Optical and Acoustical Methods in Science and Technology

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 are investigating characteristics of bentonite clay and clinoptilolite in case of Cs(I), Th(IV), U(VI) sorption.

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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 is 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 energodipersive X-ray analysis (EDX) spectra were measured using the Roentec EDX detector mounted on the LEO 1430VP scanning electron microscope (SEM). 50-point microanalysis were averaged and used for statistics.

The FT-IR photoacoustic (FT-IR/PA) 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 cm^{-1} range at the resolution of 4 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 $CaCl_2$, 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 reviewed.

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

3.1. The EDX analysis

The EDX 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

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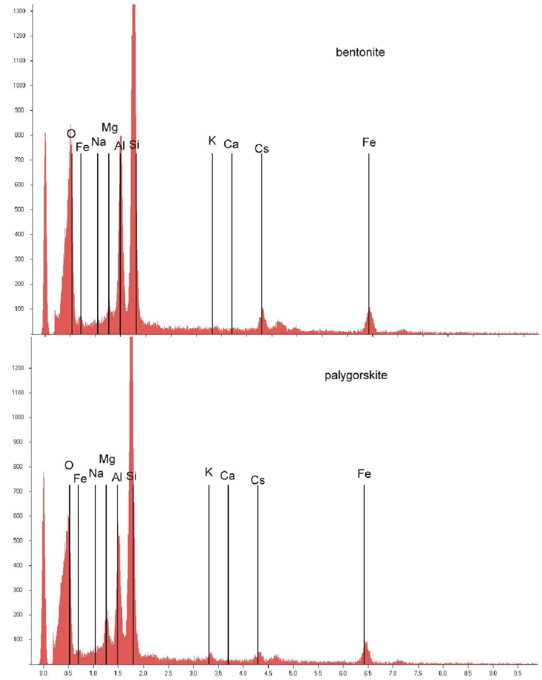

Fig. 1. EDX spectra of investigated aluminosilicates after sorption process (x axis — energy, y axis — counts).

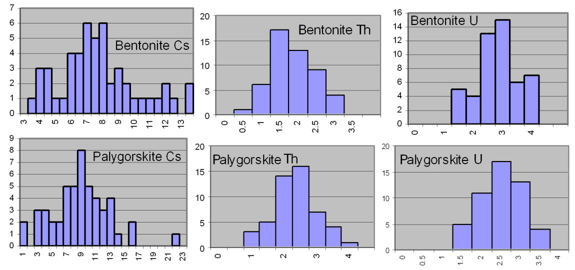

Fig. 2. Surface heterogeneity of selected aluminosilicates after sorption process (EDX data, x axis — concentration, y axis — frequency).

investigated aluminosilicates (Fig. 1). Based on the histograms we can determine places with different sorption power on the aluminosilicates surface (Fig. 2). As can be seen, in each sample there exist more than one type sorption power places.

3.2. Palygorskite — FT-IR PAS spectra description

The peak at 3616 cm^{-1} is characteristic of this mineral and corresponds to the OH stretching vibrations in M_2–OH groups (where M = Al^{3+} or other trivalent cations) (Fig. 3). The low intensity peak at 3583 cm^{-1} corresponds to vibrations of zeolitic and coordination water blocked in palygorskite channels. The peaks between 3550–3350 cm^{-1} correspond to vibrations of zeolitic and coordination water. The peak at 3549 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 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 cm^{-1} corresponds to bending vibrations of zeolitic and adsorbed water. In the region 1200–400 cm^{-1} there occur characteristic bands for silicates, mostly related to stretching vibrations of M–O (where M = Si, Al). The peak at 1190 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 cm^{-1} there appears a doublet of M–O or Si–O stretching vibrations. The signals at 1039 cm^{-1} and 989 cm^{-1} correspond to Si–O stretching vibrations. The sharp signal appearing at 914 cm^{-1} is responsible for Al–Al–OH group's deformations. The arm between 896 cm^{-1} and 867 cm^{-1} corresponds to bending vibrations of Al–Fe–OH groups. At 834 cm^{-1} there exists a signal of Al–Mg–OH bonds vibrations [1–7].

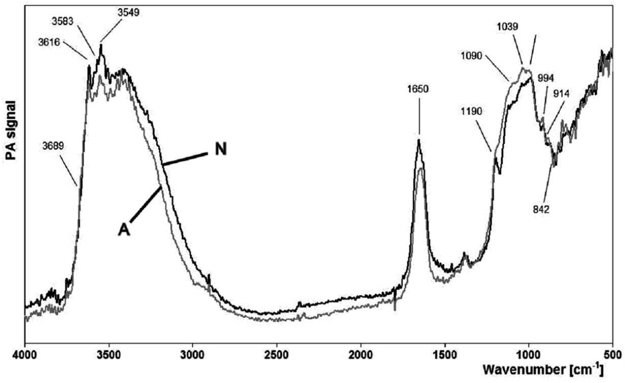

Fig. 3. FT-IR PAS spectra of palygorskite (N — natural form, A — Na form).

3.3. Bentonite — FT-IR PAS spectra description

The peak at 363 cm^{-1} corresponds to stretching vibrations of Al(Mg)–OH (Fig. 4). The bands between 3550–3350 cm^{-1} are related to coordination and zeolitic water stretching vibrations. At 3450 cm^{-1} H_2O stretching band can be found. The asymmetric signal at 1650 cm^{-1} corresponds to bending vibrations of zeolitic and adsorbed water. Near 1090 cm^{-1} area there exists doublet of M–O or Si–O stretching vibrations. The peaks at 1147 cm^{-1}, 1050 cm^{-1} and 997 cm^{-1} correspond to Si–O stretching bond vibrations. The sharp signal appearing at 914 cm^{-1} is responsible for Al–Al–OH group's deformations. The sharp peak at 875 cm^{-1} is related to deformations of Fe–Al–OH groups. Silicate vibrations band exists at 796 cm^{-1}. The signal at 628 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 compari-

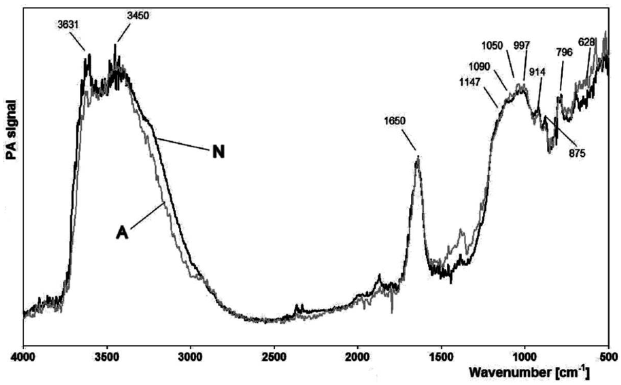

Fig. 4. FT-IR PAS spectra of bentonite (N — natural form, A — Na form).

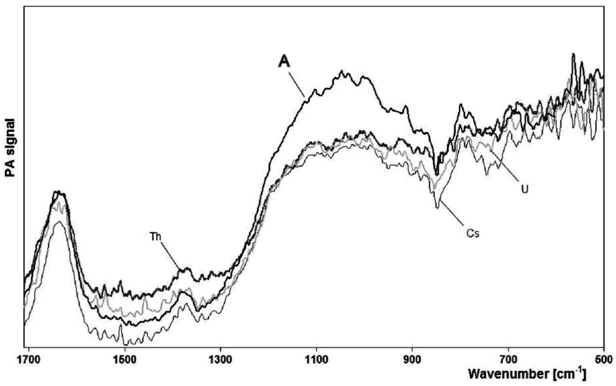

Fig. 5. FT-IR PAS spectra of four forms of bentonite (A — Na form, Cs(I), Th(IV), U(VI)).

son with Na-form. Intensities and wave numbers of many peaks are changed. Especially, there can be seen decay of 1190 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 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 cm^{-1} and 1640 cm^{-1}. The Th(IV) and U(VI) ions are more hydrated than Cs(I) ions and implement coordinated water to clay structure [1–4].

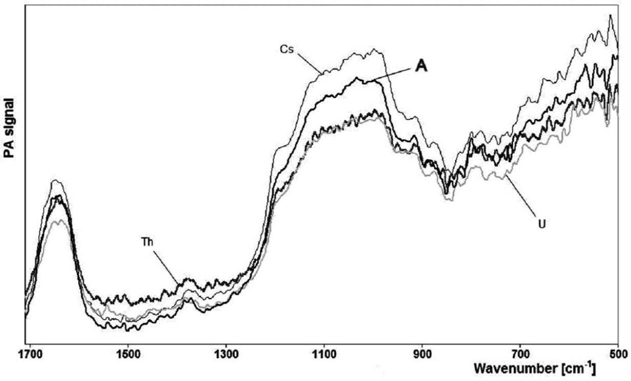

Fig. 6. FT-IR PAS spectra of four forms of palygorskite (A — Na form, Cs(I), Th(IV), U(VI)).

4. Conclusion

The 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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