

# é p í t ő a n y a g

A Szilikátipari Tudományos Egyesület lapja

Journal of Silicate Based and Composite Materials

## A TARTALOMBÓL:

- Fresh and hardened properties of self-compacting repair mortar made with a new reduced carbon blended cement
- Preparation of particle-reinforced mullite composite ceramic materials using kaolin and IG-017 bio-origin additives
- The influence of composition, microstructure and firing temperature on the density, porosity, and shrinkage of new zeolite-alumina composite material
- Composite materials based on zeolite-montmorillonite rocks and aluminosilicate wastes
- Clay- and zeolite-based biogeo sorbents: modelling and properties
- Possibilities for reducing the permeability of normal and lightweight aggregate concrete



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# Fresh and hardened properties of self-compacting repair mortar made with a new reduced carbon blended cement

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## Abstract

The present work investigates the effects of the use of waste brick as fine additive material (FAM) by partial replacement to the Ordinary Portland Cement (OPC) on the fresh and hardened properties of self-compacting repair mortar (SCRM) in order to produce a new reduced carbon blended cement. Waste brick which was available in a brick factory, was finely ground to obtain waste brick powder (WBP) before being incorporated in SCRM at substitution levels of 5%, 15% and 25%. SCM was tested at fresh state with mini slump flow and mini V-funnel flow time. At hardened state, compressive and flexural strengths and ultrasonic pulse velocity (UPV) were measured. The results indicated that the particles size of WBP is coarser compared to the OPC. The use of WBP decreased the slump flow and increased in the same time the flow time. Including WBP in SCRM decreased not only the compressive and flexural strengths but also the UPV of SCM. WBP can be suitably used at replacement rate of 5 or 15% to produce a new reduced carbon blended cement. From environmental point of view, introducing WBP has a positive impact in decreasing the amount of CO<sub>2</sub> released from cement plants into the atmosphere. Good correlations were found between strength and substitution levels of WBP.

Keywords: Self-compacting repair mortar, waste brick powder, substitution, blended, strength, environment

Kulcsszavak: öntömörödő javító habarcs, téglapor, helyettesítés, kevert, szilárdság, környezet

## 1. Introduction

Self-compacting mortar (SCM) is highly fluid mortar that can flow and fill all formwork under its own weight.

The self-compactability property allows using SCM as a repair material for reparation and rehabilitation of damaged reinforced concrete in congested area or with complicated shape. For ensuring the self-compactability of SCRM, two parameters must be taken into consideration: the use of superplasticizer (SP) and the incorporation cement and FAM with high volume [1]. As it known, SP reduces the water/cement ratio and provides more fluidity in the mixture and leads to higher compressive strength. The incorporation of FAM plays an important role in ensuring the resistance to segregation and bleeding. Without the use of FAM, self-compacting concrete (SCC) or mortar need a high content of OPC, and this can lead to many problems such as the increase in the cost production, the high consumption of energy and natural resources and high amount of CO<sub>2</sub> emitted into the atmosphere.

As concrete is the most widely used building material with amount of 12 billion tons per year, which corresponds to a consumption of 1 m<sup>3</sup> / person / year [2-3]. Its manufacture uses a binding material which is most often Portland cement. It is well known that the production of cement is very expensive in terms of economics, and polluting in terms of environment impacts. Moreover, the quantity of cement produced globally is growing remarkably, it was estimated at 3.6 trillion tons in 2011 and will rise to 5.8 trillion tons in 2050, which will increase the

CO<sub>2</sub> emissions from 3.24 trillion tons to 5.22 trillion tons (1 kg of cement produced emits 0.9 kg CO<sub>2</sub>) [4-5]. It is noted that the cement industry sector is responsible for 5% to 8% the global amount of CO<sub>2</sub> emitted into the atmosphere [6]. The most effective solution is to reduce the amount of clinker produced by replacing it with FAM having similar properties to clinker. Blast furnace slag, fly ash, silica fume, natural pozzolana, limestone fillers are the additive materials most used in the cement industry. The use of FAM have shown a great interest in the latest years from the industrial and constructor in reason of their technical, economical and environmental advantages impact. Pastes, mortars and concretes incorporating FAM showed better properties such as the low rate of hydration, low permeability, low consumption of Portland cement and low-impact environmental materials related to the low emissions of CO<sub>2</sub> [7-9]. Slag, fly ash, silica fume, limestone are the most used FAM in the world. Another source of FAM is the calcined clays such as metakaolin, brick powder or bentonite. It is known that these calcined clays were obtained by calcination or thermal treatment of kaolin, brick clay or bentonite, respectively [10-11]. Calcined clays are considered as pozzolanic materials and have a positive effect especially on mechanical and durability properties of concrete. FAM from agriculture waste such as rice husk ash (RHA) and sugarcane bagasse ash were successfully used in the production of SCC [12-14]. The characteristics of concretes and mortars are strongly influenced by the type, source, chemical, mineralogical, physical and mechanical properties of FAM [15-20]. Many researches papers that studied the possible use of



FAM to prepare mortar or concrete for rehabilitation and repair of reinforced concrete structures were published in the recent days [21-25]. Benabed et al. [21] were investigated the effect of limestone powder as a partial replacement of crushed quarry sand on properties of self-compacting repair mortars. They concluded that the use of limestone powder in repair mortar and concrete application would offer technical, economical and environmental advantages for concrete producers.

The main objective of this work is to investigate the effects of waste brick powder as substitute of the Ordinary Portland cement on the fresh and hardened properties of self-compacting repair mortar in order to produce a new reduced carbon blended cement. In this research work, waste brick powder was incorporated at substitution levels of 5, 15 and 25%, keeping all the other ingredients and proportions constant. The mortar mixtures were tested at fresh state to evaluate the flowability, filling ability and the risk to bleeding or segregation. At hardened state, compressive and flexural strengths and ultrasonic pulse velocity were determined at ages of 1, 3, 7, 28 and 90 days.

## 2. Materials and experimental tests

### 2.1 Materials

According to the European Standards EN 197-1, Ordinary Portland Cement (OPC, CEMI 42.5) was used in all SCRM mixes. The waste brick powder, which is used as mineral admixture, was obtained from brick waste in a brick factory. The chemical composition and physical properties of the OPC and WBP are presented in Table 1. It was noted that WBP is mainly consisted of silica (65.93%) with low percentage of alumina. Strength activity index showed that WBP has acceptable pozzolanic reactivity with strength activity index of 0.75 at 28 days.

In order to determine the particle size distribution of cement and WBP, laser distribution analysis was performed and the results are shown in Fig. 1. The results indicated that the WBP has a continuous particle size distribution as the OPC. Table 1 gives the diameter of particles corresponding to 10, 50 and 90% of passing. It can be observed from this table that about of 50% of WBP particles have a size lower than 44.32 μm, contrary to the cement in which 50% of particles have a size lower than 12.35 μm. These results demonstrates that WBP is coarser than the OPC.

Fig. 2 shows the results of SEM of WBP. This test gives a great idea about the particle shape of the material tested and confirms the obtained results for particles size distribution (Fig. 1). Scanning electron microscope (SEM) exam was also performed on OPC and WBP and it is presented in Fig. 2. It can be concluded from Fig. 2 that WBP has coarser and more angular particles shape compared to OPC.

As fine aggregate, river sand was used with a maximum size of 5 mm, density of 2.6, coefficient of absorption of 0.59% and water content of 0.03%. The chemical admixture used to produce various mixtures, is a polycarboxylates based high-range water reducers superplasticizer (SP). It has a specific gravity and pH of 1.07 g/cm<sup>3</sup> and 8 respectively.

Component	OPC	WBP	
SiO <sub>2</sub> (%)	18.83	65.93	
CaO (%)	61.54	6.78	
MgO (%)	1.27	2.25	
Al <sub>2</sub> O <sub>3</sub> (%)	4.20	14.60	
Fe <sub>2</sub> O <sub>3</sub> (%)	5.31	5.24	
SO <sub>3</sub> (%)	1.96	0.05	
K <sub>2</sub> O (%)	0.49	3.13	
TiO <sub>2</sub> (%)	0.20	0.74	
Na <sub>2</sub> O (%)	0.21	0.14	
P <sub>2</sub> O <sub>5</sub> (%)	0.29	0.13	
Loss on ignition (%)	5.70	1.02	
Specific density	3.11	2.54	
Activity index i <sub>28</sub>	-	0.75	
Finesses characteristics	Finesses	3300	2925
	d <sub>10</sub> (μm)	1.19	3.17
	d <sub>50</sub> (μm)	12.35	44.32
	d <sub>90</sub> (μm)	40.53	100

Table 1 Chemical composition and physical properties of OPC and WBP  
1. táblázat OPC és WBP kémiai összetétele és fizikai tulajdonságai

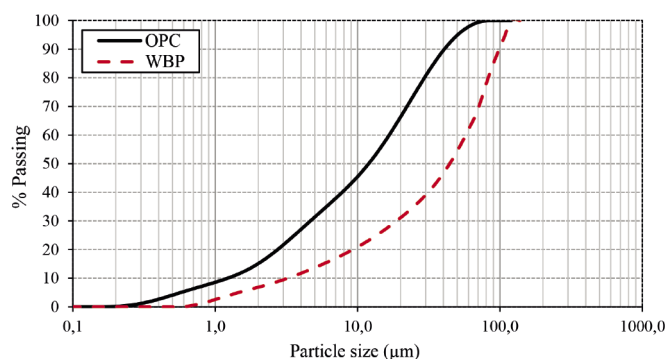


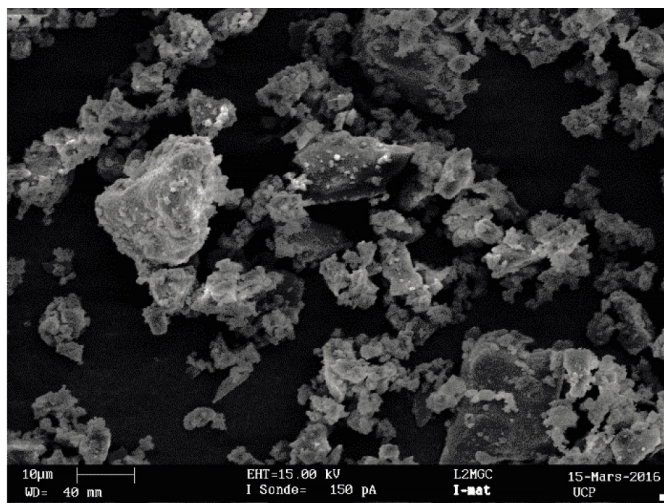
Fig. 1 Particle size distribution of OPC and WBP  
1. ábra OPC és WBP szemmegoszlás diagrammja

### 2.2 Mix proportion design

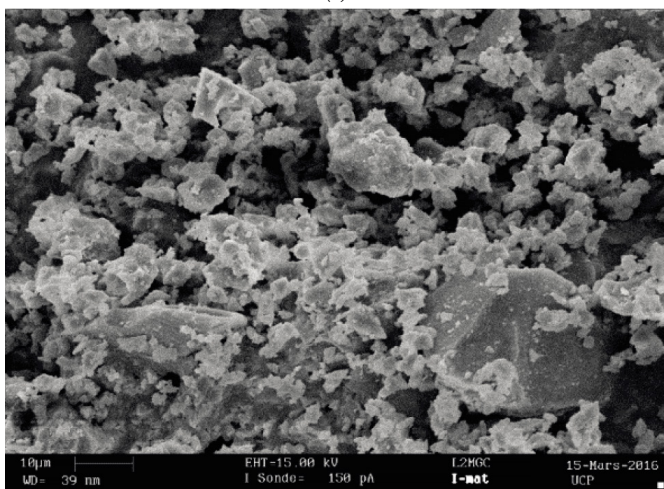
Four mixtures were prepared to study the effect of the WBP on the fresh and hardened properties of SCM. WBP was included at substitution levels of 0, 5, 15 and 25%. In all SCM mixtures, the amount of binder (OPC+WBP), water to binder (W/B) ratio and dosage of SP were kept equal to 692.65 kg, 0.4 and 0.8%, respectively. The mix proportions of SCM are given in Table 2.

Mix- tures	W/B	Constituents						
		OPC (kg/m <sup>3</sup> )	WBP (%)	WBP (kg/ m <sup>3</sup> )	Sand (kg/ m <sup>3</sup> )	Water (kg/ m <sup>3</sup> )	SP (%)	SP (kg/ m <sup>3</sup> )
0WBP	0.4	692.65	0	-	1300	278.89	0.80	5.54
5WBP		658.02	5	34.63				
15WBP		588.75	15	103.90				
25WBP		519.59	25	173.16				

Table 2 Mix proportions of SCM  
2. táblázat Az alkalmazott betonreceptúrák



(a)



(b)

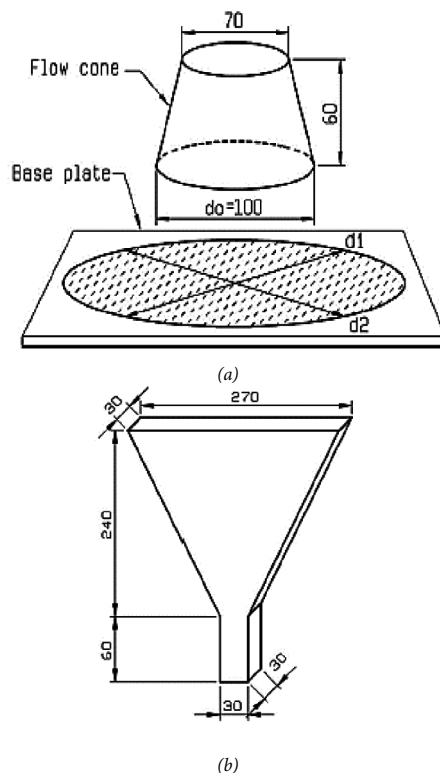
Fig. 2 SEM of: (a) OPC and (b) WBP

2. ábra OPC (a) és WBP (b) pásztázó elektronmikroszkópos felvételen

### 2.3 Test procedure

#### 2.3.1 Fresh mortar

The mini slump flow and mini v-funnel tests were conducted to characterize the flowability, filling ability and stability of fresh mortar. In the mini slump flow (Fig. 3.a), a truncated cone mold was filled with mortar and lifted upwards. The final diameter of the mortar through two perpendicular directions was measured and the mean is calculated. Slump flow ranging between 27.5 and 33.5 cm are suggested to obtain a slump flow of 55-85 cm for SCC [26-27]. The flow time T25 is the time to reach a circle of diameter of 25 cm corresponding to the flow time T50 measured in SCC was also determined [28]. It can be noted that it is possible to evaluate the trend to segregation or bleeding of SCM through visual control. The mini v-funnel was filled completely with mortar and the bottom outlet is opened allowing to the mortar to flow out (Fig. 3.b). The v-funnel flow time Tv which is the elapsed time (s) between the opening of the bottom outlet and the time when the light becomes visible from the top was measured [29].



Dimensions in mm

Fig. 3 Self-compacting mortar tests, (a) schematization of the mini-slump flow test, (b) mini V-funnel test

3. ábra öntömörödő habarcs vizsgálat, (a) mini-rokadásvizsgálat sematikus ábrája, (b) mini V-tölcséres vizsgálat

#### 2.3.2 Hardened mortar

From each mortar mixture, prismatic specimens of 40×40×160 mm in size were cast. After casting, all specimens were covered with plastic sheets for 24 hours, before they unmolded and transferred to conservation in conditioned room at 20±2 °C and 100% relative humidity until the time of test. For each mix, three specimens were used to determine flexural strength and pulse velocity values and six specimens to measure compressive strength at 1, 3, 7, 28 and 90 days. All these measures were carried out following European Standard EN 196-3 [30] and ASTM C597-97 [31].

## 3. Results and discussion

### 3.1 Fresh mortar properties

The results of slump flow and flow time T<sub>25</sub> of mortar mixtures with and without WBP are illustrated in Fig. 4. The values of slump flow varied between 29.3 and 31.4 cm. The use of WBP at replacement rate of 5% increases the slump flow, whereas a replacement rate of 15% slightly decreases the slump flow, but a replacement rate of 25% decreases significantly the slump flow. In contrary, increasing the amount of WBP until 5% slightly reduces the flow time T<sub>25</sub>, but replacements rate of 15% or 25% increases the flow time T<sub>25</sub>. For mixtures including 5% of WBP, the quantity of WBP are very low and it is completely coated by the cement particles. However, the effect of WBP is more pronounced in SCM mixtures having 15% and 25% of WBP since the quantity substituted is higher. In addition, the angular shape and coarse particles of WBP are assumed to



reduce the flowability of SCM leading to lower values of slump flow. It should be noted that, all SCM mixtures were visually examined and no risk to bleeding or segregation was observed.

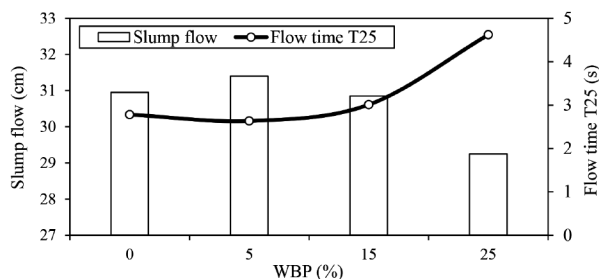


Fig. 4 Slump flow and flow time  $T_{25}$  of mortar mixtures with percentage of WBP  
4. ábra Roskádásos terület és folyási idő ( $T_{25}$ ) a WBP mennyiség függvényében

Fig. 5 depicts the evolution of flow time  $T_v$  for all mortar mixtures. The v-funnel flow time increases with increasing the percentage of WBP. The values of v-funnel flow time ranged from 3.8 to 5.2 s, these values are in the range recommended by EFNARC 2-10 s [29]. Incorporation of WBP at 5, 15 and 25% increases the v-funnel flow time by 9, 13 and 38%, respectively. Generally, the mortar viscosity is expressed by the T25 or  $T_v$  flow time. This means that the use of WBP increases the viscosity of SCM which is attributed to the angular shape and to the coarse particles of WBP which increase the resistance to the flow and consequently the viscosity of SCM.

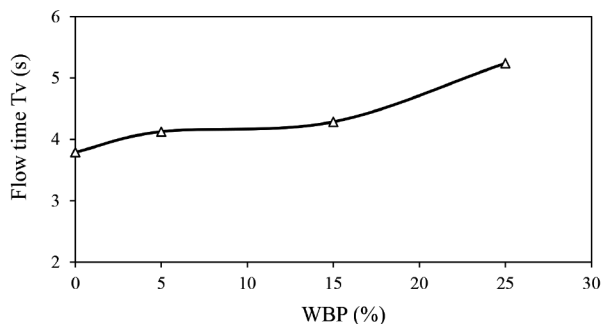


Fig. 5 Flow time  $T_v$  of mortar mixtures with percentage of WBP  
5. ábra Folyási idő ( $T_v$ ) a WBP mennyiség függvényében

### 3.2 Hardened mortar properties

Fig. 6 presents the values of the compressive strength for mortar mixtures with plain cement and WBP. It was observed that the compressive strength of all SCM mixtures increases with increase in age of curing which attributes to the continuous of the hydration. SCM with plain cement presented the highest values of compressive strength at all age of curing, exception for 3 days of curing in which mixtures contained 5% of WBP shown the higher compressive strength. Introduction of the WBP in SCM mixtures slightly decreased the compressive strength for substitution rate of 5 or 15% but considerably for substitution rate of 25%. The decrease in the compressive strength of 5WBP, 15WBP and 25WBP mixes at 28 days is about 6.3, 10.6 and 35.3%, and about 9.8, 13.6 and 38.6%. This means that there is no strength gain in mixtures containing WBP after 28 days. WBP is considered as pozzolanic material but it is coarse than the cement which meaning that its fineness is low, so the pozzolanic activity did not take place at 90 days

since the fineness played an important role in the pozzolanic activity [32].

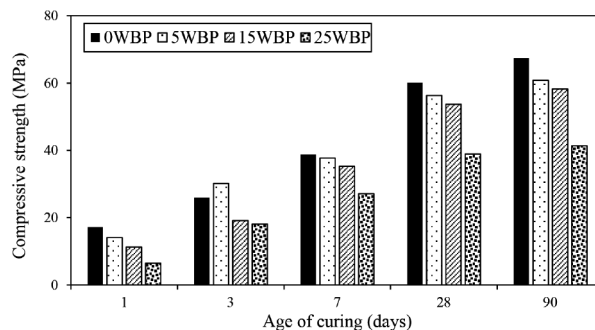


Fig. 6 Compressive strength of mortar mixtures with percentage of WBP  
6. ábra Nyomószilárdság a WBP mennyiség függvényében

The values of UPV of all mortar mixtures are shown in Fig. 7. UPV is a non-destructive test that allows assessing the internal structure of the mortar or concrete without damaging the tested element. UPV increases with increase in the age of curing. The use of WBP in SCM mixtures caused a decrease in the UPV. The UPV of mixtures containing 5 or 15% of WBP are slightly inferior to those of control mixture, but mixtures with 25% of WBP show a high reduction in the UPV. Similar results were reported by Şahmaran et al. [32].

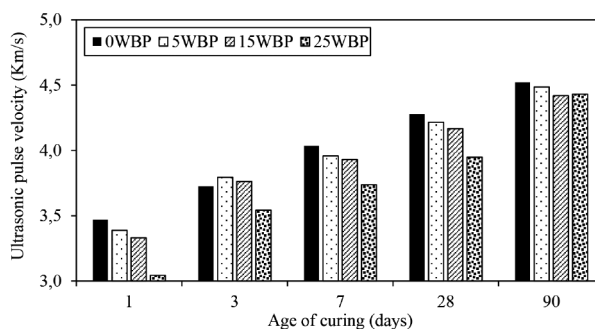


Fig. 7 Ultrasonic pulse velocity of mortar mixtures with percentage of WBP  
7. ábra Ultrahangos impulzus sebesség a WBP mennyiség függvényében

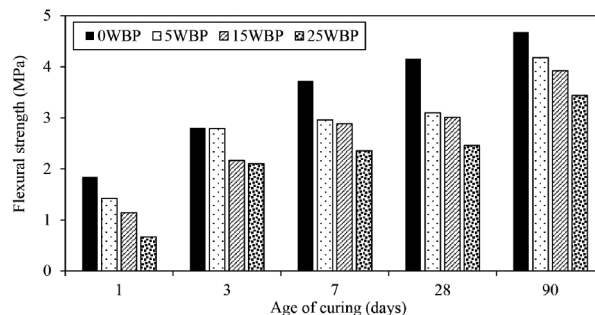


Fig. 8 Flexural strength of mortar mixtures with percentage of WBP  
8. ábra Hajlító szilárdság a WBP mennyiség függvényében

In Fig. 8, the flexural strengths of mortar mixtures with plain cement and WBP are plotted as a function of the age of curing. Due to continued hydration, it was observed that the flexural strength increases with an increase in the age of curing. Compared to the mixture with plain cement, it appears that the introduction of WBP decreases the flexural strength and as the amount of WBP increased the flexural strength decreased.

### 3.3 Environmental benefit of WBP blended cement

Cement industry is one the most source of CO<sub>2</sub> emission in civil engineering field. The production of 1 kg of cement releases into the atmosphere about 0.9 kg of CO<sub>2</sub>. Fig. 9 shows the quantity of CO<sub>2</sub> emission related to the binder for all SCRM mixtures. The results have shown a reduction in the amount of CO<sub>2</sub> when cement is replaced by waste brick powder. Using replacement level of WBP of 5%, 15% and 25% reduces the CO<sub>2</sub> emission to 401.85, 359.55 and 317.25 kg, respectively. In recent study, Kavitha et al. [33] have reported that replacing cement by metakaolin with rates ranging from 5% to 15% decreased the CO<sub>2</sub> emission by 4% to 11%.

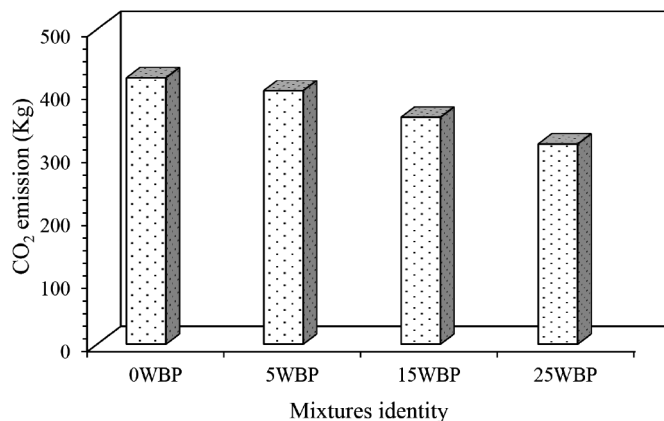


Fig. 9 Environmental impacts of mixtures with percentage of WBP  
9. ábra Különböző WBP adagolású keverékek környezeti hatása

### 3.4 Correlation between mechanical properties and substitution levels of WBP

In order to understand the relationship between mechanical properties (compressive strength  $f_c$ , flexural strength  $f_t$ ) and the percentage of waste brick powder, correlations were realized between them and the results are shown in Figs. 10 and 11, and Table 3. It was noted from the obtained results that the polynomial correlation between mechanical properties and the substitution level of waste brick powder for different age of curing was found good to excellent with very acceptable coefficient of regression. It should be noted that other correlations were also explored, but obtained results showed that these correlations are not strong compared to the used correlation.

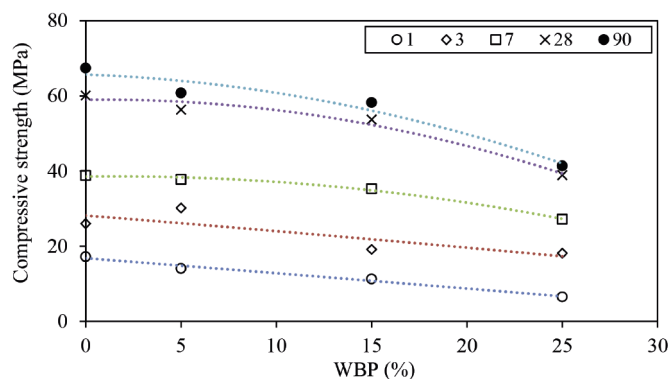


Fig. 10 Correlation between compressive strength and percentage of WBP at different ages  
10. ábra Nyomószilárdság és WBP mennyiség összefüggése különböző korú keverékek esetén

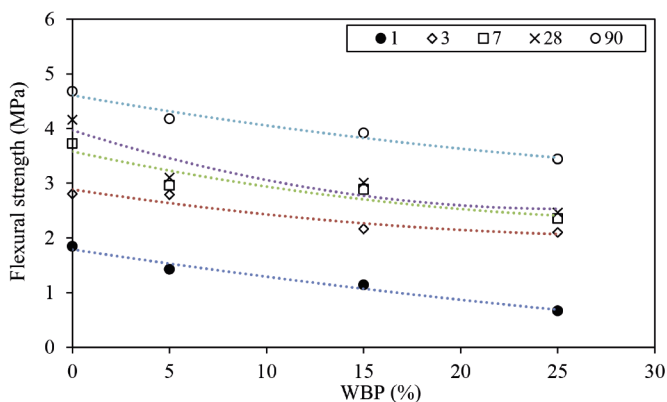


Fig. 11 Correlation between flexural strength and percentage of WBP at different ages  
11. ábra Hajlítósilárdság és WBP mennyiség összefüggése különböző korú keverékek esetén

Age	Correlation between $f_c$ and percentage of WBP		Correlation between $f_t$ and percentage of WBP	
	Regression equation	R <sup>2</sup>	Regression equation	R <sup>2</sup>
1	$y = -0.0005x^2 - 0.3937x + 16.789$	0.98	$y = 0.0004x^2 - 0.0537x + 1.7889$	0.98
3	$y = -0.0012x^2 - 0.4032x + 28.147$	0.91	$y = 0.0009x^2 - 0.0542x + 2.8866$	0.90
7	$y = -0.0207x^2 + 0.0671x + 38.5$	0.96	$y = 0.0012x^2 - 0.0757x + 3.5806$	0.86
28	$y = -0.034x^2 + 0.0641x + 58.962$	0.96	$y = 0.0022x^2 - 0.1134x + 3.969$	0.95
90	$y = -0.0306x^2 - 0.1808x + 65.676$	0.94	$y = 0.0006x^2 - 0.0613x + 4.6069$	0.96

Table 3 Regression equations and coefficients for different ages  
3. táblázat Regressziós összefüggések és koefficienseik különböző korú minták esetén

## 4. Conclusions

Based on the experimental results and the analysis performed, the following conclusions can be drawn:

- SEM analysis indicated that the particles size of waste brick powder are coarser compared to the cement.
- At fresh state, self-compacting repair mortars with waste brick powder have shown low fluidity and high viscosity. But, values of slump flow and flow time are acceptable by the recommendations of self-compacting mortars production.
- The use of waste brick powder with a fineness lower than the cement resulted in a decrease in the compressive, flexural strength and the ultrasonic pulse velocity.
- WBP can be suitably used at replacement rate of 5 or 15% to produce a new reduced carbon blended cement.
- Adding WBP could be positive from the environment point of view because of its availability as a local waste. This means also that WBP is an interesting alternative material to produce eco-friendly self-compacting mortar.
- Several correlations between hardened properties (compressive and flexural strength) and the percentage of waste brick powder were explored. These results show that there is a good polynomial correlation between the studied properties compared to other correlations.



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# Preparation of particle-reinforced mullite composite ceramic materials using kaolin and IG-017 bio-origin additives

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## Abstract

In this research work, the possibilities of producing advanced ceramics from traditional, relatively inexpensive raw materials were studied. Powder mixtures from kaolinite and IG-017 bio-original additive were milled and uniaxially pressed to pellets, then pre-sintered in the electric kiln under oxidation and oxygen-free atmosphere at 1250 °C. The pre-sintered specimens were then further sintered in nitrogen gas at 1600 °C. The produced specimens were tested on composition, microstructures and morphologies using several characterization techniques including X-ray diffraction (XRD), scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDAX). The conducted experiments by the authors have shown that it is possible from traditional kaolinite to develop technical ceramic specimens with increased physical and mechanical properties based on formed amorphous phases, mullite crystals, micro and nano carbon fibers.

Keywords: carbonization, ceramic, composition, microstructure, mullite, sintering  
Kulcsszavak: karbonizáció, kerámia, összetétel, mikroszerkezet, mullit, szinterezés

## 1. Introduction

In recent years, there is a huge demand in many industries for new low-density materials with enhanced physical, electrical, magnetic, mechanical, thermal or chemical properties [1-34]. Thanks to these continuously increased requirements, more and more ceramic materials and ceramic-based composites are being developed and used in various fields of industry and technology [35-46]. Mullite is a stable intermediate phase under atmospheric pressure in the  $Al_2O_3$  -  $SiO_2$  system (Fig. 1) [47]. Despite the rare occurrence of mullite as mineral, the sintered mullite crystals are playing an important role both in traditional and modern technical ceramics. Fig. 1 shows how the various crystals and phases are depending on the temperature and also reveals that pure mullite ( $3Al_2O_3 \cdot 2SiO_2$ ) melts at 1870 °C. Generally, at normal (atmospheric) pressure mullite crystals are capable to incorporate several transition metal cations and other foreign atoms into their structures depending on sintering environment and temperature [48-50].

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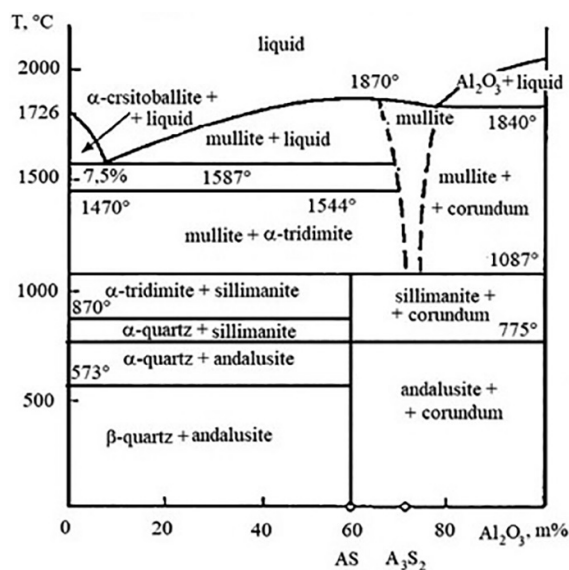


Fig. 1  $\text{SiO}_2\text{-Al}_2\text{O}_3$  phase diagram [47] (Taken from N M Bobkova: *Fizicheskaya Himiya Tugoplavkih Nemetallicheskikh i Silicatykh Materialov*, 2007)

1. ábra  $\text{SiO}_2\text{-Al}_2\text{O}_3$  fázisdiagram [47] (Átvéve: N M Bobkova: *Fizicheskaya Himiya Tugoplavkih Nemetallicheskikh i Silicatykh Materialov*, 2007)

Generally, non-oxide technical ceramics and nitride ceramics have a much higher surface hardness and compression strength than metals and metal alloys or oxide ceramics, but their production costs are usually very expensive [51]. Nitride-based ( $\text{SiAlON}$  or  $\text{Si}_3\text{N}_4$ ) materials are considered as significant and attractive structural ceramics/refractories because of their excellent properties, like high mechanical properties (e.g., strength, hardness, toughness), chemical inertness, good corrosion resistance and outstanding thermal resistance.

Silicon nitride is a non-natural mineral that needs to be synthesized by different methods [52-54]. The easiest way to produce silicon nitride from kaolin or other clay minerals is through carbothermal reduction and nitridation. The following reaction equations show the steps in which silicon carbide, silicon oxynitride, silicon nitride, and sialons are formed during the process [53-56].

1. Decomposition of kaolin at a temperature of 450 °C  
 $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O} \rightarrow \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$  (metakaolin) +  $2\text{H}_2\text{O}$  (vapor) (1)

2. Formation of mullite ( $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ ) as decomposed of metakaolin at a temperature at 1087°C

$3(\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2) \rightarrow 3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 + 4\text{SiO}_2$  (amorphous) (2)

While the temperature raises up to 1360°C, amorphous  $\text{SiO}_2$  begins to transform into crystalline  $\text{SiO}_2$ .

Carbothermal reduction and simultaneous nitridation occur at a temperature above 1400°C

$\text{SiO}_2 + \text{C} \rightarrow \text{SiO}(g) + \text{CO}(g)$  (3)

$3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 + 2\text{C} \rightarrow 3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}(g) + 2\text{CO}(g)$  (4)

3. Formation of silicon oxynitrides takes place progressively in environment richer in nitrogen under the reducing influence of the carbon

$3\text{SiO}_2 + 3\text{C} + \text{N}_2 \rightarrow \text{Si}_2\text{N}_2\text{O}$  (5)

$2\text{SiO}(g) + \text{C} + \text{N}_2 \rightarrow \text{Si}_2\text{N}_2\text{O} + \text{CO}(g)$  (6)

4. Formation of  $\chi$ -phase sialon and  $\beta'$ -sialon from mullite

$3(\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2)$  (mullite) +  $12\text{C} + \text{N}_2 \rightarrow$

$\text{Si}_3\text{Al}_6\text{O}_{12}\text{N}_5$  ( $\chi$ -phase sialon) +  $6\text{AlN} + \text{SiO}_2 + 12\text{C}$  (7)

$\text{Si}_3\text{Al}_6\text{O}_{12}\text{N}_5 + 3\text{N}_2 + 9\text{C} \rightarrow \text{Si}_3\text{Al}_3\text{O}_3\text{N}_5$  ( $\beta'$ -sialon) +  $2\text{AlN} + 9\text{CO}$  (8)

5. Formation of SiC

$\text{SiO}_2 + 2\text{C} \rightarrow \text{SiC} + \text{CO}_2(g)$  (9)

6. Formation of  $\text{Si}_3\text{N}_4$

$3\text{SiO}_2 + 6\text{C} + 2\text{N}_2 \rightarrow \text{Si}_3\text{N}_4 + 6\text{CO}$  (10)

The Si-N bonds are formed at 1200°C in the presence of carbon. These bonds are progressively formed in N-rich environment and lead to a continuous formation of silicon oxynitride compositions. Usually, these bonds are not detected by XRD but appear later in the reaction, when crystalline silicon oxynitride persists throughout the reaction and possibly containing a little amount of Al (like O-sialon and x-phase sialon). After the destruction of the mullite, the Si-O bonds survive and remain throughout the reaction, especially in the kaolinite starting material. Later in the reaction, Si-C bonds are formed. The created SiC phase behaves more like a secondary product than a transitory intermediate [54-56].

Based on the studied literatures, it can be said that mullite or mullite containment taken from kaolinite can be successfully used as a matrix material for silicon nitride particles or whiskers reinforced ceramic composites.  $\text{Si}_3\text{N}_4$  particles and whiskers can considerably enhance the mechanical strengths and toughness of both kaolinite and mullite based ceramic composites. Using conventional kaolinite or other types of clay minerals as starting materials, different micro and nano-size reinforcement materials can be produced like, SiC,  $\text{Si}_3\text{N}_4$ ,  $\text{Si}_2\text{ON}_2$  or SiAlON through carbothermal reduction and nitridation.

The aims of this work are to develop ceramic composites material with superior physical and mechanical properties using relatively inexpensive processing technology and raw materials like conventional kaolinite or other clay minerals. In this work, the authors present a part of their research on the production of carbon-containing ceramics using kaolin and a biological additive. Further these produced ceramic composite could be a potential candidate for many applications showing better mechanical properties.

## 2. Materials and Experiments

Particle-reinforced mullite composite ceramics were prepared via carbothermal reduction and nitridation techniques, commercial kaolinite powders KKA-MB and IG-017 refined bio-original additives developed and produced by IGREX Ltd. were used as starting raw materials. Stoichiometric amount of these ceramic powders were weighted using 6 different mixtures compositions as shown in Table 1. The prepared ceramic mixtures were well milled in a laboratory ball mill for 20 minutes in the speed of 200 rpm. The milled powders then uniaxially compacted at 150 MPa pressures to produce 24 cylindrical disc specimens with diameters of 20 mm for each mixture. The filling weights of specimens were 8 grams in each case. After compacting, half of the specimens were pre-sintered in normal (oxidation) atmosphere and the other half of the specimens were pre-sintered in an oxygen-free atmosphere. In both cases, the maximum pre-sintering temperatures were 1250 °C. After these, the pre-sintered specimens were well studied and later they were burned at 1600 °C using nitrogen gas in the high-temperature kiln. Fig. 2 shows the sintered specimens.

Mixture	Kaolinite	IG-017
I.	85	15
II.	75	25
III.	65	35
IV.	55	45
V.	45	55
VI.	35	65

Table 1. The volumetric relationship between components in m%  
2. táblázat Az EDAX vizsgálat során kapott elemi összetétel

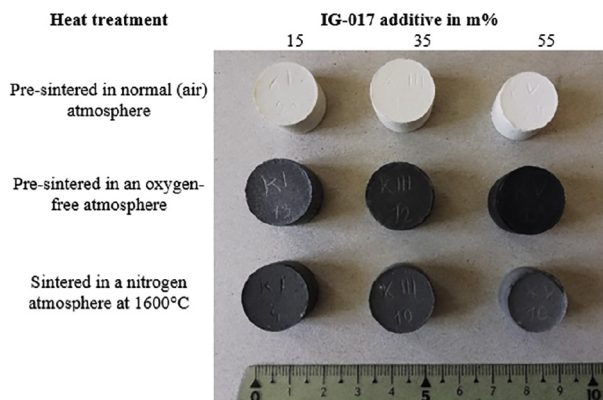


Fig. 2 The specimens after the sintering process  
2. ábra A szinterelt próbatestek

### 3. Results and discussions

Part of the authors have already shown in their earlier work some properties of the pre-sintered specimens, like volume shrinkage, weight losses, density, porosity and microstructure [57]. In this work are shown how the properties change due to sintering the specimens at a high sintering temperature (1600°C) in nitrogen gas. During pre-sintering of the specimens, firstly, drying of the samples takes place, followed by removal of the crystalline waters from kaolinite structure at approximately 450°C, parallelly gasification of the IG-017 additives occurs. Pre-sintering kaolinite at a temperature of 1250°C is high enough for the formation of mullite crystal phases and free SiO<sub>2</sub> components. Some of the specimens from each mixture were further sintered at 1600°C, where SiC and Si<sub>3</sub>N<sub>4</sub> can be formed in the ceramic product. Figs. 3 and 4 show the volume shrinkages and weight losses of the sintered samples.

Fig. 3 compares the volume shrinkage of the heat-treated ceramic products to that of the pre-sintered and crude product volumes. Oxygen deficient pre-sintered ceramic specimens exhibit higher shrinkage. In contrast, the total volume shrinkages of the two type of pre-sintered specimens were almost the same.

Fig. 4 shows the weight loss of the specimens fired at 1600°C in an Oxygen atmosphere and Oxygen-free environment. In the case of the use of a larger amount of bio-original additive, the weight of the oxidation pre-sintered samples is increased, this could be possibly due to the incorporation of Nitrogen gas into the samples. In the case of oxygen-free pre-sintered specimens, some of the carbon remaining in the material structure is discharged during sintering at 1600°C. Examination of the microstructure and elemental composition of the samples was

done by scanning electron microscopy (SEM).

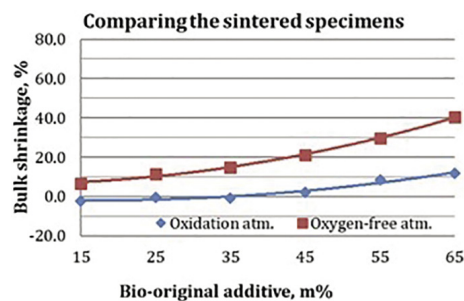


Fig 3a

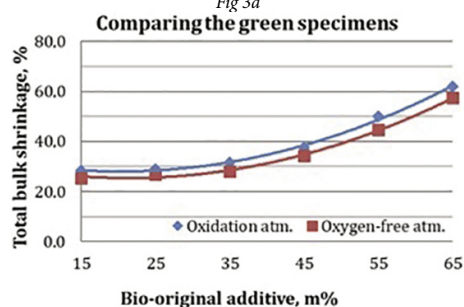


Fig 3b

Fig. 3 The volume shrinkage after sintered the specimens at 1600 °C  
3. ábra A térfogati zsugorodás az 1600 °C-os szinterelés után

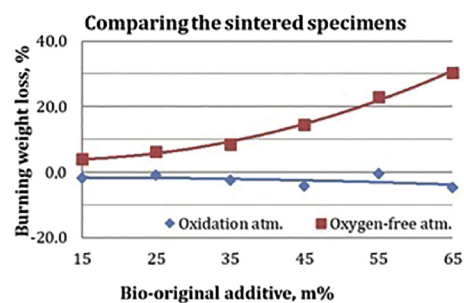


Fig 4a

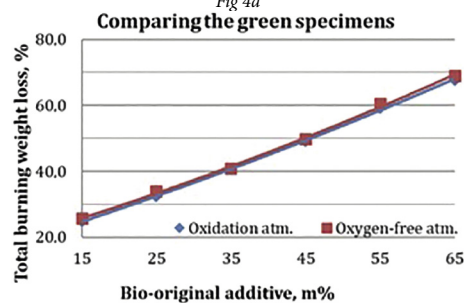


Fig 4b

Fig. 4 The weight losses after sintered the specimens at 1600 °C  
4. ábra A tömegvesztés az 1600 °C-os szinterelés után

Fig. 5 shows the outer surface and breaking surface of a specimen made with 15 m% bio-additive pre-sintered in an oxidation atmosphere and then heat-treated in nitrogen at 1600°C. It can be clearly seen on the crushed surface that it has a high degree of porosity, from which the open pores and capillaries are significant on the surface. Based on the elemental composition determined by EDAX, the sample has a significant carbon and titanium at the surface, indicating that carbon and titan-containing surface layer has been formed during higher-temperature combustion. In the case of specimens with higher biological additive content, the surface of the pressed ceramic specimens was slightly nitrated.



Based on the EDAX test, the specimen contains 45 m% IG-017 has 1.51 m% nitrogen content (Table 2).

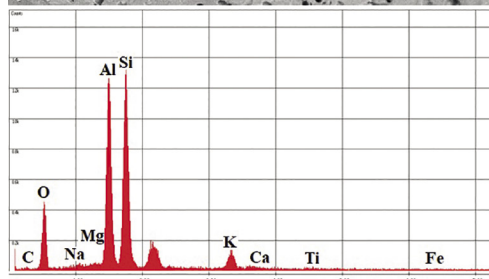
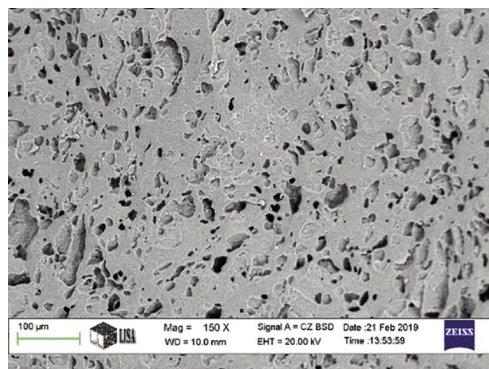


Fig 5a

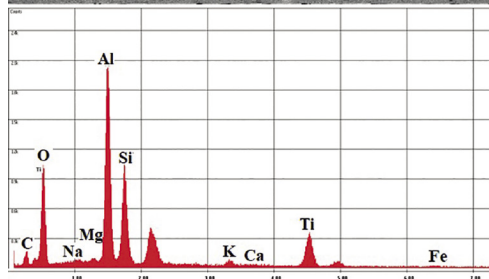
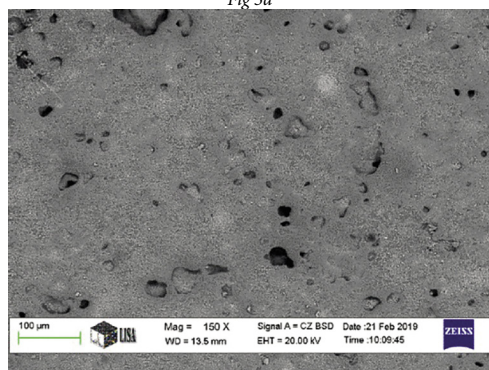


Fig 5b

Fig. 5 The breaking surface (a) and outer surface (b) of the examined specimen from the I. mixture

5. ábra A I. keverékből származó minta belső, töretfelülete (a) és külső felülete (b)

The authors measured the oxide and phase composition of the sintered specimens with XRD test. After pre-sintering the specimens, the main phase was mullite with a large amount of amorphous glass phase and a small amount of quartz or cristobalite. During oxygen-free pre-sintering, carbon fibres were formed. After high-temperature heat treatment, the oxygen-free pre-sintered samples consisted of 60% mullite, 32% amorphous phase and 8% carbon fibres. Compared to the pre-sintered sample, the amount of carbon fibres in the sample was reduced (Table 3).

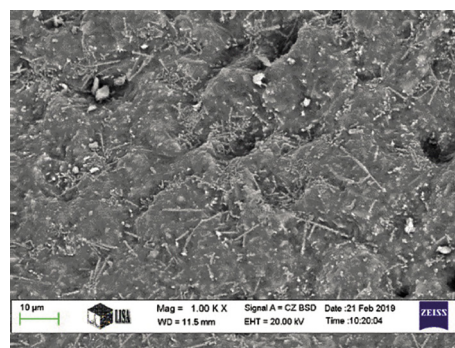


Fig 6a

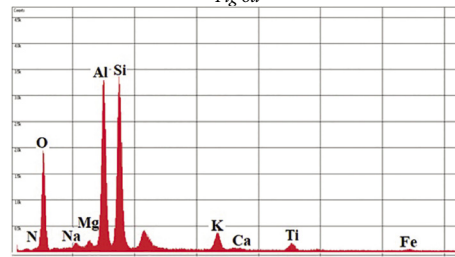


Fig 6b

Fig. 6 The microstructure (a) and elemental composition (b) of the examined specimen from the IV. mixture

6. ábra A IV. keverékből származó minta mikroszerkezete (a) és elemi összetétele (b)

Mark of test specimen mixture	I.		IV.	
	Location of EDAX test	inside	surface	
Elemental compositions, in m%	N	0	0	1.51
	C	1.88	11.61	0
	O	24.00	32.81	31.81
	Na	0.47	0.54	0.81
	Mg	0.37	0.39	0.84
	Al	26.28	24.70	23.30
	Si	40.04	16.71	32.75
	K	4.59	1.15	4.33
	Ca	0.61	0.42	0.46
	Ti	0.67	10.98	2.83
Fe	1.09	0.69	1.37	

Table 2 The elemental composition based on EDAX test  
2. táblázat Az EDAX vizsgálat során kapott elemi összetétel

Sintered atm.	Phase %	SUM	Mullite	Quartz	Cristo-balite	Amorph glass	Carbon fiber
			Al <sub>6</sub> Si <sub>2</sub> O <sub>13</sub>	SiO <sub>2</sub>	SiO <sub>2</sub>	SiO <sub>2</sub>	C
		100	53	2	5	40	0
Oxidation	SiO <sub>2</sub>	61.95	14.95	2	5	40	
	Al <sub>2</sub> O <sub>3</sub>	38.05	38.05				
		100	48	4	1	32	15
Oxygen-free	SiO <sub>2</sub>	50.54	13.54	4	1	32	
	Al <sub>2</sub> O <sub>3</sub>	34.46	34.46				
	CO <sub>2</sub>	54.96					54.96
		100	60	0	0	32	8
Nitrogen gas (1600°C)	SiO <sub>2</sub>	48.92	16.92			32	
	Al <sub>2</sub> O <sub>3</sub>	43.08	43.08				
	CO <sub>2</sub>	29.31					29.31

Table 3 The oxide- and phase composition of the sintered specimens from IV mixture  
3. táblázat A IV. keverékből készült minta oxid- és fázisösszetétele

## 4. Conclusion

In this research, the authors have successfully produced carbon-reinforced mullite ceramics using conventional kaolin minerals and IG-017 biological additive. Moreover, they continue their research on the production of mullite ceramics reinforced with silicon nitride particles or whiskers. Compared to the green products data, the weight loss and volume shrinkage of the prepared specimens after sintering at 1600 °C were not influenced by the pre-sintering atmosphere. However, the elemental and phase composition of the final products are significantly influenced by the type of applied pre-sintering process. In the case of specimens with higher biological additive content, the surface of the pressed ceramic specimens was slightly nitrated.

## 5. Acknowledgements

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# The influence of composition, microstructure and firing temperature on the density, porosity, and shrinkage of new zeolite-alumina composite material

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## Abstract

In this research work, new zeolite-alumina composite materials were prepared by mechanical activation and reactive sintering method. A detailed investigation of structure and microstructure of the raw materials and the produced ceramic samples have been precisely examined using X-ray diffraction (XRD) and scanning electron microscopy (SEM). Based on the raw material compositions, microstructure, and firing temperature, different characteristics were examined including, density, shrinkage, porosity and water absorption. The authors have found that the compositions and the firing temperature play a major role in the microstructure and the properties of the final product.

Keywords: zeolite-alumina ceramics, composite materials, mechanical activation, reactive sintering.

Kulcsszavak: zeolit-alumínium-oxid kerámia, kompozit anyagok, mechanikai aktiválás, reaktív szinterezés.

## 1. Introduction

The research work in the field of ceramics technologies has been highly grown in the recent years [1-34]. Among ceramics materials, zeolites which represent a class of crystalline minerals have been highly utilized in a wide range of applications including chemical and petrochemical industries for catalysis, adsorption and the elimination of heavy metal ions from industrial wastewaters. Zeolites offer fascinating properties like high surface area, ion-exchange capacity, high adsorption efficiency and the ability to act as a host in preparation of nanocomposite materials [35]. These outstanding characteristics assigned to the unique structure of zeolites which contain a large number of uniformly distributed micropores. The research work in zeolite is motivated not only by the need to synthesise new materials with expected potential applications [36]. But also the necessity to understand the formation of these interesting materials and to control their microstructure [37]. Zeolite-based composite materials have attracted a great deal of interest as technical materials due to

the interesting complex composition and good mechanical behaviour [38]. Despite the huge research works conducted on zeolite-based composite materials [39-43], view previous works have been conducted concerning the influence of ceramic reinforcement in zeolite-based ceramic composite [44-46].

In this research study, zeolite-based Alumina ceramic composite materials were produced through mechanical activation and reactive sintering technique. The structure and microstructure of the raw materials and the final product have been investigated via X-ray diffraction (XRD) and scanning electron microscopy (SEM), moreover, the effect of composition, firing temperature on the density, porosity, and shrinkage was studied. These new zeolite-alumina mixtures

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which relatively inexpensive materials could be a potential candidate for many technical applications showing better properties.

## 2. Experimental method

### 2.1. Synthesis of Zeolite - alumina composite materials

Zeolite-based alumina composite ceramic materials were prepared through the mechanical activation and reactive sintering method. Zeolite powders from Tokaj region (Hungary) and  $\text{Al}_2\text{O}_3$  powder (98 %; MOTIM) were used as raw materials. An appropriate amount of these ceramic powders was carefully weighted using different compositions as shown in Table 1, then the prepared mixtures were milled and mixed in Retsch PM 400 planetary ball mill for 15 minutes in 150 rpm using silica balls. The milled powders then used to make cylindrical discs with a diameter about 25 mm and thickness of 10 mm using uniaxial pressing machines under a pressure of 500 MPa. The prepared specimens were sintered at different temperatures (1100°C, 1150°C, 1200°C and 1250°C) in a programmable furnace for 3 h, with a heating rate of 60 °C/h.

Zeolite %	Alumina %
100	0
90	10
80	20
70	30
60	40
50	50

Table 1 The composition of the raw materials used to prepare the mixtures  
1. táblázat Az alapanyagokból készített keverékek összetétele

### 2.2. Characterization

The raw materials were characterized by Rigaku Miniflex II X-ray diffractometer (XRD) operated in the Bragg-Brentano geometry and the samples were scanned between  $2\theta$  of 0-70° with a scanning rate of 1°/min and a step size of 0.01016° using  $\text{CuK}\alpha$  radiation ( $\lambda = 1.54184 \text{ \AA}$ ). For the computer-based investigation, DIFFRACT measurement software was used.

The topographical feature and the surface morphology of both raw materials and the prepared ceramic samples were examined using scanning electron microscopy (SEM) (Model TM-1000, HITACHI). The prepared samples were examined under several magnification values using secondary electrons.

## 3. Results and discussion

### 3.1. Structures

The relationship between the sintered temperatures and composition of the produced ceramics is shown in Fig. 1. It is well seen that using different sintering temperatures lead to varieties on the colour of the ceramic samples as well as differences on the shrinkage of the prepared discs. These could be attributed to the fact that above 1100°C zeolite starts to recrystallize and leads to physicochemical reactions which could highly affect the microstructure of the complex ceramics structure, as well as the properties.

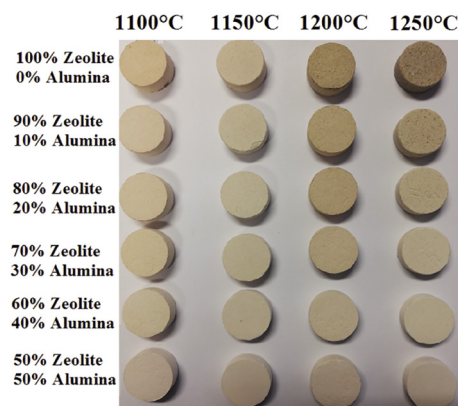


Fig. 1 Samples with different composition sintered at different temperature (1100 °C, 1150 °C, 1200 °C and 1250 °C)

1. ábra Az összetétel és az égetési hőmérséklet (1100 °C, 1150 °C, 1200 °C és 1250 °C) hatása a szinterelt zeolit mintákra

Fig. 2 exhibits the XRD pattern of natural zeolite. The analysis of the sample confirms the existence of different minerals, Table 2 reveals the chemical composition and the percentages of the different compounds.

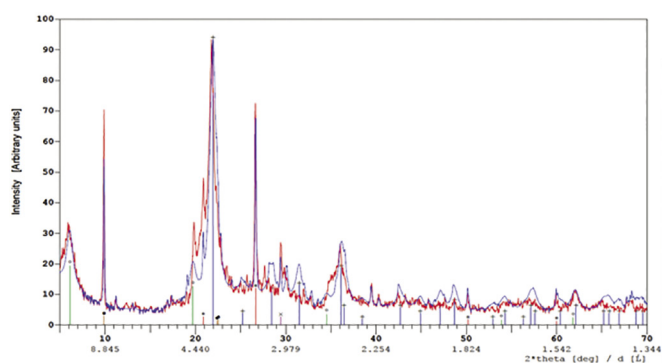


Fig. 2 XRD diffractogram of the natural Zeolite

2. ábra A természetes zeolit XRD diffraktogramja

	Quartz	Cristo- balite	Montm- rillonite	Calcite	Clinopti- lolit	Total
wt %	8.00	50.00	30.00	2.00	10.00	100.00
CaO				1.12		1.12
SiO <sub>2</sub>	8.00	50.00	19.13		5.79	82.92
Al <sub>2</sub> O <sub>3</sub>			4.06		1.89	5.95
MgO			3.21			3.21
Na <sub>2</sub> O			0.74		0.57	1.31
CO <sub>2</sub>				0.88		0.88
H <sub>2</sub> O			2.87		1.60	4.47
Loss on ignition	0.00	0.00	2.87	0.88	1.75	5.50

Table 2 Mineralogical constituents, chemical composition and loss on ignition (LOI) of the natural zeolite in wt%, resulted from XRD analysis

2. táblázat A természetes zeolit ásványi XRD vizsgálata során megállapított összetevői, kémiai összetétele és izzítási vesztesége (LOI) tömeg%-ban

### 3.2. SEM investigation of the raw materials

Fig. 3 shows secondary electron images of the natural zeolite and alumina powders. The typical grains size of zeolite and alumina were found to be in the range of 0.5 - 25 μm and 0.5-



50 μm, respectively. While Fig. 4 shows the fractured surface of the produced ceramics samples (80% zeolite-20% alumina) sintered at 1100 °C and 1200 °C, it is clear that increasing the firing temperature leads to reduce the pores of the produced ceramics hence increase the density.

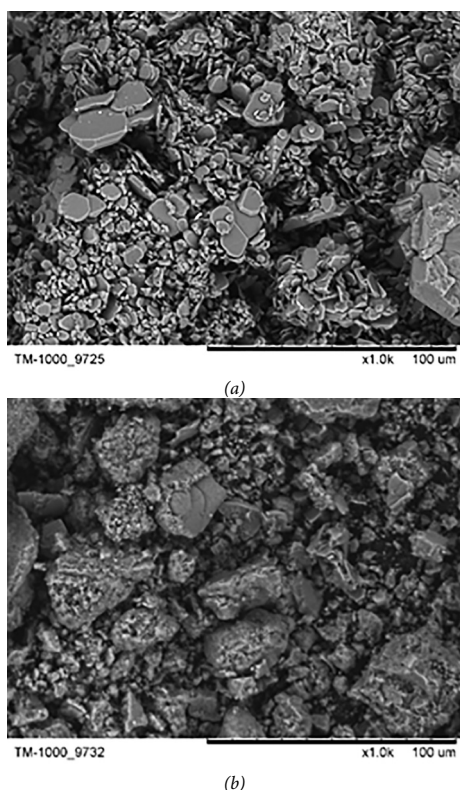


Fig. 3 SEM images of a) natural zeolite and b) alumina powders  
3. ábra A természetes zeolit a) és az alumínium-oxid por b) mikroszerkezete (SEM)

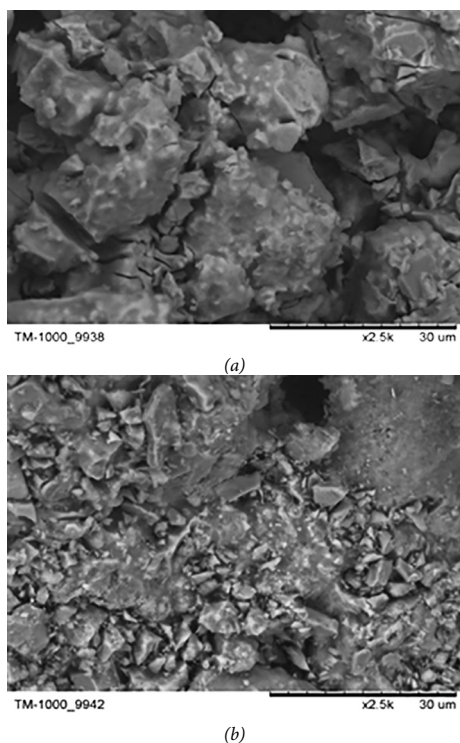


Fig. 4 SEM images of the fractured surface of 80% zeolite-20% alumina sintered a) at 1100 °C, b) at 1200 °C  
4. ábra Az 1100 °C-on a) és 1200 °C-on b) szinterelt 80 m% zeolit és 20 m% alumínium-oxid felhasználásával készült minták töretfelülete (SEM)

The composition and sintering temperature show a substantial impact on the final density of sintered ceramic samples. The pure zeolite exhibits low density, this could be assigned to the highly porous structure of the zeolite. As the amount of alumina % increasing, the density of the produced samples is gradually increased, likewise, increasing the sintering temperature also leads to increase in the density of the prepared discs, which also confirmed by SEM (Fig. 4). Pure zeolite sintered at 1100 °C offers the lowest density about 1.6 g/cm<sup>3</sup>, on the other hand, 50% zeolite- 50% alumina samples sintered at 1250 °C displays the highest density of approximately 2 g/cm<sup>3</sup>. The effect of composition and sintering temperature is shown graphically in Fig. 5.

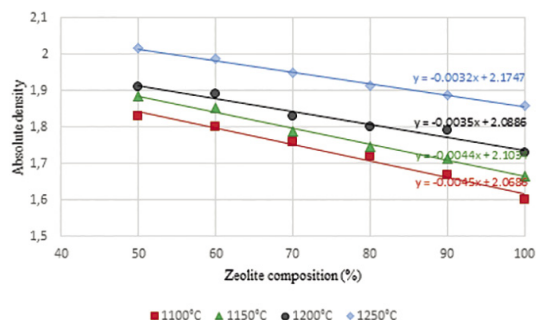


Fig. 5 The density of the zeolite-alumina samples sintered at different temperatures  
5. ábra A különböző hőmérsékleteken szinterelt zeolit-alumínium-oxid minták sűrűsége

The firing shrinkages of the produced specimens as a function of zeolite composition prepared at different sintering temperatures (1100 °C, 1150 °C, 1200 °C and 1250 °C) are shown in Fig. 6. 50% zeolite- 50% alumina samples fired at 1100 °C exhibits the lowest shrinkage of approximately 5%, with decreasing the % of alumina in the sample, the firing shrinkage is progressively increased, furthermore, increasing the sintering temperature is highly increase the firing shrinkage. Pure zeolite sintered at 1250 °C shows the highest firing shrinkage about 23%.

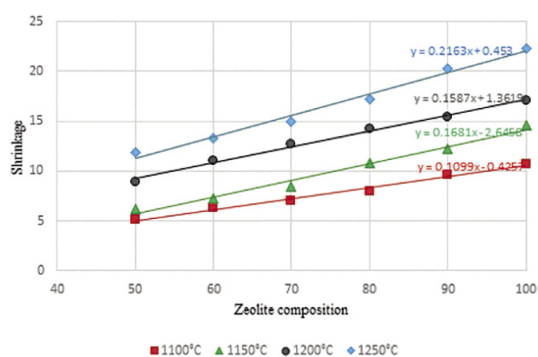


Fig. 6 The bulk shrinkage of the zeolite-alumina samples sintered at different temperatures  
6. ábra A különböző hőmérsékleteken szinterelt zeolit-alumínium-oxid minták térfogatú zsugorodása

Fig. 7 demonstrates the weight loss of the different composition of the zeolite-alumina samples sintered at variable temperatures, with increasing the sintering temperature from 1150 °C to 1250 °C the weight is highly increased from about 6% to more than 11%. Pure Zeolite shows the highest weight loss.

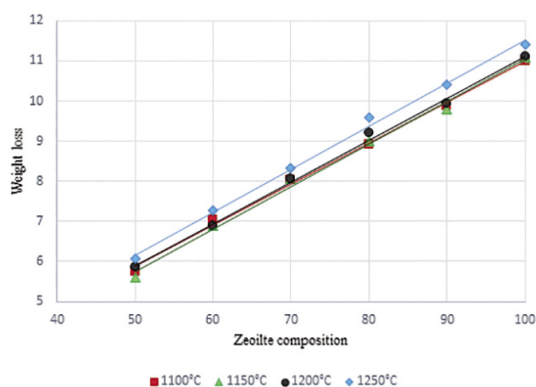


Fig. 7 The weight loss of the zeolite-alumina samples sintered at different temperatures  
7. ábra A különböző hőmérsékleteken szinterelt zeolit-alumínium-oxid minták tömegvesztése

Fig. 8 and 9 show the water absorption and apparent porosity of the prepared ceramic samples with different composition sintered in a range of temperature (1100 °C, 1150 °C, 1200 °C and 1250 °C) the two graphs are quite similar to each other, the two graphs exhibit low values of water absorption and apparent porosity when a large amount of zeolite and high sintering temperature are used.

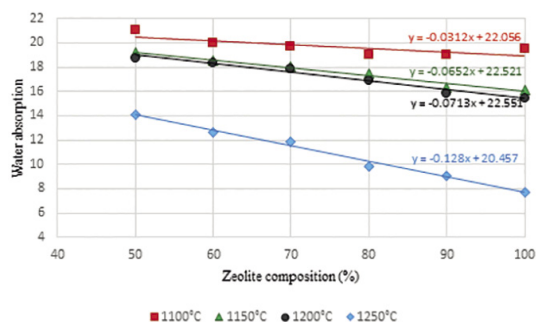


Fig. 8 The water absorption of the zeolite-alumina samples sintered at different temperatures  
8. ábra A különböző hőmérsékleteken szinterelt zeolit-alumínium-oxid minták vízfelvévő képessége

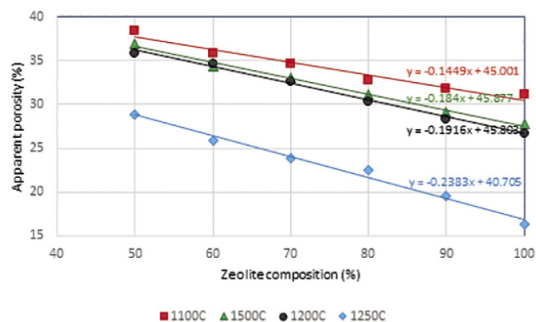


Fig. 9 The apparent porosity of the zeolite-alumina samples sintered at different temperatures  
9. ábra A különböző hőmérsékleteken szinterelt zeolit-alumínium-oxid minták látszólagos porozitása

## 4. Conclusion

In conclusion, the important notice to be enlightened is that the composition and the firing temperature can highly influence the characteristics of the final ceramics products such as density, sintering weight loss, porosity and shrinkage. The data examined in

this research work could be used to control the microstructure and, hence, the properties of sintered ceramic materials such as thermal conductivity, dilatation, thermal expansion coefficient, mechanical strength and other physical, chemical and mechanical properties.

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# Composite materials based on zeolite-montmorillonite rocks and aluminosilicate wastes

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## Abstract

The application of mineral raw materials and their wastes to modify composite materials becomes one of the promising areas of science and industry. This work presents conditions to produce composites in various systems: epoxy polymer matrix/rocks (zeolite + montmorillonite); aluminosilicate waste (coal fly ash). The properties of the initial material and the synthesized composites were studied by standard techniques, XRD and SEM. The operational properties of composites were determined: heat resistance, bending strength, tensile strength, linear shrinkage, apparent density, open porosity, water absorption and crush strength.

Keywords: composites, zeolite-montmorillonite rocks, coal fly ash, ceramics

Kulcsszavak: kompozitok, zeolit-montmorillonit ásványok, pernye, kerámiák

## 1. Introduction

The growth of industrial production and consumption of functional materials results in reducing mineral resources and forming large volumes of wastes [1-5]. Environmental problems are becoming more pronounced, special solutions are needed. The application of mineral raw materials and recycling of mineral raw wastes is one of the promising trends of modification of composite materials, an integral part of the regional economy, including creation of new technologies for the construction industry, for the regeneration of ecosystems, etc. [6-10]. The main purpose of modification of the epoxy composite material is to reduce costs and improve operational properties. We noted that the physical-technical properties of the composites based on the epoxy binder could be improved by introduction of modifying additives [11]. Natural layered and porous silicates (montmorillonite or zeolite) are used as such additives [12-14].

The specified natural materials are convenient test objects for modeling composites with desired properties. Depending on the amount of impurities, a change in the structure is possible (increasing volume of intracrystalline cavities or “swelling” of lattices) and the formation of a hybrid nanocomposite [14]. For modeling it would be interesting to show the effect on the physical and chemical properties of the composite by

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the organomodifier, which is a mixture of rocks containing montmorillonite and zeolite. Deposits of montmorillonite or zeolite formed over several thousand years. Therefore, they can have very different mineralogical, chemical, morphological and grain size structures, depending on their position and location within the deposits and strata. We presented results of study of the physical and chemical features of the synthesis of the polymer composite material in the epoxy-polymer matrix/rock system containing zeolite and montmorillonite.

Component	SiO <sub>2</sub>	TiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	FeO	MnO	CaO	MgO	K <sub>2</sub> O	Na <sub>2</sub> O	P <sub>2</sub> O <sub>5</sub>	SO <sub>3</sub>	loi	Total
<b>Analcime-montmorillonite rock</b>	56.50	0.95	19.42	7.71	0.28	0.04	0.68	1.62	1.54	1.65	0.10	-	9.35	99.84
<b>Coal fly ash</b>	61.24	1.06	16.87	12.69	2.30	0.06	1.86	2.01	K <sub>2</sub> O	Na <sub>2</sub> O	P <sub>2</sub> O <sub>5</sub>	0.11	0.9	99.87

Table 1. The chemical composition in wt. % of analcime-montmorillonite rock and fly ash  
1. táblázat Az analcime-montmorillonit ásvány és a pernye kémiai összetétele

The application of aluminosilicate wastes for composite ceramics is also becoming a modern innovative trend. For example, the possibility of obtaining glass ceramics and ceramics from coal fly ash with the addition of natural raw materials and industrial wastes: quartz, clay, talc, broken glass, dolomite, wastes from the processing of borax and titanium was shown [15–19]. However, there are very few studies in the field of ceramics synthesis with application of only fly ash [20, 21]. In this paper we showed the possibility of obtaining ceramics from fly ash without addition of other components and revealed conditions for obtaining materials with optimum strength and water absorption properties.

The aim of the work is to obtain new knowledge in the field of formation, stability of phase transformations and aggregation of ultrafine substances and creation of composite materials with desired properties based on natural and technogenic raw materials.

## 2. Materials and experiments

### 2.1. Materials

Montmorillonite – (nanoclay) – clay mineral of the subclass of layered silicates. The crystalline structure of montmorillonite allows using surface active centers and changing the dimensions of interlayer voids and injecting “foreign” molecules into them [13].

Zeolites – aluminosilicates of alkali and alkaline-earth metals – are porous bodies characterized by a specific framework structure and regular pore geometry (intracrystalline cavities and channels) into which foreign molecules can penetrate after dehydration. By variation of the exchangeable cations and the aluminosilicate framework (i.e., type of zeolite), it is possible to regulate the physical and chemical interactions involving sorbed molecules [22, 23]. In this paper the aluminosilicate minerals of the zeolite class were represented by analcime.

Samples of analcime-montmorillonite rocks, selected from the Veslyana zeolite deposit (Koinskaya zeolite area, Komi Republic, Russia), were used as the mineral component. The mineral composition of the analcime-montmorillonite rocks: montmorillonite - 35, analcime - 25, quartz - 20, feldspars - 10, kaolinite - 5, calcite – 5 %. The chemical composition is presented in Table 1. We described more details of the mineral composition of the analcime-montmorillonite rocks, their physical and chemical properties and their application in [4, 10, 24, 25].

The present study used a commercially available epoxy resin based on diglycidyl ether of bisphenol-A (DGEBA) with the trademark ED-20, and the curing agent was isomethyltetrahydrophthalic anhydride (iso-MTHPA). The chemical structures of the materials are shown in Fig. 1 a, b.

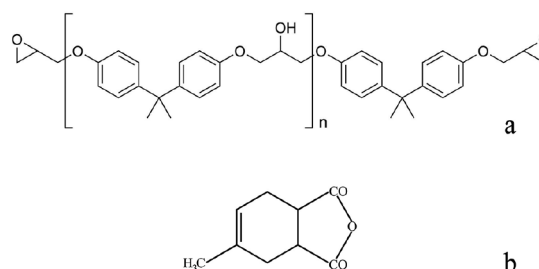


Fig. 1 Chemical structures of diglycidyl ether of bisphenol-A,  $n=0.98$  (a) and isomethyltetrahydrophthalic anhydride (b)

1. ábra A biszfenol-A,  $n = 0,98$  (a) és izo-metil-tetrahidro-ftálsav-anhidrid (b) kémiai szerkezete

Coal fly ash and slag are industrial wastes from the combustion of coal in thermal power plants. To obtain ceramic materials we used the coal fly ash from thermal power plants of Vorkuta town, which use hard coal from the mine “Vorgashorskaya” (Pechora coal basin, Russia). XRD analysis revealed quartz, mullite, magnetite, hematite and amorphous phase (probably silicate or aluminosilicate glass). The chemical composition is shown in Table 1. Detailed information on the composition and structure of the fly ash and methods of its utilization are presented in [5, 26].

### 2.2. Preparation of composite materials

The stoichiometric quantities of epoxy resin and anhydride hardener were mixed at a mass ratio of 100 to 80 at a temperature of 75 °C. The components were stirred for 15 minutes at the same temperature to obtain a homogeneous mixture. The product is added analcime-montmorillonite rock in the required ratio. The distribution of dispersed powder was carried out on an ultrasonic generator (II - 10-0.1) for 20 minutes. Then the mixture was poured into a metal mold with non-stick coating. Degassing was carried out inside the vacuum chamber at 0.1 bar. Preparation of the epoxy composite was carried out by a three-stage curing cycle. First, the mixture was kept at 100 °C for 1 hour, then at 120 °C for 1 hour and the polycondensation mode was completed at 160 °C for 3 hours. Polymer composite sheets were cooled in the desiccator to room temperature.

To obtain ceramic materials from fly ash, the technique described in [27], was used: 150 µl of distilled water was added to 1.5 g of ash (particle size is less than 0.05 mm) and mixed thoroughly in a mortar. The resulting mixture was pressed by a hydraulic press under pressure of 7, 21 and 35 MPa and 5 min exposition. As a result, cylindrical tablets with a diameter of 10 mm and a height of 9–13 mm were obtained. For pressing the tablets under a pressure of 35 MPa, 5 % polyvinyl alcohol with a volume of 500 µl was used instead of water. Before sintering, the pressed samples were dried at 103 °C for 8 h to remove moisture. The annealing was carried out in a muffle furnace at temperatures from 800 to 1250 °C (800, 900, 1000, 1050, 1100, 1150, 1200, 1250 °C) for 2 hours.

Analcime-montmorillonite rock, % (mass.)	0	0.5	1	5	10	15
Onset temperature, °C	81	60	81	83	85	90
Max temperature, °C	123	105	124	127	128	130
End temperature, °C	149	126	140	163	161	160
Energy effect, J/g	222	246	229	218	236	211

Table 2 DSC data for the process of composite obtaining  
2. táblázat DSC adatok a kompozit előállítási folyamatához

Analcime-montmorillonite filler, wt. %	0	0.5	1	5	10	15	25
Martens heat resistance, °C	110 ± 2	132 ± 2	123 ± 2	123 ± 2	118 ± 2	115 ± 2	105 ± 2
Tensile strength, MPa	44 ± 4	63 ± 4	55 ± 4	53 ± 4	50 ± 4	45 ± 4	35 ± 4
Bending strength, MPa	110 ± 5	145 ± 5	125 ± 5	125 ± 5	120 ± 5	110 ± 5	100 ± 5

Table 3 Characteristics of the composite with analcime-montmorillonite filler  
3. táblázat A kompozit tulajdonságai analcime-montmorillonit fillerekkel

### 2.3. Methods of investigations

The phase composition was determined by DRON-4M and Shimadzu XRD-6000 diffractometers. The chemical composition was determined by the method of silicate analysis for 12/14 components.

The study of the processes, occurring at the preparation of the composite material, was carried out by the methods of differential scanning calorimetry (DSC) by Shimadzu DSC-60 device and chemical analysis for functional groups. The content of epoxy groups in epoxy oligomer and carboxyl groups in iso-MTHPA was determined by chemical analysis using standard methods [20]. The strength properties were studied by IR 5057-60 tensile testing machine, which stretched the sample with a given constant rate of movement of active clamp and load measurement with an error of no more than 1% of the measured value.

The apparent density, open porosity and water absorption were determined according to [28]. The microstructural features were examined by TESCAN VEGA 3 LMH scanning electron microscope with Oxford Instruments X-Max energy dispersive attachment. The crush strength was measured using a universal testing machine (model WDW-T100) at a loading rate of 1 mm/min.

## 3. Results and discussion

### 3.1. Epoxy polymer matrix/ analcime+montmorillonite rock

The data obtained by DSC and chemical analysis for functional groups showed no interaction between components of the polymer matrix and the filler particles, i.e. we can say that the improvement of the operational properties of the material is resulted from the physical adsorption caused by hydrogen bonds, forming an additional strong lattice compensating for the growth of heterogeneity and imperfection in the boundary layers.

Fig. 2 shows a characteristic view of DSC curves of the hardening process upon receipt of a composite material. Table 2 shows the onset, maximum and end temperatures of the exothermic peak, as well as observed exothermic effect of the reaction. It is noted that with the increase of the content

of analcime from 1 to 15 wt.%, there is a slight increase of the temperatures of the onset of the reaction during preparation of the composite material. At the same time for ED-20+iso-MTHPA+analcime-montmorillonite rock mixture at low concentrations of the filler (about 0.5 wt.%), oligomer molecules in the adsorption layer are likely to be ordered because of orientation of its polar groups (glycidyl, hydroxyl) with respect to the particles of analcime-montmorillonite containing rock, which creates a “kinetically advantageous” order in it and catalyzes the hardening process, which starts at 20 °C lower temperature. The thermal-temporal mode of hardening was at: 100 °C - 2 h, 120 °C - 2 h, 160 °C - 3 h.

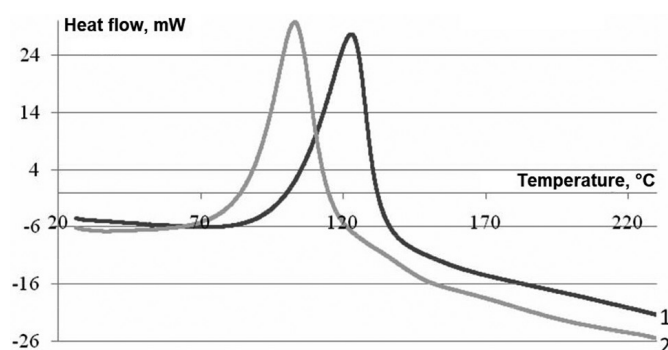


Fig. 2 DSC curves of polymerization process in the systems: 1 - ED-20+iso-MTHPA; 2 - ED-20+iso-MTHPA+0.5 wt.% analcime-montmorillonite rock

2. ábra A polimerizációs folyamat DSC görbéi: 1 - ED-20 + izo-MTHPA valamint 2 - ED-20 + izo-MTHPA + 0,5 tömeg% analcime-montmorillonit ásványrendszerekben

The study of the performance characteristics of the composite (Table 3), such as Martens heat resistance, bending strength, tensile strength, showed that for samples with a filling of 0.5 wt.% had the best results due to the effect of small additives. The improved performance is associated with the formation of reinforcing frame filler particles, the orientation of macromolecules and their transition into thin hardened films, but the main factor is the adhesion of the polymer to solid surfaces. Generally, adhesion in polymers is resulted from physical (including hydrogen) bonds, which form an additional strong lattice, which compensates the growth of heterogeneity and imperfection in the boundary



layers. However, with increasing interaction of the polymer with the surface of the filler particles, internal stresses also increase and weaken the composition. This interaction changes the structure and properties of the material in the boundary layers, the latter increases proportionally with the growth of the specific interface.

The increase of the content of the filler (from 1 to 10 wt. %) results in the decrease of modifying effect, and filling more than 15 wt. % affects properties of the polymer matrix.

### 3.2. Ceramics on the basis of coal fly ash

The experiments showed that sintering of samples occurred at 1050 °C and above. The chemical composition of the sintered samples did not generally differ from the chemical composition of initial coal fly ash. The sintered samples showed a low content of FeO, associated with its oxidation to Fe<sub>2</sub>O<sub>3</sub> when heated, and sulfur, which had volatilized at burning of the organic part of the ash (unburned carbon).

Fig. 3 showed diffraction patterns of the initial fly ash and ceramic materials obtained at temperatures from 800 to 1200 °C. Unlike the original fly ash in the sintered samples, peaks of magnetite, converted to hematite, were not diagnosed. With the increase of burning temperature, the intensity of reflections of quartz decreased, and the intensity of mullite increased. At 1200 °C cristobalite was formed.

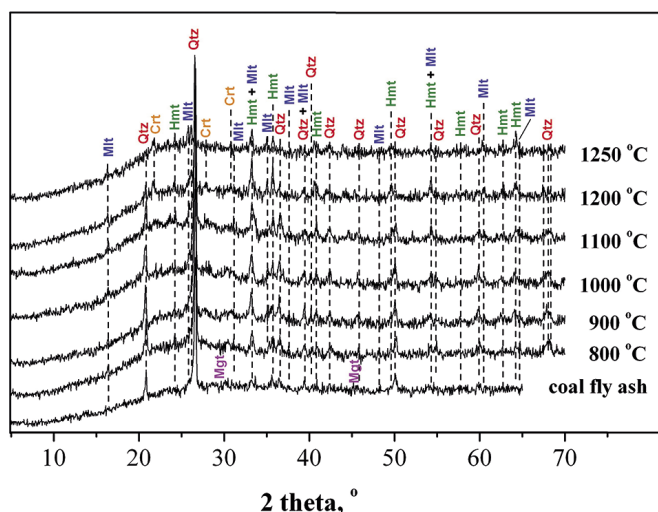


Fig. 3 XRD patterns of fly ash and samples annealed at temperatures of 800–1250 °C. Mlt - mullite, Qtz - quartz, Mgt - magnetite, Hmt - hematite, Crt - cristobalite

3. ábra 800–1250 °C hőmérsékleten lágyított pernye XRD mintái. Mlt - mullit, Qtz - kvarc, Mgt - magnetit, Hmt - hematit, Crt - cristobalite

We determined linear shrinkage, apparent density, open porosity, water absorption and crush strength for the obtained ceramic samples.

Linear shrinkage of the samples pressed at 7 and 21 MPa and annealed at 1100–1150 °C was 7.6–11.6%. Annealing at 1200 °C and higher temperature results in increasing in sample diameter by 2.6–4.8% with formation of internal pores, i.e. porous ceramics is obtained. The behavior of samples obtained at a pressure of 35 MPa is somewhat different: shrinkage is fixed only at 1100 °C; with increasing temperature the sample diameter increases by 8.1%.

The apparent density of the sample pressed at 7 MPa increases from 1.5 to 2.0 g/cm<sup>3</sup> in the temperature range of 1050–1150 °C. With the increase of apparent density, a significant decrease of open porosity and water absorption occurs. Thus, the open porosity is reduced by 20 times (from 38 to 1.9%), water absorption – 26 times (from 25 to 0.9%). Annealing at 1200 °C and higher temperature contributes to the formation of internal pores and, accordingly, to the decrease of the apparent density up to 1.2 g/cm<sup>3</sup>. The open porosity of porous ceramics was 1.1–1.4 V %, water absorption was 0.8–1.1 wt. %.

Pressing at 21 and 35 MPa allows increasing apparent density of ceramics, reducing open porosity and water absorption at a given firing temperature. Thus, a sample obtained at 35 MPa and a firing temperature 1100 °C is characterized by a rather high apparent density (2.46 g/cm<sup>3</sup>) and low open porosity and water absorption (0.4 and 0.2 wt. %, respectively).

Fig. 4 shows SEM images of the surface of ceramics obtained at various temperatures and pressing pressures. The surface of the samples pressed at 7 and 21 MPa and sintered at 1100 °C looks rough and uneven, which indicates relatively poor sintering. As the temperature rises to 1150 °C, the ash particles stick together, forming a smoother and more uniform surface, which leads to the increase in density and strength. In the samples sintered at 1200 °C, large pores with sizes up to 200 and 600 nm are observed for pressing pressures of 7 and 21 MPa, respectively. The formation of pores is resulted from softening of glass phase of the ash simultaneously with formation of gas phase. The sample, pressed at 35 MPa and sintered at 1100 °C, has the densest and flat surface. Pore formation of samples pressed at 35 MPa was detected at a temperature of 1150 °C.

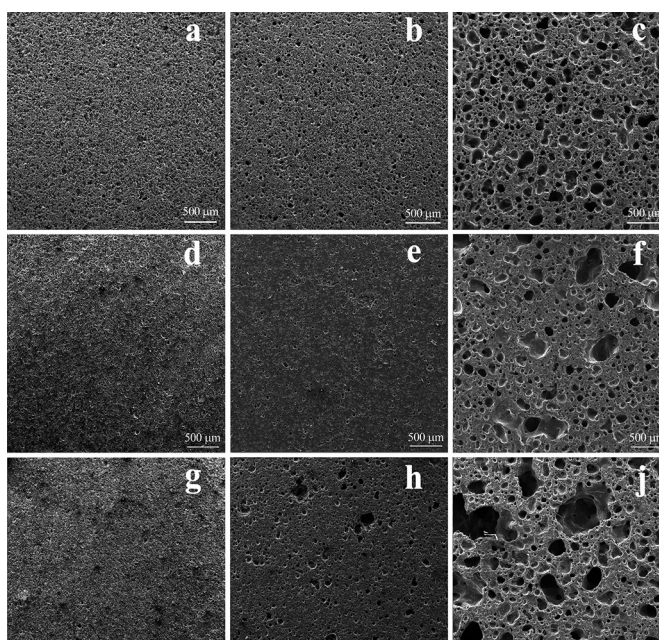


Fig. 4 SEM images of the surface of ceramics obtained at the following values of pressing pressure and firing temperature, respectively: a) 7 MPa, 1100 °C, b) 7 MPa, 1150 °C, c) 7 MPa, 1200 °C, d) 21 MPa, 1100 °C, e) 21 MPa, 1150 °C, e) 21 MPa, 1200 °C, g) 35 MPa, 1100 °C, g) 35 MPa, 1150 °C, and) 35 MPa, 1200 °C

4. ábra A kerámia felületének SEM képei az alábbi sajtoló nyomás és égési hőmérsékleteknél: a) 7 MPa, 1100 °C, b) 7 MPa, 1150 °C, c) 7 MPa, 1200 °C, d) 21 MPa, 1100 °C, e) 21 MPa, 1150 °C, e) 21 MPa, 1200 °C, g) 35 MPa, 1100 °C, g) 35 MPa, 1150 °C, and) 35 MPa, 1200 °C

It was established that the annealing temperature significantly affected the crushing strength, unlike the pressing pressure. Thus, the crush strength of samples pressed at 7 and 21 MPa and sintered at 1100 °C was 63 and 76 MPa, respectively. At a firing temperature of 1150 °C, this parameter increased significantly and amounted to 135 and 129 MPa, respectively. Increasing the firing temperature to 1200 °C leads to the formation of large internal pores, as a result of which the crush strength is sharply reduced to 39 and 21 MPa.

Thus, we showed that the pressing pressure and the firing temperature affected the characteristics of ceramics: apparent density, water absorption, open porosity, crush strength. According to their technological characteristics, the materials obtained can be used for the production of building ceramics.

#### 4. Conclusions

The paper is devoted to composites based on analcime-montmorillonite rocks and aluminosilicate wastes (coal fly ash). We emphasize an important role of integration of mineralogical and technological features of the material composition for predicting behavior in the technological processes of composite formation and their operational characteristics.

The conditions for obtaining a composite polymer material in the epoxy-anhydride matrix/analcime-montmorillonite system have been studied. The optimal conditions (T, P) for the formation of the operational characteristics of composites (heat resistance, bending strength, tensile strength, etc.) are shown.

Improving performance properties of composites is associated with P, T conditions, physical adsorption and effect of "small additives".

It is shown that the mechanism of phase transformations in the considered systems (epoxy polymer matrix/analcime+montmorillonite or aluminosilicate waste (fly ash)) can form new phases, the physical and chemical parameters of which meet the requirements of materials exploitation, expand the list of goods and reduce environmental risks.

#### 5. Acknowledgments

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# Clay- and zeolite-based biogeosorbents: modelling and properties

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## Abstract

This work presents data on the mineral and chemical composition of zeolite-containing and clay rocks considered as carriers for oil-oxidizing microorganisms, as well as their textural characteristics. The authors proved the use of mineral sorbents based on clay and zeolite-containing rocks for design of a biogeosorption material of destructive type. The minerals met the requirements for oil sorbents (environmental compatibility, oil capacity, feasibility), and were biocompatible with Biotrin consortium. Hydrocarbon-oxidizing microorganisms combined with mineral sorbents had a significant destructive potential. The degradation of petroleum hydrocarbons by biogeosorbents modeled on 551, 541-31, 539-40 samples were 77, 60 and 65.5 % for 4 days, respectively.

Keywords: biogeosorbents, clays, zeolites, Biotrin, petroleum hydrocarbons, *n*-alkanes, biodegradation, sorption

Kulcsszavak: biogeoszorbensek, agyagok, zeolitok, Biotrin, ásványolaj-szénhidrogének, *n*-alkánok, biodegradáció, szorpció

## 1. Introduction

Today, zeolite and zeolite-alumina composites, based on zeolite and clay rocks, are used in a wide area of industry and everyday life primarily as sorbents because of their technical, chemical, biological and medical properties. Water and soil pollution with hydrocarbons during exploration, mining, transportation, storage and processing should be noted to remain a significant environmental problem.

Many oil sorbents [1-8] are known to be divided into inorganic, natural organic and organic-mineral, and synthetic. Sorbents are evaluated mainly by their capacity to hydrocarbon pollutant under static conditions, the degree of hydrophobicity, the potentials for desorption, regeneration or utilization of the sorbent. Of course, the availability of raw materials and their cost must not be forgotten. Inorganic both sorbing and filtering materials include various types of clays, diatomite rocks, sand, zeolites, tuffs, pumice, etc. The methods for regenerating sorbents are processing with extractants or surfactants and burning, which causes secondary environment pollution [9].

The experience of the authors [10-13] shows that decontamination techniques using sorbents, biopreparations

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and zeolite and clay based biogeosorbents, which correlate with similar studies of zeolite and zeolite-alumina composites [14-16] are economically and environmentally desirable. Biopreparations composed of viable cells of microorganisms able to degrade hydrocarbon pollutants set the new trend in these studies. Such microorganisms are characterized by different physiological and biochemical properties, such as thermotolerance, osmophilicity, optimal pH for growth, capability of metabolize different classes of hydrocarbons.

Sample No	Rock	Description	Deposit/occurrence
551	Analcime-containing	Brownish-gray argillite	"Veslyana", Koinskaya zeolite area
541-31	Clinoptilolite-containing clay	Dark gray clay	Chim-Loptyuga oil shale deposit, Yarenga oil shale region
539-40	Glaucanite-containing	Green calcareous clay	Chim-Loptyuga oil shale deposit, Yarenga oil shale region

Table 1 Collection of zeolite-containing and clay rocks for use as mineral carriers of oil degrading microorganisms  
 1. táblázat Zeolit és agyagtartalmú anyagok kollekciója olajpusztító mikroorganizmusok ásványi vivőanyagaként való felhasználásra

The production of biopreparations involves several disadvantages of freeze drying. Firstly, the supernatant fluid, containing pool of extracellular enzymatic activities, is removed, and secondly, the freeze drying may cause death of the most of the microorganisms. Thirdly, not all associations of microorganisms can restore destructive activity after freezing exposure, which eliminates the feasibility of the use of many biological products in winter [17].

The production of biogeosorbents based on mineral raw materials solves problems both of increasing efficiency of microorganism cell immobilization, preserving their viability and biochemical activity by replacing freeze drying with the immobilization of microorganisms with a sorbent, and utilization of sorbent materials. In environmentally unfavorable conditions, sorbents act as a transport base for microorganisms, which allows up to 10 years anabiosis. Another advantage, compared with biopreparations, is the economic efficiency associated with a decrease in the amount of biogeosorbent used in the process of bioremediation [8, 18].

High ion-exchange and sorption capacities of clay and zeolites result in their wide use in environmental protection: to purify drinking water and industrial effluents, to regenerate soil, to remove harmful gases from industrial emissions [19-24]. The ability of clays and zeolites to absorb and retain water allows effectively immobilizing microorganisms and their metabolites on the surface. The sorption binding of hydrocarbons reduces toxicity of the environment to the microorganisms and fixes the substrate in close proximity to the microbial community. As a result, this raw material is a mineral fertilizer; it is not necessary to utilize the biogeosorbent [25].

To describe the interaction of oil and clay particles in aquatic microcosms, Lee et al. [26] suggested the term oil-mineral aggregates (OMA) and identified three types of the aggregates: droplet, solid, and flake aggregates. Droplet aggregates are represented by the smallest oil droplets surrounded by individual mineral particles or their floccules. In solid aggregates, oil and mineral bodies of various shape up to tens of micrometers are mixed. Flake aggregates are ordered thin sheets and can reach the millimeter size range. Solid oil-mineral aggregates, formed in microcosms with the participation of clays and zeolites, attach to minerals, which increases their size [27].

The aim of the work is to model biogeosorbents based on clay and zeolite rocks and Biotrin biopreparation, to study their sorption and oil degrading properties.

## 2. Objects and methods of research

The objects of study were:

1. Zeolite-containing and clay rocks of the European Northeast of Russia (Table 1).

2. Strains of microorganisms in the composition of Biotrin biopreparation [28]:

- bacteria *Pseudomonas yamanorum* VKM B-3033D, isolated from highly contaminated soil of the railway bed in the area of Syktyvkar [29];
- yeast *Rhodotorula glutinis*, VKM Y-2998D [30];
- microalgae *Chlorella vulgaris* Beijer. f. *globosa* V. Andr. IPPAS C-2024.

### 2.1 Biogeosorbent Modeling

The biomass of bacteria was cultivated meat-peptone broth: per 1 dm<sup>3</sup> of tap water: peptone – 20 g, NaCl – 3.0 g; KCl – 1.0 g; MgSO<sub>4</sub>×7H<sub>2</sub>O – 0.5 g at a temperature of 15–25 °C for 3-5 days of liquid phase fermentation process.

Yeast biomass was cultivated on the Čapek medium: per 1 dm<sup>3</sup> of water: sucrose – 20 g, NaNO<sub>3</sub> – 5.0 g; KH<sub>2</sub>PO<sub>4</sub> – 1.0 g; KCl – 0.5 g; MgSO<sub>4</sub> × 7H<sub>2</sub>O – 0.5 g, at a temperature of 15–25 °C for 5 days of liquid phase fermentation process.

Microalgae biomass was cultivated on the Tamiya medium: per 1 dm<sup>3</sup> of water: KNO<sub>3</sub> – 5.0 g; FeSO<sub>4</sub> × 7H<sub>2</sub>O – 0.003 g; MgSO<sub>4</sub> × 7H<sub>2</sub>O – 2.5 g; KH<sub>2</sub>PO<sub>4</sub> – 1.25 g, at a temperature of 15-25 °C for 10 days of liquid phase fermentation process.

The suspensions obtained were combined into Biotrin biopreparation. The biogeosorbents were produced by application of Biotrin biopreparation (cell titer 10<sup>9</sup>) directly to the mineral carriers with a particle size of 0.1–0.25 mm in the ratio of 1 part of the biopreparation to 6 parts of the sorbent.

### 2.2 Preparation of oil polluted water (model water sample)

0.5 g of oil was added to 100 cm<sup>3</sup> of Czapek's medium without sucrose. It was aerated in a shaker at 180 rpm for 4 days at room temperature and natural light. The water was filtered. The total petroleum hydrocarbon (TPH) content in the reference sample was 0.121 ppm, which was 2.4 times higher than the standards of maximum permissible concentrations in the water of fishery reservoirs in Russia [31].

### 2.3 Experimental design

Prepared water polluted with oil was poured into 250 cm<sup>3</sup> flasks and 1 g of initial sorbents and biogeosorbents based on them were added. The experiment was carried out for 4 days at room temperature, natural light, aeration in a shaker (180 rpm).

TPH in the model water sample, in the oil-mineral aggregates formed was analyzed fluorimetrically using Fluorat-02 liquid analyzer [32].

The qualitative and quantitative determination of the content of *n*-alkanes was carried out by Trace DSG (Thermo) chromatomass spectrometer in the mode of selective ion detection (SIM) at an electron energy 70 eV. SIM scanning was carried

out in three ions with masses 57, 71 and 85, characteristic of saturated hydrocarbons. *N*-alkanes in the chromatogram were identified previously in the mode of the full ion current using their standard solutions. The quantitative content of *n*-alkanes was studied by the internal standard method (the internal standard – *n*-decane, 0.05 mg/cm<sup>3</sup>) [33].

### 3. Results and discussion

The mineral and chemical compositions of the initial mineral carriers are previously published by Shchemelinina et al. [34].

Cultured strains of microorganisms were immobilized on the sorbents, and their surface was studied using a scanning electron microscope. As seen in Fig. 1, there are clusters of Biotrin microorganisms, fixed on the surface of mineral carriers.

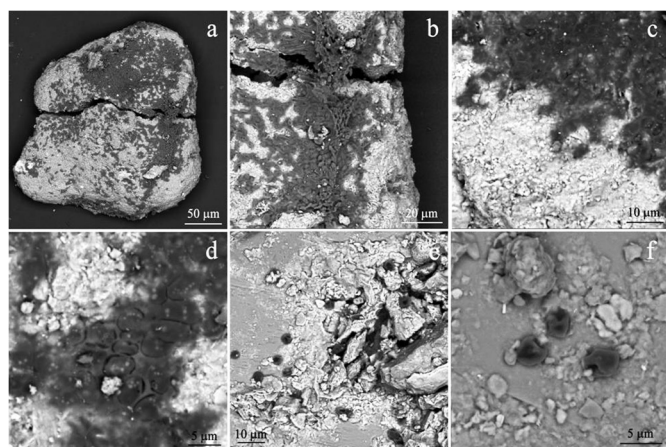


Fig. 1 SEM images of the surface of mineral carriers (light) with immobilized oil degrading organisms (dark) in the mode of backscattered electrons: a – d – *R. glutinis* yeasts, e – f – *C. vulgaris* f. *globosa* microalgae

1. ábra SEM képek az immobilizált ásványok (világos) valamint olajjal roncsolt organizmusok (sötét) felületéről visszaszórt elektronok módszerével: a – d – *R. glutinis* élesztő, e – f – *C. vulgaris* f. *globosa* microalga

The sorption was evaluated in relation to TPH of the initial sorbents and biogeo sorbents modeled. Earlier researches pointed out analcime-containing rock 551, clinoptilolite-containing clay 541-31, and glauconite-containing rock 539-40 as the most promising as sorbents and carriers for Biotrin biopreparation.

The analysis of the water in the microcosms after application of both analcime-containing rock 551, and biogeo sorbent based on it confirms the reliable high water purification levels, but variations in treatments with sorbent/biogeorbent are insignificant, and important differences are noted in sample 551. Samples of clinoptilolite-containing clay 541-31 and biogeo sorbent based on it showed the efficiency of TPH reduction. Significant differences in TPH content in both water and OMAs of 539-40 glauconite-containing sample are observed (Table 2).

Sample	TPH content in water, ppm	TPH content in OMA, mg/g
551	0.111±0.015	57±9
	0.044±0.005	250±30
541-31	0.058±0.008	100±16
	0.035±0.004	250±30
539-40	0.072±0.009	20±3
	0.024±0.003	58±9
Reference sample	0.121±0.015	-

Table 2 TPH content in the microcosms when the initial sorbents and biogeo sorbents based on them applied

Note: in the numerator – biogeo sorbent applied, in the denominator – sorbent applied. The indicated values did not exceed 1% variance for TPH.

2. táblázat Az elemi térfogatokban a TPH-tartalom jelentkezése szorbensek és biogeo sorbensek alkalmazása esetén

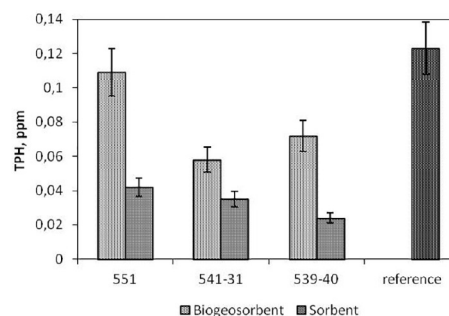


Fig. 2 TPH content in water samples when applying various sorbents and biogeo sorbents based on them

2. ábra A TPH-tartalom a vízmintákban különböző szorbensek és biogeo sorbensek alkalmazása esetén

The experiment showed (Fig. 2) that the initial samples of these sorbents exhibited adsorption activity with respect to TPH. As a result of the application of these samples into oil-contaminated water, the content of pollutant in water decreases in 4 days by 63, 71 and 80% for samples 551, 541-31, 539-40, respectively. When the biogeo sorbents based on clay and zeolite-containing rocks are applied into polluted water, water purification efficiency decreases (8, 52, 40%, respectively), which indicates a decrease in the sorption properties of mineral carriers after immobilization of microorganism cells. The decrease in the sorption properties of the biogeo sorbents is probably caused by decreasing specific surface because of adhesively fixed biomass of microorganisms. This is confirmed by experimental data on the specific surface area of sorbents and biogeo sorbents (Table 3). In almost all the cases, the specific surface area of the raw sorbents is higher than the specific surface area of the biogeo sorbents. When microorganisms are immobilized on the sorbents, the specific surface area decreases by 1.01–8.75 times.

The hydrocarbon biodegradation in samples 551, 541-31, 539-40 is 77, 60 and 65.5% for 4 days, respectively (Table 2).

Sample No.	Specific surface area, m <sup>2</sup> /g	
	without degassing	with degassing at 25 °C, 2 hours
551	13.65	8.24
	13.79	16.67
541-31	8.56	11.32
	10.60	10.03
539-40	2.17	2.72
	8.19	23.80

Table 3 Specific surface area of sorbents and biogeo sorbents

Note: in the numerator – biogeo sorbent, in the denominator – sorbent.

3. táblázat A szorbensek és a biogeo sorbensek fajlagos felülete



We identified C16-C33 *n*-alkanes in the water samples studied (Table 4).

Sample	$\Sigma C_{16-33}$ $\mu\text{g}/\text{dm}^3$	$\frac{\Sigma C_{16-23}}{\Sigma C_{24-36}}$
551	$\frac{5.54}{6.55}$	$\frac{0.22}{0.42}$
541-31	$\frac{2.28}{2.36}$	$\frac{0.15}{0.29}$
539-40	$\frac{0.7}{8.97}$	$\frac{0}{0.23}$
Reference	13.53	0.52

Table 4 Alkanes in oil-contaminated water after application of sorbents and biogeosorbents

Note: in the numerator – biogeosorbent, in the denominator – sorbent

4. táblázat Alkanák olajos vízben szorbensek és biogeoszorbensek alkalmazása után

The major part of normal alkanes covers the homological series in the range C16 to C33 with maxima of C29 and C31. Odd alkanes in the range of C25, C27, C29, C31, C33 prevailed. The ratio of light ( $\Sigma C \leq 23$ ) to heavy molecules ( $\Sigma C > 23$ ) is 0.52 (Table 4, Fig. 3).

When sorbents applied, the qualitative and quantitative distribution of alkanes is significantly different in oil-contaminated water. After analcime-containing rock 551 application (Table 4, Fig. 3A), the alkane content decreased 2.1 times compared with the reference. Mass concentrations of C28 and C30 prevailed over all other individual compounds. Light ( $\Sigma C \leq 23$ ) to heavy molecules ( $\Sigma C > 23$ ) ratio was 1.9 times lower, and the ranked homological series are dominated by hydrocarbons with the numbers of carbon atoms C27, C29, and C31.

Application of sorbent and biogeosorbent based on clinoptilolite-containing clay 541-31 reduces the amount of *n*-alkanes by more than 5 times (Table 4, Fig. 3B), but the differences within the variants are not significant. The distribution curve of the mass concentrations of alkanes in water after applying of biogeosorbent became identical to the curve after applying of sorbent.

The bulk of alkanes in water after processing with glauconite-containing rock 539-40 is represented by C17 – C33 homologues and amounts to  $8.97 \mu\text{g}/\text{dm}^3$  (Table 4, Fig. 3C), reduced by 34% relative to the reference with a reliable concentration of C27, C29, C31 homologues in the microcosm. Due to the low mass concentrations of homologs, the identification of patterns of distribution is difficult.

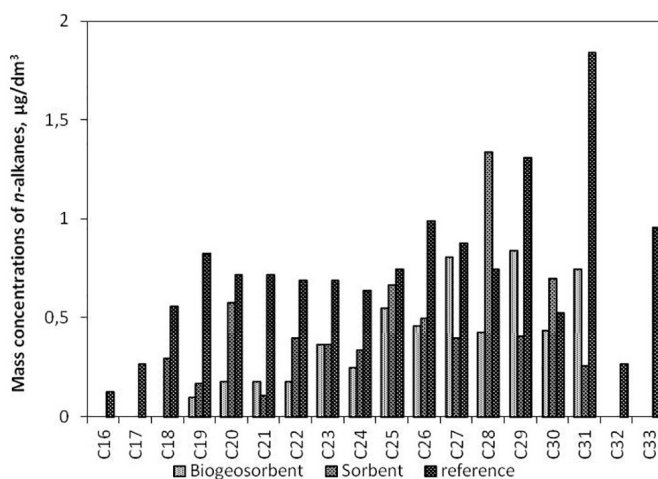


Fig.3A

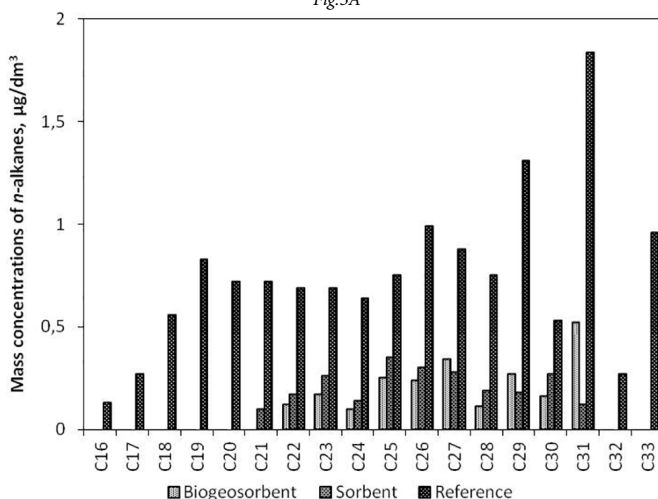


Fig.3B

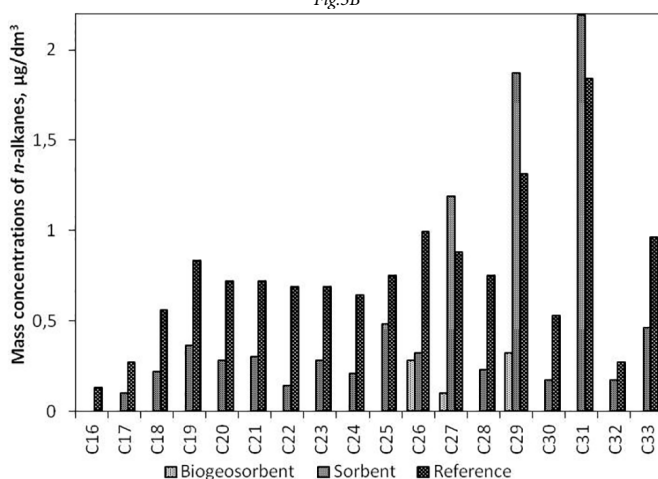


Fig.3C

Fig. 3 Distribution of mass concentrations ( $\mu\text{g}/\text{dm}^3$ ) of alkanes in the aqueous samples. A – after application sorbent 551 and biogeosorbent based on it; B – after application sorbent 541-31 and biogeosorbent based on it; C – after application sorbent 539-40 and biogeosorbent based on it  
3. ábra Az alkanák tömegkoncentrációjának ( $\mu\text{g}/\text{dm}^3$ ) megoszlása a vizes mintákban. A - 551 szorbenssel és biogeoszorbenssel kezelve; B - 541-31-es szorbenssel és biogeoszorbenssel kezelve; C - 539-40-es szorbenssel és biogeoszorbenssel kezelve

Our experiments confirm the data obtained by Netzer et al. [35] that the formation of aggregates contributed to TPH removal from the water because of accumulation and

biodegradation. Solid oil-mineral aggregates can be attached to minerals, which increase their size [27]. It was noted (Fig. 4) that TPH accumulation in the aggregates formed by biogeosorbents was significantly lower (by 77, 60, 66% for biogeosorbents modeled on 551, 541-31, 539-40 samples, respectively) than in the aggregates based on the minerals studied, which is most likely related to the biodegradation of hydrocarbons accumulated by the cells of Biotrin consortium.

In OMA sample of the analcime-containing rock 551 (Table 5, Fig. 5A), we identified C16–C32 *n*-alkanes, the total content was 11.84 µg/g, the proportion of light alkanes in the composition was 2.33. C17, C18 homologues dominated. The data indicate that the sample is capable of holding light alkanes, which under natural conditions undergo weathering processes. In OMA of 551B, the amount of alkanes is threefold decreased (3.89 µg/g), C19–C31 compounds were identified without a clear predominance of any homologs. The light ( $\Sigma C \leq 23$ ) to heavy molecules ( $\Sigma C > 23$ ) ratio was 0.57.

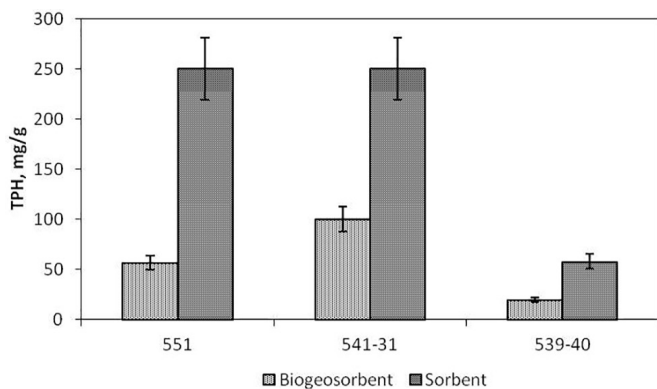


Fig. 4 TPH content in OMA  
4. ábra TPH-tartalom az OMA-ban

The decrease in the *n*-alkane content in the water of the microcosm was also accompanied by the accumulation in OMAs [26, 36, 37]. Different homolog sequences were identified in the samples.

Sample	$\Sigma C_{16-32}$ µg/dm <sup>3</sup>	$\frac{\Sigma C_{16-23}}{\Sigma C_{24-32}}$
<b>551</b>	3.89 <u>11.84</u>	0.57 <u>2.23</u>
<b>541-31</b>	5.14 <u>8.84</u>	0.34 <u>1.14</u>
<b>539-40</b>	9.11 <u>8.28</u>	0.19 <u>0.31</u>

Table 5 Alkanes in oil-polluted water after the use of sorbents and biosorbents  
Note: in the numerator – biogeosorbent, in the denominator – sorbent  
5. táblázat Alkánok olajjal szennyezett vízben szorbensek és bioszorbensek használatát után.

The major part of normal alkanes in the OMA sample based on clinoptilolite-containing clay 541-31 covers the homological series in the range of C16 – C30, the mass concentrations of C17, C19 prevail over other individual compounds. The light ( $\Sigma C \leq 23$ ) to heavy ( $\Sigma C > 23$ ) ratio was 1.14 (Table 5). In OMA of the biogeosorbent, the amount of alkanes is lower by 42% and amounted to 5.14 µg/g, the part of light alkanes is 0.34. Fig. 5B shows that the distribution of alkanes  $C > 23$  in OMA of the sorbent and the biogeosorbent is identical.

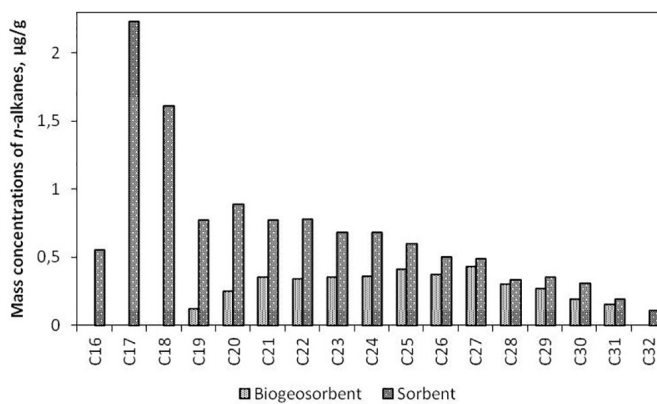


Fig. 5A

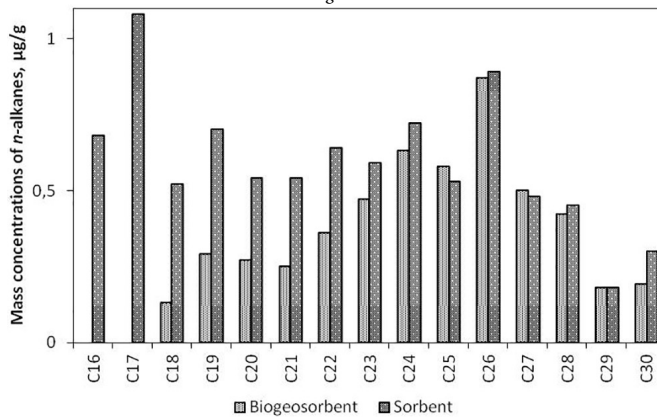


Fig. 5B

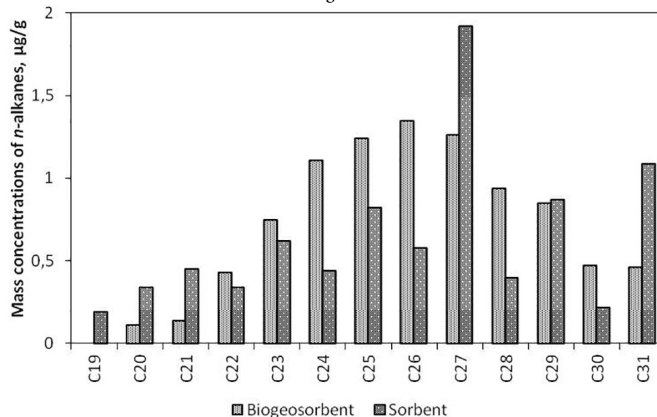


Fig. 5C

Fig. 5 Distribution of mass concentrations (µg/g) of alkanes in OMAs. A – sorbent 551 and biogeosorbent based on it; B – sorbent 541-31 and biogeosorbent based on it; C – sorbent 539-40 and biogeosorbent based on it

5. ábra Az alkánok tömegkoncentrációinak (µg/g) megoszlása az OMA-kban. A – 551 szorbenssel és biogeoszorbenssel kezelve; B – 541-31-es szorbenssel és biogeoszorbenssel kezelve; C – 539-40-es szorbenssel és biogeoszorbenssel kezelve

In OMA of sorbent and biogeosorbent of glauconite-containing rock 539-40, C19 – C31 *n*-alkanes were identified, there were no significant differences in the total content of alkanes (8.28 and 9.11 µg/g, respectively (Table 5)). However, the distribution pattern of individual compounds is different (Fig. 5C): OMA of the biogeosorbent accumulates C24–C28 compounds, while C27 homologue prevails in OMA of the sorbent.

Thus, the course of the process of biodegradation of hydrocarbons can be traced quite clearly by the distribution

of alkanes in OMAs. The ratio of normal alkanes changes, lighter alkanes degrade more quickly. The predominance of odd chains occurs when alkanes are formed in the microcosms as a result of microbiological transformation of organic matter [37]. The dominance of odd long-chain homologues of alkanes indicates that both oil and biomass characterized by a similar type of *n*-alkanes spectrum are the main sources in OMAs of biogeosorbents [39]. Probably, microorganisms convert them into the corresponding fatty acids, followed by incorporation directly into cellular lipids.

#### 4. Conclusion

Our experiments resulted in modelling of biogeosorbents, in which clay and zeolitic rocks of the European Northeast of Russia are carriers for oil-oxidizing microorganisms of Biotrin biopreparation immobilized on them. Among the samples studied, the most promising as a sorbent and carrier of Biotrin biopreparation are analcime-containing rock 551, clinoptilolite-containing clay 541-31, and glauconite-containing rock 539-40. Samples of the initial sorbents show high adsorption of hydrocarbons.

During the immobilization of microorganism cells on the surface of mineral carriers, we revealed decreasing sorption properties, but at the same time, the microorganisms supported the oxidation of hydrocarbons. The TPH biodegradation in the biogeosorbents modeled on 551, 541-31, 539-40 samples for 4 days is 77, 60 and 65.5%, respectively. The analcime-containing rock 551, clinoptilolite-containing clay 541-31 are capable of holding volatile low molecular weight alkanes.

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# Közönséges és könnyűbetonok permeabilitásának csökkentési lehetőségei

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## Abstract

Possibilities for reducing the permeability of normal and lightweight aggregate concrete

In the present study, concrete mixtures with various porosity and low water-cement ratio were investigated. In case of concrete mixtures with low water-cement ratio, there is a practical benefit to the use of porosity reducing surface treatment agents in order to reduce permeability. Normal and lightweight aggregate concrete mixtures were tested for the purpose of extended researches. Based on this information obtained, we could choose the corresponding aggregates for the concrete mixtures and the necessary tests for water penetration. Quartz gravel with 4/8 aggregate fraction as normal concrete and 4/8 aggregate fraction type 7N of expanded clay aggregate for lightweight concrete was used. Treatment layers with different behaviour in case of testing were chosen. From the point of view of selecting the concrete type, it was easy to see that the subject had available antecedents. The water-cement ratio, the paste content and the consistency of these two concrete mixtures were the same, so we could make relevant comparisons. The specimens were separated into four groups in both cases. The first group was tested with untreated surface, the other specimens applied different surface treatments. The purpose of the compressive strength tests was to measure the strength differences between normal and lightweight aggregate concrete mixtures. The next step was to measure the permeability of the concrete types with water tightness test, Karsten-tube test, German Water Permeability Test and determine the apparent porosity. Test results based on current standards were evaluated. We compared the results of different surface treatments per group and determined the best performing surface treatment per assay and overall.

Keywords: concrete, permeability, water tightness, additional water insulation, surface treatment, lightweight aggregate concrete, expanded clay gravel

Kulcsszavak: beton, permeabilitás, vízzáróság, utólagos vízszigetelés, felületkezelés, könnyűbeton, duzzasztott agyagkavics

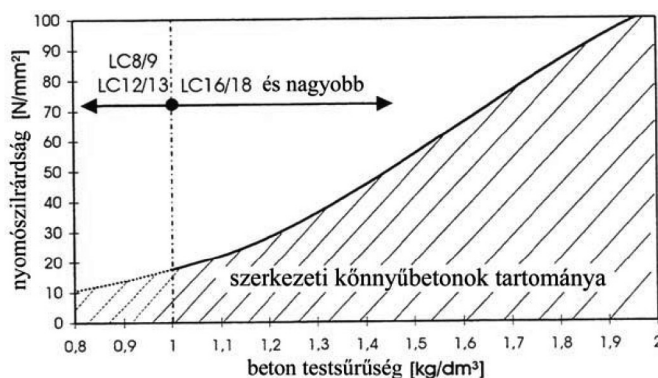
## 1. Bevezetés

A beton egyik legfontosabb tulajdonsága, a sok más anyagjellemzőjét is nagyban befolyásoló porozitás. A porozításhoz (pórusméret eloszlás, teljes és látszólagos porozitás) szorosan köthető továbbá a beton élettartama, tartóssága.

Közelítésként alkalmazható, hogy egy térfogatszázalék pórustartalom növekmény kb. 5 % nyomószilárdság-csökkenést eredményez. A különféle károsító anyagok is a kapilláris pórusokon keresztül jutnak a betonba, illetve a környezeti hatásokból származó betonkárosodásokat is jelentősen befolyásolja a beton porozitásának mértéke, jellege. Fontos ezért a porozitás ismerete, ami többféle módszerrel is vizsgálható.

A pórusok százalékos arányát mérhetjük közvetlenül, de a látszólagos porozításra következtethetünk közvetett módon, a beton víz- vagy gázáteresztő-képességének mérésével is. Bizonyos vizsgálatok azt mutatják, hogy a beton levegő- és vízáteresztő képessége kiválóan jellemzik a betonnak a gáz-, illetve folyadékállapotú agresszív közegek behatolásával szembeni ellenállóképességét, ami így egy adott beton tartósságának jellemző mértéke lehet. [1] Az építőanyagok

testsűrűségének csökkentése (lehetőleg a szilárdság minél kisebb mértékű csökkenése mellett) fontos eszköze az önsúlycsökkentésnek, így karcsúbb, esztétikusabb megjelenésű szerkezetek építhetők, ami kisebb anyagfelhasználást eredményez. A lehetséges támaszköz (l) a szilárdság ( $f_c$ ) és a testsűrűség ( $\rho$ ) hányadosával egyenesen arányos:



1. ábra A könnyűbeton szilárdságának változása a testsűrűség függvényében [3]

Fig. 1 The compressive strength of lightweight aggregate concrete in function of the body density [3]

Ez az arányszám a betonok testsűrűségének csökkentésével, illetve szilárdságának növelésével jelentősen javítható. Könnyűbeton széles szilárdsági és testsűrűségi tartományban készíthető. A kisebb testsűrűségű könnyűbetont hőszigetelő célra készítik, LC 16/18 szilárdsági osztálytól felfelé pedig szerkezeti betonként, egészen LC 80/88-ig. [2]

Az általam vizsgált könnyű adalékanyagos könnyűbeton és a közönséges betonok közt alapvető különbség az erőátadódás módja, ugyanis a könnyű adalékanyagot tartalmazó könnyűbetonoknál a teherhordásban nagyságrendileg nagyobb arányban vesz részt a cementkő, mint az adalékanyag.

## 2. Célkitűzés

A kutatás célja annak elérése volt, hogy a már jól működő összetételnek olyan alternatíváját dolgozzuk ki, ami képes maradéktalanul teljesíteni a vele szemben támasztott követelményeket, azaz nagy nyomószilárdság és kis vízbehatolás jellemezze a minél kisebb testsűrűség elérése mellett, továbbá költséghatékony legyen. A kutatás végső célja egy hídgerendákhoz megfelelő betonösszetétel kifejlesztése könnyű adalékanyagok alkalmazásával, amin belül mi foglalkoztunk a felületi porozitás és permeabilitás problémakörével.

Korábban végeztek már vizsgálatokat a kutatás előzményeként e kutatás alapjául szolgáló betonösszetételekkel, ezek közül a legnagyobb szilárdságot eredményezőből kiindulva kezdtük meg egy saját összetétel kidolgozását, az eredeti betonösszetétel ugyanis amellelt, hogy kiválóan megfelelt minden követelménynek, sőt messze túl is lépte azokat (pl. a nyomószilárdságot), gazdaságtalannak bizonyult a felhasznált anyagok magas költségei miatt.

Ezért arra törekedtünk, hogy a könnyűbeton szilárdságának és környezeti hatásokkal szembeni ellenállásának változása ne legyen arányos a keverék előállításának költségeivel, azaz nagyobb arányban csökkenjen a beton bekerülési költsége, mint a minősége. A másik kritikus pont a tartósság, ami a nagy magasságú vagy fesztávú szerkezeteknél is kiemelt fontosságú. Hidak esetén sarkalatos pont a felhasznált beton vízzárósága, kloridionok behatolásával szembeni ellenállósága, illetve fagyállósága. Amennyiben a vizsgált beton eleget tesz a vízzárósági követelményeknek valószínűleg a fagyállósága is megfelelő lesz, ugyanis csekély felületi porozitás esetén a víz kis mennyiségben jut a szerkezetbe, így kisebb valószínűséggel okozhat kárt az esetlegesen bejutott és megfagyó víz és egyéb vegyi ágensek.

Az általunk készített kísérleti terv tartalmazza két lényegesen eltérő betonösszetétel keverését, az ezekből készült próbatetek permeabilitásának kísérleti mérését GWT-készülékkel, Karsten-csővel módszerrel, illetve a látszólagos porozitás és a nyomószilárdság mérését. Fontos volt szem előtt tartani, hogy a betonok porozitása lényegesen eltérő legyen, amit elsősorban a szemcseporozítással szabályoztuk, ezért készítettünk egy betonkeveréket kvarckavics adalékanyaggal, egyet pedig igen porózus (felületén nyitott pórusokkal) duzzasztott agyagkavics adalékanyaggal.

A különböző betonösszetételekből készült próbatetek, a vizsgálatokat megelőzően eltérő felületkezelési eljárásokat alkalmaztunk (a gyártó által megadott alkalmazási útmutató

alapján), amivel a permeabilitás javítására törekedtünk, ezeknek az eredményességét összevetettük az etalon próbatetekkel (közönséges beton) és a felületkezelés nélküli könnyűbeton próbatetekkel.

## 3. Felhasznált anyagok, kísérleti és vizsgálati eljárások

Vizsgálataink során az etalon, kvarckavics adalékanyagos beton mellett duzzasztott agyagkavics könnyű adalékanyaggal készült betonnal foglalkoztunk. Fontos megemlíteni, hogy a keverések során felhasznált cement, a kvarc adalékanyag és a duzzasztott agyagkavics is külön-külön ugyanazon szállítmányból származott, így az anyagminőség egyenletes és az eredmények jól összehasonlíthatók. A duzzasztott agyagkavics gyártáshoz első lépésként üledékes, duzzadóképes, finom eloszlásban szerves anyagot tartalmazó agyagot bányásznak ki, az agyagot finomra őrlik, majd homogenizálják, granulálják és apró darabokban a forgó klinker kemencében 1200 °C hőmérsékleten kiégetik. Itt először az agyagdarabok megszáradnak, majd a külső felület megolvad. A hő befelé haladásával a belső rész szervesanyag tartalma kiég, a keletkező gázok az agyagszemeket felfújják, majd a köpenyt felszakítva távoznak. Így a kihűlt golyó külső kemény klinkeres héjjal és egy pórusos belső szerkezettel rendelkezik. [5] A duzzasztott agyagkavicsot többféle sűrűségben, többféle szemcse nagyságban, törten, vagy egészben, vagy a kettő keveréként is állítják elő és forgalmazzák. A duzzasztott agyagkavics adalékanyagként sok pozitív anyagtulajdonsággal bír, számunkra különösen fontos a kis testsűrűségén felül, a közel gömb alakja és szilárd külső burkolata, ami hozzájárul a nagyobb betonszilárdság elérhetőségéhez. [6]

Az 1. számú betonkeverék (kvarc adalékanyag) előállításához a korábbi kutatásokat alapul véve, a legnagyobb nyomószilárdságú könnyűbeton összetételből indultunk ki és cseréltük az adalékanyagok kvarcra (a megfelelő korrekciók elvégzése mellett).

A 2. számú betonkeverékhez már az új hagyományos keverék adatait vettük alapul. Az alkalmazott vízmennyiség kiinduló értéke az etalon, azaz a kvarckavics adalékanyagos összetétel vízmennyisége volt, ezt a könnyű adalékanyag által felvett víz mennyiségével korrigáltuk. Ebből kiindulva a receptet addig finomhangoltuk, amíg a két betonkeverék megegyező konzisztenciával nem bírt, a frissbeton konzisztenciáját terülméréssel ellenőriztük.

Három gyártó eltérő hatásmechanizmusú felületkezelő termékeit választottuk ki a vizsgálatokhoz, ezek alapján soroltuk be a próbateteket négy csoportba:

Az I-es jelű minták mindkét betonkeveréknél a kontrolcsoportot jelentik, ezek a próbatetek nem estek át semmilyen felületkezelési eljárásos.

A II-es számú felületkezelőszer használata az építőiparban elterjedt, bár más területeken. Leginkább ipari padlók felületkeményítésére használják, mivel egy ellenálló réteget képez a betonok felületén, ezáltal megvédi a külső fizikai és kémiai behatásoktól. Esetünkben azért volt releváns a használata, mert kiváló pórustömítő is. Egyetlen hátránya a másik kettőhöz képest, hogy hosszan tartó, vízzel való



érintkezés hatására kismértékű kioldódás jelentkezhet a betonfelületen. [7]

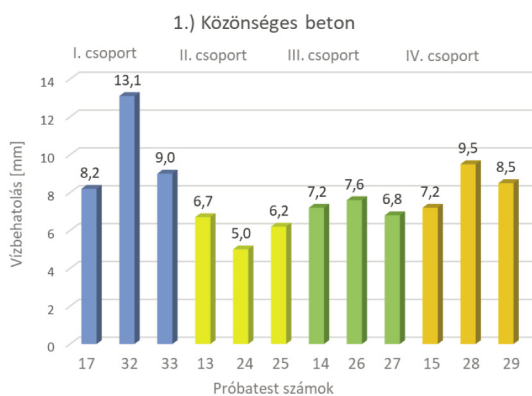
A III-as számú felületkezelőszer egy szilíciumvegyületeken alapuló diszperzió. Betonfelületeken alkalmazva hidrofób hatást fejt ki és a szennyeződésekkel szemben is ellenállóbbá válik. Ezáltal a beton időjárásállóbbá válik és csökkenti a vízbehatolás mélységét.

A IV-es számú felületkezelőszer elsősorban előregedett vagy hibás betonszerkezetek javítására használják. A vízzel telített betonszerkezetben kémiai reakció útján fejt ki hatását, a pórusokba behatolva kikristályosodik.

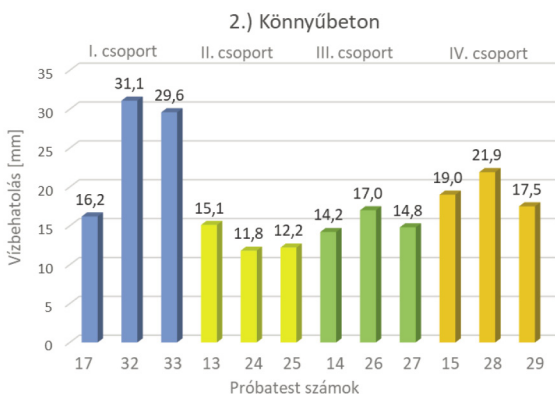
Minden elvégzett vizsgálatnak 3 szabványos 150 mm élhosszúságú próbatestet vetettünk alá az egyes felületkezelési csoportokból, keverékenként, azaz összességében 24 próbatestet eredményeiket használtunk fel minden vizsgálat kiértékelésénél. A nyomószilárdsági értéket 28 napos korban, az MSZ 4798:2016 szabvány szerint vizsgáltuk. [8] A közönséges betonkeverék C60/75, a könnyűbeton esetében LC 35/38 jelűek az említett szabvány szerint.

#### 4. Eredmények

A vízzáróság vizsgálatból kapott eredményeket az 2. és 3. ábrán tüntettük fel a mért értékekkel együtt.

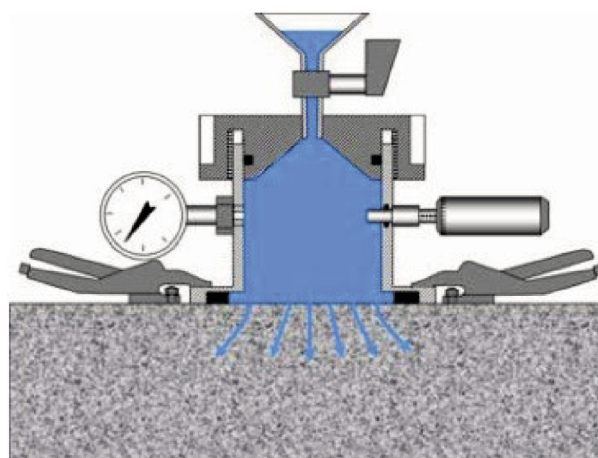


2. ábra Közönséges beton vízbehatolás értékei  
Fig. 2 Water penetration of normal weight concrete

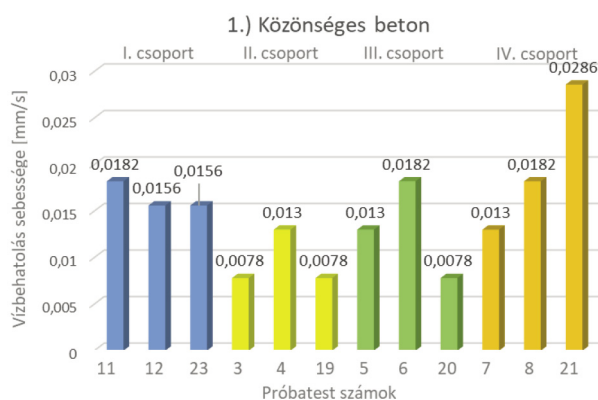


3. ábra Könnyűbeton vízbehatolás értékei  
Fig. 3 Water penetration of lightweight concrete

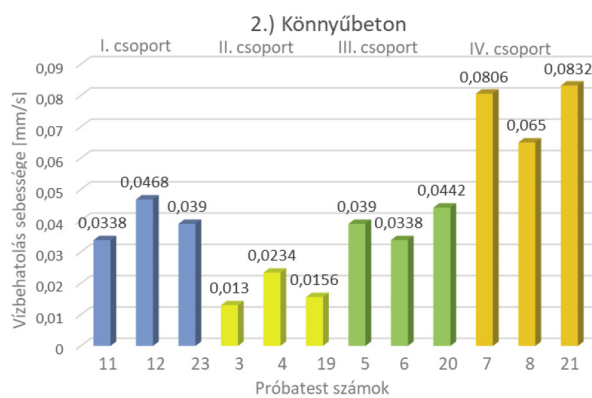
A GWT kísérleti összeállítása a 4. ábrán, a kapott eredmények az 5. és 6. ábrán láthatóak.



4. ábra GWT permeabilitásvizsgáló készülék [4]  
Fig. 4 GWT appliance [4]



5. ábra Közönséges beton GWT vizsgálati eredményei  
Fig. 5 Normal weight concrete GWT results



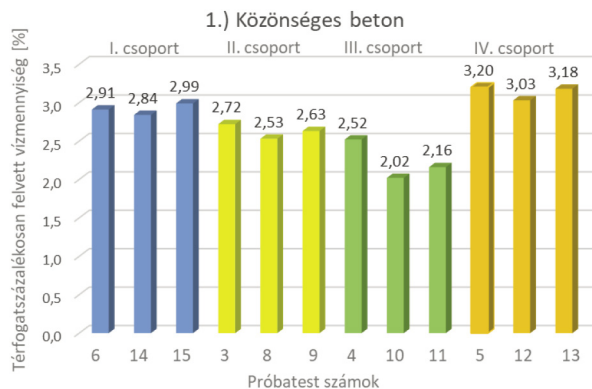
6. ábra Könnyűbeton GWT vizsgálati eredményei  
Fig. 6 Lightweight concrete GWT results

Az említett ábrákon megfigyelhetők a IV. felületkezelési csoport kiugróan magas értékei. Erre a kezelőanyag maga után hagyott vékony, felületi rétegének nagy rövid idejű vízfelvétele lehet a magyarázat. A korábbi vízzárópadon végzett vizsgálattal együtt szemlélve ezek az értékek arra mutatnak, hogy a porózus felületi rétegen túl a beton felülete alá hatolva fejt ki pórustömítő hatását, ezért a rövid időtartamú víznyomás és vízbehatolás ellen végzett vizsgálatok félrevezetőek lehetnek ebben az esetben.

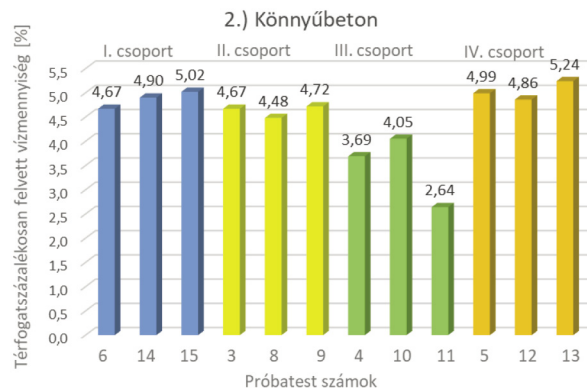
A Karsten-csöves vizsgálati eredmények a 7. és 8. ábrán láthatók, ahol a könnyű adalékanyagos beton esetében jól

érvényesül, a felületen lévő adalékanyag szemcsék pórusait eltömítő felületkezelőszerek hatása.

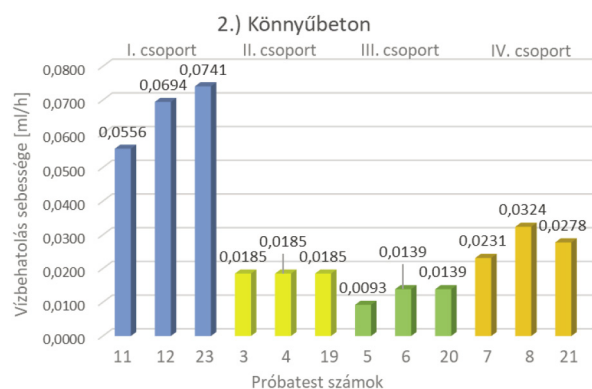
nem képez kovasavat, tartós víz hatására képes újra feloldódni és lemosódni a felületről.



7. ábra Közönséges beton Karsten-csöves vizsgálat eredményei  
Fig. 7 Karsten-tube test of normal weight concrete



10. ábra Könnyűbeton térfogatszázalékos vízfelvétele  
Fig. 10 Water absorption of lightweight concrete by volume



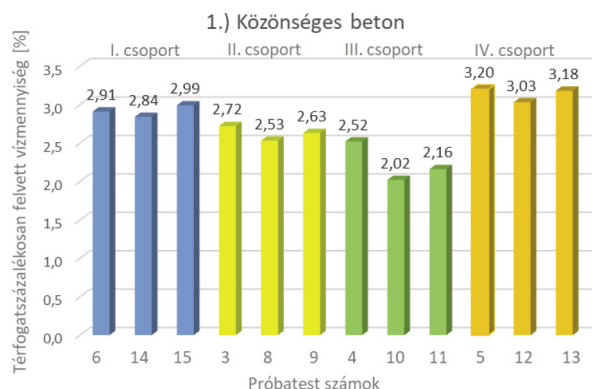
8. ábra Könnyűbeton Karsten-csöves vizsgálat eredményei  
Fig. 8 Karsten-tube test of lightweight concrete

Az látszólagos porozításvizsgálat során az egyes próbatestek által térfogatszázalékosan felvett víz mennyiségét mértük, ezek az eredmények láthatók a 9. és 10. ábrán.

## 5. Konklúzió

A kiértékelés alapján kijelenthető, hogy könnyű adalékanyag betonnál van létjogosultsága a pórustömítő felületkezelő szerek alkalmazásának alacsony víz-cement tényező mellett is. A vizsgálatok során kapott eredményekből látható, hogy az egyes kezelések hatása könnyű adalékanyag betonnál fokozottan érvényesül.

Összességében a vizsgálatok rámutattak, hogy vízfelvétel és vízzáróság szempontjából is előnyösebb a II. és III. számú szer a IV.-nél. A mérési eredmények alapján a III. számú felületkezelőszert javasolt további vizsgálatokhoz és ilyen területen történő alkalmazásra, jobb tartóssága miatt. A kutatás során tapasztaltak arra mutattak rá, hogy a hosszabb ideig tartó vizsgálatok és a nyomás alatt végzett vizsgálatok valószínűleg relevánsabb értékeket adnak, mint pl. a gyors lefolyású GWT vizsgálat. Ezért az ilyen irányultságú vizsgálatokhoz a továbbiakban ezek a módszerek/eljárások lehetnének mértékadók.



9. ábra Közönséges beton térfogatszázalékos vízfelvétele  
Fig. 9 Water absorption of normal weight concrete by volume

A IV. felületkezelési csoportnál ismételtén mért nagy értékek a korábban részletezett fizikai tulajdonságoknak tudhatók be. A jövőben érdemes lehet a habarcszerű réteg eltávolítása után megismételni a kísérletsorozatot, mivel a vékony réteg nagy porozitása miatt nagymértékben torzíthat az eredményeken.

Ennél a vizsgálatnál a III. felületkezelési csoportnál enyhe visszaoldódás volt tapasztalható. Az a vízűveg mennyiség, ami

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## A TETŐTÉR BEÉPÍTÉS KÖNNYEBBEN

Budapest – 2019. szeptember 25.

**Idén március 15-től változás történt a tetőtér-beépítésére vonatkozó szabályozásokban. Számos kedvező változások közül az egyik, hogy már a beépítési százalékba nem kell beleszámítani a tűzvédelmi előírások teljesítését szolgáló építményeket és a felvonót, valamint ezek a kötelező zöldterületből is elvehetnek. De mindez csak a már meglévő tetőterekre érvényes - új építés esetén nem!**

Az építési törvény módosításával már olyan tetőterek beépítésére is lehetőség nyílik, amelyekre korábban nem volt. Ez nem csak családi házaké, hanem országosan minden tetőterre alkalmazható. **Már a magastetős** régi bérházak, műemléki épületek padlásterői is beépíthetőek lettek, ráadásul nemcsak lakhatási célra. Az építkezés az OTÉK értelmében nem számít bővítésnek, ha a beépítéssel nem nő az épület térfogata – azaz nem változik a tető formája, valamint nem kerül hozzáépítésre semmi, pl. felvonó, lépcsőház. Ez még nem jelenti azt, hogy tűzvédelmi vagy egyéb szempontból ne kellene a hasznos alapterület bővítését a vonatkozó előírások szerint értékelni.

Látszólag úgy néz ki, hogyha nem bővítjük az épületet, az esetek többségében mindehhez **sem építési engedély sem egyszerű bejelentési eljárás sem kell.** Ennek megítélésében igen óvatosan kell eljárni, ugyanis ha az építési tevékenység műszaki tartalma alapján bármely hatóság részéről eljárást igényel (pl. lift, jelző oltó berendezés tervezés), vagy eltérést kell kérnünk a vonatkozó előírásoktól (építési, tűzvédelmi, műemlékvédelmi, stb.) akkor persze mindez nem állja meg a helyét. Meglévő épület esetében igen ritka, hogy minden jelenlegi előírás betartható. Ha engedélyekre nem is, de *kivételi tervre engedélyt nem igénylő esetekben is szükség van*, ha a Kivételi kódexben meghatározott feltételek fennállnak.

Fontos továbbá, hogy **az új szabályozás nem érinti az Országos Tűzvédelmi Szabályzatban (OTSZ) meghatározott követelményeket, amelyeket továbbra is kötelező betartani.**

### TŰZVÉDELMI ELŐÍRÁSOK VÁLTOZÁSA

Korábban megeshetett, hogy a tűzvédelemhez szükséges építmények (pl. menekülésre szolgáló lépcsőház, felvonó) létrehozása túllépte volna a telek maximális beépítési százalékát. Mostantól ezek a zöldterületből is elvehetnek, így egy újabb szabályozási engedmény teszi lehetővé a tetőterek beépíthetőségét, ami több lakásos társasházak esetén költséghatékonyságot jelent. Arra azonban figyelni kell, hogy a tűzvédelmi előírások teljesítését szolgáló építmények csak a telek beépíthető részére kerülhetnek. A **hozzáépítés**, még egy tűzvédelmi lépcső esetén is bővítést jelent, amit kötelező bejelenteni, vagy engedélyeztetni!

### MILYEN HŐSZIGETELÉS ALKALMAZHATÓ A TETŐTEREK ESETÉBEN?

A magastetők szigetelésénél itthon leggyakrabban kőzetgyapot, vagy üvegyapot szálás szigetelőanyagokat szokás használni. Kedvező tulajdonságain túl azért is, mert tűzvédelmi szempontból nem érinti korlátozás a beépíthetőségüket.

Az OTSZ ugyan az egyalakos lakó és alacsonyabb kockázati osztály besorolású épületek esetében alacsony tűzvédelmi osztály besorolású szigetelés használatát is megengedi, de ettől függetlenül érdemes olyan szigetelő anyagot választani, amely egy tüzeset során jobban teljesít. Az alacsony tűzvédelmi osztály besorolású hőszigetelő anyagokkal az a probléma, hogy éghető anyagok, melyek tűz esetén ko-

moly problémákat okozhatnak, beépíthetőségüket a tűzvédelmi előírások lényegesen korlátozzák. Ezért magasabb kockázati osztályba sorolt épületeknél nem is használhatók. **Mindig ellenőrizzük, hogy a szigetelőanyag teljesítmény nyilatkozata milyen tűzvédelmi osztályt tartalmaz**, az megfelel-e arra célra amire használni kívánjuk.

A ROCKWOOL kőzetgyapot szigetelő anyagai nem éghetőek, tüzeset során számottevő füstöt nem fejlesztenek. Vannak a családi házaknál tetőszerkezet szarufái közé akár utólag is beépíthető megoldások, és ezek például bármelyik budapesti belvárosi magasépület, bérház tetőbeépítésénél is alkalmazhatóak.

### ALÁTÉT FÓLIA

Az alátét fóliáknak csapadék és a szél ellen is védelmet kell nyújtania a megfelelő hőszigetelési hatékonyság érdekében, de tűzvédelmi szempontból is sokat számít, hogy melyet választunk. A legtöbb fólia E-tűzvédelmi osztályú, könnyen éghető anyag. Az OTSZ szerint, ez alatti tűzvédelmi besorolású fólia (F tűzvédelmi osztály) nem használható, és ezt a legtöbb termék teljesíti is. Kaphatóak azonban olyan fóliák, amelyek B osztályúak, azaz jóval nagyobb tűzvédelmet nyújtanak.

### A TETŐSZERKEZET TŰZVÉDELMI KÖVETELMÉNYEI

Az OTSZ előírása szerint **a tetőszerkezetnek, a szerkezet egészére vonatkozóan, magas A1-A2-es tűzvédelmi osztály besorolást kell teljesítenie.** Utólagos tetőtér-beépítése során tehát nem csak a szigetelésnek, hanem a szerkezetnek is teljesíteni kell az OTSZ-ben előírtakat! Ez korántsem egyszerű kérdés, mivel bár az egyes építési anyagok külön-külön általában rendelkeznek tűzvédelmi vizsgálati eredményekkel, de ha összeépítünk két terméket már nem olyan egyszerű megállapítani az adott szerkezet tűzvédelmi osztályát és tűzállósági teljesítményét. **A tűzvédelmi osztály besorolás szinte mindig függ attól, hogy milyen tűzvédelmi osztályú hőszigetelő anyagot építünk be** a tetőszerkezetbe. Bár alacsonyabb kockázatu épületeknél megoldható mindez alacsonyabb tűzvédelmi osztályú anyagokkal is, de sokkal jobb, ha már ezekben az esetekben is nem éghető szálás szigeteléseket alkalmazunk, amik nem csak tűzvédelmi, hanem például akusztikai szempontból is előnyösebbek.

Végezetül tartsuk észben, hogy jövőre a tűzvédelmi **előírások megváltoznak.** 2020. január 22-től már a módosított OTSZ szerint kell majd tervezni az épületeket!

További sajtóinformáció:

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# ESCM

EUROPEAN SOCIETY  
FOR COMPOSITE MATERIALS

THE SCIENTIFIC,  
ENGINEERING  
AND INDUSTRIAL  
COMMUNITY  
INVOLVED WITH  
COMPOSITE  
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## THE SOCIETY

### OBJECTIVES OF THE SOCIETY

ESCM is a European, non-governmental, non-profit scientific and engineering organisation with the following objectives:

- To encourage the free interchange of information on all those aspects related to composite materials which are of interest to the scientific and engineering community.
- To provide a Europe-wide forum for the discussion of such topics, e.g. by organising the ECCM (European Conference on Composite Materials) and more specialised symposia related to composites.
- To guide and foster the understanding and utilisation of the science and technology of composite materials.
- To promote European co-operation in the study of topics in composite materials science and technology.
- To promote liaison with engineering and scientific bodies throughout Europe with similar aims and to serve as a facilitator for communication between such bodies.
- To foster an environment for timely and cost-effective research, development and implementation of advanced technology in composites.
- To encourage the education of young specialists in the disciplines supporting composite materials science and technology.
- To recognise individuals of outstanding achievement in the science, technology, engineering, and application of composite materials.