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# Cement Hydration with Ultrasound Treated Clinoptilolite

**Vytautas Sasnauskas\*, Gediminas Rinkevičius,  
Deividas Martinavičius, Danutė Vaičiukynienė, Ernestas Ivanauskas**

Kaunas University of Technology, Faculty of Civil Engineering and Architecture  
Studentu st. 48, LT-51367 Kaunas, Lithuania

**Aras Kantautas**

Kaunas University of Technology, Faculty of Chemical technology  
Radvilenu st. 19, LT-50254 Kaunas, Lithuania

\*Corresponding author: [vytautas.sasnauskas@ktu.lt](mailto:vytautas.sasnauskas@ktu.lt)

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There are many cement replacement materials and one of them is zeolites. Zeolites are crystalline solids structures made of silicon, aluminum and oxygen that form a framework with cavities and channels inside where cations, water and/or small molecules may reside. In this study natural zeolite clinoptilolite was used. Clinoptilolite is the most popular natural zeolite mineral with the chemical formula  $(\text{Na}, \text{K}, \text{Ca})_{23}\text{Al}_3(\text{Al}, \text{Si})_2\text{Si}_{13}\text{O}_{36} \cdot 12\text{H}_2\text{O}$ . The present paper shows the results of using ultrasound treated clinoptilolite as Portland cement replacement material. The duration of ultrasound treatment was 5 min, 10 min, and 20 min. Results showed that the XRD of ultrasound-treated clinoptilolite slightly differs in comparison to conventional clinoptilolite. The cement samples with 5% and 10% clinoptilolite substitute provide the strength increase, 30% significantly reduces the strength compared to control samples. The heat measurements of Portland cement paste hydration, containing clinoptilolite, showed that the clinoptilolite slightly increases the duration of hydration, but hydration temperature is lower than in the controls samples. The experimental results suggest that ultrasound-treated clinoptilolite positively influence cement hydration processes, consolidation kinetics, CSH formation; the mechanical strength of the samples is increased. Typical content of Portland cement substituting does not exceed 20% of mass of Portland cement in samples. Reducing the consumption of Portland cement with substituting it with ultrasound treated clinoptilolite is preferred for reasons of environmental protection.

**KEYWORDS:** Cement hydration, clinoptilolite, ultrasound, zeolite.

## Introduction



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Pressure increase changes with pressure decrease in half-wave of the liquid phase during ultrasonic waves' propagation in liquids. The pressure pulsation amplitude becomes quite large and quickly growing the gas - vapor mixture filled bubbles begin to form in pressure decrease areas in the liquid at high energy intensity ( $> 2.5 \text{ W/cm}^2$ ). The bubble volume decreases very quickly and they collapse at pressure increase phase. This phenomenon is called cavitation. Shock wave forms in bubble collapse place.

It is possible to observe the whole range of physical - chemical phenomena, if bubbles' collapse intensively takes place in liquid. Physical - chemical phenomena are: solid surface destruction (if aluminum foil will be placed to acoustic cleaner, so after a few minutes the holes will appear, and even after a while it will be completely destroyed in the smallest particles), mixing of immis-

cible liquids (e.g., oil with water), acoustic cavitation, intensive mixing, solid and liquid material dispersion, polymerization or depolymerization reactions under certain conditions, and a number of other phenomena.

Reduction of carbon dioxide emissions into the environment is currently one of the most important objectives in cement industry, and at the same time in construction industry. More production and use of cements with a part of clinker, replaced by mineral additives, i.e., limestone, pozzolan, slag, zeolite, etc. are the main means of this problem solving.

Clinoptilolite is the most common natural zeolite mineral with the chemical formula  $(\text{Na}, \text{K}, \text{Ca})_{2-3}\text{Al}_3(\text{Al}, \text{Si})_2\text{Si}_{13}\text{O}_{36} \cdot 12\text{H}_2\text{O}$  (Brek, 1976).

Application of ultrasound can influence the size and morphology of the crystals, crystallization time and the crystallinity of the zeolites (Askari et. al., 2013).

(Yeong et. al., 2014) showed that the crystallization time was reduced by introducing ultrasonic pre-treatment from 7 days to 3 days, without affecting the structure, morphology and  $\text{CO}_2$  adsorption capacity of the resulting zeolite-T.

(Solyman et. al., 2013) revealed that sonication of parent zeolite samples affects unit cell dimensions and their crystal size. FTIR-spectroscopic analysis indicated that sonication may decrease the pore opening and cause framework structure defects. TEM and SEM micrographs showed that sonication broke-up and re-ordered zeolite crystals with longer time resulted in a different morphology relative to parents and also change the particle size.

NaP zeolite nano crystals were synthesized by sonochemical method at room temperature with 3 h of crystallization time. The effect of ultrasonic energy and irradiation time showed that the crystallinity of the powders decreased with increasing sonication energy, but phase purity remained unchanged. Sonication energy facilitates the formation of active radicals which are responsible for rapid crystallization of zeolite phase (Pal et. al., 2013).

Clinoptilolite may be used as pozzolan due to its reactive  $\text{SiO}_2$  content and ion exchange properties. Strength development and other properties of cements depending on the percentage of zeolite blend ratios were researched and the results were found positive in scientific studies performed on the usability of natural zeolite as cement blend material (Yilmaz et. al., 2007).

The use of clinoptilolite in the mortars increases the strength values. Clinoptilolite replacement decreases water absorption and porosity of the mortars. Clinoptilolite incorporated mortars show better durability than of the control mortar. The exploitation of clinoptilolite can lead to a considerable economic benefit (Bilim, 2011).

The evolution of phase contents showed that the addition of natural zeolites accelerates the onset of  $\text{C}_3\text{S}$  hydration and precipitation of CH and AFt. Kinetic analysis of the consumption of  $\text{C}_3\text{S}$  indicates that the enveloping of C-S-H layer is thinner and/or less dense in the presence of alkali-exchanged clinoptilolite pozzolans. The zeolite pozzolanic activity is interpreted to depend on the zeolite exchangeable cation content and on the crystallinity. The addition of natural zeolites alters the structural evolution of the C-S-H product. Longer silicate chains and lower C/S ratio are deduced from the evolution of the C-S-H *b*-cell parametre (Snellings et. al., 2010).

The most significant effects are in reduction in chloride permeability, a significant reduction in expansion due to alkali-aggregate reaction, and an improved resistance to acid and sulfate attacks, all of them are related to the overall densification of the microstructure, alkali-binding capacity of zeolite-blended cement pastes, and pozzolanic consumption of calcium hydroxide component of portland cement hydration in the paste (Jana, 2007).

Utilization of mineral additives in concrete increases the durability of concrete. The mechanical and physical properties of concrete improve the usage of zeolite, fly ash and ground granulated blast furnace slag. Ettringite and ASR gel formation in the microstructure of the composite against

sulfate attack was limited with the usage of zeolite, fly ash and ground granulated blast furnace slag (Karakurt, Topçu, 2011).

Blended cements containing high volume of natural zeolite were studied there. Hydration characteristics and paste microstructure were investigated also. No free  $\text{Ca(OH)}_2$  in pastes at the end of 28 days of hydration was observed. Crystal structure of zeolite completely decomposed at the end of 28 days. Similar 28-day compressive strength to that of reference Portland cement was found (Uzal, Turanlı, 2012).

Hydration heat development in blended cements containing natural zeolite was analyzed. Natural zeolite accelerates the onset of  $\text{C}_3\text{S}$  hydration and boosts the first phase of  $\text{C}_3\text{A}$  hydration. The second phase of  $\text{C}_3\text{A}$  hydration gains on importance with the increasing zeolite dosage. Effectiveness of natural zeolite as a binder decreases with the increasing dosage when its content is higher than 10% (Tydlitát, Zákoutský, Černý, 2014). Modified zeolite additive increases the compressive strength. It is related to active  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  present in the modified zeolite (Vaičiukynienė et. al., 2013). The aim of this research is to determine the influence of ultrasound treated clinoptilolite on cement hydration.

## Methods

A Portland cement of CEM I 52.5R type with a Blaine surface specific area of  $370 \text{ m}^2/\text{kg}$ , its mineral composition:  $\text{C}_3\text{S} = 50.7 \%$ ;  $\text{C}_2\text{S} = 18.5 \%$ ;  $\text{C}_4\text{AF} = 14.2 \%$ ;  $\text{C}_3\text{A} = 9.7 \%$ , initial binding of 130 min, finish after 215 min, bending length after 28 days of 8,1 MPa, compressive strength of 57,6 MPa was used for all mixes.

Physical properties of investigated clinoptilolite are: bulk density is  $2370 \text{ kg/m}^3$ , specific surface is  $144 \text{ m}^2/\text{g}$ , purity is not less than 90%. Chemical composition:  $\text{SiO}_2 = (71.5\%)$ ,  $\text{Al}_2\text{O}_3 = 13.1\%$ ,  $\text{Fe}_2\text{O}_3 = 0.9\%$ ,  $\text{TiO}_2 = 0.2\%$ ,  $\text{CaO} = 2.1\%$ ,  $\text{MgO} = 1.07\%$ ,  $\text{P}_2\text{O}_5 = 0.033\%$ ,  $\text{K}_2\text{O} + \text{Na}_2\text{O} = 5.03\%$ ,  $\text{F} = 0.025\%$ .

The X-ray powder diffraction data was collected by a DRON-6 X-ray diffractometer with Bragg-Brentano geometry using Ni-filtered Cu  $K\alpha$  radiation and graphite monochromator, operating with the voltage of 30 kV and emission current of 20 mA. The step-scan covered the angular range of  $2^\circ - 70^\circ$  in steps of  $2\theta = 0.02^\circ$ .

Specific powder surface was measured by Blaine method (EN 196-6:2010). The cement paste hydration temperature measurements were performed with 8-channel USB TC-08 Thermocouple Data Logger (temperature measurement range from  $-270$  to  $+1820 \text{ }^\circ\text{C}$ ).

Ultrasonic treatment was carried out by BANDELIN electronic UW3400 device with 200 W of power. Particle size distribution and specific surface area were determined by "Mastersizer 2000" instrument from Malvern. Red light was produced by helium-neon laser and blue light was obtained from a solid phase source.

Sample constant flow was steady and the ratio of water and solid material was constant and equal to  $W/S = 0.35$  during all test. The compositions differed by the contents of Z0, Z1 or Z2: 0%, 5%, 10%, 20% and 30% mass. Formed test samples were hardened for 28 days and 90 days. The test procedure of hardened cement paste compressive strength was applied according to the EN 196-1.

Toni Technik 2020 press was used to determine mechanical characteristics of the samples.

## Results and discussions

Clinoptilolite was used as a substitute for cement; it contains heulandite and quartz in addition to the basic mineral clinoptilolite (Fig. 1). Zeolite water suspension was ultrasonically treated for 0, 5 min, 10 min and 20 min. It was determined that increased 1,000 nm peak after the dispersion is characteristic to heulandite and decreased 0.316 nm peak is attributed to clinoptilolite (Fig.1.).

The results of granulometric analysis showed that the particle size of the clinoptilolite depends on the ultrasound processing time (Fig. 2). Most predominant (90 %) particle size of untreated clinoptilolite is 277.8  $\mu\text{m}$  and specific surface was 5744  $\text{cm}^2/\text{g}$ , then after 5 minutes of ultrasonic treatment their size was 221.8  $\mu\text{m}$ , 137.9  $\mu\text{m}$  size was obtained after 10 min and 152.0  $\mu\text{m}$  size was obtained after 20 minutes. Specific surface of clinoptilolite particles after 5 min of ultrasonic treatment has decreased from 5745  $\text{cm}^2/\text{g}$  to 5324  $\text{cm}^2/\text{g}$ , and specific surface particles increased after longer time of their ultrasound treatment, respectively, after 10 min and 20 min to

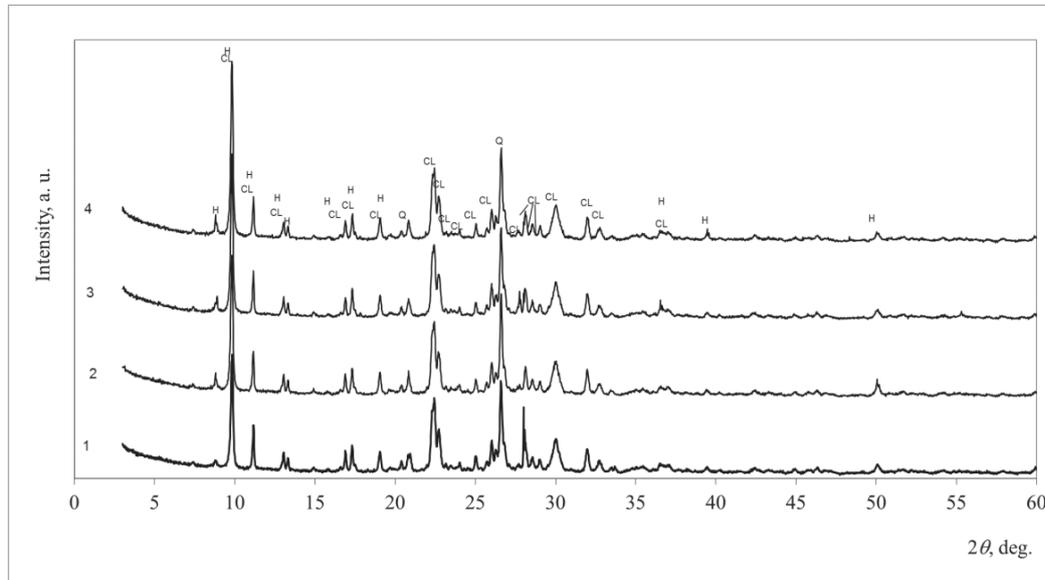


Fig. 1

X-ray diffraction patterns of ultrasonically treated clinoptilolite. Treatment time: 1) 0 min, 2) 5 min, 3) 10 min and 4) 20 min. Notes: CL is clinoptilolite, H is heulandite, and Q is quartz

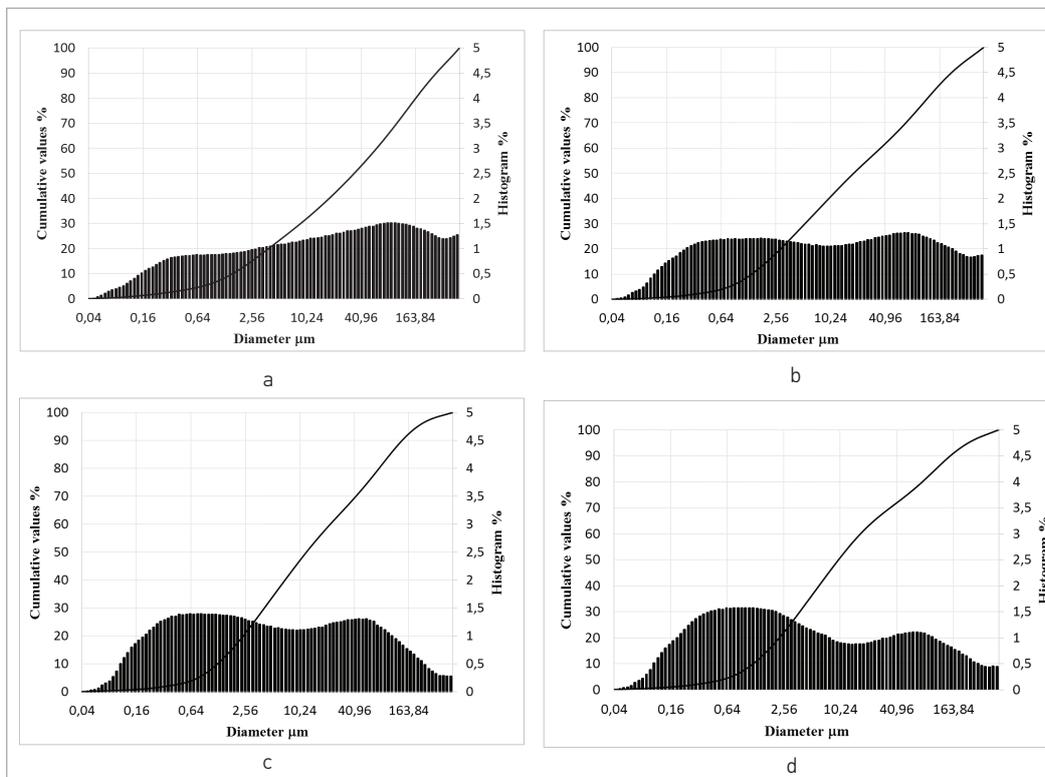


Fig. 2

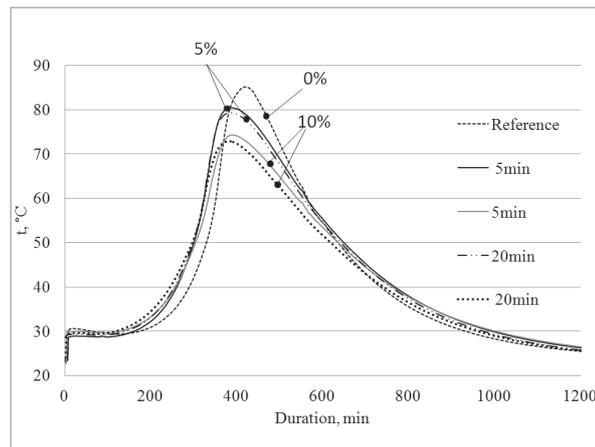
Clinoptilolite particle size distribution histograms. Ultrasonically untreated clinoptilolite (a), processed by ultrasound clinoptilolite: for 5 min (b), for 10 min (c) and for 20 min (d)

6090 cm<sup>2</sup>/g and 6817 cm<sup>2</sup>/g. Thus, particles get smaller when the ultrasonic processing time is increased up to 20 minutes, specific surface increases, but specific surface decreases after 5 min of clinoptilolite ultrasound treatment. It is likely that the polymerization and depolymerization reactions occurred in the cavitation fluid after 5 minutes.

Cement paste samples were prepared for further investigation where a part of Portland cement was replaced by clinoptilolite. The hydration of the paste was investigated: cement paste hydration temperatures and time were determined (Fig. 3). The maximum hydration temperature (85 °C) was of the control sample, i.e., the sample without clinoptilolite.

Fig. 3

Hydration temperature kinetic curves of cement paste with 5 and 10% ultrasound treated clinoptilolite. Ultrasound treated duration: 5 and 20 min



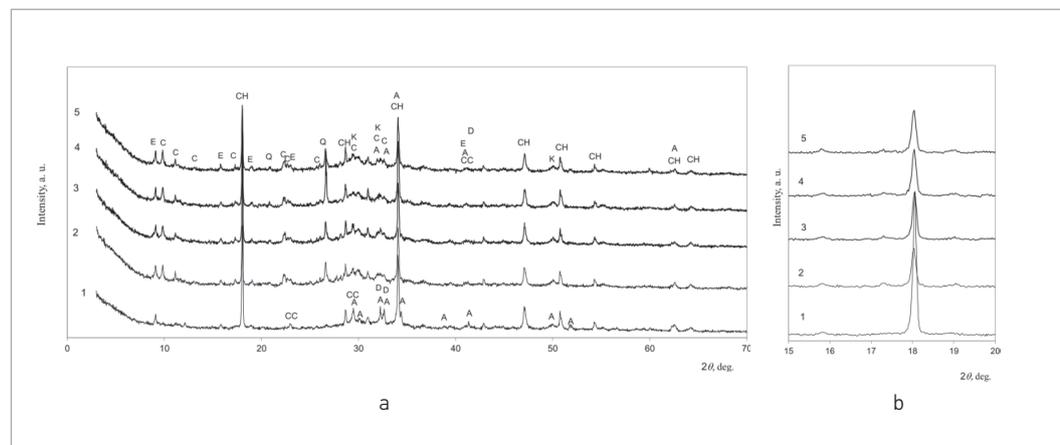
Hydration peaks decreases using clinoptilolite as a replacement for Portland cement, i.e., their temperature is 79.8 °C and 79.4 °C using 5%, and 74.3 °C and 72.9 °C with a 10% of Portland cement replacement. Hydration duration time using clinoptilolite decreases from 417 min to 383 min and 389 min respectively using 5% and 10% clinoptilolite substitute. Comparing the cement paste samples with ultrasound-treated and untreated clinoptilolite it can be said that the additive ultrasonic treatment because of its higher specific surface slightly reduces the duration of hydration peaks.

X-ray diffraction analysis results of the hydrated samples (Fig. 4) show calcium silicate hydrate, alite, belite and portlandite, as well as small amount of ettringite dominated in the hardened cement paste with and without supplementary cement material. Not all zeolite content completely reacts having replaced 20% of Portland cement by clinoptilolite, and part of it remains as a filler in cement stone (Fig. 4a). The main portlandite peak (0.493 nm) intensity decrease (Fig. 4 b) can be seen in a cross-reference of control sample with samples where a part of Portland cement is changed by clinoptilolite. This may be related to clinoptilolite pozzolanicity and the Portland cement amount reduction in the mixture.

Clinoptilolite substitute of 5% and 10% in the samples increases their strength, and then subsequently decreases, but remains still close to the strength of the control sample (Fig. 5). 11.5%

Fig. 4

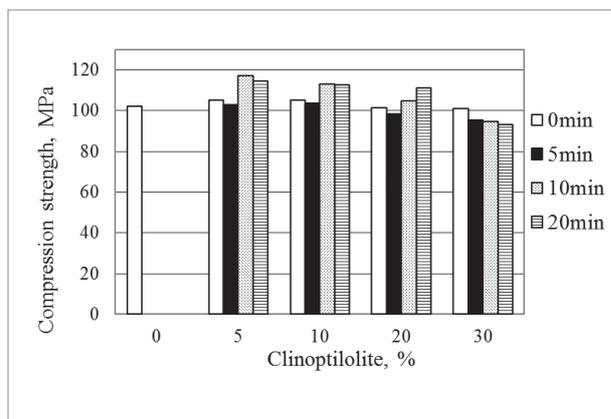
X-ray diffraction patterns of hardened cement paste after 28 days. Clinoptilolite content accounts for 20 %: reference sample (1); clinoptilolite without sonication (2); clinoptilolite 5 min sonicated (3); clinoptilolite 10 min sonicated (4); clinoptilolite 20 min sonicated (5); Notes: CH – portlandite; A – alite; K – calcium silicate hydrate; D – belite; C – clinoptilolite; E – ettringite



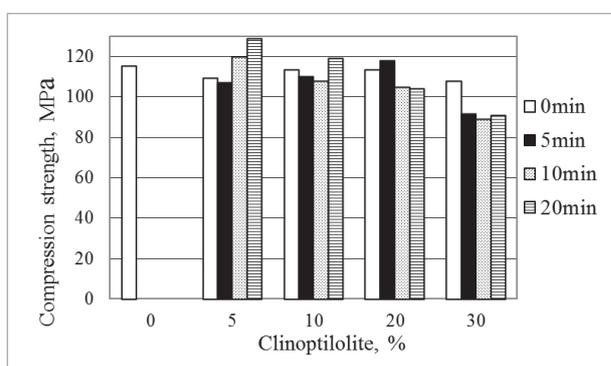
and 8.7% increase in strength is obtained after treatment of clinoptilolite by ultrasound for 10 min and 20 min respectively, using 5% of clinoptilolite and comparing to the samples with 5% of untreated by ultrasound clinoptilolite. Similar sample strength dependence is during both after 28 days and after longer hardening duration of 90 days. This allows the use of ultrasound-treated clinoptilolite additive in cementitious samples respectively over a wide range.

By treated clinoptilolite with ultrasound for 5 minutes, it was determined that no significant effect on samples mechanical - physical properties found. Increasing the ultrasonic treatment duration it was observed that the compressive strength of samples increases. This is related to the treated clinoptilolite surface morphology and specific surface characteristics change. The optimal duration of clinoptilolite treatment was 10 min. After 28 days of hydration the highest compression strength was for samples, forming with 5 % clinoptilolite, which was ultrasound treated 10 min.

The research of ultrasound treated clinoptilolite has shown that it can be used in concrete technology as Portland cement substitute. Physical mechanical researches with ultrasound-treated clinoptilolite in Portland cement paste showed that the compressive strength of the samples increased significantly compared with untreated clinoptilolite additive. Ultrasonically treated clinoptilolite additive in concrete technology allows using it in concrete mixtures for special use areas, such as: aggressive waste storage container industry, thus solving relevant ecological problems.



a



b

Fig. 5

The compressive strength after 28 days (a) and 90 days (b) of cement stone with 0, 5, 10, 20 and 30% of clinoptilolite, treated by ultrasound for 0, 5 min, 10 min and 20 min

## Conclusions

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## About the authors

### VYTAUTAS SASNAUSKAS

#### **Assoc. Professor**

Kaunas University of Technology,  
Faculty of Civil Engineering and  
Architecture

#### **Main research area**

Building materials

#### **Address**

Studentu st. 48, LT-51367  
Kaunas, Lithuania  
Tel. +370 37 300465  
E-mail:  
vytautas.sasnauskas@ktu.lt

### GEDIMINAS RINKEVIČIUS

#### **Student**

Kaunas University of Technology,  
Faculty of Civil Engineering and  
Architecture

#### **Main research area**

Building materials

#### **Address**

Studentu st. 48, LT-51367  
Kaunas, Lithuania  
Tel. +370 37 300465  
E-mail:  
gediminas.rinkevicius@ktu.edu

### DEIVIDAS MARTINAVIČIUS

#### **Student**

Kaunas University of Technology,  
Faculty of Civil Engineering and  
Architecture

#### **Main research area**

Building materials

#### **Address**

Studentu st. 48, LT-51367  
Kaunas, Lithuania  
Tel. +370 37 300465  
E-mail:  
deividas.martinavicius@ktu.edu

### DANUTĖ VAIČIUKYNIENĖ

#### **Professor**

Kaunas University of Technology,  
Faculty of Civil Engineering and  
Architecture

#### **Main research area**

Building materials

#### **Address**

Studentu st. 48, LT-51367  
Kaunas, Lithuania  
Tel. +370 37 300465  
E-mail:  
danute.palubinskaite@ktu.lt

### ARAS KANTAUTAS

#### **Assoc. Professor**

Kaunas University of Technology,  
Faculty of Chemical technology

#### **Main research area**

Building materials

#### **Address**

Radvilenu st. 19, LT-50254  
Kaunas, Lithuania  
Tel. +370 37 300163  
E-mail:  
aras.kantautas@ktu.lt

### ERNESTAS IVANAUSKAS

#### **Assoc. Professor**

Kaunas University of Technology,  
Faculty of Civil Engineering and  
Architecture

#### **Main research area**

Building materials

#### **Address**

Studentu st. 48, LT-51367  
Kaunas, Lithuania  
Tel. +370 37 300465  
E-mail:  
ernestas.ivanauskas@ktu.lt