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Leaching of F-type fly ash based geopolymers

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Abstract

Geopolymers are the synthetic analogues of natural zeolitic materials. Geopolymeric materials possess excellent mechanical properties, including fire and acid resistance. These properties make geopolymers an alternative construction material compared to Portland cement. Most waste materials such as fly ash, blast furnace slag and mine tailings contain sufficient amounts of reactive alumina and silica that can be used as source materials for in situ geopolymerisation reactions. Alkali-activation of aluminosilicate solids using alkaline hydroxide and/or silicate solutions can be used to synthesize inorganic geopolymeric binders or alkali-activated cements, displaying excellent physical and chemical properties. In this experimental study the effects of curing conditions on physical and mechanical properties and on the microstructure of geopolymer pastes were investigated. F class fly ash was activated by 12M sodium hydroxide and sodium silicate solutions. Geopolymer pastes were cured at 40°C, 80°C and 120°C for 6, 15 and 24 hours respectively. The samples were tested for compressive strength at the ages of 7, 28 and 90 days and the effect of aging was also investigated. After 28 days of curing, the samples were crushed and were extracted using leaching tests. USEPA TCLP (toxicity characteristic leaching procedure) method was applied for leaching tests. Inductively Coupled Plasma-Optical Emission Spectroscopy was used to determine the content of leach solution. For 28-days samples, microstructure of the samples were observed by X-ray diffractometry(XRD), Scanning Electron Microscope(SEM)/Energy Dispersive X-Ray(EDX) Spectrometer, and Fourier Transform Infrared Spectroscopy(FTIR) techniques. The results showed that the curing temperature and time are important parameters affecting the mechanical properties and microstructure of geopolymers.

Keywords: Geopolymer; fly ash; leaching

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1. Introduction

As energy demand increases worldwide, millions of tones fly ash is generated by power plants. Fly ash can be usedin some applicationsofcement and concrete industry. The rest of fly ash is disposed of[1,2].Although balanced disposal in landfills, there is always a risk to water sources due to heavy metals in the structure of fly ash [3]. Fly ashes obtained from coal combustion systems contain Ca, Fe, Na, K, Mg, Mn impurities [2]. Since strategies are developed to prevent environmental pollution, as a by-product fly ashes should be utilizedas valuable material[1].By geopolymer technology fly ash can be converted to a valuable material with contribution to environment [3].

Fly ashes generally includegreat extent of Al-Si glass phases and small amount of crystalline phases. Glass phases are commonly considered as major reactive components in the structure of fly ash [2].Due to high content of amorphous silica and alumina, fly ashes are suitable raw materials for geopolymers.When fly ash is mixed with alkali solution, alumina and silica dissolve to obtain precursors for reaction [4].

Geopolymers are generally used to describe the structures consist of a polymeric Si-O-Al framework. They are similar to synthetic zeolites but have amorphous microstructures. Geopolymerisation mechanism includes dissolution, migration and polymerization of Al and Si precursors. Soluble silicates can be added to increase the concentration of dissolved silicon species to fasten the polymerization [5].

Geopolymer technology can be used in various applications such as binders in solidification/stabilization systems which are highly effective methods for immobilization of waste materials including heavy metals. Fly ash based geopolymers are attractive systems due to their low-cost and feasibility. Besides immobilization, geopolymeric systems can be utilized to stabilize low level radioactive wastes [6].Geopolymer systems show similarities with cement binders used in encapsulation mechanisms which are considered to be either physical or chemical. Heavy metals are involved into the structure and balance the charge or remain physically bounded to surrounding network[5].

2. Methods

F-type fly ash was activated by sodium hydroxide and sodium silicate solutions. 12M of sodium hydroxide solution was prepared, cooled down and mixed with sodium silicate solution. Both sodium hydroxide pellets and sodium silicate were technical grade. The solution mixture were added to fly ash and mixed with mechanical stirrer for 15 minutes to obtain homogeneous paste. The paste then was cast into the steel moulds. To investigate the effect of curing conditions on physical and mechanical properties of geopolymers, pastes were cured at the temperatures of 40°C, 80°C and 120°C for 6, 15 and 24 hours.After 7, 28 and 90 days aging, compressive strength tests were carried out on the specimens. 28 days aged samples were crushed and were extracted in accordance with US EPA method.

According to US EPA method, the pH of acetic acid was adjusted to 4.93±0,05 before leaching experiments. The crushed samples and acetic acid solution were placed into beakers with liquid/solid ratio of 20 and extracted for 18 hours [7]. After filtration, Inductively Coupled Plasma-Optical Emission Spectroscopy was used to determine the content of leach solution.

The microstructure of the samples were obtained by X-ray diffractometry (XRD), Scanning Electron Microscope (SEM)/ Energy Dispersive X-Ray (EDX) Spectrometer, and the bond structure by Fourier Transform Infrared Spectroscopy(FTIR) techniques.

3. Results

The compressive strengths of the geopolymer pastes cured at the temperatures of 40°C, 80°C and 120°C for 6, 15 and 24 hours are given in Table 1.

Table 1. The compressive strength of the geopolymer pastes at the ages of 7, 28 and 90 days

Temperature (°C)	Duration (hour)	The compressive strength at 7 days (MPa)	The compressive strength at 28 days (MPa)	The compressive strength at 90 days (MPa)
40	6	4,45	21,18	31,82
40	15	7,71	23,51	30,89
40	24	6,97	22,20	23,27
80	6	18,52	28,82	36,89
80	15	33,22	34,92	41,23
80	24	30,66	37,47	47,29
120	6	20,09	33,24	25,33
120	15	39,72	33,74	37,66
120	24	33,60	51,45	36,95

The compressive strengths of 7 days aged samples are given in Fig.1.Test results have revealed that the compressive strengths of samples cured for 24 hours were lower than those of the samples cured for 15 hours. As the temperature increased the strength of geopolymers increased.

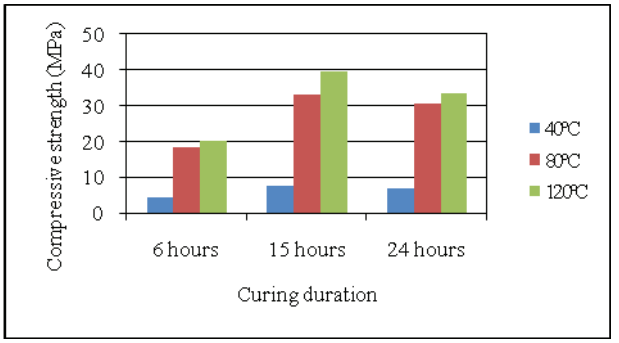

Fig. 1. The compressive strengths of samples at 7 days

The compressive strength of the samples at 28 days areindicated in Fig.2. According to the results, the strengths of the samples cured at 40°C increased as the curing duration increased from 6 hours to 15 hours, but at 24 hours the strengths of the specimens decreased. The compressive strengths of pastes cured at 80°C and 120°C for 6, 15 and 24 hours increased with increase in curing duration. Moreover, the strengths of the geopolimers increased with increase curing temperature. When the curing duration was 15 hours, the strength of paste decreased as the temperature increased from 80°C to 120°C.

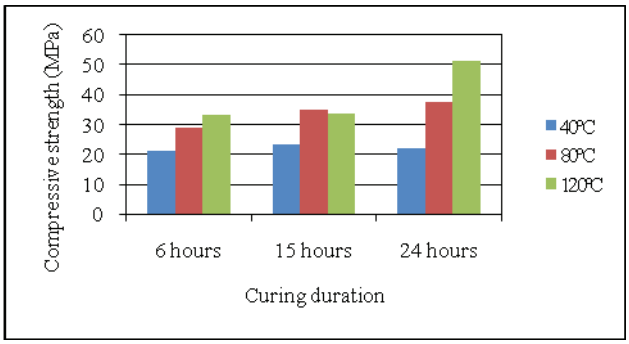

Fig. 2. The compressive strengths of the samples at 28 days

The compressive strengths of the samples at 90 days are given in Fig.3. After 90 days aging, for the samples cured at 40°C, the strength decreased with increasing curing duration. The compressive strengthsof specimens gradually increased with increase in curing duration for curing temperatures of 80°C. However,the maximum compressive strength was attained in 15 hours for the samples cured at 120°C.It was interesting that the compressive strengths decreased beyond 15 hours curing for all curing temperatures.

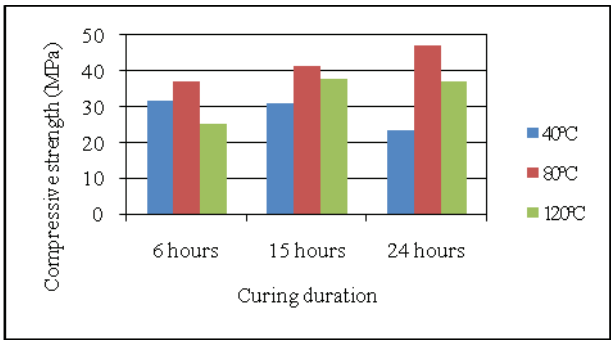

Fig. 3. The compressive strengths of the samples at 90 days

Generally the compressive strength of the geopolymers increased with aging, except for the samples cured at 120°C for 6 and 24 hours. The maximum compressive strength was obtained as 51.45 MPa at 120°C curing temperature and 24 hours curing duration for 28 days aged sample.

The amount of the heavy metal content in the leaching solutions of geopolymeric pastes, the fly ash which used as a source for geopolymerisation and US EPA Standards are given in Table 2.

Table 2. The amount of the heavy metal content in the leaching solutions

Temperature (°C)	Duration (hour)	As (ppb)	Hg (ppb)	Zn (ppb)	Pb (ppb)	Cr (ppb)	Cd (ppb)
40	6	<0.377	<3.096	<1.461	<8.065	9.855	<1.95
40	15	<0.377	<3.096	20.74	8.699	16.18	8.034
40	24	<0.377	<3.096	<1.461	<8.065	14.01	8.761
80	6	<0.377	<3.096	<1.461	<8.065	8.251	<1.95
80	15	<0.377	<3.096	35.39	<8.065	8.774	6.435
80	24	<0.377	<3.096	<1.461	10.69	22.88	<1.95
120	6	<0.377	<3.096	<1.461	<8.065	14.95	<1.95
120	15	58.86	47.42	17.14	<8.065	12.13	<1.95
120	24	191	177.6	<1.461	<8.065	10.84	<1.95
Fly ash		400	394.2	<1.461	<8.065	57.52	<1.95
US EPA Standards		0.005	0.0002	0.3	0.005	0.005	0.001

It is clear from Table 2, the heavy metal contents of the geopolymer samples were lower than those of the fly ash used in the synthesis. Especially arsenic and mercury were successfully immobilized in the geopolymeric network. The extracted solution of the samples cured at 120°C for 15 and 24 hours contained higher amounts of As and Hg than other samples did. It was interesting that Zn, Pb and Cd contents of the solutions obtained from some geopolymers were higher than those of the solutions of fly ash.

The XRD diffractogram of the sample cured at 120°C for 24 hours is illustrated in Fig.4. XRD result have shown that the main geopolymeric structure consisted of quartz and mullite crystals.

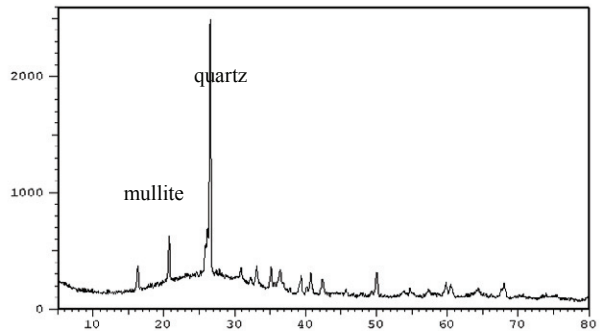

Fig. 4. The XRD diffractogram of sample cured at 120°C for 24 hours

Fig. 5 indicates the FTIR spectrum of the geopolymer sample. The strong peak at ~1000cm^{-1} is associated with Al-O and Si-O asymmetric stretching vibrations and is the fingerprint of the geopolymerisation[8]. The bands seen at 3593cm^{-1} and 1644cm^{-1} are stretching vibration of -OH and bending vibrations of H-O-H respectively. At 1460cm^{-1} atmospheric carbonation was observed [9]. In the region of 775-650cm^{-1}, the bands are attributed to symmetrical vibrations of tetrahedral groups and the band at 558cm^{-1} is due to double-ring linkage [10]. The peak at ~460cm^{-1} is assigned to in-plane bending of Al-O and Si-O linkages [8].

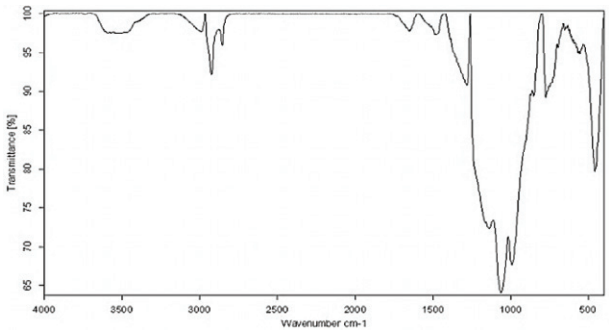

Fig. 5. FTIR spectrum of sample cured at 120°C for 24 hours

The SEM image for the same geopolymer sample is given in Fig.6. The image shows the gel phase and crystallsexisting in the structure.Moreover, some pores and spaces originated from reacted fly ash particles and unreacted fly ash particles were observed.

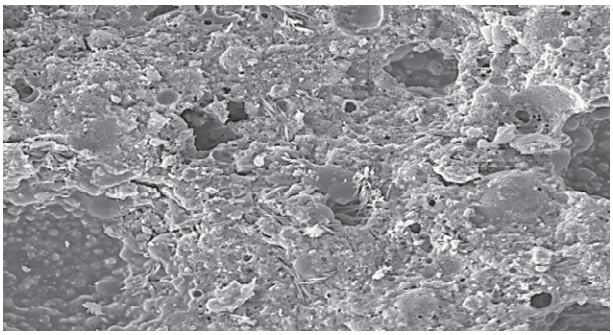

Fig. 6. SEM micrograph of sample cured at 120°C for 24 hours

EDX analysis of the gel phase is given in Table 3. It is clear that the gel phase contains high amount of SiO_2 as desired.

Table 3. EDX analysis of gel phase

Element	Weigth (%)
Aluminium	5.73
Silicon	39.73
Oxygen	51.44
Sodium	3.10

4. Discussions

The compressive strengths of geopolymersgenerally increased with aging. However it was interesting that the decreases in compressive strengths with aging were observed for some specimens. This can be attributed to the brittle structures of these specimens [11].

The leaching experiments showed that heavy metals like As and Hg immobilized in the structure effectively. The content of leachates obtained from some geopolymerswere higher than those of raw material due to contamination.

FTIR spectrum and XRD diffractogramindicated that the geopolymeric structureshavebeen achieved. In SEM micrograph some pores most probably due to long curing duration were observed. It was considered that water in the structure evaporated fast because of high curing temperature causing large pores.

Acknowledgement

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