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Structural changes of aluminum cement-based mortar with biochar addition

Paweł Woliński[1], Andrzej Szewczak[2*], Wojciech Andrzejuk[3], Paweł Ogrodnik[4], Grzegorz Łagód[5], Piotr Woyciechowski[6], Grzegorz Adamczewski[6], Estera Michaluk[7], Janina Kopyra[8]

[1] Faculty of Technical Sciences, Academy of Applied Sciences Mazovia, Sokolowska 161, 08-110 Siedlce, Poland
[2] Faculty of Civil Engineering and Architecture, Lublin University of Technology, Nadbystrzycka 40, 20-618 Lublin, Poland
[3] Faculty of Technical Sciences, John Paul II University in Biała Podlaska, Sidorska, 95/97, 21-500 Biała Podlaska, Poland
[4] Faculty of Civil and Environmental Engineering, Warsaw University of Life Sciences, Nowoursynowska 159, 02-776 Warsaw, Poland
[5] Faculty of Environmental Engineering and Energy, Lublin University of Technology, Nadbystrzycka 40B, 20-618 Lublin, Poland
[6] Faculty of Civil Engineering, Warsaw University of Technology, Armii Ludowej 16, 00-637 Warsaw, Poland
[7] Innovation Research Center, John Paul II University in Biała Podlaska, Sidorska 95/97, 21-500 Biała Podlaska, Poland
[8] Faculty of Natural Sciences, University of Siedlce, 3-go Maja, 08-110 Siedlce, Poland
* Corresponding author's e-mail: a.szewczak@pollub.pl

ABSTRACT

The article presents the results of analyzing the structural changes of samples made of cement mortar. In addition to sand, cement with a higher aluminum oxide content was selected as a mortar component. Biochar, obtained as a product of burning production waste in the wood industry, was intended as an additive affecting the variability of the results. Biochar addition amounted to 1%, 3% and 5% by weight of cement. The samples were subjected to temperature changes. For this purpose, the material was subjected to two phenomena: high temperature (400°) and 150 freezing and thawing cycles. In the study, the authors focused on the possible changes occurring in the internal structure of the material. The possible course of the formation of cracks in the material subjected to variable physical factors, as well as the primary structure, studied by means of the SEM method, were presented. The gathered material complements the previously conducted tests focusing on changes in compressive strength and flexural strengths of reference samples and those prepared according to the described formulations. The results of the study indicate the possibility of using biochar as an additive to mortars allowing them to change their response to different temperatures by affecting the process of water transport inside the material.

Keywords: biochar, aluminate-calcium cement, building composites, frost resistance, high-temperature impact.

INTRODUCTION

Concrete is undoubtedly one of the most studied construction materials. It is employed in the construction of various buildings, such as residential, public housing, public utilities, as well as other structures [1–3]. It is common to use concrete for building massive hydrotechnical structures, road surfaces, airports, towers and masts. In each of these cases, specific properties of concrete are taken into account, including: durability, non-combustibility, availability, relative ease of execution. However, concrete also exhibits certain disadvantages, such as brittleness, the energy consumption required for the production of cement (the basic ingredient of concrete), and the acquisition of aggregates [4, 5]. Given these aspects, it is easy to understand why so many researchers are trying to find various alternative additives and admixtures for concrete so that its composition and conditions of use can be further optimized. One important aspect is the placement of elements made of concrete under outdoor environmental conditions characterized by changing temperature field [6, 7]. In addition, in building structures there is a risk of fires, which significantly affects the operating conditions and the safety of users.

Among the relatively new solutions in the field of additives and admixtures for concrete, the use of several materials is becoming more common [8, 9]. An interesting direction of current research is the use of ceramic (silicon-aluminum) cenospheres obtained during the combustion of hard coal, which constitute one of the fly ash fractions, for concrete and cement composites [10–12]. Cenospheres are an excellent insulating and filling material used in composite technologies. In the case of thermal impacts, the main cause of degradation of cement composites at high temperatures are micro-cracks, resulting from different thermal properties of the cement matrix and aggregate [13]. Previous studies [14, 15] have confirmed that the use of cenospheres for concrete mix can be an effective method of increasing the mechanical parameters of concrete or cement composites. In another study [16], the authors conducted experimental research on a light cement composite with the addition of cenospheres. After more than 90 days of curing, the samples prepared for testing were heated to temperatures of 105, 200, 400, 600, 700, 800 and 1000 °C. The tests carried out showed a significant improvement in compressive strength compared to traditional concrete. After heating to 600 °C, the samples retained 92% of their initial strength, and after heating to 1000 °C – about 60%. The resulting material is characterized by low density (1450 kg/m^3) and reduced thermal conductivity (0.60W/mK) at 20 °C. The feature that determines the suitability of cenospheres for use in the production of materials resistant to high temperatures is their increased mullite content. Other applications of cenospheres in materials engineering also include their use as fillers in polymer technology, especially in the case of polyurethanes and polyesters. They can be used in the production of lightweight concrete [9].

An interesting, still developing direction of research related to the improvement of operating parameters is the use of concrete with fibers made of different materials and having various forms and dimensions [17, 18]. The main purpose of using fibers is to control cracks at the stage of loading, increase strength, modulus of elasticity and a number of other properties. Compared to steel and carbon-glass fibers, polymer fibers are attractive due to their high ductility, which affects the flexural strength of cement-based materials [19–21]. Polyamide (PA) and polypropylene (PP) fibers are successfully used in cementitious composites to improve hardness and impact resistance, control shrinkage cracking, and significantly increase the energy absorption capacity of materials. Habib et al. [22] conducted research to determine the effect of synthetic fibers (glass, nylon and polypropylene) on the mechanical properties of mortars. The research described in [23] also demonstrated a beneficial effect of plastic fibers on the mechanical properties of concrete exposed to high temperatures. Polymer fibers are important not only in the operational phase of concrete. There are numerous studies indicating the effectiveness of using fine polypropylene fibers to reduce the effects of excessive shrinkage of concrete and mortars, especially chemical and thermal shrinkage [24, 25]. The possibilities of using various types of fibers, the method of adding them to cement composites, thickening and selecting the optimal amount while maintaining the operational parameters of the mixtures, mainly workability and consistency, were described in the research.

According to the presented idea of sustainable development, an interesting alternative for improving selected operating parameters is the use of biochar [26, 27]. This is a material created through thermal treatment processes (pyrolysis) of waste from various sources, such as agricultural wood processing. Due to its physico-chemical characteristics and grain morphology, biochar can be treated as a modifier of the cement matrix combining the features of a mineral additive and microfiber. Biochar is also widely regarded as an effective method of carbon sequestration [28, 29]. So far, the experience in the use of biochar as a component of cement concretes is not substantial. The published works have shown that the effect of the addition of biochar on strength may be different – it depends mainly on the type of biochar (i.e. the type of biomass constituting the raw material), its amount and the pyrolysis temperature during which it was produced [30, 31]. In the work [32], dry grain decoctions from the bioethanol industry were subjected to pyrolysis at 500 and 600 °C to produce biochar. The compressive strength of concrete with the addition of biochar in the amount of 1, 2 and 3% by weight was tested by replacing sand. The results of this study did not show any significant differences between concretes with biochar and sand-only samples. Ahmad et al. [33] found that adding a small amount of bamboo biochar to the cement composite increases its compressive strength. The amount of biochar (0.05%, 0.08% and 0.2% by weight of cement) was added to the concrete mix and, at doses of up to 0.08%, it increased the strength by as much as 20–40%. Further increasing of the amount of biochar did not bring strength benefits. It should be noted that in this study, biochar was pyrolyzed at 850 °C and then annealed at 850 °C, which stabilized its properties. There are also reports in the literature about the use of biochar to modify cement mortars. For example, in the work [32], cement mortars with the addition of biochar 1% and 2% by wt. of cement were tested. These values turned out to be optimal for increasing the compressive strength of the cement mortar. All cited studies concern composites on cements with portland clinker. The authors did not find any reports in the literature on the modification of calcium aluminate cement composites with biochar, which was the inspiration for the research presented in this article. The analysis of the current state of knowledge leads to the conclusion that there are certain possibilities of using biochar as an additive that have a beneficial effect on changes in the strength of concrete subjected to freezing and thawing conditions.

Cement-based composites are often subjected to low temperatures under operating conditions. As the temperature is lowered, the water filling pores and capillaries, increases in volume, causing cracks to expand, fuse and degrade the material. Frost resistance testing, as described in standards [4, 34, 35], is usually aimed at obtaining information on the weight loss and/or strength of specimens subjected to a certain number of freezing and thawing cycles. These effects are relatively easy to measure. Nevertheless, the possible changes occurring in the internal structure of the tested material should be analyzed, as they lead to the final obtained changes in the results of physical and mechanical parameters. The authors of the presented article present an analysis of the describable changes occurring in a specially prepared cement mortar. The composition of the mortar was selected so that it was possible to study its response to high temperatures (400 °C) and 150 freezing-thawing cycles. For this purpose, aluminum-calcium cement with increased aluminum oxide content was used. According to the research plan, biochar derived from thermal processing of waste from the wood industry was used as an additive to the mortar. The biochar addition of 1, 3 and 5% by weight of cement was analyzed. The biochar was intended to affect the process of water transport inside the material under study. Thus, it was aimed to achieve a lower degree of degradation and, consequently, greater durability of the tested mortar. The structure of the internal structure was also analyzed, along with a description of the location of the biochar grains in the cement slurry. The analysis carried out is an extension of the studies described by authors in other article, aimed at determining changes in the strength parameters of samples treated in this way.

MATERIALS AND METHODS

Materials and mixtures

Calcium aluminate cement

A series of several specimens made of cement mortar were prepared for the study. The proportions of ingredients are shown in Table 1. Calcium aluminate cement was used. It is characterized by a high content of Al_2O_3 (40%) and CaO (36%), with a low content of SiO_2 (4%). Iron oxide Fe_2O_3 (14%) is also present. This composition of the cement enables to obtain a material that is resistant to a variable temperature field in both the high and low temperature ranges. The hydration process leads to the formation of calcium aluminosilicates, calcium aluminoferrites and the typical C-S-H phase, but in a smaller amount than when using pure portland cement.

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%.

The biochar used in the research is produced via pyrolysis of wood production waste at

Table 1. Compositions of mortars for testin

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

350–700 °C. The reactive carbon content is as high as 93%. Therefore, it is possible to use the material as an additive. It was assumed that it is possible for biochar to react with cement components and form a permanent transition zone between biochar grains and cement slurry. The general characteristics of the material are shown in Table 2.

Test methods and equipment used during the tests

Mechanical parameters before and after heating and freezing

The strength tests were conducted using specimens measuring 4 × 4 × 16 cm which were tested in a two-stage test. In the first stage, the specimens were subjected to three-point bending, then in the second stage the halves obtained were subjected to compressive strength testing. The tests were carried out by means of a testing machine (Advantest 9 Controls, Milan, Italy) with a bending test modulus: speed 50 N/s, sensitivity 1 kN, range 100 kN, and a compression modulus: speed 2400 N/s, sensitivity 5 kN, range 0–3000 kN. Then, the obtained specimen halves were subjected to compressive strength testing using a test press. When testing the reference samples, the samples subjected to roasting, and the samples subjected to frost resistance test, 3 samples were used in each measurement series.

In order to determine the changes occurring in the material due to the effects of high temperature, a separate setup was built in accordance

Table 2. Characteristics of the used biochar. [36]

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%

with the recommendations of the standard [37]. Its main component was a PK1100/1 medium-temperature chamber furnace (DanLab, Bialystok, Poland). It is based on a stainless steel square tube system. The furnace is properly insulated with fiberglass fittings and mats. The furnace is powered by 230/400 V with a voltage frequency of 50 Hz. The rated power of the unit is 20 kW. The maximum temperature that the device can achieve is 1100 °C. In order to plan the time of the roasting run, the temperature-time distribution was adopted. Samples with dimensions of 4 × 4 × 16 cm were annealed to 400 °C. Temperature was recorded and measured using a PC with ThermoPro ADVETECH software. The measure of temperature resistance was the change in strength parameters produced by annealing. In order to achieve a relatively uniform temperature distribution throughout the specimen, once the desired temperature was reached, the specimen was then roasted for an hour. After this period, the samples were cooled freely until they reached a temperature of 20°C and were subsequently subjected to compressive and flexural strength tests.

The frost resistance test was carried out on 4 × 4 × 16 cm samples after 28 days of hardening. The test was carried out in the K-010 chamber (Toropol, Warsaw, Poland). In order to meet the requirements of the study [38], constant conditioning conditions were provided for the samples. After 150 cycles, differences in weight loss and flexural and compressive strength values were examined according to the above-mentioned procedure. Then the samples were saturated with water, they were removed from the water, dried with a cloth, then placed on a tray with a wooden grate and frozen in a freezer for the time assumed in the test plan with cyclic freezing and thawing. During the tests, the condition of the outer surface of the specimens was also checked for possible cracks and low temperature effects.

SEM analysis

SEM analyses were performed throughout the individual tests. This was aimed to capture differences in the internal structure of the tested composites subjected to varying temperature effects. SEM analyses were performed using TM3000 Hitachi – scanning electron microscope with EDS detector (Hitachi, Tokio, Japan).

RESEARCH RESULTS AND DISCUSSION

Effect of biochar on the mechanical strength of the mortar in all series

The changes in the values of the bending and compressive strength were strictly dependent on the series and the content of biochar. A detailed analysis of the obtained results in terms of changes in the strength parameters of the reference samples, subjected to ignition and after the frost resistance test, was included by the authors in [39]. In terms of the strength results themselves, it should be stated that the most optimal amount of biochar in the case of the reference samples was 1% in relation to the cement mass. However, increasing the content of the additive did not affect the tested parameters in the same way. The lowest strength values, compared to the samples without the addition of biochar, were recorded with the addition of 3%, however, the amount of 5% allowed for another increase in strength (comparison of the results of the BIO S3 and BIO S5 series), but these were lower results than the BIO S0 and BIO S1 series. Compared to the results obtained for the reference samples, both the addition of biochar in the amount of 1% and 3% improved the strength properties. Only the BIO S5 series showed a decrease in the results. The results after the frost resistance test were not so obvious. The conclusions presented in [39] indicate a very diverse effect of the addition of biochar on the mechanism of sample degradation under the influence of 150 freeze-thaw cycles. The percentage changes in the bending strength values were the largest. In this case, however, the results obtained in the BIO S5 series are the best presented. Such a diverse effect of the addition of biochar on the obtained results led to the need to analyze changes in the internal structure. It was necessary to address the issue of water transport and absorption by the material, because, as the results clearly indicate, it plays a key role and has a decisive influence on the obtained relations of the individual series.

SEM analysis

The SEM analysis included two main stages. In the first one, the results of which are presented in Figure 1, the structure of pure biochar was analyzed. Similarly to the research described in [40–43], it was shown that the structure of biochar depends on the direction (Figure 1b). In longitudinal section, biochar has a longitudinal,

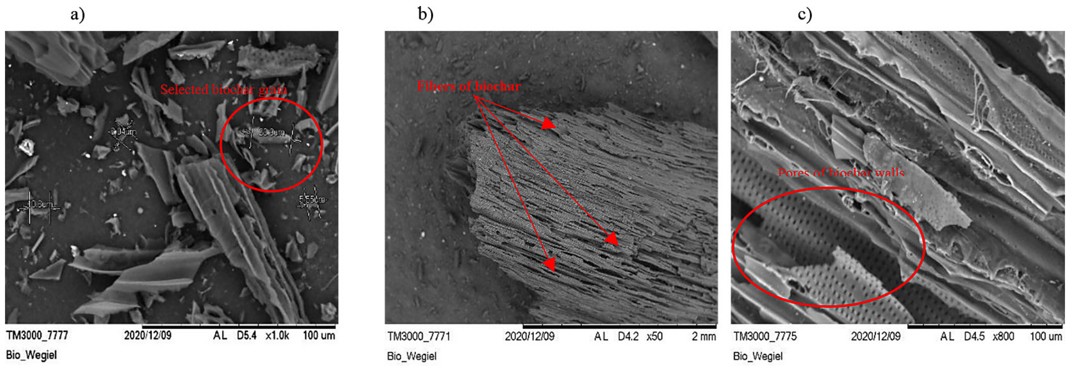

Figure 1. Morphology of biochar grains: (a) various grain shapes and sizes, (b) fibrous nature of the grain, (c) porous internal structure of the grain

fibrous structure. At high magnification (Figure 1c), perforated walls separating individual fibers are visible. Their presence, as well as the laminar structure of the biochar grains themselves, significantly facilitates the transport of water and other chemical compounds inside the additive.

The pores and fibrous structure of biochar give rise to the possibility of several possible relationships. When analyzing the effect of biochar on flexural strength, according to the already drawn conclusion, the fibrous structure can cause strengthening of the tensile zone of the composite. However, the very specific arrangement of channels and pores of the biochar is more relevant. As noted and presented in [40, 42], their diameter, shape and distribution in the cement composite largely depend on the raw material from which the biochar is made. Their presence is very clearly visible on SEM images (Figure 1), they have a different structure in the overall picture of the internal structure of the mortar. Owing to them, as mentioned earlier, it is possible to absorb water and ensure its free movement in the composite, not only in the form of liquid, but water vapor as well [44].

As the second part of SEM analysis, the main focus was on locating biochar grains inside the cement composite, which was the tested mortar, and determining the compatibility of biochar with the structure of the grout (Figure 2).

The photos showing the contact zone of the slurry and biochar also yield a number of answers to the correlations obtained earlier (Figures 2a and 2b). The transition zone is a very important part of the internal structure of the composite. In the case of biochar, it can be shaped in a specific way. Studies described in [40, 41] indicate a high content of carbon, and a low content of other elements, mainly calcium, magnesium and silicon in the overall composition of biochar [40, 43]. The presence of these elements under specific conditions of high and low temperature promotes enhanced carbonation. This effect is particularly evident in the frost resistance results. The water released from the pores of biochar can participate in the secondary hydration of the composite components [42, 45]. The presence of aluminous cement, that is, cement with an increased content of aluminum and iron oxides, can lead to the formation of structures that strengthen the composite. No calcite accumulation was found in the contact zones between the grout and biochar grains [42].

The formation of temporary chemical bonds between carbon and some of the compounds formed by cement hydration, mainly van der Waals interactions and other molecular bonds, is highly possible. However, it is difficult to determine a significant effect on these reactions. Although the carbon in biochar is considered to be chemically active, for the formation of calcium carbonate in the mortar to occur, it would need to be further oxidized to form carbon dioxide. Instead, it is to be expected that the hydration reaction in the vicinity of biochar grains occurs intensively. This is because biochar, as already described, has the ability to significantly store and accumulate water [41]. This water can pass between the outer and inner surfaces of the biochar grain walls. As it is shown in Figures 1 and 2 in schematic form, the transition zone between the main slurry and biochar is not as differentiated as the similar zone between the slurry and sand grains. Figure 1c and Figure 2 b,c show a clear boundary, which is the wall of the biochar grains. In front of it, the structure of the grout is not significantly different from the grout filling the spaces between the aggregates. Nevertheless, one should consider the slightly different structure of

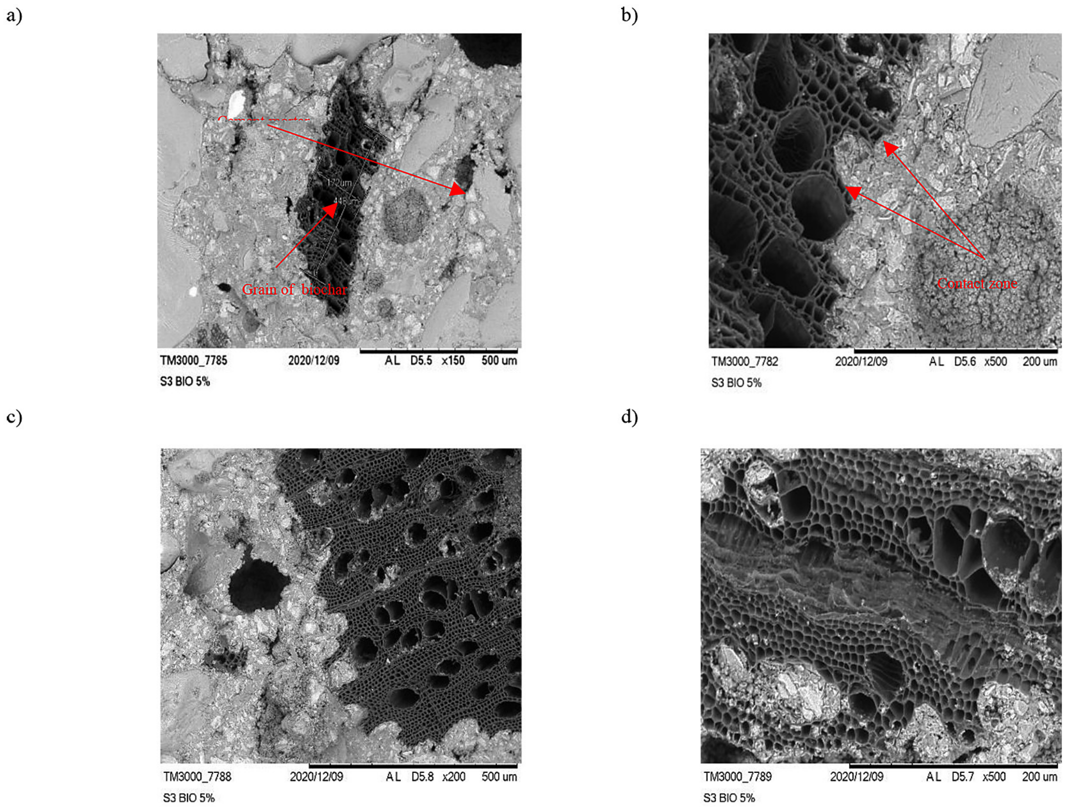

Figure 2. SEM picture of tested samples, a) biochar grain in a cement mortar matrix, b), c) contact zone between mortar and biochar, d) hydration products inside biochar grains

the transition zone resulting from possible bonds with the biochar. It should be expected that if such bonds occur, they are formed between carbon, hydrogen and silicon atoms.

It is also important to observe some of the hydration products inside the biochar (Figure 2d). This means that the components of the slurry, i.e. calcium oxides, aluminum oxides, iron oxides and water can penetrate inside the biochar and fill the volume of its pores. However, complete filling of the pores is not possible due to probable limitations on particle movement caused by conditions in the grout structure. The main issue is the possibility of an effect in which hydration of the slurry occurs faster outside the grains. In the case of hydration occurring inside them, the molecules involved in reactions (1) and (2) must first overcome the barrier that is the wall of the biochar grain, and only then can they hydrate. This process is too slow for the free movement of oxides to take place. However, water itself, as confirmed in other studies of biochar properties, has the ability to move freely between the biochar and the slurry. This movement and the reduction of freezing water during the frost resistance test.

The influence of biochar on the structure of the material subjected to calcination

In order to thoroughly analyze the phenomena occurring in the tested mortar during roasting and frost resistance tests, it is also necessary to refer to two basic reactions occurring during cement hydration [46]:

$$6CaO\ SiO_2 + 9H_2O \rightarrow 6CaO \cdot SiO_2 \cdot 9H_2O \quad (1)$$

$$3CaO\ Al_2O_3 + 12H_2O \rightarrow \rightarrow 3\ CaO \cdot Al_2O_3 \cdot 12\ H_2O \quad (2)$$

To understand the beneficial effect of the presence of biochar in the tested mortar, it is worth analyzing the changes in the structure of the composite shown in Figure 3.

The initial structure of the composite is compact, containing a natural arrangement of aggregate (in this case – sand), and a slurry composed of the products of cement hydration, primarily the C-S-H and C-A-H phases [34]. Both phases contain chemically bound water. The pores present in the grout (closed and connected by a capillary system) are the result of water movement during the hydration reaction and maturation of

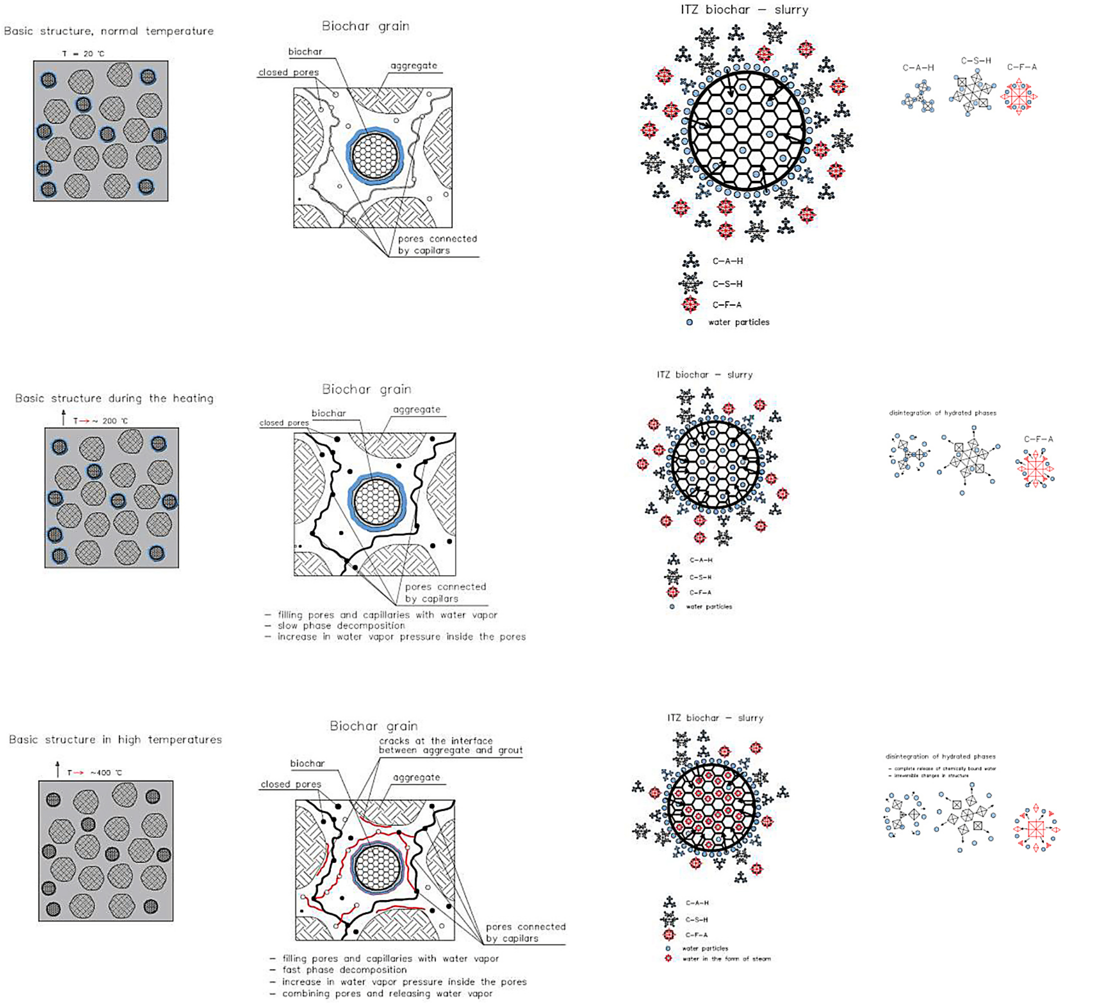

Figure 3. Schematic diagram of changes occurring in the tested composite during high temperature roasting

the samples. Their arrangement largely depends on the course of cement hydration and the w/c ratio. The presence of biochar introduces new elements into such an ordered, albeit heterogeneous, structure. In cross-section, biochar grains have a very pronounced tubular structure, resembling a honeycomb arrangement [40, 42]. The presence of reactive forms of carbon and the specific structure of biochar promotes the accumulation of more water molecules within it. Therefore, the formation of the biochar-slurry transition phase may be facilitated due to the higher affinity of the phases containing calcium, silicon, aluminum and iron oxides contained in the cement to the zones where hydration can proceed quicker and more smoothly. Part of the water can also infiltrate into the biochar grains via diffusion. An increase in temperature initially leads to typical changes in cementitious composites.

Water in liquid or chemically bound form begins to transition to a gaseous state due to thermodynamic changes. Water vapor begins to fill pores and capillaries, in which pressure increases. Eventually, as the system seeks a certain equilibrium state, the water vapor seeks escape routes from the composite. The rate of change occurring depends on the rate of temperature rise. In concretes, when the temperature rise is rapid, the water vapor leaving the material can lead to dynamic spellings and degradation of the outer layer of the concrete [47, 48, 49]. In the tested mortar, the temperature rise was uniform, which prevented violent phenomena from occurring. Nevertheless, reaching a temperature of 400 °C caused a number of specific changes. Part of the water contained in pores and capillaries and chemically bound was released and permanently left the material. Biochar, due to its properties, may have contributed to a more favorable and less degrading process of disruption of the internal structure of the mortar. Some of the water, as a result of its natural retention around the biochar, may have retained its liquid form longer. Water vapor, which in a composite without carbon additives would have caused a significant increase in pressure inside the material, had a much easier path of escape from the material through the channels in the biochar. In this way rapid destruction of samples due to rapid crack propagation was avoided. The material does not crack so dynamically cracks do not appear suddenly and are not so wide. Their range is also significantly reduced. It is not possible to completely eliminate the cracking process, which results from the specific

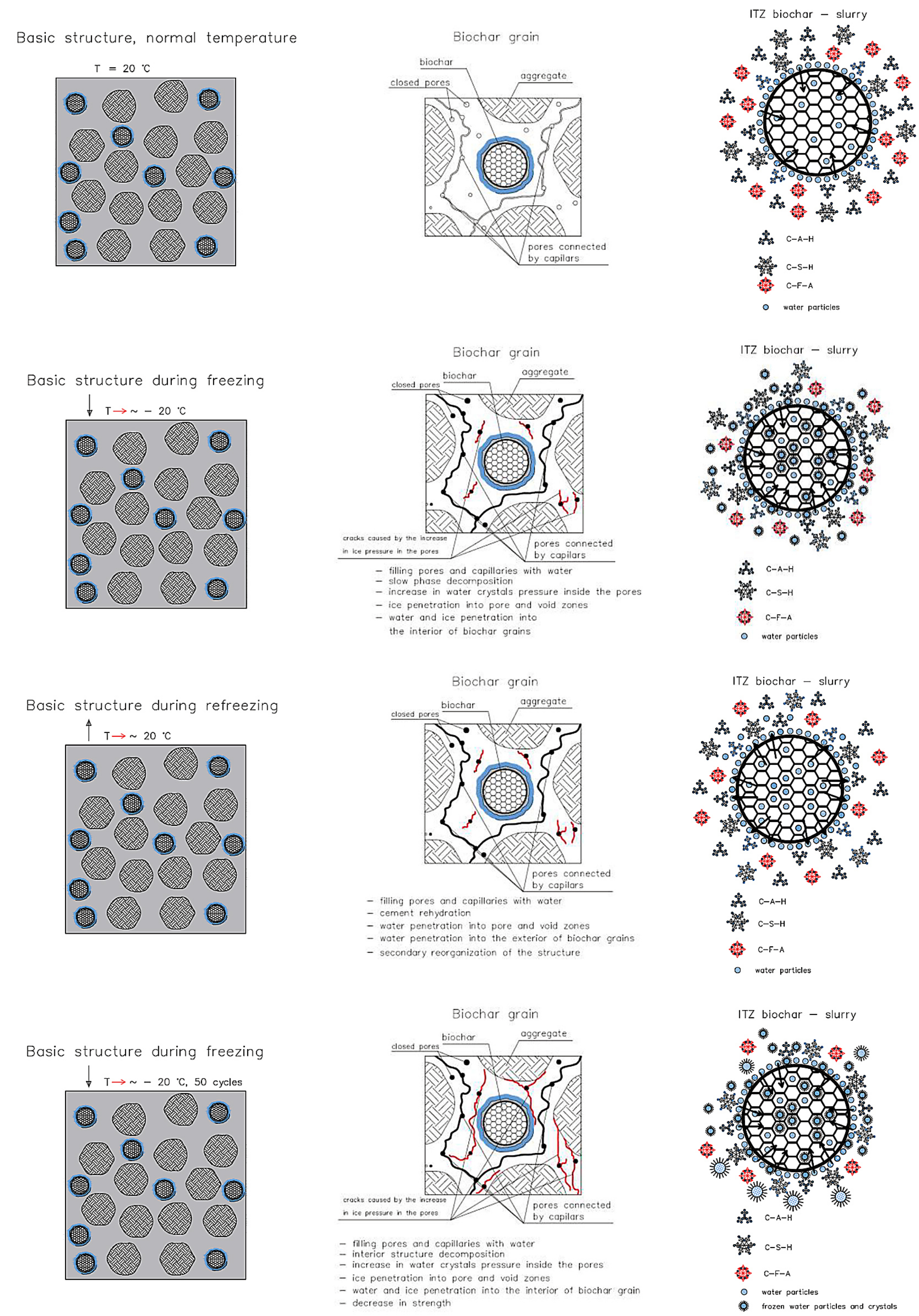

Figure 4. Behavior of the tested composite and its structure during freezing-thawing cycles

structure of the material, but it is possible to reduce this process by adding biochar.In this way, the rapid destruction of the samples was avoided.

Nevertheless, certain processes had to take place with the increase in temperature, namely the decomposition of cement hydration products [48, 50]. While biochar can retain some water in the material or facilitate its release in the form of water vapor, it is not an additive that allows preventing the very negative effects of high temperature on the material. Hence, the declines in strength values associated with the decomposition of cement slurry components. It should also be considered that the contact zone between grout and biochar is more resistant to degradation than the same zone between grout and aggregate. This is because quartz aggregate, which contains a high silicon content, heats up much faster, and thus the C-S-H and C-A-H phases in the aggregate contact zone are destroyed [46].

Mortar behavior during freeze-thaw cycles

As in the case of sample roasting, it is also possible to analyze the structure of composites with the addition of biochar (Figure 4).

In an intact structural arrangement, biochar grains are distributed between aggregate grains in the cement slurry. The contact zone between the biochar and aggregate, due to the elevated water content, promotes the accumulation of hydration products, C-S-H and C-A-H phases [8, 46]. Part of the accumulated water can, by diffusion, also pass into the interior of the biochar particles, making the additive a kind of regulator of the water content needed for the hydration reaction. The drop in temperature is associated with progressive changes in the structure of the mortar. The main reason corresponds to the issue of increasing ice volume (by about 9%) during freezing. The number of pores and capillaries also regulates the effect of freezing water. In the case of high porosity, the amount of space for freezing water in the voids also increases. However, ordinary mortars are not characterized by increased porosity. The distribution of pores, both closed and connected by a series of capillaries, is uniform. In this situation, the increasing volume of ice will lead to the slow expansion of pores, mainly through the formation of cracks. Initially, they are relatively small. The grout-aggregate and grout- biochar contact zones can be particularly sensitive to freezing. This is because ITZs are characterized by a more heterogeneous structure than in other grout zones. However, theoretically the most sensitive zones will be those in which the accumulation of water, as a result of hydration or other processes resulting precisely from the type of additive, will be significant.

The transition zone of grout – biochar is an example. However, owing to the specific properties of biochar, manifested primarily by its cellular structure, freezing may not be so unfavorable. The diffusive movement of water between the outer and inner zones of biochar leads to several phenomena. During freezing, some of the water can penetrate into the biochar [26, 27]. This happens as a result of the difference in water concentration at the wall boundary of the biochar molecule. Some of the water accumulated around the biochar will naturally freeze, causing partial disruption of the accumulated hydration products. Also, the chemically bound water in C-S-H and C-A-H crystals undergoes partial physical transformations, although the overall physicochemical situation must also be taken into account [51, 52]. Chemically bound water, as in the case of roasting conditions, undergoes physical transformations last. Water filling pores and capillaries and water accumulated in ITZs undergo them first.

The penetration of water into the biochar is not as unfavorable as the filling of pores in the grout. The volume of channels and pores in biochar is much larger, so even if water penetrates into the interior of the biochar grain and is transformed into ice there, it has enough space for the crystals to grow freely without adversely affecting the biochar itself. As a result, the process of creating cracks caused by water freezing is reduced. Their width and scope are not as significant as in the case of ordinary mortar without the addition of biochar. The ITZ zone itself between the grout and biochar through which the most intensive water movement takes place is also in a way protected by providing space for water to freeze inside the biochar grains. Therefore biochar should be considered an additive that effectively reduces the adverse effect of freezing on the structure of mortars prepared in this way. During thawing, the cycle reverses. The water contained in the ice returns to a liquid state, filling the cracks that form during freezing. Subsequent freezing cycles lead to degradation of the internal structure of the composite. The proportion of newly formed cracks increases, some of which are formed at the aggregate grain – slurry and slurry – biochar interface. The chemically bound water also freezes. This is because during successive cycles, the crystals that are products of cement hydration become less stable, relocate and become disturbed. Thus, the chemically bound water finds an easier way to leave the molecules of the grout phases and takes part in the physical transformations that water undergoes in pores and capillaries. In this situation, water can permanently leave the molecules of the phases due to movement inside the composite.

Relating the phenomena that occurred to the recorded changes in strength, one can see a clear influence of biochar, however, it is strictly dependent on the amount of biochar in the composite. In the BIO S0 series, one can see a proportional trend in the decrease in both flexural and compressive strengths with an increase in the number of freeze-thaw cycles. All other series showed a deviation from this trend, but it is difficult to find some proportion of these changes in relation to the amount of biochar. The BIO S1 series showed a relatively immediate, steady decrease in compressive strength, which did not change with the number of cycles. Flexural strength, despite a significant decrease after 50 cycles, finally increased again after 150 cycles. This already gave some insight into the phenomena taking place in the composite. During thawing, in each successive cycle, the water released from the biochar grains took part in re-strengthening the structure of the mortar. The authors made the assumption of so-called "secondary hydration", as mentioned earlier. Increasing the amount of biochar to 3% (BIO S3 series) significantly contributed to some stabilization of these processes. On the other hand, the amount of biochar 5% (BIO S5 series) even made some kind of anomaly, as evidenced by the temporary increase in flexural strength after 25 cycles. As for compressive strength, this parameter behaved similarly to the BIO S1 series.

To sum up, biochar significantly regulates the effect of freezing and thawing on the state of the mortar. Admittedly, it is not able to strengthen the composite explicitly, as an additive. This is because biochar itself is more of an additive that affects the physicochemical processes in the mortar, and regulates the movement of water in the samples. However, the effect on regulating water movement in the composite may mitigate the negative effects of freezing-thawing cycles. The presence of biochar helps provide physical space for the growth of ice crystals and the accumulation of water, which is involved in the hydration of cement phases during thawing. These processes are not as intense as in the case of hydration during mortar maturation from the moment the samples are formed. Thus, pores and capillaries are also not formed dynamically and there is no risk of significant chemical shrinkage.

CONCLUSIONS

The conducted research allowed drawing the following conclusions:

- the subject of the study was biochar derived from the pyrolysis of forest biomass as a component of mortars with aluminous-lime cement,
- undoubtedly, biochar has an impact on the structural changes of the composites studied, due to its ability to affect the transport of water inside the microstructure of the mortar biochar as an additive offsets the adverse effects of both high and low temperatures,
- the picture of frost damage at higher biochar content is curious: fibrous particles of biochar, which are not damaged by frost, combine with microcracks in the sample,
- by influencing the transport of water inside the mortar, biochar regulates the process of crack formation, reduces their destructive effect and delays the complete destruction of the sample,
- the addition of biochar is not able to completely inhibit the process of crack formation; The authors consider the option of combining biochar with dispersed reinforcement in the form of fibers as a further reinforcement of the composite.

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