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Chapter

Low-Emission, Cementless Binders and Concrete: Future Proof Materials

Krystyna Rajczyk, Wiesław Kurdowski, Paweł Pichniarczyk and Grzegorz Janus

Abstract

In the chapter, the results of testing the possibility of obtainment of the high-performance binder and concrete based on alkali activated fly ash and other aluminosilicate wastes or industrial wastes are presented. The discussed topic is framed in terms of requirements and actions taken by the cement industry, which lead to a decrease in carbon dioxide emissions. In terms of carbon footprint, cementless, geopolymer concrete is determined as a more advanced material for civil engineering because of its ability to not contain the clinker component and still be able to reach, by its properties, the level of high-performance cementitious materials. In the presented paper, some of the properties of hardened geopolymer composite material are improved. It was established that the addition of thermally processed waste material, containing metakaolin, radically increases the strength and durability of geopolymer concrete. By means of completed research methods, such as X-ray diffraction (XRD), scanning electron microscopy (SEM) coupled with energy X-ray dispersion spectroscopy (EDS) and thermal analysis DTA-DTG, the influence on changes in the structure of hardened geopolymer material due to the increase in its strength and durability during low-temperature exposure is explained.

Keywords: alkaline activation, geopolymer binder, cementless concrete, low-emission materials

1. Introduction

Geopolymers are inorganic amorphous aluminosilicates. Geopolymers are made up of chains of AlO_4^{5-} and SiO_4^{4-} tetrahedra that are irregularly connected by these tetrahedra. These chains are arranged in layers, and between them, there are cations of sodium as well as groups of OH and H_2O. In this structure, there are periodic cations of aluminium, surrounded by four oxygen atoms [1].

The geopolymer binder binds and hardens as a result of many chemical reactions between aluminosilicate oxides in a strongly alkaline environment, forming three-dimensional polymer chains Si–O–Al–O [2, 3]. The geopolymerisation mechanism is highly dependent on the nature of alkaline activators as well as the chemical

composition of precursors. The components used as precursors for geopolymerisation are low calcium aluminosilicates, e.g. silicious fly ash or blast-furnace slag. As shown in the figure, in addition to fly ash and granulated blast-furnace slag, raw materials such as metakaolin, halloysite and volcanic tuff are good precursors (**Figure 1**). According to Davidovits [2], the process of geopolymerisation consists of four main stages (dissolution, diffusion, polycondensation and hardening). This process was also described in a similar way by Glukhovsky [1]. De Silva et al. [3] suggested a three-step description of the geopolymerisation process (dissolution, agglomeration and polycondensation). Currently, one of the most important experts in the technology, microstructure and process of geopolymerisation of geopolymer materials is an Australian professor – John Provis, who promotes renaming geopolymers as Alkali-Activated Materials (AAM) [4].

Geopolymers are cementless, hardened, mechanically resistant materials with properties similar to natural stone or well-known concrete. The bonding process of such materials is different compared with the hydration process of cement, which involves the hydrolysis of calcium silicates and the formation of a hydrated C-S-H phase, with the simultaneous release of calcium hydroxide. The bonding process of geopolymers is slower compared with cement bonding. However, according to the literature, this time is sufficient to use the geopolymer binder to obtain concrete [2].

The preliminary research, held in the 1970s of the twentieth century in Poland, had led to development of geopolymer material by alkaline activation of granulated blast-furnace slag [5–8]. These studies were pioneering research in the country, which was a starting point for the numerous studies on geopolymer binder in other research centres such as Ł-ICIMB in Cracow, AGH in Cracow, Cracow University of Technology, and Poznan University of Technology. As it turned out, the volcanic tuff from Filipowice proved to be a good precursor for obtaining geopolymer materials [9].
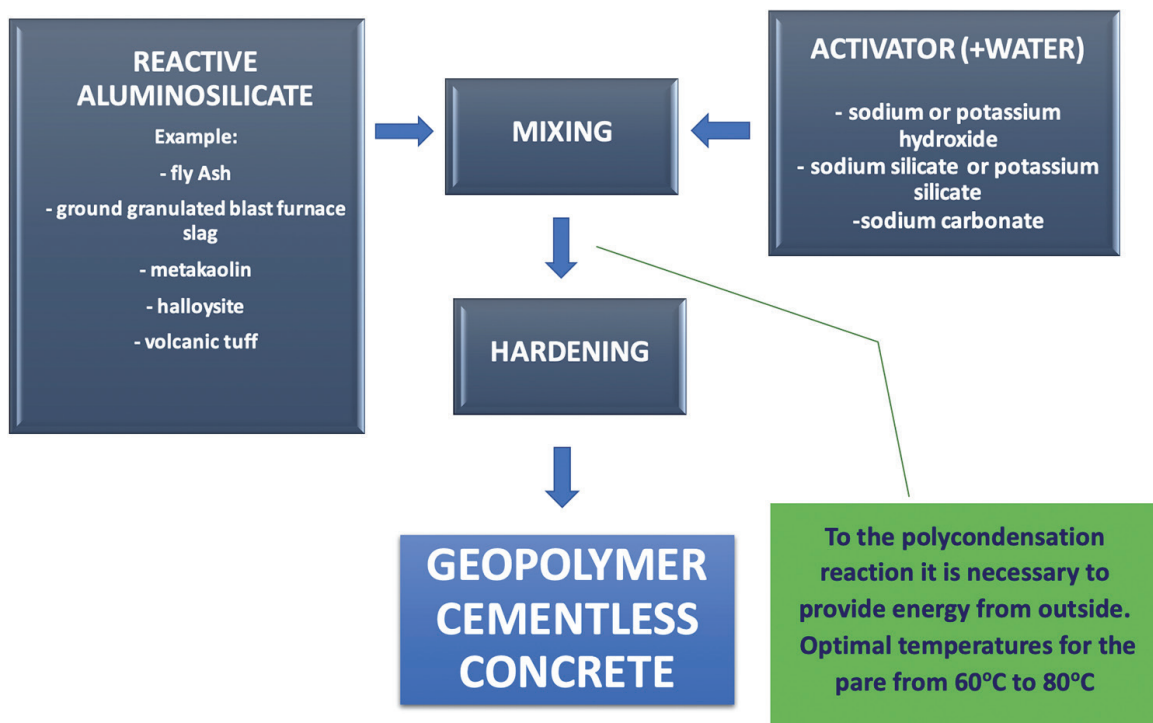

Figure 1.
Scheme for obtaining geopolymers.

In addition, the authors of the cited study have shown that post-mining waste such as coal shale [10], fly ash from lignite combustion [11] and calcined clay [12] can be an attractive material for the production of geopolymer binders.

The Ł-ICIMB (Łukasiewicz Research Network – Institute of Ceramics and Building Materials) has been conducting research on the use of fly ash from national power plants as a precursor for the production of geopolymer concrete [13–15]. Based on the XRD, SEM and thermal studies, it was found that the binding and hardening processes of cementless binder, based on fly ash, are the result of the dissolution of the active components of fly ash in a solution of sodium hydroxide. Obtained gel of silicoaluminates crystallises to form a hydrated sodium aluminosilicate of the sodalite or other type of zeolites such as: hydrosodalite, zeolite P, chabazite-Na and faujasite [16]. The resulting phases are durable and resistant to water and ambient environment, as confirmed by long-term strength tests [15, 17].

The degree of suitability of fly ash for geopolymerisation is determined by the SiO_2/Al_2O_3 ratio [18] and the CaO/SiO_2 ratio [19, 20] in fly ash, which determine the content of active components, which enter the solution under the influence of an alkaline activator [21]. According to the literature, most fly ashes have suitable properties, allowing the obtaining of binding cementless binders [18, 22]. However, as shown in [13, 15], the most advantageous fly ash allowing the production of high-strength binders and concrete is silicious micro-fly ash. The ability to convert the fly ash into geopolymer material is related mainly to the glassy phase composition, degree of gradation and loss of ignition [23–25].

Many studies have been conducted on the production of geopolymer materials based on fly ash [13, 17, 26–28]. The properties of hardened materials depend not only on the properties of the precursors, but also on the used activators. The most commonly used activators are sodium or potassium water glass, NaOH or KOH solution or a mixture of these compounds at experimentally determined proportions and concentrations [29–32]. The use of hydrothermal treatment (low-pressure steaming or autoclaving) accelerates the geopolymerisation reaction [16, 33, 34].

Geopolymer binder and concrete are widely considered to be low-carbon materials. Recently, many research centres around the world are undertaking research in the field of technology to obtain such materials. This has been included in the Roadmap of the European Cement Association (CEMBEREAU) as one of the options for reducing direct carbon dioxide emissions from the cement industry [35]. Taking into account that the cement industry is currently responsible for around 7% of anthropogenic CO_2 emissions [36], the proposal of the use of geopolymer binders in a partial exchange for high-energy and energy-consuming cement binders can significantly reduce the environmental burden and protect raw materials resources by increasing the use of waste materials and industrial waste. However, according to the literature review, most of the available studies have used either large quantities of alkaline activators or thermal processing in order to obtain geopolymer materials with properties comparable to or superior to traditional cement concrete. Such procedures raise production costs and energy consumption [37].

However, high cost of activators is a serious hindrance in the wide and industrial application of cementless geopolymer materials. This main reason hinders the competitiveness of alkali activated binders to Portland cement in spite of a much less energy-consuming of geopolymer binders. According to the data presented in [38], almost 60% of carbon dioxide emission from the process of producing geopolymer materials is associated with the production of alkaline activators. Therefore, some authors of publications on the production of geopolymer concrete believe that

this technology does not lead to a significant reduction in carbon dioxide emission [39–41]. When making a reliable assessment of the environmental impact of the production and use of geopolymer materials, it is important to pay attention to the method of calculation and the data adopted by the authors. As Davidovits [42] explains, taking into account the life cycle of concrete, the production and use of geopolymer concrete lead to a reduction in CO_2 emissions. Furthermore, a majority of the authors believe that using geopolymer concrete instead of traditional cement concrete reduces CO_2 emission into the atmosphere [43–46].

The development of geopolymer technologies is justified because of the environmental and economic aspects, as well as the expectations of civil engineers. This technology is currently under research not only in the sphere of aggregate concrete but also in the technologies of obtaining lightweight geopolymer concrete [47, 48], self-compacting geopolymer concrete [43, 49] and even geopolymer foam concrete [44] or reinforced geopolymer concrete [27, 47].

The number of publications devoted to geopolymer concrete is constantly growing. In 2019–2020, it amounted to around 5200 and was almost twice as high as in 2017–2018 and more than eight times as high as in 2011–2012 [50]. However, only about 10% of the publications concern research on the aspects of construction and engineering applications [28], while the remainder is confined to laboratory-scale research [48, 51]. Despite many studies, the results of which can be observed in numerous publications [27, 28, 43, 44, 47–49, 51–54], geopolymer concrete has not received international appreciation as a construction material. It seems to be necessary to develop standards for the production of geopolymer concrete and procedures for designing geopolymer concrete structures [50].

An example of one of the first uses of geopolymer concrete is the building of the University of Queensland – Global Change Institute (GCI). The structure of this four-storey building is constructed from, among other, suspended slab floors and facade panels made of geopolymer concrete. The precursor used for the production of geopolymer concrete was a mixture of fly ash and blast-furnace slag [55]. In Australia, a widely developed technology is the production of sewer pipes, railway sleepers, burial crypts, culverts and wall panels from geopolymer concrete [56, 57]. Currently, one of the largest applications of geopolymer concrete is the element of the taxiway at Brisbane West Wellcamp Airport [58]. Long-term durability studies preceded the use of this concrete as a structural material [57]. However, according to Srividya et al. [50], in the current state of knowledge, it is necessary to further document the durability of such material under different exposure conditions and over a longer period of time. Regardless of ongoing research around the world, extensive literature reviews summarising scientific achievements in the field of geopolymer concretes have been published in recent years [37, 50].

The presented chapter presents the results of research on geopolymer materials obtained in the process of alkaline activation of fly ash and on geopolymer concrete with their participation. The optimal parameters of the activator quantity and the cure method for obtaining high-strength concrete were determined in previous works [13, 15]. Preliminary research carried out at the Ł-ICIMB on the development of an active additive for cement and concrete based on domestic kaolin resources has led to the establishment of optimal conditions for the thermal processing of raw clay for the conversion of the kaolin component into amorphous metakaolin [59]. The chapter also presents extensive studies and their results on increasing the durability of concrete in a low-temperature environment by enriching the concrete formula with kaolin mineral additive which were partially discussed in [15].

2. Research materials

Three types of fly ash were selected for the study: siliceous fly ash from hard coal combustion (FA1, FA2), fluidised fly ash from lignite combustion (FA3) and calcareous fly ash (FA4, FA5, FA6). FA2 ash, termed 'micro-fly ash' was selectively sampled. The FA5 and FA6 calcareous fly ashes were subjected to special treatment to improve some of their properties. The carbon fractions were extracted and rejected from the FA5 and FA6 ash. Moreover, the FA6 ash was additionally ground after the separation of the carbon fractions. **Figure 2** shows SEM image of the ashes used in the study.

Based on SEM image observations, it was found that the ashes used in the studies differed significantly in size and shape of the particles. While micro-fly ash (FA2) is characterised by fine oval-shaped particles (**Figure 2A**), calcareous fly ash is characterised by a more irregular shape (**Figure 2B**). The additional grinding of the calcareous ash after extraction of the carbon fractions (**Figure 2C**) resulted in the release of fine particles from conglomerates of larger ash particles as shown in **Figure 2D**. As a result of this procedure, very fine-grained ash was obtained. The results of the laser analysis obtained for FA2 and FA6 ashes are shown in the diagram (**Figure 3**).
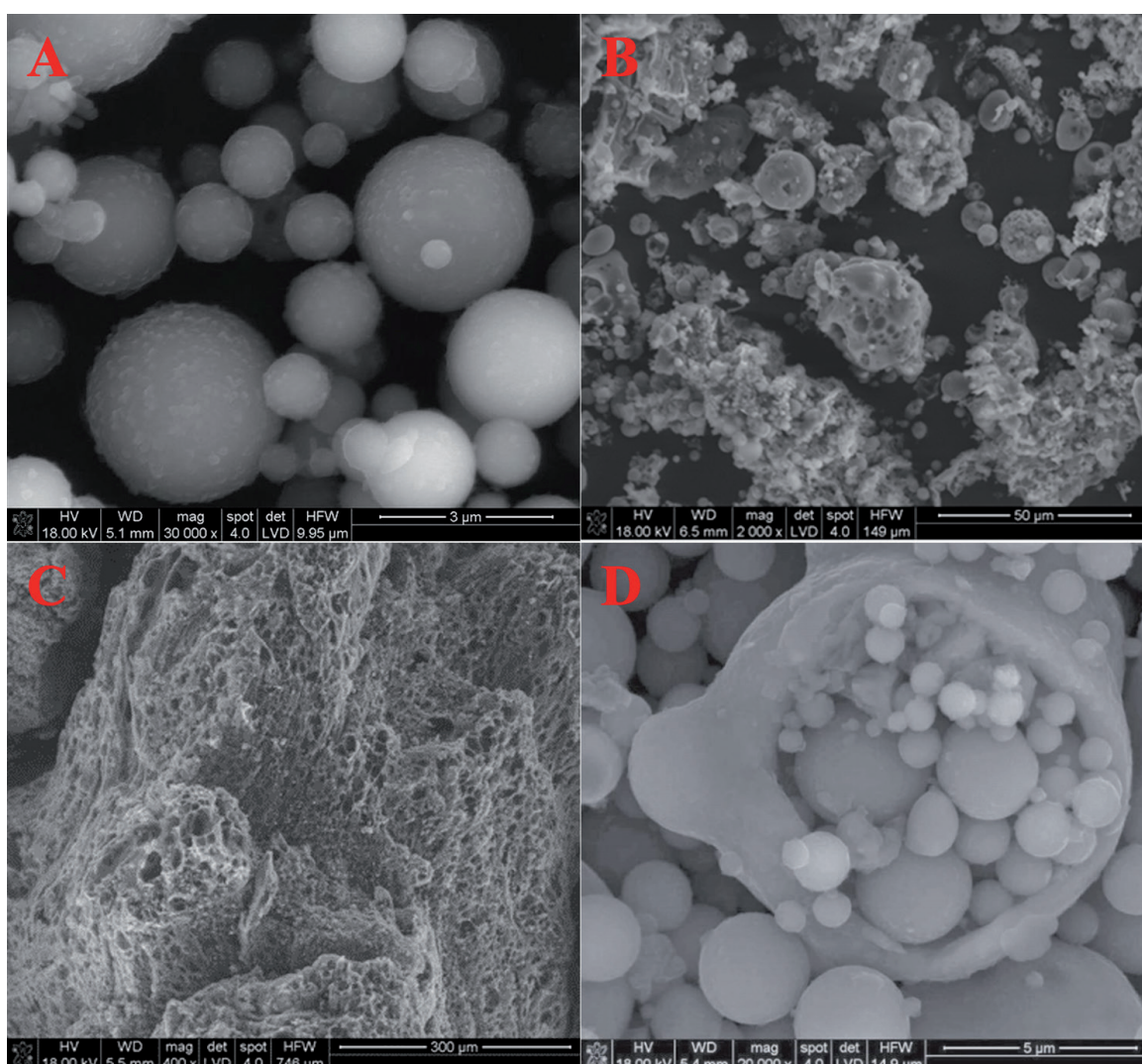

Figure 2.
SEM image of: A: 'micro-fly ash' - FA2, B: calcareous fly ash after the carbon extraction - FA5, C: extracted carbon particles from calcareous fly ash -FA4, and D: calcareous fly ash after additional grinding - FA6 [60].
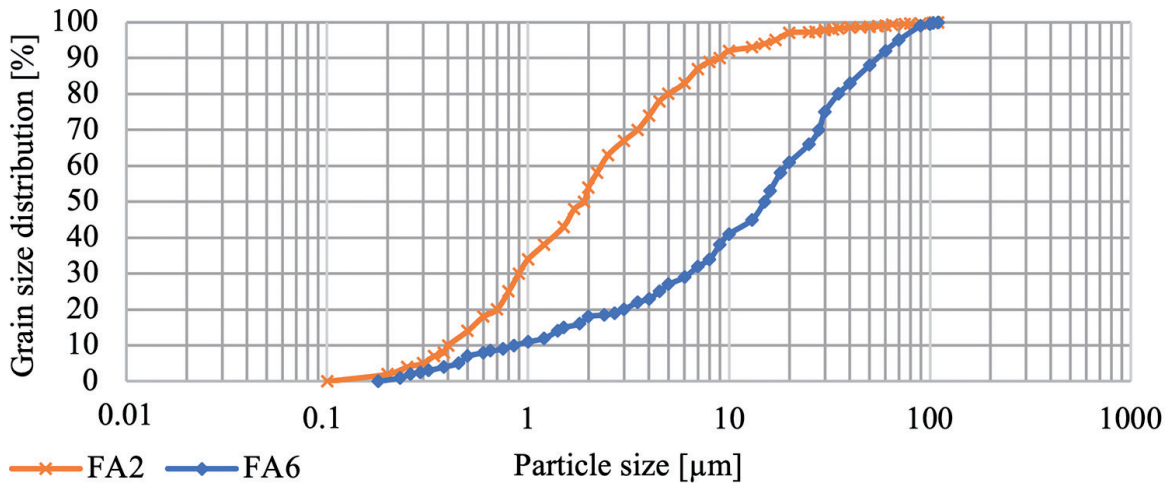
Figure 3.
Cumulative curve of particle size distribution of FA2 and FA6 fly ashes.

FA2 and FA6 ash particles showed significant differences in the granulometric distribution of these samples. FA2 fly ash is characterised by a predominant number of grains smaller than 10 μm (more than 90%). The maximum FA2 ash particle size was about 50 μm. The FA6 fly ash sample is characterised by larger particles. The percentage of particles smaller than 10 μm is about 40%, despite the additional grinding of the ash. The maximum particle size for this sample is about 100 μm. By analysing the particle size distribution curve of FA6 fly ash, it can be concluded that this material has a particle accumulation in the range of 10–60 μm and 0.5–1 μm.

As an additive to increase the durability of geopolymer concrete, a material containing a metakaolin component obtained by calcination of waste clay was used in the studies. The conditions of calcination were established on the basis of XRD studies and on the basis of the results of studies obtained using thermal analysis [13]. The phase composition of the clay used, as determined by XRD studies, is shown below.

The clay used contains significant amounts of calcite (**Figure 4**, **Table 1**). As can be seen from **Figure 4**, characteristic lines for calcite of considerable intensity are observed. The other components of the clay are kaolinite, quartz and a trace of minerals with a total content of less than 1%.
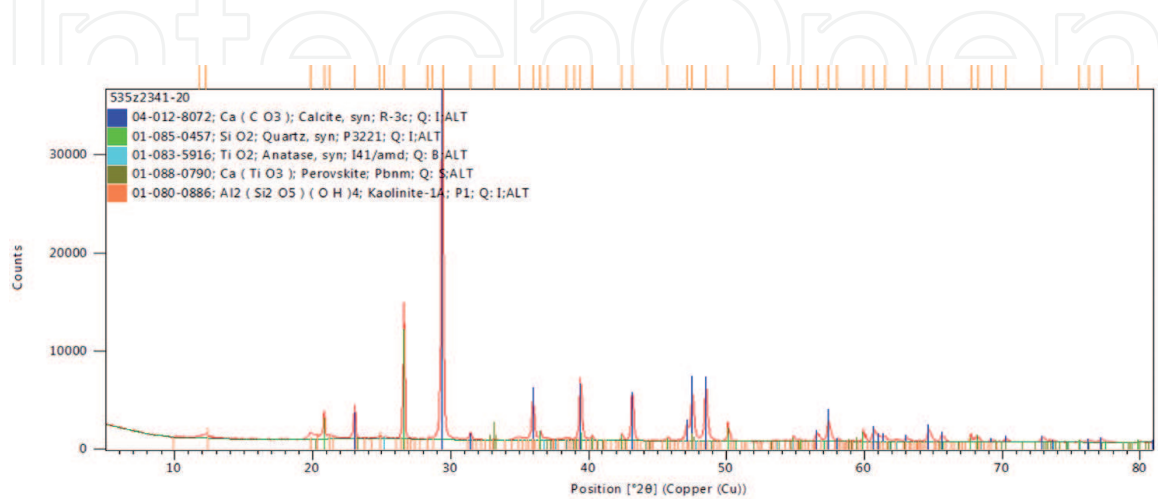

Figure 4.
XRD pattern of the raw waste clay.

Material	Quantitative contribution of phase composition [%]	Standard deviation [%]
Calcite	67.7	0.38
Kaolinite	17.9	0.42
Quartz	13.6	0.14
Anatase	0.40	0.06
Calcium titanate	0.40	0.10

Table 1.
Quantitative phase composition of the raw waste clay.

Based on DTA and DTG curves, dihydroxylation of kaolinite present in the waste clay begins in the temperature above 400°C, with the maximum of the endothermal effect at the temperature of 560°C (**Figure 5**). As a result of dihydroxylation, the metakaolin arises. According to Kurdowski [61], simultaneously with further temperature increase, the OH⁻ ions are eliminated and the structure of metakaolin is destroyed. The spinel phase of aluminosilicate and silicon is formed. Further temperature increase leads to conversion of these phases into mullite.

The DTA and DTG curves (**Figure 5**) also show an endothermic effect with a maximum temperature of 800°C associated with the decomposition of calcite. According to the accepted assumptions, the thermal activation temperature used in the waste clay studies should lead to the transformation of kaolinite into metakaolin, preventing its crystallisation into mullite. In addition, the thermal activation of clay assumes the lowest possible calcination temperature to prevent the complete decomposition of calcium carbonate in order to achieve the lowest possible level of CO_2 emissions. For
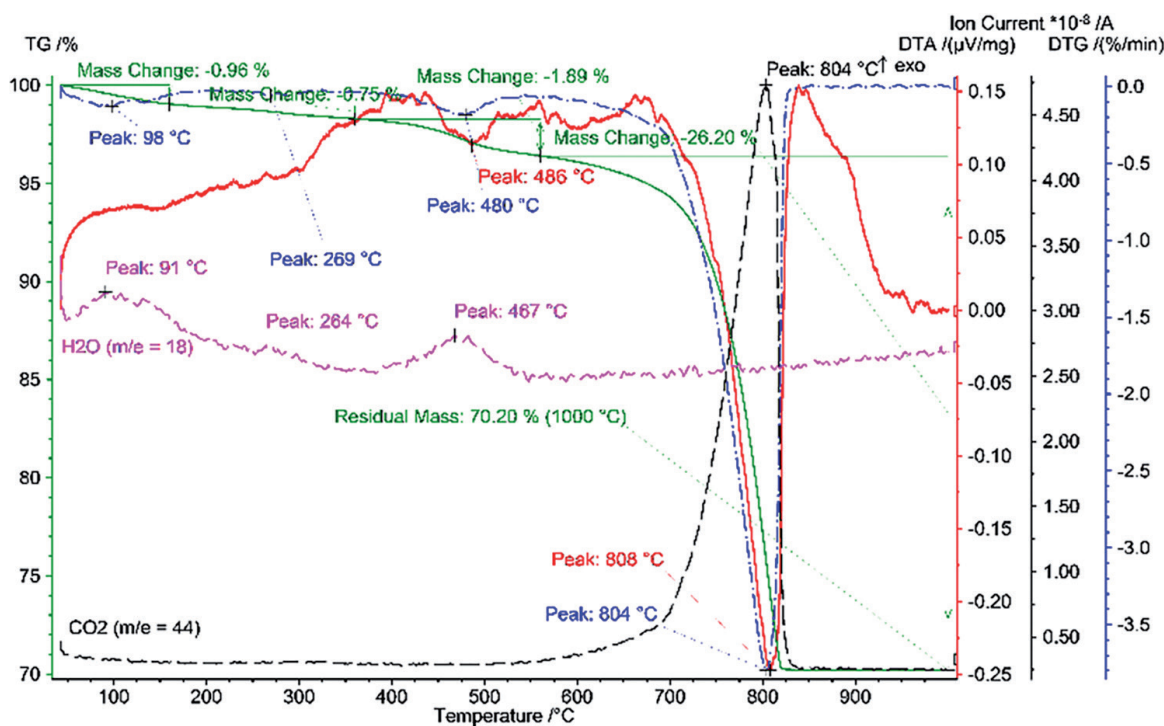

Figure 5.
DTA and DTG curves of the raw waste clay sample.

the waste clay used in the study, the time of calcination was established to 2 hours and the optimum temperature of this process was determined as 700°C.

3. Geopolymer binder forms alkali-activated fly ash

The fly ash was activated using the 8 M NaOH solution. The ratio of the alkaline solution (as an activator) to the fly ash was determined experimentally. It was 0.5 or 0.6 depending on the applicable fly ash. The samples in the form of prisms with dimensions of 40 x 40 x 160 mm were prepared for testing. After ash paste was obtained, the samples were cured under low-pressure conditions at 80°C with an ongoing 24-hour heating-maturing-cooling cycle. The samples were then subjected to compressive strength tests, which are summarised in **Figure 6**.

In addition, to determine the effect of curing conditions of alkali-activated micro-fly ash (FA2), strength tests of hardening samples of geopolymer binder under ambient conditions were carried out. **Figure 7** shows the results of the compressive strength tests of the curing samples at room temperature and humidity. It has been observed that, without the use of low-pressure steam curing conditions, curing the geopolymer binder at room temperature (20**°C**) and air humidity of about 50% for a period of up to 56 days does not lead to the obtaining of high strength. Hardened geopolymer binder
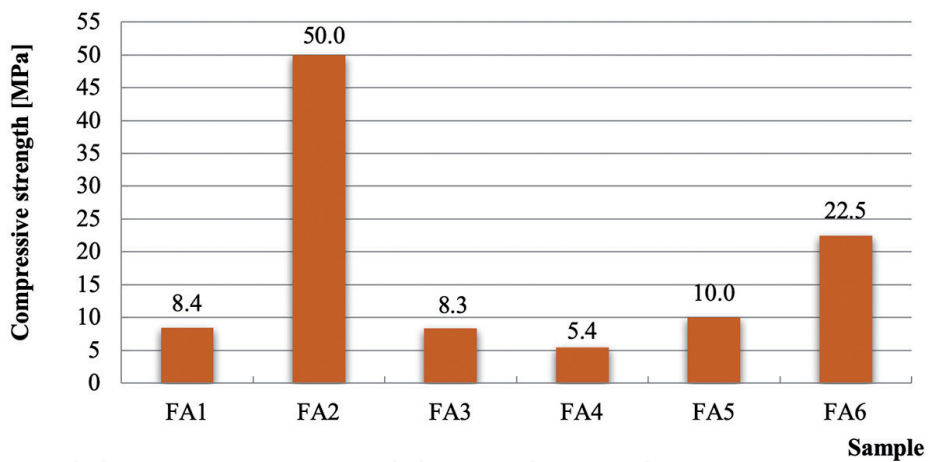
Figure 6.
Compressive strength of the fly ash pastes activated with the 8 moles/dm^3 NaOH solution and steam cured under low pressure at 80°C [13].
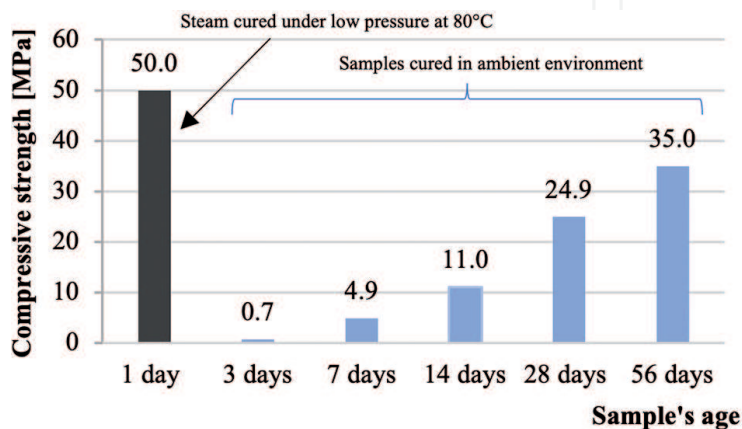
Figure 7.
The influence of the curing condition on the compressive strength of alkali activated fly ash FA2.

after this period obtained a compressive strength of 35.0 MPa, while immediately after the low-pressure steam process, it achieved a compressive strength of 50.0 MPa. In addition, white coating forms on samples that harden at room temperature, which does not occur when subjected to the low-pressure steam curing process.

Figure 8A shows the microstructure of the hardened geopolymer (FA2) characterised by the highest compressive strength. SEM image observations show a porous geopolymer structure formed between the fly ash particles under the influence of alkaline activation. The formed geopolymer phase adheres closely to the fly ash particles, forming a compact structure of hardened material (**Figure 8B**). A larger ash particle with a diameter of about 30 μm is visible in the test area.

The studies carried out at a higher magnification, together with the EDS analysis, made it possible to identify the composition of the formed compounds. At selected points of this sample, EDS analysis shows the formation of the geopolymer microstructure around the ash particles under the influence of alkaline activation with a variable Si/Al ratio (**Figure 8B** and **Table 2** p. 2, p. 3 and p. 4).
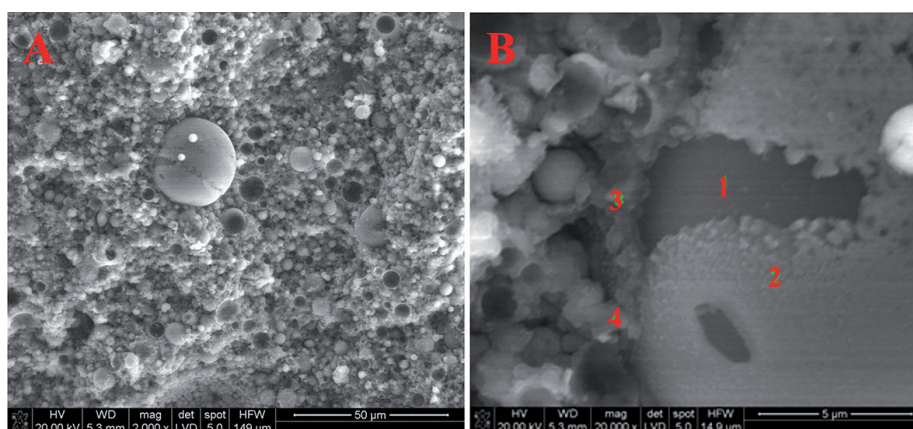

Figure 8.
SEM images of: A: of the hardened binder obtained from the FA2 (magnification 2000), and B: magnification 20,000 [13].

Point	Na	Mg	Al	Si	S	K	Ca	Ti	Fe	O
1	3.57	0.78	19.8	31.8	0.00	6.96	0.64	0.00	5.16	31.3
2	2.57	0.73	16,0	41.2	0.41	7.99	0.48	0.00	1.31	29.4
3	7.42	1.48	14.9	27.6	0.44	3.89	1.31	0.00	5.09	37.8
4	7.96	0.99	13.1	17.8	1.45	2.14	1.91	0.41	4.48	48.8

Table 2.
*EDS analysis of selected points in the micro region (marked in **Figure 8B**) of the binder obtained from the FA2 ash (atomic percentage (%)) [13].*

According to XRD analysis, quartz and mullite derived from fly ash are present in the hardened geopolymer paste (**Figure 9**). Identified reflections for hydrosodalite, recorded on the diffractogram, prove the presence of this phase in the hardened matrix of the material obtained from FA2 fly ash in alkali activation process.
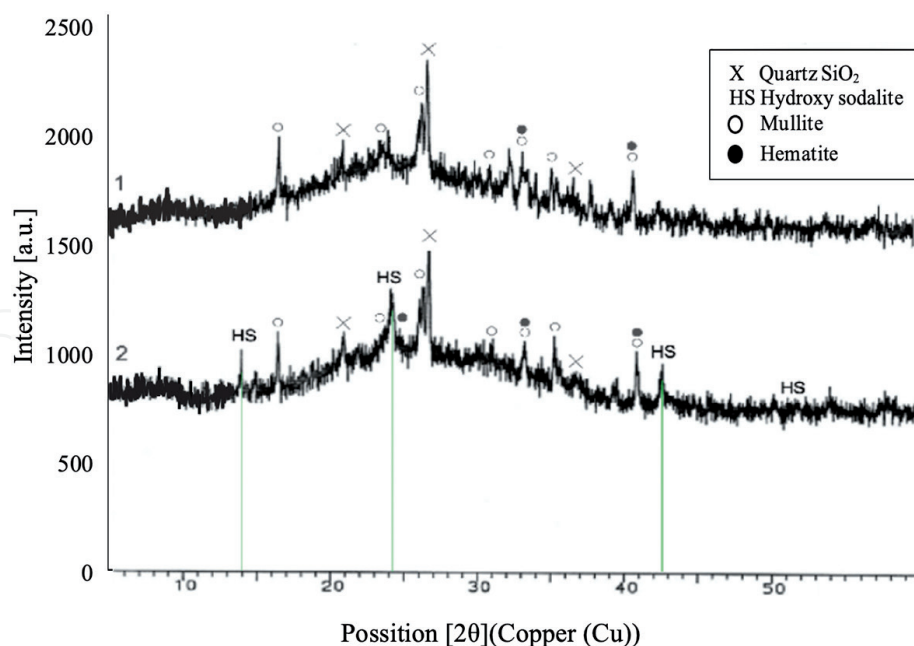
Figure 9.
XRD pattern: 1) – of the FA2 fly ash, 2) – of the hardened geopolymer paste obtained from the FA2 ash [15].

4. Development of geopolymer cementless concrete based on fly ash

The compositions of concrete mixes to obtain cementless geopolymer concrete were determined on the basis of the principles of designing ordinary concrete, assuming that in place of cement, the ashes selected for the study were used as the binder component in the concrete mix.

To prepare the reference concrete (B0FA1), the developed concrete mix was used, where the content of binder was 260 kg/m^3 in which 23% of cement was replaced by silicious fly ash (FA1). This fly ash is coherent with requirements from PN-EN 450 standard. Three aggregates' fractions were used: fine sand (0/2 mm), fine gravel 2/8 mm and gravel 8/16 mm. Apart from the micro fly ash (FA2), during the BFA2 + G mix preparation, the mineral additive – calcined at 700°C waste clay was added in place of 15% of micro fly ash FA2. The 8 mole/dm^3 NaOH solution was used as the activator, while for the BFA2 + G concrete mix, the mixture of 8 mole/dm^3 NaOH solution with water glass with an SiO$_2$/Na$_2$O molar modulus of 2.5 was used. **Table 3** shows the designations of the concrete samples, consisting of a member containing the type of initial components used to obtain the cementless geopolymer concrete.

5. Compressive strength test results of geopolymer concrete

The concrete mixes, after being cast into 100 x 100 x 100 mm cubes, were cured at 80°C under low-pressure steam conditions. In **Figure 10**, the compressive strength of tested geopolymer concretes hardened in 24 h low-pressure process is shown. From all tested concretes, which contain different fly ashes subjected to alkali activation by 8 mol NaOH solution, the highest compressive strength (26.6 MPa) was obtained by BFA2 concrete; however, it does not receive the value of compressive strength for reference concrete (30.8 MPa). BFA2 + G concrete with the addition of waste clay is characterised by exceptionally high compressive strength (73.5 MPa), exceeding the

Concrete designation	Binder	w/s	Kind of activator	Compressive strength [MPa]
B0 FA1	77% OPC + 23% FA1	0.5	—	30.8
BFA1	FA1	0.5	8 M NaOH	14.8
BFA2	FA2	0.5	8 M NaOH	26.6
BFA3	FA3	0.6	8 M NaOH	5.5
BFA6	FA6	0.6	8 M NaOH	10.6
BFA2 + G	85% FA2 + 15% calcined waste clay	0.6	8 M NaOH/Na_2SiO_2 = 1/2	73.5

Table 3.
List of materials used as a binder to obtain geopolymer concrete and kind of the activator [15].
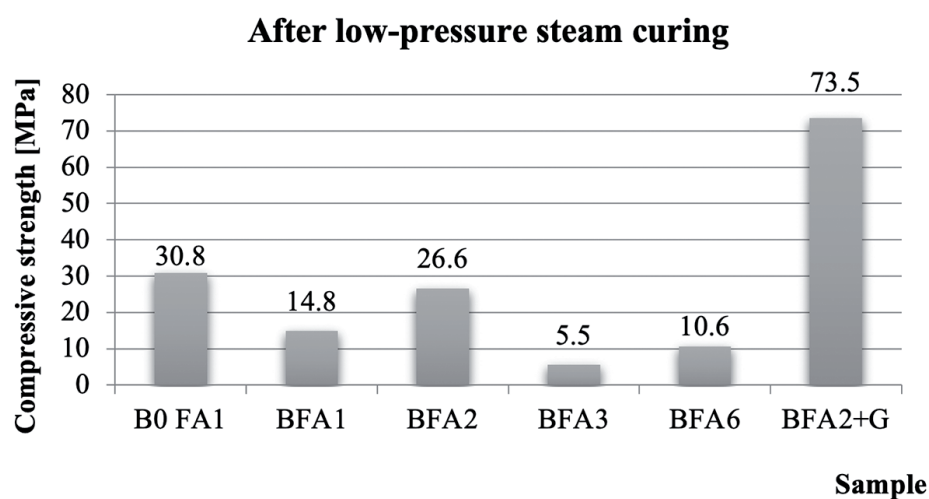
After low-pressure steam curing

Figure 10.
Compressive strength of concrete samples after low-pressure steam curing [15].

strength of the cement reference concrete samples by almost 180%. In order to check the influence of the environmental conditions under which the samples were cured after steam curing, they were additionally stored in ambient conditions and in water at temperature of 20°C.

The concrete samples were additionally stored for a period of 28 days, both in ambient condition and in water, they did not lose the original strength, which they had obtained immediately after steam curing and obtained the high compressive strength, sometimes exceeding those of the initial sample. **Figure 11** shows the compressive strength of samples of the tested concretes after the low-pressure steam curing, stored additionally 28 days in water and in the ambient condition. To test the freeze-thaw resistance of the developed geopolymer cementless concretes, concrete samples were subjected to impact of low temperature. Unfortunately, not all samples of geopolymer concretes passed this test, which include of 150 freeze-thaw cycles. All samples prepared exclusively from fly ash as a binder, were completely destroyed, some of them after only 50 freeze-thaw cycles. The modification of the BFA2 concrete composition by replacing fly ash with 15% of a specially prepared additive—calcined waste clay—significantly improved the frost resistance of the geopolymer BFA2 + G concrete (**Figure 12**).
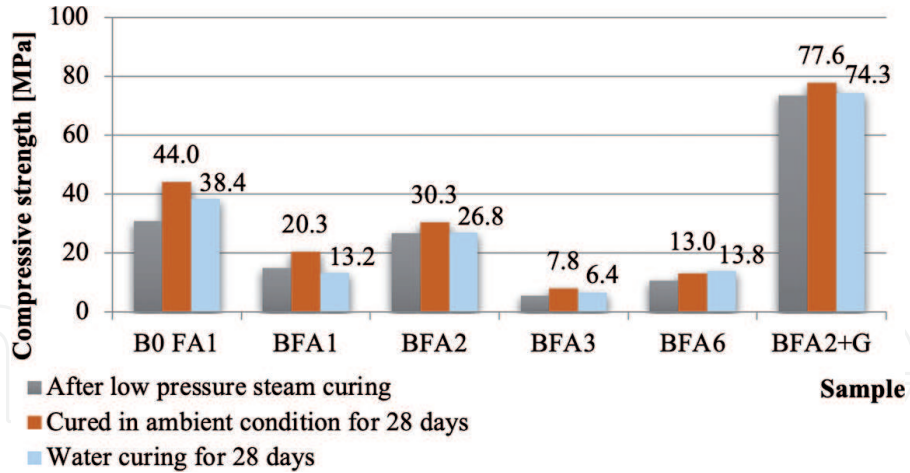
Figure 11.
Compressive strength of the concrete samples stored in ambient conditions and in water for 28 days after steam curing [15].
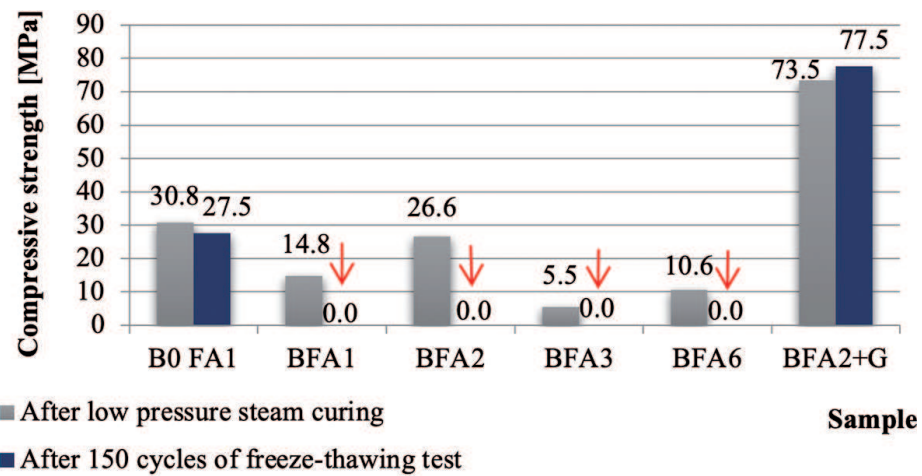

Figure 12.
Compressive strength of the geopolymer concretes after steam curing compared with the samples after frost resistance testing [15].
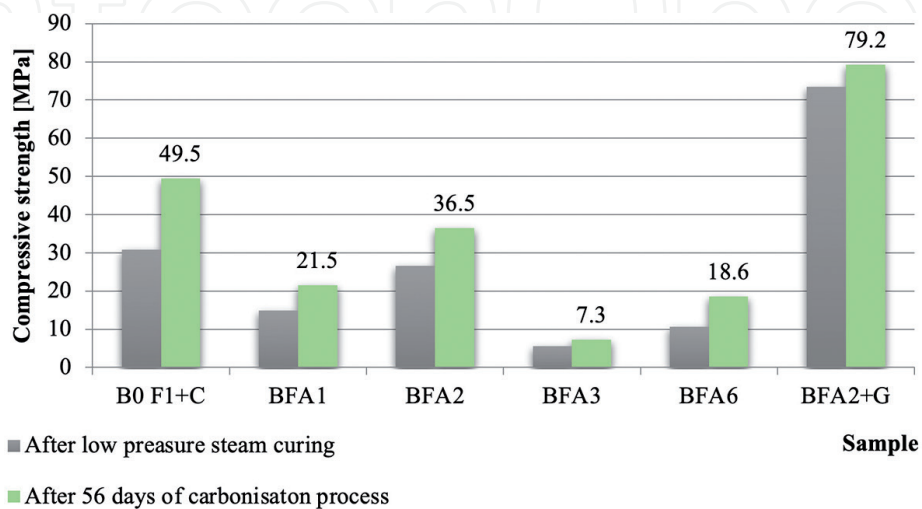

Figure 13.
Compressive strength of geopolymer concretes after low-pressure steam curing compared with the results of tests after carbonisation process.

Studies on the effect of carbonisation on the durability of the obtained geopolymer concrete were carried out in a test chamber. The pre-steamed samples were stored for another 28 days in ambient conditions and then were placed in a chamber, where they were subjected to the impact of high concentration of CO_2 (4%) for 56 days. The geopolymer concrete samples obtained higher strengths after the carbonisation process (**Figure 13**), which means that the samples after a period of preliminary steaming and further exposure show an increase in strength. The process of low-pressure curing does not lead to the achievement of the maximal strength of the material.

6. Microstructure of high-strength geopolymer concrete

The tests were carried out on the sample of the BFA2 + G concrete, which, due to the results achieved and the potential possibilities of use, as well as scientific value, raises universal interest. It is a cementless concrete made from secondary and waste materials which, after alkaline activation and subjected to low-pressure steam curing, was characterised by high compressive strength, high freeze-thaw resistance and durability both during curing in ambient conditions and in water and after conducting the carbonisation tests.

Figure 14 shows photograph exemplifying the structure of the fracture surface of the concrete sample after 3 years of storage in ambient conditions.

Further testing was carried out on the sample of the BFA2 + G, obtained by alkaline activation of fly ash with the addition of calcined clay. **Figure 15** shows the image under the scanning microscope of the microstructure of the fractured surface of the BFA2 + G concrete sample after 3 years of storage under ambient conditions. The test sample, extracted from the solidified matrix that bonds the aggregate particles, is not homogeneous. It contains partially reactivated fly ash particles. (**Figure 16A**) or more degraded fly ash particle (**Figure 16B**) which is a result of alkaline activation. The geopolymerisation products occur in a different morphology (**Figure 17** and **18**). The basic filler is a material formed by the reaction of the phase components of fly ash with an alkaline activator, which surrounds the unreacted fly ash particles (**Figure 15A**). The extender, formed by the alkaline activation of the components of the fly ash with the addition of calcined clay, is visible between the particles of the aggregate and the sand, which has a compact microstructure well bonded to the aggregate surface (**Figure 15A**). This substance consists mainly of silicon, aluminium and sodium. In the

Figure 14.
Macroscopic image of the structure of a geopolymer concrete sample.
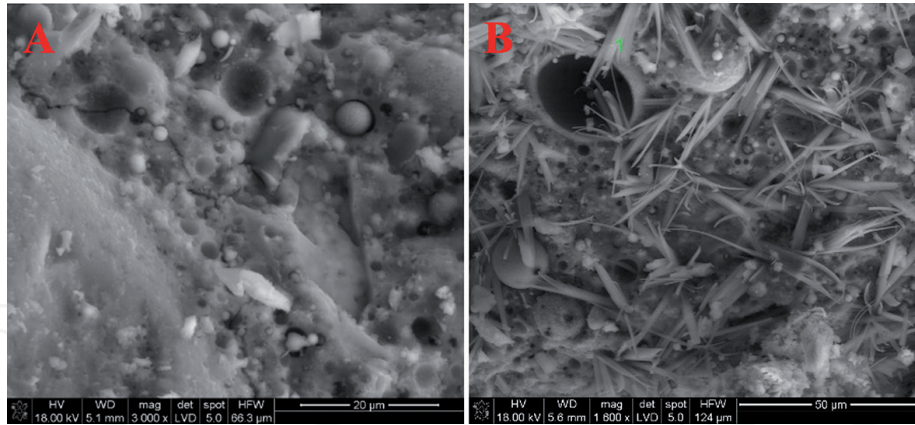
Figure 15.
SEM images of selected areas of the BFA2 + G concrete sample: A: zeolite phase of alkaline fly ash activation products [15] and B: clusters of crystalline, hexagonal crystals [15].
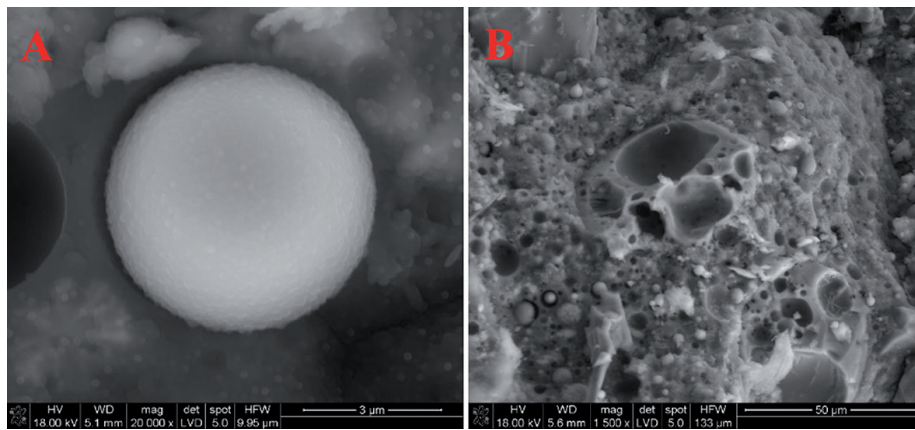

Figure 16.
SEM images of: A: partially reactivated fly ash particle with geopolymerisation products surrounding it and B: degraded fly ash particle as a result of alkaline activation.
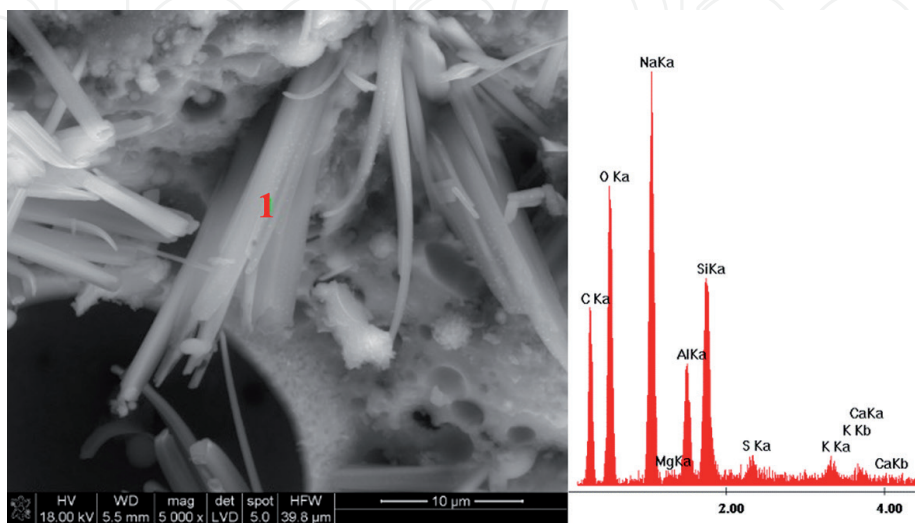

Figure 17.
The morphology of alkaline activation products in the form of needle-shaped, hexagonal crystals. They are the needle crystals of the zeolite group with high sodium content [15].
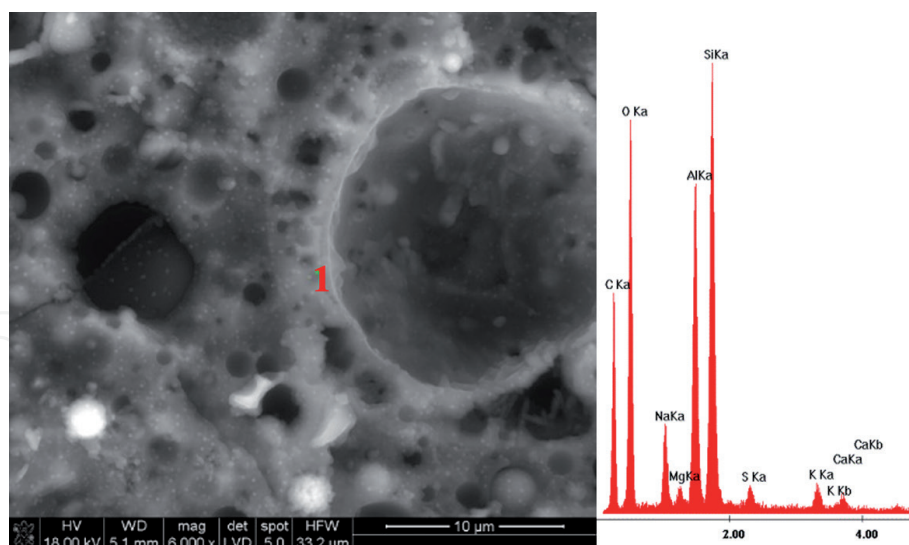
Figure 18.
SEM image of alkaline activation products formed around the surface of fly ash particles [15].

observed area of the sample, round, smooth ash particles are visible, which indicates that the alkaline reaction with the ash components occurs mainly in their surface layer (**Figure 18**). This is a normal phenomenon. They mainly contain silicon and aluminium and are characterised by a high sodium content. This component comes from the activator. In addition to the amorphous extender, clusters of crystallised hexagonal needle-like forms of the zeolite group are visible (**Figures 15B** and **17**).

Analysis of the phase composition conducted in the papier [15], as well as the SEM studies (**Figure 17** and **18**), indicates the content of crystalline phases in the test sample, originating from the base materials used. These include quartz, mullite, haematite and calcite. Based on the recorded in the papier [15] peaks with 'd' values of 4.7 Å and 3.64 Å on XRD pattern, it can be assumed that cancrinite ($Na_6Ca_2Al_6Si_6O_{24}$ $(CO_3)_2$), a zeolite occurring in hexagonal needle-like forms, is present in the tested sample. The cluster of needle-like forms shown in **Figure 17**, with the EDS analysis carried out at point 1, indicates the possibility of the formation of this compound. The results of elemental X-ray microanalysis shown in the table show significant differences in the composition of geopolymer compounds formed as a result of the alkaline activation of FA2 ash with the addition of clay (**Table 4**).

The identified cancrinite (**Figure 17**, **Table 4**) contains significantly more sodium than the zeolite formed around the surface of the fly ash particle (**Figure 18**, **Table 4**). The content of this compound in concrete with other zeolites, such as hydrosodalite, formed by alkaline activation of fly ash, has been indicated by many researchers, as described by Davidovits [62] and Zhao et al. [63].

Probably, this phase crystallised from the amorphous precursors under the influence of CO_2 from the air, in which the developed geopolymer concrete was kept during the 3-year conditioning period. More likely, the crystallisation of this phase seems to be

Point	Na	Mg	Al	Si	S	K	Ca	Fe	O
1 on **Figure 17**	14.5	0.13	1.37	3.30	0.15	0.44	0.47	0.80	46.1
1 on **Figure 18**	3.00	0.59	8.02	12.2	0.64	1.04	0.66	1.21	33.5

Table 4.
*EDS analyses of selected points in the micro region on **Figures 17** and **18** (atomic percentage (%).*

caused by alkali activation of mineral components of calcined clay which includes apart from metakaolinite some amounts of undecomposed calcite. This thesis could be based according to tests carried out by Esaifan et al. [64], who proved the presence of both minerals: hydrosadalite and cancrinite by conducting the synthesis of those zeolites' minerals from calcite-containing clay under hydrothermal conditions. Calcite is a source of the necessary Ca^{2+} ions required to form cancrinite. This phase can crystallise already in a use of NaOH solution, not only by using a mixture of sodium silicate with NaOH solution [64]. In the results interpretation of XRD tests, the structure of hydrosadalite and cancrinite tested by Barnes et al. [65] turned out very helpful. According to these authors for those mineral phases on XRD pattern, many common diffraction peaks occur. The main identifying peaks for cancrinite unlike hydrosadalite are 4.67 Å and 3.24 Å.

7. Discussion

The presented work is based on the results of many years of studies carried out at Ł-ICIMB in Cracow, aiming the decrease of CO_2 emission from cement and concrete production. One of many ways of achieving this aim is the development of new, low-emission binders and concrete, which could complement the so-called classic materials such as cement and cement concrete and replace cement in certain areas of its application.

In the conducted research, focused on utilisation for obtaining the cementless binders and concrete, commonly available fly ashes from Polish power plants. According to conducted freeze-thaw tests, all samples of geopolymer concretes containing as a binder fly ash had been damaged after 150 freeze-thaw cycles. Even BFA2 concrete, despite high fresh compressive strength, failed this test. Especially low freeze-thaw resistance was demonstrated by geopolymer concretes based in alkali activated fluidised fly ash and untreated calcareous fly ash. After 50 cycles of freeze-thaw, those concretes were totally destroyed. The modification attempt of increasing the durability of concrete by addition of calcinated clay, as a partial replacement of fly ash, became a success. This test was conducted for the BFA2 concrete, which is characterised by the highest compressive strength among from tested concretes. Although it is known that the addition of metakaolin increases the strength of the fly ash based geopolymer [66], the results presented in this chapter are difficult to interpret unambiguously because, at the same time, the type of activator was changed, introducing 30% of water glass in place of sodium hydroxide. Consequently, the structure of the geopolymer filler of the hardened BFA2 + G geopolymer concrete is different compared with BFA2 concrete containing the same silicious micro fly ash from coal combustion.

The results obtained confirm the statements of numerous authors on the possibility of shaping the functional properties of geopolymer materials by selecting the suitable base materials, the type and quantity of activator, as well as hardening conditions. Currently, one of the factors determining the development of geopolymer in civil engineering will be the cost of material production. Therefore, it is advisable to look for cheaper, alternative activators. Reducing the carbon footprint is also an important element. It is worth paying attention to the comparison of the CO_2 emission reduction and the calculation of the carbon footprint in relation to the cement material. Only the analysis carried out for products with identical technical characteristics can be considered a conclusive comparison.

Taking into account the tendency to reduce coal burning in the energy sector, it should be noted the possibility of the limitation the extraction of the best

for geopolymer concrete, silicious fly ash. This will be followed by work on the identification of other aluminosilicate precursors from both waste materials and industrial waste. A suitable example is an attempt to obtain appropriately transformed calcareous fly ash as the main component of cementless geopolymer concretes. The presented results of the use of refined calcareous fly ash, through the separation of carbon fractions and additional grinding, confirmed the possibility of obtaining cementless geopolymer concrete from such a material. A similar effect was obtained by Blaszczyński and Król [67], who, as one of the few authors, also obtained a geopolymer binder from tentatively refined calcareous ashes by removing carbon particles and pre-grinding them. Ash of this kind has not found application as an ingredient for cement production, so there are great opportunities for its acquisition.

For the widespread production of structural materials based on geopolymer binders and concrete, it is necessary to carry out long-term durability studies and develop guidelines for testing procedures and standard requirements so that the geopolymer material "native to ancient Egypt" with the new name AAM (Alkali-Activated Material) becomes the material of the future [4].

8. Conclusion

Part of the research results on the development of geopolymer concrete based on waste aluminosilicate materials, in particular fly ash, were published in the journal Cement Wapno Beton [15]. Results of tests, showed in this chapter, make a significant contribution, which led to interpret the phenomenon that occurs during alkali activation of chosen aluminosilicates industrial wastes. It has extended current knowledge in a field of geopolymer materials.

Among the fly ashes described, selected for research as base materials for obtaining cementless binders and geopolymer concretes, the best properties were demonstrated by fine-grained, specially selected siliceous fly ash from hard coal combustion—so-called micro fly ash.

It was demonstrated that a large role in the formation of the microstructure of the hardened geopolymer concrete showing high durability under the tested conditions of exposure to both water and ambient condition and low temperatures can be attributed to the modification of developed geopolymer microstructure by the presence of metakaolin and calcium carbonate in the calcined at 700°C clay [14, 60, 64, 66]. This modification resulted by the occurrence in the geopolymer microstructure, in which needle-like forms were identified using a scanning microscope, which, following other authors, can be attributed to the formation of cancrinite [64, 68].

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Conflict of interest

The authors declare no conflict of interest.

Author details

Krystyna Rajczyk[1]*, Wiesław Kurdowski[2], Paweł Pichniarczyk[1] and Grzegorz Janus[1]

1 Łukasiewicz Research Network – Institute of Ceramics and Building Materials, Kraków, Poland

2 Cement Wapno Beton Foundation, Kraków, Poland

*Address all correspondence to: krystyna.rajczyk@icimb.lukasiewicz.gov.pl

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