East European Journal of Physics. 1. 295-300 (2025)
DOI:10.26565/2312-4334-2025-1-35 ISSN 2312-4334

POSSIBILITIES OF USING UKRAINIAN CLINOPTILOLITE (SOKYRNYTSIA DEPOSIT) IN NUCLEAR ENERGY

Oleksii Yu. Lonin[a]*, **Volodymyr V. Levenets**[a], **Oleksandr P. Omelnyk**[a], **Andriy O. Shchur**[a]
[a]*National Science Center "Kharkiv Institute of Physics & Technology",*
1, Akademichna St., Kharkiv, 61108, Ukraine
**Corresponding Author*: *a_lonin@kipt.kharkov.ua, a_lonin@ukr.net*

Received December 17, 2024; revised February 2, 2025; accepted February 10, 2025

The clinoptilolite from the Sokyrnytsia deposit belongs to the zeolite family and is known for its application as sorbents in nuclear energy. The sorption of cesium, strontium, cobalt, and europium ions by clinoptilolite has been studied. The research examined how the composition and structure of clinoptilolite influence sorption. Sorption properties were assessed using the sorption coefficient, which quantitatively measures clinoptilolite's interaction with radionuclides. The results revealed that clinoptilolite exhibits the highest sorption efficiency for cesium (87.0%) and strontium (80.5%). Europium showed a sorption efficiency of 73.0%, while cobalt exhibited a lower sorption efficiency of 60.0%. The study established an ion exchange sequence for these ions in the sorption process and observed a dependency on the ionic radius of the sorbed ions. The presence and concentration of competing ions significantly affected the sorption efficiency. For instance, sodium ions in the solution reduced sorption by up to 25%, depending on the radionuclide. Increased sodium ion concentration caused an additional 26% to 40% sorption reduction. Similarly, tripling the strontium concentration in the solution reduced the sorption effect. The sorption experiments were conducted under both static and dynamic conditions. Radionuclide content was determined using the characteristic X-ray emission (XRE) method. This technique analyzes the characteristic X-ray radiation of radionuclides excited by a proton beam. The experiments were carried out at the analytical nuclear-physical complex "Sokil." Samples were irradiated in the XRE channel, where targets were placed in a cassette within an irradiation chamber under a vacuum of 10^{-4} Pa. The proton beam, with a current of 200 nA and an energy of 1600 keV, was used to excite the X-ray radiation of cesium, strontium, and cobalt atoms. The characteristic X-ray radiation of the K-series of strontium atoms was detected using two detectors: the XR-100CR Si-PIN X-ray detector and the Ge(HP) detector. Considering its established radionuclide selectivity sequence, the clinoptilolite from the Sokyrnytsia deposit can be utilized in Ukraine's nuclear energy industry.

Keywords: *Zeolite; Cesium; Strontium; Cobalt; Europium*
PACS: 82.75.Jn, 68.43.-h, 28.41.Kw

INTRODUCTION

Zeolites were first discovered by F. Cronstedt in 1756. He observed that stilbite swelled and released water when heated. This phenomenon led him to coin the term "zeolite," derived from the Greek words for "boiling stone." To date, 47 minerals have been classified as zeolites. Zeolites belong to the group of framework aluminosilicates [1]. They are found on every continent, but natural zeolites do not fully meet the demands of industry and energy sectors. Thanks to advances in modern chemistry, scientists have significantly expanded the range of zeolites, enhancing their properties to suit industrial and practical applications. Currently, more than 120 synthetic zeolites are known [1].

One of the natural zeolites is clinoptilolite. It is a component of sedimentary rocks of volcanic origin. Its name originates from the Greek words "klino" (κλίνω; inclined), "ptilo" (φτερών; feather), and "lithos" (λίθος; stone). Clinoptilolite has an aluminosilicate framework formed by the connection of AlO_4 and SiO_4 tetrahedra at their vertices. An example of the atomic arrangement in the structure of clinoptilolite, typical for zeolites, is shown in Fig. 1 [2].

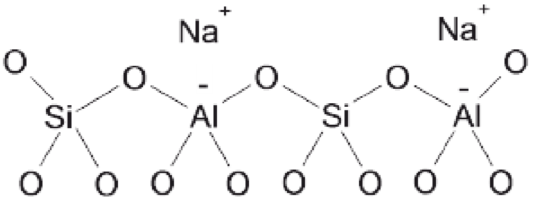

Figure 1. The fundamental structural unit of zeolites [2]

The framework features a system of cavities interconnected by channels, where cations and water molecules are located [3–6]. The cations in the channels can be exchanged for other cations. Exchangeable cations in clinoptilolite include Na^+, K^+, Ca^{2+}, Mg^{2+}, Fe^{3+}, and others (Fig. 2).

The composition and content of exchangeable ions in clinoptilolite vary depending on the deposit. For instance, the clinoptilolite content in the rock from the Neombarian region of Armenia is 85–87% [7], while in the Sokyrnytsia deposit in the Zakarpattia region of Ukraine, it ranges from 75% to 96% [8]. Such significant compositional variations highlight the need for additional quality control when using clinoptilolite as a sorbent in energy and industrial applications.

Cite as: O.Yu. Lonin, V.V. Levenets, O.P. Omelnyk, A.O. Shchur, East Eur. J. Phys. 1, 295 (2025), https://doi.org/10.26565/2312-4334-2025-1-35

Clinoptilolite has been utilized as a sorbent in nuclear energy. It was first employed during the cleanup of the Three Mile Island Nuclear Power Plant accident (USA) in March 1979, where it was used to absorb cesium [9]. The positive results of this application laid the groundwork for recommendations by the International Atomic Energy Agency (IAEA) [10].

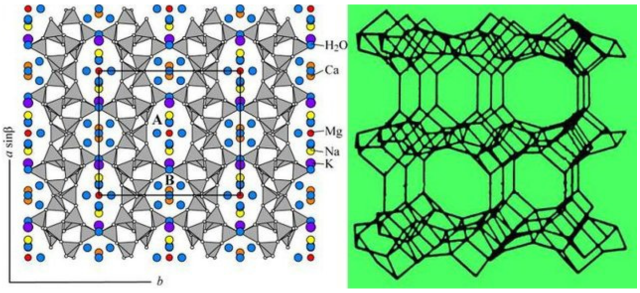

Figure 2. Crystalline structure of clinoptilolite [4]

During the cleanup of the Chornobyl Nuclear Power Plant accident (Ukraine) in April 1986, clinoptilolite was used as a radionuclide sorbent based on IAEA recommendations. Approximately 150,000 tons of zeolite sand were employed. However, clinoptilolite did not yield the expected results, unlike the Three Mile Island accident. The main reason for its limited effectiveness was the complex and diverse radionuclide contamination caused by the Chornobyl accident, which included high activity levels and a broader range of radionuclides.

This study aimed to summarize the research on the sorption of radionuclides by clinoptilolite from the Sokyrnytsia deposit, which may be present in liquid waste generated by nuclear energy facilities. Based on the results, an ion exchange series for clinoptilolite was developed to facilitate its use in mitigating radionuclide contamination.

METHODS AND OBJECTS OF THE STUDY

Objects of the Study

The object of the study was clinoptilolite from the Sokyrnytsia deposit in the Zakarpattia region of Ukraine. Two fractions of clinoptilolite were examined: 0.1 mm and 3–5 mm. The fractions were selected depending on the sorption method (static or dynamic).

Nitrates of cesium, strontium, and cobalt were used as radionuclide sources. Europium was also studied, with its source being an oxide dissolved in acid.

Methods For Studying Sorption Properties

Sorption Under Static Conditions

A 100 ml solution of nitrates was prepared using distilled water as the solvent. A 0.1 g sample of clinoptilolite (0.1 mm fraction) was used as the sorbent. Ten milliliters of the prepared solution were added to the sorbent. The mixture was periodically stirred, and the sorption process was monitored for 24 hours. Samples of 0.5 ml were taken at intervals of 1, 6, and 24 hours. For europium, a separate solution was prepared with the addition of 0.1 N hydrochloric acid.

Sorption Under Dynamic Conditions

A 500 ml solution of nitrates was prepared using distilled water as the solvent. A 2.0 g sample of clinoptilolite (3-5 mm fraction) was used as the sorbent. Dynamic sorption conditions were modeled using a setup (Fig. 3) [11]. The setup included a pump, a sorption column with a cartridge, a reservoir, and a measuring unit. The cartridge had a diameter of 8 mm and a height of 25 mm.

To evaluate the completeness of the sorption processes, 40–80 sorption cycles were performed, with periodic sampling. Dynamic sorption of europium was not conducted due to the use of acid as the solvent.

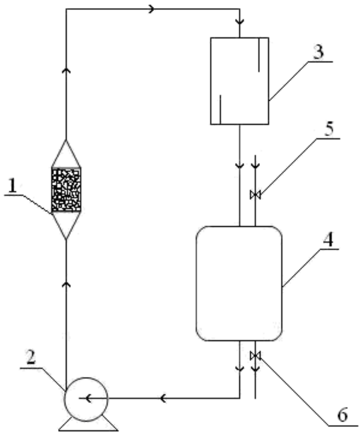

Figure 3. Diagram of the sorption setup:
1 - Sorption column; 2 – Pump; 3 - Measuring device; 4 - Collection reservoir; 5, 6 - Inflow and outflow valves respectively

Preparation of Targets

Targets were prepared using carbon substrates made from carbon rods. The carbon substrates were rectangular, measuring 10 mm in length, 5 mm in width, and 2 mm in thickness. A solution (0.05 ml) containing a mixture of cesium, strontium, and cobalt isotopes was applied to the substrate and dried at 35°C. The solution was applied using an automatic pipette with adjustable volume.

Determination of Radionuclide Content Using the XRF Method

The radionuclide content was determined using the X-ray fluorescence (XRF) method. This method analyzes a proton beam's characteristic X-ray emission of radionuclides excited. This part of the work used the "Sokil" analytical nuclear physics complex [12].

Samples were irradiated with a proton beam in the XRF channel. Targets were placed in a cassette located in the irradiation chamber. A vacuum with a 10^{-4} Pa pressure was created in the chamber before measurements.

For the excitation of X-rays from cesium, strontium, and cobalt atoms, a proton beam with a current of 200 nA and an energy of 1600 keV was used. At this energy, the L-series X-ray emission of cesium atoms and K-series X-ray emission of strontium and cobalt atoms were effectively excited. The X-ray emission was measured using the XR-100CR Si-PIN X-ray detector with an energy resolution of 155 eV for the 5.89 keV line and the Ge(HP) detector. The Ge(HP) detector, made of ultrapure germanium with a crystal thickness of 8.5 mm and a sensitive surface area of 25 mm², provided higher detection efficiency for K-series X-rays of strontium (14.164 keV) compared to the Si-PIN detector. To optimize the spectral measurement conditions, collimators with diameters of 1.5 mm and 2.0 mm, as well as polyethylene filters with thicknesses of 56 µm, 100 µm, and 150 µm, and aluminum foil with a thickness of 10 µm, were tested. Based on the experimental data, a collimator with a 1.5 mm opening and a 56 µm thick polyethylene filter was selected for optimal detection of the analytical peaks while reducing background radiation interference.

The X-ray emission from strontium atoms was detected by both XR-100CR Si-PIN and Ge(HP) detectors. The external detector was placed 7 cm from the target at an angle of 135° to the proton beam direction. The X-ray emission exited the chamber through a 25 µm thick beryllium foil window.

RESULTS AND DISCUSSION

Typical spectra of cesium, strontium, cobalt, and europium confirm the feasibility of detecting these radionuclides using the X-ray fluorescence (XRF) method and the suitability of the results for assessing sorption properties. The typical spectra are presented in Figures 4-7.

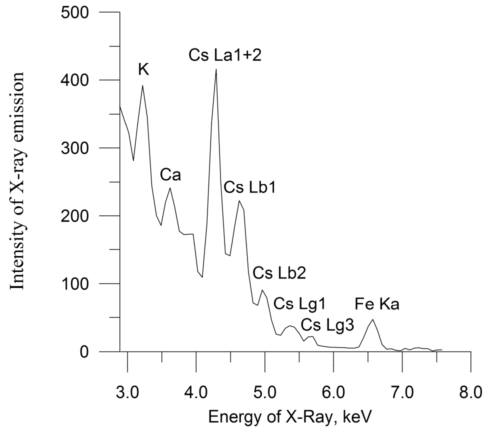

Figure 4. X-ray spectrum of the carbon target which contains 0.002 mg of cesium

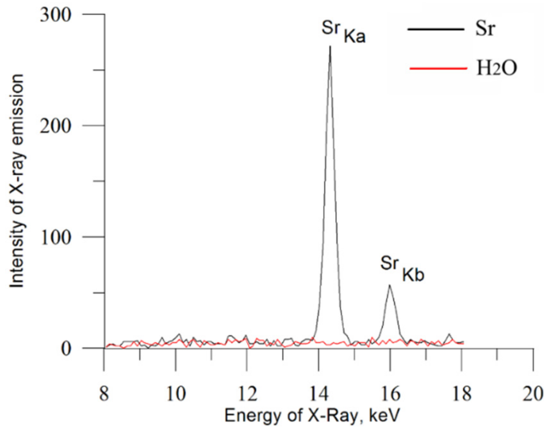

Figure 5. X-ray spectrum of the carbon target with dry water solids (H_2O), and the carbon target containing 0.0012 mg strontium (Sr)

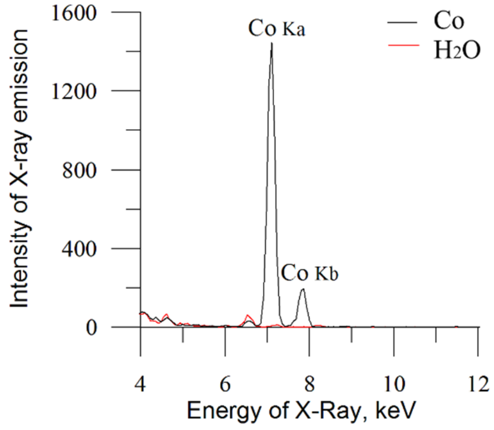

Figure. 6. X-ray spectra of the carbon target with dry water solids (H_2O) and the carbon target containing 0.0017 mg of cobalt (Co)

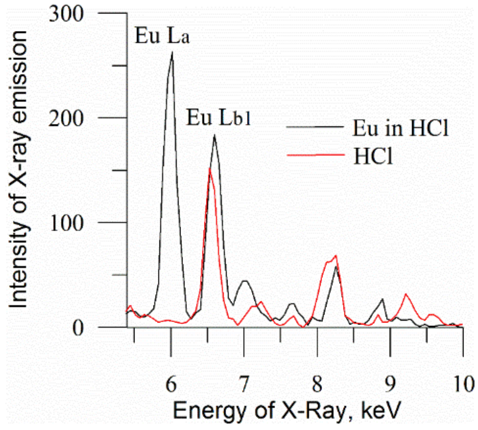

Figure.7. X-ray spectra of the carbon target with hydrochloric acid (HCl) dry residue and the carbon target containing 0.05375 mg of europium (Eu in HCl)

The sorption coefficient was used to evaluate the sorption properties quantitatively, providing insights into the interaction between clinoptilolite and radionuclides. The sorption coefficient was calculated using the formula:

$$K_s = \frac{\left(C_0 - C_p\right) \cdot 100\%}{C_0}$$

where C_o and C_p are the initial and equilibrium concentrations of the solution (mg/mL).

The sorption processes were studied under static and dynamic conditions, with adjustments made to the amount of sorbent and solution volume based on the method.

The data obtained are presented in Table 1. It was found that clinoptilolite exhibited the highest sorption efficiency for cesium (87.0%) and strontium (80.5%), followed by europium (73.0%). Cobalt displayed the lowest sorption efficiency at 60.0%.

Table 1. Sorption of radionuclides by clinoptilolite

№	Radionuclide	Sorption coefficient, %
1.	Cesium	87.0 %
2.	Strontium	80.5 %
3.	Cobalt	60.0 %
4	Europe	73.0 %

Experiments were conducted to assess the impact of competing ions and increased radionuclide concentration on sorption. These conditions were designed to simulate real-world scenarios, such as the presence of competing ions in liquid radioactive waste. Increased radionuclide concentration allowed for analyzing the performance of the sorbent under higher activity levels. The presence of competing ions, particularly sodium, significantly reduced the sorption efficiency of clinoptilolite (Table 2). For example, when sodium was present in the solution at a concentration of 0.0002 g/mL (equal to the cesium concentration in the solution), cesium sorption decreased to 46.0%. Similarly, sodium concentrations of 0.0004 g/mL reduced the sorption efficiency for cobalt and europium to 33.6% and 34.6%, respectively.

The effect of increased radionuclide concentration on sorption was analyzed using strontium as an example. A threefold increase in strontium concentration resulted in a 25% reduction in sorption efficiency (Table 2).

Table 2. Effect of competing ions and increased radionuclide concentrations on sorption

no.	Radionuclide	Radionuclide concentration, g/ml	Competing ion		Sorption coefficient, %
			Ion name	Concentration, g/ml	
1	Cesium	0.0002	sodium	- //-	87.0 %
2	Cesium	0.0002	sodium	0.0001	63.0 %
3	Cesium	0.0002	sodium	0.0002	46.0 %
4	Strontium	0.0002	- //-	- //-	80.5 %
5	Strontium	0.0006	- //-	- //-	60.6 %
6	Cobalt	0.0004	sodium	- //-	60.0 %
7	Cobalt	0.0004	sodium	0.0002	38.8 %
8	Cobalt	0.0004	sodium	0.0004	33.6 %
9	Europe	0.0005	sodium	- //-	73.0 %
10	Europe	0.0005	sodium	0.0002	47.5 %
11	Europe	0.0005	sodium	0.0004	34.6 %

The results indicate that the presence of competing ions substantially affects sorption efficiency. Sodium ions, as competitors, caused up to a 25% reduction in sorption depending on the radionuclide. Increasing the sodium concentration led to an additional 26%-40% decrease in sorption efficiency. The more pronounced effect of sodium on cesium sorption is attributed to their shared group in the periodic table (alkali metals), similar oxidation states, and competition for the same sorption sites in the clinoptilolite structure.

The effect of increased radionuclide concentration was studied using strontium sorption as an example. A threefold increase in strontium concentration reduced sorption efficiency by 20%.

Clinoptilolite demonstrates a complex sorption mechanism, involving both ion exchange and adsorption. Ion exchange occurs as a result of the need to compensate for the negative charge generated by aluminum ions interacting with the fourth oxygen ion. This charge is usually compensated by alkali metal ions, which then act as exchangeable ions. Adsorption, on the other hand, is associated with interactions between ions and the structural cavities of clinoptilolite, which are characteristic of its crystalline structure.

Based on the obtained results and the characteristics of the radionuclide ions (Table 3), it is possible to conclude the relative selectivity of clinoptilolite for these radionuclides.

Table 3. Oxidation states and ionic radii of sorbed elements

Element	Oxidation degree	Ion radius, pm
Cesium	+1	167
Strontium	+2	112
Cobalt	+2	72
Europium	+3	109

Regardless of the oxidation state of the radionuclides, the primary factor influencing sorption is the ionic radius, which allows for additional sorption, taking into account the crystalline structure of clinoptilolite. The selectivity series of radionuclides for clinoptilolite is as follows:

$$Cs^{+1} > Sr^{+2} > Eu^{+3} > Co^{+2}$$

This order corresponds to the observed sorption efficiency values and correlates with the ionic radius of the radionuclides.

The obtained data can be utilized by nuclear energy enterprises in Ukraine to optimize the use of clinoptilolite as a sorbent, both independently and as part of composite sorbents.

CONCLUSIONS

Clinoptilolite is a mineral of the zeolite group. It has been established that clinoptilolite has high sorption properties for cesium (87.0 %), strontium (80.5 %), and europium (73.0 %). The sorption properties of clinoptilolite for cobalt (60.0 %) require additional purification agents or the use of composite sorbents. Such sorption values are related to the radius of the ions to be sorbed. The large radius of the ion (cesium - 167 pm) makes it possible to perform additional sorption, taking into account the crystal structure of clinoptilolite. It was determined that the presence of competing ions (sodium) reduces sorption by 25 %. In the example of strontium sorption, it was found that an increase in the concentration of radionuclides in solution leads to a decrease in sorption by 20 %. Based on the sorption results, a range of radionuclide selectivity for Ukrainian clinoptilolite was determined. The clinoptilolite can be used in nuclear power enterprises of Ukraine, taking into account the determined range of radionuclide selectivity.

ORCID

Oleksii Yu. Lonin, https://orcid.org/0000-0002-5386-3825; **Volodymyr V. Levenets,** https://orcid.org/0000-0002-6439-0576
Oleksandr P. Omelnyk, https://orcid.org/0000-0003-2467-3632; **Andriy O. Shchur**, https://orcid.org/0000-0002-6619-4069

REFERENCES

[1] D. Breck, *Zeolite molecular sieves*, (Wiley, New York, 1974).
[2] N. Sobuś, I. Czekaj, V. Diichuk, and I.M. Kobasa, "Characteristics of the structure of natural zeolites and their potential application in catalysis and adsorption processes," Technical Transactions, **117**(1), 43 (2020). https://doi.org/10.37705/TechTrans/e2020043
[3] I. Marantos, G.E. Christidis, and M. Ulmanu, "Zeolite Formation and Deposits," in: *Natural Zeolites Handbook*, **1**, (2021). pp. 28-51. https://doi.org/10.2174/978160805261511201010028
[4] E. Chmielewská, "Natural Zeolites as Sustainable and Environmental Inorganic Resources over the History to Present," General Chemistry, **5**, 190001 (2019). https://doi.org/10.21127/yaoyigc20190001
[5] P. Miądlicki, A. Wroblewska, K. Kiełbasa, Z.C. Koren, and B. Michalkiewicz, "Sulfuric acid modified clinoptilolite as a solid green catalyst for solvent-free α-pinene isomerization process," Microporous and Mesoporous Materials, **324**, 111266 (2021). https://doi.org/10.1016/j.micromeso.2021.111266
[6] A. Mastinu, A. Kumar, G. Maccarinelli, S.A. Bonini, M. Premoli, F. Aria, A. Gianoncelli, and M. Memo, "Zeolite Clinoptilolite: Therapeutic Virtues of an Ancient Mineral," Molecules, **24**(8), 1517 (2019). https://doi.org/10.3390/molecules24081517
[7] L. Akhalbedashvili, G. Todradze, N. Kekelidze, Y. Keheyan, G. Yeritsyan, and R. Gevorkyan, Ion exchange properties of irradiated and chemically modified clinoptilolite regarding to Cs^+ and Sr^{2+}, Chemistry, Physics and Technology of Surface, **3**(1), 281 (2010). https://cpts.com.ua/index.php/cpts/article/view/38/35
[8] O.I. Ivanenko, Yu.V. Nosachova, and T.V. Krysenko, Bulletin of National Technical University of Ukraine "Igor Sikorsky Kyiv Polytechnic Institute" Series "Chemical engineering, ecology and resource saving", **4**(19), 66 (2020). https://doi.org/10.20535/2617-9741.4.2020.219786
[9] Yu. Bondar, and S. Kuzenko, Geochemistry of Technogenesis, **5**(33), 86 (2021). https://doi.org/10.15407/10.15407/geotech2021.33.086
[10] S.G. Baxter, and D.C. Berghauser, *The selection and performance of the natural zeolite clinoptilolite in British Nuclear Fuels' site ion exchange effluent plant*, SIXEP, United States: University of Arizona, Waste management. IAEA, **86**(2), 347 (1986).
[11] A.Yu. Lonin, V.V. Levenets, I.M. Neklyudov, A. O. Shchur, "The usage of zeolites for dynamic sorption of cesium from waste waters of nuclear power plants," JRNC, **303**, 831 (2015). https://doi.org/10.1007/s10967-014-3597-9
[12] S.G. Karpus, V.V. Kuzmenko, V.V. Levenets, O.Yu. Lonin, A.P. Omelnik, A.O. Shchur, and V.I. Sukhostavets, "Modernization of the analytical nuclear-physical complex SOKIL," PAST, **2**(144), 134 (2023). https://vant.kipt.kharkov.ua/ARTICLE/VANT_2023_2/article_2023_2_134.pdf
[13] V.V. Levenets, A.Yu. Lonin, O.P. Omelnik, and A.O. Shchur, "Comparison the sorption properties of clinoptilolite and synthetic zeolite during sorption strontium from the water solutions in static conditions: Sorption and quantitative determination of strontium by the method PIXE," JECE, **4**(4), 3961 (2016). https://doi.org/10.1016/j.jece.2016.09.011
[14] A.Yu. Lonin, V.V. Levenets, O.P. Omelnik, and A.O. Shchur, "Comparison of the sorption properties of natural and synthetic zeolites for the purification of aqueous solutions from cobalt: sorption of the cobalt from aqueous solutions in dynamic conditions and the quantitative determination of cobalt by the PIXE method," JRNC, **315**, 163 (2018). https://doi.org/10.1007/s10967-017-5676-1
[15] V.V. Levenets, A.Yu. Lonin, O.P. Omelnik, A.O. Shchur, "Studies of the features of the sorption of an europium by natural and synthetic zeolites for using it in the nuclear energy," PAST, 1(125), 121 (2020). https://vant.kipt.kharkov.ua/ARTICLE/VANT_2020_1/article_2020_1_121.pdf

МОЖЛИВОСТІ ВИКОРИСТАННЯ УКРАЇНСЬКОГО КЛІНОПТИЛОЛІТУ (СОКИРНИЦЬКОГО РОДОВИЩА) В ЯДЕРНІЙ ЕНЕРГЕТИЦІ

О.Ю. Лонін, В.В. Левенець, О.П. Омельник, А.О. Щур
Національний науковий центр «Харківський фізико-технічний інститут»,
1, вул. Академічна, 61108, Харків, Україна

Кліноптилоліт Сокирницького родовища відноситься до цеолітів. Цеоліти мають застосування в ядерній енергетиці в якості сорбентів. Досліджено сорбцію кліноптилолітом іонів цезію, стронцію, кобальту та європію. Визначено, як особливості складу та структури кліноптилоліту впливають на сорбційні процеси. Для визначення сорбційних властивостей використовувався коефіцієнт сорбції, який давав можливість отримати кількісну оцінку взаємодії кліноптилоліту з радіонуклідами. Встановлено, що найвищі значення сорбції кліноптилоліт проявляє до цезію 87.0 % та стронцію 80.5 %. Сорбція європію складає 73.0 %. Сорбція кобальту знижується та складає 60.0 %. Дослідження встановило послідовність іонного обміну для цих іонів у процесі сорбції та виявило залежність від іонного радіусу сорбованих іонів. Встановлено залежність сорбції від присутності та кількості конкуруючих іонів. Присутність іону натрію (конкуруючого іону) в розчині веде до зниження сорбції на 25% в залежності від радіонукліду. Збільшення концентрації іонів натрію призвело до додаткового зниження сорбції на 26-40%. Встановлено, що збільшення концентрації стронцію в 3 рази веде до зменшення сорбції на 20 %. Дослідження сорбції проводилися в статичних та динамічних умовах. Визначення вмісту радіонуклідів проводилось за допомогою метода ХРВ (характеристичне рентгенівське випромінювання). Метод засновано на аналізі характеристичного рентгенівського випромінювання радіонуклідів, після збудження пучком протонів. Данну частину роботи виконували на аналітичному ядерно-фізичному комплексі «Сокіл». Опромінювання зразків пучком протонів проводили у каналі ХРВ. Мішені встановлювали у касету, яка була розташована у камері опромінення. До проведення вимірювань у камері створювали вакуум з тиском 10^{-4} Па. Для збудження характеристичного рентгенівського випромінювання атомів цезію, стронцію та кобальту використовували пучок протонів зі струмом 200 нА та енергією 1600 кеВ. Реєстрація характеристичного рентгенівського випромінювання K-серії атомів стронцію проводилася двома детекторами: XR-100CR Si-PIN X-Ray і Ge(HP). З огляду на встановлену послідовність радіонуклідної селективності кліноптилоліт Сокирницького родовища може бути використаний в атомній енергетиці України.

Ключові слова: *цеоліт; цезій; стронцій; кобальт; європій*