



Fly-ash based geopolymer mortar for high-temperature application – Effect of slag addition

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ABSTRACT

Geopolymers are used as a Portland cement alternative in some applications. The motivation for using geopolymers is their capacity of the by-products and waste incorporation, contributing to a cleaner environment. The present study aims to evaluate the impact of temperature exposure (up to 1000 °C) on the microstructure and the mechanical properties of the geopolymer mortars. Four mixes were investigated with fly ash as the main precursor with four levels of slag replacement 0, 10, 30, and 50 wt%. To evaluate damage evolution, mechanical performances and identification tests were performed: ultrasonic pulse velocity, scanning electron microscope, mercury intrusion porosimetry, thermal strains measurements, differential thermal analysis and thermogravimetry. The research aimed to develop a mortar composition that is thermally stable at high temperature. Although slag addition improves the mechanical performances of fly ash geopolymer mortar considerably (compressive strength above 100 MPa), the mortar with no slag addition yielded better performances at high temperature. In this study, manufactured mortars exhibited a 30% strength increase and doubled tensile strength at 200 °C. Moreover, for developed mixes, a compressive strength recovery of up to 90% at 1000 °C was observed, demonstrating the potential of fly ash geopolymer as high-temperature application material.

1. Introduction

In recent years, the necessity to predict the behaviour of structural elements under fire conditions is one of the main reasons that led to research on the effect of high temperature on mineral binders. Mineral binders can retain their properties at high temperatures; therefore, they can protect steel in the form of a concrete protection cover or passive fire protection for steel structural elements (Mróz et al., 2016). In terms of durability, materials such as geopolymers, which are an environmentally friendly alternative to Portland cement, are promising (Zhang et al., 2016; Zhao et al., 2021). They also present the competitive behaviour at high temperature to Portland cement (Rickard and Van Riessen, 2014). However, complete comparison of these materials is a complex task as the binder types and aggregate contents may differ significantly.

Geopolymer is a binder obtained due to the reaction of silicates and aluminosilicates raw materials with an alkaline or acidic solution. The geopolymer bonding process is called geopolymerization and combines oligomers into a large complex interconnected by covalent bonds (Davidovits, 2015). Interest in this type of mineral binder has increased owing to its capacity to utilise industrial wastes (Wasim et al., 2021) and

secondary products (Almalkawi et al., 2019) with the ability to decrease mine tailings (Capasso et al., 2019) and industrial by-product piles (H. Y. Zhang et al., 2020; Y. Zhang et al., 2020). Geopolymers can also be used in the production of binders that allow for the utilisation of construction waste (Ulugöl et al., 2021).

One of the vital factors determining the geopolymer resistance to high temperatures is its composition (Kong et al., 2007). Factors that are of particular importance include the Si/Al (silicon and aluminium) ratio, alkali content, and liquid/solid ratio (Kong and Sanjayan, 2008). The addition of a large number of alkaline substances accelerates the bonding process, making it possible to produce materials with high early strength. On the other hand, to ensure high-temperature durability, the number of alkali substances is limited, since a large amount of these substances accelerates the melting process.

Evaluating the temperature impact requires identifying the various physical and chemical changes in the matrix. During the heating, water with a different way of incorporation in the material structure is gradually released. The mechanism is very similar to observed during Portland cement materials are exposed to high temperatures (Hager, 2013). First, the free water and then chemically bonded water also as the

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hydroxyl (OH) groups evaporates. The water release from the material due to heating results in decreasing in bulk density and a progressive thermal shrinkage of the matrix, leading to cracks formation. The water vapour pressure inside the pore system of Portland cement concretes exposed to temperatures above 100 °C grows (Kalifa et al., 2000), which can promote the fire-induced spalling behaviour (Hu et al., 2009). Mróz and Hager (2017), recently summarising the findings and hypothesis concerning the mechanism of concrete fire spalling showed that it is strongly related to the permeability of the mineral matrix. Zhang et al. (2020) demonstrated that geopolymer concretes (40–80 MPa) have a good spalling resistance when rapidly heated (5–12 °C/min). When the temperature range is higher (100–300 °C) the chemically bonded water evaporates and dehydroxylation of the OH groups occurs (Duxson et al., 2007).

Moreover, the type of precursor and activator solution affects the geopolymer properties (Kong and Sanjayan, 2008). The properties of the obtained binder depend on the raw materials used at the mix preparation stage (Guo et al., 2021). Fire resistance and durability in high-temperature conditions are related to the inorganic structure of the material which is formed during the geopolymer binding (Hosan et al., 2016). This behaviour illustrates the important difference between geopolymer and cement binders (Sitarz et al., 2018), which are more seriously damaged due to dehydration and portlandite decomposition (Hosan et al., 2016). Pan and Sanjayan (2012) found that for geopolymers, the strength of the material tested at the hot stage increased until 680 °C. Similar observations of the strength improvement were done by (Fernández-Jiménez et al., 2008) and (Shaikh and Vimonsatit, 2015).

The studies presented by (Pan et al., 2018) determined the strength parameters for alkaline-activated materials with ground granulated blast furnace slag and Class F fly ash blends. The observed differences in strength in the range of temperature 300 and 600 °C suggested significant differences in the bonding structures of these materials. In a material with a mixed binder, the sodium aluminosilicate hydrate gel rich in calcium dominated N(C)ASH. The material based solely on ash binder cured at T = 60 °C exhibited a higher strength at 600 °C, and its bonding phase was based on the sodium aluminosilicate hydrate gel (NASH). From the above study, it can be inferred that the material based on FA binder yielded good performance under high-temperature conditions. However, this composite must be cured at a temperature of approximately 60 °C, which involves an additional energy input at the material manufacturing stage.

A study by (Rickard et al., 2016) on geopolymer concrete compared the high-temperature behaviour at the hot stage (tested at elevated temperatures) with the residual values (tested after cooling down to room temperature). The authors observed, differently than for cement concrete, for temperature up to 500 °C, the higher residual compressive strength than tested at the hot stage. It was considered that this was due to progressive gel geopolymerization (Pan et al., 2009), which occurred after the material had been heated to 200–500 °C (Pan and Sanjayan, 2012). At higher temperatures, the strength tested at the hot stage became higher than tested after cooling down (residual strength). This also suggests that at temperatures above 500 °C, thermal strains due to material cooling cause damage that exceeds the strength improvement resulting from progressive geopolymerization (Rickard et al., 2016). At that temperature range, the type of aggregate used, including its ability to conduct heat, was crucial to the strength of the material. The findings of (Pan et al., 2009) showed the capacity of high ductility geopolymers to compensate for the mismatch of strains between aggregates that expands and geopolymer paste that shrinks.

Interesting experimental research of (Abdulkareem et al., 2014) consisted in testing lightweight aggregate concrete, geopolymer mortars and geopolymer pastes. The strength decrease observed between 400 and 600 °C was attributed to dehydration and dehydroxylation processes. At 800 °C, the geopolymer paste specimens lost their strength completely, whereas geopolymer mortar and lightweight concrete

exhibited residual strengths of 50% and 60% of the initial value, respectively. It was concluded that the material good temperature resistance was related to the aggregate type and properties.

A review of the literature indicated that efforts were made to better understand the properties of geopolymers and to develop mixtures with increased durability at high temperature. A literature review has shown that the high-temperature properties depend strongly on the oxide composition of precursor and activator. One of the obstacles to concluding on geopolymer behaviour at high temperature is the diversity of geopolymers binder compositions that hinders the processes' identification that induces properties to change. Moreover, the comparisons of the results with other teams are difficult due to the variety of research procedures.

The present study evaluates the effect of slag addition content on geopolymer mortar behaviour at high temperature. Only one parameter changes: the ground granulated blast furnace slag content. The precursor with blended composition FA/GGBFS was characterised by various Si/Al ratios, leading to significant differences in the bonding structures of mineral materials (Pan et al., 2018). This adds to the parametrical study of geopolymer binders and contributes to developing knowledge in this field.

The research aims to develop a mortar composition that is thermally stable at high temperature. Material is considered thermally stable when is a thermal barrier for temperature-sensitive steel in reinforced element or provides passive fire protection during the temperature exposure. For this reason, a binder that maintains a satisfactory level of mechanical properties during a fire is most wanted. Previous studies presented recently (Sitarz et al., 2020) have shown that high early strength and room temperature setting is an essential advantage of fly ash (FA) and ground granulated slag (GGBFS) blends which involves energy savings at the material manufacturing stage. The research proved that high-performance materials could be produced, showing an impressive mechanical performance reaching 100 MPa at 90 days. The presented research relates to the discussion on theoretical and practical aspects of cleaner production of mineral binders using Portland cement alternatives to achieve the goal of energy-saving construction processes.

2. Testing method and material composition

2.1. Materials composition -precursor and activator

Siliceous FA and GGBFS were used as precursors to prepare geopolymer mortars. The FA density was of 2.10 g/cm³, and its composition was as follows (wt.%): SiO₂ = 52.3%, Al₂O₃ = 28.0%, Fe₂O₃ = 6.32%, CaO = 3.05%, K₂O = 2.51%. The contents were below 2%: MgO, SO₃, Na₂O, P₂O₅, TiO₂, Mn₃O₄. The detailed material characteristics were presented in (Hager et al., 2020). GGBFS used for this study had a density of 2.90 g/cm³, and was composed mainly of CaO = 43.9%, SiO₂ = 39.3%; Al₂O₃ = 7.61%, MgO = 4.15 Fe₂O₃ = 1.49%. The contents of the SO₃, K₂O, Na₂O, Cl⁻ were below 1%. Moreover, the identification of elements in the materials was made by XRF spectrometry. The content of Si and Al was in FA 24.2% and 16.9% and GGBFS 19.4% and 4.5%, respectively. Table 1 shows the change in the ratio of silicon (Si) to aluminium (Al) depending on the precursor composition. The siliceous sand had a density of 2.65 g/cm³. The particle size of the sand grains was up to 2 mm. Geosil 34417 (Woellner) sodium silicate solution, was

Table 1
The ratio of silicon and aluminium in the precursor.

Mix	GGBFS 0%	GGBFS 10%	GGBFS 30%	GGBFS 50%
Precursor Composition (wt. %)	100% FA	90% FA + 10% GGBFS	70% FA + 30% GGBFS	50% FA + 50% GGBFS
Si/Al	1.44	1.52	1.73	2.04

employed with Na₂O content 16.74%, and SiO₂ content 27.5%, and density of 1.55 g/cm³. The molar ratio of sodium silicate solution of 1.70 (MR = mol SiO₂/mol Na₂O).

Four mortar mixes were prepared using quartz sand and a geopolymer binder. Four different ratios of GGBFS were used as replacements of the part of FA. The designation of the materials reflects the amount in the percentage of the GGBFS being used to replace the FA (0–50%). The compositions were designed to provide the same weight ratios of sand to binder equal to 1.50, the alkaline solution to binder value of 0.45, and water to binder weight ratio 0.30. The binder is regarded as FA and GGBFS. The alkaline solution was composed of Geosil with additional water. However, to obtain the same volume and similar mortar density while varying the proportion of the fly ash and GGBFS mass, the amounts of the remaining components were changed, respectively. The composition of tested geopolymer mortars is summarised in Table 2.

2.2. Geopolymer mortars manufacturing

Mixing of the geopolymer mortars was performed through a mechanical process; the first step in this process is paste preparation. At first, for 10 min, the fly ash with an activator was mixed. After GGBFS was dosed another 5 min of mixing was conducted. Subsequently, 5 min mixing was applied when the quartz sand was dosed. All tested mortars were designed to obtain proper workability for mixing and casting. The samples were cast and compacted on a shaking table in 40 × 40 × 160 mm³ plastic moulds. The specimens were protected from excessive drying with a plastic lid and stored in controlled room conditions with a T = 18 ± 2 °C and relative humidity HR = 75%. All the specimens, except for mortar with 0% GGBFS, were demoulded after 1 day. The hardening process of mortars with no slag addition is slower due to limited CaO content. Those samples were demoulded after 2 days. No special temperature curing was applied. The temperature exposure to 200, 400, 600, 800 and 1000 °C was done using a Nabertherm electric furnace after 90 days from mortars casting.

2.3. Experimental methods overview

The heating with a 1 °C/min rate was conducted in temperatures in the range of 20–1000 in intervals of 200°. This heating rate follows RILEM recommendations (Schneider et al., 2007) to minimise stresses due to temperature differences between hotter surface and cooler inner part of the sample. When the temperature has been achieved, it was maintained for 2 h to provide a temperature homogenisation in the specimen cross-section. Afterwards, the samples were cooled down freely in the furnace. After removing it from the furnace, the surface of the samples was scanned (constant lighting conditions) to obtain pictures of the samples. All the tested mechanical and physical parameters were referenced to the values obtained for the unheated samples (20 °C values), and the relative changes in the tested properties were determined.

The impact of the GGBFS content on the properties of mortar after temperature exposure was investigated. Changes in the material's visual aspects (colour change and macro-cracks) and bulk density were

Table 2
Mix components for tested geopolymer mortars.

Component	GGBFS 0%	GGBFS 10%	GGBFS 30%	GGBFS 50%
	in kg per m ³			
alkaline solution	330.7	334.0	340.6	347.5
fly ash (FA)	734.9	667.9	529.8	386.1
ground granulated blast furnace slag (GGBFS)	0.0	74.2	227.1	386.1
quartz sand	1102.4	1113.2	1135.3	1158.3

observed. After cooling the specimen down, each specimen was tested in a three-point bending using an Instron machine (loading rate 50N/s), the remaining elements produced by bending tests were used to determine strength in compression (rate of loading 2400N/s). The number of samples for one bending test was 2 for 20 °C and 1 for other temperatures. The use of the bending residue for compression tests allowed to determine the compressive strength on 3 for 20 °C and 2 samples for other temperatures.

Additionally, the velocity of the ultrasonic wave propagation through the material was assessed using PUNDIT plus equipment. The ultrasonic pulse velocity (UPV) measurement is a non-destructive test method that can monitor the presence of pores, voids and cracks. It delivers information about material damage evaluation factor (Hager et al., 2013). The comparison of results obtained on unheated and heated specimens provided data on the quality of material and the level of damage caused by high-temperature exposure. The Eq. (1) gives the relation between the ultrasonic wave velocity (V) values and the material properties: ρ_0 apparent density; E_d elastic modulus and ν Poisson's ratio.

$$v = \sqrt{\frac{E_d(1-\nu)}{\rho_0(1+\nu)(1-2\nu)}} \quad (1)$$

Additionally, mortars thermal expansion was measured using a dilatometer in which samples were heated with 5 °C/min. The same rate of temperature increase was employed to heat samples (approx. 50 mg) for thermogravimetric and differential thermal analysis (7300 Exstar SII NanoTechnology).

The total porosity and pore size distribution changes due to heating were studied using the mercury intrusion method (MIP) with a Quantachrome Poremaster 60. The damage due to temperature exposure and microstructural observations were investigated with a Zeiss EVO-MA 10 scanning electron microscope. The specimens were cut and polished using anhydrous alcohol for microscopic observations taking dehydration in heated specimens into account to prevent rehydration. The test procedures and preliminary research results are presented in the authors' publication (Hager et al., 2020).

3. Testing results and discussion

3.1. Samples appearance after heating and bulk density

The samples' visual aspect is shown in Fig. 1 of the heated samples and colour change. The images were obtained with a flatbed scanner under constant lighting. The procedure was described by (Hager, 2014) and applied for cementitious binders. As a result of drying, the colour change was observed from dark grey at 20 °C to light grey shades at 400 °C. At 600 °C, a pinkish colouration was observed in all the samples. The red colouration is the effect of iron compounds oxidation. Iron is present mainly in fly ash composition, in oxides with more than 6% of Fe₂O₃. In GGBFS, the Fe₂O₃ content was noticeably lower (1.49); therefore, the observed red colouration was more visible for mortar in which the precursor contained 100% FA. No signs of chipping or spalling were observed.

The values of bulk densities are presented in Table 3, and they are related to the GGBFS content. The higher ground granulated furnace slag content yielded a density increase in density in mortars, which explains the higher strength values. With the heating increase, a gradual drop in the bulk density was observed for all materials related to the progressive drying process and dehydroxylation, leading to mass change. The mean and relative bulk density values are shown in Table 3. The relative values are calculated as the quotient of the density at the established temperature and the density of the initial unheated material.

Progressive heating of the geopolymer results in matrix and aggregates drying. Water in the material is gradually removed from the heated matrix. With temperature increase, free water is removed first, then

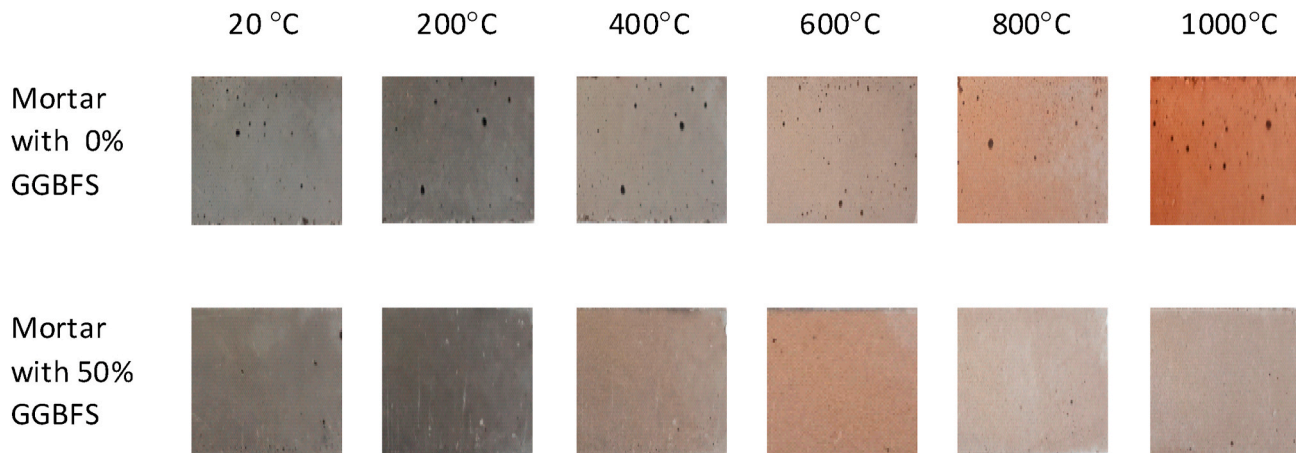


Fig. 1. Colouration change in heated mortars FA based geopolymer with 0% and 50% GGBFS.

Table 3

Mean values of densities of geopolymer mortars and density change due to heating presented to 20 °C values.

Temperature °C	GGBFS 0%	GGBFS 10%	GGBFS 30%	GGBFS 50%
	in kg per m ³ (~ 1%)			
20	1992.8 (100%)	2031.8 (100%)	2110.9 (100%)	2203.7 (100%)
200	1849.6 (93%)	1906.0 (94%)	1980.1 (94%)	2026.7 (92%)
400	1831.9 (92%)	1880.8 (93%)	1914.6 (91%)	1970.7 (89%)
600	1825.6 (92%)	1838.0 (90%)	1890.7 (90%)	1976.9 (90%)
800	1832.0 (92%)	1855.2 (91%)	1899.7 (90%)	1940.7 (88%)
1000	1818.1 (91%)	1840.2 (92%)	1916.1 (91%)	1948.4 (88%)

adsorbed water evaporates. At higher temperature, the water bound physically in the form of hydroxyl groups is removed. According to (Duxson et al., 2007), the dehydroxylation process that takes place at 250–600 °C induces shrinkage of the geopolymer binder. Nevertheless, the geopolymer binder may experience an expansion attributed to thermal dilation of water around 120 °C. As soon as the drying process starts, intensive shrinkage begins.

3.2. High-temperature exposure impact on mechanical properties

The following parameters were investigated: flexural strength evaluated in bending (f_t), compressive strength (f_c), and dynamic elastic modulus (E_d). In this section, the absolute and relative values of all listed parameters are analysed. The relative values are calculated as the quotient of the properties value at the established temperature (f_{iT} , f_{cT} , E_{dT}) to the initial unheated material absolute value (f_{i20} , f_{c20} and E_{d20}). In Figs. 2 and 3 the comparison of the results of flexural and compressive strength of the tested geopolymers are presented. The average initial flexural strength after 90 days of curing for all mortars is in the range of 6.0–8.0 MPa.

In the first test point, after exposition in 200 °C, a slight rise of approximately 10–30% in the flexural strength values for all the three mortars with 10, 30 and 50% of slag and an increase of 2.3 a factor of for the unblended FA-based mortar was observed. Afterwards, a gradual decrease in flexural strength was observed. As shown in Fig. 2, after 200 °C flexural strength decreases quasi linearly up to 600 °C as a result of progressive matrix dehydration. The result of dehydration is progressive thermal shrinkage of matrix leading to cracks formation around aggregates. Expansion of quartz sand and β - α quartz transformation at

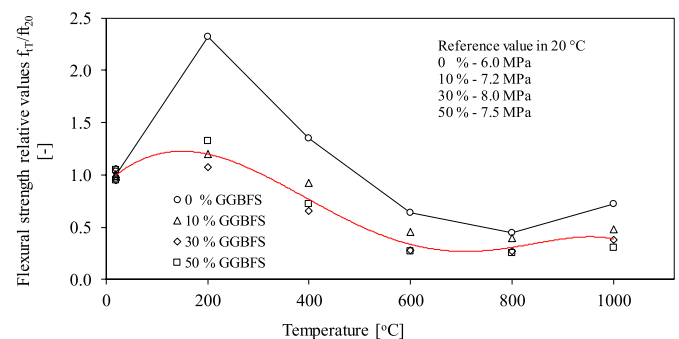


Fig. 2. Flexural strength of heated geopolymers: relative f_{iT}/f_{i20} values [-] with reference f_{iT} values in MPa.

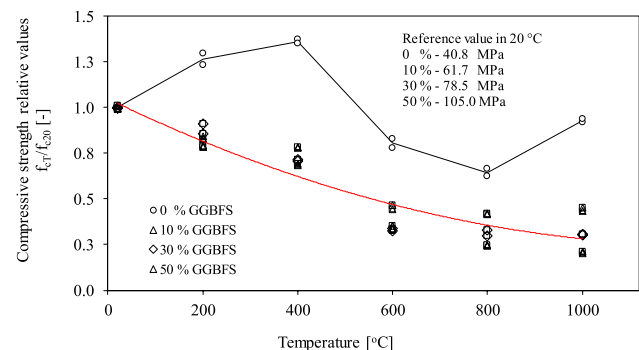


Fig. 3. Changes in compressive strength after thermal load: relative f_{cT}/f_{c20} values [-] with reference f_{cT} values in [MPa].

573 °C add up to damage progress of the material. Nevertheless, strength recovery for all mortars was observed after 800 °C, with the most significant upswing in the case of 0% GGBFS.

In Fig. 3 the evolution of strength tested in compression was depicted. The compressive strength at 20 °C, the reference values, increases along with the GGBFS content. The highest 90-day compressive strength of 105.0 MPa was observed for GGBFS content of 50%, whereas lower slag contents 0%, 10% and 30% achieved 40.8 MPa, 61.7 MPa and 78.5 MPa, respectively. As shown in Fig. 3, the progressive strength decrease was observed for all blended FA-GGBFS mortars. The reduction of f_c along with temperature follows a similar trend, regardless of the amount of GGBFS addition. The Fig. 3 comprises all test results and the line in the diagram presents mean values. Thus results from dispersion for each

temperature can be evaluated.

Mortar without GGBFS behaved differently. For mortars with the unblended precursor, an increase in strength of 30% and 40%, respectively, at 200 °C and 400 °C was observed. This can be associated with the development of geopolymerization process. According to (Pan et al., 2009), in these temperature conditions, an additional geopolymerization occurs. Strengthening effect was more noticeable for geopolymer mortars 0% GGBFS with no slag addition. During the temperature increase, when the moisture is converted into vapour, the gas pore pressure and autoclaving conditions inside the specimen can occur, which may trigger geopolymerization process resulting in a strength increase.

After temperature exposure to 1000 °C, similarly to flexural strength changes, a slight increase of strength for 10% and 30% GGBFS. Therefore, the compressive strength of unblended geopolymer mortar reached almost 90% of the initial strength value at 1000 °C. When the glass transition temperature (approx. 700 °C) is achieved, the sintering and densification of the matrix initiate.

Geopolymers with GGBFS addition shows a persistently decreasing compressive strength, resulting from changes in paste but also in the transition zone between paste and aggregate. Moreover, the incompatibility between shrinking geopolymer paste and expanding quartz aggregates induces cracking, and porosity is gradually increasing. Above 600 °C, the rate of strength fall is distinctly reduced. Fig. 3 shows clearly that compressive strength change with temperature of 0% GGBFS mortar is explicitly different from the trend curve established for blended FA-GGBFS precursor.

3.3. Elastic modulus

After the materials were exposed to high temperature and cooled down to room temperature, Ultrasonic Pulse Velocity (UPV) measurements were performed. The velocity of ultrasonic pulses variation over the temperature of the geopolymers was recently presented in (Hager et al., 2020). The obtained results indicated a clear correlation between the wave velocity and material strength and enabled the dynamic elastic modulus evaluation. Fig. 4 shows the E_d elastic modulus evolution for unblended and blended FA geopolymers.

The elastic modulus for unheated unblended mortars reached 19 GPa. For blended FA-GGBFS with 10%, 30% and 50% of slag values, the higher elasticity was observed: 23 GPa, 30 GPa and 38 GPa, respectively. The higher temperature leads to a quasi-linear elastic modulus decrease up to 600 °C. In these tests also the material with no GGBFS addition showed different behaviour with the dynamic modulus growth of 20%. A temperature of 600 °C determines the level above which the stabilisation or a slight rise in the module was observed.

The results of the UPV measurement can be a valuable indicator of damage to the material induced by temperature load and allows obtaining data on the elasticity of the material. The lowest value of ultrasonic pulse velocity at 20 °C for unblended FA geopolymer was

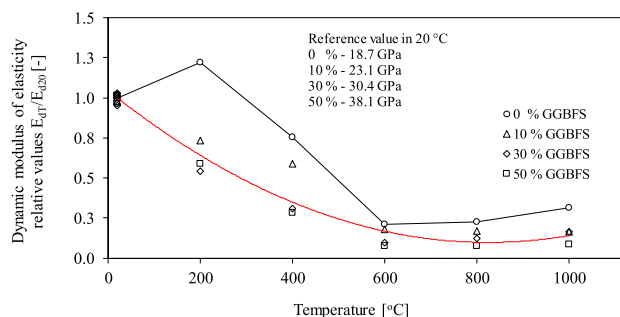


Fig. 4. Changes in elastic modulus after thermal load: relative E_{dT}/E_{d20} values [-] with reference absolute E_{dT} values in [GPa].

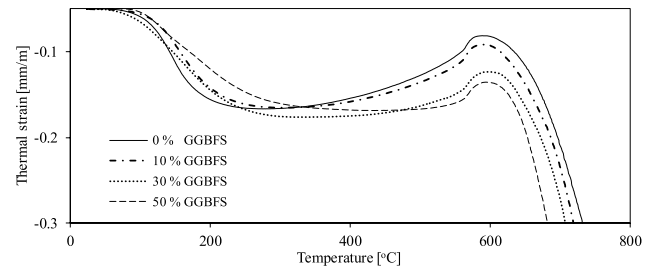


Fig. 5. Thermal deformation, heating rate 5 °C/min.

observed, and its value increase after 200 °C temperature exposure. It corresponds to the strength improvement induced by the polymerisation process. Also, the elasticity increase due to sintering is visible.

3.4. Thermal deformation analysis

For the four geopolymer mortars, the thermal deformation measurements are presented in Fig. 5. The strains induced by heating of the geopolymer mortars offers insight into dehydration shrinkage and sintering process initiation.

In the first phase (between 20 and 100 °C), shrinkage was not significant, probably due to a relatively rapid heating rate. The stage of removing free water starts above 100 °C. In the second phase (100–300 °C), weakly bound water is released. The material structure starts to damage because the shrinkage of the geopolymer paste is initiated. At temperatures above 300 °C slow dehydroxylation of the hydroxy groups occurs. After most of the water has dehydrated, there is a period when the materials exhibited relative dimensional stability. The stabilisation effect was observed in mortars with higher GGBFS content. During a further temperature increase, the slowest deformation increase was observed for the mortar without GGBFS. The impact of mortar composition was more significant at temperatures above 380 °C. Subsequently, a large expansion event occurred with a peak at 580 °C. The temperature behaviour of geopolymer composites is related to the aggregate nature and stability of aggregates at high temperature. This research relates to mortars with quartz aggregates. At 573 °C the phase transformation β to α quartz led to a volume increase of siliceous aggregates. According to (Rickard et al., 2016), 600 °C is the critical temperature for geopolymer materials with quartz aggregates.

Above approximately 600 °C, all the mortar samples start to shrink considerably because of the matrix sintering. Sintering of the sodium-aluminosilicate phase occurs leading to strength increase. It partially compensates for the strength decrease due to aggregate expansion.

The oxides content of the precursor and the nature of aggregates being used have a strong effect on material behaviour at high-temperature exposure. The shrinking paste and expanding quartz aggregate result in crack formation in the interfacial transition zone as well as cracks that are perpendicular to the aggregate surface. Shrinkage and densification of the geopolymer paste due to sintering and melting may decrease the porosity by filling cracks and voids. It is possible that sintering can promote crack closing or even their healing that could have a positive effect in the form of strength regain of previously cracked material.

3.5. Porosity and microstructure

Fig. 6 shows the MIP porosimetry results and SEM images of fly ash geopolymer mortar structures depicted at 500 \times magnification. Two mixes were selected for comparison, unblended (0% GGBFS) and containing 50% of GGBFS blended precursor. This allowed us to compare the impact of the GGBFS contribution on the structure of the unheated composite and composite subjected to high-temperature exposure. The figure illustrates the evolution of the microstructure of geopolymer

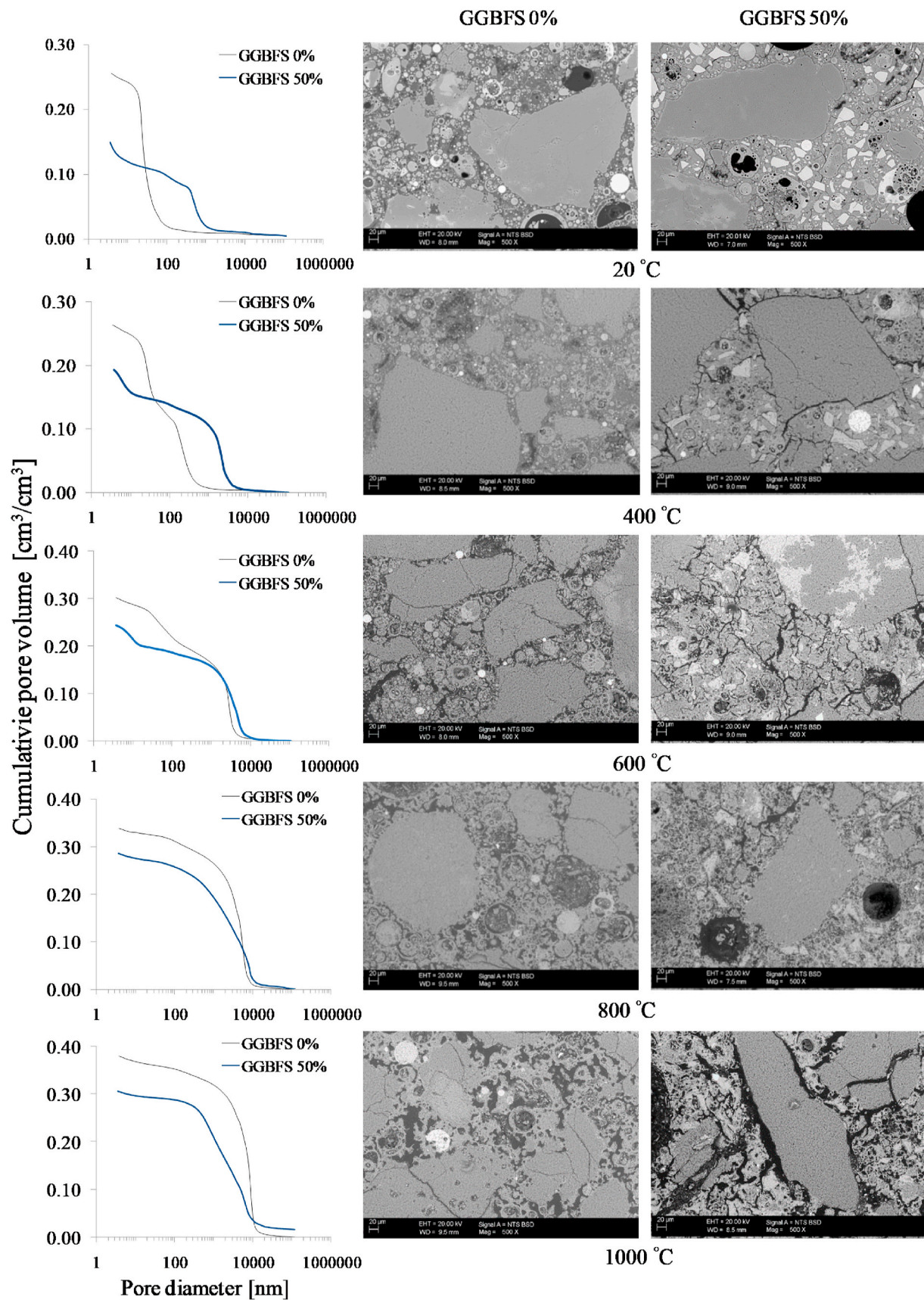


Fig. 6. SEM micrographs and MIP porosimetry of unblended FA geopolymer and blended FA-GGBFS geopolymers subjected to temperature increase (magnification 500x; polished section).

mortars observed on polished samples from 20 °C to 1000 °C.

Before heating (20 °C), the regular spherical grains of non-reacted or reacted in part fly ash grains can be observed in unblended mortars and for 50% slag blended mortars. Nevertheless, they are more frequent in the unblended matrix. For FA-GGBFS blends, numerous slag grains with whitish colour and clear edges are distinguishable. In both samples, the structure of the geopolymer gel is porous; however, micro-cracks can be easily found in the unheated matrix.

The observed changes in the mechanical parameters after high-temperature exposure are due to changes in the material structure. The structure of the unblended fly-ash is more homogeneous. The geopolymer paste cracks when the temperature reaches 600 °C. The SEM image shows the first cracks of the paste and proceeding through the transition zone between aggregates and pastes. The transversal cracks passing through the sand grains, which are visible at this temperature, are due to β - α quartz transformation. The heating of a geopolymer mortar makes its aggregate expand while the surrounding paste shrinks. As a result, the bond between the quartz sand and geopolymer paste cement weakens. At 800 °C, the effects of melting and sintering are visible in the specimen (Fig. 6). The edges of the FA grains become less pronounced, the pore structure changes, and the matrix is modified.

The changes that occur in the blended geopolymer containing slag are more pronounced. Surprisingly, in the blended FA-GGBFS matrix, cracks can already be observed in the initial texture of the unheated material. At 600 °C, the network of cracks was high. Cracks are observed similarly in the geopolymer paste volume and in the contact zone with quartz grains. At 800 °C, the beneficial effect of the melting and sintering processes on the matrix density is not very pronounced. Nevertheless, the observed results confirm the significant impact of the type of precursor used on the high-temperature behaviour of the material (Guerrieri and Sanjayan, 2010).

The cumulative pore volume porosity characteristics of the unheated mortars show a higher total porosity in the case of unblended material. The lower porosity of the blended fly ash-slag mortar resulting in higher strength parameters. In both cases, a progressive increase in material porosity was following the temperature increase. The observed trend of the changes taking place in the pore structures of individual materials was different. For unblended mortar, the total porosity values of the unheated sample and after exposure to 400 °C were comparable. The small changes in porosity corresponded to a high level of mechanical strength. Above 600 °C, the observed increase in porosity was apparent. After heating to 1000 °C, the total porosity was 60% higher than the initial value. In the case of blended FA-GGBFS mortar, the increase in porosity was significant above 200 °C. The porosity value at the final analysed temperature level (1000 °C) was higher than the initial value by more than a factor of two. The more favourable behaviour of unblended mortar indicates that the pore system created in the material allowed more efficient water transport and faster drying. The increase in porosity in blended mortar is associated primarily with cracking and had a very destructive effect on material structure and damage evolution. The microstructure observations demonstrate better behaviour at the high temperature of unblended FA geopolymer mortar with low CaO content.

3.6. Thermogravimetric analysis

TG curves are used to illustrate changes in mass with temperature increase. The total weight loss was analysed in the range of 30–1000 °C. The TGA/DTG analysis results show that geopolymer mortars demonstrated considerable weight loss at temperatures of up to 250 °C, which is associated with water evaporation, and stable material behaviour above 250 °C. After exposure to 700 °C, the specimen weight stabilised, and no further mass loss was recorded. The samples mass loss after exposure to 1000 °C reached 4.5%, 5.3%, 6.6% and 7.3%, respectively, with increasing slag content (Fig. 7).

Geopolymer mortars with a higher GGBFS content showed a more

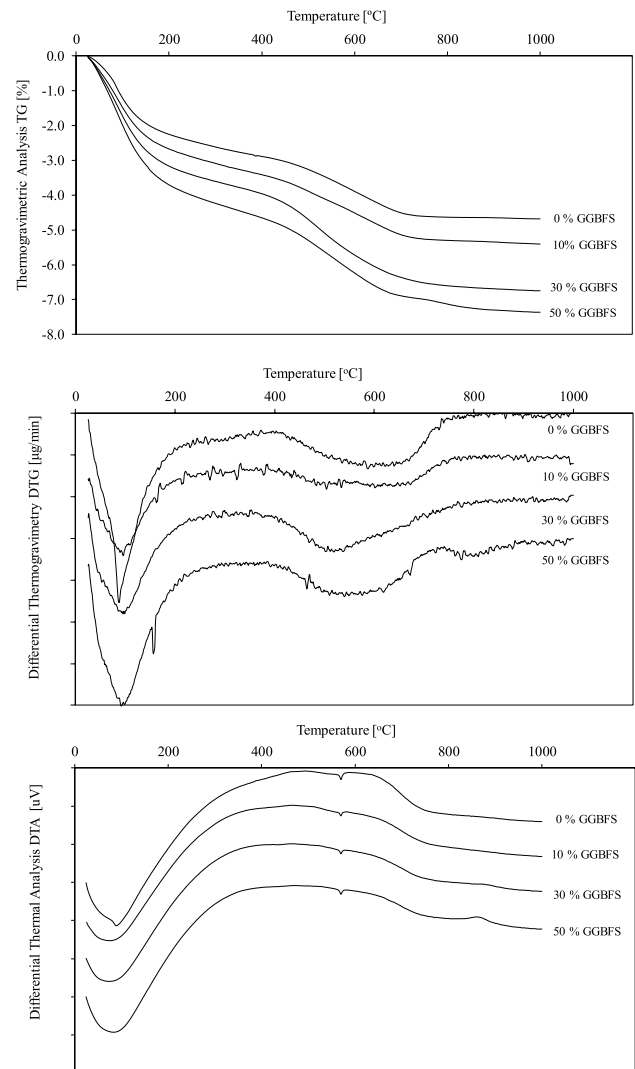


Fig. 7. TGA, DTG and DTA curves of fly ash geopolymer mortars. DTA and DTG curves shifted by 20 units to enable clear readings and comparison of values.

significant weight loss of approximately 8%. The DTG curves indicate that in all cases, the mass was released at the highest rate at a temperature of approximately 80–110 °C. Mass loss peaks were observed at 88, 98, 105, and 88 °C for mortars, with increasing slag content. In the DTA curves, this is depicted by the downward deformation of the curve because the discharge of water is an endo-energetic effect. The endothermic peak is most pronounced for unblended geopolymer, and this is attributed to the energy consumed for the continuation of geopolymerization process in unblended FA-geopolymer at 80 °C. Endothermic reactions are a favourable feature of all materials used as a fire barrier for passive fire protection (Mróz et al., 2016).

A clear peak is visible at 573 °C for all materials and is related to β - α quartz change in the sand. The upward slopes of the DTA curves at 540, 580, 605, and 610 °C for unblended and blended mortars with increasing slag content, respectively, indicate the exothermic effects related to the combustion of organic compounds contained in the material. At the same time, the trend of the TG and DTG curves shows that these processes were more intense in mortars with higher fly ash content. FA is the main source of organic compounds. Besides, in the case of 30% and 50%, the DTA curves show distinct exothermic effects at temperatures of approximately 810–850 °C, which possibly indicates matrix structural changes and the formation of crystal phases.

In Fig. 7 the DTA and DTG curves were shifted by 20 units to enable

clear readings and comparison of values.

4. Temperature-induced physical-chemical changes-a discussion

To discuss in detail the influence of temperature on changes in geopolymer mortar and to explain the observed phenomena affecting the mechanical properties of geopolymers, all observations are presented in the table below. Table 4 depicts the summary of physical-chemical changes during heating of tested geopolymers and other observations.

5. Conclusions

The conclusions below are drawn from the experiments and findings of this research:

- The geopolymer mortars, when heated, present the decrease in mechanical properties: flexural and compressive strength and elastic modulus; however, the manner of changes depends on the composition of the precursor; in particular, the slag content;
- The precursor composition affects the mechanical performances of tested mortars at room temperature. The blended fly ash-slag precursors, and Ca content contribute to developing high mechanical strength, reaching f_c at 90 days 105.0 MPa for 50% GGBFS addition; unblended fly ash mortars at 90 days have developed strength of 40.8 MPa
- For blended precursors with slag addition, its increasing content leads to increased strength at room temperature. During heating, the mechanical properties decrease with temperature followed a similar trend, regardless of the amount of GGBFS addition;
- For blended precursors FA-GGBFS, the strength parameters decrease quasi monotonously, reaching the lowest value at 800 °C. Further increase in temperature causes sintering of the matrix and contribute to a strength regain.
- For unblended mortar, 0% GGBFS, after heating at 200 and 400 °C a compressive strength increase of 30% and 40% was observed, and

flexural strength increase 120% and 40% respectively due to polymerisation progress. The microstructure of unblended FA geopolymer mortar shows a dense structure with no visible cracks; this explains the observed strength increase;

- Ultrasonic pulse velocity evaluation detects porosity changes, cracking evolution, and also polymerisation progress. UPV measurements correlate well with changes in the compressive strength after heating enabling dynamic modulus of elasticity determination.
- For unblended FA-geopolymer a strong endothermic peak was observed at 80 °C and this is attributed to the energy consumed for the continuation of geopolymerization process progressing in the matrix. Such endothermic reactions are considered a desirable feature for thermal barriers and fire protection.
- Despite a lower initial strength of FA-geopolymer (40.8 MPa) in comparison to FA-GGBFS mix (100 MPa), its behaviour of unblended mortar at higher temperatures can be considered more favourable. FA geopolymer presented nearly 90% of the initial compressive strength value after being heated to 1000 °C while for blended fly ash-slag geopolymer the strength-degradation was of nearly 50% at this temperature.
- The microstructure observations let to demonstrate better behaviour at the high temperature of unblended geopolymer mortar with low CaO content. For unblended geopolymer the structure cracks when the temperature reaches 600 °C. The sintering process at 800 °C had coarsened the structure of the matrix, and some cracks observed previously at 600 °C seem to be healed.
- The decrease in strength at high temperatures may also be due to cracking caused by thermal strains differences between shrinking geopolymer paste and aggregates that expand (mismatch of thermal strains). Moreover, the dilatometry results have shown a considerable shrinkage that begins at 600 °C induced by matrix sintering.

The investigations demonstrate that blended FA-slag geopolymers are room-temperature hardening binders with appealing mechanical performances. Nevertheless, to ensure material durability at high temperature, the slag content should be limited. In unblended geopolymers,

Table 4
Temperature induced physical-chemical changes and observations.

Temperature range	Observed physical-chemical changes	Observations
20–200 °C	water vapour pore pressure increases, autoclaving conditions inside the specimen occurs, geopolymerization triggers.	-DTG endothermic peaks, most pronounced for unblended precursor attributed to the energy consumed for the continuation of geopolymerization process in FA-geopolymer; -strength increase of unblended FA; structure densification confirmed with UPV measurements. -for rapid heating - the possibility of spalling behaviour may occur (perspective - verification needed) - mass loss leads to observed bulk density decrease
200–400 °C	absorbed water and capillary water loss; max. water release in the range 80–110 °C; weakly bound water is released.	-cracking of sand grains, matrix cracking
400–600 °C	at ca. 350 °C, some siliceous aggregates breaking up; 374 °C, water critical temperature; chemically bound water release; beginning of dehydration; dehydroxylation of hydroxy groups; 573 °C, phase change β - α in quartz, volume increase of sand grains;	- progressive decrease of strength f_c , f_t , and elasticity E_d
600–800 °C	600 °C all mortars exhibited sharp shrinkage due to the sintering process; melting begins; glass transition temperature, approx. 700 °C; sintering and melting observed, leading to the densification of the matrix; recrystallization into high melting temperature phases.	-endothermic peak due to the dehydroxylation of geopolymers - clear peak on DTA for all mortars - 600 °C, pinkish colouration occurs in all samples, which is attributed to oxidation of iron compounds -a phenomenon more pronounced for a low CaO content precursor (unblended FA) - f_c and f_t stabilisation at approx. 40% of the reference compressive and flexural strengths (f_{c20} and f_{t20}). Compressive strength of unblended mix reaches 90% of the reference value f_{c20} due to matrix densification.
800–1000 °C	800–850 °C structural changes in the material and the formation of crystalline phases; melting progresses	-intensive shrinkage, slight strength regain compared with at 600 °C -distinct exothermic effects at temperatures of approximately 810–850 °C,

the progressive polymerisation gives a positive endothermic effect at 80 °C, delaying heat transfer. The unblended geopolymers (0% GGBFS) also presents better mechanical performances at high temperature. Nevertheless, the conclusions are limited to mortars with precursor and activator compositions as outlined above. One should expect that changes in the oxide composition and the type of activator used may lead to slightly different courses of observed changes caused by heating.

6. Final remarks and perspectives

The undemanding production method, associated with good mechanical performances and unblended FA advantageous thermal behaviour, guarantees waste valorisation. Thus, efforts related to energy efficiency in construction processes are underway, contributing to more sustainable construction materials. Nevertheless, it is necessary to adapt the technology to local waste to developing alkali-activated materials. What is more, the use of local waste to produce building materials further reduces the carbon footprint associated with importing raw materials for the production of building products.

The large variation in the composition of waste materials used in the production of geopolymers causes difficulties in establishing general, universal recommendations. Thus, it is necessary to create the compositions in such a way as to use the waste materials available on the local market optimally. Unlike most of the geopolymers presented in the literature, the proposed material binds at the ambient temperature without temperature curing. Such a reduction of energy consumption in the production process of materials has a positive effect on reducing the carbon footprint of the resulting product. Bearing in mind the need to develop the technology of erecting structures towards a sustainable environment and to reduce gas emissions, further work on materials similar to those proposed in the article are, in the authors' opinion, particularly desirable.

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CRediT authorship contribution statement

Izabela Hager: Conceptualization, Methodology, Funding acquisition, Writing – original draft, and Review. **Mateusz Sitarz:** Data curation, Investigation, Visualization, Writing – original draft. **Katarzyna Mróz:** Validation, Formal analysis, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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