

CESIUM REMOVAL FROM AQUEOUS SOLUTION BY NATURAL MINERAL CLINOPTILOLITE

by

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The aim of this study was to investigate the Cs⁺ ions sorption on natural minerals clinoptilolite. The analysis of clinoptilolite and clinoptilolite with adsorbed Cs⁺ ion was conducted by X-ray diffraction, scanning electron microscopy, X-ray fluorescence, and gamma spectrometry. The specific activity of naturally occurring radionuclides in clinoptilolite was determined by gamma spectrometry by using the HPGe semiconductor detector. Obtained activity concentrations ranged from 49 Bq/kg to 810 Bq/kg for ⁴⁰K, 5.7 Bq/kg to 10 Bq/kg for ²³⁸U, 5.8 Bq/kg to 70 Bq/kg for ²³²Th(²²⁸Ac), and the presence of artificial radionuclides was not detected (¹³⁷Cs < 0.02 Bq/kg). The study of the thermal decomposition of raw clinoptilolite and Cs adsorbed clinoptilolite by differential thermal analysis is presented in this paper. The activation energy of the reaction phase transformation of raw clinoptilolite is 156.7 kJ/mol, while Cs adsorbed clinoptilolite is 121.7 kJ/mol. The lower value of activation energy reaction of the phase transformation Cs adsorbed clinoptilolite indicates that Cs which is adsorbed destabilizes the crystal structure of clinoptilolite and thus facilitates the transition to the amorphous state.

Key words: clinoptilolite, adsorption, cesium, natural radioactivity, phase transformation, differential thermal analysis

INTRODUCTION

Natural zeolites are important aluminosilicates in sorption processes [1, 2] because of their low cost and selectivity arising from their unique structural characteristics. Zeolites, inorganic polymers constituting complex and infinite three-dimensional networks, are formed from tetrahedral units of (Si, Al)_nO_{2n} whose net negative charge is balanced by positive ions trapped in the cavities of the basket like framework. The exchangeable cations, located within the framework, play a crucial role in adsorption and thermal properties of the zeolites [3]. The sorption on its particles is a complex process because of their porous structure, inner and outer charged surfaces, mineralogical heterogeneity, existence of crystal edges, broken bonds, and other imperfections on the surface. The cage-like structure of this mineral makes it suitable for ion exchange reactions. It is also reported that the adsorbed cations might be coordinated with the de-

finied number of water molecules, and located on specific sites in framework channels [4].

In environmental applications, natural zeolites have been studied extensively to remove harmful substances from wastewater by adsorption and ion exchange processes [5-8]. The ion exchange property of zeolites has been widely applied in wastewater treatment, heavy metal uptake and immobilization of heavy metals in contaminated soils [9]. The fewer studies have been published on their use in the separation, immobilization and disposal of radioactive waste-treatment that include mordenite, erionite, chabazite, and clinoptilolite [10-12]. Thermodynamic investigations have indicated an enhanced selectivity of the zeolites towards monovalent ions and especially Cs⁺ and NH₄⁺. The selectivity towards bivalent cations (Sr²⁺, Pb²⁺) is much lower [13,14].

Clinoptilolite (Na,K)₆Al₆(Si₃₀O₇₂)·20H₂O [15] is one of the most widely known zeolitic minerals – a member of the heulandite group [8]. Due to their high cation-exchange capacities and selectivity for Cs, Ba, and Sr, as demonstrated first by Ames [16, 17],

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clinoptilolite and mordenite containing rocks can retard the migration of radionuclides occurring in solution as simple cations and thus are considered as potential hosts for radioactive waste disposal [18, 19]. Moreover, zeolites can be modified by the introduction of new functional groups in order to improve its activity and selectivity for the removal of several substances [20-22]. However, impurities are present in natural zeolites, and can markedly decrease their adsorption and ion exchange efficiency. For example, there are impurities like quartz in most of the clinoptilolite deposits.

Cesium, Cs, is an alkali element ($Z = 55$) that has high solubility in water. It has several radioactive isotopes, and the most important are ^{134}Cs ($t_{1/2} = 2.06$ years), ^{135}Cs ($t_{1/2} = 2.3 \cdot 10^6$ years), and ^{137}Cs ($t_{1/2} = 30.05$ years) produced during nuclear fission processes [23]. Due to their long half lives, radionuclides ^{135}Cs and ^{137}Cs represent the main radio contaminants, regarding the cesium contamination. Radionuclide ^{137}Cs is a harmful fission product contained in low-level radioactive liquid waste. ^{137}Cs decays by beta minus emission to ^{137}Ba followed by a strong emission of gamma radiation. ^{137}Cs has a very low cross-section for neutron capture and cannot be feasibly disposed of in this way, but must be allowed to decay. Another isotope, ^{135}Cs has a potential long-term adverse impact on environment because of its mobility in final repository [24]. The Cs^+ ion can be highly mobile in aqueous media due to its low hydration energy (-276 kJ/mol) as compared to elements of larger oxidation state or smaller size, whose hydration energies can rise up to several thousands of kJ/mol. This property facilitates its involvement with the hydrological cycle, which has interfaces with the biological cycle and thus poses a potential detriment to man and to other living systems.

Due to all that was mentioned above, the object of this study was a kinetic characterization of the sorption of Cs^+ ions on natural minerals clinoptilolite.

MATERIALS AND METHODS

Natural zeolite, clinoptilolite, originated from Igroš (Brus), Serbia, was used in this work. The samples were crushed in an agate mortar and washed with distilled water in order to remove the surface dust. Grain size fractions from 0.063 to 0.1 mm were chosen for the experiment because they were proven to enable the highest uptake of metal cations [25].

The chemical composition of clinoptilolite was made by X-ray fluorescence (XRF), type UPA XRF 200 with measurement uncertainties of 0.5%.

Microstructure and morphology of samples were recorded by X-ray diffraction analysis (XRD) and scanning electron microscopy (SEM). The crystal structure of clinoptilolite was examined by X-ray diffractometer Siemens D-500, with CuK_α radiation. The diffracted X-rays were collected over 2θ range

20° - 80° using a step width of 0.02° , and measured for 1 second per step.

The investigation of surface properties of the clinoptilolite was carried out using SEM analysis (JEOL JSM 6390 LV and Oxford Instrument INCA-X-sight at 25 kV).

The clinoptilolite can be used for sorption of cations-activity carriers. The distribution of naturally occurring radionuclides in the clinoptilolite was determined by gamma spectrometry measurements. Three samples were mechanically prepared in accordance with IAEA recommendations [25], sealed in order to reach radioactive equilibrium, and measured in 500 ml Marynelly-beaker geometry. Radiological analysis was performed by means of semiconductor HPGe spectrometer (GEM30, Ortec with relative efficiency of 37% and resolution of 1.7 keV at 1332.5 keV) associated with standard beam supply electronics units. The standardized solution of the common mixture of gamma-emitting radionuclides (^{241}Am , ^{109}Cd , ^{139}Ce , ^{57}Co , ^{60}Co , ^{137}Cs , ^{113}Sn , ^{85}Sr , and ^{88}Y), traceable to the Czech Metrological Institute was used to prepare the standards, in Marynelly-beakers with active carbon and soil as a matrix, for the energy and efficiency calibration of the spectrometer.

The measurement time ranged from 155 ks to 250 ks. All spectra were recorded and analyzed using the Canberra's Genie 2000 software; net areas of the peaks were corrected for the background, dead time and coincidence summing effects, applying the calculation method of Debertain and Schotzing [26].

Mass of 1g of raw clinoptilolite were contaminated at 298 K with a solution of CsNO_3 (99.99% Alfa Aesar) concentration of 10 mg/l. Equilibrium state of solution was achieved after a sealing and shaking solution for 24 hour and after that precipitate was separated from the solution. The concentrations of Cs ions in the samples at equilibrium were determined using ICP method. Immobilization efficiency of Cs^+ ions, (%) was calculated using following equation

$$\eta(\%) = \frac{c_{\text{cation}}^i - c_{\text{cation}}^e}{c_{\text{cation}}^i} \cdot 100 \quad (1)$$

where c_{cation}^i and c_{cation}^e are the initial and equilibrated cations concentrations [mg l^{-1}].

The content of Cs in solutions was determined using flame atomic emission spectroscopy (F-AAS spectrometer, Perkin-Elmer model 5000) with measurement uncertainties of 0.3%-0.8%.

Thermal analysis

The thermal behavior of raw clinoptilolite and clinoptilolite with adsorbed Cs ions were investigated in the temperature range 20-1100 °C using a SHIMADZU DTA-50 with a linear heating rate of 10,

15, and 20 °C/min. The analysis was conducted in nitrogen atmosphere (rate flow 20 ml/min) and employing Al₂O₃ as a reference standard. The mass of all sample was 20.00 ± 0.01 mg. The measurement uncertainties were 5%.

RESULTS AND DISCUSSION

The results of the XRF analysis of the zeolitic tuff sample are presented in tab. 1. The alteration of volcanic to zeolite is associated with reduction of SiO₂, K₂O, and Na₂O contents with a proportional increasing of the Al₂O₃, MgO, CaO, and H₂O contents. Formation of zeolite appears to occur when the ration SiO₂/Al₂O₃ is between 4.27 and 6.48 and the ratio (K₂O + Na₂O)/(MgO + CaO) ranges from 1.53 to 0.76. The high overall nSi/nAl > 4 ratio in the tuff samples can be attributed the existence of significant proportion of feldspars, quartz, smectite and unaltered glass in the samples.

The results of XRPD analysis of the raw materials are shown in fig. 1. The characteristic peaks of clinoptilolite (JCPD No 25-1349) at 2θ values of 9.92,

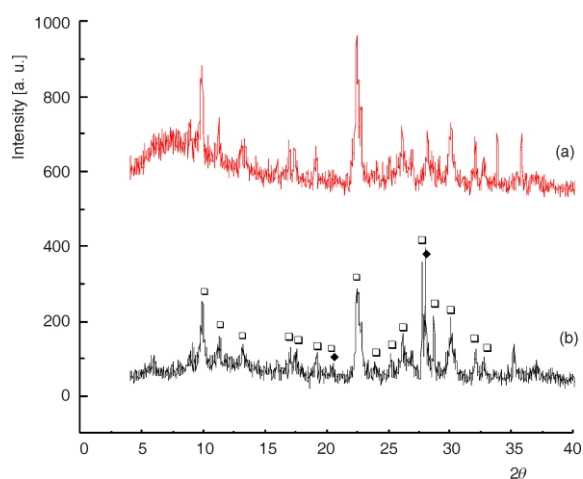


Figure 1. XRD patterns of clinoptilolite (a) and XRD patterns of Cs⁺ adsorbed clinoptilolite (□ – clinoptilolite) (b)

22.43, 25.8, 30.05, and 32° were observed in the X-ray diagrams of the samples in fig. 1.

The XRD of the Cs-loaded clinoptilolite samples revealed no meaningful change in the shape or positions of the features given in fig. 1(a) and 1(b). Some minor intensity variations were, however, obtained stemming primarily from grain size orientation of the powder samples. This problem is usually surmounted by multiple preparation and measurement of each sample. These findings indicate no change in the lattices of the minerals upon uptake of Cs⁺ ions.

Structural stability of clinoptilolite is not expected to be affected by uptake of cations [27].

The obtained specific activities of the clinoptilolite [Bqkg⁻¹] of dry clinoptilolite mass, of U-series, Th-series, ²³⁵U, ¹³⁷Cs, and ⁴⁰K obtained by gamma spectrometry, are given in tab. 2. Quoted uncertainties (the confidence level of 1σ) were calculated by error propagation calculation. The combined standard uncertainties included the efficiency calibration uncertainty and the statistical uncertainties of the recorded peaks. Results show that radioactive equilibrium in the entire uranium series is preserved in the first sample, and that it is somewhat disturbed in second and the third one; that activity ratio of uranium isotopes ²³⁵U/²³⁸U is natural within the limits of quoted uncertainties, and that artificial radionuclides were not detected in the sample. The minimum detectable activity concentrations of ¹³⁷Cs, for performed measurements were of order 10⁻² Bq/kg. The radiological analysis of clinoptilolite confirmed that it does not contain ¹³⁷Cs, what is the main recommendation for its usage as a potential material for the removal of ¹³⁷Cs isotopes from radioactive effluents.

The results of the SEM analysis of clinoptilolite and clinoptilolite incorporated Cs⁺ ions are presented in fig. 2.

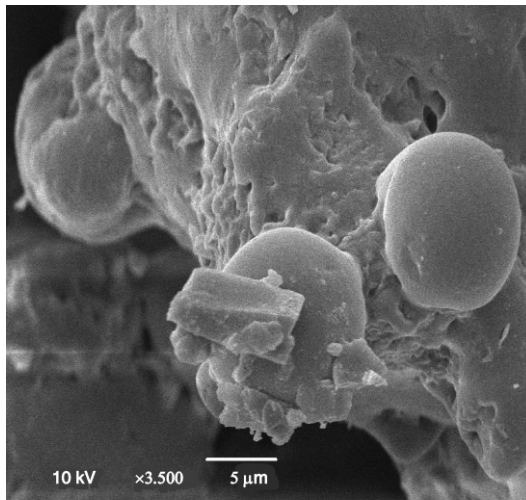
SEM images indicated that almost in all samples, zeolite powder with particles size less than 100 nm may be recognized as separated particles or in the form of larger agglomerates. Moreover, most particles have lost their initial octahedral shape and converted into spherical, elliptical or irregular shapes. By careful considerations of SEM images, some crystals with

Table 1. Chemical composition of raw clinoptilolite

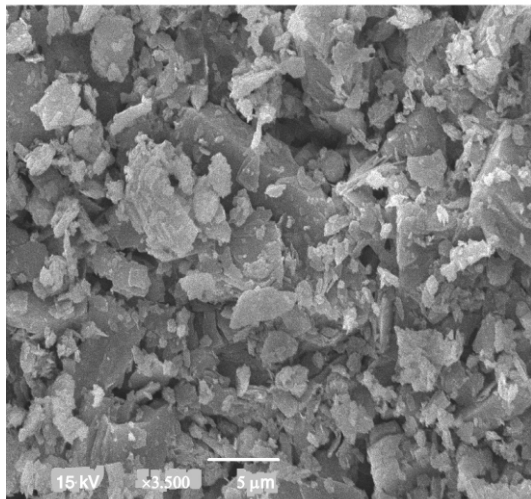
Constituents	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MnO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	LoI	Total
Average concentration [%]	70.4	0.64	12.7	4.65	0.05	3.12	3.63	0.18	3.48	0.16	0.36	100

Table 2. Radionuclide content in measured clinoptilolite samples [Bqkg⁻¹]

No.	²¹⁰ Pb		²¹⁴ Bi		²¹⁴ Pb		²²⁶ Ra		²³⁸ U		²³⁵ U		²²⁸ Ac		²¹² Bi		²¹² Pb		²⁰⁸ Tl		⁴⁰ K		¹³⁷ Cs
1	6.2	1.3	9.6	0.7	10.2	0.7	9.9	0.7	10	3	0.47	0.10	50	4	49	4	51	4	16.2	1.1	236	17	<0.01
2	44	9	31	2	33	2	32	2	56	12	1.9	0.4	70	5	69	2	72	5	22	2	810	60	<0.02
3	2.5	0.5	4.0	0.3	4.1	0.3	4.1	0.3	5.7	0.7	0.12	0.03	5.8	0.5	5.7	0.6	5.9	0.5	1.8	0.2	49.2	0.5	<0.01



(a)



(b)

Figure 2. SEM micrographs of clinoptilolite (a) and Cs⁺ adsorbed clinoptilolite (b)

sharp edges and clean surfaces were observed; with approximately 200 nm in size.

Natural clinoptilolite has a limited crystallinity thus indicating a certain degree of contamination of the structure with other minerals or amorphous glassy materials. The incorporation of Cs⁺ ions into clinoptilolite was performed using cesium nitrate Cs⁺ ions immobilized into the clinoptilolite by process of adsorption in different sites of the clinoptilolite networks. The immobilization efficiency of adsorbed Cs⁺ on the raw clinoptilolite was calculated by eq. (1). The time necessary to reach equilibrium conditions is confirmed by achieving high value of immobilization efficiency of Cs⁺ ions, *i. e.*, 97%.

Differential thermal analysis

Figure 3 presents the clinoptilolite thermogram obtained from the differential thermal analysis (DTA) anal-

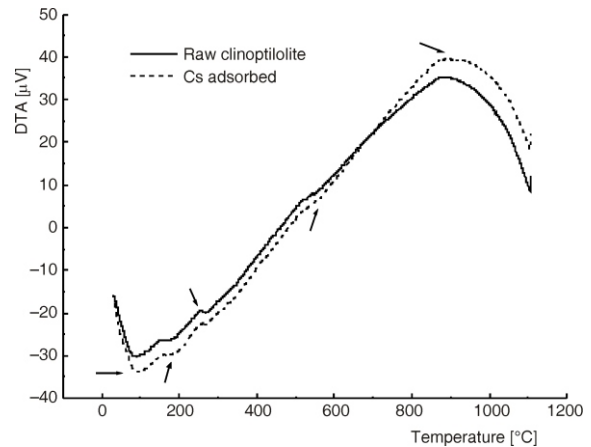


Figure 3. DTA thermogram of raw and Cs⁺ adsorbed clinoptilolite (heating rate 15 °C/min)

ysis of raw and Cs adsorbed clinoptilolite (15 °C/min heating rate).

The first endothermic peak which appears in the temperature range of 50-120 °C is attributed to the loss of water located in the clinoptilolite or other volatile species that may be present. A second endothermic peak (about 200-250 °C) characteristically broad and not well-defined, has been usually related to the loss of the hydroxyl groups that compose the clinoptilolite structure. At 450-850 °C, the DTA curve of the raw zeolite and zeolite with adsorbed Cs⁺ ion showed almost linear relationship beside one not well defined peak at temperature around 500 °C. Kurkuna *et al.*, [28] reported two forms of water – intact molecules and OH groups existing in the structure of silicate minerals (as clinoptilolite). Intact water is eliminated at below 100 °C, whereas hydroxyl groups are removed at $T > 400$ °C. According to Breck, 1974 study [29], the structural water (OH groups) is eliminated from clinoptilolite after exceeding 360 °C. Dehydration is completed above 600 °C for natural zeolite.

In differential thermal analysis, the temperature at which the peak deflection occurs for a given heating rate, is determined by both the pre-exponential factor (A) and energy activation (E_a)

$$Ae^{\frac{E_a}{RT_{\max}}} = \frac{E_a}{RT_{\max}^2} \frac{dT}{dt} \quad (2)$$

If the heating rate is changed, the peak temperature is changed. The variation of peak temperature with heating rate is governed only by the activation energy, E_a (eq. 3). Plotting $\ln \beta / T_{\max}^2$ vs. $1/T_{\max}$, as indicated by eq. (3), should give a straight line of slope $-E_a/R$ [30].

$$\frac{d \ln \frac{\beta}{T_{\max}^2}}{d \frac{1}{T_{\max}}} = \frac{E_a}{R} \quad (3)$$

The exothermic peak at high temperature was caused by the collapse of the clinoptilolite structure or transformation zeolite crystal structure into the amorphous structures and re-crystallization into a new phase, and was taken as a measure of thermal stability of clinoptilolite [31].

The parts of DTA thermograms which include temperature interval from 600 °C to 1000 °C of raw clinoptilolite and Cs⁺ adsorbed clinoptilolite ions are presented in fig. 4.

In order to investigate the energy activation of process phase transformation of clinoptilolite and Cs adsorbed clinoptilolite, Kissinger's method [32] and eqs. (2) and (3) were used. The activation energy of the reaction phase transformation of raw clinoptilolite is 156.7 kJ/mol, while Cs adsorbed clinoptilolite is 121.7 kJ/mol. The lower value of *E_a* reaction of the phase transformation Cs adsorbed clinoptilolite indicates that Cs which is adsorbed destabilizes the crystal structure of clinoptilolite and thus facilitates the transition to the amorphous state. The lower value of *E_a* is also an indication that Cs is physically adsorbed in clinoptilolite structure.

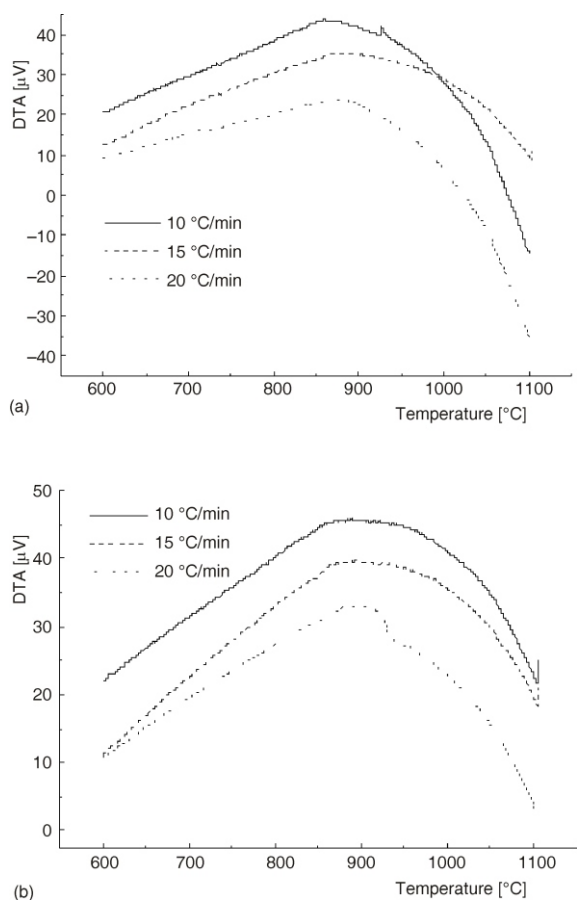


Figure 4. DTA thermogram of raw clinoptilolite (a) and Cs⁺ adsorbed clinoptilolite (b) at different heating rate

CONCLUSIONS

The radiological analysis of clinoptilolite confirmed that it does not contain ¹³⁷Cs, what is the main recommendation for its usage as a potential material for the removal of ¹³⁷Cs isotope from radioactive effluents. But, the presence of the ¹³⁷Cs in clinoptilolite is possible due to the resuspension from the ground, and therefore radiological analysis should be performed prior to other analysis. The immobilization efficiency of adsorbed Cs⁺ on the raw clinoptilolite is 97%. The broad exothermic peak for both raw and Cs adsorbed clinoptilolite which appeared in temperature range above 600 °C to 1000 °C was caused by the transformation of the clinoptilolite crystal structure into the amorphous structures. In order to investigate the energy activation of process phase transformation Kissinger's method was used. The lower value of *E_a* reaction of the phase transformation Cs adsorbed clinoptilolite indicates that Cs which is adsorbed destabilize the crystal structure of clinoptilolite and thus facilitates the transition to the amorphous state.

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AUTHOR CONTRIBUTIONS

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УКЛАЊАЊЕ ЦЕЗИЈУМА ИЗ ВОДЕНИХ РАСТВОРА КОРИШЋЕЊЕМ ПРИРОДНОГ МИНЕРАЛА КЛИНОПТИЛОЛИТА

Циљ рада је испитивање адсорпције Cs^+ јона природним минералом клиноптилолитом. Методама рендгенске дифракције, скенирајуће електронске микроскопије, рендгенске флуоресцентне спектрометрије и гама спектрометрије испитани су клиноптилолит и клиноптилолит са адсорбованим Cs^+ јонима. Гама спектрометар са HPGe полупроводничким детектором коришћен је за одређивање специфичне активности природних радионуклида у клиноптилолиту. Вредности специфичних активности су у опсегу 49 Bq/kg до 810 Bq/kg за ^{40}K , 5,7 Bq/kg до 10 Bq/kg за ^{238}U , и 5,8 Bq/kg до 70 Bq/kg за ^{232}Th (^{228}Ac). Није детектовано присуство вештачких радионуклида ($^{137}Cs < 0.02$ Bq/kg). Испитивање термичке разградње сировог клиноптилолита и клиноптилолита са адсорбованим Cs^+ јонима употребом диференцијалне термичке анализе такође је приказано у раду. Вредности енергије активације фазне трансформације клиноптилолита и клиноптилолита са адсорбованим Cs^+ јонима су 156,7 kJ/mol и 121,7 kJ/mol, респективно. Нижа вредност активационе енергије реакције фазне трансформације клиноптилолита са адсорбованим Cs^+ јонима указује да се адсорпцијом дестабилизује кристална структура клиноптилолита и самим тим олакшава прелазак у аморфно стање.

*Кључне речи: клиноптилолит, адсорпција, цезијум, природна радиоактивност,
фазна трансформација, диференцијална термална анализа*
