

The influence of the silica/sodium ratio on the fly ash geopolymer binder

V. Bocullo, D. Vaičiukynienė, V. Vaitkevičius

Department of Building Materials, Kaunas University of Technology,
Studentu St. 48, LT-51367 Kaunas, Lithuania
E-mail: danute.palubinskaite@ktu.lt

A. Kantautas

Department of Silicate Technology, Kaunas University of Technology,
Radvilenu St. 19, LT-50270 Kaunas, Lithuania

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This article investigates the properties of a geopolymer, an alternative binding material to the ordinary Portland cement (OPC), and their dependence on different SiO₂/Na₂O ratios in the system. To make the geopolymer polish coal burning fly ash consisting mainly of amorphous SiO₂ and Al₂O₃, it was activated with a NaOH solution. While many researches have been done on the Si/Al ratio influence, not many studies have examined the activator solution influence on geopolymer properties. Samples were made with 8 different mix compositions with the SiO₂/Na₂O ratio varying within 0.8–3.1. The samples were tested for compressive strength after 7, 14 and 28 days of curing. The mineral composition of each set mix was examined with XRD. Samples with the SiO₂/Na₂O ratio equal to 2.0 showed the highest compressive strength. The XRD of these samples showed the presence of low-crystallinity hydrosodalite and a small amount of mullite and quartz. The acceptable strength was shown by samples with the SiO₂/Na₂O ratio in the range of 1.5–2.5. Samples with the ratio beyond this range failed to produce enough of the necessary binding agents.

Key words: alkali-activated, geopolymer, fly ash, binding materials, compressive strength, chemical composition

Introduction

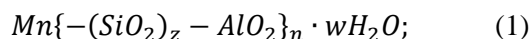
Geopolymer binder is an ecological alternative to the ordinary Portland cement (OPC). OPC is the most widely used material in the construction industry worldwide, but it has a high level of CO₂ emissions [1] because of clinker reactions and high manufacturing temperatures. To produce 1 t of OPC 0.5–0.94 t of CO₂ is emitted depending on the clinker ratio in the cement [2] due to chemical reactions where carbon dioxide is a product, and high temperatures are needed for this reaction to occur. Currently, OPC is one of the most popular building materials in the world [3], with the current consumption of 1 m³ per person per year [4]. Because of this fact, the OPC manufactures are causing at least 5–8 % of the global CO₂ emissions [4, 5].

Geopolymer binding materials or geopolymer cements are mineral molecular networks or chains bound by covalent bonds [6] and having the chemical composition similar to that of zeolites, but with a more amorphous microstructure [7].

A geopolymer is obtained by activating the SiO₂ and Al₂O₃ source material with an alkali activator

[8]. Usually, the source materials are various industry by-products like fly ash (FA), granulated blast furnace slag (GBFS), waste of fluid catalyst cracking (FCC) or any material rich in SiO₂ and Al₂O₃.

A simplified explanation of geopolymerisation can be described as several processes that occur parallel to each other: first, reactive silicates and aluminates are leached from aluminosilicate raw materials into the alkali activator solution (usually sodium hydroxide or waterglass or combination of the two); then polycondensation takes place – the released Si- and Al- tetrahedrals are polycondensed into amorphous or semi-crystalline oligomers, and different types of oligomers further polymerize forming a hardened three-dimensional synthetic network of aluminosilicates, also called geopolymer gel [9, 10]. The empirical formula of geopolymers, also known as poly(sialates), is as follows:



where M – a cation such as K⁺, Na⁺ or Ca²⁺; n – the degree of polycondensation, z – 1, 2 or 3 [11].

According to many studies, the concrete with a geopolymer binder has an equivalent strength as that of concrete with OPC. Also, it has been proven that the geopolymer concrete has a better resistance to acid attacks [12] and is more fire- and heat-resistant [13].

According to various studies, the properties of geopolymers can be affected by many factors such as the chemical composition of the raw material, the amount of activator [9]. While there are plenty of different studies on the $\text{SiO}_2/\text{Al}_2\text{O}_3$ or $\text{Na}_2\text{SiO}_3/\text{NaOH}$ (alkali activators) ratios, there is a lack of research on the $\text{SiO}_2/\text{Na}_2\text{O}$ ratio where the effect on the geopolymer of different amounts of the alkali activator is studied. In the present research, the influence of the $\text{SiO}_2/\text{Na}_2\text{O}$ ratio on the geopolymer compressive strength and chemical composition is studied.

Materials and methods

In this study, low calcium coal burning fly ash (FA) from Poland was used as a raw material for geopolymers. Currently, 750 million tons of coal FA are generated in the world every year and over 40 million tons in Europe [11]. At the moment, only 39 % of FA are utilised in the US and 47 % in Europe, while the global average is estimated to be close to 25 % [14].

Because of its chemical composition (high amounts of amorphous SiO_2 and Al_2O_3) FA may be utilized as a raw material for geopolymers [11, 15].

The XRFA elemental analysis was used to determine the chemical composition of the fly ash type F. Its elemental composition was recalculated to oxides (Table 1).

Table 1. Fly ash type F chemical composition

Oxide	Amount, %	Oxide	Amount, %
CaO	3.683	P_2O_5	1.310
SiO_2	49.468	SrO	0.106
Na_2O	0.945	ZrO_2	0.147
Al_2O_3	27.452	SO_3	0.921
MnO	0.063	ZnO	0.050
MgO	1.699	TiO_2	1.658
K_2O	4.539	CuO	0.027
Fe_2O_3	7.379	NiO	0.031
BaO	0.436	PbO	0.038

The XRD analysis shows peaks of quartz and mullite. The presence of amorphous SiO_2 is identified as a “hill” on the XRD graphic within the 2θ degree range in 18° – 30° (Fig. 1). High amounts

of amorphous SiO_2 and Al_2O_3 make FA a good raw material for the geopolymer binding material.

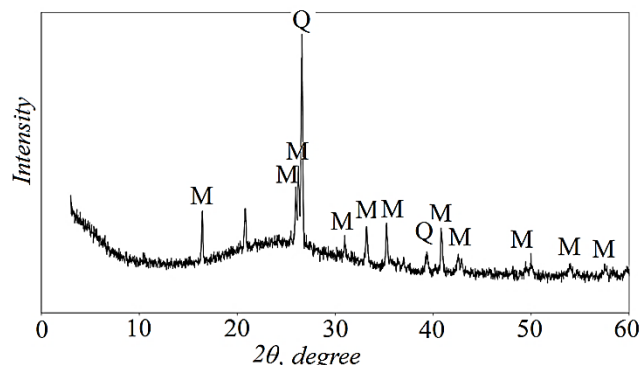


Fig. 1. XRD analysis of Fly ash. M – mullite, Q – quartz.

The XRD analysis for raw materials was performed at Kaunas University of Technology on a D8 advance diffractometer (Bruker AXS, Karlsruhe, Germany) operating at the tube voltage of 40 kV and the tube current of 40 mA. The X-ray beam was filtered with a Ni 0.02 mm filter to select the $\text{CuK}\alpha$ wavelength. Diffraction patterns were recorded in a Bragg–Brentano geometry using a fast counting detector Bruker LynxEye based on the silicon strip technology. The specimens were scanned over the range of $2\theta = 3$ – 60° at a scanning speed of 6 min^{-1} , using a coupled two theta/theta scan type.

The XRFA analysis of the fly ash type F was performed at Kaunas University of Technology on a fluorescence spectrometer S8 Tiger (Bruker AXS, Karlsruhe, Germany) operating at the counter gas Helium 2 bar.

The compressive strength of the samples was tested with a hydraulic press ToniTechnik 2020.

The fly ash was activated with a NaOH solution. The amount of NaOH was determined by $\text{SiO}_2/\text{Na}_2\text{O}$ required for a certain mix. To increase the Al_2O_3 level in the mixture, additional $\text{Al}(\text{OH})_3$ (gibbsite) was added. In the experiment, 8 different mixtures with different $\text{SiO}_2/\text{Na}_2\text{O}$ ratios have been studied (Table 2).

Table 2. Mixture design of geopolymer binder

No.	$\text{SiO}_2/\text{Na}_2\text{O}$ mol	$\text{Al}(\text{OH})_3$, g	Fly ash, g	NaOH, g	H_2O , g
1	0.8	29.94	92.23	72.7	43.3
2	1.3	33.93	104.53	45.99	41.0
3	1.5	19.97	61.49	22.47	23.1
4	1.7	21.97	67.64	22.11	24.8
5	1.9	24.95	76.86	21.58	27.4
6	2	25.96	79.93	21.41	28.3
7	2.3	29.95	92.23	20.7	31.8
8	3.1	39.94	122.98	18.93	40.4

Paste samples were cast into 20×20×20 mm moulds and left for 24 hours. After this period, the moulds were put into sealed bags to prevent drying and moved to elevated temperatures of 80 °C to ensure the best conditions for geopolymerisation.

The samples were tested for compressive strength after 7, 14 and 28 days. Crushed samples were ground for the XRD analysis.

The relative hydrosodalite crystallinity is directly proportional to intensity peaks of the investigated material [16, 17]. In this case, it was matched to the ratio of the sum of the intensity of occurred hydrosodalite peaks and the sum of the intensity of theoretical hydrosodalite peaks:

$$C_{rel} = \frac{I_{ap}}{I_{pr}} \times 100; \quad (2)$$

where C_{rel} – relative crystallinity, %; I_{ap} – intensity peaks of occurred hydrosodalite, unt.; I_{pr} – intensity peaks of theoretical hydrosodalite, unt.

Results and discussion

The samples were not tested after the first few days, because they were not yet hardened enough. The first test was run 7 days after casting.

As is seen from the strength graph (Fig. 2), the strength is more influenced by the $\text{SiO}_2/\text{Na}_2\text{O}$ ratio rather than by the curing time. The compressive strength of samples tested by the ratios varied from 5.6 MPa to the maximum 56.16 MPa, while the effect of the curing time was not as significant: in most of the cases (with a few exceptions) the strength gained within the first 7 days remained very similar.

As mentioned before, the main factor for compressive strength was the $\text{SiO}_2/\text{Na}_2\text{O}$ ratio. The strongest samples were made with this ratio in the range from 1.5 to 2.5. Within this range, the compressive strength was from 32.25 to 56.16 MPa. The peak strength (56.16 MPa) was observed at the $\text{SiO}_2/\text{Na}_2\text{O}$ ratio 2.0. Samples made from mixes that had a different ratio developed a much lower compressive strength.

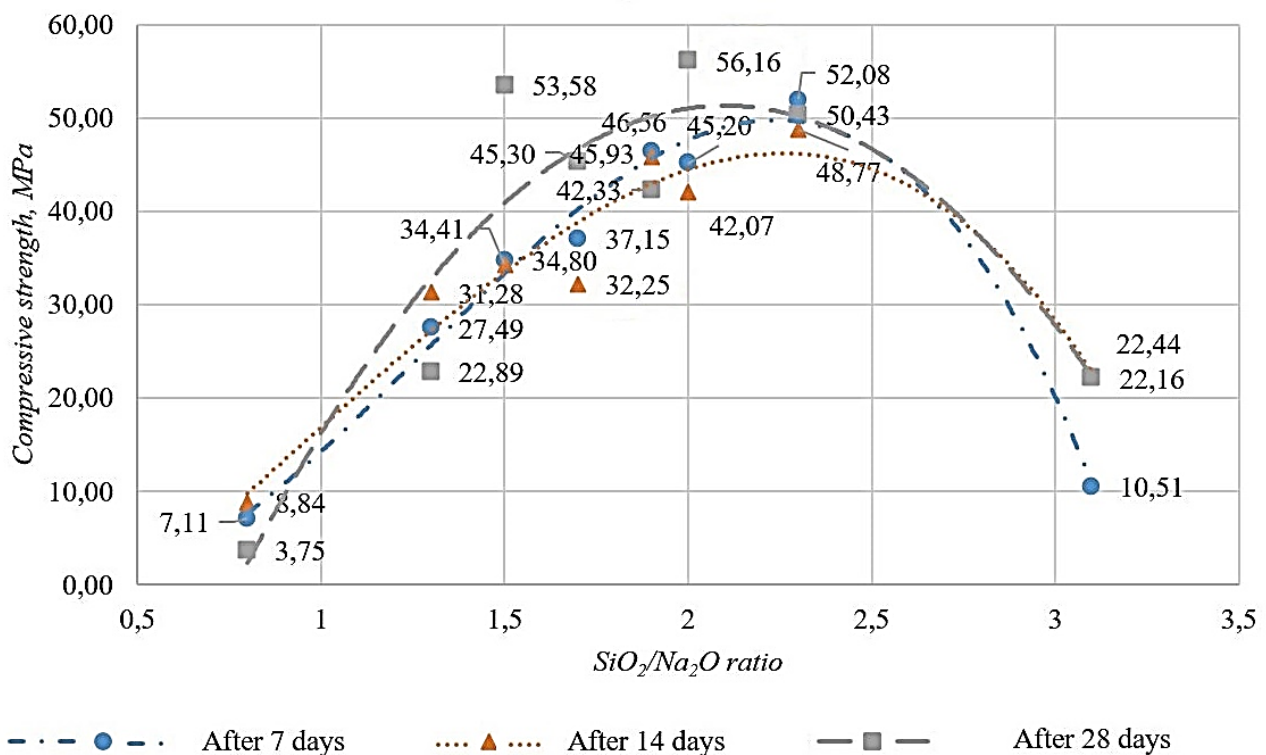


Fig. 2. Samples of compressive strength depending on the $\text{SiO}_2/\text{Na}_2\text{O}$ ratio in a mix.

The mineral composition of samples was determined using the XRD analysis. All samples with a different mix composition showed peaks for hydrosodalite (Figs. 3 and 4). The XRD diagram

which represents the strongest sample is number 6 (Fig. 4). In this sample, the low-crystallinity hydrosodalite is found with a small amount of mullite and quartz.

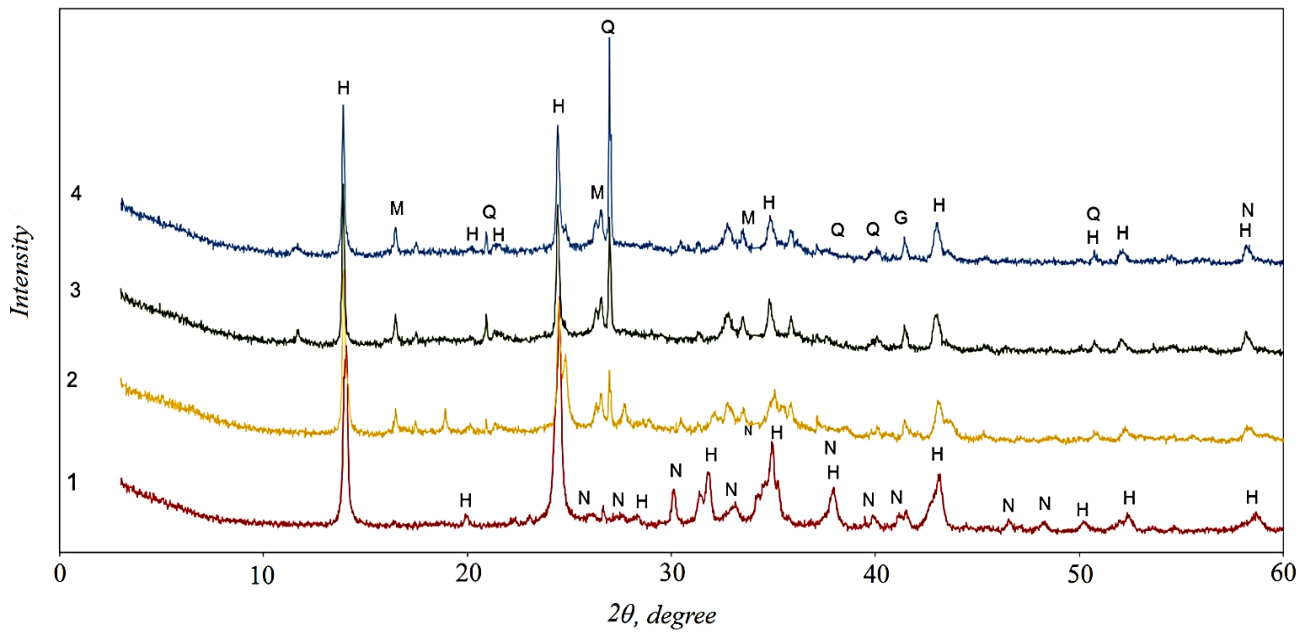


Fig. 3. XRD analysis of 1–4 mix samples. N – sodium carbonate (natrite), H – sodium aluminium silicate hydroxide hydrate (hydrosodalite), M – aluminium silicon oxide (mullite), Q – silicon oxide (α -quartz).

The weakest samples are marked as number 1 (Fig. 3) and number 8 (Fig. 4). Sample number 1 contained a high-crystallinity hydrosodalite and sodium carbonate, which doesn't provide any strength for the system. Sample number 8 (Fig. 4)

had the gibbsite ($\text{Al}(\text{OH})_3$), which is one of the geopolymer raw materials. In this case, the gibbsite didn't react and not enough of the binding agent was formed, so the system strength was very low.

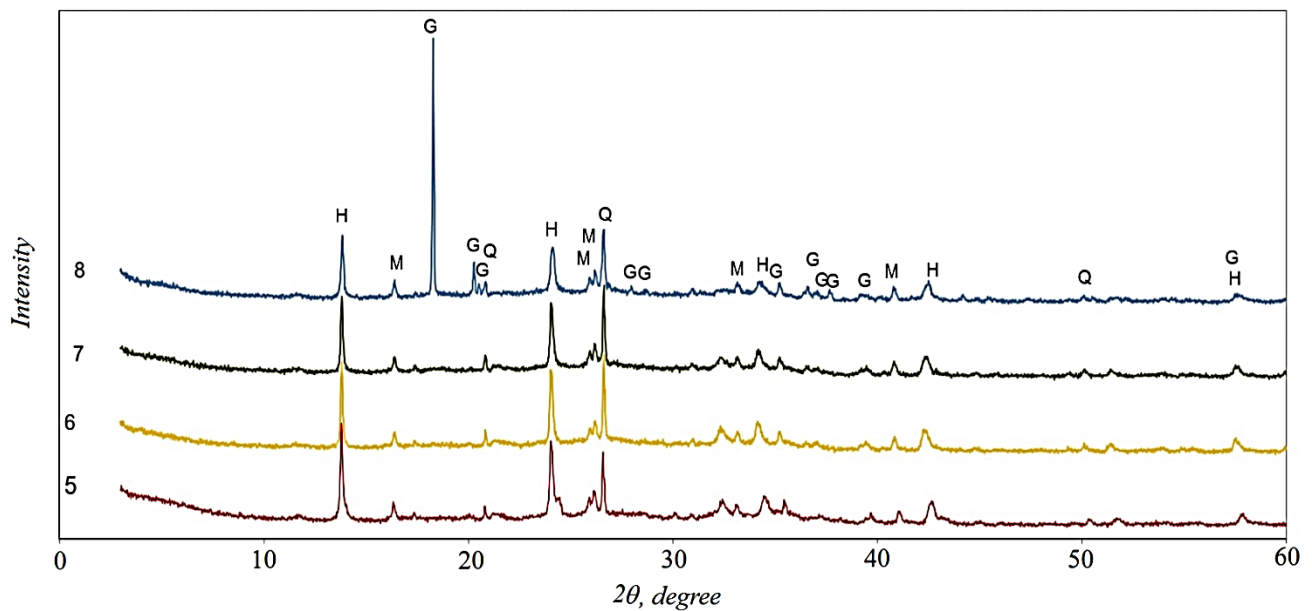
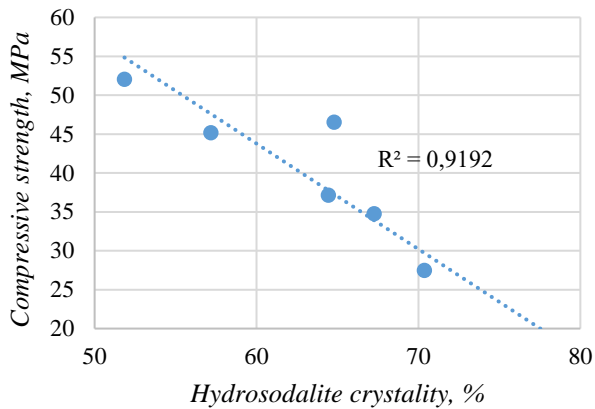
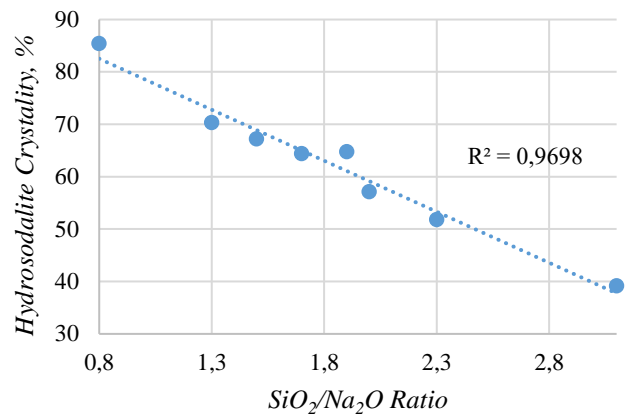


Fig. 4. XRD analysis of 5–8 mix samples. N – sodium carbonate (natrite), H – sodium aluminium silicate hydroxide hydrate, M – aluminium silicon oxide (mullite), Q – silicon oxide (α -quartz), G – aluminium hydroxide (gibbsite).



a



b

Fig. 5. The influence of hydrosodalite crystallinity on the compressive strength of samples (a) and the effect of the SiO₂/Na₂O ratio (b) on hydrosodalite crystallinity.

As is seen in Fig. 5 samples, the compressive strength decreases with a higher hydrosodalite crystallinity (Fig. 5, a). The results indicate that a bigger hydrosodalite crystallinity is obtained with a lower SiO₂/Na₂O ratio (Fig. 5, b).

Conclusions

After completing the tests, the following effects were observed:

1. The geopolymer strength can reach 50 MPa and more, which makes it equivalent to OPC.
2. The best SiO₂/Na₂O ratio to develop the maximum compressive strength is around 2.0. Satisfactory results were observed at the SiO₂/Na₂O ratio range within 1.5–2.5, otherwise the system failed to develop binding materials and to gain the compressive strength.
3. A higher SiO₂/Na₂O ratio decreases the hydrosodalite crystallinity.

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V. Bocullo, D. Vaičiukynienė, V. Vaitkevičius,
A. Kantautas

SILICIO IR NATRIO SANTYKIO ĮTAKA LAKIŲJŲ PELENŲ GEOPOLIMERINEI RIŠAMAJAI MEDŽIAGAI

S a n t r a u k a

Šiame straipsnyje aptariama alternatyvios įprastajam portlandcemenčiui rišamosios medžiagos geopolimerų savybių priklausomybė nuo sistemos SiO₂ ir Na₂O santykio. Geopolimero žaliava – lenkiški lakieji pelenai, turintys savo sudėtyje daugiausia SiO₂ ir Al₂O₃, buvo aktyvuoti NaOH tirpalu. Pasaulyje atlikta daug tyrimų, kuriuose nagrinėta tik SiO₂ ir Al₂O₃ santykio įtaka geopolimerų savybėms, ir praktiškai nebuvo iširta aktyvatoriaus įtaka.

Šiame eksperimente buvo pagaminti 8 skirtingų sudėčių bandiniai su SiO₂ ir Na₂O santykiu, kintančiu nuo 0,8 iki 3,1. Bandinių gniuždymo stipris matuotas po 7, 14, 28 parų kietėjimo. Nustatyta, kad stipriausi bandiniai gaunami (iki 56,16 MPa), kai buvo naudojamas mišinių molinis SiO₂ ir Na₂O santykis 2. XRD analizės rezultatai parodė, kad šiuose bandiniuose vyrauja mažos kristalizacijos hidrosodalitas, mulitas ir kvarcas. Bandiniuose, kurių SiO₂ ir Na₂O santykis buvo 1,5–2,5 intervale, gniuždomasis stipris kito nuo 32,25 MPa iki 56,16 MPa. Bandinių, kurie nepateko į šį intervalą (SiO₂ ir Na₂O santykis nuo 0,8–1,5 ir daugiau kaip 2,5), stipris buvo mažas. Tai galima paaiškinti tuo, kad bandiniuose nesusidarė tinkamas rišiklio kiekis.

Reikšminiai žodžiai: šarminis aktyvavimas, geopolimeras, lakieji pelenai, rišamosios medžiagos, gniuždomasis stipris.