CLINOPTILOLITE UNDER THE INFLUENCE OF PERMANENT MAGNETS AS A SORBENT FOR CESIUM, STRONTIUM, AND COBALT

O.M. Bovda, O.Yu. Lonin, V.V. Levenets, V.V. Kuzmenko
National Science Center "Kharkiv Institute of Physics and Technology", Kharkiv, Ukraine

The work examined the infusion of permanent NdFeB magnets into radionuclides (Cs, Sr, Co) sorption by clinoptilolite and composite sorbents based on zeolites. When magnets were poured onto the sorbent, during the sorption process for clinoptilolite, the sorption of cobalt increased by 10%, and strontium sorption increased by 17%. For composite sorbents, no increase in sorption of radionuclides was observed. This is associated with a portion of clinoptilolite in the warehouse, a sorbent, and a suitable place for release. The analytical part was formed using the PIXE method at the Sokil analytical nuclear physics complex.

PACS: 82.75.-z;82.80Ej;85.70.-w

The development of nuclear energy increases the demand for comprehensive protective measures. One of the protective measures used in nuclear energy is the use of natural sorbents. The use of natural sorbents allows for significant cost reduction and increased safety for personnel. Zeolites are often used for the sorption of radionuclides and the purification of liquid radioactive waste. However, the use of zeolites is associated with several limitations. The first limitation is significant changes in composition depending on the location of the deposit and its depth. The second limitation is the small range of radionuclides that zeolites can absorb. A striking example of a natural zeolite is clinoptilolite. Clinoptilolite has high selectivity for cesium but is significantly inferior in the sorption of other radionuclides.

There are mechanisms to increase the sorption properties of clinoptilolite. One such mechanism is the influence of a magnetic field on the structure of the zeolite. According to existing literature data, as well as based on the obtained data, clinoptilolite contains iron. The constant influence of the magnetic field should polarize the iron ions that are part of clinoptilolite. In the work, clinoptilolite containing iron was used. The content of Fe_2O_3 is 0.9%.

As sorbents, natural zeolite (clinoptilolite) was used, and the following sorption compositions based on zeolites were also used:

1. clinoptilolite – 100% + zeolite NaX – 0% (ClSZ_1);
2. clinoptilolite – 50% + zeolite NaX – 50% (ClSZ_2);
3. clinoptilolite – 25% + zeolite NaX – 75% (ClSZ_3).

As a permanent magnet, NdFeB magnets produced by NSC KFTI were used. Nitrates of cesium, strontium, and cobalt were used as pollutants.

In the 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. 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 mm. 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 ≥955 kA/m, and a grade of N38.

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.

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" [1]. 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 [2-4]. 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 μm 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 μm thick were used [2-4].

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 (Ks, %) was calculated using the following formula:

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

where C_0 and C_p are the initial and equilibrium concentrations of the solution, mg/ml.

According to available data, in clinoptilolite, some of the aluminum ions are replaced with iron. The iron content ranges from 0.9 to 2.5%. Therefore, magnetic fields can have a significant impact on the sorption properties of clinoptilolite. According to this task, significant changes were made to the sorption installation. The sorbent was placed in a plastic sorption column. A magnet that affects the zeolites placed in the column is located along the outer diameter of the sorption column. The obtained results of comparing the sorption of the isotope mixture with the sorbent with and without the magnet are presented in Table.

Influence of a permanent magnetic field on the sorption properties of clinoptilolite and composite sorbent

Sorbent	Sorption Cycles	Sorption coefficient (Sorption, %)		
		Cobalt	Cesium	Strontium
Clinoptilolite (ClSZ_1)	80	48%	81%	34%
Clinoptilolite (ClSZ_1)+ magnet	80	58%	70%	51%
Clinoptilolite -50+ zeolite NaX -50 (ClSZ_2)	80	79%	80%	70%
Clinoptilolite -50+ zeolite NaX -50 (ClSZ_2) + magnet	80	52%	58%	57%
Clinoptilolite -25+ zeolite NaX -75 (ClSZ_3)	80	71%	65%	66%
Clinoptilolite -25+ zeolite NaX -75 (ClSZ_3) + magnet	80	50%	60%	27%

For clinoptilolite, under the influence of a constant magnetic field during dynamic sorption, an increase in the sorption coefficient (Ks) for cobalt by 10% and for strontium by 17% was observed. At the same time, a decrease in the sorption coefficient (Ks) for cesium by 9% was noted. For composite sorbents considering a reduced share of clinoptilolite (to 50 and 25%), a decrease in sorption indicators was observed. This is due to the proportion of clinoptilolite in composite sorbents. An increase in the proportion of clinoptilolite leads to an increase in the sorption properties of the sorbent for cobalt and strontium because the composition of clinoptilolite includes iron oxides, which, unlike aluminum, are significantly affected by a constant magnetic field.

CONCLUSIONS

Experiments were conducted to determine dynamic sorption under the influence of a constant magnetic field of NdFeB magnets acting on the sorbent. The influence of the magnetic field of NdFeB magnets on the sorbent was determined. The magnet was placed on the sorption column. It was established that clinoptilolite changes its sorption properties under the influence of a constant magnetic field, due to the content of iron ions in the composition of clinoptilolite. An increase in the sorption coefficient of cobalt by 10% and strontium by 17% was observed.

For composite sorbents under the influence of a constant magnetic field of NdFeB magnets, no changes in sorption were observed. This is due to the fact that the part of clinoptilolite in the composition of the composite sorbent with the corresponding iron content is significantly smaller than in pure clinoptilolite. In the considered composite sorbents, the percentage of clinoptilolite was 50% for sorbent ClSZ_2 and 25% for sorbent ClSZ_3.

REFERENCES

1. S.G. Karpus, V.V. Kuzmenko, V.V. Levenets and others. Modernization of the analytical nuclear-physical complex Sokil // *Problems of Atomic Science and Technology*. 2023, № 2(144), p. 134-139.

2. 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 // *Journal of Radioanalytical and Nuclear Chemistry*. 2015, №303, p. 831-836.

3. V.V. Levenets, A.Yu. Lonin, O.P. Omelnik, 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 // *Journal of Environmental Chemical Engineering*. 2016, № 4, p. 3961-3966.

4. A.Yu. Lonin, V.V. Levenets, O.P. Omelnik, 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 // *Journal of Radioanalytical and Nuclear Chemistry*. 2018, №315, p. 163-169.