

Properties of Alkali-Activated Fly Ash Mortars

Effect of NaOH Concentration in Activator Solution and Curing Time

[Izabela Hager, Mateusz Sitarz]

Abstract – Non-clinker alkali-activated aluminosilicate materials provide an interesting alternative to traditional cement materials. The study described was conducted in order to determine how increasing NaOH concentration in the activator solution affects the physical properties and strength parameters of geopolymer mortar. In the paper the development of strength over time was presented.

Keywords – geopolymers, non-clinker binders, alkali-activated fly ash mortars

I. Introduction

Geopolymers are amorphous, inorganic aluminosilicate polymers with peculiar composition and properties that resemble natural stone or concrete [1]. Geopolymers are a subset of a large group of alkali-activated materials and are compounds in which the binding phase is almost exclusively aluminosilicate-based and highly ordered. They are characterised by high Al content and low Ca content [2]. The geopolymerisation process is fairly complex and the exact mechanism that causes the formation of the geopolymer network and its subsequent curing is not yet fully understood. Intensive work is being carried out in many centres around the world in order to better understand the possibilities offered by geopolymer synthesis in the manufacture of durable construction products. The synthesis of geopolymers undoubtedly results in lower carbon dioxide emissions than the production of cement and is also a less energy-intensive process. Moreover, it allows post-process waste to be utilised. Industry and the energy sector generate large amounts of waste whose storage places a considerable burden on the environment and can result in water and soil pollution. Using waste to produce new materials is a solution that is both environmentally friendly and economical [3]. Fly ash and slag can in particular be used in the geopolymerisation process. The production of geopolymers makes it possible to take advantage of hitherto unutilised raw materials and to reduce environmental pollution levels at the same time. The use of geopolymer binders in the construction sector is becoming increasingly common [4]. Non-clinker geopolymer materials provide an interesting alternative to traditional cement materials.

The usual geopolymer production process follows the following scheme: Dried and crushed pozzolanic material (e.g. fly ash or metakaolin) is mixed with an aqueous solution of the appropriate silicate (e.g. sodium or potassium silicate) and then a strong base is added, usually concentrated sodium or potassium hydroxide. After all these ingredients have been mixed, a paste that resembles cement paste is formed, which solidifies after some time. The solidification process can be fully controlled. Depending on the technological solutions employed, the solidification process may last from around dozen seconds to a few or even several dozen hours [5]. In the geopolymerisation process, the role of the raw material is to provide a source of silicon and aluminum ions. On the other hand, the role of the activator is to dissolve the base raw material; it also acts as a binder and plasticiser [6].

II. Preparation of Specimens for Testing

A. Type and amount of activator

In geopolymer technology, the role of the activator is usually played by an aqueous solution of the appropriate silicate (e.g. sodium or potassium silicate) with the addition of a strong base, usually sodium or potassium hydroxide. The purpose of the activator is to accelerate the geopolymer synthesis reaction. The activator increases the polymerisation rate by decomposing the initiator into free radicals [5]. Sodium composites typically have higher compressive strengths than potassium materials [7]. The amount of activator used to produce geopolymer mortar affects its compressive strength [8,9]. As the amount of activator is increased, the compressive strength of the finished product increases as well [10,11]. It can be assumed that there is a specific threshold amount of activator in relation to the remaining geopolymer components that will result in the best strength parameters [12]. Our research was conducted in order to determine how increasing the concentration of NaOH in the activator solution affects mortar strength parameters. For the purposes of testing, three mixtures were prepared (Table III), containing 60, 80 and 100 g of sodium hydroxide; these were designated, respectively, as G60, G80 and G100. Geopolymers were produced on the basis of fly ash from the Połaniec power plant. This is typical siliceous fly ash obtained by burning hard coal. It is characterised by high vitreous phase content. The activator was prepared in three different variants in the form of mixtures of sodium silicate (water glass) with sodium hydroxide in fixed proportions. After mixing, the solutions were cooled at -5°C for 1.5 hours.

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B. Composition, forming and curing of test mortars

In this research fly ash Połaniec was used (Tabela I), a fine particulate with pozzolanic properties. It is built of spherical, spiked grains with a density of 1900-2100 kg / m³. It is produced in the combustion of coal dust from coal process. It is obtained by electrostatic or mechanical precipitation of dusty particles from the waste gases. The main components of fly ash are SiO₂ and Al₂O₃. In addition, the composition of the material is Fe₂O₃ and a small amount of MgO, K₂O, TiO₂, Na₂O. Total content of silicon dioxide, alumina and iron (III) oxide exceeds 70% [13]. Due to the chemical composition of fly ash Połaniec is classified as a siliceous ash with a high glassy phase content. The high content of SiO₂ in the ash composition influences the high pozzolanic activity of the material [14]. Ashes are also distinguished by a low loss of ignition at around 5%.

TABLE I. PROPERTIES OF POLANIEC FLY ASH [13]

Property	Testing method	Value
Loss of ignition	EN 196-2	5 - 7 %
fineness	EN 451-2/EN 933-10	≤ 40 %
Free calcium oxide	EN 451-1	≤ 1.5 %
Reactive calcium oxide	EN 196-2	≤ 10 %
Chlorides	EN 196-2	≤ 0.10 %
Content of sulfates (VI)	EN 196-2	≤ 3 %
Density of grains	EN 1097-7	1900-2100 kg/m ³
Activity indicator		
After 28 days	EN 196-1	≥ 75 %
After 90 days		≥ 85 %
Sum of silicon dioxide, alumina and iron (III) oxide	EN 196-2	≥ 70 %
Alkali	EN 196-2	≤ 5 %
Soluble Phosphates (V)	ISO 29581-2	≤ 100 mg/kg
Phosphates (V)		≤ 5 %

TABLE II. COMPOSITION OF THE ASHES OF THE POLANIEC AND JUXTAPOSITION OF INDIVIDUAL FRACTIONS

Fraction	0 - 15 μm	15 - 30 μm	30 - 45 μm	45 - 63 μm	63 - 100 μm	100-1000 μm
Percentage %	20.27	26.79	6.70	5.07	7.66	33.51
	100 %					
Loss of ignition	5.159	3.143	2.644	1.809	1.635	1.279
SiO ₂	49.846	51.625	51.807	52.979	53.540	53.960
Al ₂ O ₃	28.323	27.883	27.883	28.204	28.493	27.232
Fe ₂ O ₃	5.039	5.839	6.444	6.559	6.356	7.653
CaO	2.890	3.372	3.333	3.039	2.799	2.860
MgO	1.763	1.777	1.726	1.685	1.629	1.684
SO ₃	0.188	0.458	0.355	0.235	0.173	0.135
K ₂ O	2.796	2.443	2.460	2.416	2.452	2.400
Na ₂ O	1.111	0.791	0.689	0.607	0.565	0.543
P ₂ O ₅	0.855	0.733	0.711	0.648	0.590	0.578
TiO ₂	1.396	1.408	1.408	1.348	1.317	1.255
other	0.634	0.528	0.540	0.471	0.451	0.421

Based on a detailed analysis of ash composition (Tabela II), one notice, that the fractions 0-15 μm and 15-30 μm represent almost half of the composition of the test sample. Large particle size with small diameters is a desirable feature in high-end geophysers [15]. In turn, larger particle size fractions are characterized by higher silica content and lower loss of ignition.

In the first stage, fly ash was mixed with the activator; subsequently, quartz sand was added to the resulting binder and all components were mixed again. 40x40x160 mm prisms were formed and compacted on a vibrating table. Immediately after being formed, all specimens were heat-soaked at 80°C for 24 hours and subsequently cured in laboratory conditions until testing.

TABLE III. COMPOSITION OF TESTED GEOPOLYMER MORTARS

Component	G 60	G 80	G 100
Fly ash [g]	800	800	800
Sodium silicate [g]	300	300	300
Sodium hydroxide [g]	60	80	100
Water [g]	150	150	150
Sand [g]	1,350	1,350	1,350
Plasticiser [% vol.]	1	1	1
Binder [% vol.]	0.66	0.67	0.68

III. Results

At 7 and 28 days after specimen formation, bulk densities of the materials tested were determined (Figure 1), followed by flexural tensile strength (Figure 2) and compressive strength testing (Figure 3); the development of both types of strength over time was analysed.

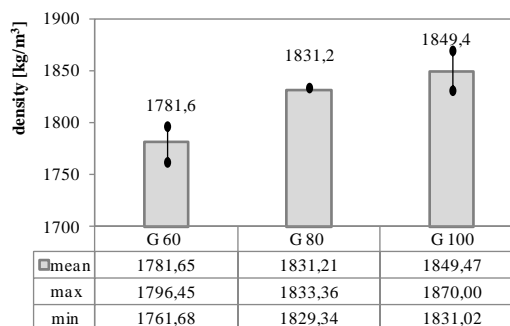


Figure 1. Density of tested mortars

A. Tensile strength

Flexural tensile strength tests were carried out according to the standard procedure for cement mortar. The results are presented in Figure 2.

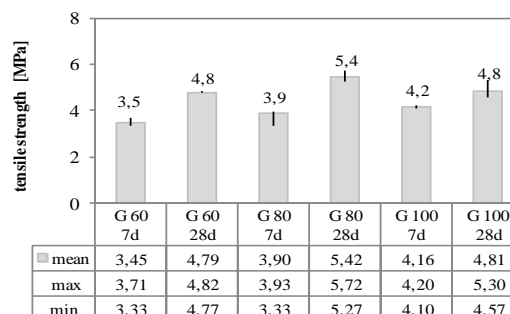


Figure 2. Tensile strength of G 60, G80, and G100 mortars

Specimen was loaded with force concentrated in the middle of the beam span and the amount of force acting on the beam was continuously recorded. The static system was that of a simply supported beam with a spacing of supports of 100 mm. On the basis of the maximum force required to destroy the specimen, flexural tensile strength of the material was calculated.

B. Compressive strength

Portions of the mortar prisms tested in bending were used for the determination of compressive strength with the use of a hydraulic press. During the test, the specimen was subjected to a compressive force until it was destroyed and its strength was determined as the ratio of the maximum force to the compressed area. The nature of destruction of geopolymer specimens was similar to the normal mode of destruction for cement mortars.

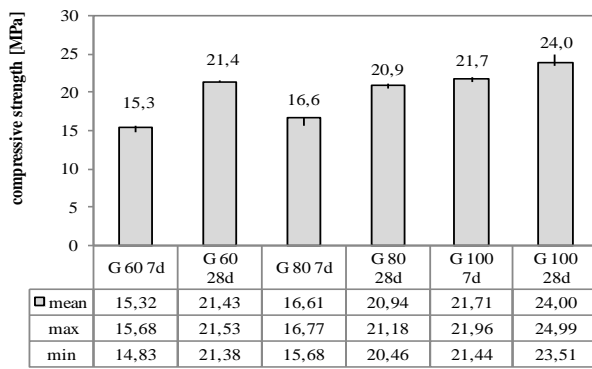


Figure 3. Compressive strength

As the amount of NaOH in the activator solution increased, the bulk density of the finished product increased as well. For specimens containing 80 g of NaOH, slight variations in bulk density between the 7th and the 28th day of curing were observed. The other specimens had higher densities after 28 days. The strength of geopolymer mortars increased over time. Those specimens that were cured for a longer period obtained higher strength parameter values. The highest increase in compressive strength (almost 40%) occurred in specimens with the lowest NaOH content of 60 g. For higher NaOH concentrations, this increase was 26% and 10%, respectively, for 80 g and 100 g of NaOH. The analysis of three point bending results demonstrated that the increase in tensile strength amounted to almost 40% for materials which contained 60 g and 80 g of NaOH in the activator solution.

Specimens with the highest content of sodium hydroxide achieved the highest strength values after 7 days of curing, whereas mortars with the lowest NaOH content exhibited the highest increases in strength between the 7th and the 28th day of curing. After 28 days, specimens containing 100 g of NaOH had the highest compressive strength and specimens containing 80 g of NaOH had the highest tensile strength. The anticipated relationship between bulk density and material strength was observed as well. As expected, materials with the highest density achieved the highest strengths.

The tests conducted have demonstrated that sodium hydroxide content of the activator solution significantly affects the strength of the resulting geopolymer. As the amount of NaOH increased, the improvement in strength parameters of the mortar was observed (Figure 4).

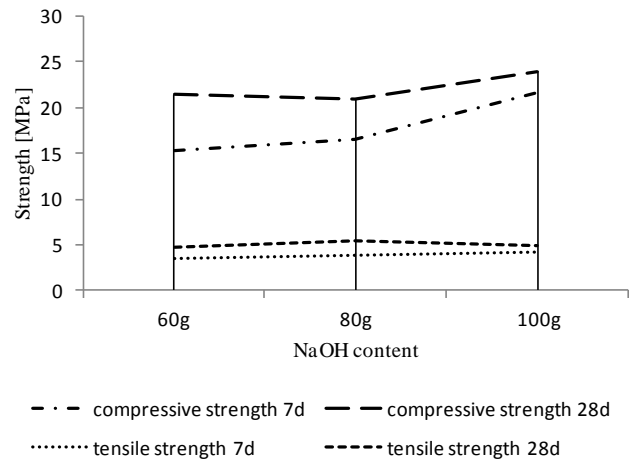


Figure 4. Influence of NaOH on strength

C. Additional Observations

For the mortars designed in the study, the optimum sodium hydroxide content ranges from 80 to 100 g per 300 g of water glass. At these concentrations, high strength is obtained and the resulting mixture consistency makes it fairly workable. Taking into account test results, it may be suspected that further increasing the amount of NaOH in the activator solution will increase strength but at the same time make the mixture less liquid, preventing proper mortar compacting. Additional problems may be caused by large amounts of heat generated by the reaction with water glass and the excess of alkaline substances in the mixture. The relatively high porosity of the specimens produced is also of note. A high pore content negatively affects mortar strength parameters. The tests conducted did not include detailed specimen porosity analysis. Based on visual observations, NaOH content had no significant effect on the porosity of the resulting material.

IV. Conclusions

- Sodium hydroxide content of the activator solution significantly affects the properties of the resulting geopolymer. As the amount of NaOH in the activator solution increases, the bulk density of specimens increases as well, but the improvement in mortar strength parameters is at the expense of the mixture becoming less workable.
- A longer curing time improves mortar strength parameters. Specimens that are cured for longer periods attain higher strength values.
- Increasing the amount of NaOH in the activator solution from 60 g to 80 g and to 100 g per 300 g water glass resulted in an increase in compressive strength after seven days by around 8% and 42%, respectively. After 28 days

of curing the differences were much smaller and resulted from variations in the development of strength over time. The highest increase in compressive strength (almost 40%) occurred in specimens with the lowest NaOH content. For higher NaOH concentrations, this increase was 26% and 10%, respectively, for 80 g and 100 g of NaOH.

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