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STRUCTURAL CHANGES IN PYROPHYLLITE INDUCED BY MECHANOCHEMICAL MODIFICATION AND ZINC OXIDE DOPING

Emina Međedović[1a], Vanja Asanović[1b], Milena Tadić[1c], Jasmina Grbović Novaković[2a], Irena Nikolić[1d], Anđela Mitrović Rajić[3a]

[1] Faculty of Metallurgy and Technology, University of Montenegro, Džordža Vašingtona bb, Podgorica, Montenegro
[2] Centre of Excellence for Hydrogen and Renewable Energy, Laboratory of Physics, Vinča Institute of Nuclear Sciences - National Institute of Republic of Serbia, University of Belgrade, Belgrade, Serbia
[3] Institute of Technical Sciences of SASA, Kneza Mihaila 35/IV, 11000 Belgrade, Serbia
[1a] emedjedovic8@gmail.com, 0009-0001-9573-3252
[1b] vanjaa@ucg.ac.me, 0000-0001-8592-3266
[1c] milenak@ucg.ac.me, 0000-0001-7321-8842
[2a] jasnagn@gmail.com, 0000-0002-8481-6407
[1d] irena@ucg.ac.me, 0000-0001-6781-3485
[3a] andjelamitrovicfh@gmail.com, 0000-0003-3004-8139

Abstract

This study investigates the structural modifications of natural pyrophyllite that occur following mechanochemical treatment and subsequent doping with zinc oxide. Pyrophyllite ore with an initial particle size of approximately 180 µm was mechanically milled using a SPEX Mixer mill at 30 Hz for 15 minutes. Mechanochemically activated samples were then doped with 2 wt% ZnO and subjected to the same milling conditions. The structural and morphological transformations of the samples were examined using X-ray diffraction (XRD), scanning electron microscopy equipped with energy-dispersive spectroscopy (SEM-EDS), and particle size analysis by laser diffraction. XRD analysis revealed a decrease in reflection intensity, accompanied by broadening of the reflections, indicating a disorder in the crystal structure of the modified pyrophyllite sample. The introduction of zinc oxide led to a further decrease in peak intensities. SEM analysis revealed the formation of aggregates in the mechanically milled sample. The decrease in particle size was observed for doped samples. Particle size analysis confirmed a reduction in median particle size from 172 µm to 3.997 µm after milling, with a slight increase to 4.980 µm following ZnO doping. Specific surface area increased significantly with mechanochemical activation, from 0.04 m²/g to 2.25 m²/g, and slightly decreased to 2.06 m²/g after doping. These results confirm the effectiveness of mechanochemical treatment and ZnO doping in modifying the structural and surface characteristics of pyrophyllite, implying potential for enhanced sorption capacity, which is necessary for removing pollutants from wastewater.

***Keywords**: Pyrophyllite, mechanochemical modification, doping, sorption*

1. INTRODUCTION

Pyrophyllite, with a chemical formula $Al_2Si_4O_{10}(OH)_2$, has a continuous layered structure and is typically found in combination with other minerals such as quartz, mica minerals, kaolinite, epidote, and rutile [1]. Pure pyrophyllite consists of 28.3% Al_2O_3, 66.7% SiO_2, and 5% H_2O [1]. The water, which is distributed between two silica tetrahedral layers, is linked with aluminium to form an “aluminium hydroxide” layer - [$Al(OH)_3$]. The structural lamellae mainly depend on van der Waals forces, and they are easily slipped under shear action, making them an ideal pressure-transmission medium [2]. The physicochemical and mechanical properties of pyrophyllite enable its application in various fields, including metallurgy, ceramic material production, and the chemical industry [2], as well as in the pharmaceutical industry, pesticide production, paints, plastics, cement, and rubber manufacturing [1]. Pyrophyllite can be used as a substitute for

kaolinite in ceramic and pottery production, and it can also replace talc in many fields, particularly in the pharmaceutical industry and medicine [1].

Pyrophyllite's layered structure provides a large surface area for adsorption. It is resistant to most chemical attacks, making it suitable for harsh industrial wastewater environments. The mechanochemical process is an effective method for producing fine-structured products from raw materials, including clay minerals [3], which not only causes a decrease in particle size but also induces structural changes that lead to an increase in chemical reactivity [4]. Mechanical milling of solid substances causes various phase transformations, cracks, and the formation of new surfaces [5]. It was found that the mechanochemical activation of pyrophyllite may affect its structural order and reactivity [3,4]. In the present study, we will investigate how doping mechanochemically activated pyrophyllite with zinc oxide induces the development of a new structure and enhances the characteristics of the resulting material.

2. EXPERIMENTAL

The powder of pyrophyllite with a particle size of about 180 μm originating from the ore deposited in Parsovići (Bosnia and Herzegovina) was mechanically milled using a SPEX Mixer mill 5100 for 15 minutes at 30 Hz, while the ratio of the weight of the balls to powder was 10:1. Mechanochemicaly activated pyrophyllite was then doped with 2% of zinc oxide - two powders where subjected to the mechanical milling for 15 minutes at 30 Hz.

The crystal structure of the samples was examined using a Philips PW 1050 diffractometer with nickel-filtered CuK$\alpha_{1,2}$ radiation (λ =0.1540 nm). The X-ray spectra have been recorded in the (2θ) range from 5° to 80° in steps of 0.02° for 10 s. The microstructure of natural pyrophyllite, activated pyrophyllite and doped samples was examined by scanning electron microscopy (SEM) using FEI SCIOS 2 Dualbeam. A Malvern 2000 Mastersizer laser scattering particle size analyser has been employed to determine the particle size distribution of samples. The designated resolution range of the system was sub-micrometre to 2 mm. As the suspension medium, 2-propanol was used. All samples underwent ultrasonication for 10 minutes before measurement. All measurements were conducted at a uniform stirring speed and obscuration level.

3. RESULTS AND DISCUSSION

X-ray diffraction (XRD) analysis has revealed that natural pyrophyllite ore consists of pyrophyllite, kaolinite, muscovite, quartz, and calcite. Mechanochemical modification of pyrophyllite ore results in changes to its crystal structure. Compared to the initial sample, the XRD profile of the mechanically modified pyrophyllite sample showed a significant decrease in the typical XRD reflection intensities (Figure 1). In addition, the broadening of the reflections was also observed. In the case of pyrophyllite doped with 2% zinc oxide, the diffraction results show a decrease in the intensity of the diffraction peaks.

Compared to the initial sample of pyrophyllite ore, which contains particles with rough surfaces and non-uniform sizes, and single particles showing a laminar structure [6], morphological characterisation of mechanochemically modified pyrophyllite using scanning electron microscopy with energy-dispersive spectroscopy (SEM-EDS) has shown significant disruption of laminar structure, and smaller particles formed by fragmentation form aggregates (Figure 2). SEM analysis of material obtained by doping modified pyrophyllite with 2% zinc oxide reveals changes in surface morphology, including the distribution of oxide particles over the surface of pyrophyllite, which maintains a laminar structure with a slight increase in roughness (Figure 2). Chemical composition of the particles is shown in Table 1.

The effect of mechanochemical activation and doping on the pyrophyllite with zinc oxide on particle size distribution is shown in Figure 3. The values of specific surface area and d (0.1), d (0.5) and d (0.9) particle size of examined samples are presented in Table 2. The median particle

size of natural pyrophyllite decreased from 172 μm to 3.997 μm during mechanical milling, while doping caused an increase to 4.980 μm. Mechanical milling resulted in a change in the structure of the pyrophyllite, leading to an increase in the specific surface area from 0.04 m²/g to 2.25 m²/g. In contrast, additional doping induced a slight decrease to 2.06 m²/g. Repeated fracture during treatment leads to a significant reduction in particle size, thereby increasing the specific surface area of the material particles. Increasing the specific surface area of pyrophyllite through mechanochemical modification implies that its sorption properties will be improved, which are necessary for removing pollutants from wastewater.

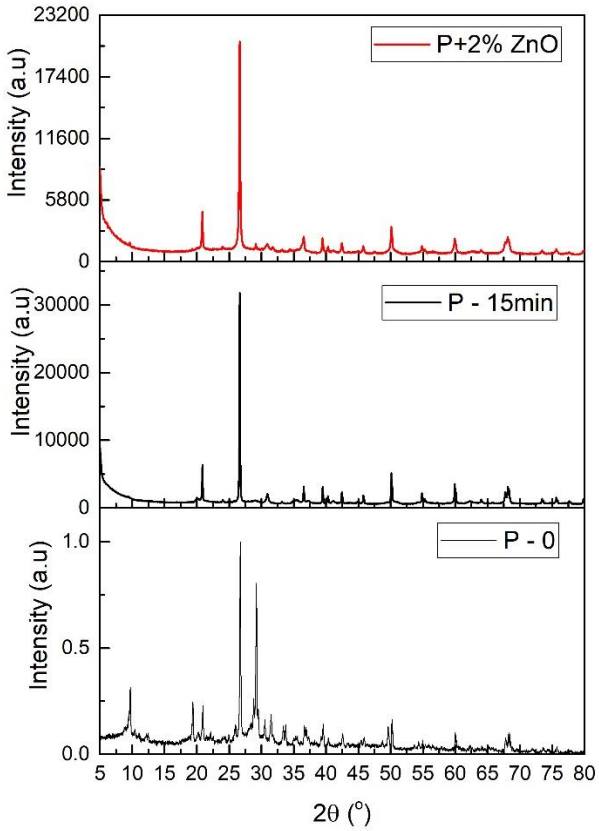
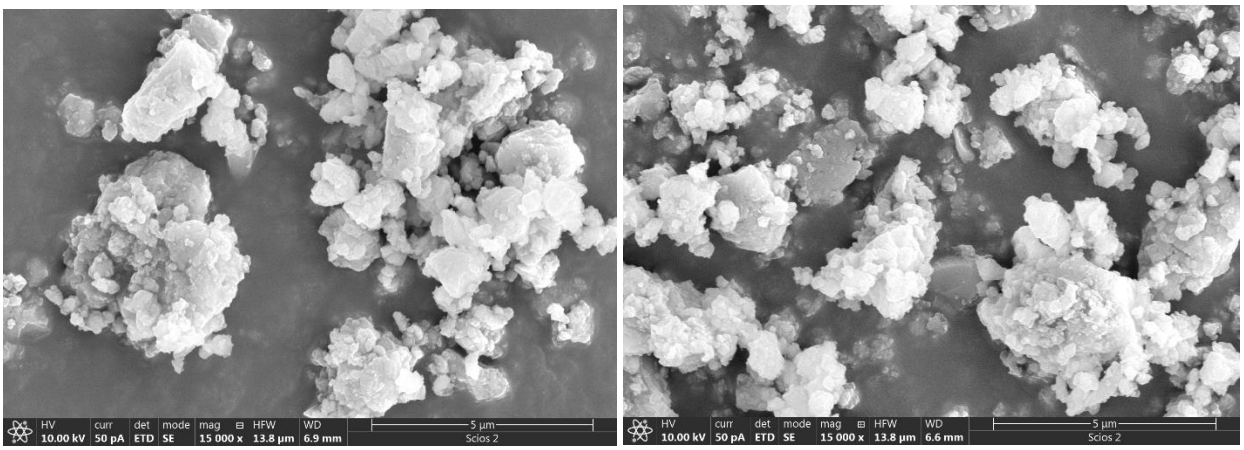


Figure 1. XRD patterns of natural pyrophyllite ore (P – 0), modified pyrophyllite (P – 15 min) and doped pyrophyllite (P+2%ZnO)



a) b)

Figure 2.SEM micrographs of mechanically modified pyrophyllite and doped pyrophyllite

Table 1. Chemical composition of the particles

Specimen	Chemical composition [weight %]									
	Si	Al	O	Mg	Ca	K	C	Zn	Na	F
modified pyrophyllite	30.284	11.220	46.957	1.786	4.153	0.832	4.000		0.202	0.566
doped pyrophyllite	32.409	8.704	44.902	0.995	2.279	0.759	6.896	3.056		

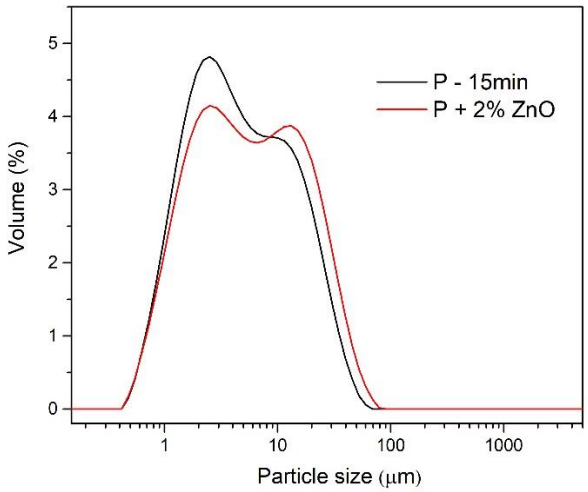


Figure 3. Particle size distribution of pyrophyllite sample (P – 15 min) and doped pyrophyllite (P+2%ZnO)

Table 2.Specific surface area and particle size of examined samples

Specimen	Specific surface area [m^2/g]	d (0.1) [μm]	d (0.5) [μm]	d (0.9) [μm]
modified pyrophyllite	2.25	1.135	3.997	18.105
doped pyrophyllite	2.06	1.180	4.980	22.542

4. CONCLUSION

Mechanochemical activation significantly alters the structural and morphological properties of natural pyrophyllite, reducing particle size and increasing specific surface area due to repeated fracture and increased disorder. Doping with 2 wt% zinc oxide further modifies these characteristics, slightly increasing particle size and influencing surface morphology. The combined treatment demonstrates an effective approach for tailoring the microstructure and enhancing the reactivity of pyrophyllite, potentially expanding its applicability in areas such as pollutant adsorption.

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