THE INFLUENCE OF A MAGNETIC FIELD ON THE SORPTION OF RADIONUCLIDES BY CLINOPTILOLITE AND COMPOSITE SORBENTS BASED ON ZEOLITES

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Two methods of using permanent NdFeB magnets and their impact on the sorption of radionuclides (Cs, Sr, Co) by clinoptilolite and composite sorbents based on zeolites are discussed. Sorption processes were considered under dynamic conditions with liquid circulation. No changes in sorption processes were observed when magnetic treatment was applied to solutions containing radionuclide ions. The natural zeolite clinoptilolite and synthetic zeolites NaX and NaA were considered at this stage. In the work, clinoptilolite from the Sokirnitske deposit in the Zakarpattia region of Ukraine was used. Ukraine possesses significant deposits of clinoptilolite. When magnets were applied to the sorbent during the sorption process, an increase in cobalt sorption of 10% was observed for clinoptilolite, and strontium sorption increased by 17%. The influence of a magnet on clinoptilolite is due to the presence of iron ions in the composition of clinoptilolite. The iron content ranges from 0.9% to 2.5%. The composition of the composite sorbent included clinoptilolite and synthetic zeolite NaX. No increase in radionuclide sorption was observed for composite sorbents, likely due to the presence of clinoptilolite in the sorbent composition and the corresponding iron content. The analytical part of the study was carried out using the PIXE (Particle Induced X-ray Emission) method on the analytical nuclear-physics complex “Sokil.” The energy range of the accelerator was 200-2000 keV. The complex made it possible to carry out all the main methods of analysis using ion beams. The targets were placed in the exit, at the Chamber for PIXE. To excite the atoms of cesium, strontium, and cobalt a proton beam with an energy of Ep=1400 keV was used.

Keywords: Clinoptilolite; Synthetic zeolite; Dynamic sorption; Cesium; Strontium; Permanent magnet

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The challenging conditions of modern times indicate a growing threat of technogenic accidents related to nuclear energy. The causes of accidents can stem not only from technical failures associated with the operation of nuclear facilities but also from armed conflicts near nuclear energy facilities and threats associated with the activities of terrorist groups. Given these factors, there is an increasing demand for sorbents that can be used in nuclear energy. The main criteria for the use of sorbents are the ratio of sorbent effectiveness to its cost. In such circumstances, the use of natural sorbents comes to the forefront. One such sorbent is zeolites. However, the use of zeolites is associated with several limitations. The first limitation is significant variations in composition depending on the location of the deposit and its depth. The second limitation is the limited range of radionuclides that zeolites can absorb. A notable example of a natural zeolite is clinoptilolite. Clinoptilolite exhibits high selectivity for cesium but lags in the sorption of other radionuclides. Therefore, one effective approach to using clinoptilolite is the creation of composite sorbents by adding synthetic zeolites that do not have the mentioned limitations. The application of synthetic zeolites is effective for the sorption of strontium and cobalt.

There are alternative methods to enhance the sorption properties of clinoptilolite besides creating composite sorbents. Special attention is required for the use of zeolite activation methods, which can increase sorption properties without a significant increase in the cost of sorbent production. Such methods include thermal activation and the activation of sorbents using a magnetic field. The possibilities and results of thermal activation were discussed by us earlier.

The potential application of magnets to increase sorption has been explored by various authors [4]. When considering the possibility of magnetic activation of sorption processes, we chose permanent magnets as our preferred option. This decision was influenced by factors such as the mobility of the sorption setup and the elimination of the need to seek additional power sources for alternating current magnets.

The experiment was divided into two directions:
1. The influence of a permanent magnet on a solution containing radionuclides that was moving through a system of pipelines.
2. The influence of a permanent magnet on the sorbent located in the sorption column.

The impact of the permanent magnet on the solution involved placing the magnet on the pipeline of the sorption setup. As a result, cesium ions present in the solution and moving through the pipeline system of the sorption setup were subjected to the influence of magnetic fields. This was expected to enhance the interaction of polarized ions with the exchange centers of the sorbent.

Another approach involved the continuous influence of magnets on the sorbent. The idea of the magnetic influence on the sorbent is related to the composition of natural zeolite (clinoptilolite). According to existing literature and based on the data we obtained; iron is part of the composition of clinoptilolite. The continuous influence of a magnetic field should...
polarize the iron ions that are part of clinoptilolite's composition. Some authors conduct additional synthesis of zeolite to increase the magnetic influence on clinoptilolite. This synthesis involves additional treatment of zeolite intending to increase the iron content. In our work, we did not perform additional treatment and used zeolite with its natural iron content. The Fe₂O₃ content is 0.9%. Some aluminum atoms in the clinoptilolite structure are replaced with iron atoms (Figure 1).

Figure 1. Structure of clinoptilolite with the substitution of aluminum ions by iron ions

It should be noted that synthetic zeolites do not contain iron in their composition unless specified by the synthesis conditions. The synthetic zeolites considered in the study do not contain iron in their composition.

The study examined two mechanisms of the influence of permanent magnets on the sorption of radionuclides by clinoptilolite and composite sorbents.

The first mechanism investigated the effect of permanent magnets on a solution containing radionuclides. The influence of magnets was expected to enhance the polarization of radionuclide ions and increase their sorption when interacting with the exchange centers of zeolites.

The second mechanism studied the influence of permanent magnets on clinoptilolite due to the presence of iron ions in its composition.

All experiments were conducted without protection from the Earth's magnetic field, which generally ranges from 2.5·10⁻⁵ T (at the magnetic equator) to 6.5·10⁻⁵ T (at the geomagnetic poles). With knowledge of the distribution, it is possible to determine the intensity of the magnetic field at the research location for sorption. However, the magnetic field created by the NdFeB magnet is 1.26 T, which is significantly higher than the Earth's magnetic field, and therefore, the latter was not considered.

MATERIALS AND METHODS

Research Objects

Experiment Objects and Materials As sorbents, natural zeolite (clinoptilolite), synthetic zeolite NaX, and zeolite NaA were used. In the work, clinoptilolite from the Sokirnitske deposit in the Zakarpattia region of Ukraine was used. Ukraine possesses significant deposits of clinoptilolite. Additionally, the following sorption compositions based on zeolites were utilized:

1. Clinoptilolite - 100% + Zeolite NaX - 0% (CISZ₁).
2. Clinoptilolite - 50% + Zeolite NaX - 50% (CISZ₂).
3. Clinoptilolite - 25% + Zeolite NaX - 75% (CISZ₃).

NdFeB magnets manufactured by NSC KIPT [10,11] were used as permanent magnets.

Cesium, strontium, and cobalt nitrates were used as contaminating substances.

EXPERIMENT ON DYNAMIC SORPTION WITH THE PLACEMENT OF MAGNETS ON THE PIPELINE

The design of the setup for dynamic sorption, which had been used previously, was modified to accommodate the use of magnets [12].

Before the solution passed through the sorption column on the pipeline, two magnets were installed (Figure 2). The pipeline had a diameter of 16 mm, and two square magnets, each measuring 30×30 mm with a magnet thickness of 6 mm, were installed on the pipeline. The magnetic force of these magnets was approximately 13 kg, with a residual magnetic induction of 1.22 - 1.26 T. The magnet's grade was N38. Using this setup design, 40 cycles of sorption were conducted with clinoptilolite and synthetic zeolites NaX and NaA.

EXPERIMENT ON DYNAMIC SORPTION WITH MAGNETS PLACED ON THE SORPTION COLUMN

In the second scheme, a magnet was used to activate the iron that is part of clinoptilolite, resulting in a change in the material used for the sorption column (plastic). Taking into account that the magnet may affect the pump, the positioning of the sorption column relative to the pump was changed (Figure 3). For magnetic treatment, two magnetic discs were used, which were positioned around the sorption column filled with sorbent. For a greater impact of the magnets, the sorption column was made of polymer materials. The external diameter of the sorption column was 16
The magnetic discs had an inner diameter of 16 mm, an outer diameter of 40 mm, and a magnet thickness of 10 mm. The magnetic force of the magnet was approximately 13 kg, with a residual magnetic induction of 1.22 - 1.25 T, the coercive force from magnetization $\geq 955$ kA/m, and a grade of N38.

**PREPARATION OF TARGETS**

To prepare the targets, a carbon substrate made from carbon rods was used. The carbon substrate had the shape of a rectangle with dimensions of 10 mm in length, 5 mm in width, and 2 mm in thickness. A solution containing a mixture of cesium, strontium, and cobalt isotopes was applied to the carbon substrate in an amount of 0.05 ml and dried by heating to 35°C. The solution was applied using an adjustable volume automatic pipette.

**ANALYTICAL PART OF THE EXPERIMENT**

The analytical investigations of Co, Sr, and Cs content were performed using the PIXE method (Particle Induced X-ray Emission). The analytical part of the work was carried out at the analytical nuclear-physical complex "Sokil" [13]. The energy range of the accelerator was 200-2000 keV. Targets were placed in a cassette located in the irradiation chamber. Before conducting measurements, a vacuum was created in the chamber with a pressure of $10^{-4}$ Pa. To excite characteristic X-ray radiation (XRR) of Cs, Sr, and Co atoms, a proton beam with a current of 200 nA and an energy of 1400 keV was used [12, 14, 15]. At this energy, the characteristic X-ray radiation of the L-series of cesium atoms and the K-series of strontium and cobalt is effectively excited. Measurement of characteristic X-ray radiation was carried out using the XR-100CR Si-pin X-ray detector. The detector was located outside the irradiation chamber at a distance of 7 cm from the target, at an angle of 135° to the direction of the proton beam. XRR exited the chamber through a 25 $\mu$m thick beryllium foil window. In previous studies to determine the content of cesium, strontium, and cobalt ions, for the optimization of spectrometric conditions for XRR spectra formation, a collimator with hole diameters of Ø 1.5 mm and polyethylene absorbing films 150 $\mu$m thick were used [12, 14, 15]. X-ray spectra were processed using the WinQXAS code.

**RESULTS AND DISCUSSION**

To determine the sorption properties, a sorption coefficient was used to quantitatively assess the interaction of clinoptilolite and composite sorbent with radionuclides. The sorption coefficient (Sorption, %) was calculated using the following formula (1):

$$\text{Sorption, %} = \frac{(C_0 - C_{eq}) \times 100\%}{C_0}. \quad (1)$$

where $C_0$ and $C_{eq}$ are the initial and equilibrium concentrations of the solution, mg/ml.

**INFLUENCE OF A PERMANENT MAGNETIC FIELD ON THE SOLUTION**

The research aimed to investigate the effect of magnets on a cesium solution during sorption by zeolites in dynamic conditions. The solution was circulated through the setup while being exposed to the magnetic field of the magnets. Analysis of the sorption properties of natural and synthetic zeolites was conducted for their potential use in nuclear energy for the immobilization of high-level radioactive waste. The obtained data indicates that the introduction of magnets into the sorption scheme leads to a 1% change in sorption, which falls within the experimental error of -5%. The sorption process for clinoptilolite in dynamic conditions consists of two stages: rapid and slow. The rapid stage occurs from the 1st to the 30th sorption cycle and is characterized by a quick increase in the sorption coefficient. This is associated with the establishment of partial sorption equilibrium in the solution-adsorbent system. The slow stage of sorption takes place from the 30th to the 40th sorption cycles and is characterized by a gradual increase in the sorption coefficient. It was found that sorption equilibrium for clinoptilolite is achieved after 30 sorption cycles (Figure 4). The maximum value of the sorption coefficient after 30 sorption cycles is 82.46% when using clinoptilolite and 81.50% when using clinoptilolite with magnetic treatment of the solution.

Next, the data for cesium sorption by synthetic zeolites was examined. For zeolite NaX, saturation is achieved after 20 sorption cycles (Figure 5). The fast sorption stage occurs from the 1st to the 20th cycle. The sorption coefficient for zeolite NaX is 82.45% when using only zeolite NaX and 83.40% when using zeolite NaX with magnetic treatment of the solution.
For zeolite NaA, saturation occurs after 10 sorption cycles (Figure 6). The fast sorption stage occurs from the 1st to the 10th cycle. The sorption coefficient after completing the fast stage is 68.15% when using only zeolite NaA and 69.30% when using zeolite NaA with magnetic treatment of the solution.

The use of magnets on the pipeline during dynamic sorption of cesium by zeolites does not lead to significant changes in sorption and falls within the experimental error. Zeolite NaA did not exhibit significant sorption values. Further research considered the influence of clinoptilolite and composite sorbents based on clinoptilolite and synthetic zeolite NaX in different ratios. Synthetic zeolite NaX showed good sorption properties.

**EFFECT OF A PERMANENT MAGNETIC FIELD ON THE SORBENT**

According to available data, in clinoptilolite, a portion of aluminum ions is replaced by iron ions. The iron content ranges from 0.9% to 2.5%. Therefore, magnetic fields can have a significant impact on the sorption properties of clinoptilolite. With this in mind, significant changes were made to the sorption setup (Figure 3). The sorbent was placed in a plastic sorption column, and an external magnet, affecting the zeolites inside the column, was located on the outer diameter of the sorption column. The results for a mixture of isotopes and different sorbents are presented in Figures 7-9, and a comparison of sorption with and without the magnet is provided in Table 1. The results in Figures 6-8 indicate that the influence of a permanent magnetic field on the sorbent exhibits unexpected characteristics, resulting in non-typical jumps in the sorption of the examined isotopes for composite sorbents. One of the reasons is the presence of isotopes (ions) in the solution with different atomic radii, which significantly affects the mobility of ions and their distribution in sorption structures. For clinoptilolite, when subjected to the influence of a permanent magnetic field during dynamic sorption, there is an increase in Ks (cobalt) by 10% and Ks (strontium) by 17%, with a 9% decrease in Ks (cesium). For composite sorbents, considering the reduced portion of clinoptilolite (down to 50% and 25%), as well as the changes introduced in the sorption setup (Figure 3), a decrease in sorption indicators is observed. This is related to the contribution of clinoptilolite to the composite sorbents. An increase in the proportion of clinoptilolite leads to enhanced sorption properties of the sorbent for cobalt and strontium. This is because clinoptilolite contains iron oxides, which, unlike aluminum, are significantly affected by the permanent magnetic field.
CONCLUSIONS

Experiments were conducted to determine the dynamic sorption under the influence of a permanent magnetic field of the NdFeB magnet, which acted on both the solution and the sorbent.

It was established that the influence of a permanent magnetic field of the NdFeB magnet on the cesium solution moving in the pipeline during dynamic sorption did not increase the sorption coefficients of zeolites. This is because the parameters of the experiment considered in the work (the magnet and the flow rate of the solution) require further research and clarification.

The second part of the work aimed to determine the influence of the magnetic field of NdFeB magnets on the sorbent located in the sorption column. It was found that clinoptilolite, under the influence of a permanent magnetic field, changes its sorption properties due to the presence of iron ions in its composition. An increase in the sorption coefficient for cobalt by 10% and strontium by 17% was observed.

For composite sorbents, there were no changes in sorption under the influence of the permanent magnetic field of the NdFeB magnet. This is because the portion of clinoptilolite in the composition of the composite sorbent with a certain iron content is significantly lower than in pure clinoptilolite. In the composite sorbents considered, the percentage of clinoptilolite was 50% for the CISZ_2 sorbent and 25% for the CISZ_3 sorbent.

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ВІЛЯВ МАГНІТНОГО ПОЛЯ НА СОРБЦІЮ РАДІОНУКЛІДІВ КЛІНОПТИЛОЛІТОМ ТА КОМПОЗИЦІЙНИМ СОРБЕНТОМ НА ОСНОВІ ІОНИ ІОНОЦЕЛОТ

Олексій Ю. Лонин, Володимир В. Левєнць, Олександр М. Бовда

Відомо, що магнітне поле впливає на фізичні очікування в процесах сорбції різних мінералів. В нашому випадку використано комплекс кобальт-алюмінієвий. Магнітне поле змінювалося в діапазоні від 0 до 1 Тл. В результаті було встановлено, що сорбційна ефективність збільшується зростанням магнітного поля.

Ключові слова: магнітнополе, рівень радіонуклідів, сорбційна ефективність, кобальт-алюмінієвий комплекс.

REFERENCES


