Synthesis and microstructural properties of a geopolymer cement with high silica materials

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Activities conducted in this study can be divided into two general sections: synthesis and analysis and identifies the properties. A geopolymeric cement production process includes two steps of thermal activation and alkaline activation. Geopolymers are cementitious materials synthesized by a polycondensation reaction between an aluminate and silicate. The geopolymeric structures of the products were investigated by Fourier transform infrared spectroscopy (FTIR), X-ray powder diffraction (XRD) and scanning electron microscopy (SEM). XRD results showed that there are no significant differences between the XRD patterns of geopolymers and metakaolin. The structure of the geopolymer is typically an amorphous phase lacking periodically repeated atomic ordering. By studying the FTIR spectra after alkali activation, shifting the main band by changing the wave number causes a new product formation and changes in the environmental chemical bonding and also results in microstructural changes towards metakaolin. SEM results showed that the integrated phase is obtained as a result of a geopolymerization process. An increase in the curing time changes the morphology and a more integrated phase is obtained, thus the strength increases.

Key words: Geopolymer, Metakaolinite, Compressive strength, Microstructure.

Introduction

In 1978, Davidovits created the term "geopolymer", to characterize new materials with the ability to transform, polycondense and adopt a shape rapidly at low temperatures similar to "polymers" [1]. Usually, a geopolymer can be synthesized at ambient temperature or slightly above, by activating an aluminosilicate using an activator composed of aqueous hydroxide and a silicate. It is a colloid reaction with a low water content in the system. The aluminosilicate used in the reaction is mostly in solid powder form while the activator can be easily constituted by a NaOH or KOH solution and a sodium silicate solution or potassium silicate solution [2].

The polymerisation process involves a chemical reaction under highly alkaline conditions on Al–Si minerals yielding polymeric Si–O–Al–O bonds with the empirical formula $M_n [-(Si-O_2)_z-Al-O]_n \cdot wH_2O$, where n is the degree of polymerization, z is 1, 2 or 3, and M is an alkali cation, such as potassium or sodium [3].

The polymerisation reaction is a geosynthesis which involves a naturally occurring silico-aluminate mineral such as kaolin or metakaolin and an activation solution [4]. The synthesis is similar to organic condensation polymerisation [5, 6, 7]. A wide range of applications have been proposed for geo-polymers because they can have similar properties to Portland cement such as high flowability, fast setting, high strength, and fire and blast resistance [8].

Experimental Procedures

The most common substances used in geopolymer cements are kaolin. Geopolymers of metakaolin and sodium silicate were synthesized. The chemical compositions of these materials gathered from different sources, on which laboratory tests were conducted on geopolymer specimens, are presented below (Table 1).

Kaolin used in this study was subject to a thermal treatment at 800 °C for 5 h, in order to achieve the dehydroxylated state.

In this investigation the mortar was a mixture of metakaolin, sodium hydroxide, alkaline silicate solution and water. The paste mixture was cast into $50 \times 50 \times 50$ mm^3 cubic-shaped moulds, vibrated for compaction and sealed with a lid to minimize any loss of evaporable water. Then samples were cured at 75 °C for 6 h and then they were placed without any mold at ambient temperature for 7 and 28 days.

The geopolymeric structures of the products were

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Table 1. Chemical composition (%)

Constituents	(%)
SiO_2	73.5
Al_2O_3	15.5
Fe_2O_3	0.5
MgO	0.25
Na_2O	0.2
K_2O	02
TiO_2	0.04
CaO	2-3
LOI*	7

* Loss on ignition.

Table. 2. Compressive strength of geopolymers synthesized by kaolinite.

Geopolymer	Curing Temperature (°C)	Curing time (days)	Compressive strength (MPa)
G_1	75	7	34
G_2	75	28	52

investigated by Fourier transform infrared spectroscopy (FTIR), X-ray powder diffraction (XRD) and scanning electron microscopy (SEM).

Results and Discussions

As shown in Table. 2. an increase in curing time from 7 to 28 days, make compressive strength increase of the sample.

Samples with a curing time of 28 days have the highest value of compressive strength. In this study, a small sample of the powder products was scraped off the surface of the hardened paste to conduct the XRD test. In addition, XRD of kaolinite and metakaolin was also carried out to serve as reference samples Fig. 1.

XRD patterns of the geopolymer samples are shown in Fig. 1. Several sharp characteristic peaks can be seen in Fig. 1. According to the XRD-pattern, these peaks were identified as kaolin and quartz.

The main phases of the geopolymer are $CaCO_3$ and quartz, which partially provides SiO_2 for the geopolymerization reaction. In respect of the X-ray diffractogram of metakaolin, kaolin and quartzes are induced by metakaolin, and in the process of geopolysisation, the kaolin and quartzes do not take part in the reaction. With respect to the X-ray diffractogram of metakaolin, quartz is an impurity in the metakaolin.

For that type of structural change XRD analysis is not appropriate, so these changes are currently assessed by infrared emission spectra analysis (FTIR).

Fig. 2. Shows the IR spectra of the raw material
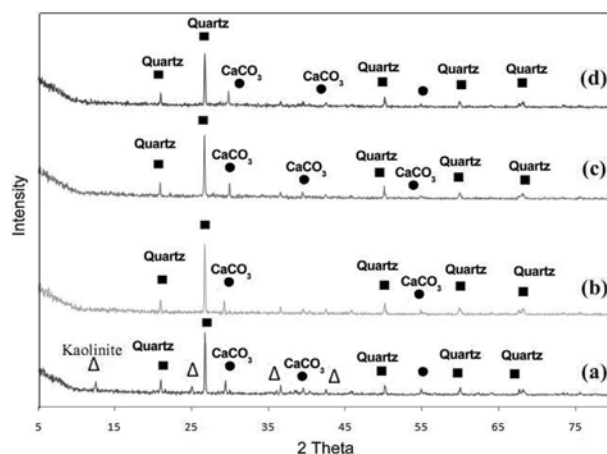
Fig. 1. X-ray diffraction pattern, a) kaolin powder, b) metakaolin powder, c, d) G_1 and G_2 geopolymeric samples
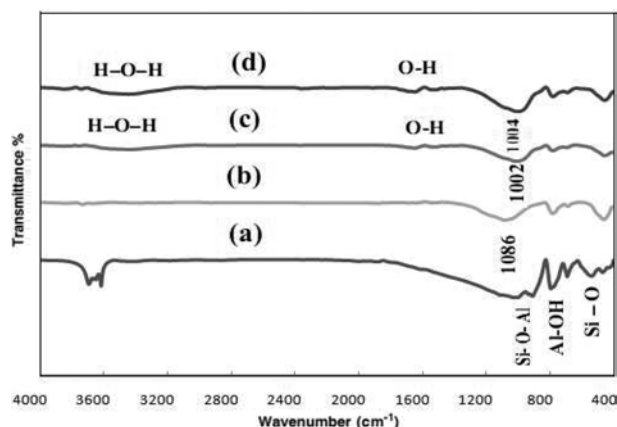
Fig. 2. FTIR spectra, a) kaolin, b) metakaolin obtained from the calcinations of primary kaolin, c, d) geopolymeric samples obtained by alkaline activation of the G_1, G_2

kaolinite and metakaolinite and the corresponding geopolymer.

The broad adsorption bands on the IR spectrum of the metakaolinite around 1086, 826, and 469 cm^{-1} are assigned to the Si-O stretching vibration, Si-O-Al vibration, and exural vibration, respectively. The most characteristic FTIR band in the geopolymeric systems appears in the wavenumber region 990-1090 cm^{-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 lengths in relation to the ones of the raw material. The strong band at 1086 cm^{-1} shifted towards the low wavenumber after the geopolymerization reaction. The chemical shift is approximately 84 cm^{-1}. This demonstrates that an obvious change in the microstructure takes place during the hydration reaction, resulting in the formation of new products with a different microstructure from metakaolin. The 1086 cm^{-1} peak is caused by symmetrical vibration of
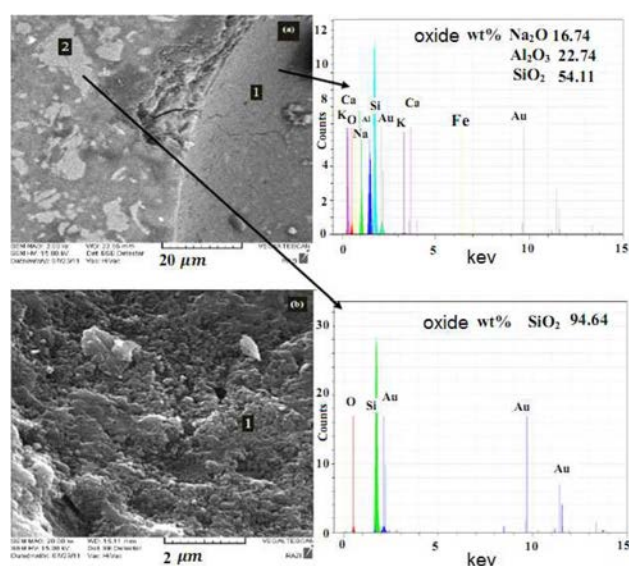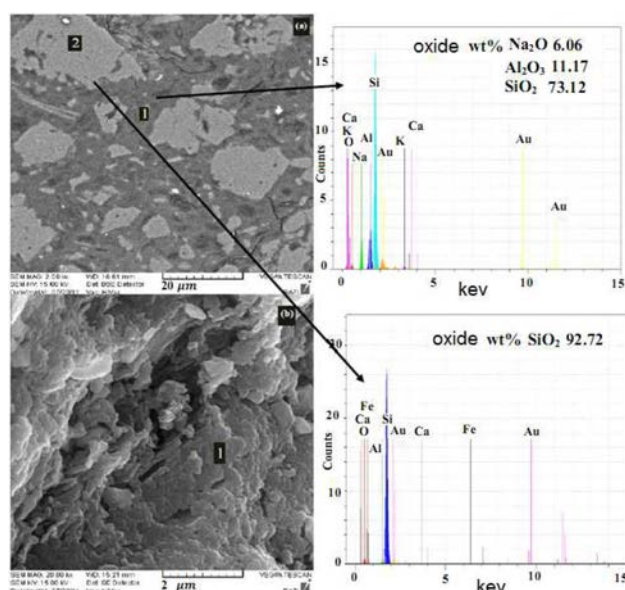
Fig. 3. a) SEM image of microstructure and G_2 sample EDS. SEM image of G_2, with zone 1 showing no reaction with quartz particles and zone 2 showing the geopolymeric matrix, b) SEM image of the microstructure of one at a higher magnification.

Fig. 4. a) SEM image of the microstructure and G_1 sample EDS. SEM image of G_1, with zone 1 showing no reaction with quartz particles and zone 2 showing the geopolymeric matrix, b) SEM image of the microstructure of zone 1 with a higher magnification.

the Si–O bond.

The large shift towards the low wavenumber may be attributed to the partial replacement of SiO_4 tetrahedral by AlO_4 tetrahedral, resulting in a change in the local chemical environment of the Si–O bond. The broad bands in the region of 1652–3445 cm^{-1} characterized the spectrum of stretching and deformation vibrations of OH and H–O–H groups from the weakly bound water molecules which were adsorbed on the surface or trapped in the large cavities between the rings of geopolymeric products.

For the microstructural investigation and elemental analysis, some high strength samples were chosen and as shown in Fig. 3 the study was conducted by a scanning electron microscope (SEM). As seen, despite having a similar FTIR and XRD spectrum, the SEM images show that the have different microstructures. Generally geopolymeric cements are composite materials that are formed from a gel phase field that did not react with the crystalline phases. This crystalline phase can arise from impurities in the raw materials or in the process of recrystallization. As seen clearly these samples were formed by two different individual and different phases that in the SEM images are different from each other due to the different contrast. Phase 1: a geopolymeric matrix and phase 2: where there was no reaction with quartz particles (sharp peaks observed in the XRD spectrum can be attributed to the existence of these particles).

Fig. 3-a and 4-a show the low magnification image of the microstructure of samples of G_2 and G_1 Metakaolin at 75 °C for 7 and 28 day was used as a curing process. As seen in these two figures two separate phases have formed a gel and a phase without a reaction.

Are seen G_1, G_2 samples are composed of geopolymeric phase. It can be easily seen in Fig. 3-b (with respect to Fig. 4-b), that it has more Integration and less porosity. So it should have the highest compressive strength and this is compatible with the results. But with this difference in 7 day samples, phase 2 was constructed from large particles and is make in terms of volume and weight. It seems that over time some of SiO_2 particles were dissolved in the quartz phases and enter the initial phase (geopolymer) that causes it to become smaller in second phase quartz. For the 28 day sample the morphology has changed and an integrated phase is obtained. Sample G_2 has 94.2% SiO_2. In this image according to the compressive strength results of other samples, it seems that quartz particles play a filler role and cause an improvement in the compressive strength.

Conclusions

The following conclusions can be drawn from this study:

1. An increase in curing time from 7 to 28 days, increase the strength of samples. Samples with a curing time of 28 days have the highest value of the compressive strength.

2. Peaks observed in the XRD patterns are associated with quartz. This phase played the role as a filler. In this case, the amount of free crystalline silica in the structure can have an effect on the mechanical properties.

3. In the FTIR spectra a change in the position of the most important bonding peak of AI-O-Si in the spectra of samples towards the position of this peak in the

metakaolin spectrum occurs (A shift to smaller wave numbers) indicates the formation of a geopolymer gel.

4. SEM results showed by increasing the curing time, unreacted phase (quartz) became smaller, the morphology changes and a more integrated phase occurred and thus the strength increased.

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