Curing Time and Temperature Effect on the Resistance to Wet-Dry Cycles of Fly Ash Added Pumice Based Geopolymer

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Abstract

The effects of curing regimes varying combinations of temperatures (ambient, 60 °C, 75 °C, 90 °C, 105 °C) and durations (4h, 8h, 24h, 48h, 96h, 168h) on the performance of fly ash added pumice based geopolymer pastes were investigated in this study. The precursor raw material consists of 70% pumice dust and 30% fly ash (FA). Alkali activator was prepared by mixing 10M sodium hydroxide (SH) solution and liquid sodium silicate (SS) in the ratio of SS/SH=2. Activator to precursor ratio was fixed as 0.45. Compressive strengths were determined at the 28 days of age as well as after exposure 5 wetting-drying (w-d) cycles. In addition, Fourier Transform Infrared Spectroscopy (FTIR) tests were conducted on the fresh and hardened geopolymer pastes in order to examine the effect of curing conditions to the structural changes and reaction products. The results show that in the case of 60 °C and 75 °C, the strength of the w-d conditioned samples increased steadily as the curing time increased. However, longer curing times of more than 24 hours are not beneficial for high curing temperatures (90 °C and 105 °C). The maximum strength after the w-d cycles is obtained for the curing conditions of 60°C/168h (74.4 MPa). Also, FTIR analysis confirmed that the hardened geopolymer paste transformed into a more coordinated structure and soluble carbonate compounds were reduced at 60 °C and 168 hours curing condition.

1. Introduction

Portland cement (PC) is the most widely used binder material in the construction industry, and world cement production, which was 0.6 billion tons/year in 1970, increased to 4.1 billion tons/year in 2019. Most of cement production is carried out in developing countries, especially China. In 2019, China produced more than half of the world's cement production with 2.2 billion tons of production in 2019 [1]. A large amount of energy is consumed in Portland cement production, and the energy spent corresponds to two-thirds of the total energy use in the production of non-metallic minerals [2]. The energy usage in normal Portland cement production for the cement plant with an annual capacity of 1.6 million tons, which is located near limestone mines and uses dry processing technique for clinker production, is 4015 MJ/ton [3].

In terms of CO₂ emissions, cement production industry is a sector that has significant negative effects to environment. In other words, in Portland cement production, limestone (CaCO₃) is divided into CaO and CO₂ during the calcination process and CO₂ is released to the atmosphere. Relevant CO₂ emissions for clinker production are about 860 kg CO₂/ton [3]. Considering the emission caused by energy consumption during heating up to 1500 °C and grinding of raw materials, approximately equal amounts of CO₂ are released into the atmosphere for each batch of cement production [4].

Studies are underway to reduce the environmental negative effects of this energy-intensive production process of conventional cement. For example, Oral and Saygin (2019) evaluated six different strategies to reduce CO₂ emissions of the cement industry in their study [5]. One of the methods that reduce the environmental impacts of conventional concrete is to reduce the amount of cement used and thus the amount of energy consumed and emission values by utilizing waste products such as fly ash or slag replacement of cement. With this method, the amount of cement in the concrete mixture can be reduced by 50-60% [6]. The complete elimination of Portland cement in concrete production using alternative binders such as alkali active cement,

calcium sulfoaluminate cement, magnesium oxycarbonate cement (carbon negative cement), super sulphate cement and geopolymer binders is also being investigated [7].

The fact that geopolymer (GP) based concretes need less energy than conventional concretes reduces the carbon dioxide emission in production by up to 64% and can be more economical depending on the mixture proportions [6, 8]. In addition to being economic and environmentally friendly, physical and mechanical properties such as high early strength, low permeability, freeze-thaw resistance, resistance to chemical effects, superior fire resistance are the prominent features of geopolymer concrete [7, 9]. This type of binder has the potential to be applied in a wide variety of fields, from construction to the automobile industry, from medical applications to aircraft technology [10].

Geopolymers are three-dimensional aluminosilicate materials with ceramic-like properties that are produced and hardened at ambient or elevated curing temperatures. Geopolymerisation is a process of forming an amorphous or semi-crystalline polymeric structure consisting of silicate (Si-O-Al) and siloxo (Si-O-Si) bonds as a result of heterogeneous reactions of powder aluminosilicate oxides dissolved in high alkaline solution medium [11]. The inorganic polymer network consists of SiO₄ and AlO₄ tetrahedral structural units that are connected together by sharing oxygen atoms (Fig. 1). In order for a stable structure, negatively charged aluminum atoms must be balanced with proportionally positive ions such as Na⁺, K⁺ which come from alkali solution (Fig. 1) [12].

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Figure 1 Geopolymer structure of Davidovits Model [10]

Geopolymers can be obtained by activating powdered materials, such as fly ash, metakaolin, mine wastes, volcanic ashes having high levels of SiO_2 and Al_2O_3 with solutions of alkaline hydroxide (e.g. sodium hydroxide) and/or alkaline silicates (e.g. sodium silicate). Generally, the process of geopolymer forming is described in three stages [13]:

- (i) Dissolution of powder precursor materials in strong alkaline solution,
- (ii) Formation of Si and/or Si–Al oligomers in the aqueous phase,
- (iii) Polycondensation of the oligomeric units in the aqueous phase to form an inorganic polymeric material.

In order to utilize for inorganic polymer (geopolymer) production, raw materials should have mainly three properties; (i): amorphous or semi-crystalline molecular structure, (ii): high amount of reactive aluminosilicates and (iii) large specific surface area i.e. fineness. Fly ash and pulverized pumice are two materials that fulfill these conditions sufficiently. Fly ash which is a kind of industrial waste material captured in the chimney filters of coal-fired power plants is widely investigated for usage in geopolymer production and conventional concretes [14–16]. Pumice is an aluminosilicate type natural lightweight volcano rock which is similar molecular structure as fly ash. Therefore, powdered pumice can be activated in alkaline environment for inorganic polymer production [12].

Studies continue in the literature in order to determine the production conditions and mixture content required for a good geopolymerization for different precursor materials. Curing conditions also have a significant impact on the geopolymerization process. It is reported that the curing temperature (25–145 °C) and time (2–24h) highly effects the dissolution of precursor aluminosilica material independent of alkali metal solution molarity in the range of 8–16M. This situation is explained as increasing in the kinetic energy of the system at elevated temperatures and so the solvent molecules breaks the solute molecular bonds and hold an intermolecular attraction, more efficiently [17]. In order for geopolymer reactions to take place properly and to accelerate, initially enough amount with a suitable ratio of precursor material must be dissolved in the reaction medium. Muniz-Villarreal et al. (2011) stated in their study on geopolymer that the calorimetric curve peaks were very short at curing conditions lower than 50 °C, indicating dissolution and formation of hydroxy species and insufficient formation of oligomers [18]. Also, it is stated in some other literature that at least 65 °C curing temperature is required especially for volcanic rock based geopolymers [19–22]. Besides, at low temperatures, aluminate dissolves faster than silica. Therefore, if the curing temperature and time increases, the Si/Al ratio increases in the initial reaction environment. For fly ash as precursor material, the Si/Al mass ratio of the dissolved materials increased from initially 3.8 to 5.3 within 24 h when the dissolution temperature is 65 °C [17]. Further, dissolution type namely congruent or incongruent may be important for geopolymerisation process. In congruent type which is predominant for waste aluminosilicate materials such as fly ash, the generation of soluble aqueous monomeric species of Si and Al take place. The dissolution type of aluminosilicate minerals (e.g. pumice containing feldspars) is considered incongruent and causes predominantly oligomeric molecular units to be released into the composition [11]. In this case, adding liquid silicates (e.g. sodium silicate) to the mixture to

increase the proportion of dissolved silicate monomers in the starting medium is beneficial for stable geopolymerization [11]. The positive effect of heat treatment on the pumice based geopolymer is confirmed in the literature via experimental study for the temperature range of 25–85 °C [23]. For that study, the curing temperature of 65°C and 48 hours of duration gave the best results having compressive strengths up to 40 MPa at the age of 28 days. However, for another study, it has been stated that the effect of curing time of more than 24 hours on strength is negligible [7, 24].

In order to reveal the effect of curing time beyond 24 hours on geopolymer performance, it was investigated in an experimental study by applying a temperature cure between 60–105 °C for up to 168 hours, in this study. In addition, many geopolymer studies in the literature have focused on strength as a performance indicator. However, for a high strength geopolymer material, it is possible that the carbonated excess alkali metal cations (Na^+ , Ca^{++}) which are not balanced in the geopolymer reactions will be dissolve from the body in wet environment resulting in strength decrease and also effloresces [25]. Especially, durability against w-d cycles is an important parameter for the design of open air structures that are exposed to wetting-drying periods in service life such as concrete roads, drainage systems and hydraulic structures [26]. Therefore, in this study, the effects of curing regimes at varying temperature and time combinations on the properties of FA-pumice based geopolymer were investigated by performing compressive strength tests before and after w-d cycles. The results showed that curing treatment at 60 °C and 75 °C up to 168 hours increased the strength by almost twice compared to 24-hour heat curing time and approximately 13 times compared to ambient curing. The highest strength value (82.8 MPa) for dry conditions was obtained at curing temperature and time combination of 75°C/168h. However, the strength of this sample after wetting and drying decreased by 21% to 65.6 MPa. Although the sample cured at 60°C/168h had relatively lower strength (78.9 MPa) in dry conditions, it showed the best resistance to the effect of w-d cycles, and its strength decreased by only 6% to 74.4 MPa. Furthermore, it was confirmed by FTIR analysis that the geopolymerization reactions develop properly and the leachable carbonate compounds decrease at 60°C/168h curing condition.

2. Materials and Methods

2.1. Materials

2.1.1. Pumice

Pumice is a low density volcano sourced natural material where hollow pores are formed by the release of the gases in its body as it solidifies after the molten lava comes to the earth surface. Pumice is widely used as aggregate in lightweight concrete production especially in countries where it is available locally or easily imported [27]. Since it contains chemically high amount of silica + alumina ($\text{SiO}_2 + \text{Al}_2\text{O}_3 > 75\%$) and has an amorphous and semi crystalline structure as a result of sudden cooling, powdered pumice is possible to be used in the synthesis of inorganic aluminosilicate polymer (geopolymer). Depending on the chemical structure of the magma, pumice is formed as acidic (with a SiO_2 content of more than 66%), basic (with a SiO_2 content between 52–45%) or neutral (SiO_2 content between 66–52%) types [28]. The Ağrı mountain pumice used in the study has a neutral character and its chemical content is given in Table 1. Based on X-ray fluorescence (XRF) test results, the pumice has high amount of silicate and aluminate and the amount of SiO_2 is three times higher than Al_2O_3 . According to the XRD pattern determined using the Tongda TD-3500 X-ray diffractometer (XRD) device, its mineralogy has a semi-crystalline structure and the presence of Albite crystal ($\text{NaAlSi}_3\text{O}_8$), which is a sodium-weighted feldspar mineral. XRD patterns of pumice and FA are presented in Fig. 2. Pumice has been ground to a similar fineness level of fly ash to achieve sufficient activity and used 70% of the precursor raw material in geopolymer samples. The passing ratio of the ground pumice from the 45 μm sieve was determined as 84%.

Table 1. Chemical composition of pumice and fly ash (%mass)

	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	K ₂ O	Na ₂ O
P	57.60	18.95	4.82	5.20	3.32	-	-
FA	56.53	25.96	6.54	1.51	2.54	3.88	1.17

2.1.2 Fly ash (FA)

This fly ash used in this study were obtained from Thermal Power Plant Çatalağzı in Turkey. This plant causes environmental problems by releasing 2500 tons of fly ash per day. However, these ashes have a potential use in the construction industry with their chemical composition, suitable activity values and physical properties. Çatalağzı FA is classified as low lime fly ash (F type fly ash) class according to ASTM C 686 and as silico-aluminous fly ash class according to its chemical composition [29]. The chemical content of fly ash determined according to XRF spectrometry test results is presented in Table 1. This FA is a suitable material for geopolymer synthesis due to its high content of SiO₂ and Al₂O₃, amorphous structure and high fineness. For this study, FA was used as a source of alumina and silica in the production of geopolymer test samples at a rate of 30% in the precursor raw material.

Figure 2. XRD pattern of fly ash and pumice

Table 2. Sodium hydroxide and sodium silicate properties which was used in this study.

	SH (solid)	SS (liquid)
Molecular formula	NaOH	Na ₂ O.2SiO ₂
Molecular mass (g/mol)	40.01	182.15
Color	White	Gel (Colorless)
Density (g/cm ³)	2.13	1.39
Na ₂ O (%)	-	12.00
SiO ₂ (%)	-	24.50
H ₂ O (%)	-	63.50

2.1.3. Liquid alkaline activator

Sodium hydroxide (SH) in the form of solid flakes was dissolved in the de-ionized water in order to obtain 10 Molar NaOH solution. After 24 hours, the alkali activator was prepared by mixing sodium hydroxide solution and the liquid sodium silicate in the ratio of SS/SH=2. The properties of SH and SS which were used in this study are presented in Table 2. Liquid alkaline activator to precursor material ratio is fixed as 0.45 for this study.

2.1.4. Geopolymer paste preparation

FA-pumice based geopolymer pastes were prepared according to the designated ratios given in Table 3. In the geopolymer mixes, the molar water to Na ratio was 6.97. The total batch composition consisted of pumice: 48.28 wt%, fly ash: 20.69 wt%, solid sodium silicate: 7.55 wt%, solid sodium hydroxide 3.25 wt%, and total water: 20.23 wt% (coming from SS liquid and 10M SH solution). To produce the designed geopolymer pastes, solid SH particles were first added into de-ionized water and thus 10 Molar SH solution was prepared. After 24 hours, the SH solution and the liquid SS were mixed so that the liquid alkaline activator was prepared. After a further 24 hours, 70% by weight ground pumice and 30% fly ash powder was mixed for 8 minutes in a planetary mixer until it became homogeneous. 45% by weight of alkaline liquid was added to the prepared powder and mixed for an additional 8 minutes. The obtained paste was poured into cubic plastic molds of 20x20x20 mm³ size and then the samples were dropped 240 times over 2 cm above the drop table to allow trapped air to escape.

Table 3. Mix proportions and curing conditions.

SH (10M)	315 g
SS	630 g
FA	630 g
Pumice	1470 g
Curing temperature (°C)	Ambient, 60, 75, 90, 105
Curing duration (Hours)	4, 8, 24, 48, 96, 168
Performance tests	Comp. str. (28days), density, water absorption, comp. str. after 5w-d cycles, FTIR analysis

Subsequently the placed samples were covered with nylon film and put in laboratory ovens to stay at the temperature and time appropriate to the designated curing conditions given in Table 3. In the study total 25 different curing conditions which are the combinations of four different curing temperatures and six curing duration and one ambient curing were applied. At the end of the curing periods, the samples taken from the oven were removed from the molds and kept in the laboratory to complete the 28-day test age. Afterwards, performance tests were conducted.

2.2. Methods

2.2.1. Density and water absorption

In order to determine the water absorption and density of the geopolymers, the weight of three 28-day cube samples from each curing series was measured as (A). The three samples were then soaked in water for 24 hours and weighed in water as samples (B). Finally, the saturated weight was weighed in air (C). Water absorption values were calculated using the equation $\text{Water absorption (\%)} = ((C - A) / A) \times 100$, and densities were determined using the equation $\text{Density} = (A / (C - B))$. Mean values for densities and water absorption are reported in Table 4.

2.2.2. Compressive strength tests

The compressive strength values of geopolymer samples cured under 25 different curing conditions were measured on the 28th day by using 20x20x20 mm³ solid cubic specimens. The loading rate in the unconstrained compression test was 0.8 MPa per second. To evaluate the durability performance of geopolymers against wet environments, 28-day samples were conditioned with 5 w-d cycles. First, the samples were kept in water for 24 hours, and then these samples were taken from the water and kept at room temperature for 48 hours. This 72 hour (3 day) period is considered a w-d cycle. After 5 w-d cycles, samples were subjected to compression tests and their strengths were determined. Test results are given in Table 4 and are also graphically presented in Figure 3.

3. Results and Discussion

3.1. Strength test results

According to the compressive strength tests, ambient cured control samples give the lowest strength as 6.2 MPa at the age of 28d. Application of heat curing between 60–105 °C increased the compressive strength of the geopolymer mixes compared to the control sample. The reason is that the higher curing temperatures accelerates the dissolution of solid particles and improves the polymerization reaction of the precursors in the first geopolymerization of the system [17, 18]. However, as a result of the high temperatures acting for a long time, negative mechanisms can also act simultaneously and cause a decrease in strength [24, 30]. Therefore, each geopolymer system is expected to have its own optimum curing temperature and curing time. In this study, that optimum curing conditions of FA-pumice based geopolymer system was investigated. The effect of curing temperature/time combinations on the 28-day compressive strength of FA-pumice based geopolymer pastes is graphically presented in Fig. 3.

When the 28-day strength values in Fig. 3a are examined, it is seen that the strengths gradually increase as the curing time increases at 60 °C curing temperature. The strength value (78.9 MPa) in the curing condition of 60 °C/168 hours reached almost 13 times the strength of the control sample (6.2 MPa) which is cured at room temperature. Similar results reported in literature that longer curing time improves the polymerization process resulting in higher compressive strength for 60 °C curing temperature [31, 32].

Table 4. Mean values of densities, water absorptions, compressive strengths before and after w-d cycles.

Curing temp/time (°C/hrs)	Density (gr/cm ³)	Water absorption (%)	28d Comp. str. (MPa)	Comp. str. after w-d (MPa)
-	1.65	~*	6.2	0.0*
60/4	1.76	~*	25.3	0.0*
60/8	1.89	4.8	44.5	15.1
60/24	1.94	6.8	46.5	27.1
60/48	1.95	7.5	57.2	28.8
60/96	1.95	6.6	62.0	46.2
60/168	1.98	3.6	78.9	74.4
75/4	1.89	5.1	50.4	29.9
75/8	1.90	5.9	49.3	33.2
75/24	1.88	7.0	46.2	37.6
75/48	1.90	6.5	61.9	49.9
75/96	1.96	5.6	67.2	54.9
75/168	2.00	5.5	82.8	65.6
90/4	1.74	5.4	44.1	25.2
90/8	1.83	5.3	56.3	26.1
90/24	1.80	2.6	40.2	36.7
90/48	1.84	2.7	38.7	44.0
90/96	1.87	6.8	25.4	26.1
90/168	1.83	7.1	22.2	32.1
105/4	1.80	6.6	40.4	20.0
105/8	1.80	4.1	46.7	20.7
105/24	1.83	3.0	61.1	33.8
105/48	1.80	6.4	45.6	34.3
105/96	1.85	6.8	44.4	29.1
105/168	1.87	6.9	33.4	24.9

* Since these samples became too weak after being kept in water for 24 hours, their surface saturated weights could not be measured and therefore water absorption values could not be calculated. Also, these examples lost their strength after w-d cycles.

Among the 4 hour cured samples, the highest strength value (50.4 MPa) was reached at 75 °C. In case of temperature 75 °C, with curing

times longer than 4 hours, a slight decrease in strength occurs and then the strength continues to increase with curing times longer than 24 hours. At 75 °C, the highest strength value among all samples (82.8 MPa) was obtained in 168-hour samples, which is the longest curing time.

At curing temperatures higher than 75 °C, the strengths appear to generally decrease especially beyond the 24 hours curing times. In the case of 90 °C, the maximum strength (56.3 MPa) was achieved in 8 hours curing time and in the case of 105 °C, the maximum strength (61.1 MPa) was achieved in the 24 hours curing time. Longer exposure beyond these times for these high temperatures, caused a gradual decrease in strength. The decrease in strength beyond 75 °C temperatures can be explained in two ways. While high temperatures accelerate the geopolymer reactions, the time required for dissolution decreases, consequently, it prevents the breakage of the precursor solid materials and the formation of oligomer and alumina/silica-hydroxy species in sufficient amount in the liquid phase [18]. In addition, due to the high curing temperature and the rapid exothermic reactions, the water quickly discharged from the prematurely hardened body causes shrinkage and a low-strength microstructure containing voids and cracks [22, 30].

Figure 3. The effect of the curing temperature and time on the compressive strengths before w-d cycles (a) and after w-d cycles (b).

In the case of 90 °C and 105 °C, this negative effect continues to increase as the temperature curing time extends, in parallel liquid silicates harden as a result of drying without taking part in geopolymer reactions. Instead of the beneficial effect of longer temperature curing, liquid environment and molar balance are disrupted, a harmful situation becomes a matter. When these results

are evaluated, it can be said that taking measures (such as steam cure and insulation) to keep the water in the body in case of high temperature and long-term curing will make a positive contribution [32].

Drying and solidification of liquid silicates and carbonation of non-balanced alkali cations in high temperature and long-term curing condition contributes to strength in dry environment. However, this is undesirable and in this case, a poor quality geopolymer paste with low durability and low resistance to water influence is produced. For this reason, with the effect of silicate and carbonates leached by water, there are significant decreases in strength after w-d cycles (Fig. 3b). Unlike the others, the strengths of the 90°C/48h and 90°C/168h samples increased slightly after the wet-drying effect. This can be explained by the fact that the water entering the pores of the samples during the 5 w-d cycle lasting 15 days in total transforms the solution medium inside cracks and pores into a state where geopolymer reactions can resume and continue. Later, new reaction products are formed in the pores and this provides strength gain. However, the strength gain is not linear, as the detrimental effects caused by w-d cycles such as expansion-contraction and leaching of soluble compounds take place simultaneously alongside these beneficial reactions.

3.2. Durability performance against wetting and drying effects

During their service life, most engineering structures such as concrete pavements and water structures are often exposed to environmental influences such as wetting and drying. For this reason, it is important to examine the resistances of the concretes used in such structures to the w-d effects in order to represent their behavior under service conditions. In this study, 28 days after the geopolymer pastes production, all the samples subjected to 5 w-d cycles and then their compressive strengths were determined.

Compressive strengths of the w-d conditioned samples are presented in Fig. 3b. As can be seen from the figure, ambient cured control sample completely lost its strength after w-d cycles. Similarly, the sample which cured at 60 °C for 4 hours lost its strength of 25.3 MPa after w-d cycles. This situation shows that geopolymerization is not achieved at a sufficient level in case of no or inadequate heat curing. When temperatures are low that silicate and aluminates in the precursor raw materials (FA and pumice) cannot be dissolved in sufficient quantity and at appropriate ratios and that the reactions required for geopolymerization cannot occur in a sufficient level. Especially at low temperatures, silicates are dissolved later and to a lesser extent than aluminates, so the resulting geopolymer products have undesirable low Si/Al ratio. It is reported that the formation of a solution medium containing silicate and aluminate monomers necessary for a good geopolymer synthesis can be achieved by increasing the curing temperature and time [17]. Otherwise, high amount of positive ions (Na^+ , K^+ etc.) coming from the alkali solution cannot be compensated by relatively few negative charge of AlO_4^- in the geopolymer network according to the Davidovits Model (Fig.1) [33].

Excess geopolymer phase-out substances in the medium prevent the development of a close and tight geopolymer structure. Unbalanced cations (Na^+ , K^+ , Ca^{++} etc.) causing carbonation compounds and unreacted soluble silicates present in the gel phase can leach by the water effect, causing the decrease in strength of the geopolymer paste. If the polymerization has not been at a level to maintain its volumetric stability, the geopolymer structure is completely destroyed after the water effect. Other samples had a good resistance against the w-d cycles. In the case of 60 °C and 75 °C, as the curing time increased, the strengths of the w-d conditioned samples increased steadily (Fig. 3b). Among all the geopolymer pastes, the maximum strength after the w-d cycles is obtained as 74.4 MPa for the conditions of 60°C/168h. The results show that curing condition of 168 hours at 60 °C is the best for FA-pumice based geopolymer paste synthesis. However, in the case of 90°C and 105°C, the increase of the curing time up to 48 hours increased the strength and decreased the strength for prolonged curing beyond 48 hours (Fig. 3b).

3.3. Fourier Transform Infrared Spectroscopy (FTIR)

FTIR tests were conducted, in order to examine the effect of curing temperature and duration combinations to the structural changes and reaction products of FA-pumice based geopolymer pastes. Agilent Cary 630 model spectrometer device ($650\text{--}4000\text{ cm}^{-1}$) was used for FTIR analysis. FTIR spectroscopy results is presented in the graphical form of transmittance vs wavenumber. In Fig. 4, the spectra lines of fresh geopolymer paste, control sample, heat cured samples at 60°C, 75°C, 90°C and 105°C for 96 hours are presented. The broad and intense peaks in 3319 and 1638 for fresh geopolymer paste show the H-OH bending and -OH symmetric and asymmetric stretching functional groups. This bands are attributed to the water and possibly -OH groups in the oligomeric solute species given in Fig. 6 [10, 34, 35].

Figure 4 Changes in FTIR spectra due to the increase in curing temperature

Figure 5 Changes in FTIR spectra due to the increase in curing time

Figure 6 Possible oligomeric solute species in fresh geopolymer paste [10, 35]

As a result of exothermic geopolymerization reactions, which are schematized in Fig.7, these functional groups turn into new products and the released water evaporates away from the body [10]. This material in paste form turns into a more coordinated hardened geopolymer structure similar to the model in Fig. 1 with the continuation of the reactions over time. Therefore, the peaks of these functional groups (H-OH and -OH) seen in the fresh paste have almost completely disappeared in the hardened geopolymers.

Figure 7 Exothermic geopolymerization reaction mechanism for sialate and sialate-siloxo species, described by Davidovits [10].

The shoulder band located at 867 cm^{-1} shows the vibration mode of the Al-O bonds in the geopolymer reaction products involved AlO_4^- groups [36]. In the FTIR graphs (Fig. 4) where the effect of temperature increase is examined, this shoulder started to disappear as the temperature increased up towards 75°C and appeared again beyond this curing temperature level towards 105°C . The changes around the shoulder band at 867 cm^{-1} shows the geopolymerisation level and it is compatible with the changes in strength values after wetting and drying. The disappearance of the shoulder in this band indicates that the geopolymerization is of good quality and a high strength material has been formed. As a matter of fact, the strength value after w-d cycles for $75^\circ\text{C}/96\text{h}$ curing condition, where this peak disappears, is the highest among 96 hour cured samples.

In order to examine the effect of curing time on geopolymerization at 60 °C curing condition, which exhibits the highest strength value after w-d cycles, FTIR analysis of samples produced with increasing curing times was executed and presented in Fig.5. In FTIR spectra, sharp small peaks around the 1450 cm⁻¹ band show O-C-O anti asymmetric stretching vibration attributed to sodium carbonate (Na₂CO₃) formed by atmospheric carbonation [36]. Fig. 5 shows that as the curing time increases for 60 °C, the intensity of these bands showing the carbonation decreases. This reduction of carbonation can be explained by the neutralization of Na⁺ and Ca⁺⁺ cations by negatively charged AlO₄⁻ groups in the geopolymer space network (Fig. 1), which are highly developed in the cured pastes at the appropriate temperature and time as at 60°C/168h.

Fresh paste and hardened geopolymer samples show a wide and intense peak in the range of 900-1300 cm^{-1} . This band is an important fingerprint of geopolymer materials and shows Si-O-T (T: Si, Al Tetrahedral) the asymmetric stretching functional group [37]. Unlike fresh paste, it is seen that the intensity at this peak value is less for hardened samples. This situation can be interpreted as the dissolved silicates and aluminates in monomer and oligomeric forms in the fresh paste are included in the space network structure by establishing new bonds with geopolymerization reactions, thus the peak intensity decreases. In addition, with the increase of geopolymerization in hot cured samples, the location of this peak has shifted towards a larger wavelength. While the band location in fresh paste is at 963 cm^{-1} , the increase in the wavelength (987 cm^{-1} for 90°C/96h) of the peak location in the samples treated with heat curing indicates that the coordination in the SiO^{n} structure increased and more polymerized Q^3 and Q^4 structured units were formed. In case of increasing curing time further, the wavelength of the peak of this band decreased a little (981 cm^{-1} for 60°C/168h) and also Al-O related shoulder band of 867 cm^{-1} is disappeared. This situation shows that the tetrahedral AlO_4^- units are more involved in the geopolymer network and polymerization progresses, thus forming a stronger and more stable structure resistant to water influence and carbonation.

4. Conclusions

FTIR spectra, compressive strengths and the resistance to w-d cycles of FA-pumice based geopolymers which is produced varying curing temperatures and times were examined in this study and the following conclusions were reached according to the test results.

High compressive strength in dry conditions does not guarantee the production of a quality geopolymer material. However, the compressive strength value measured after the wetting and drying periods is an important indicator of the geopolymerization level.

FTIR analysis is suitable method to evaluate the quality of geopolymerization and resistance to water impact. There is agreement between FTIR spectra and strength values after w-d cycles.

Ambient curing (about 22 °C) was insufficient for the synthesis of FA-pumice based geopolymers with satisfactory strength and durability. Ambient cured control samples give the lowest strength and totally lost its strength after w-d cycles.

The curing of 75°C/4h has been evaluated as a suitable condition for prefabricated production of materials to be used in dry conditions due to its short curing time with low energy consumption and sufficient strength.

Increased curing time up to 168 hours for medium temperatures (60 °C and 75 °C) improves performance, provided that the samples were sealed. However prolonged cure times beyond 24 hours is not beneficial for the high curing temperatures (90 °C and 105 °C). The optimum curing time at which the best performance achieved is depending on the curing temperature value.

FA-pumice based geopolymer concrete can be a suitable material for the production of prefabricated paving stones and drainage system elements required for concrete road constructions.

Declaration of Conflict of Interests

The author(s) declare(s) that there is no conflict of interest.

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