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Preparation and mechanical activation of extremely fine limestone and zeolite in a stirred media mill

The thesis of doctoral (Ph.D.) dissertation

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1. Introduction

There are basically two ways to produce nanoparticles. One is the build-up technology (eg. thermal and precipitating processes) that starts from the molecule (a bottom-up process) and the other is the reverse particle size reduction process (top-down process) for example milling of the material in mills (grinding).
Today ultrafine grinding (<5 μm) or even nano grinding (<500 nm) is gaining ground in the industry. The widespread use of these products - in the pharmaceutical, food, chemical, paint and ceramic sectors - is fuelling the development of technologies and equipment worldwide.
The properties of a bulk material can be divided into two main groups from a grinding point of view, (1) characteristics of the material dispersion state such as particle size distribution, particle shape and surface morphology and interfacial properties, and (2) structural properties of the material such as crystal structure, amorphousness, microstructure, inhomogeneity inside the particle and stratification. The general purpose of grinding is to decrease the particle size or to increase the specific surface area. During grinding, however, not only the dispersion properties can be varied but also the structural properties of the material (Rácz & Csőke 2016). This phenomenon is particularly characteristic of the so-called high-energy-density-mills such as vibrating mill, planetary and stirred media mill (Baláz 2008).
Raw material preparation technologies containing such processes serve sustainable development by treating our minerals economically, as of the resulting fine-ground product is needed much less in industrial use. In addition, the specific market value of high added value submicron ground material is well above the value of conventional minerals. At the same time, the products thus produced are widely used in the industry, such as fillers, thickeners, additives, dispersants, pigments in the field of cosmetics, paper, paint, plastics, construction industry and agriculture.
Zeolites are very useful, which, thanks to their special structure, can be used in different industrial areas (Hannus 2012). Their use is most significant in the field of the environment and within that in water purification. However, based on recent researches, it is experimented in pharmaceutical processing, in agriculture as a fertilizer carrier, in construction, as cement substitutes, and they are used in many cases. The essence of the methods is based on small particle size, high specific surface area, increased reactivity and cation exchangeability. Generally, zeolite ground material is produced by micro- or nano-grinding. However, these processes are extremely energy-intensive since the grinding efficiency in this particle size range is generally very low. For this reason, grinding energetic optimization and managing product properties are extremely important.
Therefore, the social exploitation of this research work is to produce high-added-value product from our domestic raw material stocks, such as zeolite, using the above-developed and optimized grinding technology in a cost-effective way. The fine-grinding research of the materials at the University of Miskolc Institute of Raw Material Preparation and Environmental Processing has a tradition: Professor Gusztáv Tarján (Tarján 1974) researched about the processes in ball mills and movement of the grinding media, Professor Pethő Szilveszter (Pethő 1986) examined mainly the field of modelling of crushing and classification with computerized process control, Professor Barnabás Csőke (Csőke 2005) investigated the mathematical

modelling of crushing and milling, sizing of mills and grindability. Gábor Mucsi (Mucsi et al. 2013) deals with the grindability and mechanical activation of minerals, Ádám Rácz (Rácz 2014) studies grinding and shaping in a dry stirred media mill. I joined this long tradition of research in 2013 as a Ph.D. student.
Among the Hungarian scientific schools operating in the field of grinding, addition to the University of Miskolc, it should be mentioned the SZIKKTI, CEMKUT and Veszprém University, where Professor Béla Beke (Beke 1974) and Professor Ludmilla Opoczky (Opoczky 1977), Professor Zoltán Juhász (Juhasz & Opoczky 1990) and Éva Kristófné Makó, are internationally renowned professionals working and worked. In my research studies, besides the known foreign publications, I was very much relying on the work of the Hungarian researchers as well.
During the detailed study of domestic and international literature, I found that no article was published that would deal with zeolite systematically grinding in a wet stirred media mill.
Based on the above, the overall scientific goal of my research is to create a method of measure and evaluation that is complex enough to optimize the operational and mechanical conditions of zeolite milling in such a way as to be capable of deliberately controlling the product's fineness and its structure while constantly monitoring the flow behaviour of the suspension.

2. Scientific antecedents of the dissertation

Based on the literature and the scientific history, it can be stated:

- When the processes in stirred media mills were described, it became clear that there are many factors influencing the grinding and dispersing effect (Mölls & Hörnle 1972).
- For stirred media mills, Kwade (Kwade 2004) has introduced a model to estimate optimum parameters when some experimental data are available. This is the so-called stress model that shows the relationship between the product's fineness in terms of energy consumption and the most important operating parameters for stirred media mills.
- Stress energy of grinding media (SE_{GM}) describes the effect of three parameters in a combined form: (1) circumferential velocity of the rotor, (2) the density and (3) the size of the grinding media. Thus, the specific grinding work and the stress energy are the two most important factors in the grinding of brittle materials in a stirred mill: there is a specific relationship between the product's fineness and the specific grinding work for each stress energy (Kwade & Schwedes 2007).
- In stirred media mills, only a small portion of the energy invested in the milling process is used to grind the particles. Most of the energy is transformed into heat because of several processes (e.g. deformation of the grinding media and friction). It is important to optimize the process to minimize the amount of energy invested and to reduce the wear of the grinding media (Faes & Kwade 2013).
- The properties of zeolites (ion exchange capacity, reactivity, etc.) can be improved by mechanical activation (Kosanović et al. 2004; Xie & Kaliaguine 1997; Huang et al. 1995).

Based on the results presented above, I have identified the following deficiencies:

- After studying the literature on the effect of mechanical activation of zeolites, it can be concluded that the process of mechanical activation has not been systematically investigated during stirred media milling.
- The available literature mainly focuses on material-based investigations, less pay attention to the optimization of production and grinding conditions (machine and operating parameters). Primarily only the grinding time is changed as a variable parameter.
- There is no analysis method that is complex enough to evaluate zeolite wet stirred media milling (product fineness or material structure) while continuously monitoring the flow behaviour of the slurry.
- The relationship between grinding energy indicators (specific grinding work, stress intensity) and zeolite dispersion and structural properties has not been revealed yet. This helps to precisely dimension and design the technology.
- The production of nanoparticles depends not only on the ability of the particle to break but also on the aggregate stability of the crushed particles and the rheology of the slurry. However, the use model ignores the change in the rheological properties of the suspension.
- An adequate method hasn’t been yet developed for online tracking of rheological changes in stirred media milling. This is extremely important for mill design, where grinding of non-Newtonian suspensions is usually done. Rheological behaviour can limit the grinding process.
- In this particle size range, special attention must be paid to crystal structure changes and amorphization.

3. The objective of my scientific work

Based on the results presented above, the main objectives of my studies and research are as follows. On the one hand, with systematic laboratory experiments, a submicron-sized zeolite product is prepared with the aim of using a stirred media mill in wet mode and optimizing the machine parameters of the process. In addition, inquiring into dispersion (particle size distribution, specific surface), structural (mineral phase composition, amorphous, crystalline size), transport (rheological) properties and chemical composition of the most commonly obtained nano size (<100 nm) particles; exploring the relationships between the particle characteristics and the production conditions. The social significance of this research is that the high-added-value products can be prepared from domestic raw material resources.

4. Description of model materials, description of tests performed, experimental equipment, test plan

Model materials, methods, and experimental equipment

To perform the experimental tests, I selected two model materials, a relatively homogeneous composition, and an inhomogeneous material, namely limestone, and zeolite. The limestone sample material was used for the development of the analysis methodology, primarily for the development of the tube rheometer, and zeolite for systematic mechanical activation experiments.

During my experiments at the Institute of Raw Material Preparation and Environmental Processing, I used the Netzsch Mini-Cer mill for grinding, which was performed under laboratory-specific conditions for nano-grinding tests. During grinding, a Horiba LA-950 V2 particle analyser was used to determine the particle size distributions and the calculated specific surface values.

The developed online rheology measuring system enables the monitoring of rheological changes in ultra-fine grinding in stirred media mill in wet mode. Therefore, an additional online tube rheometer for the Netzsch MiniCer mill was developed and installed. The original peristaltic pump of the NetzschMiniCer was used as the main pump to drive the suspension through the measuring pipe sections. Two measuring pipe sections made by stainless steel were connected serially (D_1 = 10 mm, L_1 = 1.6 m, D_2 = 9mm, L_2 = 1.6 m) with four pressure gauges. If there are two measured pressure loss - flow rate points for a given operational condition, two parameters non-Newtonian rheological model can be fit. Of course, the flow rate can be changed, and many points of the pseudo shear curve can be measured. The pressure losses of the test pipe sections were measured by no dead space gauge pressure transducers ($\Delta p_1 = p_1 - p_2$; $\Delta p_2 = p_3 - p_4$). The flow rate was determined indirectly. The applied peristaltic pump is a positive displacement pump.

The oxidative composition of the starting materials (limestone and zeolites) was determined by WD-XRF RIGAKU Supermini 200-type WDXRF, in which the source is an air-cooled 200 W Pd-ray tube with 50 kV voltage and 4.0 mA current excitation.

By oscillation spectroscopy methods, vibrations and periodic oscillations of bonds (bound atomic groups) in molecules or crystalline materials can be investigated, thus indirectly detecting chemical and local structural information (Hegman et al. 2011). Measurements were performed using the Jasco FT-IR 4200 in reflection mode using diamond ATR.

The composition of the starting and the mechanically activated samples was determined by X-ray powder diffraction, the main parameters of the apparatus were: XRD, Bruker D8 Advance, Cu-Kα radiation, 40kV and 40mA generator plant, parallel beam geometry with spherical mirrors, Vantee- 1 detector detector with aperture 1º, with a measurement time of 0.007 ° (2θ) / 24 sec.

Transmission electron micrographs from the starting and the mechanically activated samples of zeolite were made with an FEI Technai 200 kV transmission electron microscope.

My experiments were carried out according to the following inquiry plan.

Experiments with limestone mainly contributed to the development of the tube rheometer. Thus, the primary purpose of these experiments was to test the operation of the tube rheometer with a relatively homogeneous composite material. Among the grinding parameters, I examined the effect of concentration of suspension. During the experiments, I studied the rheological behaviour of the material online, and I followed the structural changes of the material with FTIR analysis.

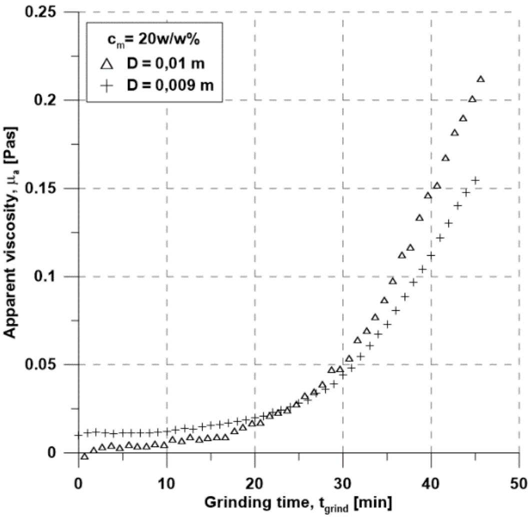
In the second stage of my studies, zeolite samples were the primary material for systematic mechanical activation experiments. To optimize the grinding parameters, I studied the effect of concentration and stress energy. Different stress energies were achieved by changing the grinding media size and the rotational speed of the rotor. In case of optimal grinding parameters, I examined the change of the structural properties of the zeolite due to grinding. Changes in the structure of the zeolite were measured by FTIR measurements, mineral composition by XRD measurements, suspension rheology by online tube rheometer and nano-structure by TEM method. Then I established relationships between characteristics of the mill and the material properties of the zeolite.

5. Scientific results, theses

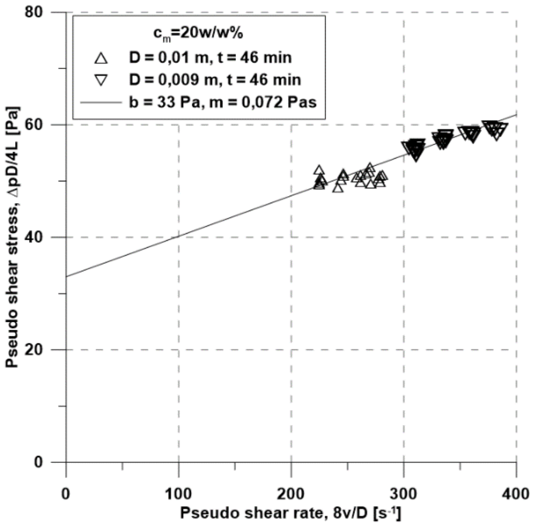
1. A measuring and evaluating method were elaborated that is appropriate to evaluate in a complex way the dispersion and structural properties of the ground product of brittle material grinding in a wet stirred media mill, while the flow behaviour of the slurry is also followed.

Figure 1. Complex measuring and evaluating method

2. It was proved by experiments that the online tube-rheometer and the method of measurement are suitable for monitoring the rheological behaviour of Newtonian and non-Newtonian suspensions during stirred media milling.



a.



b.

Figure 2. Rheological data of the c_m = 10w/w% suspension. a – Apparent viscosity versus grinding time. b – Pseudo shear curves.

3. It was found that the limestone suspensions with the original Newtonian rheological behaviour become Bingham plastic caused by high energy density milling in stirred media mill in reaching a certain (10 m^2/g) geometric specific surface area between 10-30m/m% of the concentration.

Table 1. Measured rheological and grinding parameters

Grinding time [min]	b [Pa]	τ_0 [Pa]	μ [mPas]	η [mPas]	x_{50} [mm]	SN [$\cdot 10^{10}$]	SSA [m^2g^{-1}]	W_f [$kJkg^{-1}$]
C_m= 10 w/w%								
59 (Newtonian – Bingham transition)	**0**	**0**	**0.028**	**28 (μ)**	**0.22**	**646**	**11.08**	**10100**
60	4	3	0.024	24	0.22	652	11.72	10300
120	14	10.5	0.063	63	0.18	979	20.54	20500
180	23	17.25	0.082	82	0.12	1300	21.63	30400
C_m = 20w/w%								
24 (Newtonian – Bingham transition)	**0**	**0**	**0.024**	**24 (μ)**	**0.36**	**98**	**11.05**	**2300**
46	33	24.75	0.072	72	0.20	216	12.71	4300
C_m = 30w/w%								
12 (Newtonian – Bingham transition)	**0**	**0**	**0.017**	**17 (μ)**	**0.42**	**36**	**8.54**	**730**
28	30	22.5	0.073	73	0.22	78	12.33	1830

4. FTIR measurements showed the structural changes in limestone during grinding, which is the shift of the band around 1400 cm^{-1}. It was found that the higher the concentration, the less specific grinding work needed to occur the relative banding intensity change.

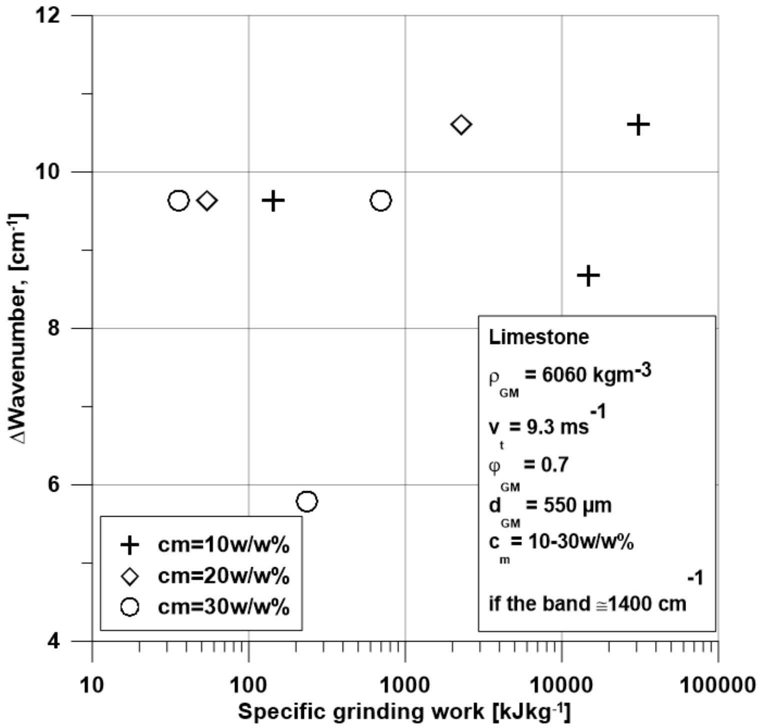
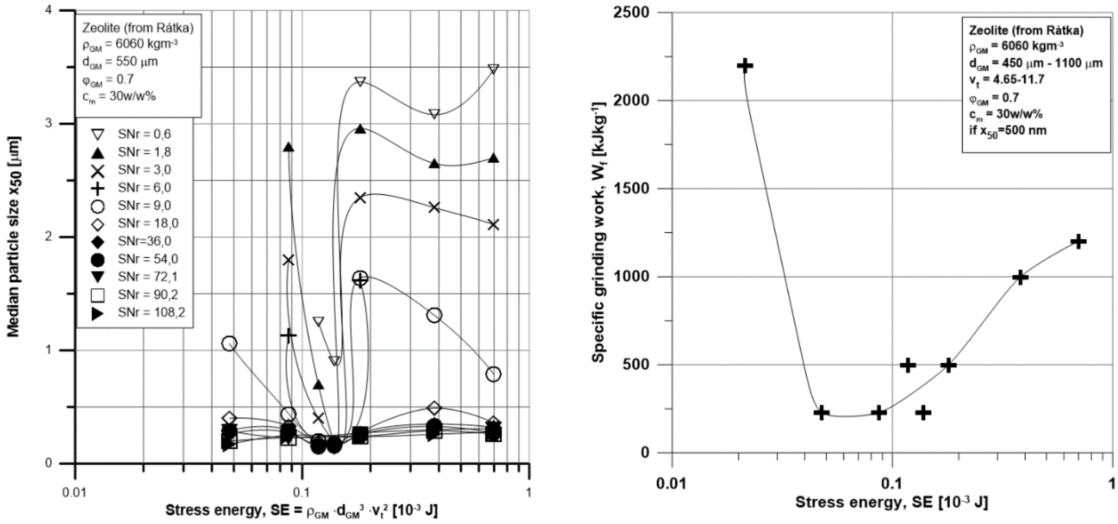


Figure 3 Changes in the wavenumber of the absorption band around 1400 cm^{-1} as a function of specific grinding work during grinding of limestone

5. Using the measuring and evaluation method described in the first thesis and using the Kwade stress model, an optimum machine, and operating parameter system can be established in case of a systematic nano grinding examination of zeolite in a stirred media mill. By using a small number of the experiment, a minimum amount of grinding energy can be obtained to determine the optimum suspension concentration and the stress energy, which can be achieved by the size, density and rotor circumferential speed of the grinding media.



a. b.

Figure 4 a. Median particle size as a function of stress energy for given stress numbers; b. Specific grinding work as a function of stress energy if the required median particle size is 500 nm

6. It has been established that in the case of zeolite grinding, the specific grinding work of the required product fineness has a minimum value as a function of the solids concentration.

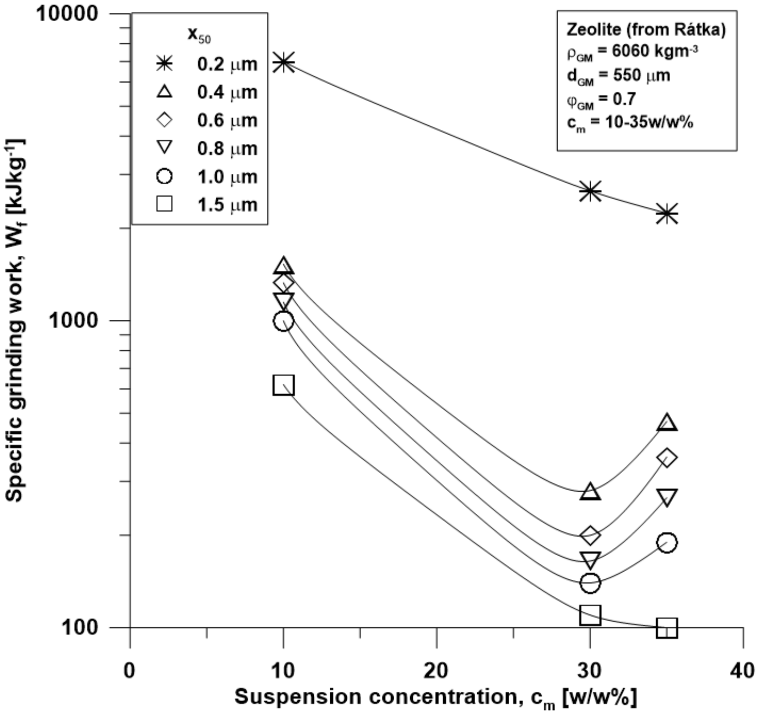
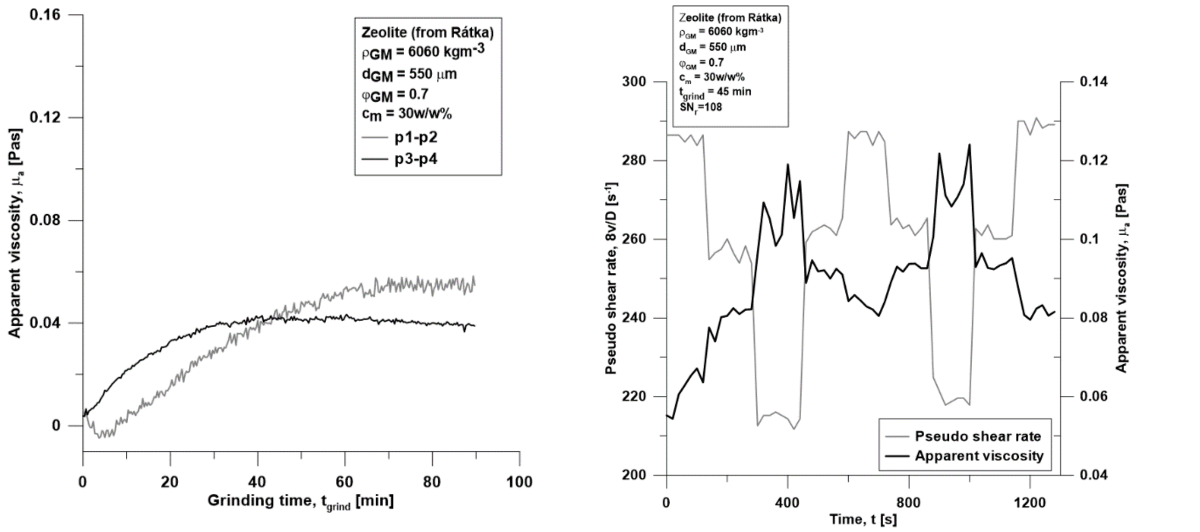


Figure 5 Specific grinding work required to produce different median particle size product depending on the concentration of the solid

7. By measurements, it proved that the viscous resistance of zeolite suspension changes during grinding and with the grinding time progressively the ground zeolite suspension has a time-dependent non-Newtonian rheological property.



a. b.

Figure 6. a. Apparent viscosity during continuous milling (SE = 0.0872 · 10^{-3} J); b. Pseudo shear rate and apparent viscosity as a function of the time required for tube-rheometer testing (SE = 0.0872 · 10^{-3} J and SNr = 108)

8. During the mechanical activation of zeolite, the change of clinoptilolite and amorphous content can be described by the power function of the specific grinding work. Based on these, I showed that amorphization took place in all three grinding (Rittinger, aggregation, and agglomeration) phases.

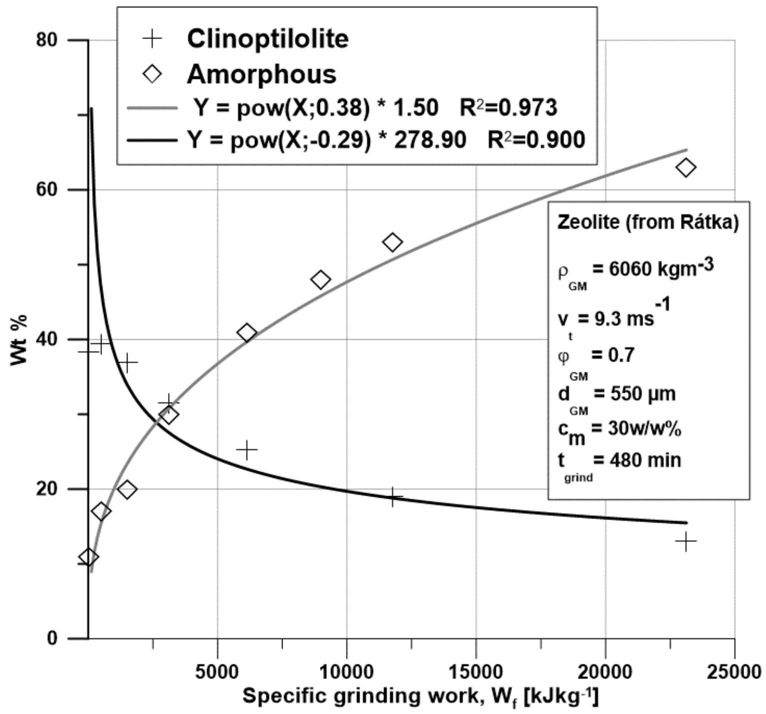
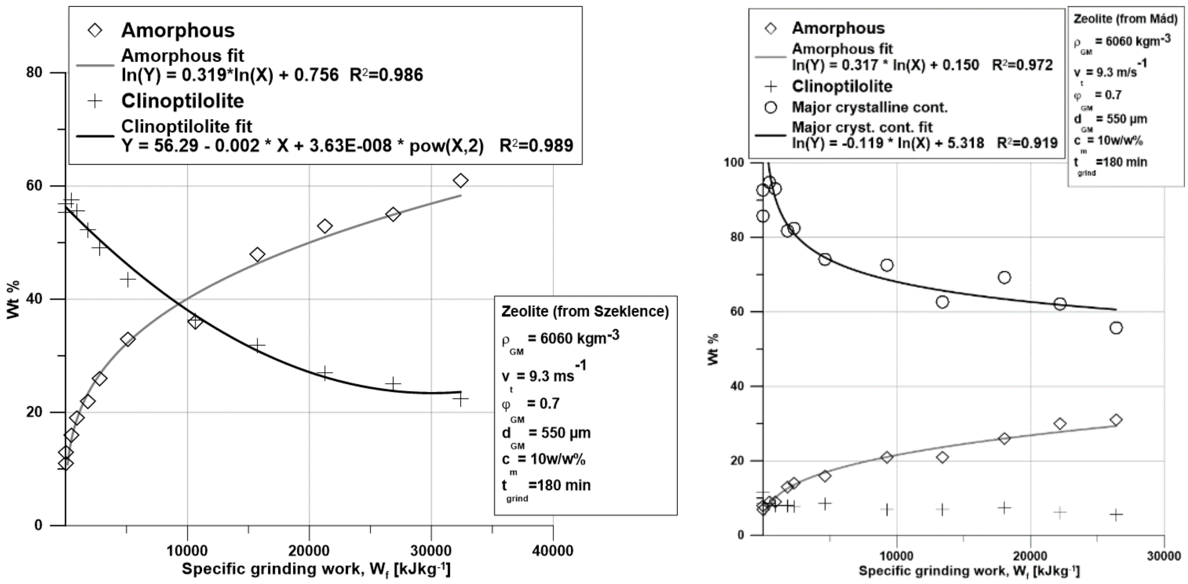


Figure 7. Changes in the main phase composition of zeolite from Rátka during grinding

9. It has been found that during the mechanical activation of zeolites with different compositions, different amorphization takes place under the same milling conditions. In

the case of homogeneous, high clinoptilolite containing zeolite (from Rátka and Szeklence), the clinoptilolite content decreases in the amount of amorphization, both changing with power function. While inhomogeneous zeolite (from Mád) is also amorphized with the major crystalline content (clinoptilolite, cristobalite, heulandite, montmorillonite, and smectite) also decreases with a power function.



a. b.

Figure 8. a. Changes in the main phase composition of (homogeneous) zeolite during grinding; b. Change of main phase composition of (heterogeneous) zeolite during grinding

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