DIATOMACEOUS EARTH: A PRECURSOR IN THE SYNTHESIS OF NEW MATERIALS

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Abstract: *This paper presents the results of research on diatomaceous earth as a possible precursor for obtaining new materials. Diatomaceous earth from the Kolubura Basin was used, where it is present as an accompanying mineral raw material. In the synthesis process, it was ion-exchanged with a diluted 0.25 M $MnNO_3$ solution. After that, the samples were annealed in a temperature range of 800 to 1100 ºC. A new phase of the mineral akatoreite ($Mn_9Al_2Si_8O_{24}(OH)_8$) was obtained. In the characterization process, the method of X-ray powder diffraction on a polycrystalline sample and the method of a scanning microscope were used.*

Key words: DIATOMACEOUS EARTH, AKATOREITE, X-RAY POWDER DIFFRACTION ANALYSIS, SEM/EDS METHOD

INTRODUCTION

Kolubara Coal Basin is one of the largest in Serbia, covering about 600 km^2 [1]. It was formed in a partially isolated bay of the Paratetis Sea with marine deposits of the Baden, Sarmatian, Pannonian and Pontic ages. The transgression of the sea towards the south formed, during the Pontus, two different ones sedimentary belts with coal deposits. they are separated by a regional dislocation in the W-E direction [2]. The deposit of lignite are concentrated in three coal basins within the EPS: Kolubarski, Kostolački and Kovinski, Figure 1.

Figure 1, Kolubarski Basen

Legend: *1. Field"Kruševica, 2. Field "Rudovci, 3. Field "A", 4. Field"B", 5. Polje "C", 6. Field "Baroševac", 7. Field "E", 8. Field "D", 9. Field "Turija", 10. Field "Stepojevac", 11. Field "Veliki Crljeni", 12. Field "Volujak-Vreoci", 13. Field "G", 14. Polje "F", 15. Field "Šopić" Lazarevac, 16. Field"Tamnava-Istok", 17. Field "Tamnava-Zapad", 19. Field"Trlić", 20. Field "Zvizdar", 21. Field "Ruklade".*

The concentration of economically significant reserves of non-metallic raw materials in the accompanying sediments of lignite deposits has long been established. As mineral raw materials, there are clays of different quality, sand, gravel, coal tailings, diatomaceous earth, fly ash. The diversity of the mentioned raw material base in terms of technology and the possibility of producing a wide range of products for the needs of the construction industry, metallurgy, chemical and glass industry are more reasons for defining and valorizing the accompanying mineral raw materials in the lignite deposits here. Due to the size of the deposit and its diverse lithological composition, it was divided into the Eastern and Western parts of the Kolubara coal basin. In this basin, the most important non-metallic mineral raw materials were singled out: diatomaceous earth, quartz sand, ceramic-refractory clays, siltstones, various types of plastic clays, brick clays and gravel. Gravel is used to make the lower and upper bearing layers of road constructions [3]. Brick raw material is represented by montmorillonite-illite clays, which are used for the production of bricks and pancakes.

Diatomaceous earth is a biogenic sedimentary rock consisting of very small shells of diatom skeletons (from 70-80%). Of the admixtures, it regularly contains significant amounts of clastic materials of the sandy fraction, clay minerals, radiolarian skeletons and organic substances. Diatomaceous earth is a soft, loose and loosely bound rock, sometimes powdery. It is white in color, although due to the content of impurities it can be yellowish, greenish and gray. It looks similar to writing chalk, but it does not dissolve in hydrochloric acid. It is extremely porous and has a low specific density (0.4-0.9 g/cm^3). It is used for insulating purposes and as a filler in the industry of paper, rubber and plastics, paints, varnishes, soaps, linoleum, gramophone records. In addition, diatomaceous earth makes an excellent filtration material that is used in the beer and soft drinks industry.

This paper presents the results of mineralogical and crystal-chemical research on diatomaceous earth (Field "B"), which was a precursor for the synthesis of new materials.

METHOD

The form of the diatomic earth, from Kolubara basen, were used as starting materials. Fully exchanged Mn^{2+} forms of these diatomic earth were prepared after several successive exchanges from 0.21 M $Mn(NO_3)_2$ solutions with the solid/liquid ratio (S/L) 1/30 [4]. The presence of different cations was determined by EDAX analysis. The sample are noted as Mn_{800}, Mn_{900} and Mn_{1000}.

The corresponding X-ray powder diffraction patterns were obtained by a Philips PW-1710 automated diffractometer, using a Cu tube operated at 40 kV and 30 mA. The instrument was equipped by a diffracted beam curved graphite monochromatic and Xe-filled proportional counter. The diffraction data of treated samples were collected in the range of 4 to 35° 2θ Bragg angles counting for 1.0 sec in 0.02° steps, for routine phase analysis.

The investigations of crystal morphology of thermally treated partially Mn-synthesized phases were carried out by scanning electron microscopy, using a JEOL 840A instrument. The investigated samples were gold sputtered in by a JFC 1100 ion sputterer.

RESULT AND DISCUSSION

SEM/EDS AND CRYSTALOCHEMICAL ANALYSIS TREATED SAMPLES

Microscopic examination revealed that diatomaceous earth consists exclusively of fossil diatomite shells that appear in spherical, needle-saw-shaped and rectangular-square forms. The most represented are rectangular-square and spherical forms, while needle-saw shaped forms are the least represented. Diatomites are isotropic, ie amorphous. Quartz occurs from crystalline silicon, but in a negligibly small percentage. The presence of carbonaceous matter was also determined in the sample. In Figure 2, a photomicrograph of diatomaceous earth with chemical analysis is presented.

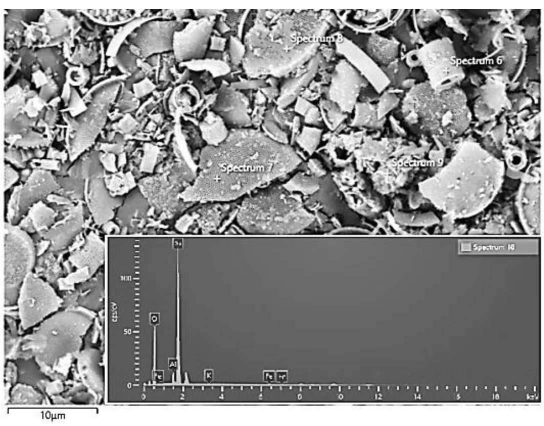

Figure 2, Photomicrograph of diatomaceous earth, with chemical analysis

Based on the chemical analysis, it was determined that SiO_2 is most present in the sample with 95.01%, Al_2O_3 3.96%, other oxides are present in a much smaller percentage (CaO 0.98%, K_2O 0.233%, Fe_2O_3 0.815%).

During the thermal treatment of Mn − modified diatomite earth at temperature of 800ºC, new Mn-diatomite earth phase was formed, akatoreite $Mn_9Al_2Si_8O_{24}$. The chemical result of Mn diatomite earth were observe during the thermal treatment (from 800 to 1100 ºC) and are presented in (Figure 3). The results of the chemical composition of ion exchange diatomic earth with Mn-cation are presented in Table 1.

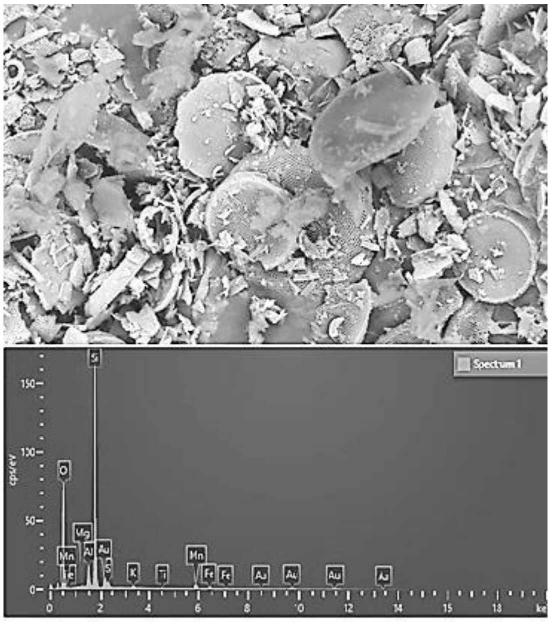

Figure 3, Photomicrograph of Mn-diatomaceous earth, with chemical analysis

Table 1, The chemical composition of diatomic earth determined with AAS and EDAX methods

Element	Weight [%]	Atomic [%]	Oxide	[%]
O	51.27	65.89		
Mg	0.15	0.12	MgO	0.24
Al	3.50	2.67	Al_2O_3	6.62
Si	38.98	28.54	SiO_2	83.40
S	1.56	1.00	SO_3	3.90
K	0.53	0.28	K_2O	0.64
Ti	0.10	0.04	TiO_2	0.17
Mn	2.94	1.10	MnO	3.80
Fe	0.96	0.35	FeO	1.24
Total	100	100.00		100

The chemical analysis of Mn-diatomic earth (see Table 1) revealed that the starting diatomic precursore, were not completely modified with Mn $^{2+}$. The Si: Al ratio does not change during the ion exchange process. During the thermal treatment of Mn-modified diatomic earth at temperature of 800 ºC, new phase Akatoreit $Mn_9Al_2Si_3O_{24}$ were formed. The structural changes of Mn-diatomic earth phase were observe during the thermal treatment (from 800 to 1000 ºC) and are presented in (Figure 4 a-c).

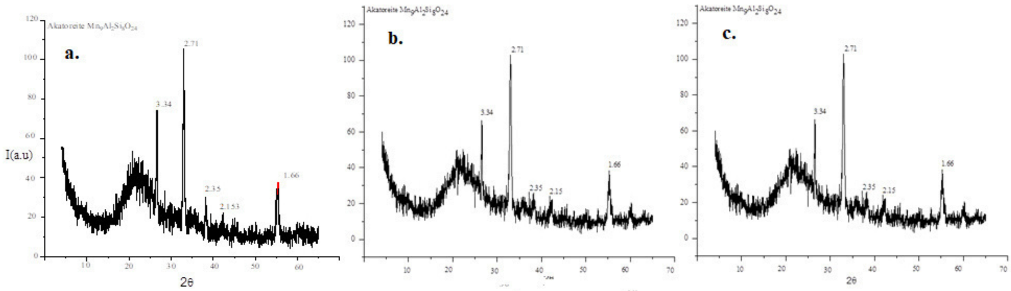

Figure 4, Comparative X-ray diagrams of thermally treated Mn-diatomaceous earth powder

Based on the X-ray powders diagrams, we can see that at a temperature of 800 ºC, a new phase of $Mn_9Al_2Si_3O_{24}$ with the most intense peak of *d* value is formed at 2.71. Akatoreite is a hydrous manganese aluminosilicate, which belongs to the sorosilicate group. It occurs as vitreous, orange-brown,massive to radiating twinned columnar araggregate sin a manganiferous metachert and carbonate lens [5].

We can conclude that in the ion exchange of diatomaceous earth it is possible to obtain a new silicate phase, in this case the sorosilicate Akatoreite, Figure 5.

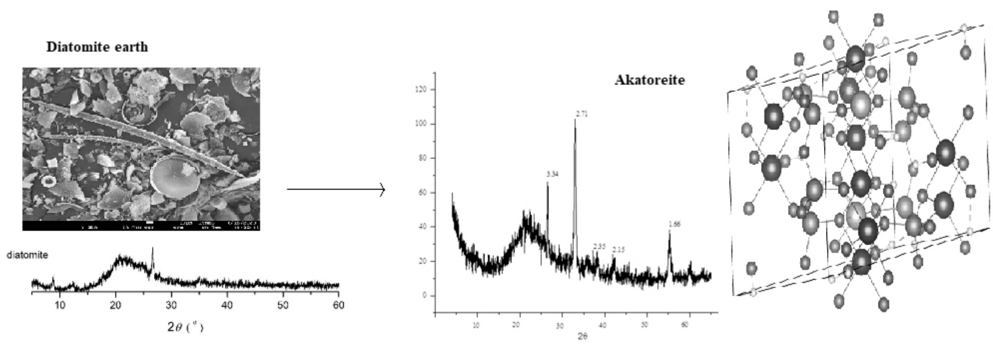

Figure 5, Thermally treated Mn-diatomaceous earth (from initial to thermally treated sample)

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