KAUNAS UNIVERSITY OF TECHNOLOGY

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RESEARCH OF STRUCTURE AND PROPERTIES OF GEOPOLYMER CONCRETE FROM INDUSTRIAL WASTE

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KAUNO TECHNOLOGIJOS UNIVERSETAS

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GEOPOLIMERINIO BETONO IŠ PRAMONĖS ATLIEKŲ STRUKTŪROS IR SAVYBIŲ TYRIMAS

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INTRODUCTION

Relevance of work

Geopolymer concrete is an ecological alternative to ordinary Portland cement (OPC) concrete. In present day, the OPC concrete is the most popular construction material with global production of over 8 billion tonnes and the number increasing (Rivera, De Gutierrez, Mejia, & Gordillo, 2014). Due to the production process, up to 0.95 t of CO_2 is emitted for every 1 t of OPC. All in all, the concrete industry is responsible for 7% of global CO_2 emission (Worrell, Bernstein, Roy, Price, & Harnisch, 2009).

Geopolymer concrete, often referred to as alkali-activated material (AAM), has potential to replace OPC in concrete production (Pacheco-Torgal, Castro-Gomes, & Jalali, 2008). Geopolymers are obtained by activating aluminosilicate materials with an alkali solution. Shi, Krivenko and Roy (2006) emphasise works of Khul and Chassevent who described the principle of alkali activation in 1930; the first breakthrough by Glukhovski's research in 1957 and works of Davidovits in 1979. Glukhovski described a material as "soil cement" which had a $Me_2\text{-}O\text{-}MeO\text{-}Me_2O_3\text{-}SiO_2\text{-}H_2O$ structure (Me – metal). In 1979 prof. Davidovits suggested term Geopolymer, suggesting it is a non-organic polymer (Shi et al., 2006).

There is an on-going scientific discussion on the terminology, whether the geopolymers are alkali-activated materials or is it a separate group. Davidovits suggests that geopolymers are a different group of materials because, according to Davidovits (2013), alkali-activated materials, unlike geopolymers, do not have a polymeric structure. Shi, Jiménez, & Palomo (2011) suggest two groups of alkali-activated materials a) systems with a high calcium content and b) systems with a low calcium content. The latter are often referred to as Geopolymer (Provis & van Deventer, 2014). Shi (2011) concludes that the term "geopolymer" is more suited for commercial use, as is the term "Portland cement", rather than for scientific use (Pacheco-Torgal et al., 2008).

Alkali activation and geopolymerisation occurs when raw material rich with SiO_2 and Al_2O_3 is in contact with an alkali solution, a.k.a. the activator solution (Pacheco-torgal, Jalali, & Castro-Gomes, 2008). The most common activators are NaOH, KOH, Na_2SiO_3, while Na_2CO_3, Na_2SO_4, etc. are sometimes used as supplementary material in activator solutions (Shi et al., 2006, Pacheco-torgal et al., 2008). The most common raw materials are fly ash (FA), blast furnace slag, metakaolin. Most researchers agree that alkali activation happens in three stages: (1) leaching, (2) orientation and (3) hardening. The activation process starts when aluminosilicate raw material contacts an alkali-activator solution. The Al^{+3}
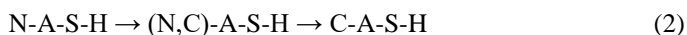
and Si^{+2} ions leach into the alkali solution. Leaching mostly depends on the type of activator and contact time (Shi et al., 2006; Pacheco-torgal et al., 2008; Feng, Provis, & Deventer, 2011; Rattanasak & Chindaprasirt, 2009). The second stage can go in two ways: after the formation of dissolved particle accumulations coagulated structures star forming – harden gel phase starts growing; or polycondensation starts immediately after the start of leaching (Pacheco-torgal et al., 2008). The final product of alkali activation reactions is hardened alkali aluminosilicate hydrate gel. Depending on raw material it can be N-A-S-H gel or, if Ca^{2+} ions are present, C(N)-A-S-H, C-A-S-H and C-S-H gels (Pacheco-torgal et al., 2008).

When calcium is not present in the first stage, leaching-coagulation happens: the OH^- ions redistribute electric charge around Si-O-Si bonds, making them weaker. It allows new -Si-OH and -Si-O$^-$ compounds to form. Negative charge is compensated by connecting an alkali cation (like Na^+); this prevents the new compounds going back to Si-O-Si. The second stage involves coagulation and condensation – the accumulation of ionic species favours contact between disaggregated products and polycondensation begins. The reaction products are amorphous $Na_2O-Al_2O_3-SiO_2$ compounds. The third stage is condensation-crystallisation. $Na_2O-Al_2O_3-SiO_2$ compounds react with silica-gel binding powder (such as FA) particles (Palomo, Krivenko, Kavalerova, & Maltseva, 2018).

When materials with a high calcium content (e.g. fly ash type C, blast furnace slag) are activated, the reaction occurs in a slightly differently. Additional reactions occur where Ca^{2+} replaces such alkali as Na^+ in the newly formed Si-O-Na-OH forming Si-O-Ca-OH. Ca^{2+} also plays an important role in the early stages of hydration, where C-S-H gel forms. Activation of materials with a high Ca content resembles the hydration of OPC. The main reaction products are C-A-S-H and C-S-H gels (Palomo et al., 2018).

To produce alkali-activated concrete that has properties equivalent to OPC concrete, often several raw materials are mixed, i.e. hybrid systems are created. The most frequent material combinations are fly ash (type F) and blast furnace slag; FA (Type F), blast furnace slag and OPC; FA (type F) and OPC. The activation reaction products of these combined materials are N-A-S-H and C-A-S-H gels. These reaction products do not form as separate gels, but rather interact and go through structural changes: the newly formed N-A-S-H, which is a common reaction product of aluminosilicate, and the C-S-H gel, which is an OPC hydration product; the gels modify in this order (Garcia-lodeiro, Palomo, Fernández-jiménez, & Macphee, 2011):

$$C\text{-}S\text{-}H \rightarrow C\text{-}(A)\text{-}S\text{-}H \rightarrow C\text{-}A\text{-}S\text{-}H \qquad (1)$$

$$N\text{-}A\text{-}S\text{-}H \rightarrow (N,C)\text{-}A\text{-}S\text{-}H \rightarrow C\text{-}A\text{-}S\text{-}H \qquad (2)$$

As seen in the transformations above, calcium which was applied in the system with OPC modifies the N-A-S-H gel where it replaces sodium as a charge-balancing cation forming a (N,C)-A-S-H gel (García-lodeiro, Maltseva, Palomo, & Fernández-jiménez, 2012; Palomo et al., 2018) which gradually transforms into C-A-S-H. The transformation continues until there is enough of calcium content (Garcia-lodeiro et al., 2011).

It is reported that materials with an OPC additive are denser, have lower porosity, water absorption and higher compressive strength, they are also able to carry on activation in ambient temperatures.

The aim of this work

The aim of this work is to design alkali-activated (geopolymer) concrete with by-products of the industry and to determine its properties.

To achieve the aim the following goals are set:

1. To determine the influence of SiO_2/Na_2O and Al_2O_3/Na_2O molar ratios on the strength and mineral composition of hardened geopolymer paste;
2. To evaluate the influence of the OPC additive on the compressive strength and mineral composition of hardened geopolymer paste;
3. To investigate the mechanical properties of geopolymer mortar with an OPC additive activating different aluminosilicate materials;
4. To investigate the mechanical properties and durability of FA concrete activated with NaOH and NaOH – Na_2SiO_3 mixtures.
5. To prepare recommendations for the production of alkali-activated (geopolymer) concrete.

Scientific novelty of the research

According to the results of the research, geopolymer fly ash concrete was developed with a compressive strength more than 50 MPa. In the production, an additive of Portland cement and sodium hydroxide – water glass activator mixture was used. A new geopolymer binder was developed using biomass bottom ash and silica gel with fluoride compounds when fluoride is bonded with sodium during hydration.

Practical significance of the dissertation

The research results presented in the thesis are significant in development of sustainable construction technologies, more specifically in the technology of ecological concrete and the utilization of production by-products in the concrete

production. This ecological concrete is developed by replacing Portland cement with various industrial waste, which are usually stored in landfills, like coal fly ash, biomass bottom ash, AlF_3 production waste – silica gel and sulphur slime.

Statement presented for defence

1. At the presence of a high alkali content ($SiO_2/Na_2O \geq 2.3$) rapid carbonation reactions take place in the system forming Na_2CO_3 which causes a lack of sodium to achieve geopolymerisation.
2. OPC can have a positive influence on the mechanical properties and durability of fly ash geopolymer concrete when Na_2SiO_3 is present.

Approbation and publication of research results

The results of the research are published in Romanian Journal of Materials, two scientific publications were published in journals included in International data bases: one in Sustainable Architecture and Civil Engineering and one in Chemical Technology. The results of this dissertation have been reported in six proceedings of five international conferences: Baltsilica 2016, Advanced Construction 2016, 5th and 6th International conference on Hazardous Materials and Waste Management "Crete 2016" and "Crete 2018" (two publications in 2018), Sustainable concrete: materials and structures, "International Conference Malta 2018".

1 METHODS AND MATERIALS

1.1 Materials

Three industry by-products were used as raw materials for alkali activation and concrete production: coal burning fly ash (FA), biomass bottom ash (BBA) and AlF_3 production waste – silica gel (PWS) and sulphur slime (SS).
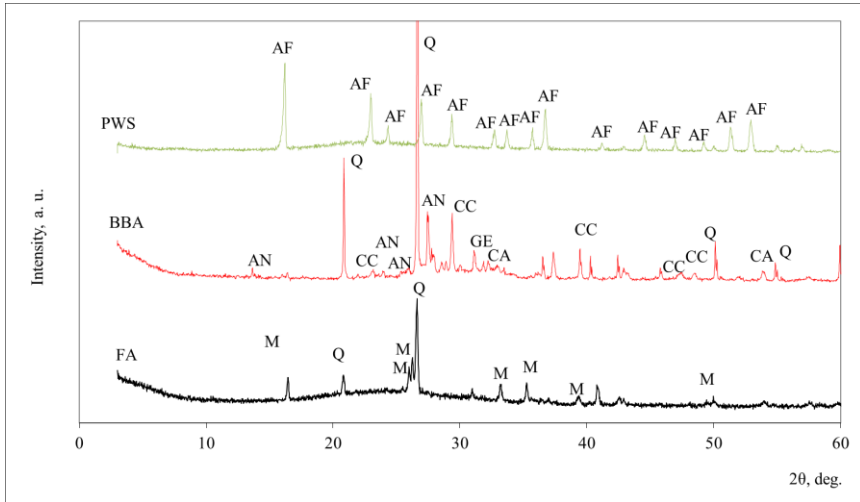
Fig. 1. XRD analysis of the raw materials. Notes: Q – quartz (78-1252), CA – calcium oxide (4-777), CC – calcite (72-1652), AN – anorthoclase (75-1631), GE – gehlenite (79-2421), AF – aluminium fluoride hydrate (35-827), M – mullite (79-1454)

The presence of amorphous SiO_2 is identified as a halo peak on the XRD graph within 2θ degree range 18°–30° (Fig. 1). XRF elemental analyses were used to determine the chemical composition of the raw material and the elemental composition was recalculated to oxides. The results are shown in Table 1.

Fly ash type F is considered to be an excellent material to synthesize geopolymers (Riahi et al., 2012; June et al., 2010; Olivia & Nikraz, 2012). With reference to XRD analysis (fig. 1.), the peaks of quartz (78-1252) and mullite (79-1454) refer to the major minerals of this material. High amounts of amorphous SiO_2 and Al_2O_3 make FA the right raw material for geopolymer binding. The bulk density of the F Class FA that has been used in the research is 1.84 g/cm^3 and was determined with helium pycnometry.

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Table 1. The composition of FA, BBA, PWS

FA					BBA			
Oxide	Amt., %	Oxide	Amt., %		Oxide	Amt., %	Oxide	Amt., %
CaO	3.683	P_2O_5	1.310		CaO	48.978	P_2O_5	5.048
SiO_2	49.468	SrO	0.106		SiO_2	22.39	SrO	0.06
Na_2O	0.945	ZrO_2	0.147		Na_2O	0.281	Rb_2O	0.024
Al_2O_3	27.452	SO3	0.921		Al_2O_3	2.509	ZrO_2	0.039
MnO	0.063	ZnO	0.050		MnO	0.347	SO_3	0.582
MgO	1.699	TiO_2	1.658		MgO	8.286	ZNO	0.041
K_2O	4.539	CuO	0.027		K_2O	8.686	TiO2	0.328
Fe_2O_3	7.379	NiO	0.031		Cl	0.04	CuO	0.02
BaO	0.436	PbO	0.038		Fe_2O_3	2.179	BaO	0.161

PWS	
Oxide	Amt., %
Al_2O_3	5.68
SiO_2	72.23
F	21.01
CaO	0.42
Fe_2O_3	0.66

The average particle density of BBA was 2.24 g/cm^3. XRF elemental analysis was used to determine the chemical composition of raw material. Elemental composition was re-calculated to oxides and is reported in Table 1. According to the XRD analysis (Fig. 1) BBA consists of quartz (78-1252), calcium oxide (4-777), calcite (72-1652), anorthoclase (75-1631) and gehlenite (79-2421).

The third material which was used in this research was AlF_3 production waste – silica-gel (PWS). The largest part of PWS consists of $SiO_2 \cdot nH_2O$, where SiO_2 is in the amorphous state (Vaičiukyniene, Vaitkevičius, Kantautas, & Sasnauskas, 2012). It is known that amorphous SiO_2 could be used as an OPC additive because of its pozzolanic properties (Provis, Lukey, & Van Deventer, 2005). PWS is a product of silicahexaflouride acid neutralisation. This acid is obtained from manufacturing phosphoric acid. The silicahexaflouride process reaction is as follows:

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$$H_2SiF_6 + 2Al(OH)_3 \rightarrow 2AlF_3 + SiO_2 \cdot nH_2O + H_2O + Q \qquad (3)$$
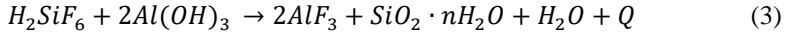
The XRD analysis shows that the material consists of crystalline $AlF_3 \cdot 3.5$ H_2O (Fig 2). The XRF analysis shows that the largest part of the AlF_3 production waste consists of SiO_2 and Al_2O_3.

Some supplementary materials were used in the experiments: laboratory reagents – NaOH, $Al(OH)_3$; and commercially available water glass (Na_2SiO_3) and OPC CEM I 52,5R.

1.2 Methods

AAM and geopolymer paste moulds were kept sealed in ambient temperature for 24 hours then moved to 60°C for 24 hours. After a curing period, the samples were demoulded and dried. The compressive strength of AAM and geopolymer paste samples was tested after seven, 14 and 28 days. The test was performed on a hydraulic compression machine Toni Technik 2020. The paste samples were 20×20×20 mm cubes.

Sample composition was analysed with XRD after the samples were compressed. XRD was performed with X-Ray Diffraction "Bruker D8 Advance" operating at tube voltage of 45 kV and tube current of 40 Ma, with a copper source (Cu). Samples were scanned over a range of $2\theta = 5°$ to $55°$, at a scanning speed of $1°$/minute. XRF was used for elemental analysis of raw material with a Fluorescence spectrometer S8 Tiger (Bruker AXS, Karlsruhe, Germany) operating at the counter gas Helium 2 bar (XRFA analysis) to determine the chemical composition of fly ash (FA).

SEM – EDS was used for microstructure and elemental analysis of AMM and geopolymer paste samples. The test was performed with FEI Quanta 200 FEG scanning microscope and with an energy-dispersive X-ray spectrometer Bruker XFlash 4030.

AAM concrete samples were 70×70×70 mm cubes and mortar samples were 40×40×160 mm prisms. Different sample sizes were required for different tests. These samples were sealed in moulds after formation and kept in ambient temperature for 24 hours, then moved to 60°C for 24 hours. After the curing period they were demoulded and dried.

A compressive strength test was carried out on the concrete cubes after seven, 14 and 28 days. A hydraulic compression machine Toni Technik 2020was used for the test.

An elastic modulus was determined according to standard ISO 1920-10:2010. During the test, the mortar prisms were placed in a frame and loaded 40%

of its destructive load for 3 times and strains and deformations were monitored during loading/unload. Static elastic modulus was calculated:

$$E = \frac{\sigma_a - \sigma_b}{\varepsilon_a - \varepsilon_b} \cdot 100 \tag{4}$$

where E – elasticity module, MPa; σ_a – Maximum load (40% $F_{C, Cub.}$), MPa; σ_b – minimum load ($\approx$ 0.5 MPa), MPa; ε_a – relative deformation at maximum load; ε_b – relative deformation at the lowest load.

The carbonation of AAM concrete was evaluated by measuring the depth of the carbonated layer. Carbonation depth was measured in 28-day-old sample and compared with the depth after keeping samples in a carbonation chamber for 56 days (CO_2 concentration 1%, temperature 20°C). To measure the carbonation depth, samples must be split and sprayed with phenolphthalein solution then the carbonated layer does not present purple colour.

Porosity was determined by using the water absorption kinetics test. To calculate porosity, open porosity, closed porosity dry sample mass, sample mass after 48 h of drowning and sample mass in the water must be measured. Sample density is calculated:

$$\rho = \frac{m_d}{m_{48} - m_w} \cdot 1000, kg/m^3 \tag{5}$$

here: m_{48} – sample mass after 48 h of drowning, g; m_d – dry sample mass, g; m_w – sample mass in the water (after 48 h drowning), g.

Water volume absorption ($W_{p(t)}$) of the sample is equal to open porosity (P_o):

$$P_o = W_{p(t)} = \frac{W_p \rho}{1000}, \% \tag{6}$$

Here: W_p – water mass absorption, %, ρ – density, kg/m³.

Porosity can be calculated with equation:

$$P = \left(1 - \left(\frac{\rho}{2690}\right)\right) \cdot 100, \% \tag{7}$$

Here: ρ – density, kg/m³.

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Then closed porosity (P_c) is equal to:

$$P_c = P - P_o, \%\qquad\qquad(8)$$

To measure the danger of ASR, the test was carried out according to standard ASTM C1260. During the test 40×40×160 mm prisms are placed in 1 mol/l NaOH, 80°C solution and measured after one, three, seven, and 14 days. Deformations are recalculated into relative deformations. According to the regulations of standard ASTM C1260, concrete is resistant to ASR when relative deformations are under 1 mm/ 1m after 14 days.

Resistance to freeze/thaw was evaluated with a testing method regulated by standard SS 137244:2005. According to the regulations, the top surface of the samples is exposed to a NaCl solution (concentration 3%) and cycles of freeze/thaw (from -20 to +20°C) are applied for 56 days (chamber does one cycle per day). Other surfaces are insulated from the effect. After 56 days, mass loss from the affected sample is measured. According to the regulations of standard SS 137244:2005, mass loss must be under 1 kg/m^2.

2 PROPERTIES OF THE ALAKLI-ACTIVATED MATERIALS AND GEOPOLYMER PASTE

2.1 The influence of SiO_2/Na_2O ratio on the properties of the geopolymer paste

To determine the influence of SiO_2/Na_2O ratio on geopolymer paste the samples with 5 different compositions were made (table 2). Geopolymer paste was produced with fly ash (FA) alkali-activated with a NaOH solution.

Table 2. Sample compositions

No.	SiO_2/Na_2O mol	Al(OH)$_3$, g	FA, g	NaOH, g	H$_2$O, g
F-1	0.8	29.94	92.23	72.7	43.3
F-3	1.5	19.97	61.49	22.47	23.1
F-6	2	25.96	79.93	21.41	28.3
F-7	2.3	29.95	92.23	20.7	31.8
F-8	3.1	39.94	122.98	18.93	40.4

Compressive strength results peaked at SiO_2/Na_2O ratio 2.0 (F-6) reaching 56.16 MPa (Fig. 2). Reasonably good results (between 32.25 MPa and 56.16 MPa) were obtained with SiO_2/Na_2O ratio range 1.5–2.3.
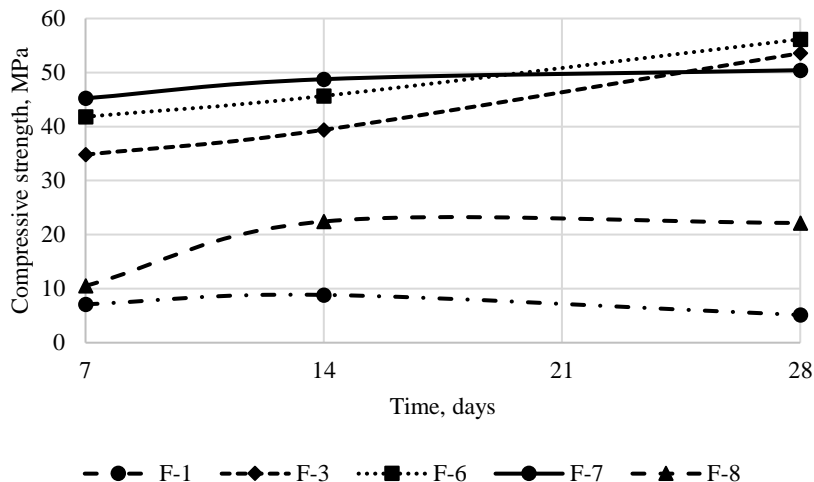
Fig. 2. Compressive strength test results

The lowest compressive strength belongs to samples with the highest (F-8) and the lowest (F-1) SiO_2/Na_2O ratio, reaching 22.16 MPa and 5.13 MPa, respectfully. Sample F-1 has the lowest SiO_2/Na_2O ratio, thus after alkali activation process the sample presents the highest intensity peaks of hydrosodalite and sodium carbonate, which could be reason for the lowest compressive strength presented by sample F-1. NaOH promotes the formation of hydrosodalite because Na^+ dissolves the aluminium and silica source from FA. As dry mix compositions of all samples have $Al(OH)_3$ with high intensity crystalline phase of gibbsite, together with NaOH gibbsite of $Al(OH)_3$ work as catalysts. The free Na^+ or sodium of pore solution in the material reacts with CO_2 for 6 days after curing and before testing, and since F-1 has the highest NaOH concentration in its starting chemical composition it also has the highest amount of free Na^+ after alkali activation process. The presence of Na_2CO_3 confirms this (Fig. 3).

Sample F-8 has a relatively low compressive strength and it presents low intensity hydrosodalite peaks in XRD analysis as compared to other samples, no sodium carbonates and high intensity crystalline phase of gibbsite from raw material at the age of 28 days. It can be explained by an insufficient amount of NaOH, SiO_2/Na_2O of 0.8 (Table 2) which is one of the main components in N-A-S-H gel formation (which is the main product of the alkali activation process) as well as in the formation of hydrosodalite and sodium carbonate crystals.
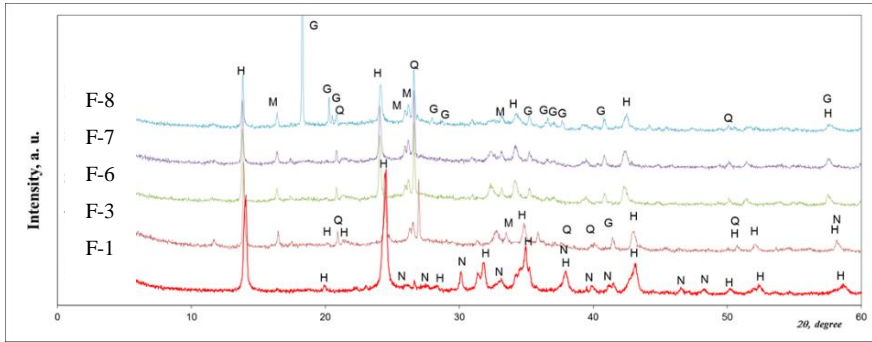
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Fig. 3. XRD analysis. Notes: N – natrite (76-1108), H – hydrosodalite (72-2329), M – mullite (84-1205), Q – quartz (78-1252), G –gibbsite (33-18)

A higher compressive strength is presented by sample F-6, which, has more N-A-S-H in its structure in comparison to sample F-1 (Fig. 3) but in comparison to sample F-8 it has less hydrosodalite and no sodium carbonate.

N-A-S-H gel (main product of alkali-activation) formation has been detected by halo at 15°–35° moving to 20°–40° (Garcia-lodeiro et al., 2011). All samples after alkali activation present quartz, mullite and gibbsite from FA as well as new crystalline phases defined as hydrosodalite (72-2329) – sodalite-group zeolites which are a common by-product of N-A-S-H gel.

SEM – EDS was performed for F-1, F-5 and F-8 compositions. The SEM pictures of samples F-1 (Fig. 4) present crystallic particles similar to hydrosodalite. The most of peak patterns, in the EDS analysis of selected points, are common to a general geopolymer pattern consisting of Si, Al, O, and Na peaks. Nevertheless, some points have unusually distinct Na peaks – the atomic weight Si/Na ratio in these cases are between 0.01–0.08, indicating an overdose of activator solution. It suggests that at the presence of sodium rapid carbonation takes place and the remaining sodium is not enough to contribute in alkaline activation. Due to lower density and a lack of alkali activation product the compressive strength of these samples was significantly reduced.
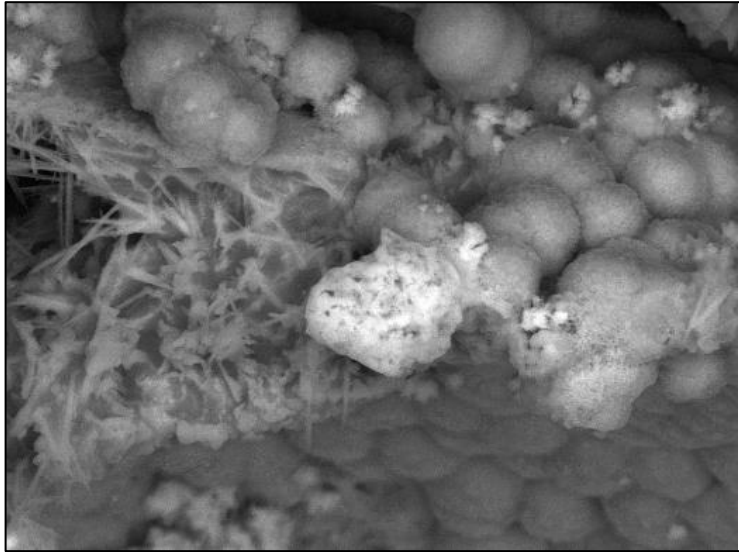
Fig. 4. SEM microphotograph of sample F-1 with magnification ×1000

Sample F-6, which develops the highest compressive strength, presents a dense microstructure consisting of hydrosodalite and N(C)-A-S-H gel. The FA particles appear to be partly dissolved, as indicated by the spherical voids on the surface, which suggests that alkali activation took place. A dense and more homogenous structure is presented by sample F-6 (Fig. 5). Fig. 5 also shows FA particle with voids indicating that it was affected by an alkali solution – activation took place. According to EDS, the Si/Na ratios were between 0.69–1.59 with the majority around 1. It appears to have a homogenous dense structure consisting Si, Al, O, and Na, which are the main elements forming geopolymer chains. Some points feature Ca, which enters the Si–O–Al–O skeleton and compensates the loading on Al atoms. These atoms can connect an individual chain of Si–O–Al–O through and make the structure with stronger at the presence of substances containing Ca (Skvara, Kopecky, Nemecek, & Bittnar, 2006).
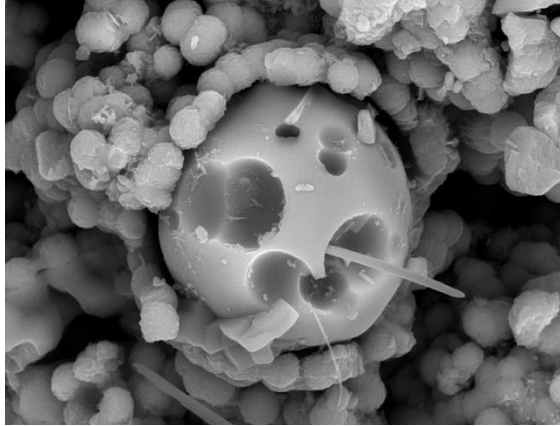
Fig. 5. SEM microphotograph of sample F-6 with magnification ×1000

SEM pictures of sample F-8 shows a presence of many unreacted FA particles. EDS analysis indicates that these particles are surrounded by the aluminosilicate matrix. A general image of sample microstructure with Na_2O/SiO_2 shows many unreacted FA particles, and the Si/Na ratio in the most characteristic points rises up to 12.30 and, in most cases, is more than 2 which is significantly more compared to previous cases, indicating that there were not enough alkalis to dissolve FA particles. These factors widely contributed to a loss of compressive strength in samples with this composition.
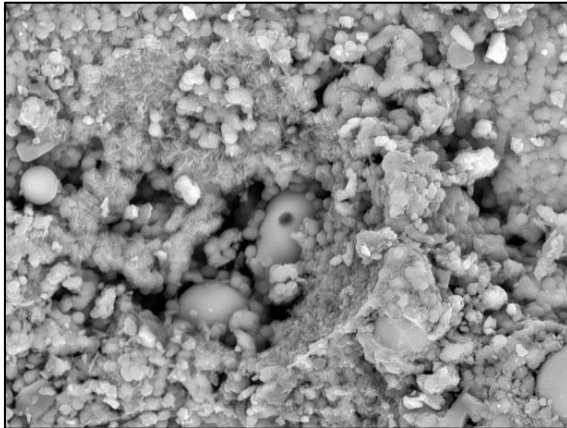
Fig. 6. SEM microphotography of sample F-8 with magnification ×1000

In the tested conditions, the best SiO_2/Na_2O ratio range for compressive strength development was between 1.5–2.3, but the optimal composition was with 2.0 SiO_2/Na_2O ratio reaching 56.16 MPa after 28 days.

An insufficient SiO_2/Na_2O ratio causes an overdose of sodium in the system which leads to sodium carbonate formation due to rapid carbonation, therefore there are not enough alkalis for activation. If the SiO_2/Na_2O ratio is too high, there is not enough alkalinity for geopolymerisation.

2.2 The influence of Al_2O_3/Na_2O ratio on the properties of geopolymer paste

An experiment was carried out using fly ash (FA). To evaluate the influence of Al_2O_3/Na_2O ratio, four compositions were made with different ratios. The ratio was changed by adding additional $Al(OH)_3$ into the system. Mix-1 was the control mixture without any additional $Al(OH)_3$, for the sake of simplicity it was marked as "0". $Al(OH)_3$ additive ratios were 0.5, 1.0 and 1.5 (Table 3).

Table 3. Mix design with different $Al(OH)_3$ amount

No.	SiO_2/Na_2O	$Al(OH)_3$, mol	SiO_2, mol	NaOH, mol	H_2O, water/solid
Mix-1	2.0	0	2.0	1	0.25
Mix-2	2.0	0.5	2.0	1	0.25
Mix-3	2.0	1	2.0	1	0.25
Mix-4	2.0	1.5	2.0	1	0.25

Compressive strength test results (Fig. 7) clearly show a decline of compressive strength with a higher amount of Al_2O_3 content. Mix-1 samples without additional $Al(OH)_3$ were the strongest reaching 26.17 MPa after 28 days. Other mixtures had smaller compressive strength after the same time: Mix-2 reached 16.27 MPa, Mix-3 – 9.98 MPa and Mix-4 – 9.76 (Fig. 7). It is worth mentioning that Mix-1 samples reached most of their strength within the first seven days, while samples with other compositions had much slower compressive strength development.
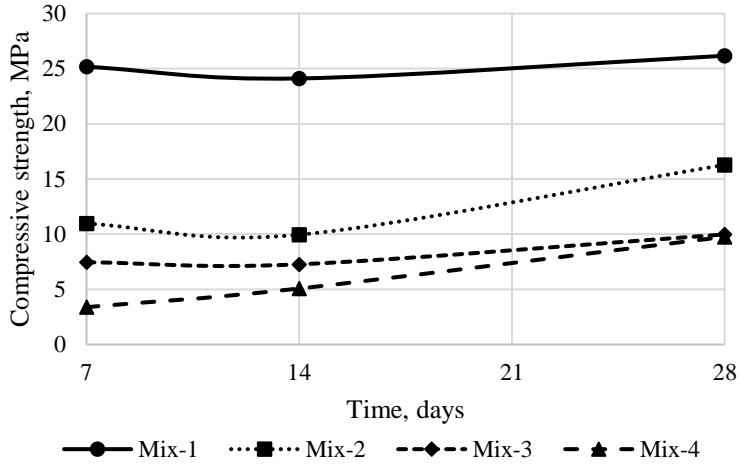
Fig. 7. Compressive strength of FA geopolymer

XRD patterns of geopolymers are normally identified through a featureless halo peak centred approximately at 27° to 29° 2θ (Fig. 8), which is attributed to the N-A-S-H gel – the primary binder present in geopolymer systems (Provis et al., 2005). High intensity peaks determine the crystalline minerals present in the sample. In samples with FA class, a common peak was observed in Mixes 2, 3 and 4 at 18° 2θ, which shows the greatest intensity for higher $Al(OH)_3$ quantity levels (Ryu, Lee, Koha, & Chung, 2013).

Mix-1 showed a diffuses halo peak at around 24° to 36° 2θ, confirming that the major phase of geopolymer was amorphous (Li, Wang, & Jiao, 2013). The Mix-2 pattern showed a weaker halo peak pattern that tended to slightly disappear in Mix-3 and Mix-4. This showed that the addition of $Al(OH)_3$ did not contribute to the geopolymerisation process and this was further confirmed by the compressive strength results which showed a decline in strength with the addition of $Al(OH)_3$ in the mix.
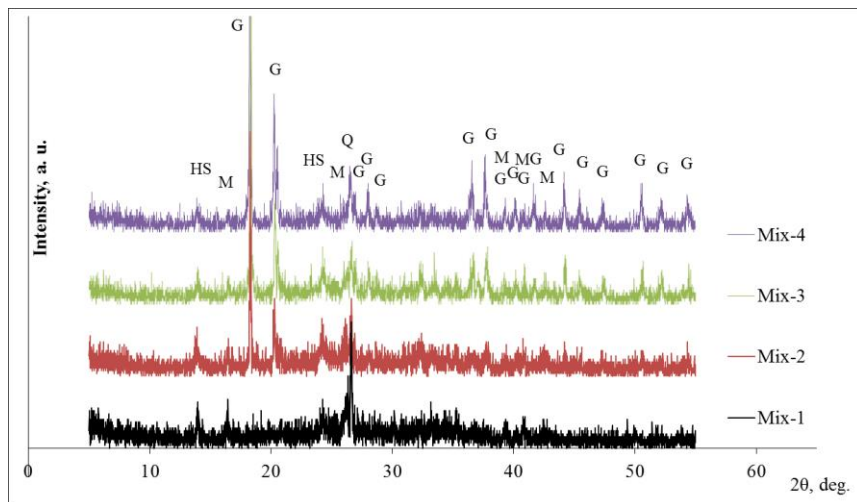
Fig. 8. XRD analysis of hardened geopolymer samples with FA. Notes: G – gibbsite (7-324), M – mullite (84-1205), HS – hydrosodalite (72-2329), Q – quartz (78-1252)

Moreover, Mix-3 and Mix-4 showed numerous peaks that in Mix-1 and Mix-2 were not present. This further supports the theory that the peaks representing minerals in the mix constituents do not participate in geopolymerisation (Grinys, Bocullo, & Gumuliauskas, 2014). Another observation was noted at the edge of the curve, from $5°$ to $12°$ 2θ. This slight curve at the edge could result in the formation of meso-material of poorly crystalline nature with a pore size range of 20 to 50nm (Rattanasak & Chindaprasirt, 2009).

Furthermore, XRD analysis shows no presence of N-A-S-H gel, since these are associated with broad peaks around $28°$ to $35°$ 2θ, or C-A-S-H phases, which are associated with main peaks at $30°$ 2θ (Pangdaeng, Phoo-ngernkham, Sata, & Chindaprasirt, 2014).

Previous research has shown that the addition of Al^{+3} ions increased the mechanical strength of geopolymers. In this research, the addition of $Al(OH)_3$ resulted in a reduction of the compressive strength. Therefore, further studies should be performed to investigate the performance of the $Al(OH)_3$ in the geopolymerisation process. All the samples were cured at $50°C$ for 28 days.

2.3 The influence of SS on the properties of hardened biofuel ash paste

There are many ways to make alkali activation more effective, such as mechanical activation or acceleration of geopolymerisation reactions. Mechanical

activation is grinding the BBA. The specific surface and reactivity are increased by grinding (Marjanović, Komljenović, Baščarević, & Nikolić, 2014; Soutsos, Boyle, Vinai, Hadjierakleous, & Barnett, 2016). According to Marjanovic et al. (Marjanović et al., 2014), mechanical activation promotes dissolution and polycondensation of geopolymers, reduces the degree of crystallinity and enhances the availability of aluminium, therefore more homogeneous geopolymer gel is formed (Marjanović et al., 2014). BBA were grinded for 30 min with a ball mill.

To accelerate the geopolymerisation reactions additional Na_2SO_4 can be used. This material has already been used for FA activation and it can significantly increase the compressive strength. Donaello et al. (Donatello, Palomo, & Fernández-Jimenez, 2013) claims that Na_2SO_4 salt works as a source of alkali metal during activation of FA amorphous phases. Na_2SO_4 reduces the binding time, induction period and accelerates the development of compressive strength. It is noted that the most effective amount of Na_2SO_4 is approximately 2–4% of the FA mass (Shi et al., 2006).

In the experiment, Na_2SO_4 was mixed into the paste with an activator solution. Na_2SO_4 forms when sulphur form sulphur slime reacts with NaOH:

$$NaOH + S + H_2O \rightarrow Na_2SO_4 + H_2O \qquad (9)$$
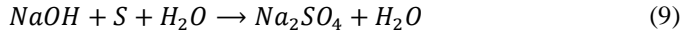
There were five compositions of alkali-activated BBA with different amounts of sulphur slime tested during the experiment:

Table 4. Mixture composition

SS, %	Mass parts, %				$SiO_2/$ Na_2O mol	$SiO_2/$ Al_2O_3, mol
	$Al(OH)_3$	BBA	NaOH	H_2O		
0	16.7	51.4	13.8	18.2	2.0	1.0
0.5	16.7	51.4	13.8	18.2	2.0	1.0
1	16.7	51.4	13.8	18.2	2.0	1.0
2	16.7	51.4	13.8	18.2	2.0	1.0
5	16.7	51.4	13.8	18.2	2.0	1.0

The average density of the samples was about 1250 kg/m^3. It appears that the SS additive does not affect the density of the samples.
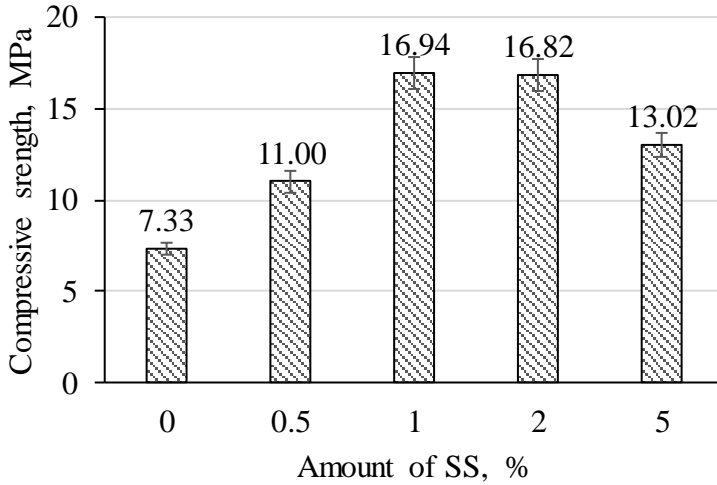
Fig. 9. Compressive strength of alkali activated BBA samples with additional SS

Additional SS enhanced the compressive strength when the amount of additive was between 0.5–2% (Fig. 9). Compressive strength gradually increases up to 1% of SS amount where it peaks reaching 16.82 MPa – nearly twice as much compared to samples without the additive. Another additional percent (2% overall) does not affect compressive strength much – 16.82 MPa. When additive amount is increased to 5%, negative influence is seen, since compressive strength reduces to 13.02 MPa.
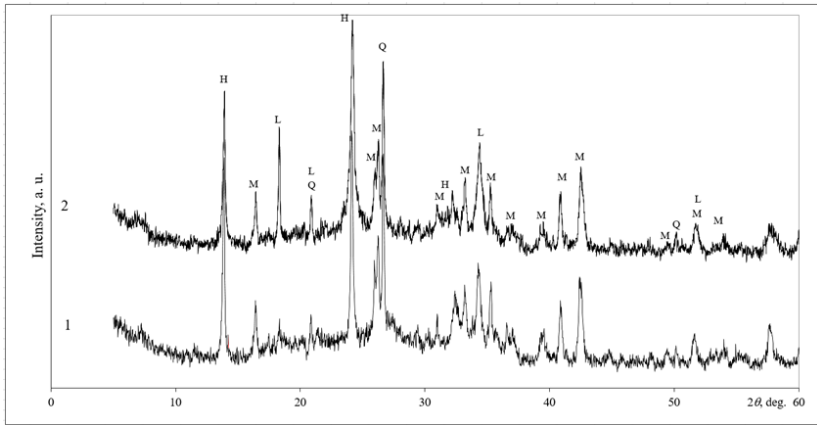
Fig. 10. XRD analysis of hardened geopolymer BBA paste with Na_2SO_4. Notes: 1 – control sample (no SS), 2 – 2% SS, Q – quartz (78-1252), M – mullite (84-1205), H – hydrosodalite (72-2329), L – calcium aluminium silicate hydroxide hydrate (76-1808)
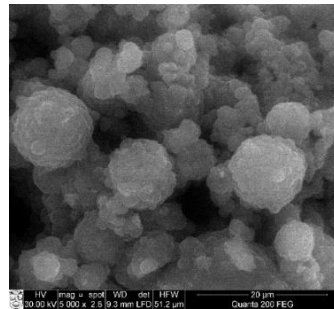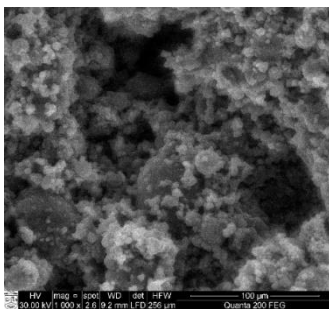

A   B

Fig. 11. SEM images of hardened BBA geopolymer paste without SS

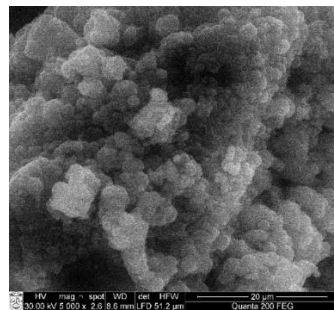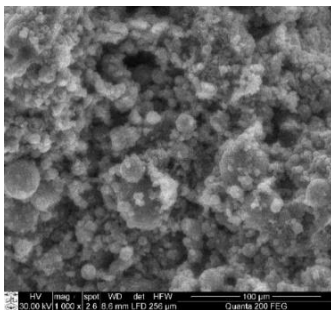A   B

Fig. 12. SEM images of hardened BBA geopolymer paste with SS

When Na_2SO_4 is present, the peaks of hydrosodalite and calcium aluminium silicate hydroxide hydrate are more intense (Fig. 10). It does correlate with the results of compressive strength test. Additionally, SEM images show a denser microstructure with no visible voids (Fig 12). Na_2SO_4 transforms amorphous compounds to crystalline compounds making their microstructure even denser as compared to samples without SS (fig. 11).

The additive is effective for increasing compressive strength of alkali-activated biomass bottom ash. A small amount of the additive (up to 2%) can double the value of compressive strength.

2.4 Alkali-activated FA paste with additional Portland cement

Ordinary Portland cement (OPC) is used in AMMs and geopolymers to enhance their properties (Posi et al., 2016). The experiment was carried out with four compositions partially replacing FA with OPC (Table 5). The material proportions are determined by previous experiments.

Table 5. Sample composition for 1l paste

Composition (OPC %)	FA, g	CEM I 52.5 R, g	Water, g	NaOH, g
0	1145.8	0.0		
5	1088.5	54.4	347.5	244.3
10	1031.3	103.1		
15	974.0	171.9		

OPC indeed has a positive effect on the compressive strength of the hardened paste sample. Samples with 15% OPC additive developed the highest compressive strength – 47.66 MPa after 28 days (Fig. 13). Samples without OPC developed 43.30 MPa after 28 days (Fig. 13). Samples with the OPC additive were stronger during entire period of the experiment.
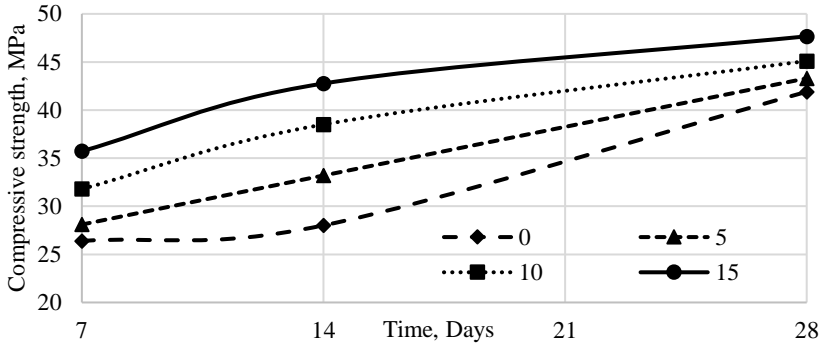
Fig. 13. Compressive strength of harden geopolymer with OPC additive
(0 %, 5 %, 10%, 15 %)

The mineral composition of the control samples (0% OPC) and the samples with 15% OPC additive were analysed with XRD (Fig. 14).
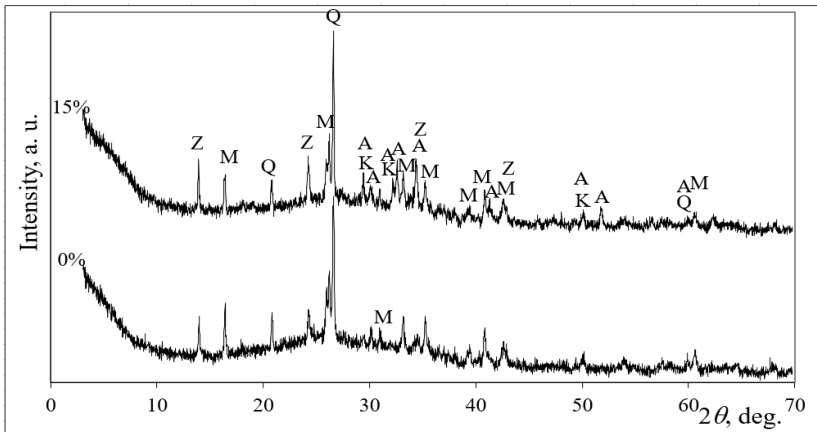

Fig. 14. XRD analysis. Notes: Z – Z-sodium zeolite; M – mulitte, A – alite, K – calcium silicate hydrate, Q – quartz.

A common feature of alumo-silicate material, i.e. the halo peak of indistinct peaks, was featured at 20°–40° 2θ in both cases. During activation, sodium zeolite formed in both samples; it is a common compound for an alkali-activated material. Samples with OPC featured additional peaks of C-S-H, a product of OPC hydration. Also, the peaks of sodium zeolite were more intensive. Quarts and mullite, which are minerals inherited form FA, were present in both compositions.

25

Also, some unreacted alite, a clinker mineral usually found in OPC, was present in the sample with OPC additive.

Control sample (without OPC) and sample with 15 % OPC was selected for SEM analysis. In SEM images revealed that there are no visible unreacted FA particles in both tested specimens (fig. 15). Control specimen appeared to have homogenous microstructure, but nevertheless some voids up 30 μm diameter were noted (fig. 15 a).

Samples with OPC additive appeared to have denser microstructure: with few relatively small voids with diameter up to 10 μm (fig 15 b).
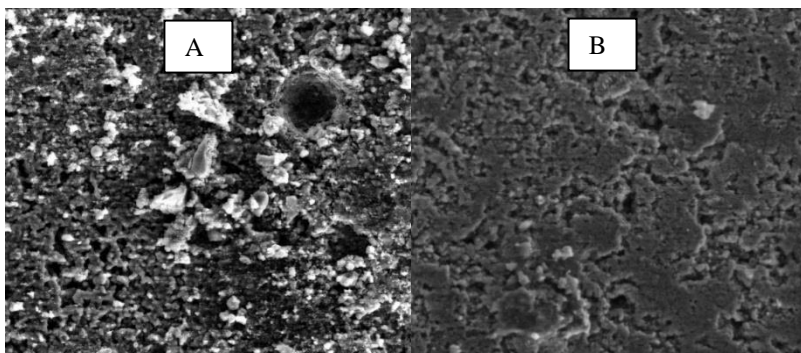

Fig. 15. SEM image of activated fly ash (A) and activated fly ash with OPC additive

By partly substituting FA with OPC in AAMs compressive strength and density are increased. It can be attributed to the formation of C-S-H and a denser microstructure

2.5 The influence of activator solution containing Na_2SiO_3 (water glass) on the properties of hardened geopolymer paste

The aim of the experiment is to compare the properties of hardened geopolymer paste activated with and without water glass. To achieve this, four different compositions were studied (table 5).

The first two compositions, as in the previous chapter, were the control samples, the composition of which was without OPC and with 15% OPC, both activated with a NaOH solution. Because of the same materials and curing conditions the data from the previous chapter is compared to the newly designed compositions were FA and FA with 15% OPC are activated with a NaOH and Na_2SiO_3 (water glass) mixture.

Table 6. Mixture design for 1 l.

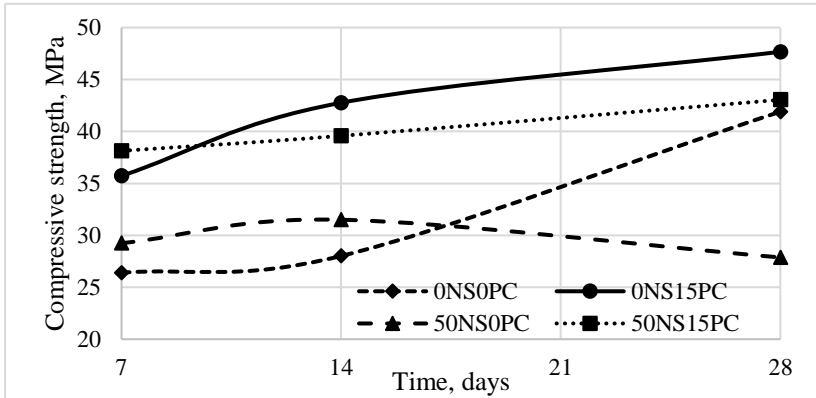| Comp.	FA, g	OPC	Water, g	NaOH, g	Na_2SiO_3, g
0NS0PC	1145.8	0.0	347.5	244.3	0
0NS15PC	974.0	171.9			
50NS0PC	1145.8	0	173.75	122.1354	295.8
50NS15PC	974.0	171.9			

Fig. 16. Influence of Na_2SiO_3 on the harden geopolymer compressive strength

After 28 days, samples activated with an activator containing water glass were weaker compared to samples activated with the NaOH solution (Fig. 16). Compressive strength of I composition samples reached 41.9 MPa and 0NS15PC reached 47.7 MPa, while samples activated with NaOH and Na_2SiO_3 (50NS0PC and 50NS15PC) reached 27.9 MPa and 43.1, respectively. It is worth mentioning that samples with water glass in their compositions tend to reach their final strength more rapidly, 50NS0PC samples reached the compressive strength of approximately 30 MPa within 7 days and 50NS15PC samples were even stronger than 0NS0PC and 0NS15PC after the same period. The compressive strength of samples 0NS0PC and 0NS15PC grows more gradually and eventually surpasses that of 50NS0PC and 50NS15PC.
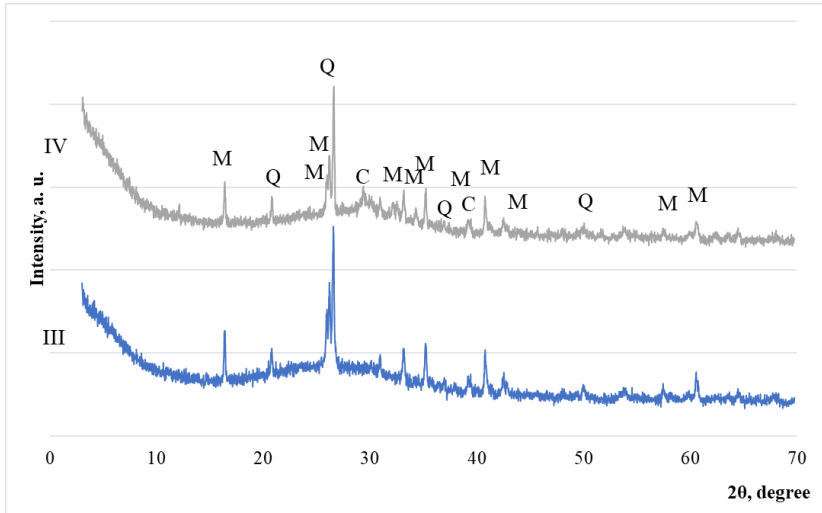
Fig. 17. XRD analysis of III and IV composition samples. Notes: M – mullite, Q – quartz, C – calcite.

XRD analysis of 50NS0PC and 50NS15PC are shown in Fig. 17; the XRD analysis of 0NS0PC and 0NS15PC are in Fig. 14 in the previous chapter (marked as 0% and 15%, respectively). 50NS0PC and 50NS15PC had peaks of mullite and quartz inherited minerals form FA. Unlike 0NS0PC and 0NS15PC (Fig. 14) 50NS0PC and 50NS15PC (Fig. 17) did not show any peaks of sodium zeolite.

Although new crystal phases were not found in 50NS0PC and 50NS15PC, the halo peak was clear in XRD analysis (Fig. 14). In the 50NS0PC halo peak was in 20°– 35° 2θ range and in 50NS15PC halo peak moved up to 25° – 40° 2θ.

2.6 Alkaline Activation of hybrid Cements Binders Based on industrial by-products

To evaluate the influence of OPC on geopolymer concrete, prisms (size 40×40×160 mm) with FA, BBA and PWS were formed. There were nine prisms of each batch and they were tested after seven, 14 and 28 days. During the experiment, prisms were kept in an oven at 50°C. Elevated temperature is proven to have a positive effect on geopolymerisation. The composition of mixtures is given in Table 7.

Table 7. 1l geopolymer mortar composition

Mixture design		Mix 1	Mix 2	Mix 3	Mix 4
FA	Agg., g	1350.00			
	Water, g	244.46			
	NaOH, g	171.85			
	FA, g	740.04	703.04	666.04	629.04
	OPC, g	0.00	37.00	74.00	111.01
	SiO_2/Na_2O	2.70	2.61	2.52	2.43
	Al_2O_3/SiO_2	0.33	0.32	0.32	0.32
	CaO/SiO_2	0.08	0.14	0.21	0.28
BBA	Agg., g	1350.00			
	Water, g	327.53			
	NaOH, g	95.78			
	BMBA, g	740.04	703.04	666.04	629.04
	OPC, g	0.00	37.00	74.00	111.01
	SiO_2/Na_2O	2.24	2.21	2.17	2.13
	Al_2O_3/SiO_2	0.07	0.07	0.07	0.07
	CaO/SiO_2	2.34	2.41	2.47	2.54
PWS	Agg., g	1350.00			
	Water, g	244.46			
	NaOH, g	214.00			
	PW, g	740.04	703.04	666.04	629.04
	OPC, g	0.00	37.00	74.00	111.01
	SiO_2/Na_2O	3.33	3.20	3.06	2.93
	Al_2O_3/SiO_2	0.05	0.05	0.05	0.05
	CaO/SiO_2	0.01	0.05	0.1	0.15

Additional OPC additive had different effects for the samples with different materials (Fig. 18). In most cases, OPC additive significantly improved the compressive strength (Fig. 18), especially when raw material was FA and PWS. FA sample control mix (0% OPC) achieved the compressive strength of 29.67 MPa (Fig. 3a) after 28 days. Samples with 5% OPC additive achieved and the compressive strength of 44.60 MPa (Fig. 18b). Furthermore, within 14 days these

samples reached 98% of final compressive strength, while the control samples reached only 61%. FA samples with 15% OPC substitute gained the highest strength: after 28 days, the compressive strength was 50.99 MPa, which is additional 20 MPa (Fig. 18d) compared to samples without additional OPC. Similar observations can be noticed in samples with 15% OPC additive (Fig. 18d). Only samples with 10% OPC substitute did not improve the compressive strength for reasons yet to be understood (Fig. 18c).
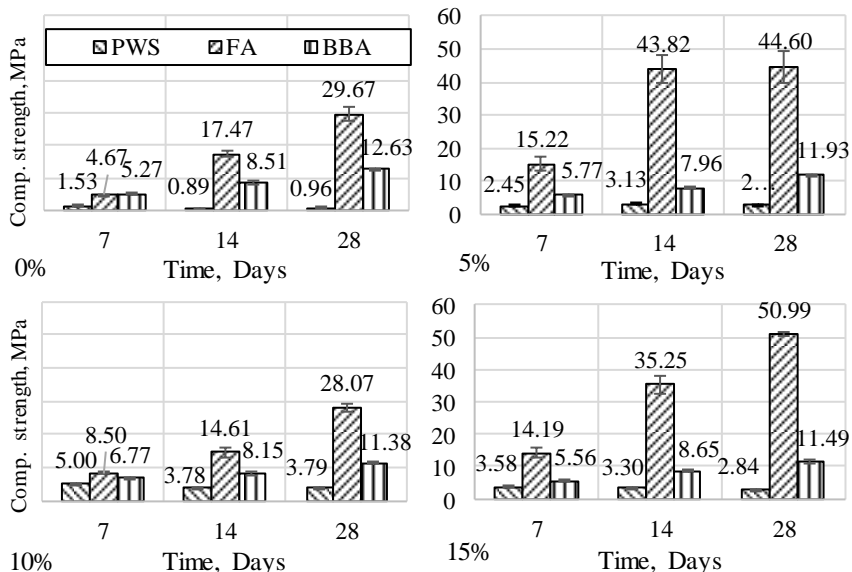

Fig. 18. Compressive strength of hardened binder, (a) – 0% OPC, (b) – 5% OPC, (c) – 10% OPC, (d) – 15% OPC

BBA samples did not develop additional compressive strength and in some cases even lost some after adding OPC to blends. In general, with little exceptions, the compressive strength of the samples remained similar. Geopolymer with BBA gained most of its strength within the first 7 days and which then remained more or less the same despite whether additional OPC was used or not.

PWS samples with OPC substitute, similarly to samples with FA, gained additional compressive strength. But unlike the samples with FA, PWS samples gained most of their additional strength (flexural and compressive) after adding 5% OPC substitute, and larger addition did not have much effect. Nevertheless, PWS samples remain to be the weakest in most instances among materials tested even with the gain of additional compressive strength due to OPC substitute. Exceptions were noted at 7-day-old flexural strength of 10%
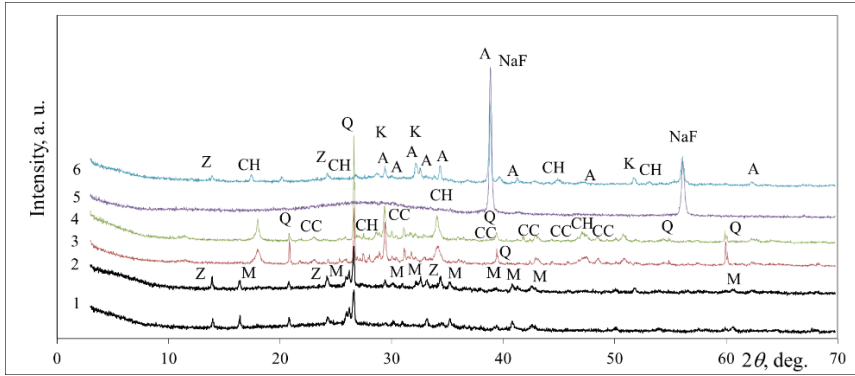
30

Fig. 19. XRD analysis. Notes: 1 – FA (0% OPC), 2 – FA (15% OPC), 3 – BBA (0% OPC), 4 – BBA (15% OPC),5 – PWS (0% OPC), 6 – PWS (15% OPC); Z – sodium zeolite (31-1270); M – Mullite (84-1205), A – alite (13-272), K – calcium silicate hydrate (33-306) Q – quartz (78-1252), CC – calcite (81-2027), CH – portlandite (44-1481), NaF – villiaumite (4-793).

XRD analysis of the binder showed that additional OPC formed C-S-H, which should have contributed to strength development, since it is a primary binding agent in OPC concrete (Fig. 19). Despite the formation of C-S-H in the hardened binder samples of BBA, concrete samples did not gain any strength in most of the cases. This phenomenon could be explained by the formation of portlandite (Ca(OH)$_2$), since peaks in XRD showed a presence of this compound (Fig. 19). This is a relatively weak compound which does no contribute to strength development. Ca(OH)2 formed because of two reasons: there was not enough SiO$_2$ to react (BBA contains only 22.39% of SiO$_2$, while FA contains 49.47%), possible there was large amount of CaO (48.98%).

Despite the fact that PWS mortar samples were significantly the weakest, just like FA samples, PWS samples gained additional strength and the XRD analysis of the binder revealed an additional formation of zeolites and C-S-H gel in the system (Fig. 19). The raw material consists mainly of amorphous SiO$_2$ (over 70%) and only a fraction of CaO (0.42%). Fluoride compounds were also present in the raw material. During hydration, fluoride bonded with sodium forming NaF (villiaumite, 4-793), which had distinct peaks (Fig. 19).

2.7 Mechanical properties and structure of geopolymer concrete

For the compressive strength test 70×70×70 mm cubic concrete samples were produced, their compositions for 1 m^3 are given in Table 5.

Table 8. Mixture compositions for 1 m^3.

Ingredient	Unit	0NS0PC	0NS15PC	50NS0PC	50NS15PC
Sand 0/4	kg	583			
Gravel 4/16		729			
Water		238		119	
FA		719	611	719	611
NaOH		166		83	
Na$_2$SiO$_3$		0		202	
OPC		0	108	0.00	108
SP		0			13

Elastic modulus and porosity tests require 40×40×160 mm prisms. Due to different specimen size, the mortar samples were formed (Table 7).

Table 9. Mixture composition for 1 m^3.

Ingredient	unit	0NS0PC	0NS15PC	50NS0PC	50NS15PC
Sand 0/4	g	1758			
Water		319		160	
FA		964	819	964	819
NaOH		223		111	
Na$_2$SiO$_3$		0		135	
OPC		0	145	0	145
SP		0			13

Superplasticizer "Schomburg SP56" was required for IV to ensure workability when OPC is used with water glass.

Unlike geopolymer paste samples, the additional OPC in alkali-activated FA concrete have reduced the compressive strength. After 28 days, 0NS0PC reached 21.4 MPa, while 0NS15PC was only at 17.5 MPa (Fig. 20). Even though it is often claimed the heat of the OPC hydration is beneficial to geopolymerisation and Ca presence accelerates reactions, from C-A-S-H gel also, the result is opposite during NaOH activation.
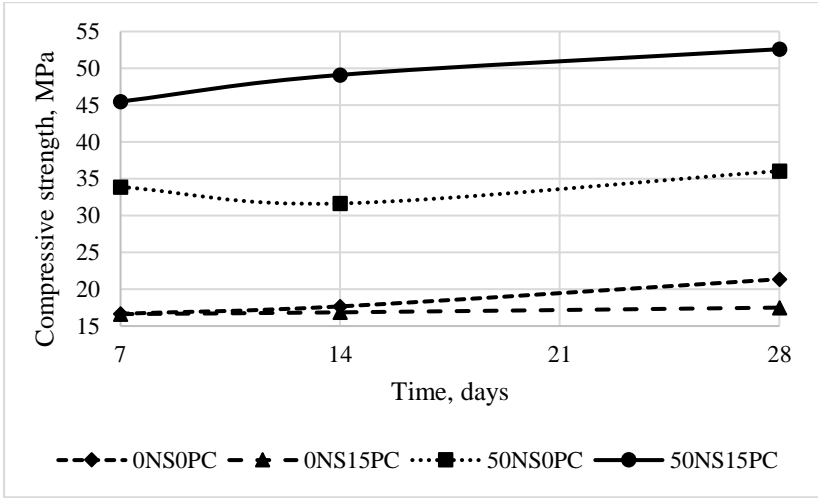
Fig. 20. Compressive strength of FA geopolymer concrete

The presence of Na_2SiO_3 has a significant effect on compressive strength development. FA geopolymer concrete activated with a NaOH and Na_2SiO_3 mixture (50NS0PC) reached 36.1 MPa of compressive strength after 28 days. The effect is even bigger with OPC; 50NS15PC reached 52.6 MPa after 28 days (Fig. 20). The 50NS15PC composition samples had the biggest elastic modulus of 14026 GPa.
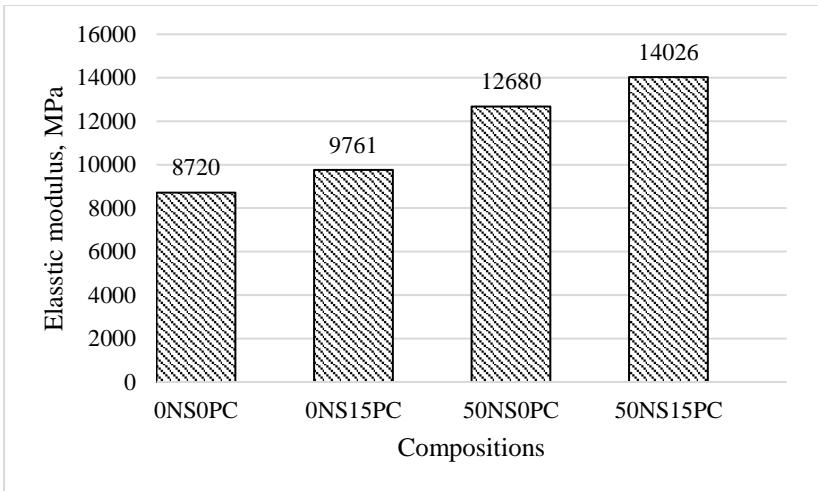

Fig. 21. Elastic modulus of geopolymer mortar

The density (Fig.20) and porosity (Fig. 21) are affected by composition design. With additional OPC (0NS15PC and 50NS15PC), density tends to grow and porosity reduces. Meanwhile, the presence of Na_2SiO_3 (50NS0PC and 50NS15PC) has the opposite effect (Fig. 20 and Fig. 21).
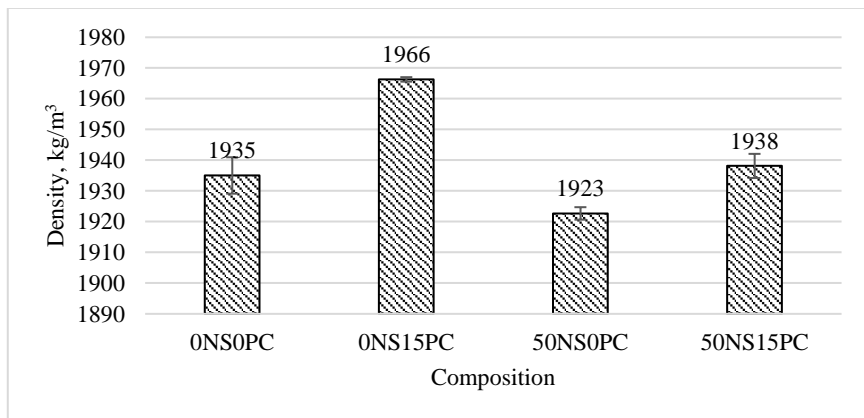

Fig. 22. Density of mortar prisms

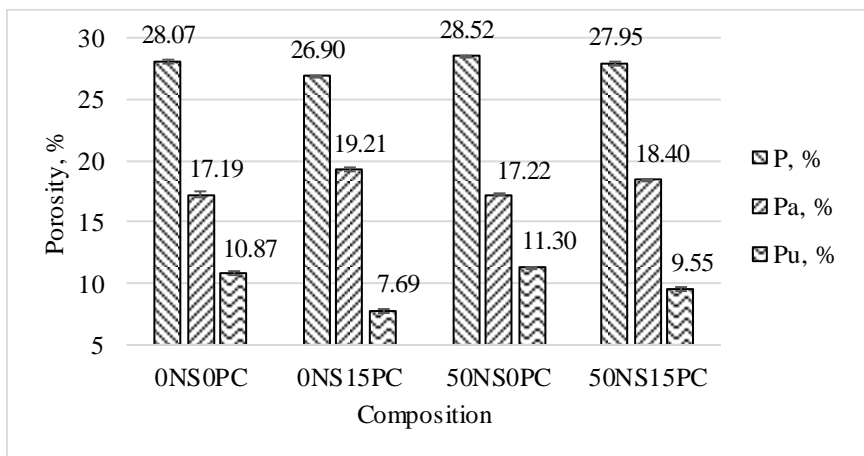**Fig. 23.** Porosity of mortar prisms. Notes: P – porosity, Pa – open porosity, Pu – closed porosity

The porosity of 0NS0PC concrete was 28.1%, closed porosity was 10.9%; the porosity of 0NS15PC was 26.9%, closed porosity was 7.7%. It can be concluded that the presence of OPC reduced porosity. The porosity of 50NS0PC was 28.5, closed porosity was 11.3 which shows that porosity is slightly bigger

with Na_2SiO_3; the porosity of 50NS15PC was 27.95%, closed porosity was 9.6%, which is slightly less than 50NS0PC indicating that OPC is balancing the effect of Na_2SiO_3 on porosity.

2.8 Durability of geopolymer concrete

Three different conditions were chosen to evaluate the durability of geopolymer concrete: alkali-silica reaction (ASR), resistance to freeze and thaw, and carbonation. Prisms in the size of $40\times40\times160$ were used for the ASR test consisting of glass shatters in the mixture to simulate reactive aggregates. Freeze/thaw and carbonation tests used same $70\times70\times70$ concrete cubes as were used in the compressive strength test.

Table 10. Mortar composition for ASR test, 1 m^3.

Ingredient	unit	0PC0NS	15PC0NS	0PC50NS	15PC50NS
Sand 0/4		1491			
Water		319		160	
FA		740	740	740	595
NaOH	kg	223		111	
Glass 4/2		176		176	
OPC		0	145		145
Na$_2$SiO$_3$		0	0	271	

The deformations in ASR mostly depended on the activator solution (Fig. 22). The samples activated with NaOH expanded relatively rapidly: after 1 day, relative deformations reached 1.41 mm/1m in 0PC0NS compositions, and 1.55 mm/1m in 15PC0NS composition. During the following days, samples deformed very little.
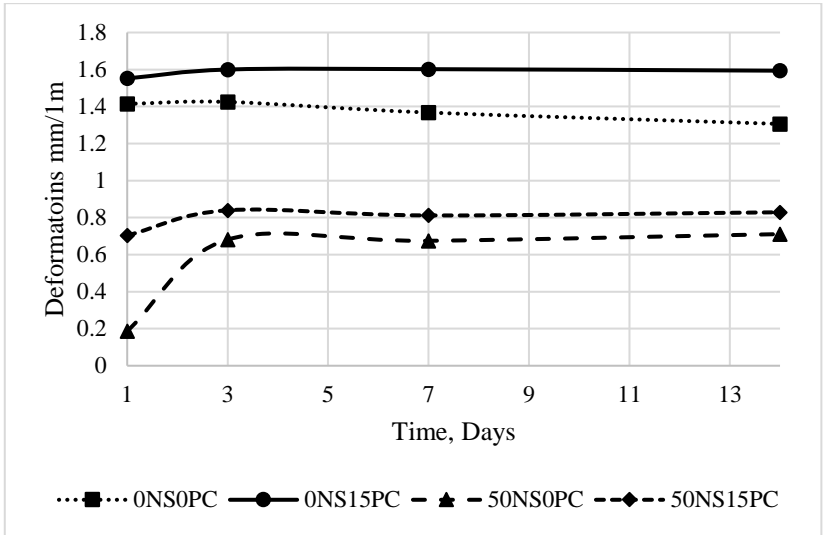
Fig. 24. Deformation during ASR test

Samples with Na_2SiO_3 in the activator solutions (compositions 0PC50NS and 15PC50NS) expanded much less: 0.71 mm/1m and 0.83 mm/1m, respectively, after 14 days of experiment (Fig. 22). The expansions of samples 50NS0PC and 50NS15PC were under 1.0 mm/1m which acceptable by the regulations of the standard.
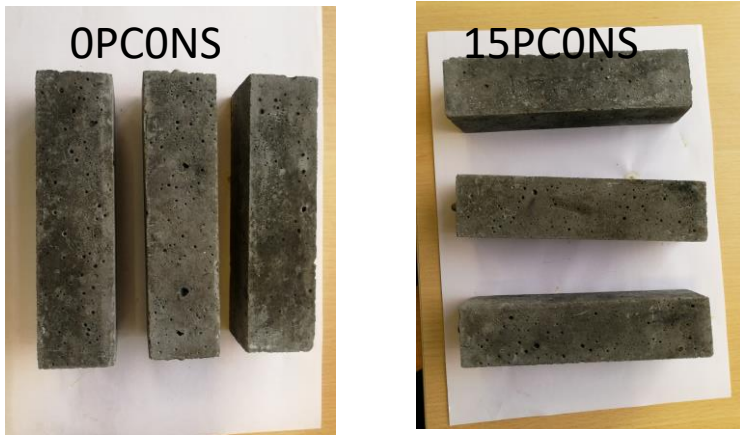

Fig. 25. ASR test samples after time in alkali solution. The sample surface is observed to be smooth without visible damage

It worth mentioning that even 0PCNS and 15PC0NS composition samples had big expansions, visually there were no ASR signs, such as crack network, local pop-outs; the surface was smooth as seen in Fig. 25.

It appears that the presence of OPC increases the resistance of geopolymer concrete to freeze and thaw cycles. When OPC is absent, the mass loss of the samples with FA concrete activated with NaOH and NaOH – Na_2SiO_3 mixture were over 1 kg/m^2, namely, 1.571 kg/m^2 and 1.265 kg/m^2 (Fig 24). For FA concrete activated with NaOH, the amount of OPC necessary to reduce mass loss to under 1.0 kg/m^2 was 10%, while concrete activated with NaOH – Na_2SiO_3 was 5%. The effect of OPC on increased resistance to freeze/thaw cycles can be attributed to reduced porosity. Also, the addition of Na_2SiO_3 makes concrete much stronger thus it can better withstand internal tensions due to ice expansions.
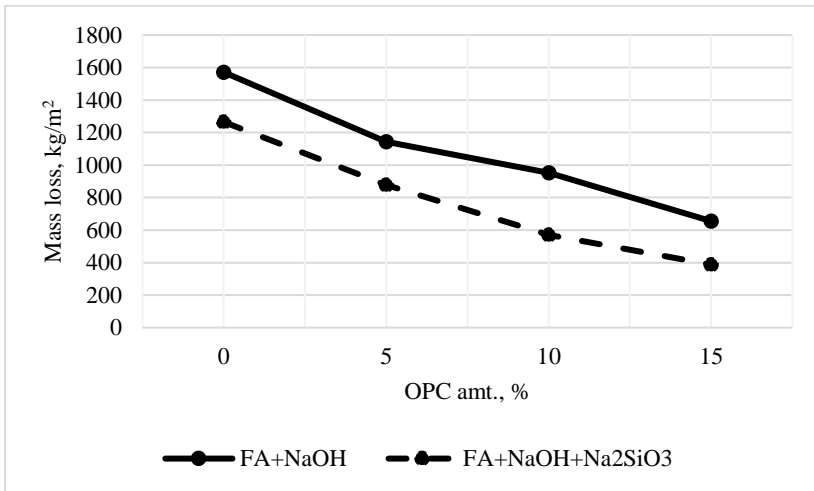

Fig. 26. Mass loss due to freeze/thaw cycles

The experiments showed that geopolymer concrete and mortar can start leaching sodium carbonate compounds, which are products of reaction with CO_2. The residue of sodium carbonate on the surface of the sample can complicate the practical use of this sort of concrete, thus carbonation is an important issue.

Carbonation was evaluated after keeping the samples in a carbonation chamber for 56 days, where the CO_2 level was increased to 1%. The carbonated layer was more shallow where OPC additive was used. Samples with 15% OPC additive were not affected by CO_2 after the first 28 days, and the depth of carbonation only reached 2.5 mm after 56 days in the chamber. The Na_2SiO_3 had the opposite effect: initially, the carbonated layer was 7.5 mm deep and after a

period in the carbonation chamber it reached 23.5 mm. When OPC is used together with Na_2SiO_3 it balances the system – carbonation was initially at 4.5 mm and after a period in the chamber it reached only 10.5 mm.
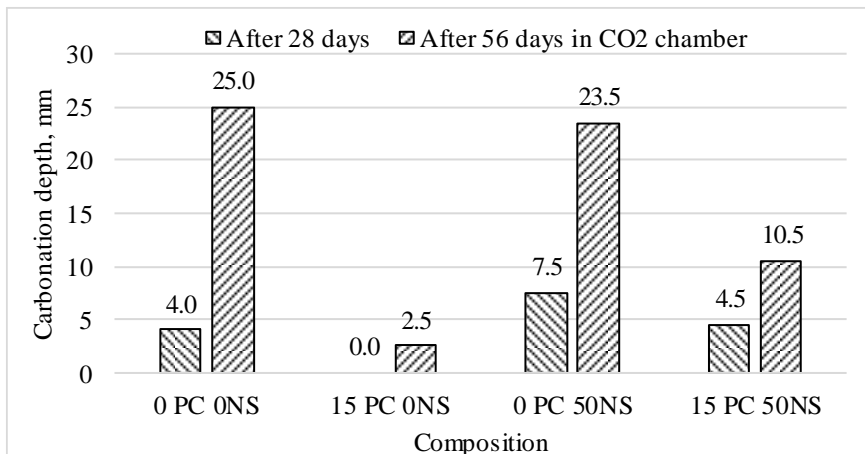

Fig. 27. Carbonation depth

These results correlate with porosity – when OPC is present it reduces porosity, thus reducing carbonation as well. If water glass tends to increase these parameters, OPC works as a balancing factor.

3 CONCLUSIONS

1. The proportions of raw materials should be selected so the SiO_2/Na_2O ratio is 2.0. If the ratio is bigger than 2.3, there are not enough alkali for the reaction to proceed, and if it is lower than 1.5, alkalis rapidly react with CO_2 thus slowing down geopolymerisation reactions. Additional $Al(OH)_3$ participated very little in geopolymerisation reactions and did not join new compounds.

2. Partially replacing FA with OPC geopolymer made the paste more homogeneous and denser, consisting of some OPC hydration products. Therefore, the compressive strength of the geopolymer stone samples with additional Portland cement was significantly bigger (additional 12% compared with samples made from just FA, after 28 days)

3. The OPC additive increased the compressive strength of the mortar samples produced form FA and PWS up to 71%, when the samples were kept in 60°C for 28 days. The increase in strength could be attributed to the denser structure and incorporated calcium in the reaction products.

4. Geopolymer concrete activated with a NaOH and Na_2SiO_3 mixture had better resistance to freeze and thaw, carbonation, ASR and developed bigger compressive strength. In the presence of Na_2SiO_3, OPC can participate in the development of compressive strength: the compressive strength of the samples with OPC additive but without Na_2SiO_3 was 17.51 MPa, meanwhile the compressive strength of the samples with Na_2SiO_3 in the activator solution was 52.6 MPa. Also, the mixture starts binding in ambient temperature. When OPC is used as an additive, a denser structure forms, which compensates for the effect of Na_2SiO_3. Due to these reasons it is beneficial to use OPC with Na_2SiO_3:
   - The expansive deformations are less significant when there are conditions promoting ASR.
   - Carbonation depth is reduced.
   - The amount of material detached due to repetitive freeze and thaw is reduced.

5. Geopolymer concrete with the best properties was obtained when 15% of FA mass was replaced with OPC. The FA and OPC mixture was activated with NaOH and Na_2SiO_3 (NaOH solution concentration 17 mol/l; NaOH and Na_2SiO_3 mixture ratio 1:1). Aggregate and binding agent ratio 2:1.

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REZIUME

Temos aktualumas

Žmogaus veiklos sukelta klimato kaita dėl išmetamų šiltnamio efektą sukeliančių dujų šiuo metu yra viena didžiausių pasaulio problemų. Siekiant mažinti klimato kaitą, 1997 metais pasirašytas Kioto protokolas, o 2015 metais – Paryžiaus susitarimas, įpareigojantys pasirašiusias šalis mažinti išmetamų šiltnamio efektą sukeliančių dujų kiekį.

Portlandcemenčio gamyba yra viena didžiausių CO_2 skleidėjų – vien šio produkto gamyboje išskiriama apie 7 % viso pasaulio metinio CO_2 kiekio. Tokį didelį skaičių lemia tai, kad portlandcemenčio betonas yra pati populiariausia statybinė medžiaga pasaulyje, o portlandcemenčio gamybos procese reikalingos aukštos temperatūros perdirbant klintis. Pagaminus 1 t portlandcemenčio susidaro iki 0,95 t CO_2.

Siekiant mažinti neigiamą portlandcemenčio gamybos poveikį aplinkai, būtina ieškoti alternatyvių rišamųjų medžiagų. Šarmu aktyvuotų medžiagų betonas gali būti gaminamas visai be portlandcemenčio, t. y. būti tinkamu jo pakaitalu. Tokios rūšies betonas, dar vadinamas geopolimeriniu betonu, yra gaunamas užpildo daleles rišant šarminiu tirpalu aktyvuota aliumosilikatine medžiaga. Šarmu aktyvuotų medžiagų ir geopolimerinio betono rišimasis vyksta tada, kai šarmų tirpalas sumaišomas su aliumosilikatine medžiaga, prasideda pastarosios tirpimas, o į tirpalą išsiskiria Si^{4+}, Al^{3+} jonai. Ima formuotis N-A-S-H ir C-A-S-H geliai – kuriama kieta struktūra. Taip susidariusi matrica suriša užpildo daleles.

Šarmu aktyvuotos medžiagos ir geopolimerinis betonas naudingas dar ir tuo, kad pagrindinės žaliavos – aliumosilikatinės medžiagos, dažniausiai būna įvairios gamybos atliekos: lakieji pelenai, metalurgijos aukštakrosnių šlakas, naftos katalizinio krekingo atlieka, silikagelis ir pan. Gaminant tokį betoną galima utilizuoti didelius šių medžiagų kiekius.

Dar 1957 metais Glukhovski šarmu aktyvavo molį ir gautą medžiagą pavadino geocementu, o Davidovits 1979 metais šarmu aktyvuotas medžiagas aprašė kaip neorganinių polimerų tinklus ir juos pavadino geopolimerais. Savo veikaluose Davidovits vengia termino „šarmu aktyvuota medžiaga" ir keičia jį „geopolimeru". Taip autorius nori pabrėžti, kad geopolimerai yra sudaryti iš silicio, aliuminio ir deguonies grandžių, ir atriboti geopolimerines medžiagas nuo įprastojo portlandcemenčio betono, kadangi portlandcementis taip pat kietėja

šarminėje aplinkoje. Mokslo bendruomenėje medžiagos, sudarytos iš N-A-S-H gelio, dažniausiai vadinamos geopolimerais, o surištos C-A-S-H geliu – šarmu aktyvuotomis medžiagomis, tačiau paprastai ši riba yra neapibrėžta, kadangi N-A-S-H ir C-A-S-H geliai linkę koegzistuoti arba formuoti (N,C)-A-S-H gelį.

Nuo to laiko, kai buvo sukurtos šarmu aktyvuotos ir geopolimerinės medžiagos, jos buvo pradėtos taikyti kaip portlandcemenčio alternatyva betono pramonėje. Šarmu aktyvuotas (geopolimerinis) betonas pasižymi ekvivalentišku stiprumu kaip ir įprastas portlandcemenčio betonas, taip pat turi didesnį atsparumą rūgščių (ypač sulfidų) poveikiui.

Geopolimerinis betonas yra naudojamas praktikoje: Australijoje 2013 m. pastatytas pirmasis pasaulyje pastatas su geopolimerinio betono konstrukcijomis. Kvinslando universiteto Pasaulinės kaitos instituto (*Global Change Institute*) būstinėje perdanga surinkta iš 33 geopolimerinio lakiųjų pelenų / šlako betono plokščių. Nuo to laiko Australijoje geopolimerinis betonas sėkmingai naudojamas komerciniais tikslais.

Darbo tikslas ir uždaviniai

Darbo tikslas – sukurti šarmu aktyvuotą (geopolimerinį) betoną panaudojant pramonės atliekas, nustatyti jo savybes ir ištirti struktūrą.

Siekiant įgyvendinti darbo tikslą buvo sprendžiami šie uždaviniai:

1. Nustatyti molinio SiO_2 / Na_2O ir Al_2O_3 / Na_2O santykių įtaką geopolimerinio akmens gniuždymo stipriui ir mineralinei sudėčiai.
2. Įvertinti portlandcemenčio priedo (OPC) įtaką geopolimerinio akmens gniuždymo stipriui ir mineralinei sudėčiai.
3. Ištirti smulkiagrūdžio geopolimerinio betono su portlandcemenčio priedu mechanines savybes šarmu aktyvuojant įvairias aliumosilikatines medžiagas.
4. Ištirti NaOH tirpalo ir $NaOH$-Na_2SiO_3 aktyvatorių įtaką šarmu aktyvuotų lakiųjų pelenų betono mechaninėms savybėms ir ilgaamžiškumui.
5. Parengti šarmu aktyvuoto (geopolimerinio) betono gamybos rekomendacijas.

Mokslinis naujumas

Remiantis atliktų tyrimų rezultatais sukurtas geopolimerinis lakiųjų pelenų betonas, kurio maksimalus stipris gniuždant siekė daugiau kaip 50 MPa. Betono

bandinių gamybai papildomai naudotas portlandcemenčio priedas ir natrio hidroksido tirpalo bei skystojo stiklo šarminis aktyvatorius.

Sukurta nauja rišamoji geopolimerinė medžiaga, panaudojant biokuro pakuros pelenus ir silikagelį, su fluoro junginių priemaišomis, kai fluoras hidratacijos metu surišamas į natrio fluoridą.

Praktinė vertė

Disertacijoje pateikti darbo rezultatai yra svarbūs plėtojant darniosios statybos technologijas, t. y. ekologiško betono technologiją bei gamybos atliekų pritaikymą geopolimerinio betono gamyboje. Sukurtas ekologiškas betonas, kuriame portlandcementis yra pakeičiamas utilizuojamomis pramonės atliekomis, kurių didelė dalis yra laikoma sąvartynuose: anglies lakiaisiais pelenais, biokuro pakuros pelenais, AlF_3 gamybos atlieka – silikageliu – ir sieros rūgšties gamybos atlieka – sieros šlamu.

Ginamieji disertacijos teiginiai

1. Esant dideliam šarmų kiekiui (SiO_2 / Na_2O ≥ 2,3), aliumosilikatinės medžiagos ir šarmo aktyvatoriaus tirpalo mišinyje vyksta greita karbonizacija ir susidarius Na_2CO_3 nebepakanka šarmų geopolimerizacijai.
2. Portlandcemenčio priedas lakiųjų pelenų geopolimerinio betone gerina mechanines savybes ir ilgaamžiškumą, kai aktyvatoriaus tirpale, be NaOH, yra ir Na_2SiO_3.

Darbo aprobavimas ir publikavimas

Disertacijos tema paskelbta 1 mokslinė publikacija žurnale „Romanian Journal of Materials", įtrauktame į ISI Web of Science duomenų bazę, ir 2 straipsniai į tarptautines duomenų bazes įtrauktuose leidiniuose: „Sustainable Architecture and Civil Engineering" ir „Chemical Technology".

Disertacijoje atliktų tyrimų rezultatai paskelbti 6 pranešimuose 5 tarptautinėse konferencijose: „Advanced Construction 2016", „Baltsilica 2016", „Crete 2016: 5th International Conference on Industrial and Hazardous waste management", „Sustainable concrete: materials and structures" (Malta, 2018), „Crete 2018: 6th international conference on industrial and hazardous waste management" (du pranešimai).

Darbo apimtis

Disertaciją sudaro įvadas, literatūros analizė, metodinė dalis, tyrimų rezultatai ir jų aptarimas, išvados, 154 literatūros šaltinių sąrašas, 4 publikacijų disertacijos tema ir 3 mokslinių pranešimų, paskelbtų konferencijų medžiagos rinkiniuose, sąrašas. Disertacijos tekstas apima 132 puslapius, įskaitant 18 lentelių, 52 paveikslus ir 1 priedą.

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