

## Influence of mechanical activation on the properties of natural zeolites from Tokaj Mountain

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**Abstract.** This paper presents the results of a study of the influence of mechanical activation on morphology, specific surface area and phase composition of natural zeolite of Tokaj Mountain. During the mechanical activation of zeolites powders with specific surface area of 19-20 square meters per grams, significant changes in chemical and mineralogical compositions can be observed. The laboratory experiments had shown an intensive increase of specific surface area at the beginning of mechanical activation; a further relatively slow decrease and reduction of BET surfaces were observed. By increasing the mechanical activation time the amount of quartz, cristobalite-low, orthoclase mineral components were not stable, and their content have varied not so strongly as a decrease smectite 15 A, clinoptilolite, illite 2M1 or calcite. In addition, during the mechanical activation occurred amorphization, which was increased from 13% to 52%.

### 1. Introduction

The Tokaj Mountain region, located in the northeastern part of Hungary as part of the Carpathian Basin, is one of the most famous volcanic mountains of Hungary [1]. The interest of researchers towards natural zeolites is connected with their unique properties: an extremely high adsorption capacity, catalyzing action, thermal stability and resistance in different chemical environments [2].

The results of the study of structural, physicochemical properties of natural zeolites allow developing the theoretical bases for the directed change of useful properties of natural minerals that are required for sorption materials.

The specific surface area is a dominant parameter for zeolites [3]. To obtain the necessary magnitude of specific surfaces of materials depends not only on their chemical and mineralogical composition, but also on physical, mechanical and rheological parameters of the used materials [4, 5]. It is known that mechanical processing in ball mills can change the structure, morphology, specific surface area of zeolite-containing materials and occasionally improve their processing properties [6]. In spite of the numerous publications, the physicochemical properties of natural zeolites are still not sufficiently studied. The goal of this work was to study changes induced by mechanical activation on morphology, specific surface area, and phase composition of the natural zeolite Tokaj Mountain deposit.

### 2. Materials and Experimental Procedure



Natural zeolite from Tokaj Mountain was used as object of investigation. The mechanical activation of the powder was performed in a Retsch PM 400 planetary ball mill at 350 rpm for 600 minutes. The acceleration in planetary mill was 26.8 g. Ceramic grinding balls were used in planetary mill [7].

The crystal structure and phase composition of the zeolite before and after the mechanical activation were determined by X-ray diffraction analysis (XRD) using diffractometer Rigaku MiniFlex II with Cu-K $\alpha$  ( $\lambda = 1.5418 \text{ \AA}$ ) radiation in angular interval of 3–90° with steps of 0.04° [8]. The phases were determined by search method using powder diffraction data base file PDF2.

The morphology of the powder was analyzed using field emission scanning electron microscopy Zeiss Supra 55VP operated at an acceleration voltage of 3.5 kV. For the measurements, the samples were put on a carbon tape and covered with a gold layer.

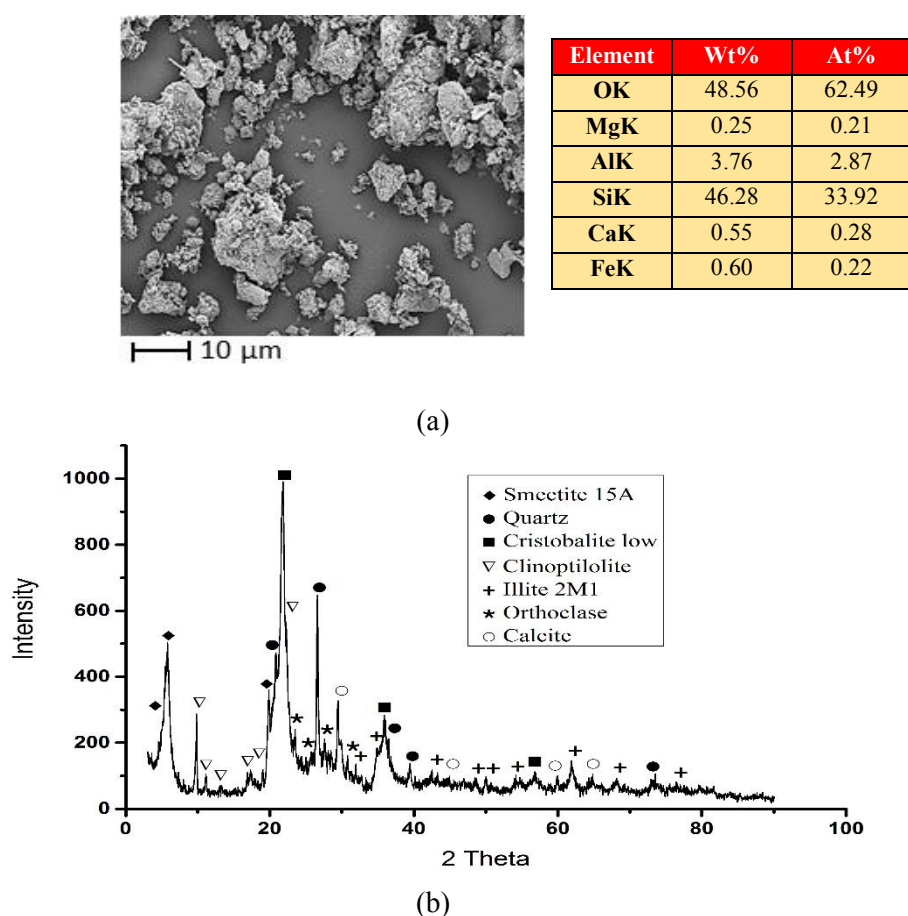
The particle size was determined by using laser diffraction particle size analyzer Horiba LA-950 in the range 0.01 - 3000  $\mu\text{m}$ .

Brunauer, Emmett, Teller (BET) surface area was determined using a micrometrics Tristar 3000 gas adsorption analyzer [9].

### 3. Results and Discussion

#### 3.1. Initial of natural zeolite powder

On Fig. 1 it is shown the elemental analysis, SEM-pictures and X-ray patterns of natural zeolite powder.

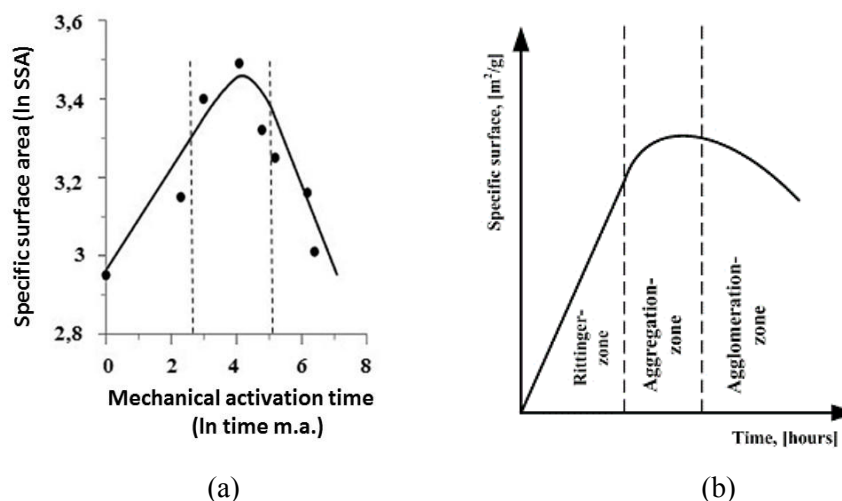


**Figure 1.** SEM-picture, elemental analysis(a), X-ray pattern(b) of natural zeolite powder

The results of elemental analysis showed that the zeolite powder in the initial state consisted of Al, O, Si, Ca, Mg, Fe. The SEM data showed that particles of zeolite powders has irregular shapes with an average particle size of 27  $\mu\text{m}$ . Calculations of the X-ray pattern showed that the structure of zeolite consists of seven different phases: smectite 15A, quartz, cristobalite-low, clinoptilolite, illite 2M1, orthoclase, calcite with value of 20%, 8%, 15%, 14%, 15%, 9%, 6% respectively. XRD results showed that the presence of amorphous phase in initial zeolite was 13%.

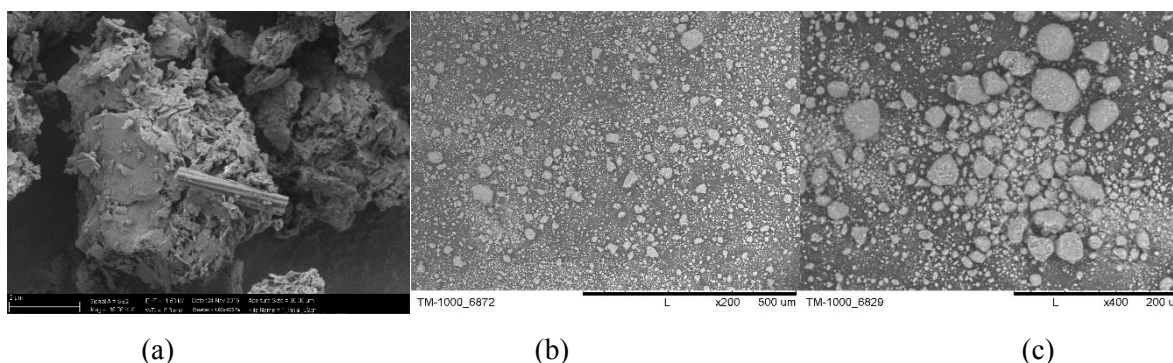
### 3.2. Mechanical activation of natural zeolite powder

Initial zeolite powder has a specific surface area of 19  $\text{m}^2/\text{g}$ . Experimental results regarding the change in BET specific surface area of zeolite samples with mechanical activation time in a planetary ball mill are shown in Fig. 2 (a). During the first 60 minutes, the specific surface area of zeolite powder increases, reaching 33  $\text{m}^2/\text{g}$ . After 120 minutes, the specific surface slightly decreases and after 600 minutes of activation, there is a significant reduction to 20  $\text{m}^2/\text{g}$ .



**Figure 2.** The dependence of specific surface area values of zeolites from mechanical activations times on logarithmic scale (a), theoretical curve (b).

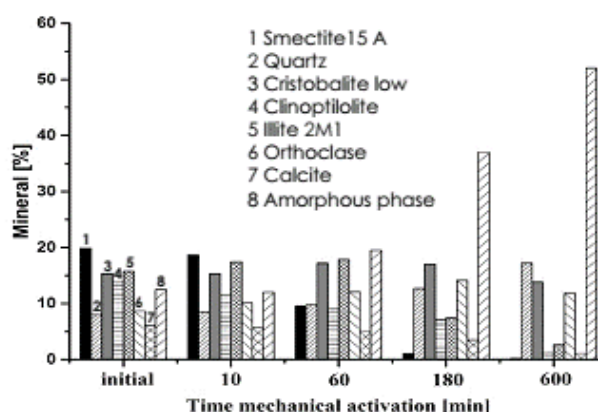
The changes of the specific surface area of the zeolites corresponding to the theoretical curve of the developed specific surface as function of the activation time is shown in figure 2 (b) – on the first stage one can observe rittinger-zone when the increase of the specific surface is proportional to the activation time; on the second stage there is an aggregation zone when the specific surface almost does not change, and the last stage - agglomeration-zone decreases the specific surface with the activation time [10-12].



**Figure 3.** SEM-pictures, initial zeolite (a), after 20 minutes (b), after 600 minutes (c) of milling time.

With the increase in the mechanical activation time there is also a change in the particles size of zeolite powder, as shown in Fig. 3. The initial zeolite-average (value in microns) was 27  $\mu\text{m}$ . After activation of 20 minutes, particle size was 5.5  $\mu\text{m}$  and after 600 minutes of milling time, the particle size became 28  $\mu\text{m}$ . Moreover, most particles have lost their initial shape and converted into a spherical shape during the mechanical activation.

The quantitative analysis of XRD patterns showed radical changes in mineralogical compositions, as shown in Fig. 4. The proportions of all mineralogical components of natural zeolite changed in dependence on the activation time. The most intensive changes can be observed in mineral components of smectite 15 A, clinoptilolite, illite 2M1 and calcite. After 60 minutes of activation time the content of smectite 15 A – decreased from 20% to 10%, clinoptilolite from 14% to 9%, meanwhile the amount of orthoclase – grew from 9% to 12%. In mineralogical composition, the considerable changes continued up to 600 minutes of mechanical activation. At 600 minutes of activation time the zeolite content of smectite 15 A, clinoptilolite, illite 2M1, and calcite reached its minimum value of 0.5%, 1%, 3%, 1% respectively, meanwhile the amount of quartz increased up to 17%. Under mechanical activation the amount of quartz, cristobalite-low, orthoclase mineral components were also not stable, but their content have varied not so strong. In addition, during the mechanical activation it occurred amorphisation, which increase from 13% to 52%.



**Figure 4.** Mineralogical composition of natural zeolite during mechanical activation.

#### 4. Conclusion

During the first 60 minutes, the specific surface area of zeolite powder increases, after 120 minutes, the specific surface slightly decreases and after 600 minutes of mechanical activation, there is a significant reduction of surface area. Most particles have converted into spherical shape during the mechanical activation.

During the mechanical activation of natural zeolite the most intensive changes observed in mineral components of smectite 15 A, clinoptilolite, illite 2M1 and calcite, and it was observed an increase of system amorphisation from 13% to 52%.

#### Acknowledgement

The research was conducted according to project RF Academy of Science № III.23.2.3.

#### 5. References

- [1] Viczián I 1997 *Clays Clay Miner.* **45** 114
- [2] Akimkhan A M 2012 *Structural and Ion-Exchange Properties of Natural Zeolite* (Croatia: Intech)
- [3] Olson E 2012 *J. of GxP Compliance* **16** 52
- [4] Gömze L A, Gömze L N, Kulkov S N 2015 *Építőanyag–JSBCM* **67** (4) 143  
<http://dx.doi.org/10.14382/epitoanyag-jsbcm.2015.24>

- [5] Gömze L A 2003 *Építőanyag–JSBCM* **55** (4) 133  
<http://dx.doi.org/10.14382/epitoanyag-jsbcm.2003.23>
- [6] Nikashina V A, Streletskii A N, Meshkova I N, Kolbanev I V, Grinev V G, Serova I B 2011 *Inorganic Materials* **47** 1341
- [7] Geber R, Kocseha I, Gömze L A 2012 *Mater. Sci. Forum* **729** 344
- [8] Song Z, Huang Y, Wang L, Li S, Yu M 2015 *Chem. Commun.* **51** 373
- [9] Dedova E S, Shutilova E S, Geber R, Gömze L A, Kulkov S N 2016 *IOP Conf. Ser. Mater. Sci. Eng.* **140** 012007 <http://dx.doi.org/10.1088/1757-899X/140/1/012007>
- [10] Gömze L A 2010 *Mater. Sci. Forum* **659** 19 [www.scientific.net/MSF.659.19](http://www.scientific.net/MSF.659.19)
- [11] Juhász Z A, Opoczky L 2003 *Építőanyag–JSBCM* **55** (3) 86  
<http://dx.doi.org/10.14382/epitoanyag-jsbcm.2003.16>
- [12] Gömze L A, 2016 APPLIED MATERIALS SCIENCE I., Compilation of Selected Scientific Papers, Published by IGREX Ltd, ISBN 978-963-12-6600-9 pp 1-189