




AKADÉMIAI KIADÓ

# Ceramic bricks with enhanced thermal insulation produced from natural zeolite

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## ABSTRACT

In this research, ceramic bricks were produced based on natural zeolite from Tokaj (Hungary) using the dry pressing technique. The microstructure, morphology and properties of the produced samples were examined via scanning electron microscopy, X-ray diffraction and X-ray fluorescence. The X-ray investigation revealed various minerals in the natural zeolite; moreover, the samples' physical and thermal properties were also investigated. The sintering temperature and composition play a major role in the microstructure and the properties of the prepared ceramic samples. The produced ceramics bricks have excellent thermal insulation and good mechanical strength. The results of this research work confirm the potential use of natural zeolite from Tokaj as an eco-friendly building material.

## KEYWORDS

natural zeolite, ceramic bricks, dry pressing, thermal conductivity

## 1. INTRODUCTION

The energy demand is expected to highly increase in the upcoming years [1–3]. Therefore, saving energy by introducing new building materials with good thermal insulation properties has drawn huge interest [4, 5]. This is basically due to the economic and environmental importance of saving energy. In the hot climate area and especially during the summer, a considerable amount of energy is used for cooling the building, while in the cold climate area, almost the same amount is used to warm the building to achieve internal comfort [6]. The heating and cooling of the building, which causes discomfort, commonly occur due to heat transmittance through the wall. Therefore, using thermally insulated materials can reduce global warming and contribute to sustainability by reducing heat gain and loss through the walls [7, 8].

Natural zeolites are microporous materials of volcanic origin. They are a well-known group of hydrated crystalline aluminosilicate minerals [9–11]; they usually contain alkali- and alkaline earth ions, and they form by weathering of volcanic glass under different geochemical conditions [12]. The zeolite framework includes  $[\text{SiO}_4]^{4-}$  and  $[\text{AlO}_4]^{5-}$  tetrahedral, which are linked together by shared oxygen atoms, to make a systematic crystal structure with various interconnected open voids where foreign atoms or molecules can be accommodated [13, 14]. The replacement of Si by Al causes the negative charge in the zeolite framework, which is generally neutralized by some cations [15].

Due to their fascinating properties, including high specific area, superior ions exchange capacity, dehydration – rehydration and their highly porous structure, zeolites could be considered as one of the environmentally cleanest materials [16]; therefore, they are a potential candidate for many applications, for example, catalysts, ion exchangers and sorbents [17, 18].

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Natural zeolites (Tokaj) are volcanic tuffs containing a low amount of zeolite (below 10%) together with quartz, cristobalite, montmorillonite and sometimes feldspar [19]. The low portion of zeolite in these materials hinder their advanced applications, but due to their superior mechanical characteristic, large porosity, and lightweight, natural zeolites are very good building materials. Many research works have been carried out regarding the use of natural zeolite in construction as an additive to the cement or masonry blocks [20, 21].

Ceramic bricks are essential building materials produced in a large amount all over the world [22]. They usually produce from clay [23–24] through grinding [25], molding, drying, and firing [26]. The clayey materials normally consist of many minerals, for instance, quartz, illite, montmorillonite, kaolinite, chlorite and feldspars. The most common shaping techniques are dry pressing, semi-dry pressing and extrusion [27]. During the firing, many processes can take place that can affect the properties of the final product. These processes involve dehydration, decomposition of some mineral phases, phase transformations and physicochemical reactions [28]. Increasing the density due to the increase in the sintering temperature leads to an increase in the thermal conductivity and mechanical strength. The bricks' thermal conductivity is highly connected to many factors, including raw material composition, firing temperature, and the porosity of the fired bricks. The thermal conductivity of ceramic bricks typically has a value of  $1.0 \pm 0.4 \text{ W/mK}$  [29].

This research aims to study the preparation of ceramic bricks from natural zeolite. Ceramic samples were sintered at a different temperatures ranging from (950–1,300 °C) and evaluated based on their physical, mechanical and thermal characteristics.

## 2. MATERIALS AND METHODS

### 2.1. Characterization of the raw material (natural zeolite)

In this work, natural zeolite, which is used as a starting raw material for the preparation of ceramic bricks, is obtained from Tokaj Mountain in north Hungary. Chemical analysis of the raw material was carried out using an energy dispersive X-Ray Fluorescence (XRF) spectrometer. After the size reduction via planetary ball milling, the chemical composition and the phase identification were made using Rigaku Miniflex II X-Ray Diffractometer (XRD). The samples were scanned between  $2\theta$  intervals of 0–70 °C with a scanning rate of 1 °C/min and a step size of about 0.01016 °C using  $\text{CuK}\alpha$  radiation ( $\lambda = 1.54184 \text{ \AA}$ ). For the computer-based investigation, DIFFRACT measurement software was used. ThermoGravimetric (TG) analysis, Differential Thermal Analysis (DTA) and Differential ThermoGravimetric (DTG) analysis of the powder samples were done at a temperature up to 1,200 °C with a heating rate of 5 °C/min in air. The topographical feature and the surface morphology

of the prepared ceramic samples were examined using Scanning Electron Microscopy (SEM) (Carl Zeiss EVO MA10 equipment work at 20 kV using a Bruker microprobe: the images were taken under BSD-SE mode. The prepared samples were examined under several magnification values. The optimal sintering temperature and the linear volume change of the natural zeolite powder were determined using a heating microscope.

### 2.2. Preparation of the ceramic samples and sintering method

Ceramic bricks based on the natural zeolite were prepared through the mechanical activation and reactive sintering method using uniaxial dry pressing. The zeolite tuffs were milled in Retsch PM 400 planetary ball mill for 15 min at 150 rpm. The milled powders were then used to make cylindrical pellets with a diameter of about 25 mm and a thickness of 10 mm using uniaxial pressing machine under a pressure of 55 MPa. The prepared pellets were sintered at different temperatures from 950 to 1,300 °C with 50 °C step in a high-temperature programmable furnace for 3 h, with a heating rate of 60 °C/h.

### 2.3. Characterization of the sintered samples

Using Archimedes principle, different properties including bulk density, apparent porosity and water absorption were determined; furthermore, loss on ignition, volume shrinkage and the thermal conductivity of the sintered ceramic samples as well as the microstructure characteristic and mineralogical composition were also examined using SEM and XRD.

## 3. RESULTS AND DISCUSSION

### 3.1. Characterization results of the raw materials

**3.1.1. XRD and XRF investigations.** Natural zeolite powder (Tokaj) contains many minerals like cristobalite, quartz, montmorillonite, calcite and clinoptilolite, which is confirmed by XRD analysis (Fig. 1). Table 1 shows the percentage of the mineralogical constituents, chemical

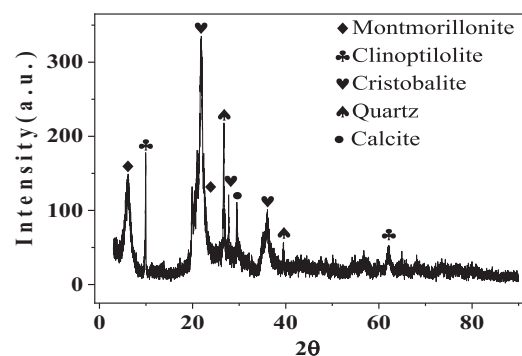


Fig. 1. XRD diffractogram of natural zeolite

Table 1. Chemical and mineralogical percentages of the natural zeolite (Tokaj, Hungary)

	wt %	CaO	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	MgO	Na <sub>2</sub> O	CO <sub>2</sub>	H <sub>2</sub> O	LOI
Quartz	8		8						0.00
Cristobalite	50		50						0.00
Montmorillonite	30		19.1	4.06	3.21	0.74		2.87	2.87
Calcite	2	1.12					0.9		0.88
Clinoptilolite	10		5.79	1.89		0.57			1.75
Total	100	1.12	82.8	5.95	3.21	1.31	0.9	2.87	5.50

composition and Loss On Ignition (LOI) of the natural zeolite in wt% obtained from XRD and XRF tests; this raw material basically contains SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>.

**3.1.2. Thermal properties of raw materials.** TG/DTA curves of the natural zeolite are shown in Fig. 2. Overall weight loss of approximately 9.3% was obtained at 1,200 °C. Firstly, a 5.29% decrease in the mass was observed in a temperature range of 40–240 °C, which accounts for the removal of free water from the natural zeolite micropores. Secondly, a 1.74% weight loss was obtained at a temperature between 214 and 548 °C, which could be attributed to the evaporation of combined water and burning of the organic content. Finally, a weight loss of 2.27% was revealed at a temperature between 550 °C and 753 °C. In DTA graph, a large exothermic peak is shown in a temperature range of 192–752.6 °C, which likely indicates the evaporation of crystalline water and the burning of organic content in the ceramic raw material. Small reactions were obtained at about 796–1,200 °C, which indicates the physicochemical reactions and phase transformation.

Figure 3 demonstrates the connection between the firing temperatures and the natural zeolite's geometrical deformation, which is done using a heating microscope in a temperature range of 25–1,400 °C. Firstly, 4% height

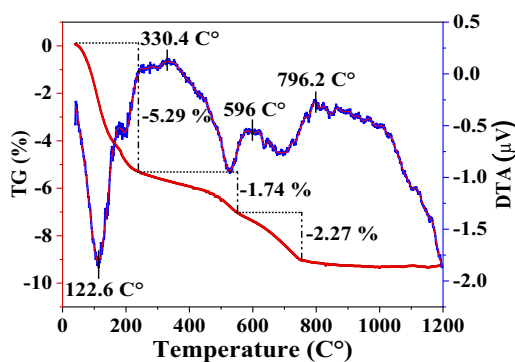


Fig. 2. DTA and TG curves of natural zeolite

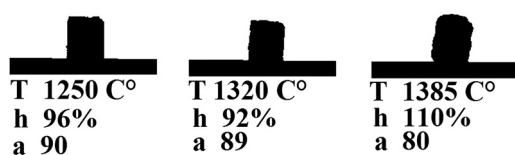


Fig. 3. Heating microscope images of the natural zeolite

shrinkage is obtained at 1,250 °C due to the effect of sintering; at high temperature (1,385 °C), 10% volume expansion is determined with a shape distortion indicating the softening state prior to the melting.

## 3.2. Characterization results of the produced samples

**3.2.1. Dimensional characteristic after firing.** Sintering at different temperatures has enormously increased the shrinkages and changed the colors of the ceramics samples, as it is shown in Fig. 4. This could be attributed to the recrystallization of zeolite, which starts with dehydration and results in some physicochemical reactions which can change the microstructure.

**3.2.2. XRD investigations.** X-ray diffraction results, which show the crystallinity and phase analysis of the raw material and fired samples, are demonstrated in Fig. 5. The XRD diffractogram of the sintered samples revealed the formation of different phases. The samples sintered at 1,000 °C confirmed the existence of silica (quartz + cristobalite) as the main component with a small portion of anorthite;

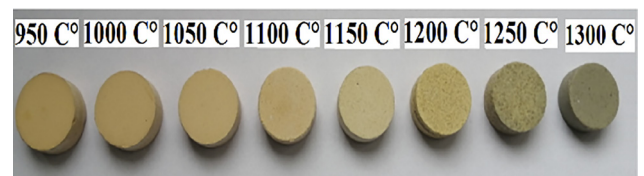


Fig. 4. Ceramic samples sintered at different temperatures

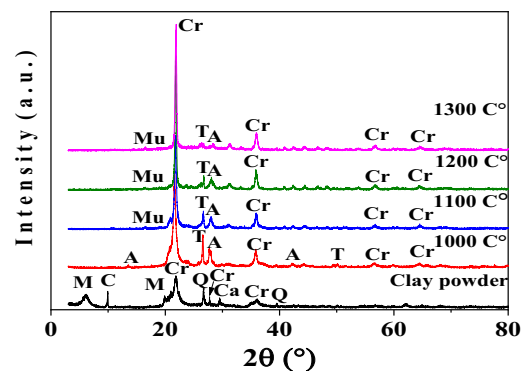


Fig. 5. XRD results of fired samples (M: montmorillonite; C: clinoptilolite; Cr: cristobalite; Q: quartz; Ca: calcite; A: anorthite; T: tridymite; Mu: mullite)

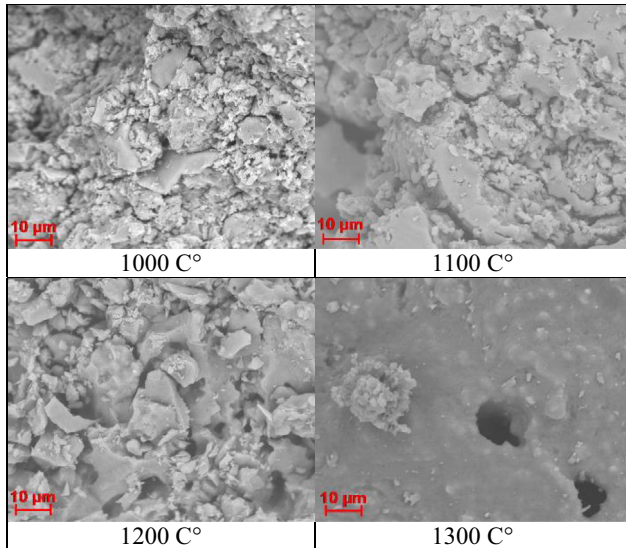
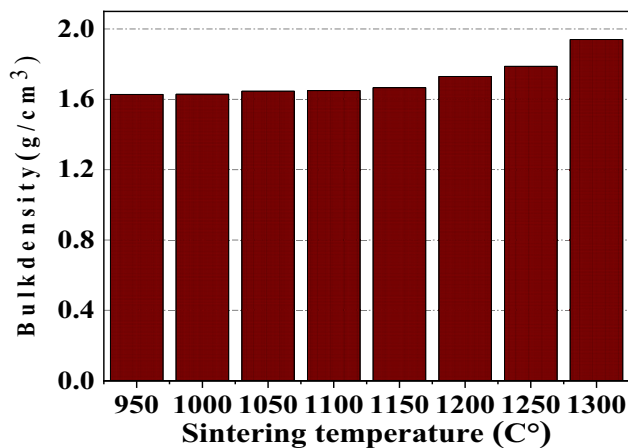


Fig. 6. SEM images of the sintered samples

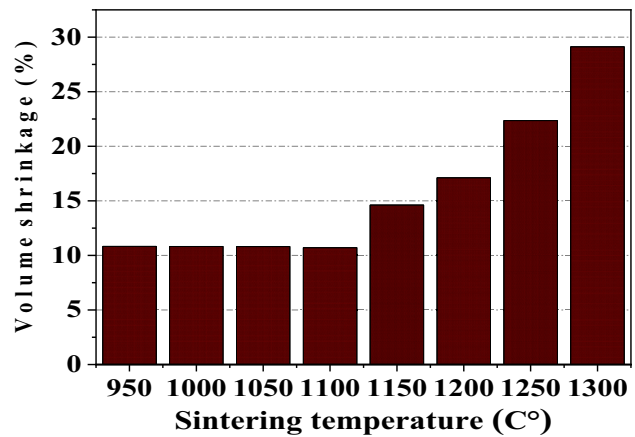
increasing the sintering temperature to 1,300 °C leads to the formation of mullite, increase the amorphous percentage and reduce the amount of anorthite.

**3.2.3. SEM examination.** The topographical feature and morphology of the fractured surface obtained from the samples fired at a temperature range of (950–1,300 °C) are shown in the scanning electron micrographs (Fig. 6). The reactive sintering process starts at 1,050 °C. It can be seen that raising the sintering temperature reduces the pore size, therefore increasing the density of the produced samples. In the samples sintered at a temperature of 1,200 °C, the pores are interconnected, forming a capillary. Furthermore, dense ceramic samples with a large amount of amorphous phase can be noticed in the samples sintered at 1,300 °C. This mainly happens due to the intensive sintering and conversion of some crystalline silica to amorphous silica.

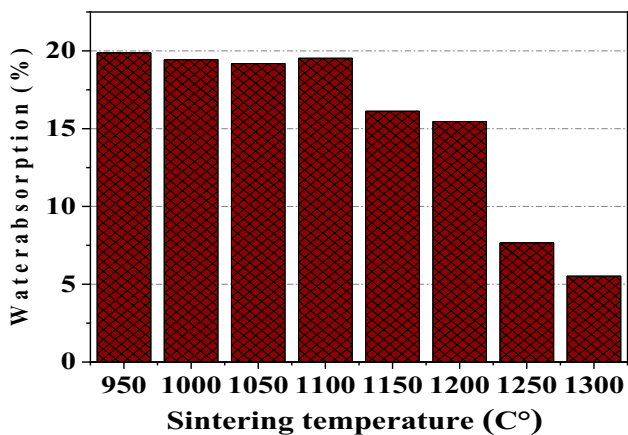
**3.2.4. Physical properties.** Upon increasing the firing temperature, several physical properties were changed, as it is shown in Fig. 7. At lower sintering temperatures (950–1,100 °C), the samples showed relatively higher dimensional stability with volume firing shrinkages of about 10%. At higher temperatures (above 1,100 °C), some minerals in the natural zeolite (montmorillonite, clinoptilolite and calcite) decompose. Furthermore, physicochemical reactions take place and lead to the formation of anorthite and mullite, as confirmed by XRD analysis (Fig. 5).



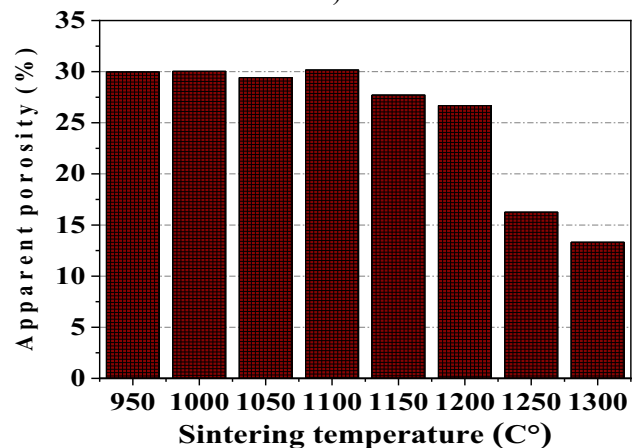
a)



b)



c)



d)

Fig. 7. The a) bulk density, b) volume shrinkage, c) water absorption and d) apparent porosity of the ceramic bricks sintered at variable temperatures

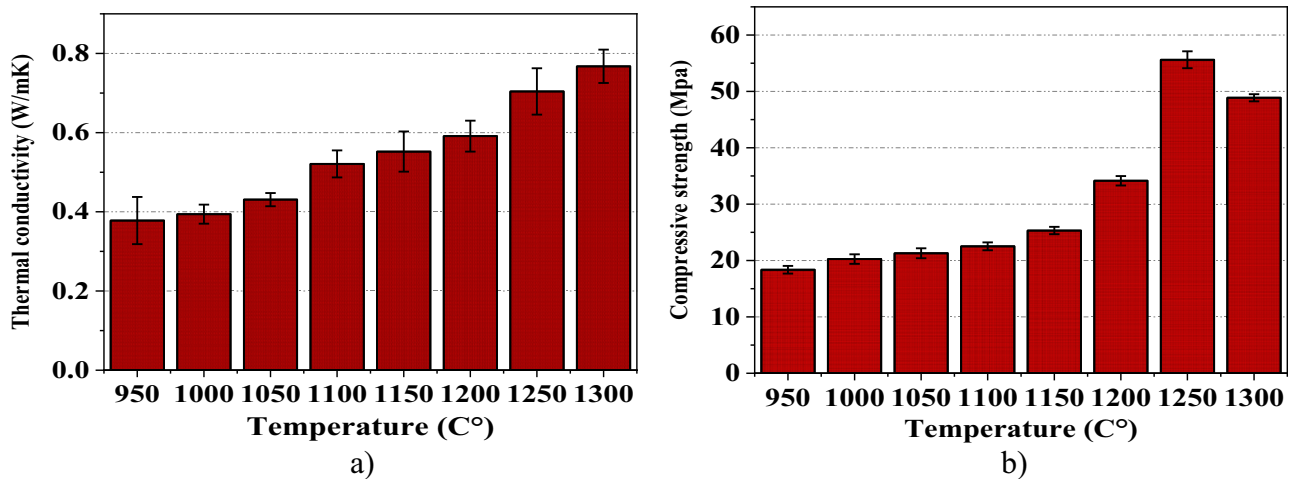


Fig. 8. a) Thermal conductivity, b) compressive strength, of the ceramic bricks sintered at variable temperatures

As a result, the volume shrinkages start to increase gradually and finally reach 29% at 1,300 °C. The values of bulk density, water absorption and apparent porosity of the prepared ceramic bricks sintered at different temperatures are shown in Fig. 7. The bulk density of the brick samples sintered at 950 °C is 1.62 g/cm<sup>3</sup>, while its porosity is 30% and water absorption is about 20%, the corresponding compressive strength is 18.3 MPa. The bulk density of the produced samples has increased from 1.62 g/cm<sup>3</sup> to about 1.85 g/cm<sup>3</sup>. The water absorption and apparent porosity reduced from 20 to 6% and from 30 to 13%, respectively, with the firing temperature increase to 1,300 °C. This change in the physical properties occurred due to the decomposition and reactive sintering process, which lead to the creation of new phases.

**3.2.5. Thermal conductivity.** The thermal conductivity of the prepared samples as a function of sintering temperatures is shown in Fig. 8a. The samples' thermal conductivity tends to increase with increasing the sintering temperature. The lowest value of thermal conductivity was 0.37 W/mK obtained from the samples sintered at 950 °C. As the sintering temperature increases to 1,300 °C, the thermal conductivity increases and reaches a maximum value of 0.76 W/mK. The main reason beyond the rise in the thermal conductivity is the sintering, which occurs at high temperature through the diffusion that reduces the porosity and therefore, increases the thermal conductivity. Usually, the material with higher porosity has higher thermal conductivity since the air absorbed into the materials' pores act as insulating materials.

**3.2.6. Compressive strength.** Compressive strength is considered one of the crucial factors determining the quality of ceramic bricks and other construction materials [30]. Figure 8b demonstrates the value of compressive strength for the prepared ceramic samples fired at variable temperatures. The results confirm that the compressive strength tends to increase with increasing the sintering temperature. This occurs due to thermally-induced volume

shrinkage and physicochemical processes, for instance, mineral decomposition and chemical reactions as confirmed by XRD test in Fig. 5, reducing the porosity and increasing the density and compressive strength. The minimum compressive strength was 18.36 MPa achieved when the ceramic bricks sintered at 950 °C; this value of compressive strength is far above the value of the standards required for the building brick which is 5 MPa. The highest value for compressive strength was 55.6 MPa obtained from the ceramic samples sintered at 1,250 °C. The compressive strength of the samples fired at 1,300 °C decreased up to 48.8 MPa. This decrease in compressive strength could be attributed to the conversion of some crystalline silica into amorphous silica.

## 4. CONCLUSION

Through the processing technique proposed, ceramic bricks were successfully produced. The properties of the final product are highly affected by sintering temperatures. A remarkable change is observed in the density, porosity, shrinkage, and color of the produced bricks. This change could be due to liquid-phase sintering associated with the formation of new phases. The XRD test confirms the formation of anorthite and mullite. The SEM analysis reveals that the porosity of the ceramic samples decreases with increasing the sintering temperature. This could be attributed to the liquid-phase diffusion of the melt into the pores. In contrast, their bulk density is noticeably increased. The sample sintered at 950 °C shows the lowest value of thermal conductivity (0.37 W/mK) with excellent compressive strength (18.36 MPa). These properties make them an outstanding candidate for bricks making. The samples sintered at 1,300 °C showed the highest thermal conductivity (0.76 W/mK), which still lies within the standards. The data examined in this research work confirm the potential application of natural zeolite from Tokaj region as efficient insulating building bricks. These studies could be used to

control the microstructure and, hence, the properties of the produced ceramic materials.

## ACKNOWLEDGMENTS

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