

## FT-IR/PAS AND SEM EDX STUDIES ON ALUMINOSILICATES MODIFIED BY CS(I), TH(IV) AND U(VI)

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*Clays and zeolites are some of the most important industrial minerals. They have practical applications in geology, agriculture, construction, engineering, process industries, and environment. This article is about one of them: radioactive waste disposal. We were investigating characteristics of bentonite clay and clinoptilolite in case of Cs(I), Th(IV), U(VI) sorption.*

**Keywords:** *industrial minerals, radioactive waste disposal*

### 1. INTRODUCTION

Clays and zeolites are some of the most important industrial minerals. They have practical applications in geology, agriculture, construction, engineering, process industries, and environment. There are many traditional applications of aluminosilicates. Some of the most important include ceramics, paper, paint, plastics, drilling fluids, foundry bondants, chemical carriers, liquid barriers, decolorization, and catalysis. Our research was focused on radioactive waste disposal from aqueous solutions by using clays (bentonite and palygorskite). Clays are cheap and widely available material, and it's interesting to investigate its characteristic in relation to Cs(I), Th(IV), U(VI) sorption.

### 2. EXPERIMENTAL

The subjected aluminosilicates (bentonite and palygorskite) are naturally mined and grinded to suitable dimensions. They are quite well homogeneous. In this form they are used in industries. The EDX (Energodipersive X-ray Analysis) spectra were measured using the

Roentec EDX detector mounted on the LEO 1430VP scanning electron microscope. 50-point microanalysis were averaged and used for statistics.

The FT-IR/PAS spectra were recorded by means of a Bio-Rad Excalibur 3000MX spectrometer equipped with a photoacoustic detector MTEC300 (in the helium atmosphere in a detector) over the 4000-400  $\text{cm}^{-1}$  range at the resolution of 4  $\text{cm}^{-1}$  and maximum source aperture. The spectra were normalized with reference to MTEC carbon black standard. A stainless steel cup (10 mm diameter) was filled with powder samples (thickness <6 mm). Interferograms of 512 scans were averaged for each spectrum.

The extraction process was conducted in 4 groups, but only 2 groups are present in this paper:

1. natural aluminosilicate,
2. sodium activated aluminosilicate  
2 M NaCl, 0,1 M HCl,
3. calcium activated aluminosilicate  
2 M  $\text{CaCl}_2$  , 0,1 M HCl,
4. 2 M HCl rinsed aluminosilicate.

Every group was shaken with three solutions (containing Cs(I), Th(IV), U(VI) ions).

Sorption microquantities of these ions from the 0,01 M nitric acid solution on the prepared aluminosilicates was investigated. As follows Cs(I), Th(IV), U(VI) ions sorption depends on sorbent preparation. In this publication only natural, and Na-form clays are review.

The recorded EDX spectra allowed to distinguish the differences between the properties of bentonite and palygorskite and those between various forms of these sorbents.

3. RESULTS AND DISCUSSION

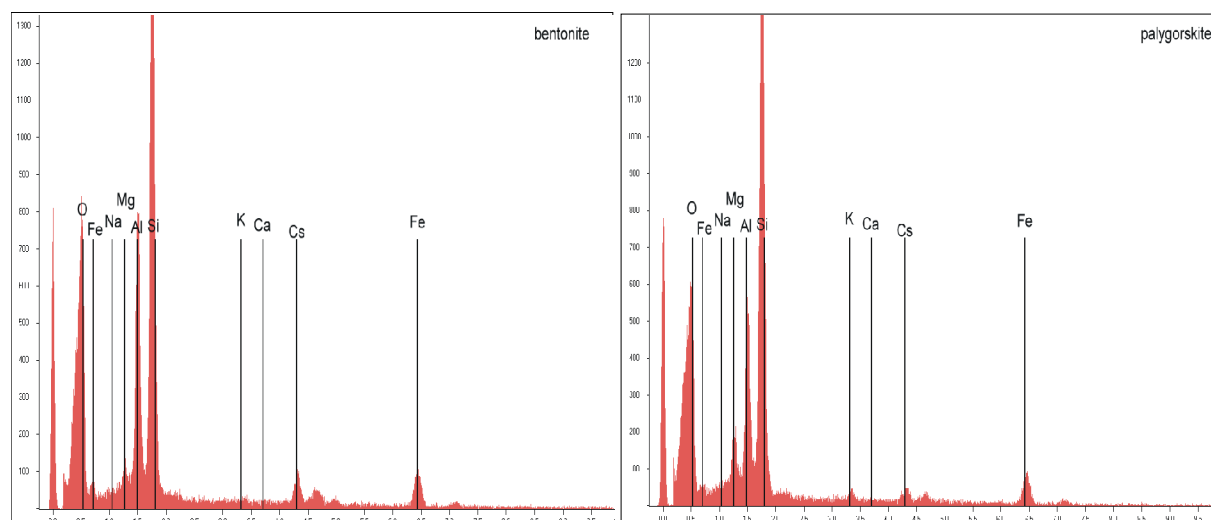


Fig.1. EDX spectra of investigated aluminosilicates after sorption process. (x axis – energy, y axis – counts).

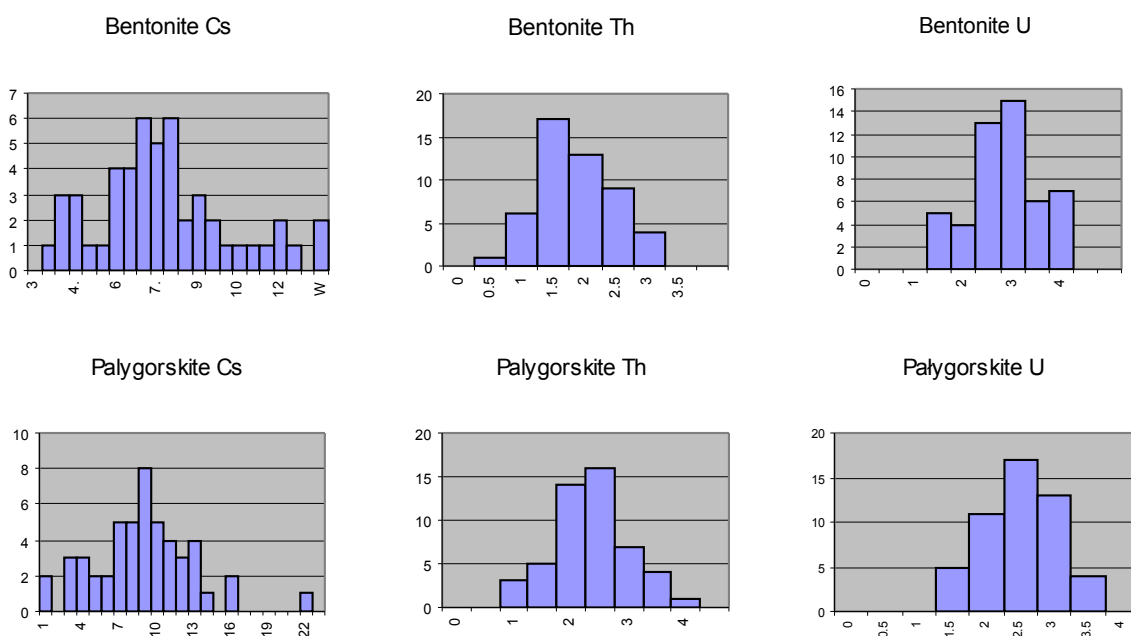


Fig. 2. Surface heterogeneity of selected aluminosilicates after sorption process (EDX data, x axis - concentration, y axis – frequency).

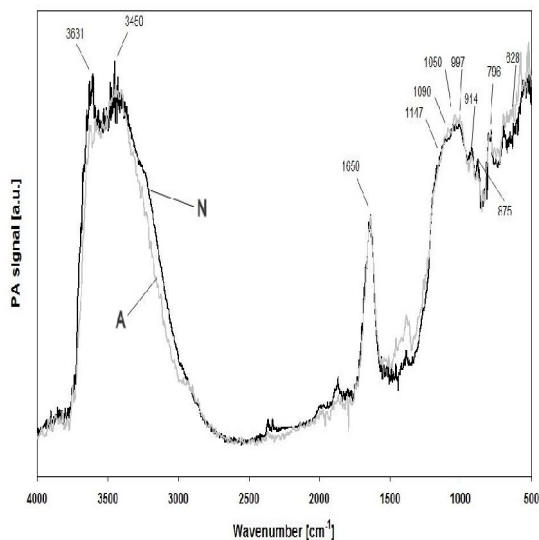


Fig. 3. FT-IR PAS spectra of bentonite (N - natural form, A - Na form).

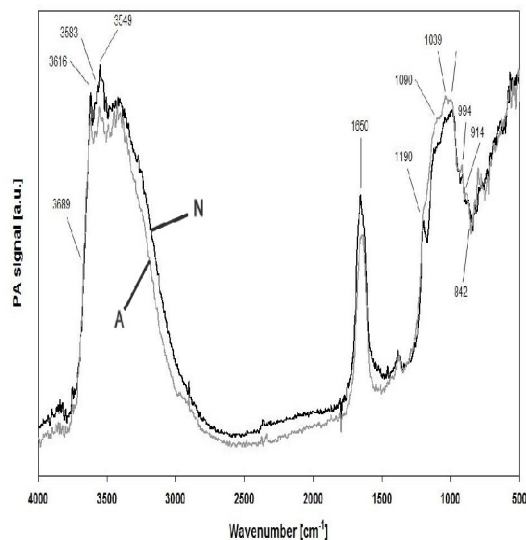


Fig. 4. FT-IR PAS spectra of palygorskite (N - natural form, A - Na form).

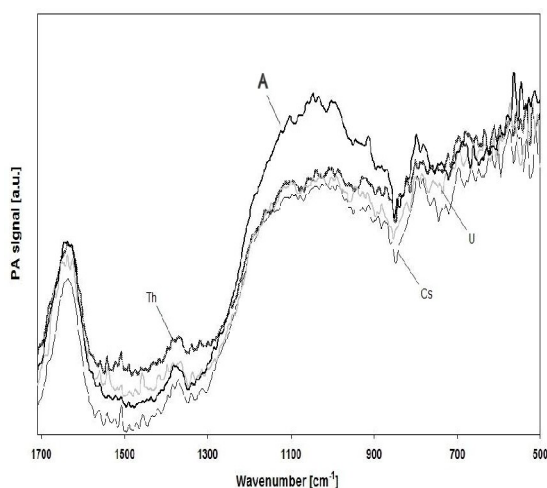


Fig. 5. FT-IR PAS spectra of four forms of bentonite (A-Na form, Cs(I), Th(IV), U(VI)).

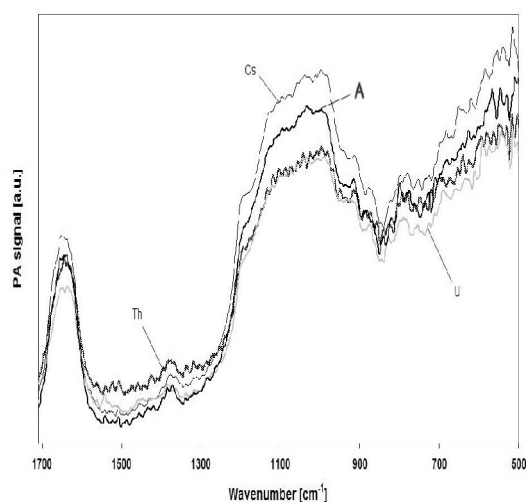


Fig. 6. FT-IR PAS spectra of four forms of palygorskite (A-Na form, Cs(I), Th(IV), U(VI)).

### 3.1. THE EDX ANALYSIS

The Energodispersive X-ray Spectroscopy is very useful to determine many physical and chemical properties for natural aluminosilicates under investigations. The EDX method is suitable to determine surface concentration histograms which allow finding places of different power of sorption on the surface of investigated aluminosilicates. Based on the histograms we can determine places with different sorption power on the aluminosilicates surface. As can be seen, in each sample there exist more than one type sorption power places.

### 3.2. PALYGORSKITE - FT-IR PAS SPECTRA DESCRIPTION (FIG. 4.)

The peak at  $3616\text{ cm}^{-1}$  is characteristic of this mineral and corresponds to the OH stretching vibrations in M2-OH groups (where  $M = \text{Al}^{3+}$  or other trivalent cations). The low

intensity peak at  $3583\text{ cm}^{-1}$  corresponds to vibrations of zeolitic and coordination water blocked in palygorskite channels. The peaks between  $3550 - 3350\text{ cm}^{-1}$  correspond to vibrations of zeolitic and coordination water. The peak at  $3549\text{ cm}^{-1}$  indicates vibrations of not only coordination water, but also those of OH in Al-Mg-OH, Fe-Mg-OH and Fe-Fe-OH group. At  $3689\text{ cm}^{-1}$  there occurs a small peak, which indicates trioctahedral character of 3Mg-OH group. Low intensity of this peak is caused by larger amount of  $M_2$ -OH group presence. The asymmetric signal at  $1650\text{ cm}^{-1}$  corresponds to bending vibrations of zeolitic and adsorbed water. In the region between  $1200 - 400\text{ cm}^{-1}$  there occur characteristic bands for silicates, mostly related to stretching vibrations of M-O ( where  $M = \text{Si, Al}$ ). The peak at  $1190\text{ cm}^{-1}$  is characteristic of palygorskite. This fact is related to the structure of this mineral, where there occurs inversion of top oxygen atom in tetrahedron which is manifested by the O-Si-O bond between crossing layers. In the area of  $1090\text{ cm}^{-1}$  there appears a doublet of M-O or Si-O stretching vibrations. The signals at  $1039\text{ cm}^{-1}$  and  $989\text{ cm}^{-1}$  correspond to Si-O stretching vibrations. The sharp signal appearing at  $914\text{ cm}^{-1}$  is responsible for Al-Al-OH groups deformations. The arm between  $896\text{ cm}^{-1}$  and  $867\text{ cm}^{-1}$  corresponds to bending vibrations of Al-Fe-OH groups. At  $834\text{ cm}^{-1}$  there exists a signal of Al-Mg-OH bonds vibrations. [1-3,5]

### 3.3 BENTONITE - FT-IR PAS SPECTRA DESCRIPTION (FIG. 3.)

The peak at  $363\text{ cm}^{-1}$  corresponds to stretching vibrations of Al(Mg)-OH. The bands between  $3550- 3350\text{ cm}^{-1}$  are related to coordination and zeolitic water stretching vibrations. At  $3450\text{ cm}^{-1}$   $\text{H}_2\text{O}$  stretching band can be found. The asymmetric signal at  $1650\text{ cm}^{-1}$  corresponds to bending vibrations of zeolitic and adsorbed water. Near  $1090\text{ cm}^{-1}$  area there exists a doublet of M-O or Si-O stretching vibrations. The peaks at  $1147\text{ cm}^{-1}$ ,  $1050\text{ cm}^{-1}$  and  $997\text{ cm}^{-1}$  correspond to Si-O stretching bond vibrations. The sharp signal appearing at  $914\text{ cm}^{-1}$  is responsible for Al-Al-OH groups deformations. The sharp peak at  $875\text{ cm}^{-1}$  is related to deformations of Fe-Al-OH groups. Silicate vibrations band exists at  $796\text{ cm}^{-1}$ . The signal at  $628\text{ cm}^{-1}$  corresponds to twisting vibrations of Al-OH and Si-O and stretching vibrations of Al-O [1-4].

Figures 5 and 6 show the FT-IR PAS spectra of impregnated clays (Cs(I), Th(IV) and U(VI)) in comparison with Na-form. Intensities and wavenumbers of many peaks are changed. Especially, there can be seen decay of  $1190\text{ cm}^{-1}$  peak in palygorskite (characteristic peak of this clay), which can be explained by bracing properties of adsorbed ions. Changes of signal at  $1650\text{ cm}^{-1}$  (belonging to zeolitic and adsorbed water) depend on the kind of sorbed ions. In the case of Th(IV) and U(VI) the signals are divided into  $1650\text{ cm}^{-1}$  and  $1640\text{ cm}^{-1}$ .

Th(IV) and U(VI) ions are more hydrated than Cs(I) ions and implement coordinated water to clay structure [1-4].

#### 4. CONCLUSION

Both methods (EDX and FTIR-PAS) are very useful in the investigations of clays under question. The EDX method is suitable to determine surface concentration histograms which allow finding places of different power of sorption on the surface of investigated aluminosilicates, but these data are incomplete without FT-IR/PAS investigations. FT-IR/PAS complements these results by giving information about structural changes after activation and sorption process of Cs(I), Th(IV) and U(VI).

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