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Research on the possibility of using biochar as a component of aluminate-calcium cement sustainable building composites

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ABSTRACT

The subject of the research presented in the article is biochar and the possibility of using this additive in aluminate-calcium cement-based mortars. The influence of this additive in the amount of 1, 3 and 5% on compressive and flexural strength was tested. It is a material created as a result of thermal transformation of organic waste of plant origin. The possibility of using this additive in cement composites has not yet been described in detail in the literature, however well inscribe within frame of sustainable development and circular economy. The aim of the research presented in the article was to design and test a mortar showing increased resistance to a number of extreme physical operating factors, including frost-resistance and the impact of high temperature, while maintaining strength parameters. The selection of material components of mortars, including the choice of calcium-aluminate cement as a binder and biochar as a partial replacement for cement, was dictated by the desire to combine all the above-mentioned mortar features in one composite. The result of the research is the development of recommendations for optimizing the composition of the biochar mortar at the future stage of implementation. A variable effect of the addition of biochar was obtained. Depending on the content of this additive, both decreases and increases in strength were noted. The presented results constitute a stage of a broader research program.

Keywords: biochar, aluminate-calcium cement, building composites, frost resistance, high-temperature impact, sustainable concrete, sustainable development, circular economy.

INTRODUCTION

The idea of sustainable development is the leading civilizational challenge of our time [Meese and Mcmaoh, 2012]. Reducing CO_2 production in construction is extremely difficult, especially considering that the construction sector consumes approx. 40% of the energy generated annually [Schneider et al., 2011]. Many publications defining "sustainable concrete of the 21st Century" emphasize the fundamental importance of durability and resistance of concrete to operational factors [Mehta and Burrows, 2001]. One of the directions of current research is the use of cement substitutes for concrete and/or the use of recycled aggregate. A well-known trend that has been adopted for years is the use of fly ash in concrete, which brings a number of benefits, including acceleration of hydration, increase in final strength and reduction of the thickness of the grout-aggregate contact zone, which has been confirmed in a number of studies, including [Wang and Ishida, 2019; Malhotra and Ramenizanainpour, 1994; Giergiczny, 2019] and has also been sanctioned in European standards [PN-EN 450-1:2012]. Microsilica, which is produced during the manufacture of silicon and metal alloys, is also widely used in the production of concrete. Its use significantly increases the strength of concrete and allows for its tight structure. In this way, it is possible to reduce the amount of cement or aggregate, and therefore also the energy needed for their production, while using post-production waste, which well inscribe within frame of sustainable development and circular economy [Neville et al., 2012; Szewczak and Łagód, 2022].

Concrete, as a heterogeneous material composed of several components, is susceptible to changes in its structure as a result of the changing temperature field [Zhang et al., 2017]. Because it obtains a specific state of its structure through the cement hydration reaction and adhesion between the cement paste and the aggregate concrete acquires a certain set of mechanical properties [Auberg and Setzer, 1988]. The impact of low and high temperatures on concrete has already been well described [Schneider, 1988; Xiao and König, 2004]. However, due to the use of new additives and admixtures in concrete, there is a need to further test this material in terms of its reaction to physical factors, especially temperature. One type of cement used to increase the resistance of concrete and mortar to high temperatures is alumina cement. There are two methods of producing calcium aluminate cement: melting a suitable mixture of bauxite and limestone or sintering in rotary kilns [Scrivener and Capmas, 2003]. This method is used in Górka Cement plant in Trzebinia (Poland) and employed in presented tests. In recent years, the method of melting in electric furnaces has been used. Currently, two varieties of calcium aluminate cement are produced, i.e. white and dark brown. Their properties depend on the purity of the ingredients in production. White alumina cements are produced from the purest varieties of bauxite and limestone. Alumina cement was primarily used for the production of mortars and refractory concrete [Pöllmann, 2012]. The cement strength in the first 24 hours can reach 90%, and the hydration process is easy even at high temperatures. The setting time is around 30 minutes. High ambient temperature does not reduce its strength properties. A specific feature of mortars and concretes with the addition of clay-lime or clay cement is increased resistance to high temperatures. For this reason, they can be used in places where variable thermal conditions occur, especially sudden temperature increases, e.g. in mining shafts. However, they are also used in the construction of industrial and residential buildings. In addition to fire resistance, they are characterized by a rapid increase in strength and a higher heat of hydration than other cements. For this reason, while maintaining concreting guidelines, they can be used, for example, in winter concreting [Bensted, 2002; Bensted and Smith, 2011]. The use of corundum aggregate modifies the thermal resistance of concrete, which can reach up to 1600 °C during the operation of engineering structures [Kursowski, 2010].

Repeated freezing and thawing has a very negative effect on the parameters of the hardened mortar mixture. This is the result of the limited rate of heat transfer and the increase in the concentration of salts that are dissolved in the previously unfrozen pore liquid [Zaharieva et al., 2004]. The higher the concentration, the lower the freezing point. It also depends on the number and size of pores. The smaller the ice crystals are, the higher the pressure ice particles are under and this is a direct result of surface tension. As a result of this phenomenon, the pore liquid freezes from the smallest to the largest pores. The transformation of water into ice increases its volume by about 9%. As a consequence, this process is striving for the outflow of its excess from the pore space. The growing ice will tend to displace water. The resulting pressure causes a phenomenon called swelling.

In order to further improve the resistance of concrete to the changing temperature field, other solutions, such as the use of metallurgical cements, basalt and hematite-based aggregates, are also employed [Wight and MacGregor, 2016; Ghali et al. 2018]. Nevertheless, clear and beneficial effects can also be achieved by using smaller quantity but equally effective additives, such as fly ash of various origins, ground clay and brick meal, as well as fibers that limit shrinkage and crack development during temperature changes [Li et al., 2022, Gagg, 2014].

Biochar is a product made from the remains of sawmill biomass, forest biomass, fruit and vegetable processing in the process of their combustion. Manure, poultry waste and palm oil are also used in its production. It is worth noting that biochar is made from the part of the biomass that has already been used and is becoming a social problem due to the need for storage and decay processes. During putrefaction, there is an emission of excessive and uncontrolled amount of greenhouse gases. Decaying biomass emits a large amount of methane and carbon dioxide into the atmosphere. It is created in the anaerobic process of biomass carbonization, which binds the carbon element into a stable structure that is resistant to gas emissions. By producing a large amount of biochar using biomass, the concentration of greenhouse gases is reduced [Malińska, 2012, 2014]. Biochar is a highly porous material made from plant waste, mainly used in agriculture as a soil improver, in animal husbandry as a feed supplement and in metalworking as a reducing agent. It can also be used to clean "grey water", as an absorber for sportswear, batteries and many other applications, in addition, it is increasingly often used in construction and health protection [Tokarski et al., 2022]. The physical and chemical properties of biochar are related to the use of biomass for its production as well as the conditions of its production, and determine its usefulness. Burned at 60 °C, it leads to the formation of a stable form, while at 400 °C, biochar still has volatile parts and other unstable compounds. The biochar obtained from rice waste is characterized by high efficiency and unique chemical properties due to the silica content in the biomass structure. The biochar of wood origin is characterized by high carbon content and high sorption properties. Physico-chemical properties can cause changes in soil nutrient content and carbon availability. The biochar derived from carbonization processes produced at low temperatures has a high content of volatiles that easily decompose in the soil, which has a positive effect on plant growth. The biochars produced at high temperatures have a structure characterized by a large surface area and a high content of aromatic carboxylic acids, which increase the absorption capacity. The use of biochar has a positive impact on ecology. This is a good way to dispose of various biodegradable waste that can have a harmful impact on the environment, including the climate [Malińska and Dach, 2014, 2015].

The appropriate selection of combinations for cement, aggregates and biochar additions allows to obtain a material that meets the criteria of sustainable development. Due to this, it is possible to obtain much more durable composite materials, resistant to physical-chemical factors. The biochar structure significantly affects the transport and maintenance of water in the composite, e.g. in mortar or in concrete [Malińska, 2012, 2014]. However, the exact process requires accurate analysis, hence the authors' idea for the research program described in the text.

Taking into account the factors described above, the authors of the following study focused on the possibility of using biochar in combination with aluminate-calcium cement to prepare mortar samples. Biochar is a material that is still relatively poorly described in the literature, although there are already first conclusions presented by scientists. A very important issue addressed by researchers which influences research results is the origin of biochar, i.e. the material used in the pyrolysis process to obtain it. Each type of biochar may cause different results. An important scientific novelty of the presented research program is the influence of biochar addition on the mechanical properties of the selected type of cement mortar. In the presented program, 1, 3 and 5% of biochar in relation to the mass of cement were added to cement mortar based on sand and clay-limestone cement, respectively. The mixes used and the planned research program were intended to demonstrate the impact of the composition used on resistance to extreme impacts of physical factors: cyclic freezing-thawing (frost resistance) and high temperature (high-temperature impacts). The induced temperature effects were related to changes in the values of two basic strength parameters of mortars: compressive and bending strength. These parameters largely determine the durability of the material and its usefulness in construction. The presented results constitute the first stage of a larger research program on the effectiveness of the use of biochar in various cement composites, which well inscribe within frame of sustainable development and circular economy.

MATERIALS AND METHODS

Research significance, scope and program of experiment

The subject of the research presented in this article is an unconventional concrete-like composite made of calcium aluminate cement and biochar in order to obtain high resistance to temperature changes. The aim of the research was to optimize the composition of the composite with mechanical properties typical for construction materials, from the point of view of frost resistance and fire resistance. A material with such durability characteristics can be found in the construction and repair of industrial facilities, where complex environmental impacts often occur. An additional aspect of research on this new composite is its compliance with the trends of sustainable development and circular economy, resulting from the use of waste biochar, which has not been widely used in the engineering of building materials so far.

The tests were carried out on mortars with a composition similar to the standard mortar according to [PN-EN 197-1]. Part of the cement was replaced with biochar in a 1:1 mass ratio, i.e. without taking into account differences in density. Superplasticizers were not used in the research to eliminate an additional factor of influence, which would certainly be the absorption of superplasticizer on biochar grains. Biochar was used to replace 1, 3 and 5% of the cement weight. The first stage of preliminary testing, not specified further, was to check the consistency with a penetrometer, according to standard [EN 1015-4.]. The consistency of all mortars with biochar was at the level of 12 mm. With regard to the designed mortars, tests of frost resistance and fire resistance were carried out, in addition to tests of basic mechanical properties: compressive and bending strength. The list of compositions is presented in Table 1.

Components and used mixtures

Calcium aluminate cement

Calcium aluminate cement produced from a mixture of bauxite and limestone was used in tests. The cement has a density of 3.05 g/cm^3 and a specific surface area with value 3250 cm^2/g. Bauxite is one of the sedimentary rocks dominated by the content of aluminum hydroxide and oxyhydroxides, such as diaspore and boehmite. Apart from the main components, bauxite also contains iron compounds, silica compounds, titanium oxides and clay minerals [Osiecka, 2005]. The content of alumina Al_2O_3 and iron oxide Fe_2O_3 in bauxite determines the class and purity of alumina cement [EN 14647:2005]. The chemical composition of the cement used is shown in Figure 1. These ingredients significantly

Table 1. Compositions of mortars for testing

Specimen designation	Component			
	Cement [g]	Water[g]	Aggregate [g]	Biochar [g]
BIO S0	450	225	1350	0
BIO S1 1%	445.5	225	1350	4.5
BIO S3 3%	436.5	225	1350	13.5
BIO S5 5%	427.5	225	1350	22.5

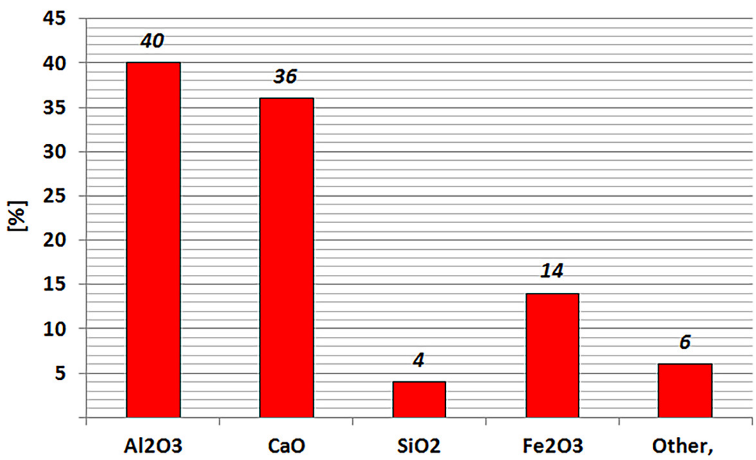


Figure 1. Chemical composition of aluminate-calcium cement used in research: Al_2O_3 – aluminum trioxide, CaO – calcium oxide, SiO_2 – silica dioxide, Fe_2O_3 – iron trioxide

influence the hydration of cement in the mortar. Thanks to them, it is possible to produce an increased amount of C-S-H phase products. The introduced metal oxides can also increase the composite's resistance to temperature fluctuations by reducing porosity.

Biochar

Biochar obtained by pyrolysis of wood material from the wood industry was used for the research. The production process is carried out at temperatures of 350–700 °C. An important feature of the material is the high content of reactive carbon at the level of 93%. Table 2 shows the main properties of the biochar used in tests.

Test methods and equipment used during the tests

Fire resistance

The test of resistance to high temperatures was carried out on a setup equipped with a PK1100/1 (DanLab, Bialystok, Poland) medium-temperature chamber furnace. The furnace is made of square tubes and stainless steel sheet. Fittings and a mat made of ceramic fibers were used to insulate the furnace. The furnace is powered by 230/400 V with a voltage frequency of 50 Hz, rated power is 20 kW and the rated temperature is 1100 °C. Samples with dimensions of 4 × 4 × 16 cm were annealed to 400 °C or 800 °C according to the adopted temperature-time distribution. Temperature registration and measurement was carried out using a PC computer with ThermoPro software ADVETECH. The measure of resistance to temperature was the change in compressive strength as a result of annealing.

The mortars intended for testing the flexural strength were subjected to annealing, with the number of tests being 3 samples each. The elements were heated in accordance with ISO 837, standardized temperature-time curve for a specific combination of loads and in a specific time [PN-EN 1992-1-1]. The temperature distribution is shown in Figure 2. The analysis of the temperature effect on elements made of the designed cement mortars was carried out in a specific time period, omitting the cooling phase. After reaching the assumed temperature, i.e. 20 °C, 400 °C or 800 °C, the samples were heated for another 60 minutes. This was to equalize the temperature in the entire volume of the sample, and then it was freely cooled to ambient temperature. The total

Table 2. Characteristics of the used biochar [product safety data]

Property name	Description
Product classification	In accordance with Regulation EC No. 1272/2008 [CLP/GHS] The substance is not classified as posing physical, health or physical hazards or for the environment
Appearance	- physical state (20 °C): solid, - color: black
Smell	Absent
Relative density	Bulk density: within the range 160–370 kg/m^3
Solubility in water	Practically insoluble
temperature of self-ignition	It does not exhibit self-heating in the UN N.4 test
Reactivity	The substance is not reactive under normal conditions of use and storage
Chemical stability	Under recommended conditions of use and storage, the substance is stable
Possibility of hazardous reactions	No hazardous reactions occur under normal conditions of storage and use. Dusts may form explosive mixtures with air
Conditions to avoid	Avoid sources of fire
Incompatible materials	Strong oxidants
Hazardous decomposition products	Under normal conditions of storage and use, the product does not decompose dangerously. In a fire environment, it can form dangerous carbon monoxide (CO)
Toxicity	The product has not been classified as dangerous for the environment
Durability and degradability	The product is readily biodegradable
Carbon element content	Above 70%
The content of chlorine, sulfur, mercury	Trace amounts, below 0.01%
Volatile content	17%
Ash content	Below 6%

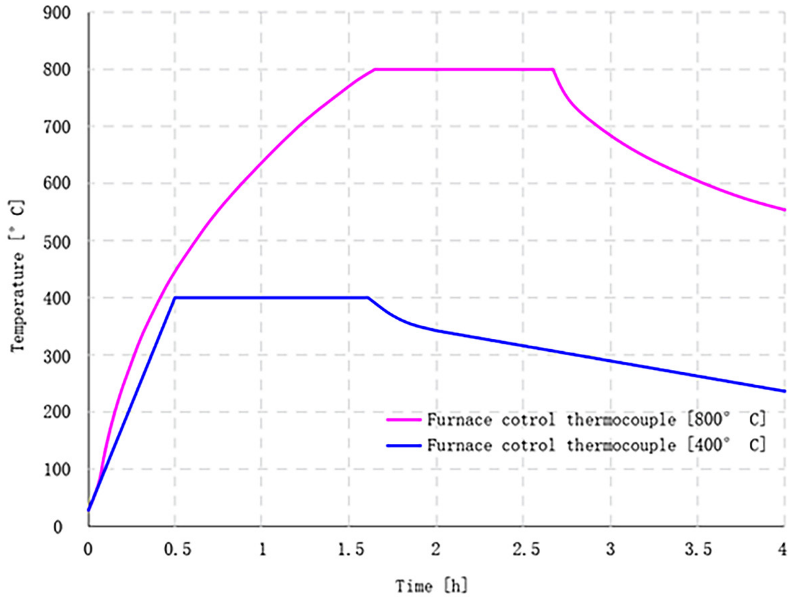


Figure 2. Temperature distribution at 400 °C and 800 °C [PN-EN 1992-1-1]

time of loading the element with a temperature of 400 °C and 800 °C was approximately – 90 and 160 minutes, respectively.

After annealing, the samples were left in a closed furnace until it cooled down completely. After cooling down, repeated bending and compressive strength tests were performed.

Frost resistance

Determination of frost resistance was carried out on 4 × 4 × 16 cm samples after 28 days of hardening. The K-010 chamber was used for testing the frost resistance of cement composites (Toropol, Warsaw, Poland). The samples were stored at 20 +/- 0.1 °C under the following conditions:

- a relative air humidity of 50–60% for the mortars hardening in air environment,
- a relative air humidity above 95% for the mortars hardening in water.

A series of samples was prepared for testing, half of which were subjected to freezing tests, the other half was intended for control testing of bending and compressive strength (the reference samples). Before testing, all samples were dried to a constant weight, weighed with an accuracy of 1 g, and then immersed in water until fully saturated. After the samples were saturated with water, they were removed from water, dried with a cloth, and then placed on a tray with a wooden grate and placed in the freezing machine for the time assumed in the test plan with cyclic freezing and thawing. The machine performs freezing and thawing cycles automatically during the test. Also, the condition of the samples should also be periodically checked, determining their physical condition (damage, cracks, disintegration of trabeculae). Reference samples should be kept in water throughout the test period. After freezing and thawing, all samples, including control samples, were dried to a constant weight and weighed with accuracy to 1 g and measurement to 0.1 mm was performed to calculate the volume. The samples were subjected to 150 cycles of freezing and thawing [PN-B-06265:2018-10].

Mechanical parameters

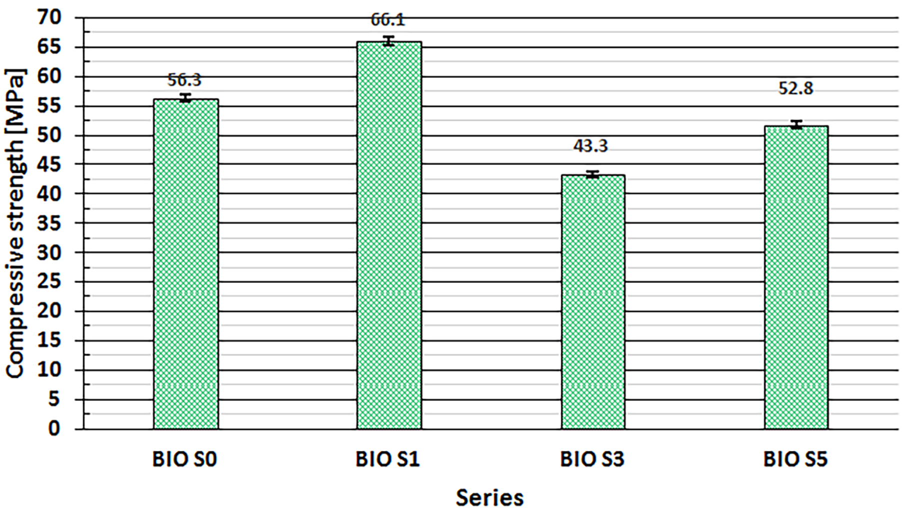
The mortars samples with dimensions of 4 × 4 × 16 cm were tested in two ways, in accordance with the guidelines of the standard [PN-EN 1015-11:2020-04]. Initially, the bending strength was tested in a three-point bending scheme. A testing machine was used for this purpose (Advantest 9 Controls, Milano, Italy) with the bending tests module: velocity 50 N/s, sensitivity 1 kN, range 100 kN, and compression modulus: velocity 2400 N/s, sensitivity 5 kN, range 0–3000 kN. Then, the obtained sample halves were subjected to compressive strength testing using a testing press. The tests were performed both for the samples not subjected to temperature tests (reference samples) as well as for the samples undergoing individual tests, i.e. high temperature resistance and frost resistance.

RESEARCH RESULTS AND DISCUSSION

Effect of biochar on the mechanical strength of the mortar

Samples in the form of bars with dimensions of 40 × 40 × 160 mm were used for testing. Each series consisted of 3 measurements. Figures 3a and 3b show the results of the strength parameters. As it was shown in Figure 3a, the impact of biochar as a substitute for part of cement on mechanical strength is very diverse. The 1% biochar content resulted in an increase in flexural strength of about 14%, with a decrease in this value of 6.2% and 24.5% at 3% and 5% biochar addition, respectively. Such changes clearly indicate the effectiveness of the addition of biochar in replacing cement. Cement composites in general are characterized by inferior flexural strength, which is mainly related to reduced tensile strength (in the case of bent beams in the lower part of their cross-section). As stated on the basis of the test results obtained, biochar can be a type of dispersed reinforcement at a relatively small amount. The 1% addition probably represents an optimal value, while the carbon itself combines with the cement during the hydration process. The final determination of this phenomenon was described in another part of the study, during SEM analysis. The results of compressive strength were more varied. The largest increase in the value of this parameter was obtained with the amount of biochar equal to 1% (17.3%). The presence of biochar in the amount of 3% caused a decrease in strength (by 23.2%), while, interestingly, a smaller decrease was recorded for the samples with 5% biochar addition (by 8.1%). Similar relationships were obtained in the studies described in [Navaratnam

a)



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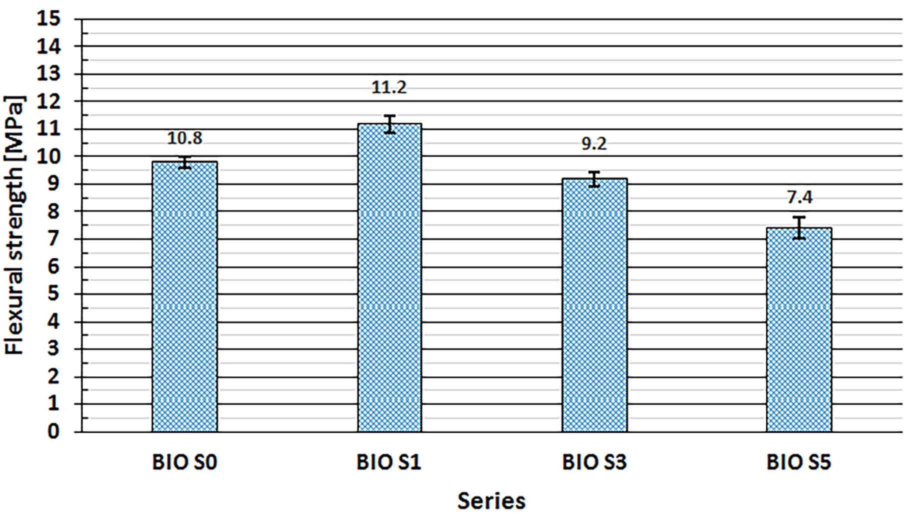

Figure 3. Compressive and flexural strength of mortar with biochar; (a) compressive strength, (b) flexural strength

et al., 2021] at relatively different biochar contents. As described in this work, different properties of biochar from different sources or obtained using other methods can also significantly change the course of changes in flexural and compressive strength. This effect may be related to the difficult compaction of the mortar during the formation of the samples, resulting from the specific, elongated and lamellar shape of the biochar grains. The internal contact zone between the cement paste and the biochar grains was devoid of air pores, which explains the beneficial effect of biochar on strength characteristics. In the studies described in [Navaratnam et al., 2021; Mensah et al., 2021], where a higher w/c ratio and different proportions of cement were adopted, an increase in compressive strength was also obtained with a relatively lower addition of biochar, and a decrease in this strength with increasing biochar content. As it can be seen from the analysis, biochar, due to the lack of sufficient research on its optimal content in this type of composites, is an additive that allows an increase in compressive strength. However, with its relatively small amount. In order to be able to determine its optimal content, possible reaction products of biochar with cement components and possible interactions between biochar and aggregate grains should be investigated. Further conclusions to confirm the results that occurred were refined after SEM analysis.

Fire resistance

The results of the changes in the values of the mechanical parameters of the tested composites are shown in Figures 4 and 5. In the case of the samples unmodified with the addition of biochar and those modified with the amount of

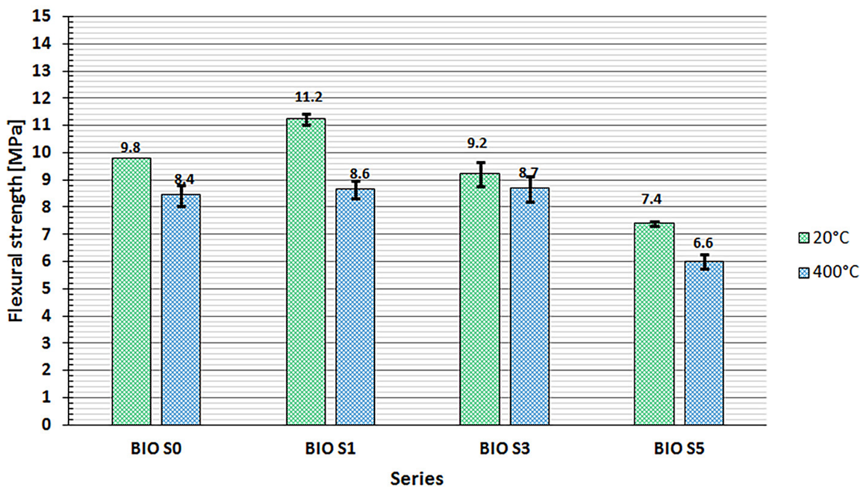

Figure 4. Test results for changes in bending strength after annealing at a temperature of 400 °C

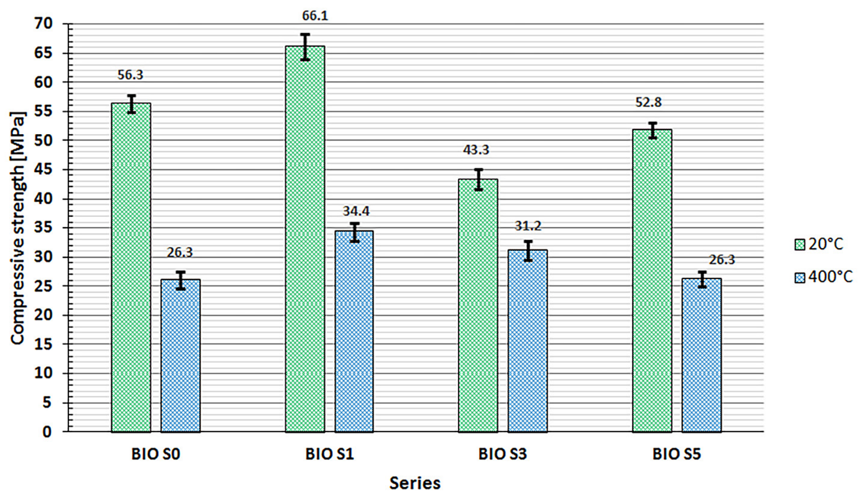

Figure 5. Test results for changes in compressive strength after annealing at a temperature of 400 °C

3 and 5%, it was not possible to carry out tests after annealing at 800 °C due to the destruction of the samples during the process. The analysis of the obtained results concerned the evaluation of the influence of both deliberately applied solutions, i.e. the addition of biochar as a material of unknown influence on cement composites and aluminum cement, the presence of which in the tested mortars was aimed at increasing resistance to high temperatures. The variation of the results shown in Figures 4 and 5 enables a better explanation and understanding of the relationships also obtained in Figure 2.

The addition of biochar in the amount of 1 and 3% allowed for relatively small decreases in flexural strength values compared to reference values. Compared to the BIO S0 series, no decrease in this strength was recorded. Only the 5% biochar content showed such a decrease of 28.6%. Significantly greater variation in flexural and compressive strength was shown by the reference samples. The compressive strength in the BIO S1 series was proportionally higher than this value in the BIO S0 series. Interestingly, although the BIO S3 series reached the lowest strength value at 20 °C, the loss on ignition was not proportional. In this case, the strength achieved a value 20% higher than that of the BIO S0 series, and only 9.3% lower than that of the BIO S1 series. The BIO S5 series showed a decrease at a similar level as the BIO S1 series, however, the achieved strength value was slightly higher compared to the BIO S0 series. Due to the use of the same type of aggregate and cement, a clear beneficial effect of the addition of biochar is evident. In the studies described in [Gupta and Kua, 2021], a similar effect was also obtained, however, for much higher contents of biochar (in the range of 5–20%), but also higher water-cement ratio. In addition, in a thoroughly described analysis in [Navaratnam et al., 2021], an adjustment of the stress-strain curve to the recorded changes in compressive strength and elastic modulus was proposed. On the basis of the work [Mensah et al., 2021], the effect of a particular type of cement on the behavior of biochar specimens subjected to high temperatures is evident. This means that there is a certain limit of biochar addition – in this case 3% – that leads to the most unfavorable impact of biochar. The fact that it is contained between a lower and a higher value, in this case 1% and 5%, is related to the method of binding biochar particles in the mortar and although it is not typical compared to other additives, similar relationships can be found in the literature obtained both for biochar (item 29) as well as for other mortar and concrete additives. The results shown in Figures 4 and 5 gave some insight into how biochar can influence the enhancement of this resistance. During setting with cement and with water, it is possible for water and grout to partially accumulate in the pores of the biochar, resulting in lesser sensitivity to elevated temperatures. The presence of aluminous cement is of great importance in the analyzed series. The molecules in its composition can form more durable structures when reacting with biochar, which are more resistant against the negative effects of roasting. As described in many studies [Novak and Kohputkova, 2018; Ma et al., 2015], cementitious composites deteriorate at high temperatures mainly due to the evaporation of water from their surface and interior and, as a result, the detachment of layers on the surface as well as the loosening of the internal structure. Of great importance is primarily the removal of chemically bound water, which is significantly involved in the hydration reactions of cement. The decomposition of the hydrate components under the influence of high temperature is also important. In this respect, biochar has some beneficial properties. Biochar under humid conditions is able to absorb about 6 times more water than its own weight. This is possible due to the arrangements of congealed fields and clusters contained in it, which can be freely filled with water. The results obtained may indicate the greater ability of these clusters to hold water and release it slowly than in the case of mortar without the addition of biochar [Gupta and Kua, 2020]. Biochar itself, as a material, may also be important in this case. Its closed clusters and pores, which will not be filled with chemically bound water, may provide an outlet for the vapor pressure of the accumulated internal material [Gupta et al., 2020; Tam et al., 2020]. The shape of the channels, which depends on the origin of the biochar, is important in this case [Navartnam et al., 2021]. Regardless of the raw material used in production, biochar itself is a product of biomass combustion, so it is not susceptible to further effects of elevated temperature. Such effects were also described in [Gupta and Kua, 2020]. On the basis of the results obtained, it was also possible to preliminarily determine the greater resistance of the tested mortars to low temperature conditions as well, due to the strengthening of the contact zone between the grout and aggregate.

Frost resistance

Table 3 summarizes the results of the frost resistance test. All the reference samples were tested at the end of the freeze-thaw cycles. The losses in mass, flexural and compressive strength after 25, 50 and 150 cycles.

It is difficult to evaluate the effect of the addition of biochar on the frost resistance of the mortar. Observations resulting from the analysis of mass changes are different than changes in mechanical properties. The addition of 1% biochar resulted in a significant increase in the weight loss of the mortar after freezing compared to the reference series. This effect is difficult to interpret in the light of the fact that with a higher addition of biochar (3–5%), weight gain after freezing was observed. With regard to mechanical properties, a beneficial effect of biochar is observed in relation to changes in compressive strength, but only in the study after 25 and 50 cycles. The effect of the addition of biochar with regard to flexural strength after freezing is surprisingly beneficial. Observation of the structure of frozen samples after the strength test leads the authors to the conclusion that it is related to the morphology of biochar grains, which in the matrix subjected to frost destruction act somewhat like microfibers, limit the development of frost microcracks.

The effect of biochar with alumina cement on strength parameters after freezing and thawing cycles is extremely variable. In the case of the BIO S0 series, attention should be paid to the typical relationships for the samples made of other unmodified mortars. As the number of cycles increases, a gradual, proportional decrease in weight can be seen. The value increases above the reference only at 150 cycles, which is due to the higher absorptivity of the samples. After 150 cycles, the internal structure of the mortar is already so disturbed and weakened by the processes of freezing and thawing of water in the capillary pores that the sample

Table 3. Results of frost resistance tests obtained for the reference samples containing biochar

Reference samples						
Specimen designation	Mass [g]		Flexural strength [MPa]		Compressive strength [MPa]	
BIO S0	558		9.8		56.3	
BIO S1	595		11.2		66.1	
BIO S3	544		9.2		43.3	
BIO S5	538		7.4		51.8	
Samples after freezing						
After	Mass from the solution	Mass relative to reference sample	Flexural strength		Compressive strength	
	[g]	[g]	[MPa]	relative to reference sample [%]	[MPa]	Relative to reference sample [%]
BIO S0						
25 cycles	556	-0.40	9.3	-4.88	52.0	-7.70
50 cycles	541	-3.00%	8.1	-17.15	45.8	-18.71
150 cycles	569.7	2.10	7.5	-23.29	42.8	-24.03
BIO S1						
25 cycles	554	-6.90	6.9	-38.50	42.2	-36.18
50 cycles	551	-7.40	5.3	-52.76	42.4	-35.88
150 cycles	557	-6.40	7.6	-32.26	42.6	-35.58
BIO S3						
25 cycles	547	0.60	8.3	-9.95	36.0	-16.90
50 cycles	560	2.90	8.1	-12.12	35.6	-17.83
150 cycles	569.6	4.70	7.3	-20.80	32.2	-25.67
BIO S5						
25 cycles	530	-1.50	9.1	23.03	36.3	-29.87
50 cycles	550	2.20	7.4	0.05	36.6	-29.29
150 cycles	540.3	0.40	7.1	-4.01	33.6	-35.09

easily soaks up water and holds it in its bulk. With the increase in the number of cycles, there was also a gradual decrease in both flexural and compressive strength. This fact, too, is directly related to the violation of the internal structure of the material subjected to an alternating temperature field. The effect of the influence of freezing and thawing cycles on the 3 afore-mentioned parameters was a point of comparison for the other series, with different biochar content.

The BIO S1 series showed decidedly different relationships. These can be seen already in the analysis of changes in the weight of the samples. Compared to the mass of the samples before the test, the BIO S1 series showed a slight fluctuation in this value. A decrease in value of about 7% was shown by samples after 25, 50 and, most importantly, after 150 cycles. This indicates some different behavior of the material. Further analysis of the results shows quite different strength parameters. Flexural strength initially decreases by about 40% after 25 cycles, then by more than 50% after 50 cycles, to finally increase after 150 cycles. This kind of relationship is not typical for cementitious composites, especially mortars. It indicates a favorable addition of biochar. Relating these results to the compressive strength values, it should be noted that despite a rather large decrease (about 36%) after the first phase of freezing-thawing cycles, the increase in the number of cycles did not cause a further decrease in this value.

Similar correlations were found for other series, with the correlations being adequate and proportional to the initial mass and values of each strength. In the BIO S3 series, an increase in the weight of the samples was established after each series of cycles. However, unlike the BIO S0 series, this did not translate to the same extent into a decrease in strength parameters. The flexural strength after 25 and 50 cycles reached a similar level, only to decrease after 150 cycles. However, the differences in decreases were not as significant as in the BIO S1 series, while there was no increase in the value of this parameter either. Compressive strength also followed similar relationships. The BIO S5 series initially showed a slight decrease in weight, and then the value oscillated around a result higher than the reference weight. A clear increase in flexural strength after 25 cycles is significant in this series. Subsequently, this parameter decreased to values practically the same as those of the specimens before the test. Compressive strength after 25 and 50 cycles reached similar levels, then decreased slightly (about 6%) after 150 cycles compared to the values of the BIO S5 series before the test.

All the correlations that have occurred have their justification in the structure of biochar, which has already been mentioned during the analysis of the results in the previous chapter, as well as in studies [Sikora et al., 2022; Tokarski and Ickiewicz, 2021]. Biochar particles can affect the state of the internal structure of the composite under study in two ways. According to an earlier conclusion, their structure itself can constitute a kind of dispersed reinforcement, reducing the effects of shrinkage and mortar failure due to the expansion of the volume of water in the material pores during freezing. The transition zone itself between the grout, aggregate and biochar can thus be further strengthened. The second issue concerns the ability of the biochar particles to hold water. The water stored during the soaking of the material inside the biochar structure, as also found in [Mensah et al., 2021; Tan et al., 2020], can take part in the secondary hydration of the cement of the inner material during its release. The structure of biochar allows the creation of special channels through which water, in various forms, can escape from the composite, thus reducing the internal pressure in the material [Navaratnam et al., 2020; Gupta and Kua, 2020]. It is likely that it does not freeze at the same rate as the water contained in the pores and capillaries of the grout or aggregate. In this situation, the decrease in strength values is due to normal phenomena that occur when testing the frost resistance of a cement composite. On the other hand, the water released from the biochar particles can re-bond part of the cement by rebuilding the C-S-H phase, which is associated with the re-strengthening of the internal structure of the material. Hence, despite the decrease in compressive strength compared to reference samples, this value is kept relatively constant. Also, secondary reinforcement of the structure can, in specific cases and with the right amount of biochar, cause an increase in flexural strength. This is most likely related to the reorganization of the structure and its temporary strengthening. The amount of biochar is also important. In the study described in [Jia et al., 2023], at a biochar content of 20–40%, there was no significant effect of biochar on frost resistance, however, no significant decrease in compressive strength was found either. It is important to determine whether this effect is somehow dependent on other temperatures. In the absence of sufficient studies, it is uncertain whether this effect is also possible with other types of cement or under other test conditions.

CONCLUSIONS

The conducted research allowed drawing the following conclusions:

- the subject of the research was biochar from pyrolysis of forest biomass as a component of mortars with aluminate-calcium cement and only in the scope of such a composite the conclusions from this research can be applied,
- the possibility of using the tested biochar in the mortar with alumina-calcium cement without negative effects was demonstrated when its dosage was limited to max. 3% by weight of cement.
- the highest strength characteristics (both for compression and bending) were obtained by the mortars with 1% biochar content,
- loss of mortar strength at 400 °C is lower than the reference sample (without biochar) until dosing 3% of the cement mass,
- the effect of biochar on frost resistance is ambiguous – the addition of 1% does not change the course of frost destruction in relation to the reference sample. The picture of frost destruction with a higher content of biochar is interesting: fibrous particles of biochar, which are not damaged by frost, join the microcracks in the sample and, as a result, the decrease in bending strength of the samples after freezing is relatively small.

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