz phase smaller. After 21 days, morphology changes and a continuous phase is obtained; as a result the sample aged 28 days has more compressive strength compared to the sample aged 7 days, which is in accordance with the obtained results.

Fig 5 shows SEM micrograph of the matrix phase (geopolymer matrix) of geopolymer samples constructed by ZS metakaolin with 7 and 28 days of curing age. As can be seen, in these samples geopolymer phase is well formed. Fig 5(a) is related to the sample 28 S 6-50. As can be clearly observed, this sample has more continuity compared to the sample in fig 5 (b) and is expected to have the greatest compressive strength, which is in accordance with the obtained results.

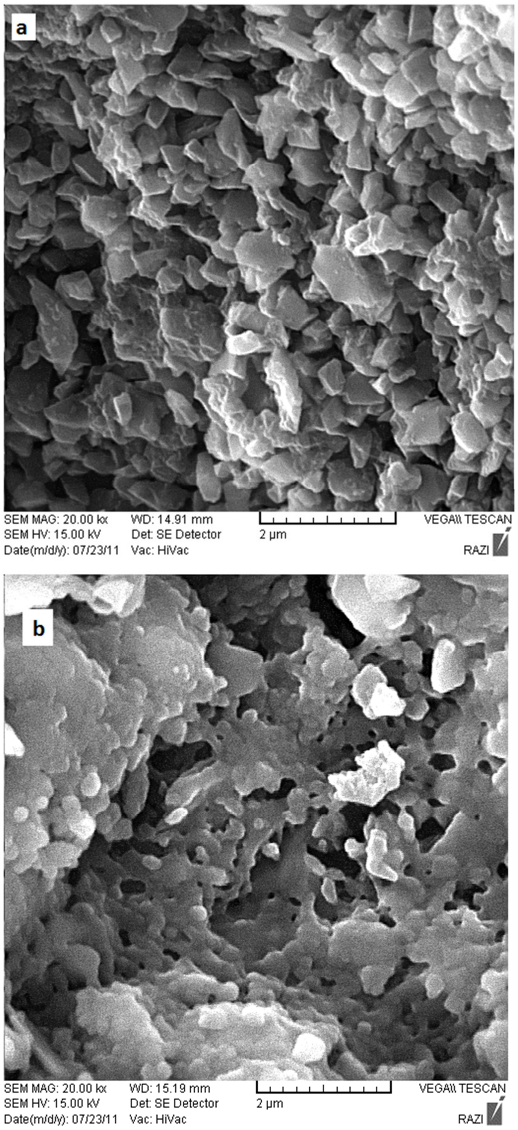


Fig.5. SEM image of microstructure of the geopolymer samples a) 28 S 6 -50 and b) 7 S 6 -50 (magnification: 20ĸx)

4- Conclusion

The results of the present study can be divided into two general categories, synthesis and analysis and identification of properties. Geopolymer samples were synthesized by mixing an amorphous aluminosilicate material and an alkaline silicate solution. The effect of curing temperature and molar ratio of Na_2O/SiO_2 on compressive strength was studied. Finally, the various properties of the obtained products were identified. These investigations included the study of crystallinity, chemical bonds and microstructure by using infrared spectrometer analysis (FTIR) and scanning electron microscopy (SEM). By inspecting FTIR spectrum after alkali activation it is revealed that with the shift of the major band with the change in the wavenumber a new product has been generated and alterations in the chemical environment of the bond as well as in microstructure compared to metakolin are resulted. SEM observations revealed that a continuous phase has been resulted from geopolymerisation process. Of course, some particles from the starting precursor which have not participated in the reaction are observed in geopolymer micrograph.

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