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SCIENTIFIC PAPER

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RESISTANCE TO FROST ACTION AND MICROBIOLOGICAL CORROSION OF NOVEL CERAMIC COMPOSITES

Article Highlights

- The incorporation of fly ash in producing more sustainable ceramic products
- Prediction of frost action mechanisms on ceramic compacts and biocorrosion resistance
- Utilization of fly ash in ceramic composites without significant deteriorating effect

Abstract

This work illustrates the prediction of frost action mechanisms on ceramic compacts and their biocorrosion resistance to fungus action. The ceramic compacts were produced from two raw materials: coal fly ash (40 wt.%) and clay material (60 wt.%). The ceramics models were made in laboratory conditions by pressing (P = 45 MPa), drying (105 °C, 3h), and sintering (1100 °C, 1 h; heating rates 3 °C/min and 10 °C/min.). The mechanisms responsible for the deterioration of the designed ceramic compacts were defined based on the values of the total porosity, pore size distribution, pore critical radius, and the Maage factor, as well as on the values of water permeability. The biocorrosion process was investigated using Aspergillus niger fungus as a model microorganism. The different degrees of fungus colonization on the designed compacts were comparatively analyzed based on the Scanning Electron Microscopy investigation results. The gained results are encouraging as they show that the utilization of fly ash (40 wt.%) in ceramic composites is possible without significant deterioration of their durability (frost action and microbiological corrosion resistance) compared with the ones whose production was based only on clay material.

Keywords: waste treatment, fly ash, ceramic, weathering, pore size distribution, thermal analysis.

One type of waste material with a high potential for the production of ceramic materials is fly ash, a by-product of coal combustion in thermal power plants [1]. As a waste material, fly ash is often stored in landfills, presenting a major source of environmental pollution in the form of dust and toxic substances, such as heavy metals and sulphur compounds. However, the ashes mostly contain particles with dimensions of (50–100) μm; therefore, no extra milling is needed. The application of fly ashes as industrial wastes from coal combustion in thermal power plants, the cement industry, road base construction, and agriculture is well known [2, 3]. The potential use of this secondary raw material in the building and construction industry minimizes the ecological footprint of this sector. In addition, it reduces the pressure on using primary raw materials such as clay materials, quartz sand, and carbonates. It contributes to the transition towards a more resource-efficient and sustainable world.

The growing interest in environmental protection shows an increasing need to utilize fly ash in producing new materials and for other reuses [4, 5]. Due to envi-

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ronmental issues, price volatility, supply chain, and pressure on valuable resources have compelled companies to look for alternative and sustainable materials and energy supplies. According to the Ellen MacArthur Foundation, "a circular economy is restorative and regenerative by design and aims to keep products, components, and materials at their highest utility and value at all times, distinguishing between technical and biological cycles" [6].

Many studies have been published regarding the benefits of fly ash as a component of the raw material composition in the production of ceramic composites [7–9]. Still, the frost and microbiological resistance of the composite ceramic materials based on fly ash have not met with the same interest and attention.

Weathering is a group of processes that leads to the decay or degradation of materials upon their exposure to surrounding environmental conditions [10]. The most dominant factors regarding the environmental damage of buildings, more precisely those with ceramic materials as their constitutive parts, are moisture, atmospheric pollution, and the presence of soluble salts and microorganisms. Even the most durable materials could be modified and ruined due to the deposition of dust and, consequently, the action of microorganisms, such as cyanobacteria, fungi, and algae [11]. It is well known that the textural properties, especially the pore size distribution and the values of the total porosity, and the mechanical properties of ceramic materials are of great interest for application in real environmental conditions [12].

In many ceramic applications, there is a growing need to predict the service life of the products based on laboratory tests. Many scientists and science groups have been working on analyzing the factors that influence ceramic materials' weathering and developing models to predict the aging of ceramic building materials (frost resistance and biocorrosion). Maage [13,14], Franke and Bentrup [15], Koroth *et al.* [16], Robinson [17], and Vincenzini [18] elaborated different models which refer to technological properties: water absorption in different outdoor conditions or textural properties (total porosity, size and specific surface of pores). They gave modeling equations based on which the frost resistance of materials could be predicted.

Porous ceramic materials in their structure always contain some quantity of moisture, i.e., of physically bound water. The presence of this water directly affects the physical-mechanical properties of ceramic materials, such as strength, shrinkage/expansion, water vapor transmission, and resistance to external conditions (resistance to frost action, soluble salts, and microorganisms). The capacity of materials to accumulate moisture within the porous system is one of the basic parameters that influence their durability and use as building materials. Namely, the existing stress in the material, when the temperature falls below 0 °C, is generated during the conversion of water into ice, leading to the formation of micro-cracks whose extent can overcome the mechanical resistance of the material, later promote inevitable damages. The material's compressive strength is directly related to textural properties and indirectly related to the frost resistance of materials [19].

The knowledge about the development and action of the defined frost action mechanism (closed container, hydraulic pressure, and micro ice lens mechanism) gives the possibility to predict the durability of building materials during the frost action.

The mechanism of a closed container [20] can be simply explained if the ceramic materials can be considered as closed system from which no water enters or leaves. In such a case, the mechanism of destruction caused by the increase of the ice volume becomes dominant due to the phase transformation of the water-ice, which is accompanied by an increase of the volume by 9%. Also, the physical size of the representative samples for this mechanism should be so small that the influence of the temperature gradient to destroy the samples can be neglected. The water saturation and the lack of air-filled pores determine the presence of this mechanism. When a porous network is partly saturated, some porosity remains occupied by air, and ice can extrude toward these trapped air gaps without creating any pressure on the porous medium. This paper determines the susceptibility to this mechanism by the number of pores with a radius smaller than 0.1 µm. With water suction availability, these pores are responsible for high water saturation causing larger expansion.

The mechanism of hydraulic pressure [20] appears when the temperature gradient cannot be neglected, as in the case of a rapid temperature drop. According to this mechanism, ice is initially formed on the surface of the samples, where the temperature is the lowest. Then, the water that does not freeze in the pores with a small radius is pressed over time under hydraulic pressure and moves through the capillary and gel pores, partially filled with ice, in the bulk of the sample. The response of the samples to this mechanism depends on the rate of ice formation (determined by the rate of freezing, total porosity, pore size distribution, and width of the pore size distribution), permeability, and the maximum distance that water has to pass until it reaches the air pore (both of which is determined by pore size distribution).

The ice-lens mechanism [20] occurs when there is a lower freezing rate and a longer freezing period. As a result, a balance between frozen and unfrozen water is established in larger and smaller pores, respectively. As a result of this mechanism, non-frozen water has more free energy than ice and moves through a pore system to the ice crystals participating in their growth. As a result, the ice, shaped like a lens (hence the name of the mechanism), grows and can cause pressure on the walls of the pores and lead to the deterioration of the material.

Although frost damage is mostly a physical process, the action of microorganisms (biocorrosion) implies several physical and chemical changes in the material caused by their metabolic activity. Physical degradation is caused by penetration, pressure, and dimensional growth of biological structures within materials. In contrast, chemical degradation is brought by the excretion of metabolic intermediates or the end products of metabolism that could have hindering or very aggressive roles. Apart from these causes, chemical degradation can also be a consequence of the process of assimilation, when microorganisms, using a mediator (water), use the material as food and energy source for enzymatic activities or ionic transfer [24].

The biocorrosion phenomenon of ceramic building materials causes structural, esthetical, and economic issues, and it strongly influences the final products' chemical and physical properties, functionality, and durability. All the mentioned facts present a good basis for research dedicated to biocorrosion resistance and the application of ceramic products in real environmental conditions [22]. Colonizing roofing tiles by organisms is progressive, heterogeneous, and slow. On the other hand, laboratory assessment of this phenomenon requires a procedure that could be conducted within a reasonable period of time. Bearing that the lichens are a major causative agent of bio-deterioration of ceramic materials, the fungus *Aspergillus niger* (*A. niger*), as a possible symbiotic partner for lichen formation, could be very useful for the laboratory colonization of the clay roofing tiles. *A. niger* fungus is the most common species of the genus *Aspergillus*, and it belongs to the saprotrophic fungi that live on inorganic substrates. This fungus is most commonly found in oxygen-rich environments where it grows on the surface of the substrate. Fungi usually grow on carbonate-rich substrates or in wet places (walls, bricks, tiles), but they can also grow in carbonate-deficient environments [23]. Water availability and physical properties, such as porosity, roughness, and substrate surface temperature, strongly impact microbiological growth. Still, no correlation has been found between the raw material characteristics and phototropic growth [24].

Considering that numerous studies have been published concerning the benefits of fly ash utilization in the production of ceramic composites and that frost resistance and microbiological corrosion have not received the same attention, our work aimed to examine the durability of composites based on fly ash and clay materials. For that purpose, was used the novel ceramic composite composed of 60 wt.% clay and 40 wt.% fly ash sintered at 1100 °C/1h, which was found as optimal in our previous work [25], where fly ash content and the sintering temperature varied from 10 wt.% to 90 wt.% and from 900 °C/1h to 1100 °C/1h, respectively. Bearing in mind all the mentioned facts, the experimental investigation presented in this work was performed by combining the exploitation capacity (resistance to freezing cycles and microbiological corrosion) and the characteristics of the novel ceramic product, i.e., its microstructural, textural, and physical-mechanical properties.

MATERIAL AND METHODS

It is a well-known fact that the mechanical properties of ceramics are very important in determining their application for any specific function. This property, together with the porosity of ceramics, is an important factor considering resistance to freezing temperatures. Bearing in mind this relationship, the idea of our work was to estimate the dominant deterioration mechanism regarding frost and biocorrosion actions of the novel ceramic composites, found as optimal in previous work [25], where a significant part of the clay material (40 wt.%) was replaced with fly ash. A detailed characterization of raw materials (clay and fly ash) and the porous final product was performed.

Material

The raw materials used for the performed investigation were: fly ash from the thermal power plant REK Bitola, Republic of North Macedonia, and clay material from a region near Bitola, Republic of North Macedonia. Production parameters of the novel ceramic composites, as well as of the ones prepared only from clay materials/fly ash, were the following: (1) fly ash content in the investigated composites was 40 wt.%; (2) particles size of the used raw materials (clay and fly ash) was less than 63 μm; (3) processing parameters: pressing parameter of the compacts was 45 MPa (uniaxial press, Weber Pressen KIP 100), and polyvinyl alcohol (PVA) was used as a plasticizer; the drying process was done in laboratory conditions at 105 °C for 3 h until the mass of the compacts was constant; (4) sintering process was performed in a laboratory electric furnace under the following conditions:

sintering temperature was 1100 °C for 1 h (air atmosphere) while the heating rates were 3 °C/min and 10 °C/min.

Six different systems were produced to investigate the influence of fly ash on the characteristics of ceramic composites: (1) the first system of novel ceramic composites (40 wt.% fly ash and 60 wt.% of clay) was sintered with the heating rate of 3 °C/min; (2) the second system was designed with the same raw materials, but sintered with the heating rate of 10 °C/min; (3) and (4) systems based only on the clay material sintered with two different heating rates of 3 °C/min and 10 °C/min; (5) and (6) systems based only on the fly ash material, sintered with two different heating rates of 3 °C/min and 10 °C/min.

Methods

The mineralogical composition of the raw materials, as well as of the novel ceramic composites, was determined by X-ray powder diffraction (XRD) analysis (model PW 1710, Philips, Germany) under the following experimental conditions: monochromatic CuKα radiation with λ=1.54178 Å wavelength in the 5–55° of 2θ range, scan rate 0.02°, 0.5 s per step.

The chemical composition of the raw materials was determined by an X-Ray Fluorescence Spectroscope, model ARL 9900XP, USA.

Water absorption of the sintered samples was determined from the difference between the total dry mass, mdry, and the surface dry mass, msur.dry, after their immersion in water (19 °C). The bulk density value was determined by the water displacement method according to EN-993. Finally, the total porosity of the samples was calculated from the results of the relative density values.

The mechanical properties, i.e., bending strength and E-modulus of the produced novel ceramic composite, are determined using a three-point bending tester (Netzsh 401/3, Germany) with a 30 mm span and a 0.5 mm/min loading rate. Furthermore, the compressive strength tests were carried out using an Instron testing machine (model 1126, Germany) with a crosshead speed of 0.5 mm/min.

The frost resistance investigation was conveyed through mercury (Hg) intrusion porosimetry: total porosity, pore size distribution, pore critical radius values, and Maage factor [26]. Hg porosimetry of the final compacts was conducted using an AutoPore IV 9500 device (Micromeritics, USA), with the possibility of achieving the pressure up to 33,000 psi (228 MPa), which enables measurement of pore radius ranging from 360 μm to 0.001 μm. In addition, the low-temperature nitrogen adsorption method (ASAP Micrometrics, US model 2000) was used to determine surface area, pore volume, the surface area of pores, and the percentage of pores smaller than 20 nm.

Low-temperature dilatation measurements were done using a Thermo Mechanical Analyzer (Model 981, Du Pont, USA) to simulate the relatively low-temperature behavior of the same ceramic composite's dried and water-saturated samples materials. These measurements were performed in the temperature interval of -40 °C up to +40 °C (thawing rate was 10 C/min). The desired low temperature (-40 °C) was achieved by holding the samples in liquid nitrogen for a defined time.

The microbiological corrosion was later artificially induced on the novel ceramic composite, which stood out as the most frost-resistant product. Finally, the biocorrosion process was performed in laboratory conditions using *A. niger* fungus. This approach was chosen based on: (1) our previous work dedicated to biocorrosion resistance of clay roofing tiles [27] and (2) the fact that the lichen, as a symbiotic life form of fungus and alga/cyanobacteria, is a major causative agent of bio-deterioration of ceramic materials [28].

The ceramic compacts were put in a sterile Petri dish. On the top surface of the ceramic models, a drop of the suspension (0.05 ml) of the *A. niger* fungus spore, with a concentration of 1.105 CFU/ml (Colony-forming units/milliliters), was added. Malt broth was used as a medium in which the spores were suspended. The specimens were submerged to a certain level in distilled water. The experiment was conducted over one month. The samples were sterilized in an autoclave with time, temperature, and pressure relation of 15 min, 121 °C, and 1.1 bar, respectively, then submerged to a certain level in distilled water to maintain humidity and exclude other environmental influences. The period of a month was chosen as long enough for the incubation of the fungus. This experiment was based on the fact that lichen is a symbiotic life form between a fungus and an alga or cyanobacteria, excreting organic acids while metabolizing the inorganic compounds of the ceramic system. The acidotic and complexing activity shown by the lichens was due to the fungal component of this symbiotic association. The degree of fungal colonization on the novel ceramic composite was comparatively analyzed with the colonization of the same fungus on the pure compacts of clay and fly ash using SEM (JEOL JSM-6460LV Scanning Electron Microscope). Before applying the spores, a number of incisions were made on the surface of the compacts, which were later used for breaking the compacts to perform SEM analysis of the cross-section to analyze the penetration of the fungus hyphae inside the compacts.

RESULTS AND DISCUSSION

Raw materials characterization

The raw materials were characterized in terms of their phase and chemical composition.

Phase composition

The XRD pattern of the fly ash (Figure 1) confirmed the presence of an amorphous phase and the following minerals: quartz, anorthite, hematite, albite, diopside, and anhydrite. In addition, the clay material used contained the following major mineral composition: quartz, feldspar, aragonite, chlorite, and calcite.

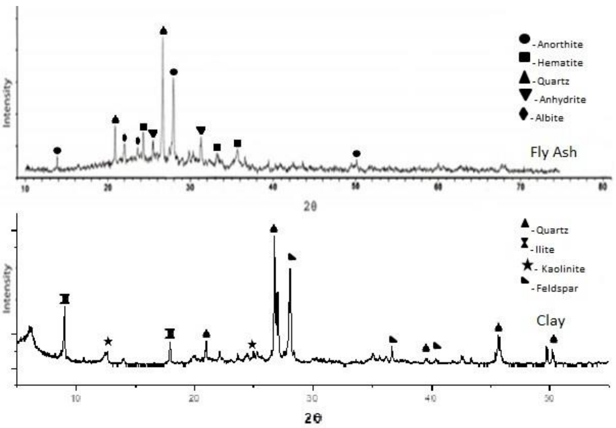

Figure 1. XRD profiles of raw materials.

Chemical composition and loss on ignition

The chemical composition (in terms of oxides) of the fly ash and the clay material is shown in Table 1. In both raw materials, there was a dominant presence of SiO_2, Al_2O_3, Fe_2O_3, and CaO. The fly ash, based on the content of SO_3, MnO, and P_2O_5, is an ecologically risky material, as already mentioned in the introduction part (pollution of surrounding areas in the form of dust and toxic substances, such as heavy metals and sulfur compounds). The identified loss on ignition (LOI) in the case of fly ash is related to the existence of unburned and partially burned coal particles.

Characterization of novel ceramic composite

XRD of novel ceramic composite

The phase composition of the novel ceramic composites, Fig. 2, based on fly ash and clay material, shows that the sintering process reduces the intensity of quartz and anhydrite peaks and promotes the formation of anorthite and diopside crystal phases. No significant differences exist in the phase composition of the samples sintered at the same sintering temperature (1100 °C) with different heating rates (3 °C/min vs. 10 °C/min). The relatively high content of CaO present in the fly ash and the clay material is the most likely reason for forming an anorthite crystal phase. Diopside [Ca(Mg,Al)(Si,Al)$_2$O$_6$], identified in the case of both

Table 1. Chemical composition of the fly ash and the clay material.

Oxide	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	MnO	P_2O_5	ZnO	PbO	SO_3	LOI	Σ
Fly ash	52.38	0.09	23.61	7.31	7.42	2.11	0.9	1.67	0.03	0.08	0.01	0.03	1.2	3.12	99.94
Clay	58.48		19.8	7.44	6.18	1.43	2.1	2.51						2.05	99.99

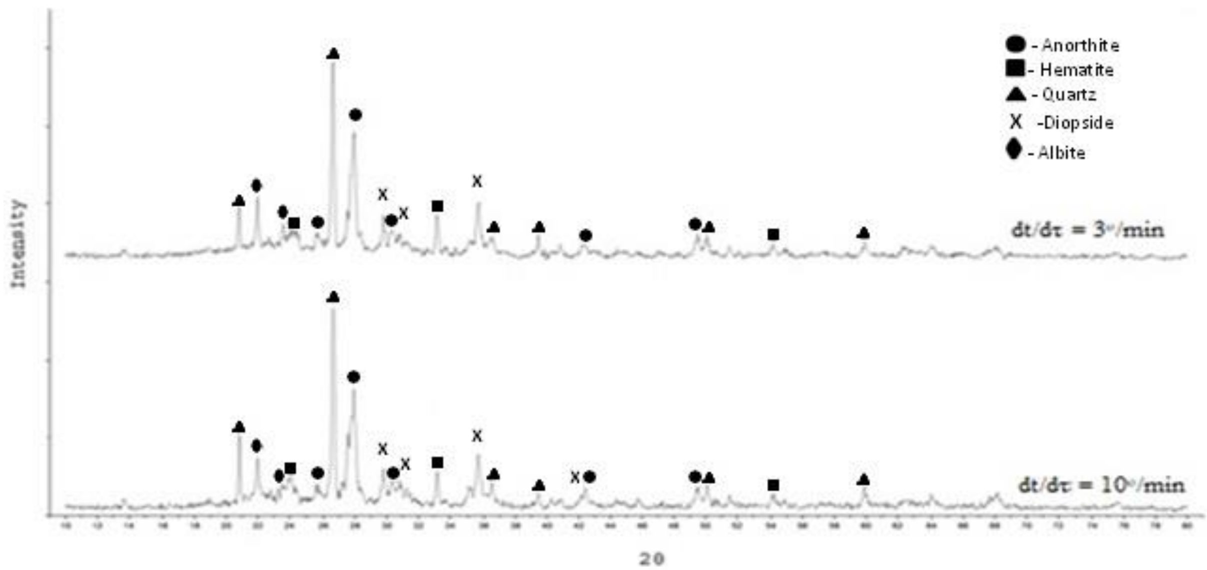

Figure 2. Diffractograms of novel ceramic composite.

systems, displays good resistance to frost action [29] due to the intercalation of its crystals. Therefore, the idea for future research is to encourage the formation of this crystalline phase.

Microstructural analysis

The SEM images of the novel ceramic composite sintered with different heating rates are given in Fig 3a (3 °C/min) and Fig 3b (10 °C/min). More closed micro pores and fewer larger pores were detected in the sample sintered with a heating rate of 10 °C/min. Therefore, this model seems to be more compact.

Physical and mechanical properties of the novel ceramic composites

It is well known that variations of physical and mechanical properties are related to sintering conditions used to obtain the desired microstructure of the samples. A dense microstructure is preferred when the produced composite is intended to resist weathering processes [30–32].

The physical and mechanical properties of the sintered models, Table 2, are a function of the sintering heating rate. The density value increased with the heating rate and vice-versa. On the other hand, a slight drop in the density value and increased porosity of the novel ceramic composite was noticed when the heating rate was reduced from 10°/min to 3°/min. These phenomena seemed to be caused by the expansion of the trapped gases during the sintering process.

According to the results in Table 2, the utilization of fly ash (40 wt.%) had a negative impact on mechanical properties and water absorption of the novel ceramic composite compared with the systems produced with 100 wt.% clay. Despite this, the values of the physical and mechanical properties of the novel composites were still solid enough for their potential application as bricks and tiles [33].

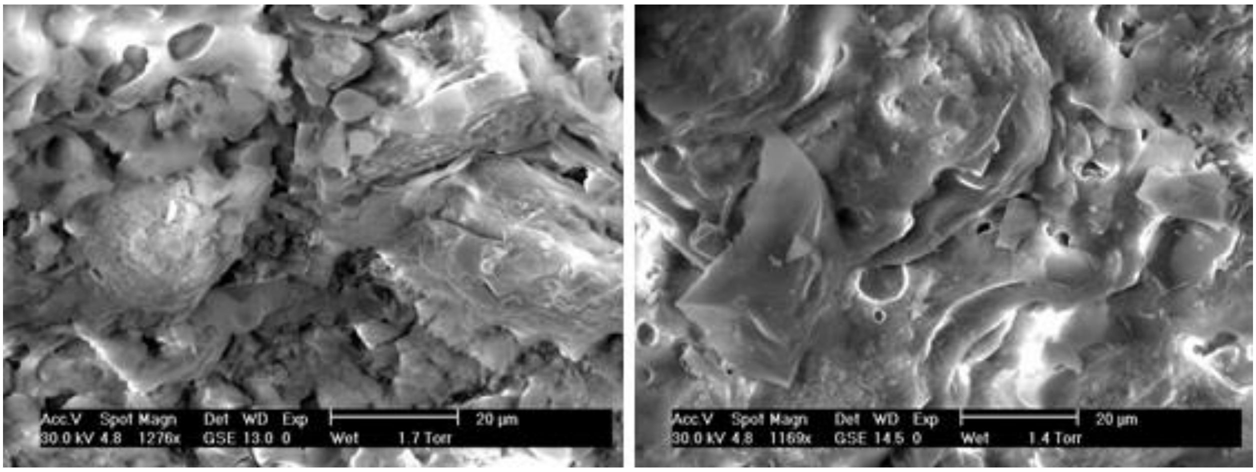

Figure 3. SEM photos of the novel ceramic composites.

Table 2. Physical and mechanical properties of the ceramic composites.

Composite	Heating rate, °C/min	Density, g/cm^3	Water porosity under the vacuum, %	Water absorption, %	Compressive strength, MPa	Bending strength, MPa	E-modulus, GPa
Novel ceramic composites	3	2.009	18.91	9.93	85.47	44.09	21.65
	10	2.089	15.70	7.02	100.01	50.47	25.35
100 % fly ash	3	1.41	38.13	25.45	10.38	11.92	5.88
	10	1.44	36.82	23.77	21.24	14.01	7.22
100 % clay	3	2.45	6.25	3.15	240.00	80.02	31.23
	10	2.47	5.43	0.34	285.00	90.00	34.12

Textural characterization

Hg porosimetry values

Based on the values of Hg porosimetry measurements, Figures 4 and Table 3, it is evident that the values of pore size distribution were significantly affected by the sintering heating rate. The samples sintered with the heating rate of 10 °/min have a broader range of pore-size distribution, Figure 4.

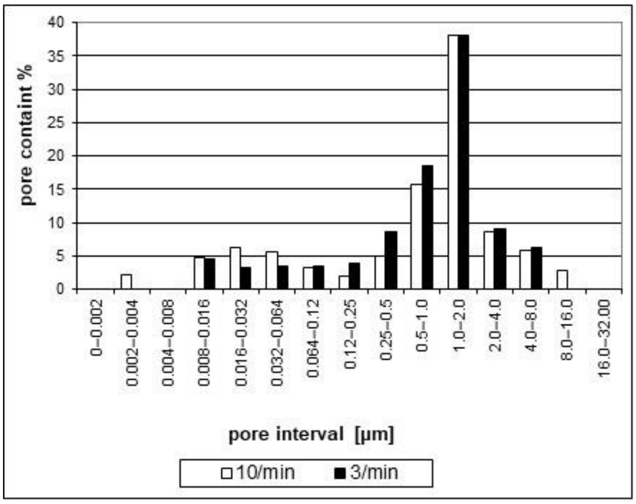

Figure 4. Pore size distribution of the composites based on fly ash and clay material sintered with respective heating rates.

The average total porosity determined by the mercury intrusion technique, Table 3, differs from the values of the total porosity measured by water absorption under vacuum. It is due to the difference between the two techniques covering different pore size intervals. Nevertheless, the total porosity was increased in both cases by lowering the heating rate from 10 °C /min to 3 °C /min.

The results of Hg porosimetry and the microstructural characteristics were used as parameters for predicting the ceramic models' frost action durability and determining the dominant frost action mechanisms [30–32]. The main parameters for this type of prediction are presented in Table 3.

The samples sintered at a lower heating rate (3 °C/min) showed different microstructural and textural properties than those sintered at (10 °C /min). It is the consequence of the microstructural heterogeneity of the green compacts, more precisely, due to the mixture of two different mineralogical raw materials. The heating rate of 3 °C/min influenced the reduction of the quantity of smaller pores (r<0.1 µm) and consequently caused the increase of the quantity of larger pores (r>3 µm), Table 3. The obtained textural and microstructure features, with a significant quantity of glass phase (Figure 3), positively influenced the resistance of the products to freezing temperatures (Magee factor is 82.45) but negatively affected the mechanical characteristics (Compressive strength values), Table 2.

Table 3. Total porosity, pore size fractions, dominant pore interval, scatter coefficient, Critical pore radius, Maage factor.

Heating rate, °C/min	Total porosity vol, %	Pore size fraction (r<0,1 µm) vol, %	Pore size fraction (r>3 µm vol, %	Dominant pore interval, µm	Scatter coefficient Cd	Critical pore radius, µm	Maage factor
3	17.29	10.4	23.55	1–2	1.28	2.83	82.45
10	10.51	16.1	17.8	1–2	1.62	3.42	58.5

As the composites, sintered at a heating rate of 10 °C/min, had a higher fraction of capillary pores (the number of pores with radius < 0.1 µm), it is evident that the closed container mechanism was adequate for this type of product.

The value of the scatter coefficient (Cd parameter) for the ceramic models sintered at 3 °C/min was smaller than that for the ceramics sintered at 10 °C/min. It means that a narrower pore size distribution and, consequently, greater sensitivity of the products to the hydraulic pressure mechanism was obtained for the models sintered with a lower heating rate (3 °C/min).

In terms of critical pore radius, the novel ceramics sintered with 10 °C/min had a larger critical pore radius value, which means that this system should have greater permeability and a lower possibility of the hydraulic pressure mechanism to be anticipated as the dominant mechanism of deterioration. This conclusion correlates well with the prediction of frost resistance based on the scatter coefficient, Table 3.

The volume (%) of pores larger than 3 µm signifies the existence of air-filled parts in the ceramic systems. Namely, these pores are large enough to facilitate the passage of water from smaller to larger pores without affecting disruptive pressures and positively influencing the Maage criteria. Therefore, in accordance with the Maage factor, the composite ceramics sintered at 3 °C /min are more frost resistant than the ones sintered at 10 °C /min.

Results of low-temperature nitrogen adsorption

The distribution of the pores smaller than 150 nm in diameter for both ceramic products is presented in Figure 5, while in Table 4, the following values are presented: specific surface area of the materials and the pores; specific pore volume; average pore diameter and percentage of the pores smaller than 20 nm in diameter.

The samples sintered with 10 °C /min had a smaller average diameter and a greater fraction of the

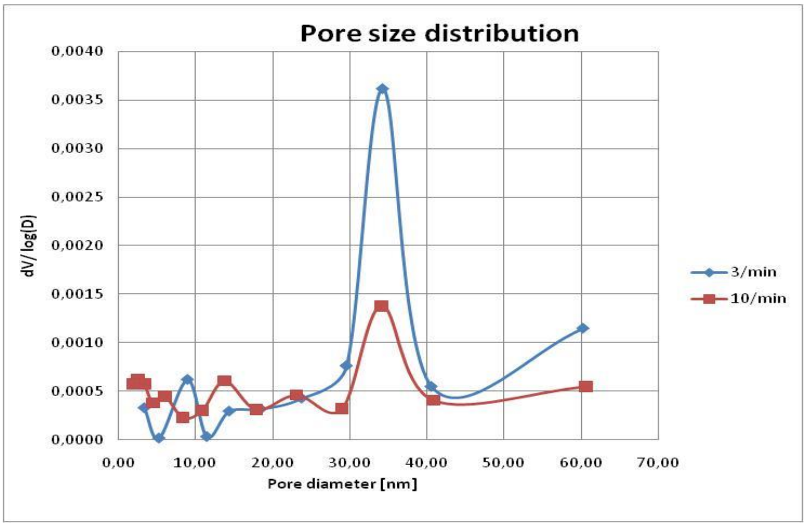

Figure 5. Pore size distribution.

Table 4. Values of the specific surface area of the materials and the pores, specific pore volume, average pore diameter, and percentage of pores smaller than 20 nm.

Heating rate, °C/min	Specific surface area of the material, m^2/g	Specific pore volume, cm^3/g	Specific surface area of pores, m^2/g	Average pore diameter, mm 10^3	Percentage of pores < 20 nm
3	1.2352	0.000694	0.1492	18.6035	20.5
10	0.9142	0.000784	0.4946	6.3439	61.6

pores < 20 nm. These results predict that the novel ceramic composites sintered with 10 °C /min will likely be more sensitive to the ice lens mechanism.

The results of the determination of frost action susceptibility to different frost action mechanisms are comparatively presented in Table 5.

Table 5 shows that the ceramic models sintered with 10 °C /min are more sensitive to the closed container mechanism and ice lens mechanism but less sensitive to the action of the hydraulic pressure mechanism.

Table 5. Summary of the dominant frost action mechanism.

Sample	Mechanism of the closed container, (ratio of pores r < 0,1 µm)	Mechanism of hydraulic pressure		Mechanism of ice lens, (percentage of pores < 20 nm)
		Rate of ice formation, Cd parameter	Permeability	
10	1	2	2	1
3	2	1	1	2

[1] Very sensitive to the specific mechanism; [2] less sensitive to the specific mechanism.

Low-temperature dilatation measurements

As the results of similar linear thermal expansion of both samples (in the temperature area 0°C to -40 °C), Figure 6 shows no major differences in the dilatation values between the dry and water-saturated samples. Therefore, based on these results, all models could be considered resistant to the action of the hydraulic pressure mechanism.

Pore structure (values of critical pore radius) and especially the scattering coefficient values showed that the models sintered with the heating rate of 10 °C /min are the most resistant to the hydraulic pressure mechanism. Furthermore, their compressive and flexural strength values, Table 2, correlate well with this estimation.

Biocorrosion resistance

The novel ceramic composites sintered with a heating rate of 10 °C /min had better stability to hydraulic pressure, which is known as the more common destruction mechanism in the case of ceramic materials [26]. Based on this fact, further investigations considering biocorrosion resistance were dedicated to this type of model sample. The obtained results were compared to the results of the products based only on

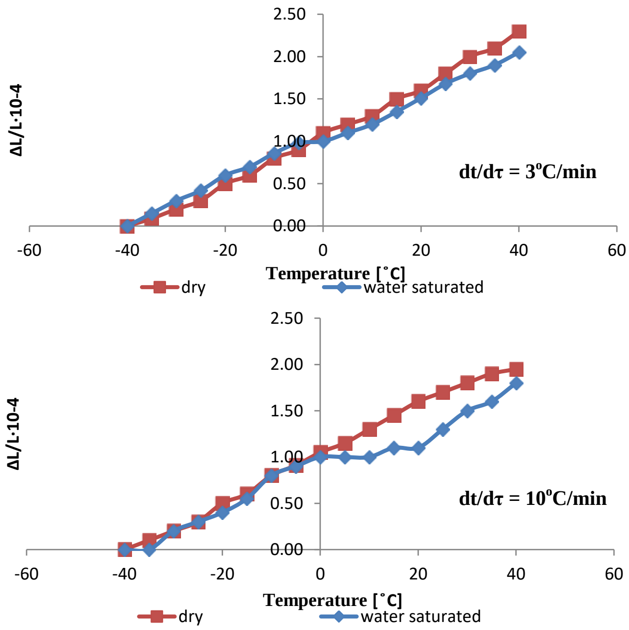

Figure 6. Low-temperature dilatation values of the composites.

the clay material/fly ash (heating rate 10 °C/min). The SEM micrographs in Figure 7 illustrate the results of the biocorrosion investigation.

The SEM micrographs show that the hyphae were present on the product's surface composed only from the clay material, Figure 7a. In contrast, the complete fungi formation was identified in the product fully designed based on fly ash, Figure 7 b. There is no sharply defined border between the outer surface and inner section, Figure 7 b, i.e., due to the high porosity of the compact, hyphae penetrate a part of the inside of the compact. In the case of the composite material, Figure 7 c and d, a very similar situation is observed as in the case of the product based only on the clay. The fungal growth on the sample surface is evident, but the beginning of the hyphae penetration into the ceramic composite structure was also noticed. It could be explained based on the fact that the colonization process of *A. niger* fungus goes through two stages [24]. In the primary stage, the colonization process is highly related to the capacity of microorganisms to attach themselves to the surfaces of the ceramic materials, while in the second phase, the textural properties are the key factors for their development [21]. Evidently, all three systems had the same surface affinity for the microorganisms, but the second stage of colonization differs as their textural properties differ. Based on the results shown in Table 2, it is evident that the changes in the values of the water absorption (indirectly, of the porosity value) from 0.34% (clay material) to 7.02% (novel composite material) and the changes from 23.77% (fly ash) to 7.02% (novel composite material), influenced the fungi growth and penetration differently. The penetration of the fungi is in good correlation with the decrease of the water absorption value. This value is more important for fungal growth and penetration than the raw material characteristics [21]. Moreover, in the case of novel products, chemical degradation and the presence of new mineralogical forms, due to the action of *A. niger*, were not observed. It is a positive result for further application of novel ceramic composites as building materials in real conditions.

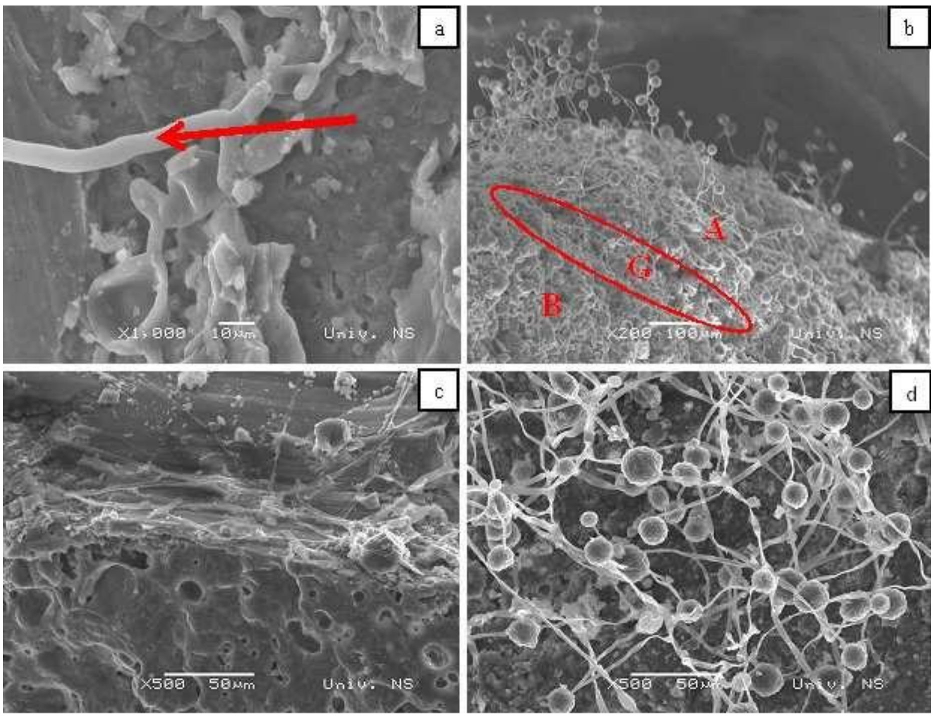

Figure 7. SEM micrographs of the final product prepared only with clay (a), fly ash (b), and the novel composite material (c and d).

CONCLUSION

The results of low-temperature dilatation confirmed satisfactory thermal stability of the formed ceramic composites (produced with different heating rates). Novel ceramic composites sintered with a heating rate of 10 °C/min, based on the results of textural properties, were more sensitive to the frost mechanisms of closed containers and ice lenses but less sensitive to the action of the mechanism of hydraulic pressure. Besides good durability regarding frost resistance properties, the simulation of biocorrosion deterioration (fungal action) initiated only aesthetic changes in the surfaces of the novel ceramic composites without chemical degradation. The results of durability investigations are encouraging, showing that the utilization of fly ash (40 wt.%) in ceramic composites is possible without the significant deteriorating effect of their resistance to frost action and microbiological corrosion action, compared with the ones produced only from clay material. Bearing in mind the high consumption of fly ash in the designed ceramic compacts (40 wt.%) and promising results regarding the resistance of the novel products in aggressive outdoor environments, the potential use of fly ash will reduce the environmental burden due to the accumulation of waste and will enable the production of more sustainable ceramic products.

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NAUČNI RAD

OTPORNOST NA DEJSTVO MRAZA I MIKROBIOLOŠKU KOROZIJU NOVIH KERAMIČKIH KOMPOZITA

U radu je prikazano predviđanje mehanizama delovanja mraza na keramičkim kompozitima, kao i analiza njihove otpornosti na biokoroziju dejstvom gljiva. Keramički kompoziti su proizvedeni od dve sirovine: lebdećeg pepela (40 mas. %) i glinenog materijala (60 mas. %). Ovi kompoziti pripremljeni su u laboratorijskim uslovima presovanjem (P = 45 MPa), sušenjem (105 °C, 3h) i sinterovanjem (1100 °C, 1h; brzine zagrevanja 3 °C/min i 10 °C/min). Mehanizmi propadanja projektovanih keramičkih kompozita definisani su na osnovu vrednosti ukupne poroznosti, raspodele veličine pora, kritičnog radijusa pora i faktora Maage, kao i vrednosti vodopropusnosti. Proces biokorozije je ispitan korišćenjem gljive Aspergillus niger kao modelnog mikroorganizma. Različiti stepeni kolonizacije upotrebnjenog mikroorganizma na dizajniranim kompozitima su uporedno analizirani na osnovu rezultata ispitivanja skenirajuće elektronske mikroskopije (SEM analiza). Rezultati dobijeni u ovom radu pokazuju da je upotreba lebdećeg pepela (40 mas. %) u keramičkim kompozitima moguća bez značajnog pogoršanja njihove trajnosti (dejstvo na mraz i mikrobiološka otpornost) u poređenju sa onima čija se proizvodnja zasniva samo na glini.

Ključne reči: tretman otpada, pepeo, keramika, starenje materijala, raspodela veličine pora, termička analiza.