

20th International Congress of Chemical and Process Engineering CHISA 2012
25 – 29 August 2012, Prague, Czech Republic

An experimental study on the mechanical and microstructural properties of geopolymers

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Abstract

Geopolymer is a new class of inorganic polymer synthesized by activation of an aluminosilicate source with an alkaline hydroxide or silicate solution. In recent years, geopolymeric materials have attracted much more attention because of their excellent mechanical properties, good chemical resistance, low shrinkage, environmentally friendly nature and long-term durability. Fly ash, considered to be a waste substance is an important aluminosilicate source material for geopolymer production since it contains sufficient amounts of reactive alumina and silica.

In this experimental study, F type fly ash was activated by 4M, 8M and 12M of sodium hydroxide and sodium silicate solutions and the effects of pH on the properties of geopolymeric samples were investigated. All the pastes were cured at 80°C for 15 hours. The compressive strength tests were carried out at the ages of 7 and 28 days. The samples aged 28 days were crushed and the degrees of reaction of all samples were determined. The microstructure of geopolymer samples were investigated by Scanning Electron Microscope(SEM)/ Energy Dispersive X-Ray(EDX) Spectrometer, X-ray diffractometry (XRD) and Fourier Transform Infrared Spectroscopy(FTIR) techniques. According to results, the compressive strength of samples increased as the molarity of sodium hydroxide increased. It was observed that the workability of the pastes was negatively affected by increase in molarity of sodium hydroxide.

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Keywords: Geopolymer; fly ash; characterisation

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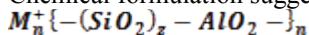
1. Introduction

As the industrialization grows in the world, the CO₂ emissions to atmosphere rise increasingly. Globally, the production of cement contributes at least 5-7% of CO₂ emissions. The greenhouse emissions of cement industry hence concrete and the impact of fly ash on the emissions have examined in many studies. Fly ash and other by-products have been discussed as supplementary cementitious material in cement and use for geopolymerisation. The studies showed that geopolymer concrete has a potential alternative to standard concrete [1].

Inorganic geopolymeric binders can be synthesized by alkali-activation of aluminosilicate source with an alkaline hydroxide and/or silicate solution. The aluminosilicate source can be industrial waste materials such as fly ash, blast furnace slag or natural materials such as mineral aggregates, natural rocks [2,3]. Geopolymers contains amorphous aluminosilicate gel consisting of three dimensional framework of SiO₄ and AlO₄ tetrahedra linked by O atoms. Alkali metal cations balance negative charge of the Al tetrahedral sites in the framework [3].

Geopolymers can be used in many fields due to their various properties like high compressive strength, low shrinkage, acid and fire resistance. Raw materials affect the chemical reactions during the synthesis hence the properties of geopolymers. Microstructure, physical, mechanical and chemical properties are also affected by the raw material type [4]. Another important factor affecting the geopolymerisation is alkali activating solution. NaOH is the most common activator affecting significantly the compressive strength and the structure of geopolymers [5]. Alkalinity affects the dissolution of raw material and the degree of polymerization. At the high concentrations of alkali activator, silicate species in the solution increases.

Chemical formulation suggested for geopolymers is:



where M⁺ is alkali cation, n degree of polymerization and z is the Si/Al ratio. Geopolymerization involves dissolution, reorientation and solidification reactions [6].

2. Methods

F-class fly ash, technical grade sodium hydroxide and sodium silicate were used for the geopolymer synthesis. In order to investigate the effect of pH on the mechanical and microstructural properties, 4M, 8M and 12M of sodium hydroxide solutions were prepared. NaOH solutions were prepared with distilled water and let cool down to room temperature. After cooling, sodium hydroxide added to sodium silicate and stirred 15 minutes to obtain homogeneity. The hydroxide-silicate mixture then added to fly ash and again stirred. Geopolymeric paste obtained after stirring poured to steel moulds. The pastes cured at 80°C for 15 hours. When curing completed, the pastes demoulded and aged for 7 and 28 days at atmospheric conditions.

For all specimens, compressive strength tests were carried out at the ages of 7 and 28 days. 28 days samples were crushed after compressive strength tests and degree of reaction determined with these samples. 3g of crushed samples added to 2M of HCl solution and stirred for 20 minutes at 60°C. After filtration samples were washed with distilled water and then acetone. The samples were dried at 70°C for 2 hours. Dried samples were added to 3% Na₂CO₃ solution and stirred for 20 minutes at 80°C [7]. Samples were again filtrated and dried at 70°C for 2 hours. Loss of ignition was determined with X-ray Fluorescence. The degree of reaction was calculated by mass difference as follows:

$$\text{Degree of reaction\%} = (m_{\text{sample}} - [m_{\text{residue}} (1 + LOI)]) / m_{\text{sample}} \times 100 \quad (1)$$

The microstructure of geopolymer samples obtained at different mediums also investigated with SEM/EDX, XRD techniques. FTIR Spectroscopy was used to investigate the bond structure of the pastes.

3. Results

The compressive strengths of geopolymers prepared by 4M, 8M and 12M of sodium hydroxide solutions are given in Fig.1.

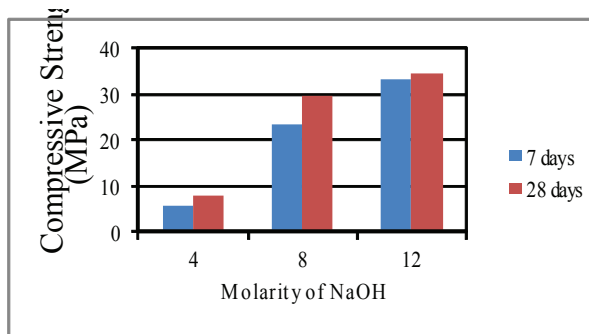


Fig. 1. The compressive strength values at 7 and 28 days

As it can be seen from the figure, the compressive strength increased with increasing molarity. When the molarity increased from 4 to 8, the compressive strength increased nearly 4 times. Results showed that for 7 days aged samples, the rise in compressive strength due to molarity was sharper than 28 days aged samples in the

interval of 8M to 12M. The maximum compressive strength was found to be 33.07 MPa at 7 days and 34.7 MPa at 28 days for the sample prepared with 12M NaOH. The results have also revealed that the effect of aging on the compressive strength was not remarkable.

The results showing the degree of reaction values of geopolymers are given in Fig.2. The loss of ignition was found as 1.6% by XRF.

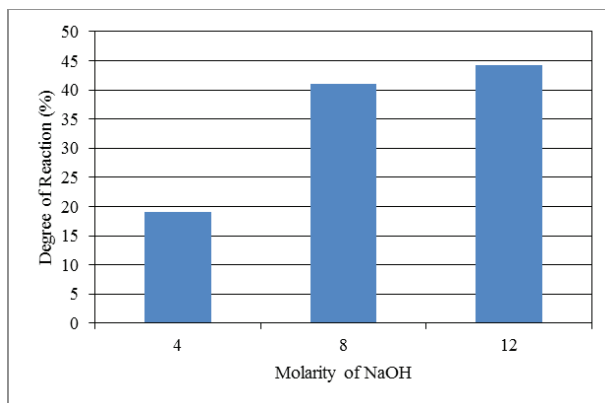


Fig. 2. The degree of reaction values of samples

The results have revealed the degree of reaction increased with increasing molarity. The degree of reaction values were determined as 19.13, 41.1 and 44.18 for the samples prepared by 4,8 and 12M of sodium hydroxide solutions respectively.

The SEM image for the geopolymer sample prepared by 12M of sodium hydroxide solution is given in Fig.3. The image shows that crystalline phases are clear and well formed, but still unreacted fly ash particles exist in the structure.

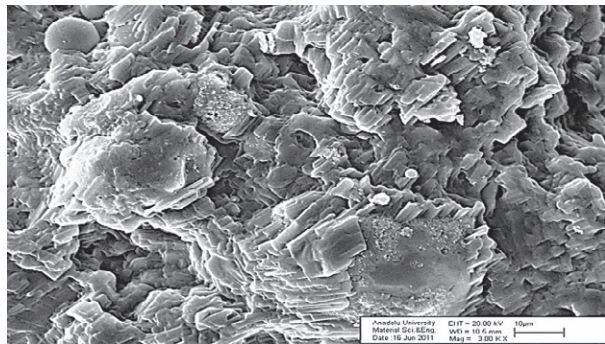


Fig.3. SEM micrograph for sample prepared with 12M

In Table 1, the EDX analysis is given. According to EDX, the crystalline phase substantially consists of aluminum, silicon, sodium and the rest are iron and potassium which are present in the fly ash.

Table 1. EDX analysis

Element	Weigth (%)
Aluminium	9,72
Silicon	11,50
Oxygen	58,72
Sodium	15,24
Iron	1,46
Potassium	3,36

The XRD diffractogram of the same sample is illustrated in Fig.4. Geopolymers exist a broad hump between $18-36^{\circ} 2\Theta$, which is the characteristic of amorphous geopolymers, in their patterns [6]. XRD result shows that the main geopolymeric structure consists of amorphous and crystalline phases. Quartz and mullite crystals were determined in the diffractogram. A hump between $15-34^{\circ} 2\Theta$ was observed in the diffractogram.

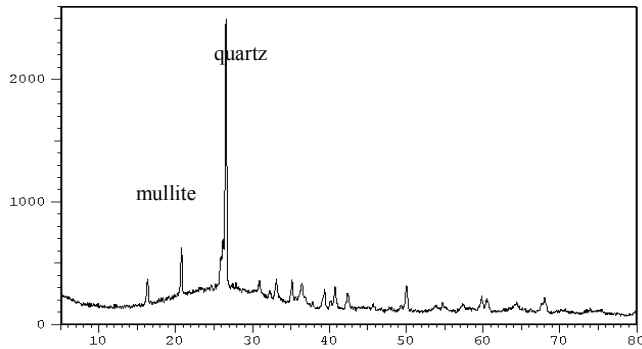


Fig. 4. The XRD diffractogram of sample prepared with 12M

Fig. 5 shows the FTIR spectrum of the geopolymer sample. The strong peak at $\sim 1000\text{cm}^{-1}$ is associated with Al-O and Si-O asymmetric stretching vibrations and is the fingerprint of the geopolymerisation [7]. The bands seen at 3593cm^{-1} is due to stretching vibration of -OH and at 1644cm^{-1} is due to bending vibrations of H-O-H. Atmospheric carbonation is evident at 1460cm^{-1} [8]. In the region of $775\text{-}650\text{cm}^{-1}$, the bands are attributed to symmetrical vibrations of tetrahedral groups. The band seen at 558cm^{-1} is due to double-ring linkage [9]. The peak at $\sim 460\text{cm}^{-1}$ is assigned to in-plane bending of Al-O and Si-O linkages [7].

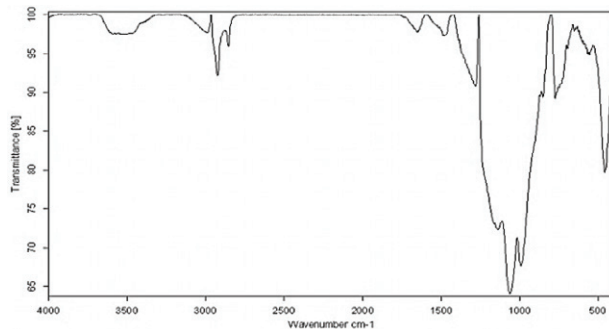


Fig. 5. FTIR spectrum of sample prepared with 12M

4. Discussions

In this study the effects of pH on the properties of geopolymers were investigated and it was found that both the compressive strength and the degree of reaction increased with increasing molarity of NaOH. The degree of reaction was not found to be significantly high. This can be attributed to the unseparated crystalline parts of the structure considered.

FTIR spectrum and XRD diffractogram have shown that that the geopolymeric structure was obtained successfully. The unreacted fly ash particles were seen in the SEM image. This can be attributed to the insufficient mixing and also curing conditions when preparing the geopolymer paste.

Acknowledgements

This experimental study was supported by the Anadolu University research project No: 080249. The ICP/OES analysis was carried out at AUBIBAM research centre.

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