Effect of Mixing Procedure and Chemical Composition on Physical and Mechanical Performance of Geopolymers

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Abstract. Nowadays geopolymer is promising and relevant material that can be effectively used in wide range of application areas. It is possible because of there are a lot of potential sources of raw materials for geopolymer synthesis. Raw components are the one of the key parameters that effect on geopolymer performance. On the other hands, the technological stages of geopolymer synthesis is no less important factor.

The purpose of this study was to determine effect of technological parameters of geopolymer synthesis such as component composition of solid state phase, alkaline activator preparation and its introduction onto geopolymer paste as well as curing temperature on performance characteristics of geopolymer.

Fly-ash based geopolymer samples were prepared with adding of different mineral components: Portland cement (PC), kaolin, metakaolin; different curing temperature conditions: ambient temperature and temperature treatment at 70 °C in oven during 24 hours; different methods of preparation and application of alkaline activator: using of fresh alkaline solution and using alkaline solution after 24 hours of cooling.

The results show that efficiency of curing temperature conditions strongly depend on component composition of geopolymer paste. Samples, containing PC and metakaolin demonstrate better characteristics after curing under ambient temperature. Samples, containing kaolin and reference composition (fly ash only) the temperature treatment in oven is the best curing method (increasing in compressive strength up to 13 times).

Using alkaline solution of NaOH after 24 hours of cooling gives a good effect on geopolymerization process and provides increasing in compressive strength value from 13 to 84 % for all experimental geopolymer pastes. However, average density for all compositions is varied slightly.

Introduction

Normally, process of geopolymerization is initiated by chemical reaction between aluminosilicate component and alkaline activator, that contains oxides of alkaline elements (Na^+, K^+) [1–10]. Review of a lot of reports and experimental data, allows proposing the basic parameters of effective geopolymer synthesis (see Figure 1).

According to Fig 1., parameters effecting on geopolymerazation process and quality of geopolymer material are, mainly, depends on characteristics of raw materials and curing conditions. So, the main parameters are the followings:

– Aluminosilicate composition of solid phase component with SiO_2/ Al_2O_3 in range of 1.5–2.5;

– Concentration of alkaline-earth elements (CaO, MgO) is 10 %, no more;

–Vitreous phase content in aluminosilicate component is 50–60 % at least;
– Presence of iron, calcium, and inert particles in fly ash [11].
– Curing under heated temperature to accelerate structure formation and consolidation processes.

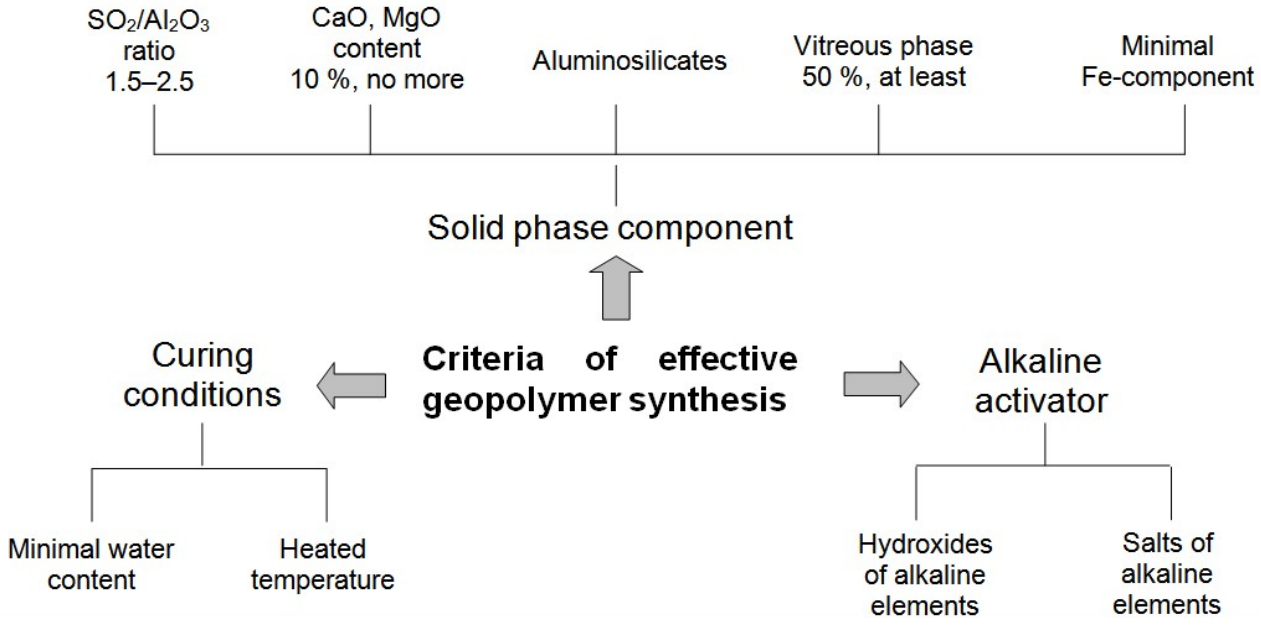


Fig. 1. Criteria of effective geopolymer synthesis according to [12–18]

According to widely accepted idea of geopolymer synthesis, the first stage of geopolymerization is alkali activating of aluminosilicate component. Here, initiating by alkaline cations the solution of aluminosilicate particles and its dissociation up to elementary units such as silicon–oxygen and aluminum-oxygenous tetrahedrons takes place.

Next stage of geopolymerization is formation of dimensional alkali-aluminosilicate framework (hydrogel).

Solution of solid phase aluminosilicate up to silicon–oxygen and aluminum-oxygenous ions and transformation of them onto liquid phase is the most important stage that influents on solidification kinetics of geopolymer. So, more reactive alkaline activator for certain aluminosilicate component initiates more intensive and full chemical reaction and provides faster strength development as well as formation of increased strength characteristics.

In literature there are data of using of different alkaline components as a geopolymer activator.

Normally, alkaline salts and alkaline oxides or hydroxides are used as an activator for synthesis alkali-activated cements, including geopolymer. These activators according to [19]:can be classified on following six groups upon chemical composition:

1. Alkali hydroxides: MOH
2. Salts of weak acids:M_2CO_3, M_2SO_3, M_3PO_4, MF, etc.
3. Silicates: $M_2O{\cdot}nH_2O$
4. Aluminates: $M_2O{\cdot}nAl_2O_3$
5. Aluminosilicates: $M_2O{\cdot}Al_2O_3{\cdot}(2\text{-}6)SiO_2$
6. Salts of strong acids: M_2SO_4

Among the all alkaline activators the leaders are the followings: NaOH, KOH, Na_2CO_3, $Na_2O{\cdot}nSi_2$ y Na_2SO_4. Application some of the above ones, for exp., K-based activators is notably limited because of its unavailability and high cost. By the other hands, K- and Na-based alkaline components are identical in reactional characteristics. They can used in solid and liquid state.

For exp., fly ash based geopolymers, with complex alkaline activator complexes such as NaOH-Na_2SiO_3 and NaOH-CaO demonstrate tensile strength values up to 4 MPa [20].

Some of studies [21, 22] report effective alkaline activation of blast furnace slag and fly ash with water glass Na_2SiO_3 and its combination with NaOH. The obtained alkali-activated cements by this activation are characterized by high values of compressive strength in range of 40–94 MPa.

Kovtun M. etc. [23].experimentally determined that using of sodium carbonate as an activating agent for low-reactive blast furnace slag initiates acceleration the consolidation process in binding system at ambient temperature and simultaneously increases the values of compressive strength from 2.5 MPa to 15 MPa.

Of course, the most preferable to use activating alkaline component that presents in structure of aluminosilicate raw materials [24, 25].

As an example of such aluminosilicate can be noted natural material – perlite. It can contain up to 10 % of cations of alkaline elements in form of Na_2O and K_2O oxides.

The presence of alkaline cations in aluminosilicate component allows avoiding the introduction of an additional amount alkaline activator or its reducing ,saving relatively high compressive strength values (up to 37 MPa). In addition, the presence of Na^+ and K^+ cations in the structure of perlite explains the equally effective use of alkali NaOH and KOH as perlite based geopolymer activators [26].

It should be noted that, studies devoted to geopolymer synthesis, are focused not only on choice of alkaline activating agent. Considerable interest is oriented to the method of its preparation and introduction into solid-phase aluminosilicate substance as well.

In the literature there are 3 methods of introducing an alkaline component:

- mixing of solid phase aluminosilicate and alkaline components with further mixing of the mixture with water [27].
- preparation of an aqueous alkali solution and its subsequent introduction into the aluminosilicate mixture [28]
- preliminary exposure of aqueous alkali solution after preparation for 24 hours, followed by adding into the aluminosilicate mixture [29]
- activation of alkaline components that presents in aluminosilicate raw materials (exp., perlite) by grinding [11].

Curing conditions of the geopolymer paste is also one of the main parameters that affect the consolidation rate, formation of the structure and operational characteristics of the hardened geopolymer paste. Curing conditions, normally, depend on the type of aluminosilicate component. In the literature, the most common conditions are moisture-humidity treatment [30], drying in an oven [31], ambient conditions [32, 33].

The purpose of this investigation was to study the influence of component composition of geopolymer paste, method of alkaline activator preparation and curing conditions on the physical and mechanical properties of geopolymer binders with different compositions.

Materials and methods

To synthesize the geopolymer binders, sodium hydroxide NaOH (98 % of purity) and the following solid-phase components were used in the study: type F fly ash (FA), kaolin (K), metakaolin (MK). MK was synthesized in laboratory conditions by calcination of kaolin in a muffle furnace for 2 hours at 700 ° C and Portland cement CEMI 32, 5N (PC).

The specific gravity of the used solid-phase raw materials was determined with a ATC helium pycnometer Pycnomatic (Thermo Fisher Scientific, Italy).

The specific surface area (SSA) was measured using a Blain machine PSH-12 (SP) (Russia).

The chemical composition of the raw materials was determined with a WorkStation ARL 9900 X-ray workstation using Co-anode radiation.

The microstructure of solid-phase raw materials was studied with a Mira 3 FesSem scanning electron microscope (Tescan, Czech Republic) operating in high vacuum (InBeam) using a high-brightness Schottky cathode. The samples were filmed with chromium.

Data of chemical composition, microstructure and basic physical characteristics of the used solid-phase mineral components are presented in Tables 1 and 2 and on Figure 3.

Table 1. Basic physical characteristics of the used solid phase components

№	Solid phase	Parameters

1	FA	1870	290
2	PC	3050	320
3	K	2610	1091
4	MK	2520	1170

Table 2. Chemical composition of the used solid phase components

Solid phase component	Oxides content, wt. %											
	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	K_2O	MgO	CaO	P_2O_5	SO_3	N_2O	LOI	$\frac{SiO_2}{Al_2O_3}$ ratio
FA	58.98	28.29	4.63	0.97	0.65	1	3.74	0.36	–	0.63	6.07	2.08
PC	19.13	5.21	3.58	0.32	0.6	1.28	65.38	–	3.47	–	0.23	3.67
K	53.8	43.4	1.02	0.58	0.56	0.21	0.01	0.06	–	0.03	4.2	1.3
MK	53.1	42.8	0.7	0.3	0.9	–	0.15	–	–	0.02	0.4	1.24

Granulometric (particle size destribution) analysis of the solid-phase components was carried out using a laser analyzer ANALYSETTE 22 NanoTec plus (Germany). Results are shown in Figure 2.

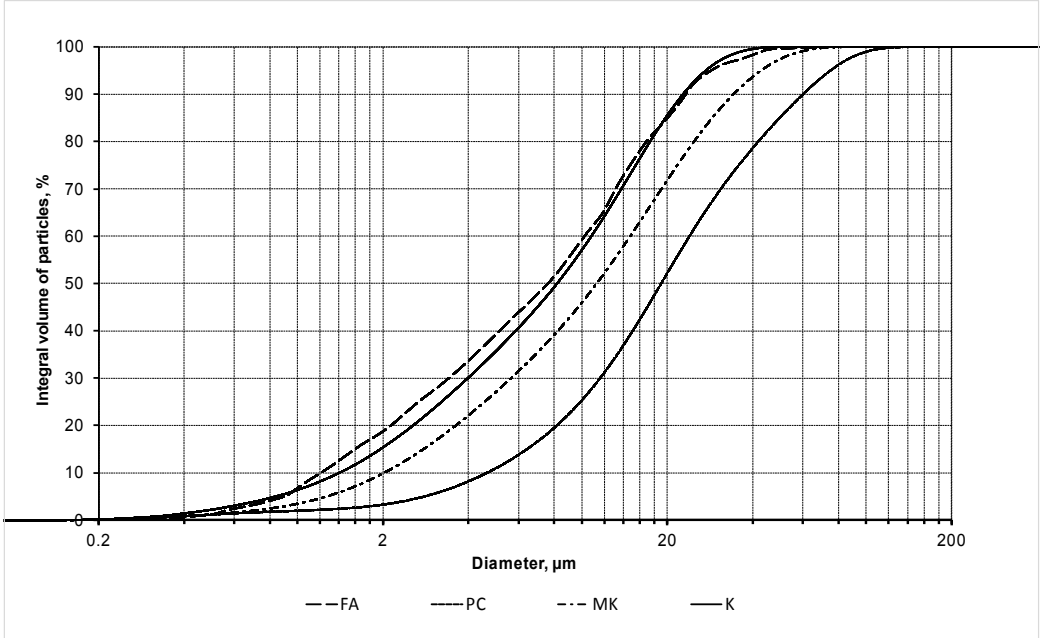
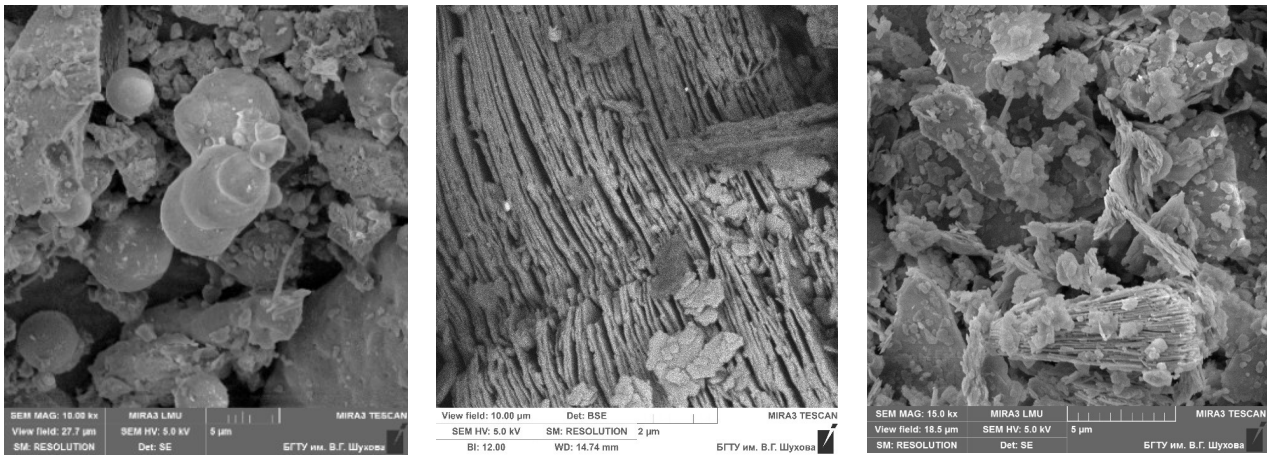


Fig. 2. Granulometric analysis of the solid-phase components

The results of the particle size distribution analysis (Figure 2) demonstrated that the range of size distribution for all used materials is from 2 to 90 microns. Portland cement size distribution is slightly differed. The particle size distribution curve is placed in size range from 2 to 150 microns.

The results of particle size distribution analysis are confirmed by SEM images presented on Figure 3.



a b c

Fig. 3. Microstructure of raw aluminosilicate materials: a - FA; b - K; c- MK

Results and discussions

Effect of curing conditions

The experimental compositions of geopolymer pastes were molded in two batches. The first batch was hardened under ambient laboratory conditions (at room temperature and natural humidity). The second batch was exposured to heat treatment (heat drying) in oven at 70 °C for 24 hours, followed by hardening under ambient laboratory conditions. The obtained results are presented on Figure 4.

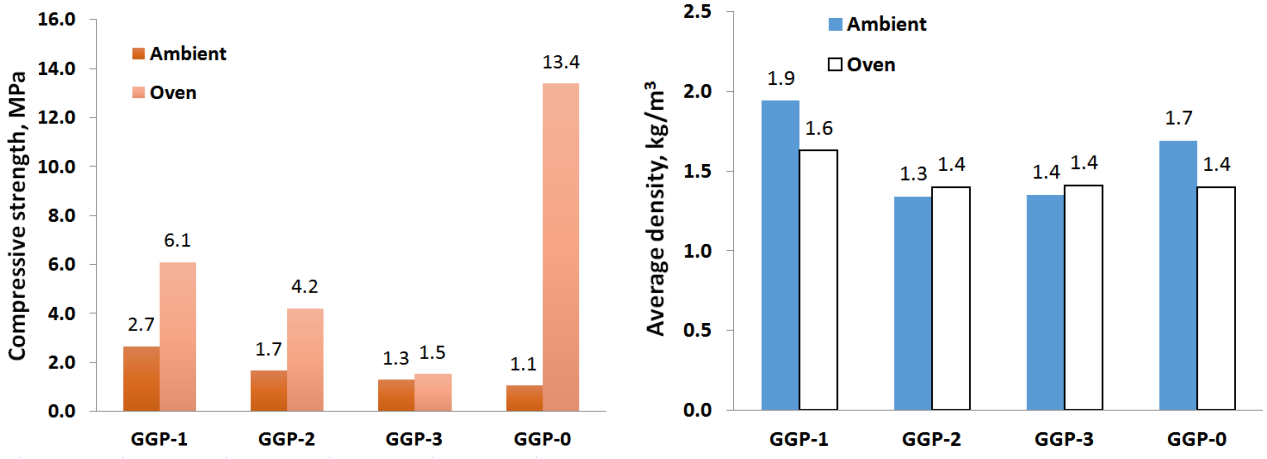


Fig. 4. Effect of curing conditions on characteristics of geopolymer paste

On Figure 4 the low strength values for the composition of GGP-3, that contains metakaolin stick out. These results are in conflict with the generally accepted concept that metakaolin is the most effective raw material for the synthesis of geopolymers both from the point of view of constant chemical composition and degree reactive activity.

However, an additional literature review allows to explain the observed phenomenon.

A number of recent studies [34–38] established and experimentally confirmed that the chemical composition of metakaolin, namely, the ratio of the main oxides of the geopolymer system, in particular the SiO_2 / Al_2O_3 ratio, is crucial in the formation of strength values of the final geopolymer paste. According to [34], the most effective range of SiO_2/Al_2O_3 ratios is varied from 2.75 to 3.75. That provides the compressive strength of the hardened stone from 20 to 62 MPa. Comparison of the results of studies reported in the study [34] and the values of the SiO_2 /Al2O_3 ratio for metakaolin applied in this work (SiO_2/Al_2O_3 = 1.24), gives a logical explanation for the obtained low strength values for metakaolin-containing geopolymers paste (Figure 4).

In addition, using the data, reported in [39, 40], geopolymers synthesized with using or based on metakaolin demonstrate a tendency for a sharp transition of the structure from amorphous to zeolite-like crystalline when curing under heated temperature. This effect causes the destruction of alkali-aluminosilicate gel, leading to a loss of strength of the composite.

Methods of alkaline activator preparation and introduction

The purpose of this study was to establish the influence of the method of alkaline activator preparation and introduction into geopolymer paste on physical and mechanical properties of geopolymers.

To synthesize the experimental geopolymer compositions, alkaline aqueous solutions prepared by two methods were used (Figure 5).

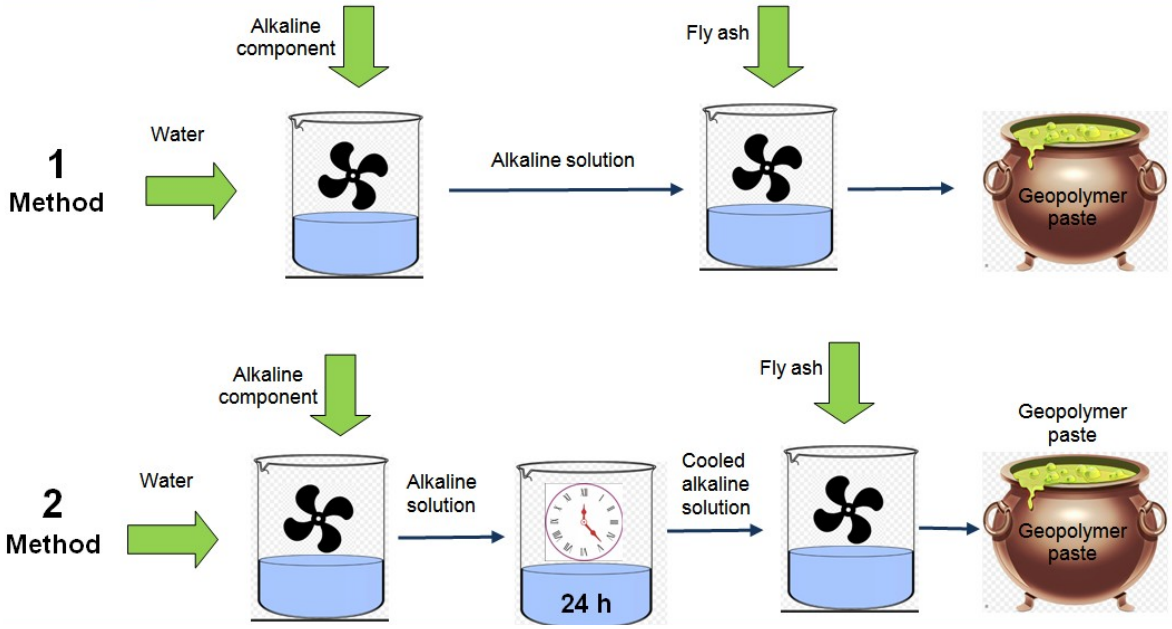


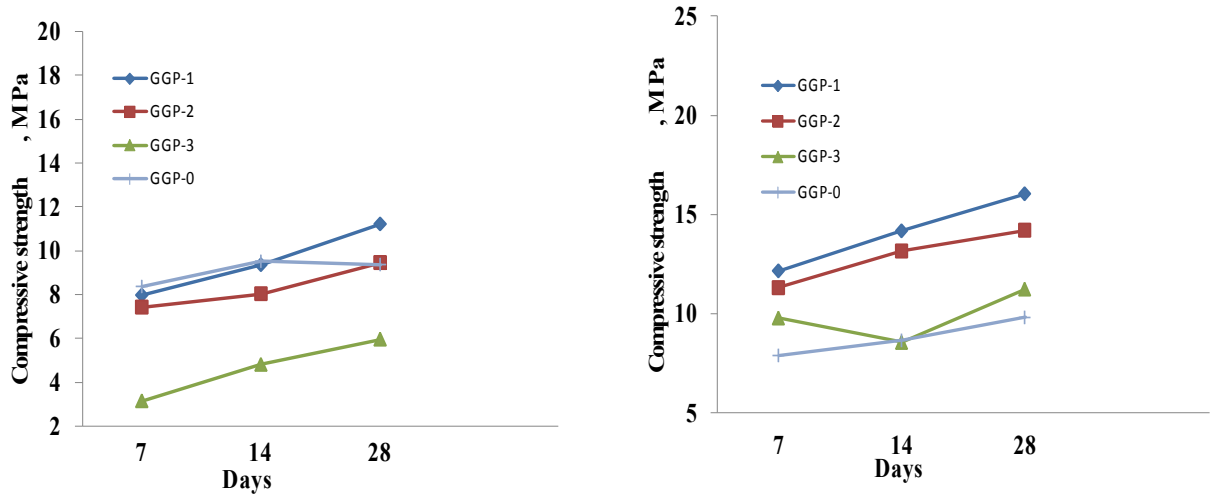
Fig. 5. Methods of alkaline activator preparation and introduction into geopolymer paste

Using the alkaline solutions obtained by methods 1 and 2 (Figure 5), the 4 compositions of geopolymer pastes were molded. The experimental compositions are presented in Table 3.

Table 3. Compositions of experimental geopolymer pastes

Composition	Components, g					
	FA	PC	K	MK	NaOH	Water
GGP-1	60	40	-	-	5	40
GGP-2	60	-	40	-	5	45
GGP-3	60	-	-	40	5	45
GGP-0	100	-	-	-	5	45

The curing regime of the molded samples consists of the following stages: the molded geopolymer samples were left for 1 day in the laboratory room under ambient conditions. Then, they were placed in oven for heat treatment for 24 hours at 70 ° C.



1 2

Fig. 6. Method of alkaline activator introduction onto geopolymer paste vs. compressive strength

Tests of samples for density and compressive strength were carried out at the age of 7, 14, 28 days.

The results of the data obtained are shown on Figures 6 and 7.

Analysis of the obtained data of density and compressive strength, demonstrated that the aging of the alkaline solution during 24 hours before its using has a positive effect on the physical and mechanical properties of all experimental geopolymer pastes. Increasing in compressive strength in the range of 13 to 84 % takes place. Decreasing in compressive strength is observed in GGB-1 samples (that contains a PC) vs. samples with the same composition, but without alkaline activator cooling during 24 hours, only.

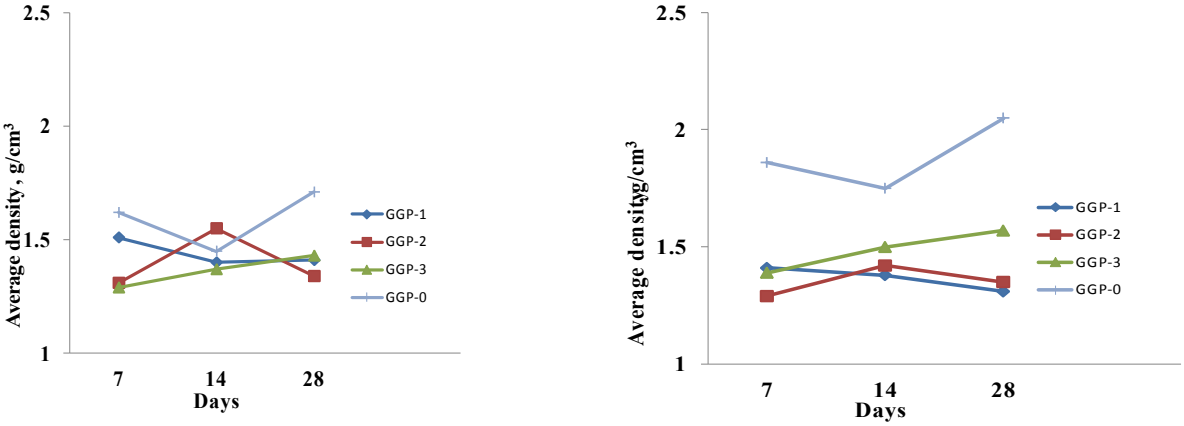


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Fig. 7. Method of alkaline activator introduction onto geopolymer paste vs. average density

The results presented in Figure 7 showed that cooling during 24 hours of the alkaline solution during 24 hours before its using leads to increasing in average density for reference composition GGP-0 from 1.7 to 2.1 kg/m^3, as well as for the GGP-3 sample from 1.3 to 1.6 kg/m^3. For the others samples, the average density values remained almost unchanged.

Based on all the above results (Figures 6, 7), it can be concluded that aging of the alkaline solution during 24 hours before its using has a positive effect on compressive strength values of geopolymer samples and almost does not affect the average density.

Summary

It was determined that the curing conditions of geopolymer pastes extremely depend on the component composition. In geopolymer systems containing PC and MK, the curing under ambient temperature is the most preferable. For reference geopolymer paste (based on fly ash only) and compositions with kaolin, the thermal drying conditions initiates increasing of compressive strength (approximately, up to 13 times).

Also, it was found that cooling of the alkaline solution of NaOH during 24 hours before its using favorably affects on geopolymerization processes, providing more monolithic and impact structure, and also provides increasing in strength characteristics from 13 to 84 %. By the other hands, this parameter almost does not affect the average density.

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