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Chemometric assessment of mechano-chemically activated zeolites for application in the construction composites

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ABSTRACT

Natural zeolites of clinoptilolite type from seven deposits were submitted to mechano-chemical activation in a Retsch ultra-centrifugal mill. The zeolite types and activation parameters were altered during the experiment with an aim to determine the optimal combination that would produce powder with adequate physico-chemical and microstructural properties for application as a binder replacement and an ion-exchanger in the construction composites. The effects of input variables (chemical composition of the samples) and process parameters (the rotor velocity and the activation period) on the efficiency of zeolite activation were investigated in terms of dependent parameters such as: specific surface area, grain size distribution, cation exchange capacity, melting point, compression strength, shrinking, water absorption and apparent porosity. Cluster analysis, Principal component analysis and Standard score analysis were applied in the assessment of the acquired product quality. Artificial neural networks (ANN) were developed in mathematical modeling of observed responses. Subsequently the ANN was compared to experimental results and the developed second order polynomial models. Developed models showed r^2 values in the 0.822–0.998 range, meaning that they were able to predict the observed responses in a wide range of processing parameters. ANN models performed high prediction accuracy (0.975–0.993) and can be considered as precise and very useful for response variables prediction. The combination of the conducted mathematical analyses isolated Z5 zeolite as a preferable type, and 20000 rpm and 30 min as an optimal activation set of parameters. Mathematically derived conclusions were confirmed by results of instrumental analyses (XRD, DTA/TG, SEM).

1. Introduction

Zeolites comprise a multitude of natural and synthetic materials characterized by differences in the chemical, physical and structural properties [6,20]. Even though these mineral resources are commonly utilized in the design of composite materials with extensive application variety, there is a difficulty in excerpting just one definition of the term "zeolite" [11,35]. The IMA–CNMMN[1] Committee defined zeolite as "a crystalline substance with a framework of linked tetrahedra, each consisting of four oxygen atoms surrounding a cation" [8].

The natural zeolite is a crystalline hydrated aluminosilicate of alkali and alkaline earths characterized by the structure that contains frameworks with dimensionally equate crystals. The frameworks are interconnected by cavities and resided by large cations and water molecules. Since zeolite comprises SiO_4 and AlO_4 tetrahedra interlocked by oxygen atoms that are situated in the structural nodes, their characteristics differ due to the varieties in the structure-directing agents and Si/Al ratio [9,21]. The presence of extra-framework exchangeable cations enables zeolite substantial ion-exchange chemistry [30,42]. Zeolites are actually a form of "molecular sieves" with interconnected micro- and mesopores and cavities. Thusly created void channel maze allows relocation of ions and molecules in and out of the structure helping the ionic exchange. The structural empty spaces in the range of molecular dimensions (3–10 A°) can provide a space for receipt of Na^+, K^+, Mg^+, Ba^+ and Ca^+ cations, and also various metal cations and transition metal ions (Co, Fe, Mn, Zn), as well as molecules and ion groups (H_2O, NH_3, CO_3^{2-}, NO_3^-) [24,44]. The ion exchange capacity and the

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[1] International Mineralogical Association, Commission on New Minerals and Mineral Names: http://www.ima-mineralogy.org/CNMNC_Strategy.htm.

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Nomenclature

V	The velocity of the rotor (number of rotations per minute), rpm
AP	Activation period (milling duration), min
ZT	Zeolite type
BD	Dry (poured) density, g/cm^3
SSA	Specific surface area, m^2/g
M_1	Mass residue/oversize on the sieve with mesh size 63 μm, %
M_2	The sum of the mass residues/oversize on sieves with mesh sizes 63-5 μm, %
M_3	Mass undersize on the sieve with mesh size 5 μm, %
d_{av}	Average grain size, μm
CEC	Cation exchange capacity, mmolM$^+$/100 g
Mp	Melting point, °C
CS_7	Compressive strength measured after 7 days, MPa
CS_{28}	Compressive strength measured after 28 days, MPa
CS_{90}	Compressive strength measured after 90 days, MPa
CS^{1000}	Compressive strength measured after firing at 1000 °C, MPa
S^{110}	Linear shrinkage after drying at 110 °C, %
S^{1000}	Linear shrinkage after firing at 1000 °C, %
WA^{1000}	Water absorption after firing at 1000 °C, %
AP^{1000}	Apparent porosity after firing at 1000 °C, %
CA	Cluster analysis
PCA	Principal component analysis
ANOVA	Analysis of variance
SOS	Sum of squares
SOP	Second order polynomial model
ANN	Artificial neural networks

hydrophilicity are the most appreciated characteristics regarding zeolite application as absorber in the construction composites.

The zeolites easy availability and the utilization cost-effectiveness have prompted the research on their physicochemical and structural properties (e.g. adsorptive and molecular-sieve activity, heat resistance, and microporous cage structure) and finding new options for their application [19,26,31,39]. Apart from the presence of exchangeable framework cations which are crucial for the adsorption ability, and a certain degree of pozzolanic reactivity, the thermal stability is another important characteristic for use of the zeolite in composite materials that are exposed to high temperature. Thereby, the zeolites found a wide application possibilities in the design of the construction composites [3,27,45], as well as for resolving of the environmental protection issues like waste water refining or heavy metal elimination [13].

The activation treatment is a common and frequently applied procedure, both on laboratory and industrial scale, when certain characteristics of the zeolitic minerals have to be improved in order to enhance over-all performance of the final zeolite based composite. The mechano-chemical activation is based on continual blending and fracturing of solid-state powdery particles in a high-energy mill without altering material's chemistry [29,38,43]. The activation enables acquiring of the desired physicochemical behavior of the zeolite, such as enhancing the insufficient adsorptive capacity, increasing the specific surface area or improving inadequate reactivity, for its application as binder replacement and/or ion-exchanger [14,46]. The objective of this work was to investigate the effects of the zeolite chemical composition and milling variables (velocity, duration) on the activated powder quality described through a number of parameters (grain size and distribution, specific surface area, cation exchange capacity, shrinkage, melting point, porosity, strength, water absorption). The experiment was constituted on multiple testing and mathematical analyzing to acquire the best milling conditions and the optimal product. The application of statistical and mathematical tools is crucial when it comes to selecting the optimal result for further application of a zeolitic material as it is described in various studies [12,25,34,37]. Analysis of variance highlights the relations between obtained results, which is usually further specified and differentiated by pattern recognition techniques (Principal component analysis, Cluster analysis), and compared by means of Standard Score analysis and Artificial Neural Networks. The optimal, statistically singled out zeolite type, in this study, was further instrumentally analyzed to perceive structural changes upon milling and to assess the possibilities of its application in composite materials. The expected outcome of the study is an optimized activation procedure for the production of zeolite with physicochemical properties, thermal behavior and morphology appropriate for the application as value-added binder and adsorbent in construction composites.

2. Experimental

2.1. Material

The natural zeolitic tuffs that were used in this study originated from the seven different Serbian deposits. Hence the zeolites of different origin have varieties in the chemistry and consequently dissimilar properties; the idea behind the work was to apply statistics and the mathematical modeling to help in choosing of the optimal result of mechanical activation for further application of the zeolitic material in the construction composites.

All acquired tuffs visually appeared as pale yellow pelitic rocks covered with limonitic film. The rock mass comprised zeolitizated volcanic ash, and small amounts of quartz, plagioclase, and biotite. The crude samples from each deposit were obtained by standard sampling campaign and submitted to initial crushing. The 10 kg sub-samples (Z1-7) were acquired by cone and quartering method. Chemical analysis was performed by X-ray fluorescence method on an ED 2000 XRF spectrophotometer (Oxford Instruments, UK). Representative samples (100 g) were pulverized in a laboratory mill prior to testing (Standard: SRPS EN196-2:2015). Averaged values are given in Table 1.

2.2. Mechanical activation

The sub-samples were comminuted in laboratory in three steps (jaw crusher, roll crusher, and ceramic-lined mill with ceramic balls) to achieve adequate activation input. An ultra-centrifugal ZM-1 mill (Retsch, Germany) was applied for the mechano-chemical activation due to rapid and efficient size reduction ability [4,38–40]. The high alloyed steel rotor (⌀100 mm, 600 W) and a variable mesh size ring sieve (120 μm, trapezoid holes) created a reacting system for energy transfer from the mill to powder. The stainless steel grinding tools were placed in a 300 ml working element. The analytical fineness of the zeolite was achieved through its repeated fracturing and welding [4]. The micronized particles flowed from the rotor towards the sieve being able to