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Alkaline Activation of Hybrid Cements Binders Based on Industrial by-Products

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Environmentally friendly building materials are becoming increasingly relevant in civil engineering in view of their contribution toward sustainable development. This research is focused on hybrid geopolymer concrete (geopolymer with ordinary Portland-cement (OPC) additive) with the objective of analysing strength development. In this research, hybrid geopolymer concrete, manufactured using biomass bottom ash, fly ash and production waste from the manufacture of aluminium fluoride (silica gel) with 4 different amounts of OPC (0%, 5%, 10% and 15%) is studied. Each blend is cured at a temperature of 50 ^{0}C and the material is tested after 7, 14 and 28 days. X-ray powder diffraction and energy-dispersive X-ray spectroscopy were used as investigation methods. The purpose of research was to study the chemical composition and the strength development in hybrid geopolymer concrete made from OPC and the industrial by-products mentioned above.

Keywords: alkali – activated cements, fly ash, geopolymer, hybrid concrete.

Introduction

Ordinary Portland-cement (OPC) is the most common building material in the world (Turner and Collins 2013)an alternative binder based on fly ash (a fine waste collected from the emissions liberated by coal burning power stations, but manufacturing OPC results in significantly high energy consumption, due to the high temperatures required. Production of 1 t of OPC produces nearly 1 t of CO_2, which all in all accounts for around 7% of annual CO_2 emissions (Turner and Collins 2013) an alternative binder based on fly ash (a fine waste collected from the emissions liberated by coal burning power stations. This is not only environmentally unfriendly due to the high carbon footprint of the material, but can have significant economic disadvantages due to additional taxes on products (Turner and Collins 2013)an alternative binder based on fly ash (a fine waste collected from the emissions liberated by coal burning power stations.

All of this encourages further research on alternative binders instead of OPC. Geopolymer concrete (GC) is a relevant alternative to OPC. Geopolymer concrete can significantly reduce the amounts of OPC consumed. In addition different production wastes (like fly ash, high furnace slag and any other waste material that has high quantities of SiO_2 and Al_2O_3) can be utilized during manufactur-

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ing of the concrete. Research suggests that GC has a higher resistance to fire, and improved performance at elevated temperatures (Abdulkareem et al. 2014)mortars and lightweight aggregate geopolymer concrete (LWAGC and in the case of acid attack (Ariffin et al. 2013).

Recently more attention has been given to research in geopolymer concrete containing OPC as an additive. These cements form when blends containing low proportions of cement and high proportions (60-70 %) of mineral additions (slag, fly ash or metakaolin) are alkali activated. According to Posi et al. (2016) the incorporation of OPC enhances the strength development of lightweight geopolymer concrete with a slight increase in the density. Posi et al. determined the optimum OPC content as 10% OPC replacement level of fly ash. The optimum curing temperature curing proposed was 60 °C. Concrete with a density of 1400 kg/m^3 and a strength of 14.5 MPa was obtained using a similar mix design with 10% OPC and curing temperature set at 60 °C. García-Lodeiro et al. reviewed the fundamental chemistry governing these new reactive systems. The authors also analyses the nature of the reaction products formed and their compatibility under different reaction conditions (2012). In the research the reaction mechanism involves a number of stages in which the original gels form in the OPC hydration, C-S-H gel and the gel precipitated in the alkali activation of aluminosilicates, N-A-S-H gel, evolve to C-A-S-H and (N,C)-A-S-H respectively (Inés García-Lodeiro et al. 2012). Pangdaeng et al. (2014) stated that the use of OPC as additive had improved the properties of high calcium fly ash geopolymer. The strength increased due to the formation of additional C–S–H and C–A–S–H gel. Curing conditions significantly affected the properties of geopolymers.

C-S-H/N-A-S-H mix of gels precipitating, did not precipitate in a pure state. Rather their composition was affected by the presence of dissolved species. In the presence of aluminium C-S-H gel development was as follows: C-S-H → C–(A)–S–H → C-A-S-H, whilst in the presence of calcium, N-A-S-H gel evolved as follows: N-A-S-H → (N,C)-A-S-H → C-A-S-H. This last conversion is not complete in these systems because the amount of calcium present is thought to be insufficient (I. García-Lodeiro, Fernández-Jiménez, and Palomo 2013).

Nath and Sarker (2015) used OPC to improve the setting and early strength properties of low calcium fly ash geopolymer concrete cured at room temperature. In the research they concluded that the presence of OPC accelerated the geopolymerisation reaction and the compactness of the gel increased with an OPC content (P. Nath and Sarker 2015). Shinde and Kadam (2016) reported that GC with OPC gives better compressive strength when compared to GC cured at ambient temperature.

In this article the development of strength and the chemical composition of hybrid GC with OPC and additive from biomass bottom ash (BMBA), coal fly ash (FA) and production waste of aluminium fluoride (PW) is studied. The aim of the research is to analyse how additional OPC affects the chemical composition and the development of strength during the first 28 days.

Methodology

The mineral composition of the material was analysed through X-ray diffraction (XRD) using on the “D8 Advance” diffractometer (Bruker AXS, Karlsruhe, Germany). The device parameters were set as follows: tube voltage - 40 kV; current - 40 mA The X-ray beam filter - Ni 0.02 mm, scanning range 2θ = 3–60°. Diffraction patterns were recorded in a Bragg-Brentano geometry using a fast counting detector “Bruker LynxEye” based on silicon strip technology. Samples for chemical composition analysis (XRD) were prepared separately without aggregate to avoid peaks that belong to minerals such as quartz in the sand aggregate. These samples were prepared keeping the same proportions and molar ratios as for the mortar samples and kept in same curing conditions. The XRF analysis of raw materials were performed on the fluorescence spectrometer “S8 Tiger” (Bruker AXS, Karlsruhe, Germany) operating at the counter gas helium 2 bar. The compressive and flexural strength of mortar samples was determined using a hydraulic machine “ToniTechnik 2020” at 7, 14 and 28 days. The mechanical properties including compressive and flexural strength of samples were determined in accordance to BS EN 196-1:2005. The sample size, load rate and other experimental parameters refer to the standard.

Materials

SiO_2 and Al_2O_3 sources

Three different industrial by-products, were used as raw materials. All materials used were a– source of SiO_2 and Al_2O_3; main components of geopolymer chains. The raw materials used were the following: biomass (timber) bottom ash (BMBA), coal fly ash (FA) and AlF_3 Production waste (PW).

BMBA was sourced from a Lithuanian biofuel boiler house. This type of ash contains large amounts of CaO. The XRD analysis for this material (**Fig. 1**) shows peaks of mullite and quartz and also the halo peak at 2θ 25° – 35° indicates the presence of amorphous SiO_2. Its chemical composition is given in **table 1**.

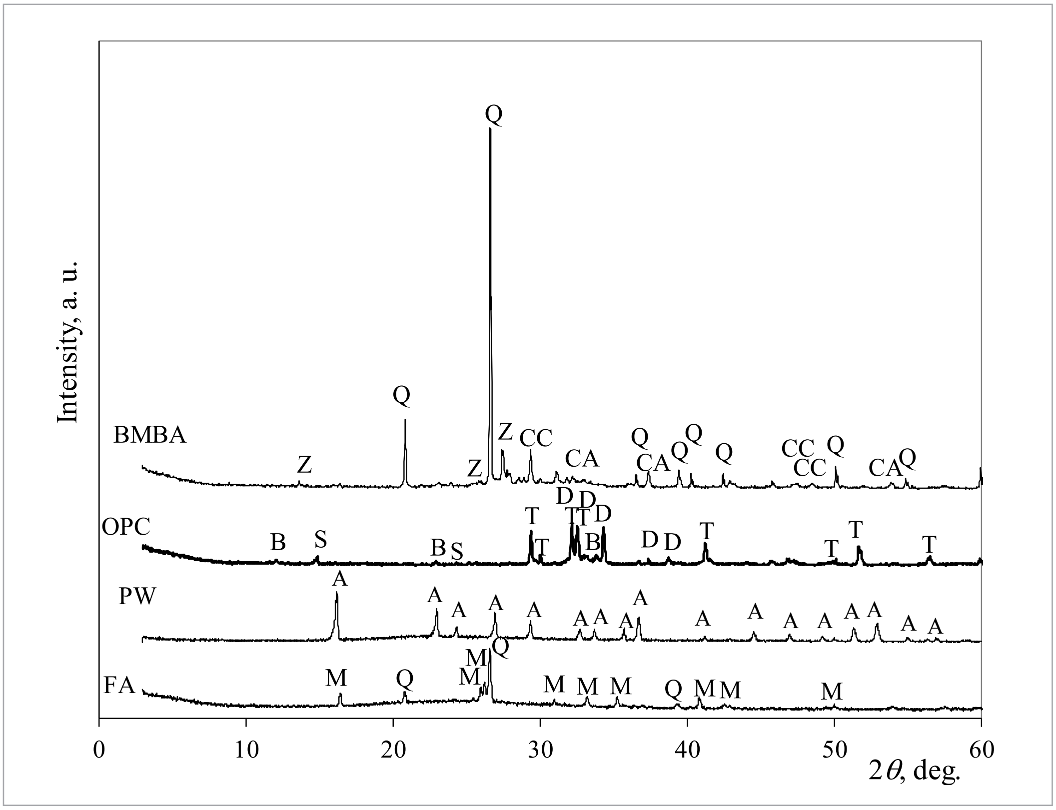


Fig. 1
XRD analysis

Notes: A - $AlF_3 \cdot 3.5H_2O$, M – mullite, Q – quartz, T – alite, D – belite, B –Brownmillerite, S – Bassanite, Z - Anorthoclase, CA – calcium oxide, CC – calcium carbonate.

Coal burning FA is one of the most popular raw materials for geopolymer concrete due to its near perfect chemical composition: FA contains large amounts of SiO_2 and Al_2O_3. These oxides form minerals of quartz and mullite according to the XRD analysis. Amorphous SiO_2 forms a halo peak at 2θ 20° – 30°. Since annual FA output is over 500 Mt it is important to utilize this waste rather than landfill it. The chemical compositions of this material are given in **table 1**.

AlF_3 production waste consists of $SiO_2 \cdot nH_2O$, where SiO_2 is in the amorphous state. AlF_3 production waste is a silicahexaflouride acid neutralisation product. This acid is obtained from the manufacture of phosphoric acid. The silicahexaflouride process reaction (1) is as follows:

$$H_2SiF_6 + 2Al(OH)_3 \rightarrow 2AlF_3 + SiO_2 \cdot nH_2O + H_2O + Q \quad (1)$$

The XRD analysis shows that the material consists of crystalline $AlF_3 \cdot 3.5\ H_2O$ (**Fig. 1**). The "halo" peak at 2θ 20° – 30° in the XRD analysis indicates the presence of amorphous SiO_2. The chemical composition is presented in **table 1**.

Table 1

Chemical composition of raw materials (XRF Analysis)

Oxide	amount, %				Oxide	amount, %			
	FA	BMBA	PW	OPC		FA	BBF	PW	OPC
CaO	3.683	48.978	0,42	57.4	ZrO_2	0,147	0,039	0	0.016
SiO_2	49.468	22,39	72,23	14.3	SO_3	0,921	0	0	4.70
Na_2O	0,945	0,281	0	0	ZnO	0,05	0,041	0	0
Al_2O_3	27.452	2.509	5,68	3.63	TiO_2	1.658	0,328	0	0.231
MnO	0,063	0,347	0	0.0428	CuO	0,027	0,02	0	0
MgO	1.699	8.286	0	2.36	NiO	0,031	0	0	0
K_2O	4.539	8.686	0	1.33	PbO	0,038	0	0	0
Fe_2O_3	7.379	2.179	0,66	3.29	Cl	0	0,04	0	0
BaO	0,436	0,161	0	0	Rb_2O	0	0,024	0	0
P_2O_5	1.310	5.048	0	0.392	F	0	0	21,01	0
SrO	0,106	0,06	0	0.0817					

Table 2

Grading range of aggregate

Size in mm	Cumulative retained, %
2,00	0
1,60	7 ± 5
1,00	33 ± 5
0,50	67 ± 5
0,16	87 ± 5
0,08	99 ± 1

Aggregate

Standard BS EN 196-1 sand was used as aggregate for mortar. Standard sand is natural siliceous sand consisting mostly of rounded particles with silica content of at least 98%. Sand is thoroughly washed, dried and accurately graded. The grading range is provided by manufacturer and presented in **Table 2**.

Portland-cement

Portland-cement is used as additive to contribute through additional C-S-H gel in the geopolymer concrete system (Yip et al. 2008). This is expected to improve the mechanical properties (flexural and compressive strength). In this research CEM I 42.5 R is used. The XRD analysis shows the presence of alite, belite, brownmillerite and bassanite – typical clinker minerals (**Fig. 1**).

In this research prisms (size 40 x 40 x 160 mm) were tested for the flexural and compressive strength. There were 9 prisms produced for each batch and these were tested after 7, 14 and 28 days. During the experimental period, the prisms were kept in the oven at a temperature of 50 °C. An elevated temperature is proven to have a positive effect on geopolymerisation (S. K. Nath et al. 2014). The composition of the mixtures is presented in **Table 3**.

Results and discussion

Additional OPC additive had different effects on the samples produced using different materials (**Fig. 2**, **Fig. 3**). In most of the cases OPC additive contributed significantly in improving the compressive (**Fig. 3**) and flexural strength (**Fig. 2**) especially when the raw material was FA and PW. The s control mix (0 % OPC) of the FA samples achieved 5.75 MPa flexural (**Fig. 2a**) and 29.67 MPa compressive strength (**Fig. 3a**) after 28 days. Samples with 5% OPC additive achieved 6.02 MPa flexural (**Fig. 2b**) and 44.60 MPa compressive (**Fig. 3b**) strength. Furthermore, within 14 days these samples reached 93% of the final flexural and 98% of the final compressive strength, while control samples reached only 59% and 61% respectively. FA samples with 15% substitute of OPC gained the biggest strength: after 28 days flexural strength was 8.02 MPa and compressive strength 50.99

Table 3
Mixtures composition

Mixture design		Mix 1	Mix 2	Mix 3	Mix 4
FA Geoplymer	Aggregate, 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 molar ratio	2.70	2.61	2.52	2.43
	Al_2O_3/SiO_2 molar ratio	0.33	0.32	0.32	0.32
	CaO/SiO_2 molar ratio	0.08	0.14	0.21	0.28
BMBA Geoplymer	Aggregate, 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 molar ratio	2.24	2.21	2.17	2.13
	Al_2O_3/SiO_2 molar ratio	0.07	0.07	0.07	0.07
	CaO/SiO_2 molar ratio	2.34	2.41	2.47	2.54
PW Geoplymer	Aggregate, 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 molar ratio	3.33	3.20	3.06	2.93
	Al_2O_3/SiO_2 molar ratio	0.05	0.05	0.05	0.05
	CaO/SiO_2 molar ratio	0.01	0.05	0.1	0.15

MPa, which amounts to an additional 20 MPa (**Fig. 3d**) when compared to samples without additional OPC. Similar observations can be noticed in samples with 15% OPC additive (**Fig. 2d** and **Fig. 3d**). Only samples with 10% OPC substitute did not present improvement with respect to the compressive strength, for reasons yet to be understood (**Fig. 3c**).

The decrease of compressive strength can occur due to modified zeolite in the system. The modified hydrosodalite possesses, the great surface and water absorption and the early strength of hardened cement paste might decrease when zeolite percentage increases (Janotka, 1995).

BMBA samples didn't develop additional compressive strength or in some cases even experienced a reduction in compressive strength on addition of OPC in the blends. In general, with some exceptions, samples lost flexural strength while compressive strength remained the same as for the control sample. Geopolymer with BMBA gained most of its strength within the first 7 days and later compressive and flexural strength remained the same irrespective on whether additional OPC was used or not.

PW samples with the OPC substitute, similarly to FA samples FA, gained additional compressive and flexural strength. But unlike samples with FA, PW samples experienced an increase in strength (flexural and compressive) with a 5% OPC substitute. However higher levels of substitution of OPC did not contribute more to the mechanical properties (flexural and compressive strength). Nevertheless, PW samples were noted to be the weakest in general, among the materi-

Fig. 2

Flexural strength of hardened binder: (a) – 0% OPC, (b) – 5% OPC, (c) – 10% OPC, (d) – 15% OPC

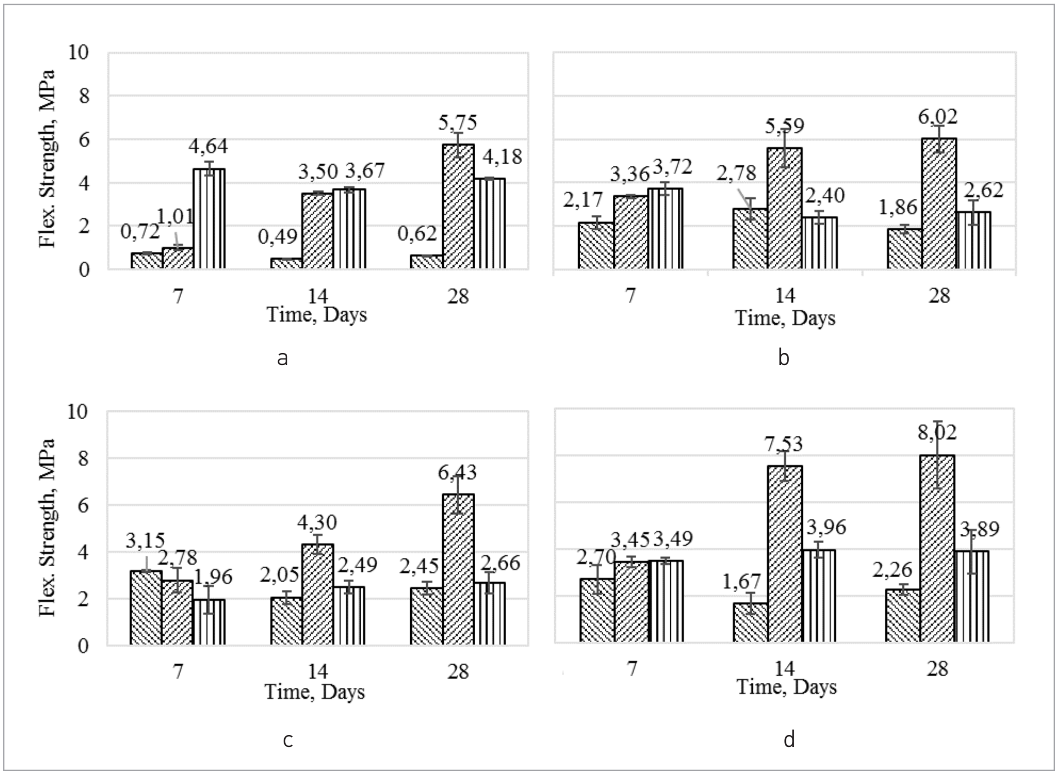
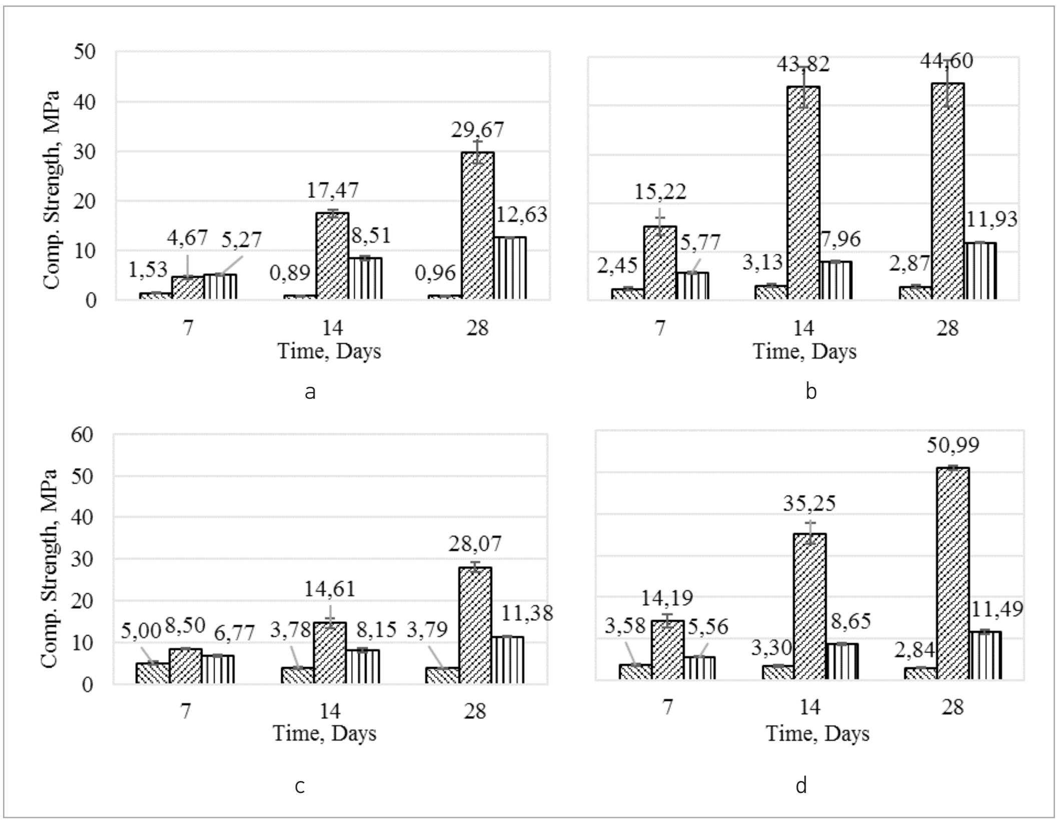


Fig. 3

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



als tested, even with the gain of additional compressive and flexural strength due to the OPC substitute. Exceptions were noted at 7 days for flexural strength with 10 % OPC substitute – the only time when PW samples showed larger flexural strength than FA and BMBA samples, and at 14 days with 5 % OPC substitute (Fig. 2c), where PW samples were stronger than BMBA samples (Fig. 2b).

Separate hardened material samples without aggregate were prepared in order to determine the chemical composition of the binder through XRD analysis. Two compositions of each raw material were selected to be tested – without OPC (control) and with 15% OPC substitute (the maximum substitute in this experiment) to see what difference additional OPC contributes to, with respect to the chemical composition in hardened samples.

Samples with FA and 15% OPC additive resulted in the largest gain in compressive and flexural strengths. XRD analysis of the binder showed that additional OPC formed C-S-H, which should have contributed to strength development, because it is the primary binding agent in OPC concrete (Fig. 4a).

Despite C-S-H formation in hardened binder samples of BMBA, concrete samples didn't gain strength in most of the cases. This phenomenon could be explained through the formation of

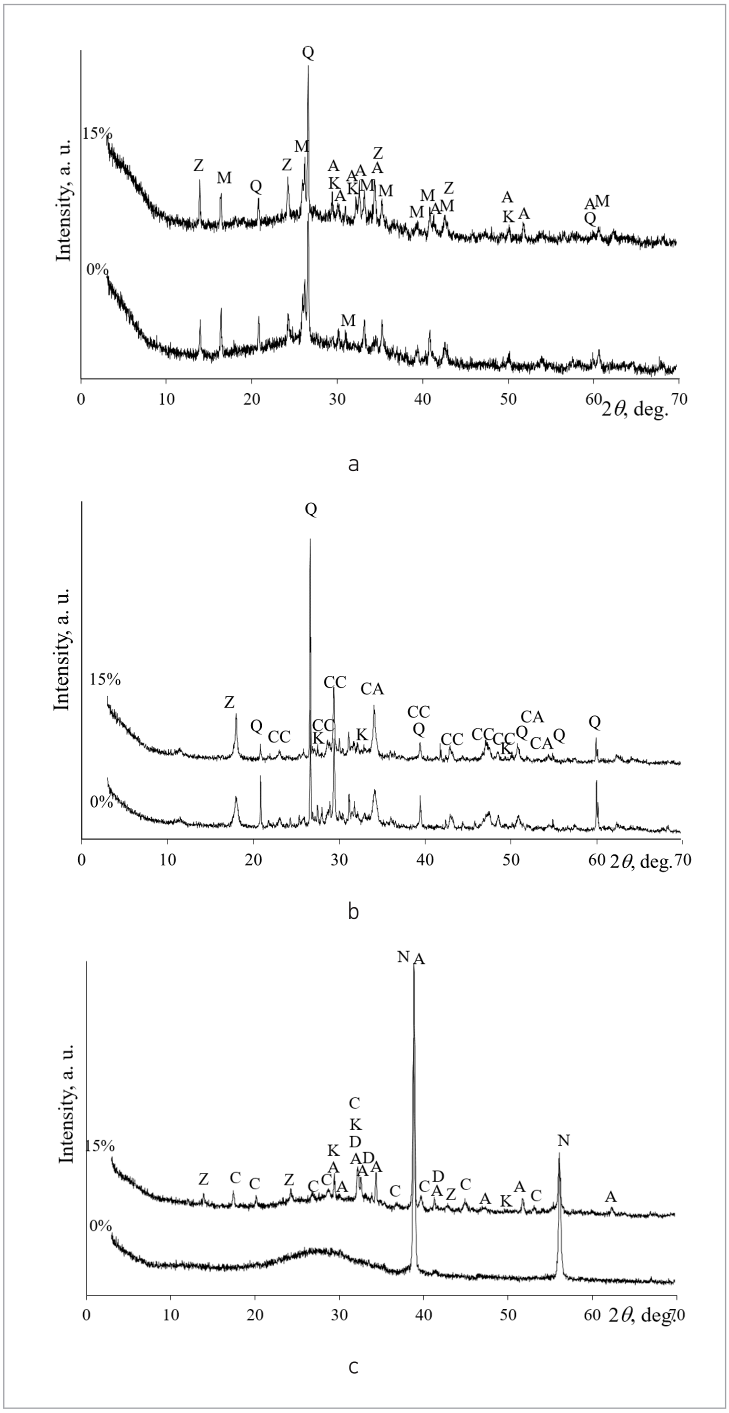


Fig. 4

XRD analysis of hardened binder. (a) Fly ash; (b) biomass bottom ash; (c) AlF3 production waste (silicagel)

Notes: Z – sodium zeolite (31-1271); M- mullite (84-1205), A – alite (13-272), K – calcium silicate hydrate (33–306), Q – quartz (78–1252), CA – portlandite (44-1481), CC – calcite (81-306), C – fluorite (2-1203), N – villiaumite (36–1455, D – larnite (33-302).

portlandite ($Ca(OH)_2$) – the portlandite peaks in the XRD showed the presence of this compound (Fig. 4b). This is a relatively weak compound and doesn't contribute to strength development. It is possible that the larger quantity of CaO (48.98%) contributed, to this and that there was not enough SiO_2 to react. BMBA contains only 22.39 % of SiO_2, while FA contains 49.47%.

Despite the fact that PW mortar samples were significantly the weakest, just like FA samples PW samples gained additional strength. The XRD analysis of the binder revealed the additional formation of zeolites and C-S-H gel in the system (Fig. 4c). The raw material consists mainly of amorphous SiO_2 (over 70%) and only a fraction of CaO (0.42%).

Conclusions

According to the results obtained, it can be concluded that OPC can be effectively used in geopolymer concrete as additive to increase the mechanical properties of concrete, whilst noting specific issues. The following observations are presented:

- Part of the raw materials used for geopolymer concrete could be substituted with OPC. The presence of OPC increases the flexural and compressive strength. The biggest strength gain was observed after 28 days with FA samples: geopolymer concrete samples reached 29.67 MPa compressive strength and those with 15% additive of OPC increased strength up to 50.99 MPa.
- Samples with 5% OPC additive gained strength more rapidly: after 14 days, 98% of its final strength was reached, while samples without OPC reached only 61%.
- The decrease in compressive strength could be caused by the formation of modified zeolite, which, according to literature, increases water absorption.
- Analysis of the chemical composition revealed that OPC forms C-S-H gel – the primary binder in ordinary concrete. In PW samples, additional OPC resulted in the formation of zeolites.
- If raw material has relatively small amount of SiO_2 and contains a lot of CaO, which is often the case with type C fly ash, the addition of OPC can result in a decrease in strength in the sample, because of the formation ($Ca(OH)_2$).

In general, the research indicated that out of the three industrial by-products considered, the FA performed significantly better. While the geopolymer binder performed satisfactorily, the addition of OPC as a partial replacement of geopolymer binder resulted in significant increase in mechanical properties of the material.

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