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MECHANICAL AND MICROSTRUCTURAL PROPERTIES OF THE FLY-ASH-BASED GEOPOLYMER PASTE AND MORTAR

MEHANSKE IN MIKROSTRUKTURNE LASTNOSTI GEOPOLIMERNIH VEZIV IN MALT IZ LETEČEGA PEPELA

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In this paper we have investigated the influence of synthesis parameters on the mechanical properties of the fly-ash-based geopolymer paste and mortars. Moreover, the influence of an addition of limestone sand on the microstructure of fly-ash-based geopolymers was investigated as well. An addition of limestone sand increased the compressive strength of the fly-ash-based geopolymer mortar, in comparison to the strength of the geopolymer paste, by changing the composition of the gel phase in the geopolymer structure and with the physical strengthening due to the presence of well connected grains of the sand. The results have shown that the compressive strength and Young's modulus of elasticity of the fly-ash-based geopolymer mortar are correlated. The values of these parameters increase as the alkali and silicate dosages increase. At one point, they reach the maximum values and then start to decrease. On the other hand, the parameters that considerably increase the compressive strength slightly decrease the flexural strength of the geopolymer mortar.

Keywords: geopolymerization, fly ash, mortar, flexural strength, compressive strength, Young's modulus

Članek obravnava raziskavo vplivov parametrov sinteze na mehanske lastnosti geopolimernih veziv in malt iz letečega pepela. Preiskovan je bil tudi vpliv dodatka peska iz apnenca na mikrostrukturo geopolimera iz letečega pepela. Dodatek peska iz apnenca je povečal tlačno trdnost geopolimerne malte iz letečega pepela v primerjavi s trdnostjo geopolimernega veziva s spreminjanjem sestave želirne faze v strukturi geopolimera in s fizikalnim utrjevanjem zaradi prisotnosti dobro povezanih zrn peska. Rezultati so pokazali pri geopolimeru iz letečega pepela povezavo med tlačno trdnostjo in Youngovim modulom elastičnosti. Vrednosti teh parametrov naraščajo z naraščanjem dodatkov silikatov in alkalij. V določeni točki dosežejo največjo vrednost in se potem začnejo zmanjševati. Po drugi strani pa parametri, ki občutno povečajo tlačno trdnost, rahlo zmanjšajo upogibno trdnost geopolimerne malte.

Ključne besede: geopolimerizacija, leteči pepel, malta, upogibna trdnost, tlačna trdnost, Youngov modul

1 INTRODUCTION

Geopolymerization is an innovative technology that can transform a variety of aluminosilicate materials with alkali activation into useful, environmentally friendly materials known as geopolymers (inorganic polymers). These materials may be successfully applied in civil engineering as a replacement for cement binders. Geopolymerization is also known as a waste-minimization technology because it may utilize waste material (coal fly ash and metallurgical slag) as raw material.

The mechanism of geopolymerisation may be summarized in a few steps:

(1) Dissolution process, in which a breaking of Al-O-Si and Si-O-Si bonds in the source material and a liberation of Al^{3+} and Si^{4+} in an alkali silicate solution occur. Together with the dissolution, a hydrolysis of dissolved Al and Si occurs, leading to the formation of aluminate and silicate monomeric species;

(2) Polycondensation of the Al and Si species in an amorphous three-dimensional aluminosilicate network (gel), in which the Si^{4+} and Al^{3+} cations are tetrahedrally coordinated as $[SiO_4]^{4-}$ and $[AlO_4]^{5-}$ and linked by oxygen bridges.[1] The negative charge of the AlO_4^- group is charge-balanced by alkali cations (Na^+ and/or K^+) [2];

(3) Hardening of aluminosilicate gel.

The empirical formula of a geopolymer is: Mn $[(\text{-}SiO_2)z\cdot AlO_2]n\cdot wH_2O$, where Mn is a cation, usually an alkali (Na^+ or K^+), *n* is a degree of polycondensation, *w* Ł 3 and *z* is 1, 2 or 3.[3]

Geopolymers may be characterized with a variety of properties like a good thermal resistance[4–6] and resistance to aggressive environment,[7,8] but the basic engineering request is a high compressive strength. Depending on the processing conditions, geopolymers may show different values of compressive strength. Engineering demands for an improvement in the mechanical properties of geopolymers have resulted in considering possible geopolymer applications in the form of mortars or concrete.[9–13]

Fly ash, the by-product from coal-fired power stations, is mainly used for a geopolymer synthesis. Although fly ash is not considered to be a hazardous waste, the high quantity of ash produced all over the world imposes the necessity of finding a solution for this environmental problem. In this sense, a utilization of fly ash through the geopolymerization process may be considered as a promising solution.

The goal of this study was to investigate the influence of the synthesis parameters, the alkali and silicate dosages, on the mechanical properties of the fly-ash-based geopolymer paste and mortar and to investigate the influence of a sand addition on the microstructural properties of the fly-ash-based geopolymers.

2 EXPERIMENT

The fly ash sourced for this investigation was supplied from the coal-fired power station Pljevlja in Montenegro. Its chemical composition is given in **Table 1**.

Table 1: Chemical composition of fly ash
Tabela 1: Kemijska sestava letečega pepela

Compound	Content, *w*/%
SiO_2	49.45
Fe_2O_3	5.23
Al_2O_3	21.77
TiO_2	0.66
CaO	13.34
Na_2O	0.46
ZnO	$4.5 \cdot 10^{-3}$
MgO	1.29
MnO	0.02
P_2O_5	0.24
K_2O	1.4
LOI*	4.35

*Loss on ignition

The geopolymer paste was prepared by mixing fly ash with an alkali silicate solution, in a solid-to-liquid ratio of 1. An alkali silicate activator was prepared by mixing the NaOH and Na_2SiO_3 solutions at the mass ratios of 1, 1.5 and 2. The concentrations of the NaOH solution were (7, 10 and 13) M and a commercial sodium silicate solution ($w(Na_2O)$ = 8.5 %, $w(SiO_2)$ = 28.5 %, a density of 1.4 g/cm^3) was used. The geopolymer paste was cast in a cylindrical plastic mould, sealed with lead and left to rest in an oven for 48 h at the temperature of 65 °C.

Geopolymer mortar was prepared by mixing the geopolymer paste with crushed limestone sand. The granulometry distribution obtained with the sieve method is given in **Table 2**. The prepared mixtures were cast into the standard 40 mm × 40 mm × 160 mm prism moulds covered with polyethylene film sheets and left in an oven for 48 h at 65 °C. After this time, the samples were allowed to cool down, then removed from the moulds and left to rest for additional 14 d at ambient temperature before any testing was performed. The samples were tested for the compressive and flexural strengths as well as the modulus of elasticity. All the tests were performed using a minimum of three samples per mortar mix.

Table 2: Analytical sieving analysis of limestone sand
Tabela 2: Analitična sejalna analiza peska iz apnenca

Sieve size opening mm	Cumulative mass fraction of a sample pass through each sieve %
0.063	3.45
0.09	7.2
0.125	10.24
0.25	15.88
0.5	28.41
1.0	54.47
2.0	74.78
4.0	97.90
8.0	100.00

The samples of the geopolymer paste were tested only for the compressive strength, while the samples of the geopolymer mortar were subjected to testing for all the mechanical properties (compressive strength, flexural strength and Young's modulus of elasticity).

The flexural strength was determined from the modulus of the rupture test, while the Young's modulus of elasticity was calculated from the linear stress/strain response prior to failure. The samples remaining from the flexural-strength tests were used for testing the compressive strength of the geopolymer mortar.

Microstructural investigations of the geopolymer mortar were carried out using the FEI 235DB focused-ion-beam system at the National Center for Electron Microscopy at Berkeley, equipped with an EDAX Genesis energy dispersive spectrometer (EDS). The SEM images were recorded with a secondary electron detector (SED). A cross-sectioning of the geopolymer paste (without a sand addition) was carried out using 1000 pA gallium ion beam and a microstructural characterization was performed using an electron beam at the 5 kV operating voltage. In order to minimize electron charging effects, a through-lens back-scattered electron detector (TLD-B) was used for image recording.

3 RESULTS AND DISCUSSION

3.1 Mechanical properties of fly-ash-based geopolymers

Mechanical properties of fly-ash-based geopolymers are of primary importance regardless of possible applications in civil engineering. One of the basic conditions for a possible use of geopolymers in construction is a satisfactory strength, which can be significantly enhanced with an addition of sand. Two of the most important factors that greatly influence mechanical properties are alkali and silicate dosages. The influence of an alkali dosage on the mechanical properties of the geopolymer paste and mortar was evaluated through the change in the NaOH concentration, while the influence of a silicate dosage was investigated through the change in the $w(Na_2SiO_3)/w(NaOH)$ ratio.

The results have shown that the mechanical properties of the fly-ash-based geopolymer paste and mortar greatly depend on the reaction parameters of the geopolymerization process. Depending on the reaction parameters, the compressive strength of fly-ash-based geopolymers may be considerably increased with an addition of sand. The change in the compressive strength of the fly-ash-based geopolymer paste and mortar as a function of the reaction parameters is given in **Figures 1** and **2**. It is evident that the compressive strength of the geopolymer mortar is considerably higher than the compressive strength of the geopolymer paste. One of the reasons for that is the fact that well connected grains of sand physically strengthen the fly-ash-based geopolymers. The compressive strengths of both the geopolymer paste and mortar increase with the increase in the NaOH concentration (**Figure 1**) and the $w(Na_2SiO_3)/w(NaOH)$ mass ratio (**Figure 2**). At one point, they reach the maximum values and then decrease. The maximum values of the compressive strength were obtained using the 10 M NaOH at the $w(Na_2SiO_3)/w(NaOH)$ mass ratio of 1.5. Moreover, the compressive strength of the geopolymer mortar is higher than the strength of the geopolymer paste by 58.7 %.

The results of the investigation of geopolymer mortars have shown that the Young's modulus of elasticity is related to the compressive strength. The increase in the NaOH concentration from 7 M to 10 M leads to an increase in the Young's modulus. The maximum value of the Young's modulus of elasticity (9.1 GPa) was reached using 10 M NaOH. A further increase in the alkaline (NaOH) dosage to 13 M slightly reduced the modulus of elasticity of the geopolymer mortar (**Figure 3**). The same behaviour of the fly-ash-based geopolymer mortar was observed with the change in the silicate dosage (**Figure 4**). The fly-ash-based geopolymer mortar reached the maximum value of the Young's modulus at the $w(Na_2SiO_3)/w(NaOH)$ ratio of 1.5. A further increase in the silicate dosage, i.e., a change in the $w(Na_2SiO_3)/w(NaOH)$ ratio, led to a reduction in the Young's modulus of elasticity. A similar observation of the influence of the silicate dosage on the Young's modulus of elasticity was observed by Duxon et. al.[14]

On the other hand, the flexural strength of the fly-ash-based geopolymer composites is inversely related to the compressive strength and Young's modulus of elasticity. The parameters that considerably increase the compressive strength and Young's modulus of elasticity slightly reduce the flexural strength of the fly-ash-based geopolymer composites. The minimum values of the flexural strength correspond to the maximum values of the compressive strength and Young's modulus of

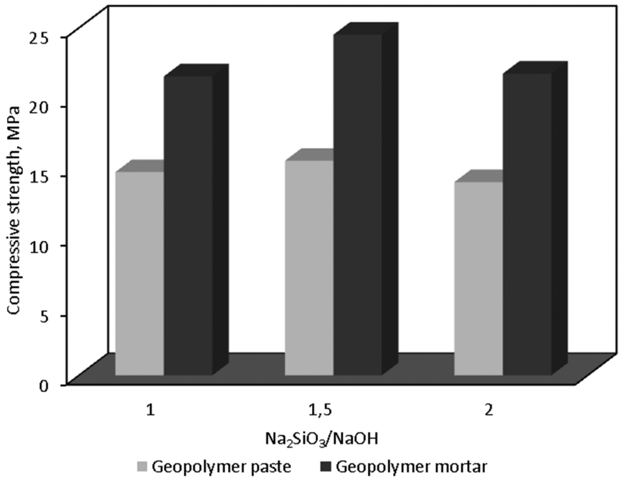

Figure 2: Change in the compressive strength of geopolymer paste and mortar as a function of the $w(Na_2SiO_3)/w(NaOH)$ mass ratio

Slika 2: Spreminjanje tlačne trdnosti geopolimernega veziva in malte v odvisnosti od masnega razmerja $w(Na_2SiO_3)/w(NaOH)$

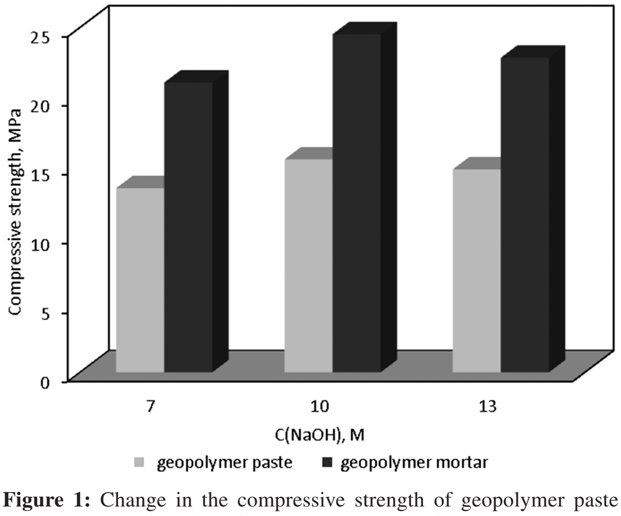

Figure 1: Change in the compressive strength of geopolymer paste and mortar as a function of the NaOH concentration

Slika 1: Spreminjanje tlačne trdnosti geopolimernega veziva in malte v odvisnosti od koncentracije NaOH

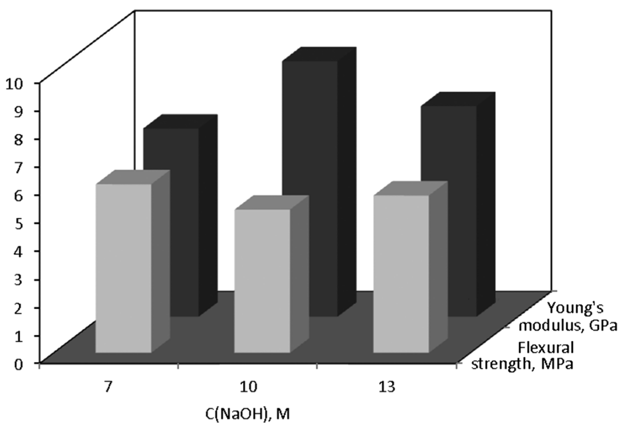

Figure 3: Change in the flexural strength and Young's modulus of elasticity of geopolymer mortar as a function of the NaOH concentration

Slika 3: Spreminjanje upogibne trdnosti in Youngovega modula elastičnosti geopolimerne malte v odvisnosti od koncentracije NaOH

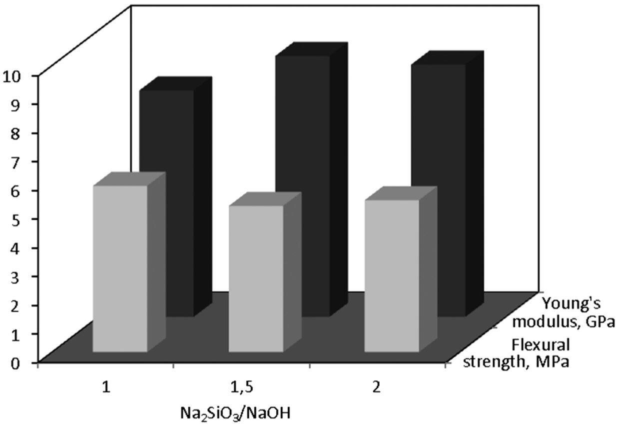

Figure 4: Change in the flexural strength and Young's modulus of elasticity of geopolymer mortar as a function of the $w(Na_2SiO_3)/w(NaOH)$ mass ratio

Slika 4: Spreminjanje upogibne trdnosti in Youngovega modula elastičnosti geopolimerne malte v odvisnosti od masnega razmerja $w(Na_2SiO_3)/w(NaOH)$

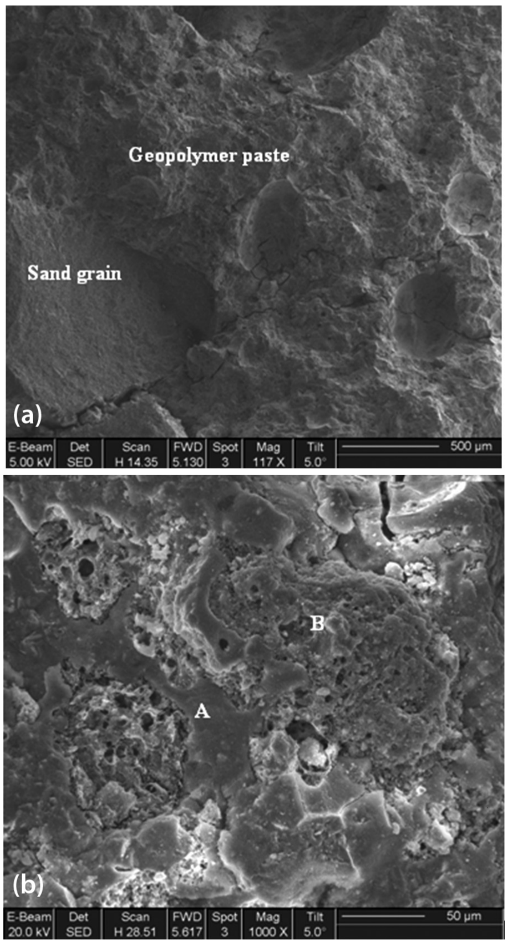

Figure 5: a) Microstructure of geopolymer mortar prepared using 10 M NaOH at the $w(Na_2SiO_3)/w(NaOH)$ mass ratio of 1.5; b) geopolymer paste (as a part of geopolymer mortar); A – gel; B – unreacted fly ash particles

Slika 5: a) Mikrostruktura geopolimerne malte, pripravljene z 10 M NaOH, pri masnem razmerju $w(Na_2SiO_3)/w(NaOH)$ 1,5; b) geopolimerno vezivo (kot del geopolimerne malte); A- vezivo; B- nereagirani delci letečega pepela

elasticity that were reached using 10 M NaOH (**Figure 3**), at the $w(Na_2SiO_3)/w(NaOH)$ ratio of 1.5 (**Figure 4**). The highest value of the flexural strength was obtained using 7 M NaOH at the $w(Na_2SiO_3)/w(NaOH)$ mass ratio of 1.

3.2 SEM –EDS microanalysis

The microstructure of the geopolymer mortar is characterized by the presence of sand grains and geopolymer paste (**Figure 5a**). The geopolymer paste consists of a gel phase (A) and unreacted fly-ash particles (B), (**Figure 5b**). The strength of the geopolymer mortar primarily depends on the structure of the gel, while the presence of the well connected grains of sand additionally strengthen the structure of the mortar. Besides, the unreacted fly-ash particles play the role of microaggregates contributing to the overall strength of the geopolymer mortar. The results of an EDS analysis of the gel phase in the mortar (**Figure 6a**) have shown a quantity of Ca that is considerably higher than the Si, Al, and Na contents. On the other hand, the results of an EDS analysis of the gel phase of the geopolymer paste prepared without an addition of sand, but with the same reaction parameters, have shown the quantities of Si, Al, and Na that are considerably higher than the Ca content.

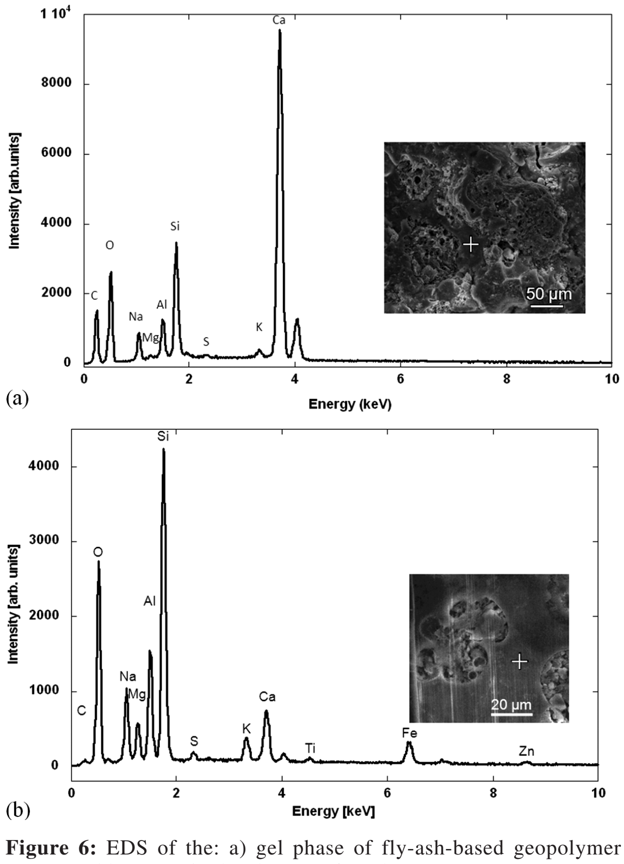

Figure 6: EDS of the: a) gel phase of fly-ash-based geopolymer mortar and b) paste (in the absence of sand)

Slika 6: EDS veziva: a) geopolimerne malte iz letečega pepela in b) veziva (brez peska)

In this case, Ca in the gel phase only originates from the fly ash (**Figure 6b**).

The previous research showed that the main gel forming elements are Si, Al and Na and that the structure of the geopolymer gel is determined by the w(Si)/w(Al) ratio.[15] But, in the geopolymer mixture with a high Ca content, the influence of Ca must be taken into account because the properties of the gel also greatly depend on the Ca content.[16,17]

Table 3: Content of elements (w/%) and their ratios in the gel phases of geopolymer mortar and paste

Tabela 3: Vsebnost elementov (w/%) in njihov delež v vezivu geopolimerne malte in lepila

Ratio	Geopolymer mortar	Geopolymer paste
w(Na)/w(Si)	0.48	0.42
w(Na)/w(Al)	1.23	1.17
w(Si)/w(Al)	2.65	2.8
w(Ca)/w(Si)	3.04	0.17
Si	6.31	17.14
Al	2.38	6.11
Ca	19.17	2.85

There is no considerable difference between the w(Na)/w(Si), w(Na)/w(Al) and w(Si)/w(Al) ratios in the gel phase of the geopolymer paste and mortar (**Table 3**). But, in the case of w(Ca)/w(Si), the ratio is considerably higher in the gel phase of the geopolymer mortar than in the geopolymer paste, which indicates a strong influence of Ca on the structure of the geopolymer mortar. On the other hand, in the gel phase of the geopolymer mortar the observed quantities of Al and Si are considerably lower than their contents in the gel phase of the geopolymer paste without an addition of limestone sand (**Table 3**). It could be that the presence of Ca in some way depletes the Al and Si dissolution, but this assumption needs to be further studied.

As the limestone sand was used for the geopolymer-mortar synthesis, it is necessary to take into account the presence of Ca in the gel phase as a result of the limestone dissolution in a strongly alkaline medium. Besides, a certain amount of Ca in the gel originates from fly ash. The reaction mechanism of the geopolymerisation varies significantly, depending on the presence of Ca in the geopolymer mixture. In the absence of Ca, the main product of the geopolymerisation process is an aluminosilicate inorganic polymer (the gel), while in the presence of Ca, additional Ca-bearing phases are formed.[18] The reaction pathway during the geopolymerization is strongly influenced by the Ca presence, because it strongly reacts with the soluble silicate and aluminate species provided during the dissolution step. This leads to the formation of a calcium silica hydrate and calcium aluminate hydrate gel phases.[19] It is considered that these Ca phases additionally strengthen the geopolymer structure, but a clear understanding of how Ca influences the reaction mechanism of the geopolymerization has not yet been established. It is assumed that the calcium silica hydrate gel fills the voids and pores within the geopolymer paste leading to an increase in the compressive strength.[18] Moreover, it is also considered that Ca is capable of acting as a charge-balancing cation within the geopolymer structure participating, in this way, in the geopolymerization process.[20]

4 CONCLUSIONS

In this paper, the influence of the synthesis parameters and a limestone-sand addition on the mechanical and microstructural properties of the fly-ash-based geopolymer paste and mortar was investigated. The results have shown that the compressive strength of the geopolymer paste may be increased by adding limestone sand. Moreover, the compressive strength correlates with the Young's modulus of elasticity of the fly-ash-based geopolymer mortars. Both the compressive strength and Young's modulus of elasticity increase with an increase in the NaOH concentration and the $w(Na_2SiO_3)/w(NaOH)$ mass ratio, reaching their maximum values at one point and then decreasing. On the other hand, the parameters that increase the compressive strength slightly decrease the flexural strength of the fly-ash-based geopolymer mortar. The maximum value of the compressive strength corresponds to the minimum value of the flexural strength of the fly-ash-based geopolymer mortar, indicating that the fly-ash-based geopolymers may be considered to be brittle materials. An addition of limestone sand increases the compressive strength of the fly-ash-based geopolymers by changing the structure of the geopolymeric gel phase. The gel phase of the geopolymer mortar is characterized by a content of Ca that is considerably higher than in the geopolymer paste, resulting in a higher compressive strength of the geopolymer mortar. In addition, the physical presence of the well connected grains of sand also contributes to the strengthening of the geopolymer mortar.

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