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In-service performance of hybrid geopolymer binders based class F fly ash

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Abstract. Production of high-performance construction materials, meeting the requirements of construction process when development of up-to-date buildings and structures is very relevant and requires the usage of effective polycomponent binding systems, including geopolymers This work studied mechanical performance, as well as strength, water absorption and water resistance of portland cement – Class F fly ash – NaOH hybrid geopolymer binding system. The bench scale testing was conducted on different mixes, including regular portland cement-based and Class F fly ash-NaOH geopolymer binders used as reference compositions. The developed hybrid binders demonstrated, that incorporation of portland cement up to 40% as a modifying agent, reduces the formation of water soluble mineral phases such as sodium carbonates and hydroxycarbonates in low reactive class F fly ash geopolymer binders. It was found, that the presence of portland cement in the system positively affects strength development and noticeably reduces water absorption and improves water resistance of the developed binders, which is related to formation of water resistant and stable calcium hydrosilicate phases (C-S-H)

Keywords: class F fly ash, Portland cement, hybrid binders, geopolymers, water resistance, compressive strength, water resistance, water absorbtion

1. Introduction

A great interest among scientists and industries in the application of alkali-activated binders [1–6], particularly, geopolymers [7–8] can be explained by a tremendous potential and availability of Class F fly ash, a coal combustion by-product, which is as a cheap source of pozzolan and supplementary cementitious materials as well as a main component for zero-cement binding systems [9–14]. The broad spectrum of applicability of the binders driven by excellent in-service performance. However, the use of cheap off-spec materials results in production of construction composites with lower exploitation characteristic, which, therefore, limits their applicability.

Early studies [15, 16] showed that geopolymers based on low quality (i.e. low chemical reactivity) class F fly ash had lower strength and freeze-thaw performance.

Considering that geopolymers are "green" zero-cement binding systems and a very efficient approach for large-volume industrial by-products utilization it is important to look for new opportunities an effective application of off-spec materials [18, 19].

In the world practice it is common to incorporate different modifying agents and mineral admixtures into a binding system in order to upgrade the quality and in-service performance of materials [20-29]. Here, we are dealing with composite binders or "hybrid binders" in the case of geopolymers.

In the world of construction material science there is the term "hybrid material". One of the widely used area of usage of this term is paints consisting of clay and organic component, that were applied by Mayas ("Maya blue paint") [30–32].

The term "hybrid binder" is used for these systems due to its various chemical history and characteristics [33–35] as well as because of several mechanisms of structure formation involved which affect the performance of final product [36].

Along with numerous advantages of industrial by-products utilization, classical class F fly ash-based geopolymer systems have extremely low or zero water resistance, which classifies the materials to be not applicable to many outdoor applications such as geotechnical and transportation infrastructure.

This research is focused on study of basic in-service performance of hybrid geopolymer binding system "Class F fly ash – portland cement". Several mixtures were prepared and evaluated in terms of density and strength performance as we as water resistance and water absorption.

2. Materials and methods

2.1. Materials.

The Class F fly ash and sodium hydroxide NaOH pellets (with purity of 98%) were used in this research as main alumosilicate component and alkaline activator respectivelly for preparation geopolymer pastes. Portland cement CEM I 42,5N (supplied by Belgorod cement, Russia) was used as a modifying mineral admixture. The chemical composition of fly ash and portland cement presented in table 1.

2.2. Methods.

In order to evaluate the effect of portland cement admixture to density and strength pervormance as well as water absorption and water resistance of geopolymer binding system a finite element analysis with two factorial experiment was applied. The computation was performed using SigmaPlot software.

Table 1. Chemical composition of fly ash and portland cement.

№	Component	Oxides content, wt. %													
		SiO_2	Al_2O_3	TiO_2	Fe_2O_3	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5	NiO	V_2O_5	ZrO_2	LOI
1	Class F fly ash	58.98	28.29	0.97	4.63	0.08	1.00	3.74	0.63	0.65	0.36	–	0.02	–	6.07
2	Portland cement	22.49	4.77	–	4.4	–	0.44	67.22	–	–	–	–	–	–	0.23

Due to strucrural and crystallographic features of vitreous phase [8] class F fly ash shows a very low chemical reactivity with alkalies based on alkali metals, particularly, with NaOH.

3. Results and discussion

In the frame of this study two sets of specimens with a total of 18 mixes of hybrid geopolymer binder pastes were prsspared and molded into the 20x20x20 mm cubes. The first set of the specimens with 9 mixes was casted and placed in oven for 24 hours, where temperature was gradually reached 70 °C and then kept constant until the end of the treatment. After, the specimens were taken out from the oven and placed to cool down in laboratory environment followed by demolding and further storage at 22±3 oC and RH 35-40% until the testing. The second set of the specimens was cured in ambient conditions at at 22±3 oC and RH 35-40%.

For the design of experiment in hybrid geopolymer binder the cement content in the range of 0-40% was chosen as a controllable imput parameter X1 and the alkaline activator content in the range of 0-10% was X2. So that the cement as a modifying agent was added to the hybrid geopolymer system in the amount of 20 and 40 % and the amount of alkaline agent was added in proportions of 5 and 10% by total weight of solid cementitious component (table 2). Compressive strength and density of hybrid composites at the age of 9 days were the output parameters of the experiment.

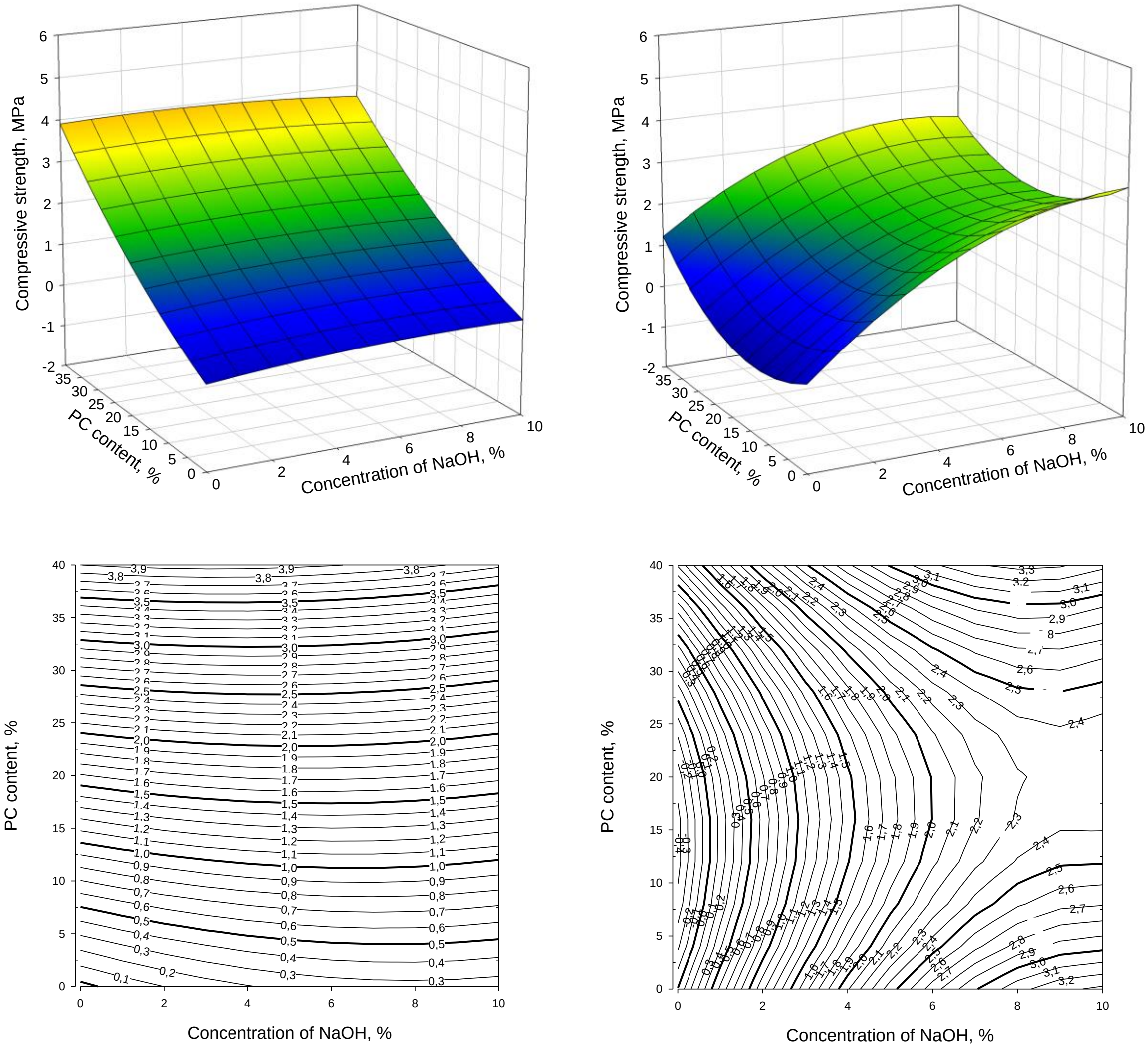
Table 2. Mix proportions of curing conditions

Mix ID	**Solid components, %**		**Activator, %**	***fc’*, MPa**	
	Fly ash	Portland cement	NaOH	Ambient conditions	Thermal treatment
1	100	0	0	0	0
2	80	20	0	1.5	0.37
3	60	40	0	3.9	0.5
4	100	0	5	0.5	1.7
5	80	20	5	2.1	1.7
6	60	40	5	3.7	3.7
7	100	0	10	0.8	4
8	80	20	10	1.3	1.6
9	60	40	10	3.9	3.2

The nomograms obtained from the two factorial design of experiment depicted in figures 1 and demonstrated that the geopolymer binders with and without portland cement in the system cured at different conditions responded noticably differently.

For classical “fly ash – NaOH – water” geopolymer binding systems in order to achieve satisfactory strength performance thermal treatment (or thermal drying) is required. With addition of cement powder as a modifying agent into the geopolymer system allows the elimination of thermal treatment and also leads to improvement of strength performance of up to 31% of the specimens cured under ambient conditions.

Such behavior can be caused by presence of some portion of hydraulic binder in the system responsible for a higher kinetics of structure formation. It is important to mention, that the hybrid geopolymer systems subjected to thermal treatment demonstrated almost the same strength performance as reference geopolymer binders. Thermal treatment causes an intensive water evaporation from the system and so prevents an effective hydration process.



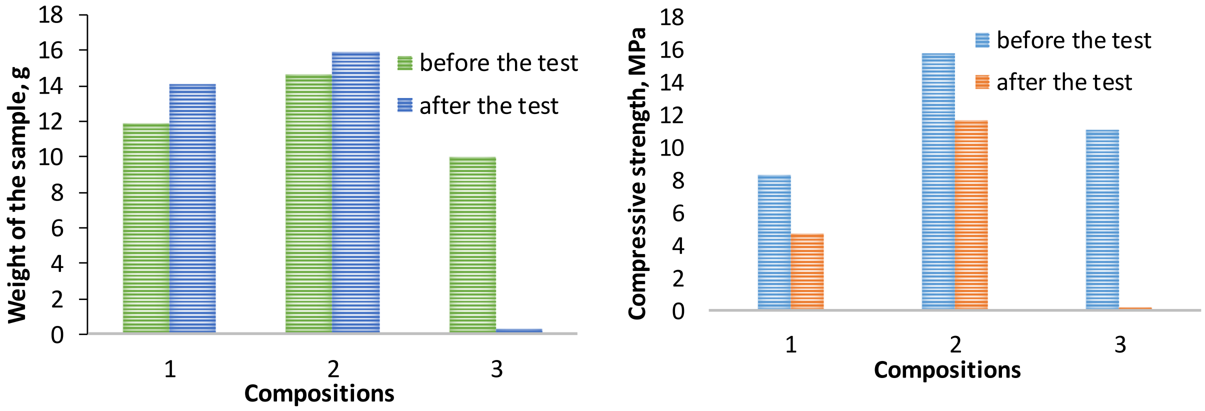
a b

Figure 1. The Effect of alkaline activator and PC content on compressive strength at a) ambient conditions; b) after thermal treatment

At the same time, geopolymerization of aluminosilicate-alkali media is intensified by temperature increase. Therefore, even an addition of up to 40% of cement into the geopolymer system which will be a subject to thermal treatment becomes detrimental in terms of strength performance.

Water resistance and water absorption of hybrid geopolymer binders

The effect of incorporation of portland cement as a modifying agent into fly ash-based geopolymer binding system was also evaluated in terms of water resistance and water absorption (figure 2, table 3). Three different mixes were prepared for this experiment which were the and a hybrid fly ash-based geopolymer binder with incorporation of 40% of portland cement (Mix 1), regular cement paste (Mix 2) fly ash-based geopolymer paste (Mix 3). After the mixes were places into molds they were stored at room temperature for 24 hours followed by thermal treatment at 70°C for another 24 hours and demolding after they cooled down to a room temperature. All specimens were testes for compressive strength at the age of 9 days.



a

b

Figure 2. The effect of portland cement incorporation into geopolymer binders on a) mass change and b) compressive strength performance

In order to evaluate water absorption response, the initial mass of the specimens was measured, and then they were placed in a water tank. The specimens were stored in such a way that the water level is slightly above the top surface of specimens. After storing in these conditions for 48 days at the temperature of 23±2 °C the mass of saturated with water specimens was measured.

In accordance with Russian standard GOST 12730.3-78 [37], water absorption was measured by mass change in % using formula (1):

$$W = \frac{m_1 - m_2}{m_1} \cdot 100 \qquad (1)$$

where m_1 – mass of dry specimen (g); m_2 – mass of specimen saturated with water (g).

Also, the parameters of water resistance of the prepared specimens were evaluated as a ratio of fc'_1 of dry specimen and fc'_2 specimen saturated with water using formula (2) [38]. For this experiment, specimens were placed in water tank so the water level is at least 20 mm above the top surface of specimens. The specimens were stored in such conditions for 48 hours at room temperature. For compressive strength test the specimens were taken out of the water tank, the excess of water was removed with wet cloth and then specimens were crashed to record strength data.

$$K = \frac{f_{c'2}}{f_{c'1}} \qquad (2),$$

where, fc'_1 – compressive strength of dry specimen, MPa;
fc'_2 – compressive strength of specimen saturated with water, MPa.

Materials are considered to be water resistant if the K value higher than 0.8.

As expected, Mix 2, which a portland cement paste performed very well in terms of strength before and after water saturation with a minimal mass change. However, Mix 3, a reference fly ash-based geopolymer paste completely failed after storing in water conditions, demonstrating a zero water resistance.

Table 3. Performance of developed hybrid geopolymer binders

Parameters	**Mix ID**		
	Mix 1	**Mix 2**	**Mix 3**
Water resistance, K	0.74	0	0.56
Water absorption, %	8.5	100	18.4
Compressive strength, MPa			
- normal conditions	8.3	15.7	11.1
- water saturated	4.6	11.7	0.2

The experimental data for Mix 1 demonstrated that the incorporation of cement powder in amount of 40 % as a modifying agent into class F fly ash-based geopolymer binding system results in reduction of water absorption of up to 82% and, also helps to improve water resistance of up to 56%.

An extremely low or zero water resistance geopolymer binders based on class F fly ash with low chemical reactivity, usually, related to presence of non-reacted fly ash in considerable amount and formation of water soluble sodium carbonates and hydroxycarbonates in the binding system as a reaction of alkaline activator and carbon dioxide, captured from atmosphere. The incorporation of portland cement into the geopolymer system causes the formation of water resistant and with higher strength calcium hydrosilicate (C-S-H) phases, typical for portland cement-based systems. This phenomenon explains an apparent improvements of strength performance as well as water resistance of the developed hybrid geopolymer binders.

4. Results and discussion

The incorporation of portland cement powder as a modifying agent into class F fly ash-based hybrid geopolymer binding system positively affects hydration reaction at ambient conditions and results in up to 30% strength improvement. Also, the developed hybrid binders demonstrated reduced water absorption and improved up to 50% water resistance vs. reference class F fly ash-based geopolymer binders, which is related to formation of water resistant and stable calcium hydrosilicate phases (C-S-H), typical for portland cement-based systems.

The incorporation of up to 40% of portland cement into geopolymer system cured at ambient conditions demonstrated a very similar strength performance vs. reference class F fly ash-based geopolymer binder cured at high temperatures.

However, while thermal treatment is favorable for classical class F fly ash-based geopolymer systems, it considerably diminishes the positive effect of portland cement in the system due to intensive evaporation of water required for hydration reaction.

Thus, the developed hybrid binding system with incorporation of up to 40% of portland cement can considerably reduce the negative effect of low chemical reactivity of class F fly ash and, so provide a considerably better in-service performance, which opens the door for wider outdoor construction application.

In addition, the elimination of thermal treatment from technological process will help to reduce ecological footprint by reduction of heat release and CO_2 emission into the atmosphere.

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