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Influence of the activator nature on mechanical properties of fly ash-based geopolymer

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***Abstract** : Geopolymers are included in the group of low-emission materials called "low-carbon" binders. The amount of CO_2 generated during production of the material may be reduced to only 10% of the CO_2 emitted during production of Portland cement, which explains the increasing interest of the construction industry in this type of binders. This paper presents a comparative study concerning fly ash-based geopolymers prepared with different formulations of activators. For aluminosilicate activation, most commonly available water glass mixed with sodium hydroxide pellets was used, as well as a specially developed aqueous silicate solution Geosil ®. The same molar ratio was used for both activators. Two geopolymer mortars were tested and compared in the aspect of their mechanical properties. Tests were made on geopolymer mixes based on fly ash (FA) with the addition of ground granulated blast furnace slag (GGBFS), with the additives constituting 10, 30 and 50%, respectively. The investigations enabled demonstration of the effect of different nature of activator on the mechanical performances at 2, 7 and 28 days. Test results show that both geopolymer mortars have obtained similar strengths. The use of a ready-made industrial activator facilitate the mix preparation process, and makes it safer due to the limited handling of NaOH pellets.*

***Index Terms** : activator, fly ash, geopolymers, fly ash, GGBFS, mechanical properties*

I. INTRODUCTION

Geopolymers are a group of low-emission mineral binders that are an exciting alternative to traditional cementitious binders in some uses [1], [2]. In the process of geopolymer synthesis, metakaolin or waste products from the energy sector, such as fly ash (FA) and ground granulated blast furnace slag (GGBFS), are used [3], [4]. Using waste products in the process of synthesis of new binders is particularly interesting from the perspective of minimising the environmental impact [5]. The cement production process is highly energy-intensive and it is also associated with high carbon dioxide emissions. The amount of CO_2 generated during production of the material may be reduced to only 10% of the CO_2 emitted inproduction of Portland cement. Given the growing requirements for reducing greenhouse gas emissions, it is necessary to develop technologies that enable at least partial reduction of the harmful impact of human activities on the environment. Geopolymer binders offer such possibility [6]. The geopolymer production process is less energy-consuming compared to cementitious binder production [6], [7]. Besides, geopolymer binders are characterised by high mechanical strength and high resistance to aggressive environmental factors, [8], [9], [10]. The geopolymer binder is produced as a result of the reaction of fine-grained raw material containing silicon and aluminium oxides with an alkaline solution [11]. Both components determine the properties of the resultant binder [12]. The most frequently used alkaline solutions are sodium or potassium silicate solutions mixed with sodium or potassium hydroxide [13]. The type of alkaline solution that has been used affects the physical parameters and strength of the material [14], [15], [16]. Research indicates that strength increases

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following the increase in metal hydroxide concentration and that the strength of geopolymers with sodium alkaline solution is higher than with potassium solution [13], [17]. Studies [18] show that an increase in the amount of sodium silicate and sodium hydroxide causes an increase in the level of geopolymerization and, as a result, an increase in compressive strength is observed. The results of studies on geopolymer binding mechanisms [19] show that the molar ratio (MR) of the alkaline solution is an essential factor in the geopolymer hardening process. When using solutions with a lower MR value, the condensation reaction between silicon and aluminium oligomers is faster and the material setting time is shortened, which also shortens the workability of the mix. For geopolymer mortars, the degree of networking of the material mainly depends on the irreversible chemical reaction. The use of an alkaline solution with lower reactivity reduces the degree of networking of the material and influences the mechanical strength of the produced material. The most commonly available sodium silicate has the molar modulus of about 2.6. For the production of geopolymers, it is necessary to use solutions with a lower module. Hence the need to lower the module with a sodium or potassium hydroxide solution. To limit the onerous process of regulating the molar module of water glass with sodium hydroxide, the researchers tested a specially developed aqueous silicate solution dedicated for geopolymer materials from the Geosil® line (Geosil® 34417 - sodium silicate) offered by Woellner. The Geosil® product contains specially formulated aqueous silicate solutions for the alkaline activation of reactive mineral fillers. The aim of the study was to compare the properties of fly ash-based geopolymer mortars made with the addition of GGBFS produced with the use of two different alkaline solutions. A mixture of sodium hydroxide pellets and sodium silicate solution was prepared, and the effect on the geopolymer mortar was compared with the Geosil® product from Woellner. The study aimed to show the supposedly inevitable differences in the obtained strength between the material, with the assumption that both solutions had a similar molar ratio.

II. MATERIALS

Geopolymer binders were based on fly ash class F, acc. to ASTM C618-12a from "Połaniec" Power plant with a varying addition of ground granulated blast furnace slag (GGBFS). Three ratios of GGBFS were used: 10%, 30% and 50%, as partial replacement of fly ash content. The oxide compositions in both raw materials are shown in Table 1 below.

Table 1. Composition of fly ash (FA) and ground granulated blast furnace slag (GGBFS)

Oxide	FA	GGBFS
SiO_2	52.30	39.31
Al_2O_3	28.05	7.61
Fe_2O_3	6.32	1.49
CaO	3.05	43.90
MgO	1.71	4.15
SO_3	0.28	0.51
K_2O	2.51	0.36
Na_2O	0.76	0.47

The fly ash (FA) and ground granulated blast furnace slag (GGBFS) used in the research have the specific gravity of 2.1 g/cm^3 and 2.9 g/ cm^3, respectively. Siliceous sand (0/2 mm) was also used to prepare the geopolymer mortars. The composition of the mortars was designed based on previous research results [20], [21]. For the purposes of comparison, two different alkaline solutions were used. The first was the specially developed aqueous sodium silicate solution Geosil® 34417 and the second was prepared as a mixture of sodium silicate solution "Chempur" (Na_2O = 11.1%, SiO_2 = 27.9%, H_2O =

61.0%) and sodium hydroxide. Both solutions were characterised by molar ratio MR=1.7. The compositions of the prepared mortars are shown in Table 2. The constant sand to binder (FA+GGBFS) ratio s/b=1.5 and water to binder ratio w/b = 0.3 were applied to all mortars.

Table 2. Compositions of geopolymer mortar per 1m³

Components	**G 10** [kg/m³]	**G 30** [kg/m³]	**G 50** [kg/m³]
Alkaline solution	334.0	340.6	347.5
Fly ash (FA)	667.9	529.8	386.1
GGBFS	74.2	227.1	386.1
Sand	1113.2	1135.3	1158.3

III. METHODOLOGY

The mortars were prepared according to the procedure recommended by Davidovits. Alkaline solutions were prepared 24h before starting the mixing. In the case of a mixture of sodium silicate and sodium hydroxide, NaOH pellets in water were first dissolved and then mixed with sodium silicate. The total amount of water used to mix the mortars was also added to the solutions. Containers with solutions have been closed to protect water evaporation. In the second step, a geopolymer binder was prepared to begin with mixing the FA with alkaline solution for 10 min, and then GGBFS was introduced and mixed for another 5 min. At the end of the mixing process, siliceous sand was added, and the mortar was mixed for 3 minutes. The workability of all mixtures allowed for adequate mixing and casting. The samples were cast in plastic moulds 40x40x160 mm and compacted on a shaking table. The samples were cured at ambient temperature (18°C±2°C) and the moulds used were also equipped with plastic lids. After one day, the samples were removed from the moulds and stored in laboratory conditions (T = 18°C±2°C, HR = 75%) until the mechanical tests were performed. The samples were able to exchange moisture with surroundings. To determine the impact of the alkaline solution on the test materials, half of all the samples were prepared with Geosil® and the rest with sodium silicate and sodium hydroxide solution. The following nomenclature was used to name the mixes Geosil® and Nasil.

The mechanical performances: compressive strength and flexural tensile strength were determined after 3, 14 and 28 days of curing. The mechanical properties of hardened mortars were tested on three samples and also the development of those parameters over time was observed. The specimens were tested in three-point bending with a constant load rate (50N/s) to failure. For the determination of compressive strength, the remaining mortar prisms from the bending test were used. The samples were tested on a hydraulic press with constant load rate (2400N/s). Mechanical parameters were obtained according to the standard procedure applicable to cement mortar. Besides, before each mechanical test, bulk densities of materials were controlled to monitor the evolution of this property during curing. The direct method was used based on the mass and dimensions of the samples.

IV. RESULTS AND DISCUSSION

Bulk density

The Fig. 1 shows the evolution of bulk density over time for samples prepared with different alkaline solution Nasil NaOH and Geosil. A decrease in bulk density over time was observed in all samples. The weight loss is caused mainly by drying. The observed differences in density between mortars with different alkaline solutions were small. After two days, the bulk densities of mortars made with sodium silicate and sodium hydroxide solutions were 2.09 g/cm³, 2.13 g/cm³ and 2.21 g/cm³ for G10, G30 and G50, respectively. In the case of mortars made with Geosil®, it was 2.05 g/cm³, 2.14 g/cm³ and 2.22 g/cm³ for samples with 10, 30 and 50% GGBFS, respectively. After 28 days, the densities reached 2.05

g/cm³, 2.07 g/cm³ and 2.18 g/cm³ for G10, G20 and G50, respectively. Similar values were noticed for samples prepared with Geosil: G10=2.01 g/cm³, G30=2.11 g/cm³, and G50=2.20 g/cm³. The results do not show any evident influence of the activator nature on the density of the material.

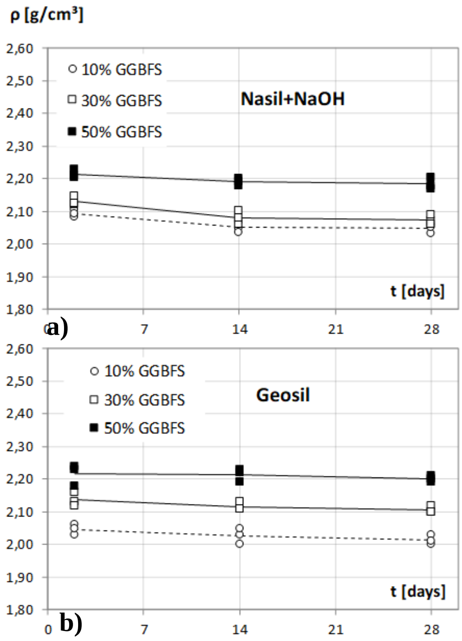
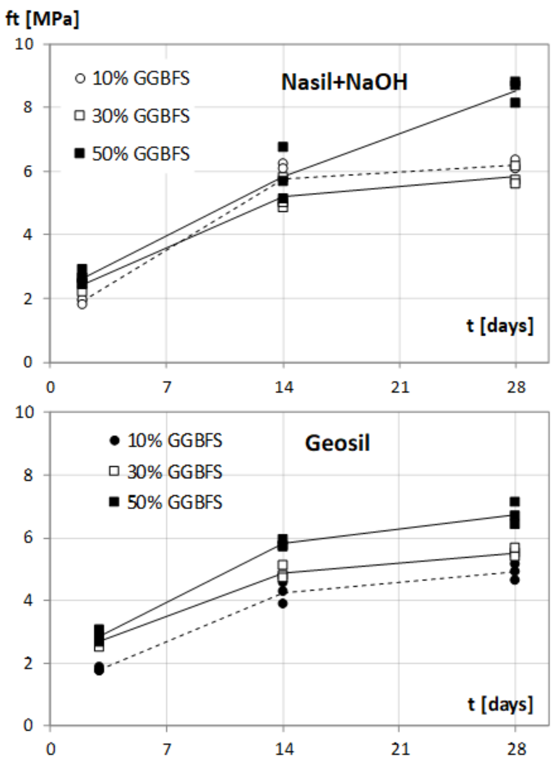


Fig. 1 The comparison of geopolymer mortar densities a) Nasil; and b) Geosil®

Flexural tensile strength

The flexural tensile strength results for FA-based geopolymer mortars with GGBFS addition prepared with two different types of sodium alkaline solutions are presented in Fig. 2.

a)



b)

Fig. 2 Evolution of flexural tensile strength in the function of curing time a) Nasil; and b) Geosil ®.

At the initial stage of curing, after two days, the flexural tensile strength values were very similar,

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irrespective of the type of alkaline solution that had been used. The flexural tensile strengths after two days were about 1.8 MPa, 2.5 MPa and 2.8 MPa for mortars with 10%, 30%, 50% GGBFS, respectively. After 28 days of curing, the differences were slightly more visible, especially for samples whose binder contained 50% of GGBFS. After 28 days, flexural tensile strength values for samples with sodium silicate and sodium hydroxide solutions reached 6.2 MPa, 5.8 MPa and 8.5 MPa for G10, G30 and G50, respectively. For comparison, samples with Geosil® solution obtained 4.9 MPa, 5.5 MPa, 5.8 MPa for binders containing 10, 30 and 50% of GGBFS, respectively. Apart from the type of alkaline solution that has been used, the GGBFS content also affects the bending strength. It has been observed that the increase in the amount of GGBFS in the binder composition is accompanied by an increase in flexural tensile strength.

Compressive strength

Fig. 3 shows the evolution of compressive strength in function of curing time for samples with different GGFBS contents and different type of alkaline solutions.

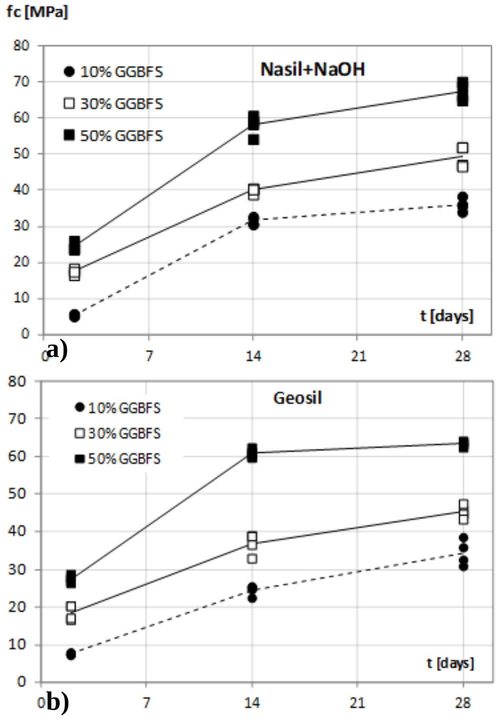

Fig. 3 Compressive strength in the function of curing time a) Nasil b) Geosil®.

Development of compressive strength over time was observed in all cases. Similarly to flexural tensile strength, the differences in compressive strength were not very significant. After two days of curing, Nasil samples with 10, 30 and 50% GGBFS content, prepared with an alkaline solution containing sodium silicate and sodium hydroxide, achieved the compressive strength of 5.4 MPa, 17.5 MPa and 24.3 MPa, respectively. For comparison, samples with the Geosil® solution obtained 7.6, 18.6 and 27.4 MPa, respectively. After 28 days, both in the case of mortars prepared with sodium silicate and sodium hydroxide solutions and in the case of mortars made with the Geosil® solution, the highest strength was observed for mortars with the binder containing 50% FA and 50% GGBFS. In both cases, the average value of compressive strength was above 60MPa. We can observe a slight influence of the activator nature on the obtained value of compressive strength. However, the impact of GGBFS content was more visible. A higher GGBFS content in the mortar composition entails an increase in its mechanical strength.

V. CONCLUSIONS

The study aimed to estimate the influence of the activator nature on mechanical properties of the fly ash-based geopolymer. In this paper, we compared the development of flexural tensile strength and the compressive strengths of geopolymer mortars made with the use of two different sodium alkaline solutions. A solution was prepared (Nasil) – a mixture of sodium silicate and sodium hydroxide – was prepared and its effect on the geopolymer mortar was compared with the product of Geosil® manufactured by Woellner. Geosil® is a range of specially formulated aqueous silicate solution for alkaline activation of reactive mineral fillers dedicated specifically for geopolymers. Both alkaline solutions used had the same molar ratio, and the study aimed to show possible differences in the obtained strength between mortars prepared with two types of alkaline solution. Test results show that the mortars with Geosil® have obtained similar strength values to materials prepared with the blended alkaline solution. In both cases, the highest strength values were reached by samples with 50% addition of ground granulated blast furnace slag after 28 days of curing in ambient conditions – the average value of flexural tensile strength was above 6 MPa and the average value of compressive strength was above 60 MPa. The impact of the amount of slag used in the binder was much more visible. The increase in the amount of slag resulted in a noticeable increase in strength parameters, irrespective of the alkaline solution used. Apart from strength parameters, we should also pay attention to the technological advantages.

The use of a specially prepared industrial Geosil® product reduces the arduous process of regulating the molar ratio of alkaline solution and sodium hydroxide. As the results of the investigation have shown, the observed features and properties of the material were almost the same. The use of a ready-made industrial Geosil® product facilitates the mix preparation process and makes it safer because we limit the handling of NaOH pellets. The geopolymer preparation process is much safer for the user and thus increases the application potential of the produced material based on this type of alkaline solution. The availability of the low-module aqueous silicate solutions will undoubtedly promote the development of geopolymer technology and foster its growth in the construction sector.

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