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Effect of Admixtures on Selected Properties of Fly Ash-Based Geopolymer Composites

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Featured Application: The aim of this work is to increase knowledge of the use of admixtures in geopolymer composites.

Abstract: This research was carried out to expand our knowledge of the effects of different admixtures on the properties of fly ash-based geopolymer composites. Three admixtures were used: a liquifying admixture based on stabilized polycarboxylates, a plasticizing admixture, and a liquifying admixture based on modified polynaphthalenes. The effect of variable activator content relative to the binder was also tested. The most favorable flexural and compressive strengths as well as water absorption were obtained in the series with a liquifying admixture based on stabilized polycarboxylates and an activator to fly ash ratio of 0.5 or 0.6. An increase in flexural and compressive strengths of 11% and 32%, respectively, was obtained compared to the series without admixtures. No positive effect was found for plasticizing admixtures or those based on modified polynaphthalenes.

Keywords: admixtures; fly ash; geopolymer; geopolymer composites

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1. Introduction

Geopolymers (composites based on alkali-activated binders) can be an alternative to cementitious composites, which are the most commonly used materials in construction. In an era of global warming, geopolymer technology is a promising concept for replacing traditional cement production and reducing CO_2 emissions. When waste materials are used as the base for geopolymers, economic and ecological benefits can be obtained [1–5]. The properties of geopolymer composites depend on the composition, especially [5–15]:

- Type of binder;
- Type of activator;
- Concentration of sodium hydroxide liquid (NaOH);
- Sodium silicate to sodium hydroxide liquid ratio by mass.

Additionally, different curing conditions affect the final properties of the geopolymer.

Binders most commonly used in geopolymers include metakaolin, fly ash, and ground, granulated blast furnace slag. Metakaolin-based geopolymers are characterized by their consistent properties, but their water demand can be a problem in their production [6,11]. Fly ash-based geopolymers show better mechanical properties [6]. Slag-based composites, on the other hand, have better resistance to aggressive environments compared to the other two [6]. The origin of the binder itself is also of great importance. The oxide composition of fly ash, for example, varies depending on the combined heat and power plant from which it was obtained. The ratio of alumina to silicon dioxide is particularly important in the production of geopolymer composites [5–14].

The most used alkali activators are sodium hydroxide (NaOH), potassium hydroxide (KOH), sodium silicate (Na_2SiO_3), and potassium silicate (K_2SiO_3), in most cases mixtures of those substances. In most studies, concentrations ranging from 4 to 14 M were used [5,7,8,12]. In most cases, the molar ratio of sodium silicate to sodium hydroxide was mainly tested at 2.0 or 2.5 [5,9,12–14,16].

The concentration of sodium hydroxide, either used as a standalone activator or combined with sodium silicates, also has a strong influence. In most studies, concentrations ranging from 4 to 14 M were used [5,6,8,9,12,14,16].

Many researchers have examined the impact of different maturation conditions [6–10,12]. In the production of geopolymers, elevated temperatures are necessary to allow them to harden. The temperature range most commonly used varied from 40 to 85 °C. Samples were treated at a higher temperature usually for 24 h.

The effect of admixtures on geopolymers is not yet resolved. Especially since, for example, the effect of plasticizing admixtures in cement concrete is well known, but in geopolymer concrete, it may be quite different. The effects of admixtures on workability and mechanical properties were mainly checked. Sometimes they were only added as an additive to improve consistency, without assessing the impact on properties [9,11,16–19].

Geopolymer composites based on fly ash (FA) and ground granulated blast-furnace slag (GGBS) are usually tested. Several studies have not found a clear improvement in properties through the use of various admixtures, including vinyl copolymer and polyacrylate copolymer, naphthalene-based, melamine-based, lignosulfonates, and modified polycarboxylates [9,12,16–18].

Gupta et al. [20] studied the effect of a polycarboxylic ether-based high-range water-reducing superplasticizer on geopolymer concrete specimens, where FA and GGBS were used in a 50:50 ratio. The most favorable results were obtained with an admixture of 3% by weight of the binder. A 15% increase in compressive strength and a reduction in water absorption of approximately 12% compared to concrete without the admixture were found.

An increase (by approximately 20%) in the strength properties of fly ash and blast furnace slag-based geopolymer concrete is also observed with the use of liquefaction admixtures based on naphthalene in an amount of approximately 0.8% by weight of the binder [21].

Xiong et al. [22] tested the effect of naphthalene- and polycarboxylate-based superplasticizers in an amount ranging from 0.1 to 2.4% by weight of the binder. The contents of the admixtures were determined to achieve the appropriate fluidity. Both admixtures improved the workability of geopolymer slurries based on fly ash and slag powder.

However, results can be found for geopolymer composites based on fly ash alone.

Mezhov et al. [23] investigated the effect of a polynaphthalene sulfonate (PNS) superplasticizer on the properties of fly ash and cement-based pastes. The admixture was added during mechanical activation of the fly ash (5% by weight of FA) or with the mixing water (0.5% by weight of binder). More favorable results were obtained by adding a superplasticizer during mechanical activation compared to the pastes with SP added by mixing water.

Laskar et al. [24] found that the third-generation water reducer based on high-range polycarboxylic ether (1.5% by weight of fly ash) improved the workability of concrete based on fly ash, but with a lower molar mass (4 M) NaOH solution that was used.

Nematollahi et al. [25] studied the effect of six types of superplasticizers (with a dose of 1% by mass of fly ash) on geopolymer pastes, two naphthalene-based, three modified polycarboxylate admixtures, and one melamine-based powder. Based on the results, it was found that the effect of admixtures depends on the type of superplasticizer. In all cases, there was a reduction in compressive strength. However, the most favorable results were obtained by using admixtures based on a modified polycarboxylate. Increased knowledge of the effects of the use of different admixtures in geopolymer composites will allow mixtures to be designed with selected properties. This is particularly important when producing geopolymers based on regionally available materials, especially local fly ash.

2. Materials

Silica fly ash from the local heat and power plant was used as a binder material. The material met the requirements of the EN 450-1 standard [26]. The chemical oxide compositions of the fly ash are presented in Table 1. Fly ash was characterized by a loss on ignition of 4.37% (according to EN 450–class A).

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

Oxide	Fly Ash
SiO_2	54.6
Al_2O_3	25.3
Fe_2O_3	4.97
MgO	1.8
CaO	2.14
Na_2O_{eq}	2.68
Na_2O	0.84
K_2O	2.8
TiO_2	1.07
P_2O_5	0.55
SO_3	0.37
BaO	0.15
SrO	0.07
Mn_3O_4	0.06

Sand in the 0–2 mm fraction was used as an aggregate. The grain size distribution of the sand is presented in Table 2.

Table 2. Grain-size distribution of sand (%).

Material	>2.0 mm	2.0–1.0 mm	1.0–0.5 mm	0.50–0.25 mm	0.250–0.125 mm	0.125–0.063 mm	0.063–0.000 mm
Sand	5.8	21.6	32.7	29.6	9.0	0.9	0.3

Three different admixtures (AD) were used: a liquifying admixture based on stabilized polycarboxylates (AD1), a plasticizing admixture (AD2), and a liquifying admixture based on modified polynaphthalenes (AD3). The characteristics of the ADs used in this study are summarized in Table 3.

Table 3. Physical and chemical properties of the admixtures.

Admixture	Characteristics	Appearance/Color	pH	Density (g/cm^3)
AD1	Liquifying admixture based on stabilized polycarboxylates	Green-amber liquid	5.0 ± 1.0	1.12 ± 0.03
AD2	Plasticizing admixture activating additives, i.e., fly ash and blast furnace slag, for high early strength	Amber liquid	4.0 ± 1.0	1.035 ± 0.03
AD3	Liquifying admixture based on modified polynaphthalenes	Brown liquid	6.0 ± 1.0	1.20 ± 0.03

The activator (AC), composed of sodium hydroxide and sodium silicate solutions, was used in this study. The sodium hydroxide solution was prepared at a concentration of 12 M using sodium hydroxide (NaOH) beads of 99% purity and distilled water. The mass of solid NaOH needed to prepare 1 dm^3 of a 12 mol/dm^3 NaOH solution was 480 g. The sodium silicate solution (Na_2SiO_3), with a specific gravity of 1.26–1.71 g/cm^3 and a modulus ratio (Ms) equal to 2.5 (where Ms = SiO_2/Na_2O, Na_2O = 12.07%, and SiO_2 = 29.35%), was used. Sodium silicate and sodium hydroxide solutions were mixed with a $Na_2SiO_3/NaOH$ ratio of 2.5 to prepare the activator.

3. Experimental Procedures

The effect of different admixtures and variable activator content on compressive and flexural strengths and water absorption of the fly ash-based geopolymer mortar was investigated in this study. The ratio of activator to fly ash was variable (AC/FA = 0.5, 0.6, and 0.7). The ratio of admixtures was held constant at 0.8% by weight of fly ash, based on the manufacturer's recommendations. To prepare the mortar, fly ash was mixed with sand for 2 min in the mixer. The activator and specific admixture were then added, and the mixing continued for another 3 min.

Based on those assumptions, the mix proportions of geopolymer mortars were prepared and presented in Table 4. Additionally, three series of control samples were prepared without admixtures.

Table 4. Geopolymer mortar mix proportions (g).

Series Code	Fly Ash	Sand	Activator	Admixture
AC/FA = 0.5 AD1	400	1600	200	3.2
AC/FA = 0.5 AD2	400	1600	200	3.2
AC/FA = 0.5 AD3	400	1600	200	3.2
AC/FA = 0.6 AD1	400	1600	240	3.2
AC/FA = 0.6 AD2	400	1600	240	3.2
AC/FA = 0.6 AD3	400	1600	240	3.2
AC/FA = 0.7 AD1	400	1600	280	3.2
AC/FA = 0.7 AD2	400	1600	280	3.2
AC/FA = 0.7 AD3	400	1600	280	3.2
AC/FA = 0.5	400	1600	200	-
AC/FA = 0.6	400	1600	240	-
AC/FA = 0.7	400	1600	280	-

For each mortar series twelve $40 \times 40 \times 160$ mm mortar specimens were cast. Samples were compacted for 20 s on a vibrating table. Then they were cured for 24 h at a temperature of 65 °C. For each series, compressive and flexural strengths, and water absorption tests were performed after 28 days of curing.

Each compressive and flexural strength test was performed on six specimens in accordance with EN 196-1 [27]. Six specimens were used for water absorption and density tests, following the PN-B-04500 standard instructions [28]. Statistical analyses were performed using Tibco Software Inc. Statistica version 13.3 software [29].

4. Results and Discussion

4.1. Flexural Strength

The 28 day flexural strength results showed an interaction between the amount of activator in the mix and the type of admixture used. The average results of the flexural strength for all the series are shown in Figure 1. The best results were obtained in the series with a liquifying admixture based on stabilized polycarboxylates and an activator to fly ash ratio of 0.6. In comparison with control samples with the same activator to fly ash ratio, an approximately 11% increase was observed when an admixture based on stabilized polycarboxylates was used. Control samples are characterized by an increase in flexural strength with an increase in activator content of about 4% and 5%, respectively. Dependence was observed in the mortar results with different admixtures.

Regardless of the activator content, the highest flexural strengths were obtained in mortars with the admixture based on stabilized polycarboxylates (AD1) (Figure 2). Changing the content of the activator did not cause much change when using the plasticizing admixture (AD2).

The greatest decrease (Figure 2) was observed when the liquifying admixture based on modified polynaphthalenes was used, approximately 11.5% and 17.5%, respectively. Higher activator content when using the admixture based on stabilized polycarboxylates did not cause an increase in the tested mechanical property when changing from 0.5 to 0.6.

The drastic decrease of the flexural strength by approximately 17% in geopolymer mortars containing the highest amount of activator was observed.

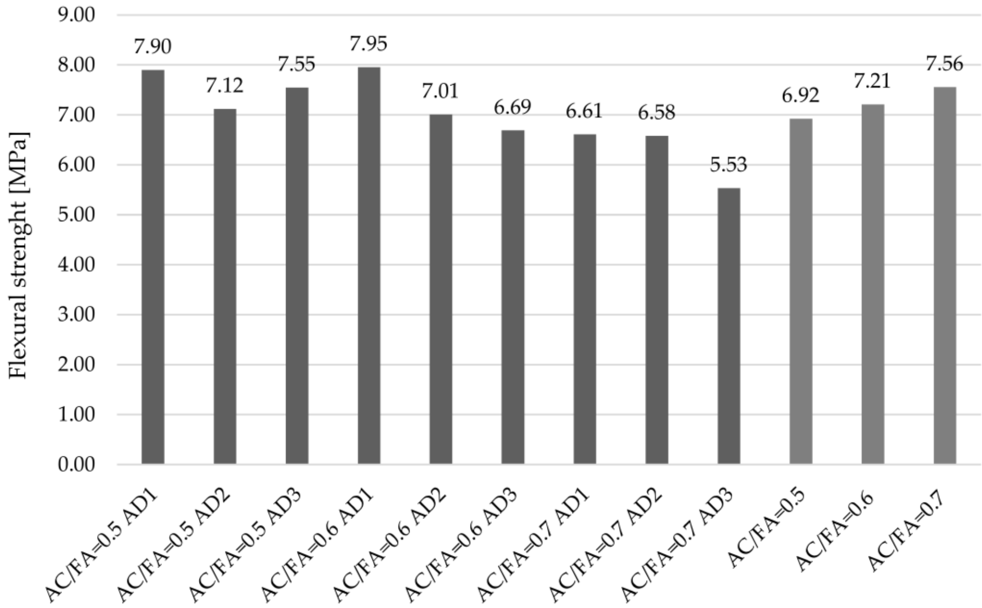

Figure 1. Flexural strength results for all series.

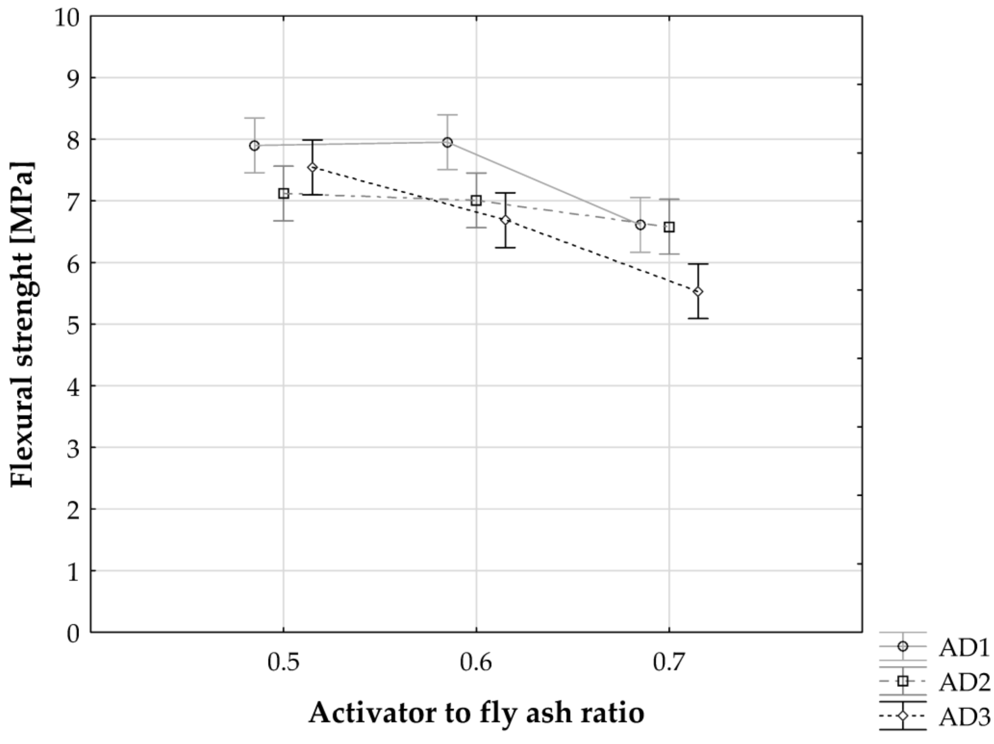

Figure 2. Flexural strength results depending on the activator to fly ash ratio (ANOVA certainty in whiskers).

4.2. Compressive Strength

The 28 day compressive strength results showed an interaction between the amount of activator in the mix and the type of admixture used. The average compressive strength results for all the series are shown in Figure 3.

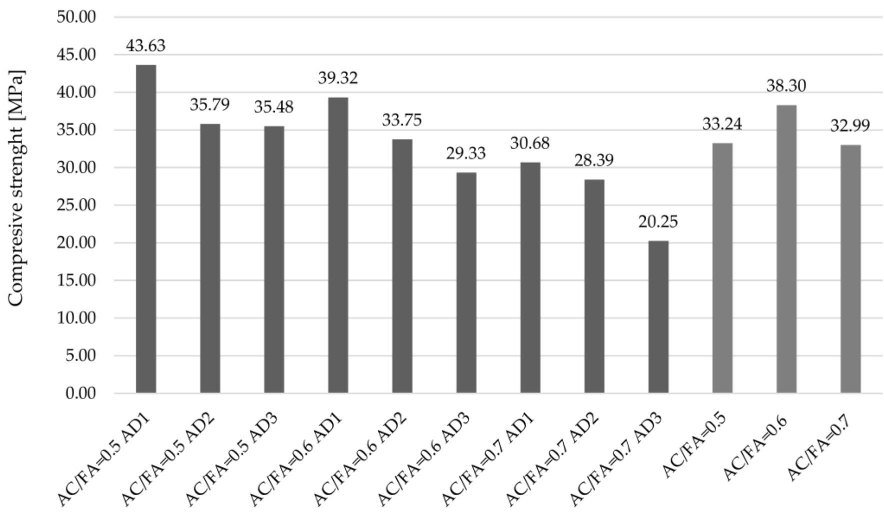

Figure 3. Compressive strength results for all the series.

The best results were obtained in the series with a liquifying admixture based on stabilized polycarboxylates and an activator to fly ash ratio of 0.5. In comparison with control samples with the same activator to fly ash ratio, an approximate 32% increase was observed when an admixture based on stabilized polycarboxylates was used. Control samples are characterized by an increase in compressive strength and an increase in activator content of about 15%. A further increase in the activator content resulted in a decrease in compressive strength of approximately 15%. Different dependencies were observed in the results of mortars with admixtures.

Regardless of the activator content, the highest compressive strengths were obtained in mortars with the admixture based on stabilized polycarboxylates (AD1) (Figure 4). These results confirm the beneficial effect of polycarboxylate-based superplasticizers achieved by Gupta et al. [20] in fly ash and GGBS-based composites. The increase in activator content caused a decrease in compressive strength regardless of the type of admixture used.

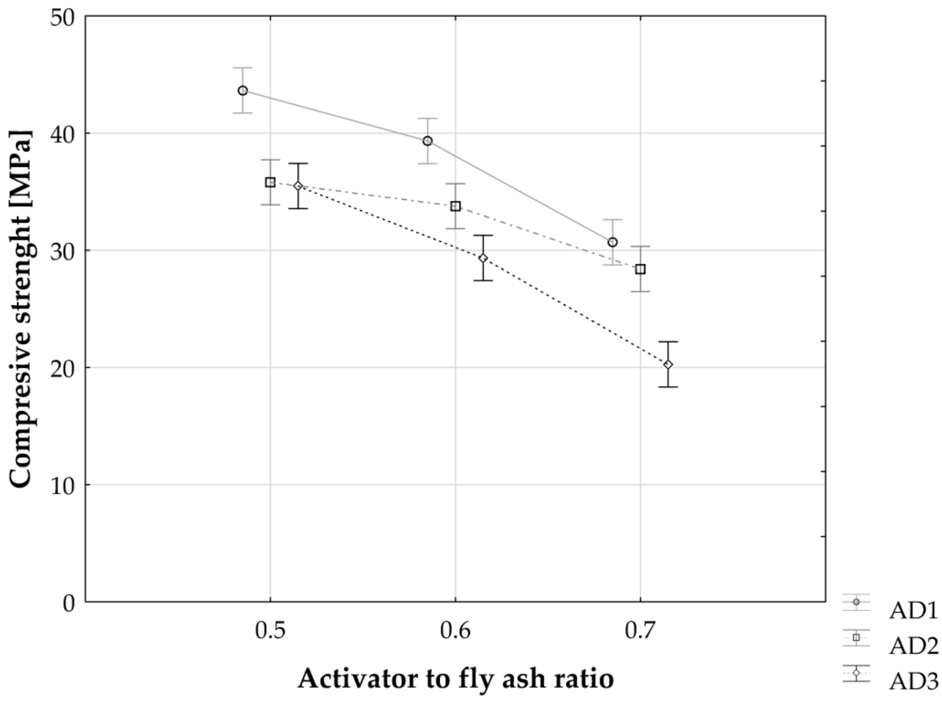

Figure 4. Compressive strength results depending on the activator to fly ash ratio (ANOVA certainty in whiskers).

In mortars with the admixture based on stabilized polycarboxylates, a total decrease of 30% was observed. In samples with a plasticizing admixture and an admixture based on modified polynaphthalenes, the decrease was 16% and 43%, respectively.

4.3. Water Absorption

Average water absorption results for all the series are shown in Figure 5. The best results were obtained in the series with a liquifying admixture based on stabilized polycarboxylates and an activator to fly ash ratio of 0.5. In comparison with control samples with the same activator to fly ash ratio, an approximate 25% improvement in properties was observed when an admixture based on stabilized polycarboxylates was used.

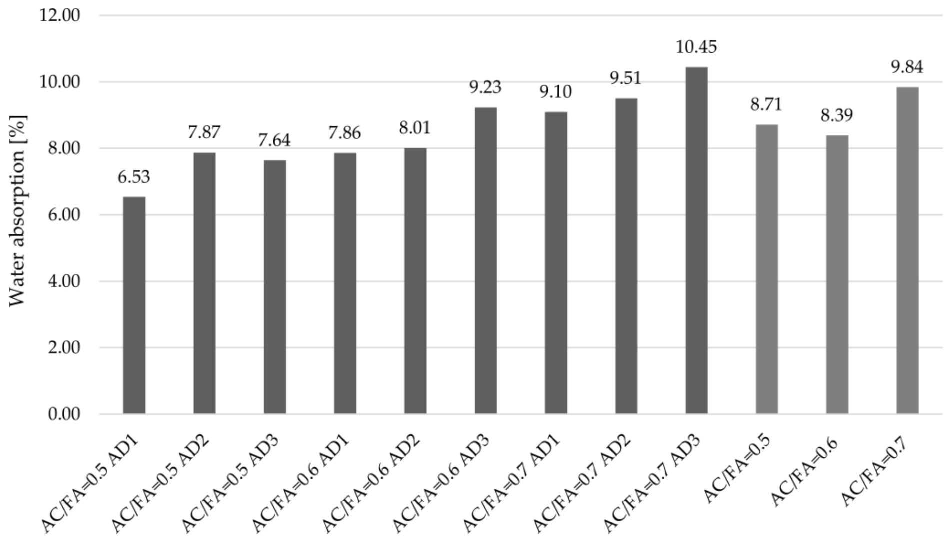

Figure 5. Water absorption results for all the series.

Regardless of the activator content, the lowest water absorptions were obtained in mortars with the admixture based on stabilized polycarboxylates (Figure 6). The increase in activator content caused an increase in the absorption of water, regardless of the type of admixture used.

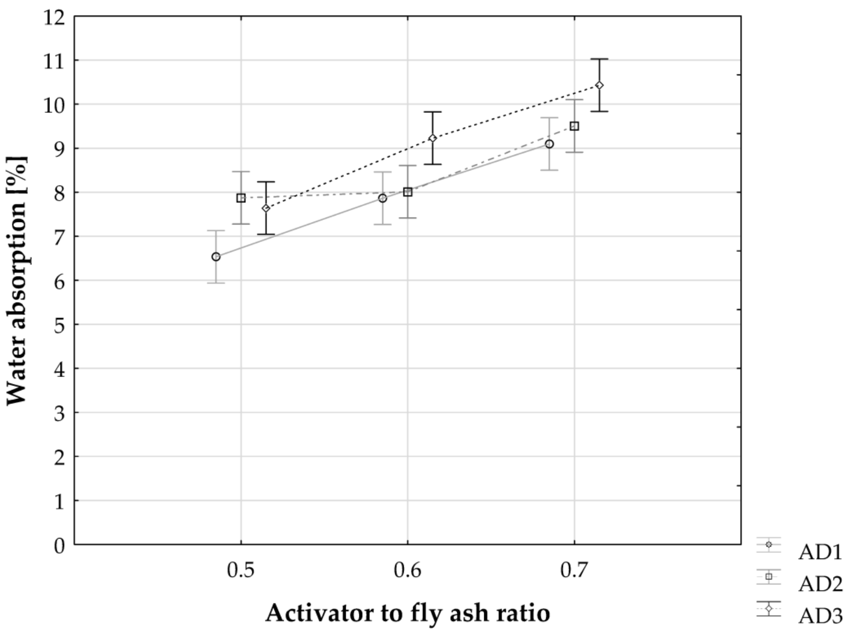

Figure 6. Water absorption results depending on the activator to fly ash ratio (ANOVA certainty in whiskers).

In mortars with the admixture based on stabilized polycarboxylates, a total increase of 40% was observed. In samples with a plasticizing admixture and an admixture based on modified polynaphthalenes, the increases were 21% and 37%, respectively.

4.4. Bulk Density Results

The average results of the bulk density for all the series are shown in Figure 7. All the series obtained similar bulk densities. However, a certain correlation can be identified. Mortars with admixtures are characterized by a decrease in the bulk density and an increase in the activator content.

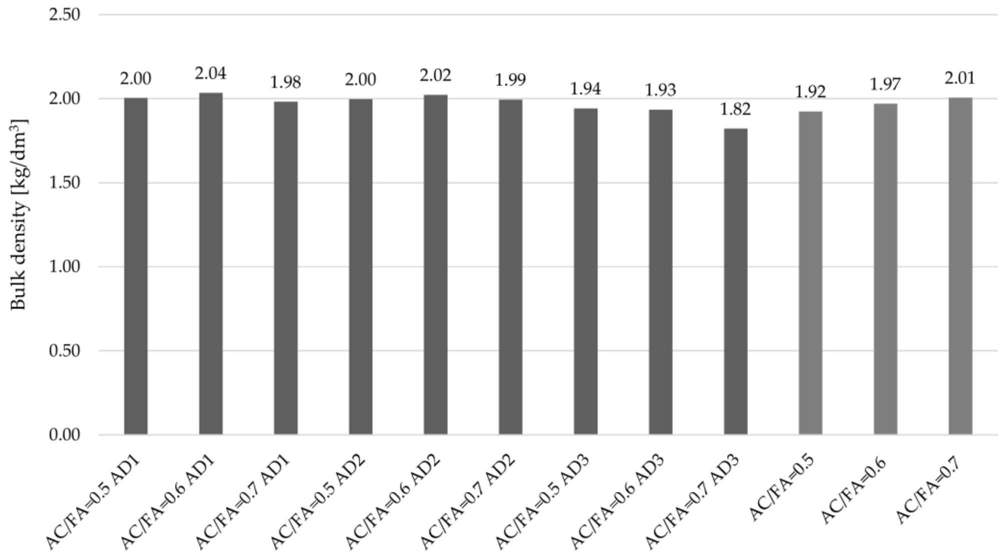

Figure 7. Bulk density results for all the series.

After flexural strength testing, all the samples were subjected to visual analysis. The series with a plasticizing admixture and an admixture based on modified polynaphthalenes were characterized by large pores visible in the cross-sections. The plasticizing admixture (AD2), according to the technical data sheet, causes an increase in volume by introducing micro air bubbles which was also observed in the samples. Thus, it was confirmed that this admixture works in a similar way in geopolymer mortars. Despite the use of a plasticizing admixture to activate the additives, i.e., fly ash and blast furnace slag, no results were obtained to conclude that the admixture activates the fly ash used to make the geopolymer composite.

5. Conclusions

The results of the analysis of geopolymer mortars indicate that their properties can be improved by using suitable admixtures. The effect of varying activator content in the geopolymer composite should also be considered:

1. The improvement in properties was achieved by the addition of the liquifying admixture based on stabilized polycarboxylates combined with a low activator content. The most favorable results were due to a more compact structure, which is confirmed by the highest bulk density as well as the lowest water absorption;
2. The increased volume and highly porous structure when the plasticizing admixture is used in the geopolymer composite have the same effect as when it is used in cement concrete. However, its additive activating properties have not been noted;
3. No positive effect was found for plasticizing admixtures or those based on modified polynaphthalenes.

The evaluation of the effect of the variable polycarboxylate-based admixture content to obtain optimal properties of geopolymer composites will be the next step in the research program. On the basis of the preliminary studies presented in this article, it will be possible to plan the next part of the study, in which the microscopic structure of geopolymer composites should be compared in relation to their composition, especially their admixture content.

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