Journal of Building Engineering 35 (2021) 102023

Contents lists available at ScienceDirect

Journal of Building Engineering

journal homepage: http://www.elsevier.com/locate/jobe

A new parameter influencing the reaction kinetics and properties of fly ash based geopolymers: A pre-rest period before heat curing

Ugur Durak [a,*], Serhan İlkentapar [a], Okan Karahan [a], Burak Uzal [b], Cengiz Duran Atiş [a]

[a] *Erciyes University, Civil Engineering Department, Kayseri, Turkey*
[b] *Abdullah Gul University, Civil Engineering Department, Kayseri, Turkey*

ARTICLE INFO

Keywords:
Sodium hydroxide
Fly ash
Geopolymer
Pre-rest period before heat curing
Microstructure

ABSTRACT

In this study, the influence of a pre-rest period before heat curing (as a new parameter), on the physical properties, flexural and compressive strength, and microstructure of geopolymer mortars and pastes produced with alkali activation of fly ash were investigated. In this context, geopolymer mortar and paste samples were prepared and pre-rested under laboratory conditions for 0, 1, 2, 3, 7, 14, and 28 days before heat curing. After the pre-rest period, the samples were subjected to heat curing at 75 °C in an oven, for 2 days. Mortar and paste samples exposed to a pre-rest period while in the fresh state before heat curing were compared with control samples without pre-resting. Water absorption, porosity, specific gravity, capillarity, flexural strength, compressive strength, and abrasion resistance tests were conducted on the geopolymer mortar samples. A reaction kinetics study using an isothermal calorimeter, XRD, and SEM analyses were performed on the geopolymer paste samples for microstructural investigations. Based on the results obtained, it was observed that the mechanical strength of the samples subjected to the pre-rest period before heat curing increased considerably compared to the reference (without pre-resting) samples. In addition, because of pre-resting, the capillarity coefficient, water permeability, and porosity of the samples decreased compared to the reference samples, and it was concluded that pre-resting improves durability-related properties. Moreover, the reaction kinetics and SEM analysis results, supporting the above findings, showed that a pre-resting period increases the geopolymeric reaction products and causes a denser microstructure.

1. Introduction

The term geopolymer was first introduced by Joseph Davidovits in the 1970s as a new alternative binding material to Portland cement [1]. A geopolymeric reaction is a chemical reaction similar to an organic polymeric chain; in the final product, it forms an alumina-silica chain that has binding property. Geopolymeric reaction takes place between glassy silica and alumina in a high pH strong alkaline catalyzing medium. The reaction is also named alkali activation and, converts glassy compositions of source matter into a solid compound matter with a robust binding property [2–6]. In general, the use of fly ash, as one of the major industrial wastes from thermal power stations, is preferred as the source material containing alumino-silicate in geopolymer production. The main reason for using fly ash is to protect both the environment and natural resources by recycling fly ash [7,8].

Portland cement production is responsible for about 7–8% of the carbon dioxide emissions to the atmosphere. Geopolymer binder is a greener material than Portland cement. While a ton of CO_2 gas is emitted into the atmosphere in one ton of Portland cement production, 0.18 ton of CO_2 gas is emitted into the atmosphere in the production of one ton of geopolymeric binder [7,9–12].

In geopolymer synthesis, silica and alumina oxides major ingredients of aluminosilicate materials, dissolve in an alkali activator solution. It includes three phases of the chemical procedure. Published literature reports that the reaction mechanism of geopolymers consist of three major steps: (1) dissolution of reactive Si and Al mainly from glassy solid phases due to OH^- attack; (2) reorientation and gelation of dissolved species; (3) polymerization and condensation of products [13–17].

The formation of geopolymerization takes place in the presence of strong alkalis such as sodium hydroxide and/or sodium silicate between alumina and silicate materials. Based on published literature, geopolymer was synthesized at room conditions in some studies and at different temperatures in others. However, geopolimerization develops slower at room temperature and faster at higher temperatures (between

---

* Corresponding author.
E-mail address: ugurdurak@erciyes.edu.tr (U. Durak).

https://doi.org/10.1016/j.jobe.2020.102023
Received 29 June 2020; Received in revised form 27 October 2020; Accepted 22 November 2020

60 and 100 °C) [3,18–21]. It has been reported that the activation energy requirement of mixtures prepared using fly ash and sodium hydroxide is higher in producing geopolymeric products compared to mixtures prepared with meta-kaolin or blast furnace slag [10,22].

Laboratory studies were carried out on fly ash based geopolymer mortars, with different molarities, different curing temperatures, and durations. Mechanical, physical, permeability and microstructural properties of the samples produced were investigated [10,23,24].

In one study, the effect of heat curing temperature on physical and mechanical properties was investigated. The fly ash based geopolymer samples cured at 85 °C for samples prepared at 9 M Na^+ and cured for 24 h had less water absorption, porosity and higher density than that of samples cured at 65 °C [23].

In another study, fly ash based geopolymer mortar was activated with NaOH and cured at 75 °C for 48 h. After heat curing, hardened geopolymer was left 28 days at room conditions before strength tests. According to the experimental results obtained, it was observed that the mechanical strength of the samples left at room conditions increased and permeability properties decreased [25].

Atis et al. carried out a parametric laboratory study and produced fly ash based geopolymer mortar samples with different Na^+ ratios (4–20%). The geopolymer mortar samples were subjected to heat curing at different temperatures (45–115 °C), durations (24–72 h), and examined mechanical properties. As a result of the study, in general, it was observed that the strengths increased as the sodium molarity increased. Improvements in strength were observed with the increase of heat curing temperature and durations. In addition, it was concluded that each parameter (molarity, temperature, curing time) has its optimum value. However, according to the experimental results obtained, the highest compressive strength was found to be 120 MPa in samples prepared with 14 M Na, exposed to 115 °C heat curing for 24 h. It was observed that the influence of heat curing on strengths was decreased particularly when the heat curing temperature was higher than 75 °C and curing duration was longer than 48 h. They stated that the maximum curing period should not exceed 48 h in fly ash based geopolymer mortar samples to be subjected to heat curing [26].

Briefly, published literature showed the rate of geopolymeric reaction accelerates with an increase in curing temperature, curing duration, and molarity of alkali activator. These findings were also supported by other researchers [15,24,27,28].

Sun and Vollpracht, carried out a laboratory study to investigate a one year geopolymerisation of sodium silicate activated fly ash and metakaolin geopolymers. They prepared fly ash and metakaolin pastes with sodium silicate, separately. An isothermal calorimetry test was conducted on their geopolymer pastes at 20, 30, 40, and 60 °C for 72 h. According to the isothermal calorimetry results, they concluded that when the temperature was increased, heat flow peak and cumulative heat value were increased for both geopolymer pastes. However, the heat flow peak and cumulative heat values of the metakaolin geopolymer pastes were found to be higher than those of the fly ash geopolymer pastes for all temperatures. It was observed that the activation energy requirement of the fly ash-based geopolymer paste samples activated by alkali was higher at all temperatures than those of the counterpart metakaolin-based geopolymer paste samples. They concluded that initial heat curing contributes to the strength development of both geopolymers [29]. However, the strength improvement of fly ash based geopolymer is more prominent than its metakaolin counterpart, revealing the temperature dependence of alkali activated fly ash [27–30]. Also, research reported that the activation energy requirement of sodium hydroxide activated fly ash is higher than that of metakaolin or blast furnace slag [10,22,29].

From the literature review above, it is understood that fly ash based geopolymer needs heat curing for hardening and geopolymerization to take place for a certain duration [18,23,31–33]. Furthermore, there are several phases in the geopolymerization process i.e. dissolution of reactive ingredients, reorientation, gelation, polymerization, and condensation of geopolymeric products [22,34–36]. These phases take time, as for any chemical process. Therefore, it was postulated that when fly ash based geopolymer is heat cured, geopolymerization takes place during heat curing in the presence of sodium ions within the presence of water in the medium to transport these ions. However, heat curing results with the geopolymerization of fly ash in the presence of alkali solution, and causes evaporation of the water present in the alkali solutions. When the water evaporates fully, then the geopolymeric reaction reaches an end and stops. Thus, generally, it results with an uncompleted geopolymeric reaction. Therefore, it was thought that if the geopolymeric reaction process was extended for a certain period as well as slowing down the evaporation of water for a certain period of time, then better geopolymeric process could take place, resulting in a geopolymeric product with better properties. This can be achieved by applying a pre-rest period to fresh alkali activated fly ash based geopolymer mortars, which allows the dissolution of the amorphous phase of fly ash. Therefore, in this work, a new parameter influencing the geopolymeric reaction, as well as properties of geopolymer, was introduced as the pre-rest period before heat curing of geopolymer. Moreover, the influence of applying the pre-rest periods to fresh mixtures of alkali activated fly ash based geopolymer on the properties of hardened geopolymer sample was investigated. A laboratory study was undertaken to achieve the aim of the study. The laboratory study was comprised of preparing fresh sodium hydroxide activated geopolymer mortar and paste mixtures made with class F fly ash. These fresh mixtures were subjected to pre-rest periods before heat curing to provide certain time for dissolution of some amorphous phases of the fly ash. Following pre-rest periods, these samples were heat cured for certain durations. Their properties, including unit weight, flexural tensile and compressive strength, and abrasion resistance on mortar samples, were measured. A microstructural study including XRD and isothermal and SEM analyses were carried out on the paste samples. The results obtained were evaluated.

2. Properties of materials and methods

2.1. Fly ash

In this study, low-lime class F fly ash, which was classified by ASTM C 618 [37], was used and obtained from the Adana Iskenderun Sugözü thermal power plant. Characterizations of the fly ash were done by XRF (The Axios XRF spectrometer by PANanalytical), XRD (Bruker Axs D8 Advance Model) analysis, and SEM imaging in the Erciyes University Technology Research and Application Center Laboratories and are presented in Table 1 and Fig. 1.

The specific weight of the fly ash used was 2.41 and the remaining fly ash on a 45 μm sieve was 12%. Pozzolanic strength activity indexes of the fly ash were 78.4% for 7 days and 91.8% for 28 days, determined according to ASTM C618 [37].

2.2. Standard sand

Rilem Cembureau Standard sand, produced by the Limak Cement Industry, was used. The sand had a maximum grain size of 2 mm. Sieve analysis and limits of the standard sand are given in Table 2, and the sand complied with TS EN196-1 [38].

2.3. Activator

As an alkali activator, sodium hydroxide was used and was obtained from Zülfikarlar Group Akça Chemicals and its purity ratio was greater than 97%. The chemical content of the sodium hydroxide is given in Table 3.

Table 1
Chemical oxide composition of fly the ash (%).

Oxide	SiO_2	Al_2O_3	Fe_2O_3	CaO	SO_3	Na_2O	Free CaO	Cl^-	LOI
Fly Ash	61.81	19.54	7.01	1.77	0.31	2.43	0.07	0.04	2.20

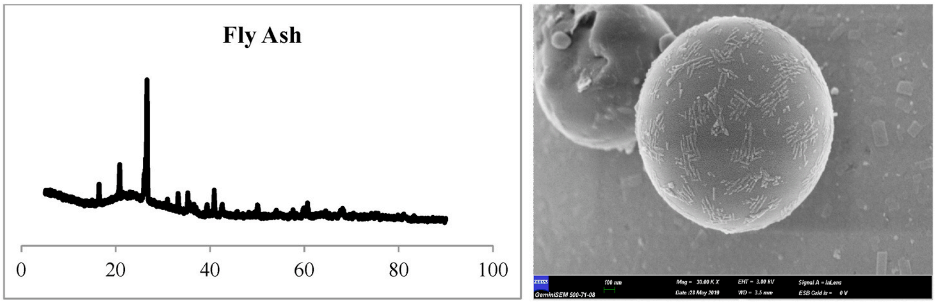


Fig. 1. XRD and SEM of fly ash.

Table 2
Grading of sand used and standard specifications.

Sieve Size (mm)	0.08	0.16	0.50	1.0	1.6	2.0
Remaining on sieve (%)	99	85	71	36	7	0
Standard Limits (%)	99 ± 1	87 ± 5	67 ± 5	33 ± 5	7 ± 5	0

Table 3
Chemical ingredients of the alkali activator (%).

NaOH	Na_2CO_3	Cl	Al	Fe	SO_4
≥ 97	≤ 1	≤ 0.01	≤ 0.002	≤ 0.002	≤ 0.01

2.4. Water

Clean and drinkable city water was used in the study.

2.5. Experimental program and test applied

The material ratios of the fly ash based geopolymer mortar mixtures produced in the experimental study were 3, 1, 0.29, and 0.1 for sand, fly ash, water, and sodium hydroxide in mass basis, respectively. The amount of materials used for mortar and paste samples are presented in Table 4. The alkaline solution and water binder ratios in the geopolymer paste samples were kept the same as in the geopolymer mortar mixtures. The prepared mortar and paste samples were subjected to a pre-rest period at room conditions for 0, 1, 2, 3, 7, 14, and 28 days and then exposed to heat curing at 75 °C for 48 h in an oven. Sample codes, pre-rest period before heat curing, and heat curing duration at 75 °C are given in Table 5. Subsequently, water absorption, porosity, specific gravity, capillarity, flexural strength, compressive strength, and abrasion resistance tests were carried out on the mortar samples that completed the 48 h heat curing period. For paste samples, reaction kinetics, XRD analysis, and SEM imaging were performed.

Prism molds with a size of 40 × 40 × 160 mm^3 were prepared using the above mixing ratio, given in Table 5, then the flexural and compressive strengths of the hardened geopolymers were done according to TS EN 1015-11 [39].

Table 4
Geopolymer mortar and paste mixture compositions (g).

	Sand	Fly Ash	NaOH	Water
Mortar	1350	450	80	130
Paste	–	450	80	130

Table 5
Mixture codes, pre-rest periods before heat curing, and heat curing duration.

Mixing Numbers For Mortars and Pastes	Pre-rest Period Before Heat Curing (days)	Heat Curing Duration (hours)
M0, P0	0	48
M1, P1	1	48
M2, P2	2	48
M3, P3	3	48
M7, P7	7	48
M14, P14	14	48
M28, P28	28	48

The Bohme abrasion test was carried out on the cubic mortar samples of 71 × 71 × 71 mm^3 according to TS 2824 EN 1338 [40]. Determination of water absorption, porosity, unit weight, and capillary water sorptivity properties were carried out according to ASTM C642 [41] and ASTM C1585 [42] on the prismatic samples of 40 × 40 × 160 mm^3.

Isothermal calorimetry measurements were conducted on the geopolymer paste samples by using a TAM Air (TA Instruments) calorimeter for pre-rest periods of 1, 3, 7, and 28 days as well as reference samples without a pre-rest period. Geopolymer pastes were placed into plastic vials after mixing. The P0 geopolymer paste sample without a rest period were immediately placed inside the calorimeter cell and measurements were conducted at 75 °C for 48 h. The P1, P3, P7, and P28 pastes were placed inside the calorimeter cells after curing in plastic vials at room conditions for 1, 3, 7, and 28 days, respectively, and then calorimetric measurements were performed at 75 °C for 48 h. The rate of reaction of geopolymer pastes was recorded as heat flow in mW units and then normalized per gram of fly ash in the geopolymer paste. Additionally, the total heat of reaction curves for the pastes were obtained as the cumulative area under reaction rate vs. time plots.

The geopolymer paste samples were prepared in accordance with the mixture composition and curing conditions given in Tables 4 and 5, respectively, for X-Ray diffraction (XRD) analyses and scanning electron microscopy (SEM).

Hardened paste samples were crushed and sieved through a 63 μm screen before XRD analysis, and then they were analyzed between 2-theta angles of 5–60° by using a Bruker AXS D8 model XRD device, operating with a CuKα X-ray source, 40 kV potential, and 40 mA current.

SEM examinations of the hardened geopolymer pastes were conducted on the fractured surfaces coated with gold/palladium to provide a conductive surface. Finally, the microstructure of the hardened geopolymer paste samples were examined by using LEO 440 SEM, equipped with an energy-dispersive X-ray analysis (EDX) system.

3. Results and discussions

3.1. Unit weight, water absorption and porosity

Unit weight, water absorption, and porosity testing results obtained from the AAFA geopolymer mortar subjected to a pre-rest period before heat curing are displayed in Table 6. Comparison between the control geopolymer mortar and geopolymer mortar with a pre-rest period before heat curing shows that there is a tendency of the sample to increase in unit weight as the pre-rest period curing increased. Unit weight of the hardened geopolymer mixture was found to be between 2.22 and 2.26 g/mm^3. From Table 6, the water absorption and porosity values of the control specimen were 4.9% and 10.6%, respectively. The water absorption and porosity values of the samples subjected to a pre-rest period were 4.7%, 4.0%, 3.7%, 3.6%, 3.6%, 2.7%, and 10.4%, 8.8%, 8.2%, 8.0%, 7.9% and 5.4% for 1, 2, 3, 7, 14, and 28-day pre-resting periods, respectively.

It was observed that the pre-rest period caused an increase in unit weight, and reduced the water absorption and porosity values of the samples. This is attributed to higher geopolymerization and denser structure caused by the pre-rest period explained in the following microstructural studies, particularly in the SEM studies.

3.2. Sorptivity

Water capillary sorptivities, including the initial and secondary sorptivity of the hardened geopolymer mortars produced in the study, are presented in Table 7. The highest initial and secondary sorptivities were obtained from the M0 mixture without a pre-rest period. The lowest initial and secondary sorptivities were obtained from the M28 mixture with the longest pre-rest period before heat curing. Table 7 shows that there is a reduction tendency in initial and secondary sorptivity of samples while the pre-rest period increases. The initial and secondary sorptivity results were found to be compatible with water absorption and porosity values.

3.3. Flexural and compressive strengths results

The study flexural and compressive strengths of the alkali activated fly ash-based geopolymer mortar samples exposed to a certain pre-rest period before heat curing and subsequently, heat cured in a 75 °C oven for 48 h are presented in Figs. 2 and 3.

Samples without a pre-resting period were considered as reference samples. As seen from Figs. 2 and 3, the flexural and compressive strengths of the control sample were 8.2 and 38.4 MPa, respectively. The flexural and compressive strengths of the samples subjected to a pre-rest period were 8.2, 10.2, 10.7, 10.8, 11.3, 11.7, 11.8 MPa and 38.4, 43.3, 48.5, 50.8, 51.0, 54.6, 59.4 MPa for 0, 1, 2, 3, 7, 14, and 28-day pre-resting period, respectively. Flexural strengths increased by up to 25%, 31%, 32%, 38%, 42%, and 44% compared to the reference mixture for 1, 2, 3, 7, 14, and 28 days pre-rest period, respectively. Similarly, compressive strengths increased by up to 13%, 26%, 32%, 33%, 42%, and 55% compared to the reference mixture for 1, 2, 3, 7, 14, and 28 days pre-rest period, respectively. Therefore, it was concluded that the flexural and compressive strength of the samples exposed to a pre-rest period was significantly higher than that of the reference sample.

As the pre-rest period duration increases, an increase in flexural and compressive strengths and significant increase rates of flexural and compressive strengths were observed. Therefore, the pre-resting phenomenon and its duration are found to be crucial for the strength properties of geopolymer. It was concluded that the pre-resting phenomenon and its duration are highly effective in contributing to geopolymerization and strength properties.

In literature, it was reported that heat curing time and degree, amount of alkaline solution, and molarity are effective parameters on the geopolymerization event and properties of geopolymer. From this study, it was concluded that the pre-rest period is a new parameter and it is as important and effective as the parameters mentioned above. Thus, a pre-rest period is introduced and defined as a new parameter, which influences the properties of geopolymer.

Table 6
Unit weight, water absorption and porosity results of mortars.

Mixture No	Heat Curing Duration	Rest Period Before Heat Curing	Unit Weight (g/cm^3)	Absorption (%)	Porosity (%)
M0	48 h	+0	2.22	4.9	10.6
M1	48 h	1 d	2.24	4.7	10.4
M2	48 h	2 d	2.24	4.0	8.8
M3	48 h	3 d	2.24	3.7	8.2
M7	48 h	7 d	2.25	3.6	8.0
M14	48 h	14 d	2.25	3.6	7.9
M28	48 h	28 d	2.26	2.7	5.4

Table 7
Water sorptivity results of the mortars.

Mixture No	Initial Sorptivity (mm/sn$^{1/2}$)	Secondary Sorptivity (mm/sn$^{1/2}$)
M0	0.0477	0.0014
M1	0.0404	0.0014
M2	0.0377	0.0011
M3	0.0304	0.0010
M7	0.0052	0.0009
M14	0.0069	0.0009
M28	0.0036	0.0009

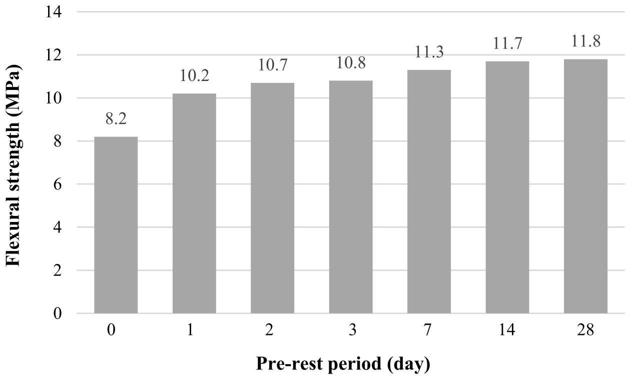


Fig. 2. Effect of the pre-rest period before heat curing on flexural strengths.

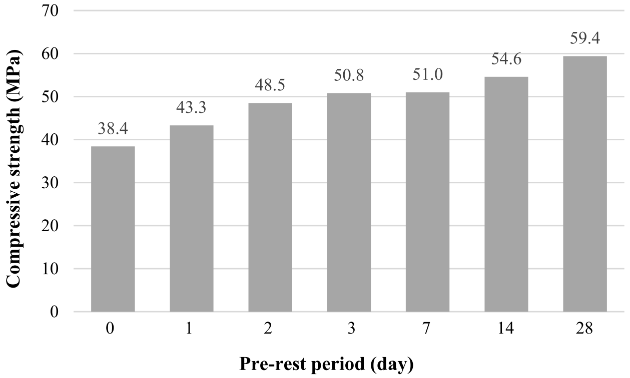


Fig. 3. Effect of the pre-rest period before heat curing on compressive strengths.

3.4. Abrasion resistance

The Böhme abrasion testing results of the alkali activated fly ash-based geopolymer mortar samples produced in this study are presented in Table 8.

As seen from Table 8, the abrasion value of the control samples were 4005 mm3/5000 mm^2. The Bohme abrasion values for the samples subjected to a pre-rest period were 3875, 3838, 3349, 3241, 2979, and 2869 mm^3/5000 mm^2 for 1, 2, 3, 7, 14, and 28 day pre-resting periods, respectively.

The abrasion values decreased by up to 3.2%, 4.2%, 16.4%, 19.1%, 25.6%, and 28.4% compared to the reference mixture for 1, 2, 3, 7, 14, and 28 days pre-rest period, respectively. Therefore, it was concluded that the Bohme abrasion value for the samples exposed to a pre-rest period was significantly lower than that of the reference sample. Increasing the pre-rest period before heat curing corresponds to a higher abrasion resistance of alkali activated fly ah based geopolymer. This is a direct result of increase in the flexural and compressive strengths of the material due to the pre-rest period. It is known that for certain material, higher strength is associated with lower abrasion value or higher abrasion resistance [43].

3.5. Reaction kinetics

The rate and cumulative heat of reaction of the geopolymer pastes are shown in Figs. 4 and 5. The geopolymer pasts were tested at 75 °C for the pre-rest periods of 1, 3, 7, and 28 days, as well as the reference sample, without a pre-rest period before testing, for the short term (1 day and 3 days) and the long term (7 days and 28 days) pre-rest periods, respectively. The cumulative heat of reaction curves of the pastes subjected to pre-rest periods before heat curing were plotted to initialize with the cumulative heat value recorded at the end of the rest period. According to published literature, the reaction mechanism of fly ash based geopolymers consists of three major steps: (1) dissolution of reactive Si and Al, mainly from glassy solid phases due to OH^- attack; (2) reorientation and gelation of the dissolved species; and (3) polymerization and condensation of the products [13–17]. The rate of heat evolution graph for the reference geopolymer paste tested without a pre-rest period (Figs. 4a and 5a) indicated that the reaction rapidly accelerates in the first hour by giving an initial exothermic peak. The first peak can be associated with the dissolution of the aluminosilicates from the fly ash particles. The reference geopolymer paste also exhibited a second and a third exothermic peak in the first 2 h. This multiple peak process is in line with published literature reported for FA based geopolymer binders cured at elevated temperatures and is attributed to structure transformation and further condensation of N-A-S-H gels at higher temperatures [13–17].

Regarding the influence of a pre-rest period duration before heat curing on hydration kinetics of FA activated by NaOH, it was clearly observed that the pre-rest period modified the reaction process significantly depending on the duration of the rest period. The longer-term pre-rest periods particularly converted the early reaction process to a single from a multiple peak exothermic heat flow. Short term pre-rest periods resulted in the peaks becoming closer whereas the 28 days pre-rest period before heat curing completely created a single-peak exothermic reaction due to the merging of multi peaks. This behavior suggests that a pre-rest period at room temperature, especially for longer periods, allows efficient dissolution of reactive species from FA particles without considerable polymerization and condensation. Heat curing after the pre-rest period in the presence of rich dissolved species causes a rapid and enhanced polymerization and condensation process with a single exothermic peak, which can be associated with strength enhancements after the pre-rest periods. The cumulative heat curves for 48 h of heat curing at 75 °C were affected considerably by the pre-rest period as shown in Figs. 4b and 5b. The final values of the cumulative heat curves at the end of heat curing were recorded as 290, 421, 423, 422, and 426 J/g for 0, 1, 3, 7, and 28 days pre-rest period, respectively. It was observed that pre-resting increased the cumulative heat of reaction of the geopolymer pastes at the end of heat curing by approximately 45%. However, no significant difference in cumulative heat values occurred as the rest period was prolonged from 1 day to 28 days.

Table 8
Abrasion resistance of the AAFA mixtures.

Mixture No	Abrasion (mm^3/5000 mm^2)
M0	4005
M1	3875
M2	3838
M3	3349
M7	3241
M14	2979
M28	2869

It was observed that the final values of cumulative heat releases increase with a pre-rest period and become asymptote to its threshold value. An attempt was made to relate compressive strength development with those final values of cumulative heat releases and these are presented in Table 9 (column 1 and 2). A closer observation of Table 9 shows that there was no proper relation between compressive strength and the final values of cumulative heat releases.

However, another attempt was made to relate compressive strength development with the area under the cumulative heat release graphs including cumulative heat releases during the pre-rest periods. The determined values of those areas are presented in Table 9 (column 3). Table 9 shows that a good relation exists between compressive strength and those areas. While, the values of areas increase, then the compressive strength of geopolymer mortar increases. This appropriately explains the increase in compressive strength through cumulative heat release.

3.6. SEM examinations

SEM image studies were carried out on the geopolymer paste samples, which were subjected to the pre-rest periods before heat curing. After completing the pre-rest period, the samples were exposed to 75 °C heat curing for 48 h. SEM images of the P0, P1, P2, P3, P7, P14, and P28 geopolymer paste samples are given in Fig. 6.

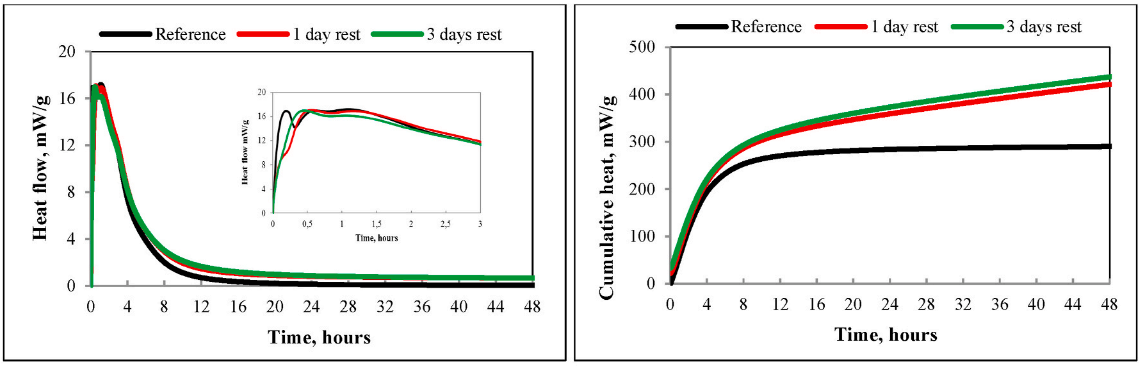
The reference geopolymer paste sample, which was directly cured at 75 °C for 2 days without a pre-rest period, consisted of partially reacted and unreacted fly ash particles as well as geopolymer gel. P0, the spherical fly ash particle dissolved in alkaline solution because of geopolymerization is seen in Fig. 6 (a). It is observed from Fig. 6 (b, c, d) that the P1, P2, and P3 geopolymer paste samples have less unreacted spherical fly ash particles. Thus, the microstructure of the geopolymer paste with low porosity became denser. In addition, the geopolymer paste samples P7, P14, and P28, as determined from Fig. 6 (e, f, g), had the least amount of unreacted fly ash particles in the geopolymer. The microstructure of the paste was much more dense and compact with very low porosity due to the pre-rest period.

As a result of the SEM examinations, it was concluded that while the pre-rest period before heat curing increases, the reacted amount of fly ash particles increases, and therefore a more dense and compact microstructure was formed.

In order for the geopolymeric reaction to take place, sodium has to be in ion form. This is possible by forming an alkaline solution of water with sodium or water with sodium hydroxide.

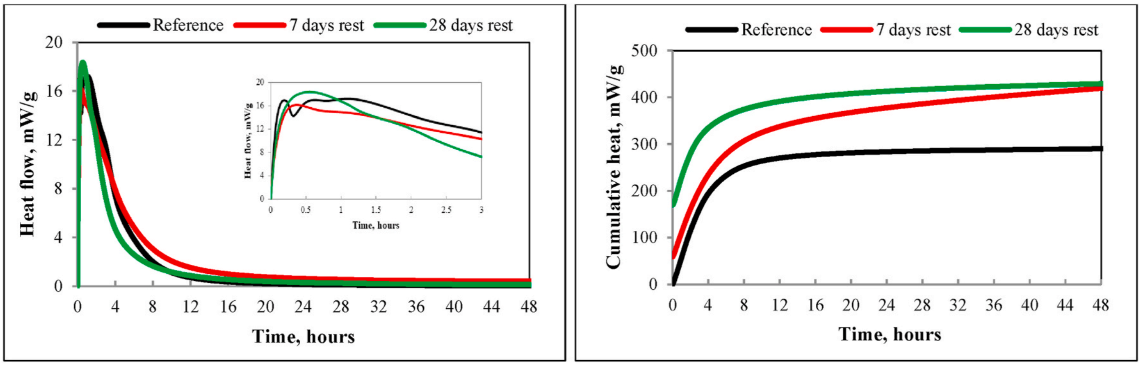
While geopolymer pastes are subjected to heat curing without a pre-rest period, the water contained in the paste sample alkaline solution evaporates rapidly with the effect of heat curing. This reduces the ion transfer, thereby limiting the formation of the geopolymeric reaction.

The alkaline solution in the samples subjected to a pre-rest period before heat curing, allows the first stages of geopolymeric reactions to take place with more regular and orderly form. Thus, the mechanical,



(a) (b)

Fig. 4. (a) Rate of hydration curves of the geopolymer pastes at 75 °C for 2 days. (b) Cumulative heat of hydration of the geopolymer pastes.



(a) (b)

Fig. 5. (a) Rate of hydration curves of the geopolymer pastes at 75 °C for 2 days. (b) Cumulative heat of hydration of the geopolymer pastes.

Table 9
Cumulative heat of hydrations.

Mixture No	Compressive Strengths, MPa	Cumulative heat of hydrations, J/g	Area of under cumulative heat of hydration curves
P0	38.4	290	46,003
P1	43.3	421	59,927
P3	48.5	423	65,786
P7	51.0	422	83,879
P28	59.4	426	302,326

durability, and microstructural properties of the geopolymer samples exposed to heat curing after the pre-rest period develop favorably.

3.7. XRD analysis results

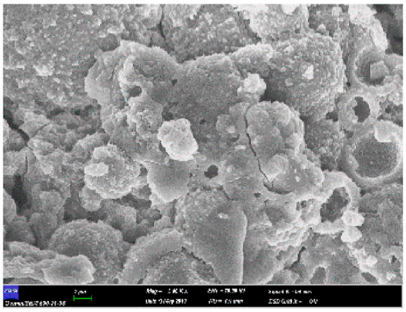
The results of XRD analysis obtained for P0, P1, P2, P3, P7, P14, and P28 geopolymer pastes are presented in Fig. 7. Many peaks of quarts, mullite, and sodalite crystalline minerals were observed due to the ingredients of the fly ash and alkali materials used, for all geopolymer pastes. There was no clear difference in the intensity of the peaks of quartz, mullite, and sodalite. The main difference between only fly ash sample and alkali activated geopolymer paste was the sodalite mineral. Sodalite mineral was not observed in the fly ash sample. Formation of sodalite can be taken as an indicator of a geopolymeric reaction between sodium ions and fly ash particles. It is not easy to identify the pattern of the geopolymeric reaction product using only XRD results [20,44–46].

In Fig. 8, the XRD analysis of fly ash and P28 samples are presented. From a closer examination of Fig. 8, the graph of the P28 sample drop down can be compared to the graph of the fly ash. The graph of fly ash humping upwards is an indication of the amorphous structure of the fly ash. In the P28 paste sample, the graph's dropping down and the flattening of the hump is explained by the dissolution of amorphous materials in the fly ash in an alkaline solution, and turning into a more crystalline structure and geopolymeric product.

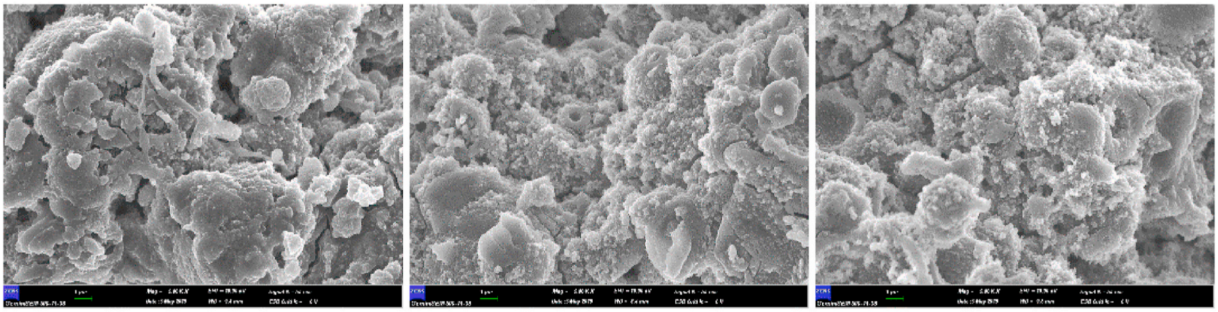
4. Conclusions

The following conclusions were made from the laboratory study carried out to evaluate the influence of the pre-rest period before heat curing on the properties of an alkali activated fly ash based geopolymer.

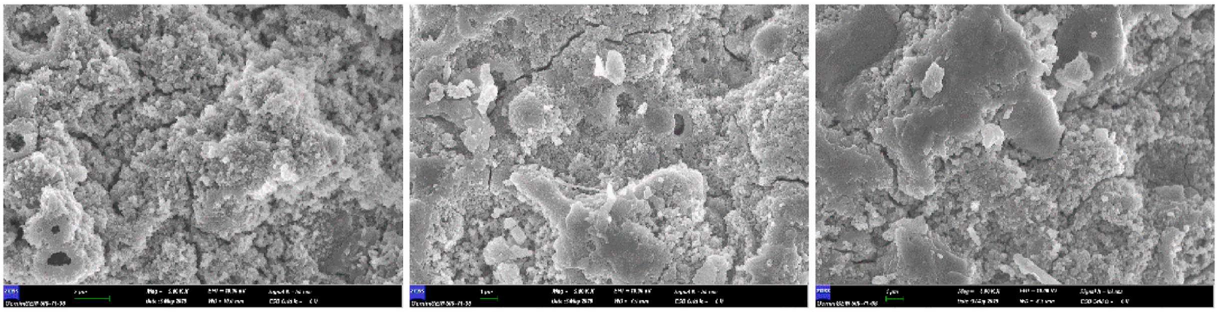
1 An applied pre-rest period before heat curing on fly ash based geopolymer mortar increased unit weight, decreased water absorption, and porosity values of the geopolymer mortar.
2 A pre-rest period resulted in an increase in the flexural and compressive strength properties of the geopolymer. The longer pre-rest period means a higher strength property.
3 A pre-rest period caused a higher abrasion resistance of the geopolymer mortar. The higher abrasion resistance was obtained from the longer pre-rest period.
4 Based on SEM pictures, it was concluded that the pre-rest period, allowing more time for ion transfer between the alkaline solution and fly ash particles, resulted with a more compact and denser microstructure, thus, resulting in better material properties.
5 XRD analysis proved that the pre-rest periods before heat curing causes the dissolution of amorphous materials in the fly ash in an alkaline solution and turns them into a more crystalline structure in the geopolymeric reaction.



(a) Reference



(b) 1 day pre-rest before heat curing (c) 2 days pre-rest before heat curing (d) 3 days pre-rest before heat curing



(e) 7 days pre-rest before heat curing (f) 14 days pre-rest before heat curing (g) 28 days pre-rest before heat curing

Fig. 6. SEM images for geopolymer pastes.

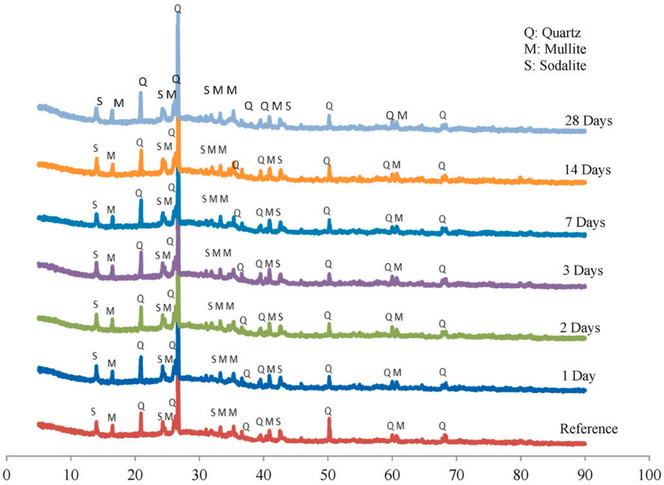


Fig. 7. XRD analysis of geopolymer paste samples.

6 Isothermal studies showed that the pre-rest periods before heat curing contribute to the geopolymeric reaction, thus increasing the compressive strength development and mechanical properties.

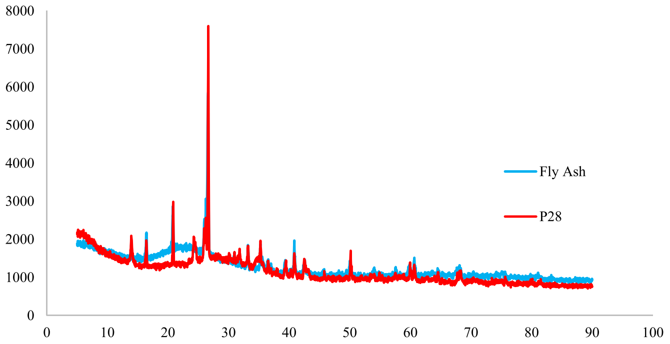


Fig. 8. XRD analysis of fly ash and P28 samples.

7 Finally, pre-rest periods before heat curing can be considered a new and rewarding parameter, which influences the geopolymeric reaction development and mechanical properties of hardened geopolymer.

Author statement

Required questions according to reviewers were answered and attached to Response to Reviewers file. Also, the changes were marked by red color in the manuscript.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgment

This work, project code FBA-2018-7931, was supported by the Erciyes University Scientific Research Project Coordination Unit.

References

[1] J. Davidovits, Chemistry of geopolymeric systems, terminology, in: Geopolymer International Conference, 2015 no. Iv.
[2] A.S. De Vargas, D.C.C. Dal Molin, A.C.F. Vilela, F.J. Da Silva, B. Pavão, H. Veit, The effects of Na2O/SiO2 molar ratio, curing temperature and age on compressive strength, morphology and microstructure of alkali-activated fly ash-based geopolymers, Cem. Concr. Compos. (2011), https://doi.org/10.1016/j.cemconcomp.2011.03.006.
[3] J.C. Swanepoel, C.A. Strydom, Utilisation of fly ash in a geopolymeric material, Appl. Geochemistry 17 (8) (Aug. 2002) 1143–1148, https://doi.org/10.1016/S0883-2927(02)00005-7.
[4] B.H. Mo, H. Zhu, X.M. Cui, Y. He, S.Y. Gong, Effect of curing temperature on geopolymerization of metakaolin-based geopolymers, Appl. Clay Sci. (2014), https://doi.org/10.1016/j.clay.2014.06.024.
[5] J.G.S. Van Jaarsveld, J.S.J. Van Deventer, G.C. Lukey, The characterisation of source materials in fly ash-based geopolymers, Mater. Lett. (2003), https://doi.org/10.1016/S0167-577X(02)00971-0.
[6] U. Durak, S. İlkentapar, İ. İ. Atabey, and C. D. Atİş, “Influence of Incubation Period on Strength Development of NaOH and Heat Cured Fly Ash Based Geopolymer Mortar,” p. 1021.
[7] C.R. Meesala, N.K. Verma, S. Kumar, Critical review on fly-ash based geopolymer concrete, Struct. Concr. (2019) 1–16, https://doi.org/10.1002/suco.201900326. October.
[8] J. Davidovits, G. Resins, Geopolymer chem istry and sustain able Dev elopment . The Poly (s ialate) term inolog y : a v ery useful and simp le model for th e p rom otion and understanding of green-chemistr y, 1980, pp. 9–16. July 2005.
[9] M.B. Ali, R. Saidur, M.S. Hossain, A review on emission analysis in cement industries, Renew. Sustain. Energy Rev. 15 (5) (2011) 2252–2261, https://doi.org/10.1016/j.rser.2011.02.014.
[10] A. Rafeet, R. Vinai, M. Soutsos, W. Sha, Effects of slag substitution on physical and mechanical properties of fly ash-based alkali activated binders (AABs), Cem. Concr. Res. (2019), https://doi.org/10.1016/j.cemconres.2019.05.003.
[11] J.L. Provis, Green concrete or red herring? - future of alkali-activated materials, Advances in Applied Ceramics (2014), https://doi.org/10.1179/1743676114Y.0000000177.
[12] M. Olivier, G.J. J, J.A.H.W. Peters, G. Janssens-Maenhout, Muntean, Trends in Global CO2 Emissions, 2013.
[13] X. Gao, Q.L. Yu, H.J.H. Brouwers, Characterization of alkali activated slag-fly ash blends containing nano-silica, Constr. Build. Mater. (2015), https://doi.org/10.1016/j.conbuildmat.2015.08.086.
[14] E. Deir, B.S. Gebregziabiher, S. Peethamparan, Influence of starting material on the early age hydration kinetics, microstructure and composition of binding gel in alkali activated binder systems, Cem. Concr. Compos. (2014), https://doi.org/10.1016/j.cemconcomp.2013.11.010.
[15] S. Chithiraputhiran, N. Neithalath, Isothermal reaction kinetics and temperature dependence of alkali activation of slag, fly ash and their blends, Constr. Build. Mater. 45 (2013) 233–242, https://doi.org/10.1016/j.conbuildmat.2013.03.061.
[16] C. Shi, R.L. Day, A calorimetric study of early hydration of alkali-slag cements, Cem. Concr. Res. (1995), https://doi.org/10.1016/0008-8846(95)00126-W.
[17] S. Song, H.M. Jennings, Pore solution chemistry of alkali-activated ground granulated blast-furnace slag, Cem. Concr. Res. (1999), https://doi.org/10.1016/S0008-8846(98)00212-9.
[18] T. Bakharev, Geopolymeric materials prepared using Class F fly ash and elevated temperature curing, Cem. Concr. Res. 35 (6) (2005) 1224–1232, https://doi.org/10.1016/j.cemconres.2004.06.031.
[19] U. Rattanasak, P. Chindaprasirt, Influence of NaOH solution on the synthesis of fly ash geopolymer, Miner. Eng. 22 (12) (Oct. 2009) 1073–1078, https://doi.org/10.1016/J.MINENG.2009.03.022.
[20] M. Komljenović, Z. Baščarević, V. Bradić, Mechanical and microstructural properties of alkali-activated fly ash geopolymers, J. Hazard Mater. 181 (1–3) (Sep. 2010) 35–42, https://doi.org/10.1016/J.JHAZMAT.2010.04.064.
[21] D. Ravikumar, S. Peethamparan, N. Neithalath, Structure and strength of NaOH activated concretes containing fly ash or GGBFS as the sole binder, Cem. Concr. Compos. 32 (6) (Jul. 2010) 399–410, https://doi.org/10.1016/J.CEMCONCOMP.2010.03.007.
[22] Z. Sun, A. Vollpracht, Isothermal calorimetry and in-situ XRD study of the NaOH activated fly ash, metakaolin and slag, Cem. Concr. Res. (2018), https://doi.org/10.1016/j.cemconres.2017.10.004.
[23] G. Görhan, G. Kürklü, The influence of the NaOH solution on the properties of the fly ash-based geopolymer mortar cured at different temperatures, Compos. Part B Eng. 58 (2014) 371–377, https://doi.org/10.1016/j.compositesb.2013.10.082.
[24] J.L. Provis, A. Palomo, C. Shi, Advances in understanding alkali-activated materials, Cement Concr. Res. (2015), https://doi.org/10.1016/j.cemconres.2015.04.013.
[25] S. İlkentapar, C.D. Atiş, O. Karahan, E.B. Görür Avşaroğlu, Influence of duration of heat curing and extra rest period after heat curing on the strength and transport characteristic of alkali activated class F fly ash geopolymer mortar, Constr. Build. Mater. (2017), https://doi.org/10.1016/j.conbuildmat.2017.06.041.
[26] C.D. Atiş, E.B. Görür, O. Karahan, C. Bilim, S. İlkentapar, E. Luga, Very high strength (120 MPa) class F fly ash geopolymer mortar activated at different NaOH amount, heat curing temperature and heat curing duration, Constr. Build. Mater. 96 (Oct. 2015) 673–678, https://doi.org/10.1016/J.CONBUILDMAT.2015.08.089.
[27] S.K. Nath, S. Mukherjee, S. Maitra, S. Kumar, Kinetics study of geopolymerization of fly ash using isothermal conduction calorimetry, J. Therm. Anal. Calorim. (2017), https://doi.org/10.1007/s10973-016-5823-x.
[28] S.K. Nath, S. Maitra, S. Mukherjee, S. Kumar, Microstructural and morphological evolution of fly ash based geopolymers, Constr. Build. Mater. 111 (2016) 758–765, https://doi.org/10.1016/j.conbuildmat.2016.02.106.
[29] Z. Sun, A. Vollpracht, One year geopolymerisation of sodium silicate activated fly ash and metakaolin geopolymers, Cem. Concr. Compos. (2019), https://doi.org/10.1016/j.cemconcomp.2018.10.014.
[30] S. Chithiraputhiran, N. Neithalath, Isothermal reaction kinetics and temperature dependence of alkali activation of slag, fly ash and their blends, Constr. Build. Mater. (2013), https://doi.org/10.1016/j.conbuildmat.2013.03.061.
[31] C.a. Strydom, J.C. Swanepoel, Utilisation of fly ash in a geopolymeric material, Appl. Geochemistry 17 (8) (2002) 1143–1148, https://doi.org/10.1016/S0883-2927(02)00005-7.
[32] P. Chindaprasirt, T. Chareerat, V. Sirivivatnanon, Workability and strength of coarse high calcium fly ash geopolymer, Cem. Concr. Compos. 29 (3) (2007) 224–229, https://doi.org/10.1016/j.cemconcomp.2006.11.002.
[33] D. Panias, I.P. Giannopoulou, T. Perraki, Effect of synthesis parameters on the mechanical properties of fly ash-based geopolymers, Colloids Surfaces A Physicochem. Eng. Asp. (2007), https://doi.org/10.1016/j.colsurfa.2006.12.064.
[34] J.L. Provis, S.A. Bernal, Geopolymers and related alkali-activated materials, Annu. Rev. Mater. Res. (2014), https://doi.org/10.1146/annurev-matsci-070813-113515.
[35] P. Duxson, A. Fernández-Jiménez, J.L. Provis, G.C. Lukey, A. Palomo, J.S.J. Van Deventer, Geopolymer technology: the current state of the art, J. Mater. Sci. (2007), https://doi.org/10.1007/s10853-006-0637-z.
[36] D. Khale, R. Chaudhary, Mechanism of geopolymerization and factors influencing its development: a review, J. Mater. Sci. (2007), https://doi.org/10.1007/s10853-006-0401-4.
[37] ASTM C618, Standard Specification for Coal Fly Ash and Raw or Calcined Natural Pozzolan for Use, merican Society for Testing and Material, 2012.
[38] TS EN 196-1, Methods of Testing Cement—Part:1 Determination of Strength, TSE, 2016.
[39] TS EN 1015-11, Mortar Testing Method, Part 11. Measurement of Compressive and Flexural Tensile Strength of Mortar, TSE, Ankara, 2000.
[40] TS 2824 EN 1338, Concrete Paving Blocks-Requirements and Test Methods, Turkish Standart, Ankara, 2005.
[41] ASTM C642-13, ASTM C642, Standard Test Method for Density, Absorption, and Voids in Hardened Concrete, 2013.
[42] ASTM C1585-13, Standard Test Method for Measurement of Rate of Absorption of Water by Hydraulic Cement Concretes, ASTM Int., 2013, https://doi.org/10.1520/C1585-13.2.
[43] A.M. Neville, Properties of Concrete, 2011, 4th.
[44] B. Lee, G. Kim, R. Kim, B. Cho, S. Lee, C.M. Chon, Strength development properties of geopolymer paste and mortar with respect to amorphous Si/Al ratio of fly ash, Constr. Build. Mater. 151 (2017) 512–519, https://doi.org/10.1016/j.conbuildmat.2017.06.078.
[45] G.S. Ryu, Y.B. Lee, K.T. Koh, Y.S. Chung, The mechanical properties of fly ash-based geopolymer concrete with alkaline activators, Constr. Build. Mater. (2013), https://doi.org/10.1016/j.conbuildmat.2013.05.069.
[46] N.N. Shao, Z. Liu, Y.Y. Xu, F.L. Kong, D.M. Wang, Fabrication of hollow microspheres filled fly ash geopolymer composites with excellent strength and low density, Mater. Lett. (2015), https://doi.org/10.1016/j.matlet.2015.09.016.