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THE CHEMICAL AND MINERAL COMPOSITION OF NATURAL ZEOLITES AND THEIR SORPTION PROPERTIES DURING OZONATION WITH DRAIN WATER FROM NUCLEAR POWER PLANTS

The article reveals the regularities of the overall process of ozonolytic destruction of organic components of model drain water from nuclear power plants and sorption of imitators of the main dose-forming radionuclides (Cs — with the isotopic ^{137}Cs label; stable isotopes of Co, Sr, Mn salts) by natural zeolite of the Sokyrnytsky deposit and sorption-reagent compounds — salts of ferrous and manganese (II). The chemical composition of the main elements of zeolite after ozonation with the addition of iron and manganese salts practically does not differ from the composition of natural zeolite. Its phase composition in the ozonation process in the presence of ferrum salts is represented by the main rock-forming mineral clinoptilolite and the secondary mineral — quartz. The main ferrum-containing phase on the zeolite surface is goethite. Secondary phases include Fe(II)-Fe(III) layered double hydroxides (Green Rust) and lepidocrocite, but their relative content is insignificant. For zeolites, after ozonation with the addition of both ferrous and manganese (II) salts, the main phases are clinoptilolite and quartz. Manganese-containing phases on the zeolite surface are represented by hausmannite Mn_3O_4 , manganese(II) oxide, and manganese oxyhydroxide $\text{MnO}(\text{OH})_2$. The iron- and manganese-containing phases deposited on the surface of the zeolite in the process of ozonation are mainly characterized by a weakly crystallized or amorphized structure. The main sorbent of dose-forming radionuclides is zeolite, not the iron- and manganese-containing compounds that formed on its surface during ozonolysis. The maximum degree of sorption of ^{137}Cs by zeolite is up to 90% when the concentration of Fe^{2+} is increased to 50 mg/dm^3 or Mn^{2+} to 100 mg/dm^3 . The degree of cobalt sorption is 97.5% at the initial typical concentration of competing cations ($\text{Fe}^{2+} — 5 \text{ mg/dm}^3$; $\text{Mn}^{2+} — 10 \text{ mg/dm}^3$) and when Mn^{2+} concentration increases to 100 mg/dm^3 . The maximum degree of extraction of Sr^{2+} and Mn^{2+} is 99.4% and 99.9%, respectively. For effective extraction of ^{137}Cs and Co^{2+} by zeolite in the ozonation process, an increase in the concentration of competing Fe^{2+} cations is permissible — 50 mg/dm^3 ; $\text{Mn}^{2+} — 100 \text{ mg/dm}^3$ in solutions. The efficiency of extraction of Sr^{2+} and Mn^{2+} practically does not depend on the concentration of competing cations (Fe^{2+} , Mn^{2+}) in the drain water solutions.

Keywords: NPP drain water, ozonation, chemical and mineral composition, sorption, zeolite.

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Introduction. In the process of operation of Ukrainian nuclear power plants, tens of thousands of m³ of water (drain water) are formed from various sources. They are contaminated with uranium fuel fission products, radionuclides (RN) of corrosive origin, various substances used to maintain the water-chemical regime and decontamination of equipment¹. According to indicators of oxidation of the drain waters they contain a small amount of organic substances.

In recent years, an optimal technology for processing of drain water and cubic residue (CR), which is a salt concentrate (200-400 g/dm³) in a liquid state, has been developed in order to avoid formation of high-salt condensate (SC)-salt concentrate with the content more than 500 g/dm³.

To date, a recognized promising technology is the sedimentation and sorption purification of the drain water and sewage from the main dose-forming radionuclides on composite industrial sorbents with subsequent cementation and conditioning in barrels and containers intended for waste disposal [1, 4]. Concentration of RN on sorbents makes it possible to reduce the volume of liquid radioactive waste (LRW), which is sent to long-term storage or disposal, by 10 or more times compared to direct LRW cementation, which makes such an approach promising and relevant [6]. The introduction of zeolites as sorbents is implemented at mobile installations NURES (Finland) and Fukushima-1 (Japan) [5]. One of the largest zeolite deposits in the world — Sokyrnytsky (industrial reserves of the mineral amount to 18.5 million tons²) is located in Ukraine. It determines the relevance of the development of effective zeolite-based sorbents of the main dose-forming radionuclides from almost all existing sources of RW at NPPs with VVER reactors. Basing on the composition of the exchange complex and the Si/Al ratio, the rock-forming zeolite of the Sokyrnytsky deposit

belongs to the low-silicon potassium-sodium clinoptilolites with a high degree of crystallinity and heat resistance, which makes it possible to use it as an effective sorbent for the extraction of ⁹⁰Sr and ¹³⁷Cs from model solutions of pre-ozonated drain water [10].

The aim of the article is to study the influence of the ozonation process of model solutions of the nuclear power plants' drain water with VVER reactors in the presence of zeolites of the Sokyrnytsky deposit on their elemental and mineral composition and sorption properties.

Materials and Methods. *Simulated drain water solution.* In the Ukrainian NPPs equipped with pressurized water-water reactors, the total salinity of the various components in the drain water mixture is on average 3-7 g/dm³ (rarely up to 15 g/dm³) [12]. The purification of drain water from radionuclides is complicated by the variety of their forms: simple and complex ions, neutral molecules and colloidal particles. The main dose-forming radionuclides are ¹³⁷Cs and ⁹⁰Sr — uranium fuel fission products, and ⁶⁰Co and ⁵⁴Mn — activation products of the circuit equipment. ¹³⁷Cs and ⁹⁰Sr are present in the ionic forms, while ⁶⁰Co and ⁵⁴Mn are mainly in the form of organic complexes with EDTA and oxalic acid. The composition of the simulated solution used in our study is presented in (Table 1). The radioactive tracer ¹³⁷Cs and salts of stable elements of Sr, Co, Mn as chemical analogues of the related radionuclides were added to the initial solution.

To increase the concentrations of Fe²⁺ (50 and 500 mg/dm³), Mn²⁺ (100 and 1000 mg/dm³) and Ca²⁺ (50 and 500 mg/dm³) ions in the initial solution, ferrous and manganese(II) sulphates were added.

Zeolite samples. In our study we used samples of tuff rock (zeolites) taken at a depth of 11-15 m from the mining pit of the Sokyrnytsky deposit. The main characteristics of the Sokyrnytsky clinoptilolite used in the research corresponded to standard TU U 14.5-00292540.001-2001.

The main rock-forming mineral is low siliceous potassium — calcium — sodium clinoptilolite with a content of up to 75-90%. Other zeolite minerals are represented by quartz and mica in the amount of approximately 12 and ≤5%, respectively [10]. A fraction of 0.25 mm was taken from the samples, washed with

¹ (2020) Behavior with radioactive waste during the operation of the nuclear power plant SE "NAEK "Energoatom", Report for 2020, Kyiv, 76 p. [in Ukrainian].

² (2017) Environmental expert evaluation of environmental impact assessment materials (EIA) "Development and mining-technical reclamation of the Sokyrnytsky deposit (site located between the 8th and 11th sections) of zeolites in the Khust district of Zakarpattia region", Kyiv, 15.12.2017, 18 p. [in Ukrainian].

distilled water from the remains of the dusty fraction with periodic stirring until the distillate was 100% transparent. The precipitate was separated and dried to air-dry state.

Ozonation conditions. Ozonation of the simulated drain water solutions was performed by ozone-air mixture produced in an ozone generator and fed into the column with the simulated drain water solution through the dispersant [10]. Then the column was heated to 60 °C, and natural bentonite was added in the ratio bentonite (g):solution (ml) = 1:100. After that, ozone was passed through the mixture for two hours. After ozonation, the simulated solution was filtered with a vacuum pump through a membrane filter. Then, the final pH, chemical oxygen demand (COD), ^{137}Cs activity and residual concentration of Sr^{2+} , Co^{2+} , Mn^{2+} were measured.

Research methods. *Scanning electron microscopy (SEM) and energy dispersion spectroscopy (EDS).* Samples of bentonite were applied on a film and sputtered with precious metals. The study was performed with a scanning electron microscope Tescan Mira 3 LMU, equipped with an energy-dispersive attachment for microanalysis. The results were obtained at the following parameters: accelerating voltage of 3-15 kV, spatial resolution: 1 nm — 30 kV and 2 nm — 3 kV, the working pressure in the chamber: high vacuum mode about 9×10^{-3} Pa, low vacuum mode 7 — 150 Pa. Pure metals, minerals, oxides and fluorides were used as standards. *X-ray phase analysis (XRD).* Phase composition of the samples was determined using DRON-3 diffractometer with a copper anode radiation (Cu K α). The scanning step was from 0.05 to 0.1 degrees, exposure equalled 4 seconds, 2 θ diffraction angles was from 15 to 90°. Patterns were collected at standard temperature. Identification was performed according to the ASTM

file. *Atomic adsorption spectroscopy.* To measure the concentration of Sr, Co, Mn and Fe in the solutions, Jarrell Ash AA-8500 single-beam dual-channel atomic absorption spectrophotometer with a flame atomizer was used.

γ -spectrometry. The activity of ^{137}Cs in aqueous solutions was measured using γ -spectrometer Atoll-1M (manufactured by OPYT enterprise, Ukraine).

Results and Discussion. The value of zeolites is determined by the aluminum-silica-oxygen framework common to them. The frame has a negative charge and this charge is compensated by cations of alkaline and alkaline earth metals and water molecules located in the pores and cavities of the frame and weakly connected to it. The structure of clinoptilolite consists of $[\text{SiO}_4]^{4-}$ and $[\text{AlO}_4]^{5-}$ tetrahedra, which, joining each other, form pores of two types with dimensions of 0.6×0.4 and 0.4×0.4 nm [14]. The pores of zeolites, connecting to each other through "windows", form a network of through channels inside the crystals. The contents of the channels represent an extra-framework subsystem — these are positively charged exchange cations Na^+ , K^+ , Mg^{2+} , Ca^{2+} , H_3O^+ compensating for the negative charge of the framework, as well as a large amount of coordination water.

Exchangeable cations are located next to the $[\text{AlO}_4]$ tetrahedron mainly in large cavities. The order and degree of extraction of exchangeable cations and Al is approximately the same. The elements can be arranged in a series that correlates with the decrease in the strength of the bonds of these elements in the structure of clinoptilolite ($\text{Si} > \text{Al} > \text{K} > \text{Ca} > \text{Na}$) [12]. If the ion exchange is carried out under conditions of complete or partial hydrolysis of metals in solution, then the phases of highly dispersed oxides and oxyhydroxides of the corresponding metal are formed on zeolites [13]. The stability of the

Table 1. Composition of the initial simulated drain water solution

Chemical compounds	Concentration, mg/dm ³	Chemical compounds	Concentration, mg/dm ³	Chemical compounds	Concentration, g/dm ³
H_3BO_3	1700	CoSO_4	132	The CaCl_2	13.9
KNO_3	1000	$\text{MnSO}_4 \cdot \text{H}_2\text{O}$	30.77	EDTA	100
Na_2SO_4	2000	$\text{Sr}(\text{NO}_3)_2$	120.5	$\text{H}_2\text{C}_2\text{O}_4$	40
NaCl	1450	CsNO_3	73.3	Lotus-M	350
NaOH (45%)	1450	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$	25	Mineralization	7035.47

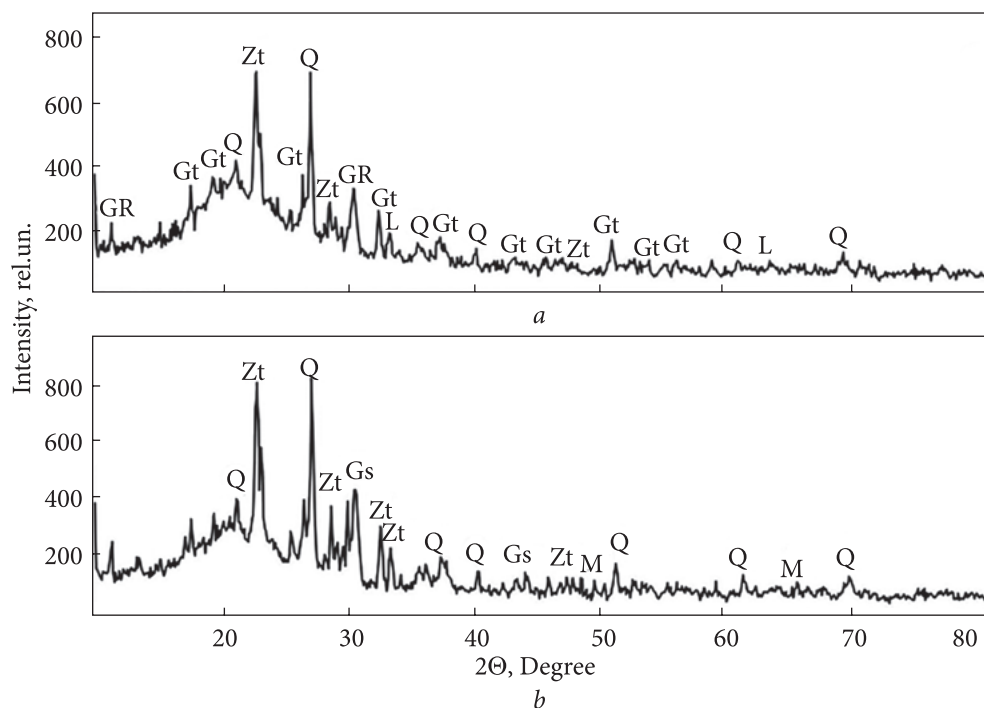


Fig. 1. Diffractograms of zeolite samples with additions (10%): *a* — iron, *b* — manganese. Legend: Zt — clinoptilolite; Q — quartz; GR — Green Rust Fe(II)-Fe(III) layered double hydroxides; Gt — goethite; Mt — magnetite; Gs — hausmannite; M — oxyhydroxide of manganese

structure of zeolites is determined by the ratio of silicon to aluminum in the crystal lattice and can vary within fairly wide limits, but there is an upper limit for aluminum, according to which its content in tetrahedral positions in silicon-aluminum-oxygen frameworks can be either less than or equal to the content of silicon, but cannot be higher than it [7]. According to the IMA (International Mineralogical Association) nomenclature of zeolites, "clinoptilolite" is characterized by a ratio of Si/Al \geq 4.

The sorption and ion exchange properties of zeolites, which determine the possibilities of their practical use for the decontamination of radiation-contaminated water environments, are affected by the morphology and composition of clinoptilolite.

According to X-ray phase analysis, the diffraction pattern of zeolite, the transformation of which took place in the ozonation process in the presence of 10% ferrum content (Fig. 1, *a*), shows the reflexes of clinoptilolite and quartz, the intensity of which is maximum. That is, ozonation conditions do not lead to the destruction of the clinoptilolite framework and loss of sorption properties. The main ferrum-

containing phase is goethite, as it was established from the results of diffractograms of the ozonation sediments of drain waters [11] for which all the reflexes characteristic of this phase can be traced. Secondary phases include Fe(II)-Fe(III) layered double hydroxides (Green Rust) and lepidocrocite, but their relative content is insignificant. Probably, the ozonation process causes the intensification of the oxidation process of soluble ferrum-containing aquacomplexes and the formation of goethite as the end product of oxidation under hypergenesis conditions.

Fig. 1, *b* shows the diffractogram of zeolite, which was transformed under the action of ozonation of drain water in the presence of aqua forms of manganese with degrees of oxidation (II, III, IV). As in the sample of zeolite with ferrum (Fig. 1, *a*), the main phases are clinoptilolite and quartz, but unlike it, the formation of phases in the case of 10% manganese is weakly expressed. The diffractogram shows slight reflexes of manganese oxides and oxyhydroxide. The most important of them are hausmannite and oxyhydroxide, which is consistent with the mineral composition of ozonation sediments of drain water [11]. It can be assumed that the

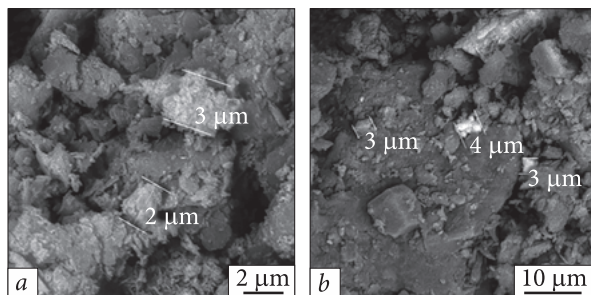


Fig. 2. SEM images of zeolite, ozonized with additions (10%): *a* — iron, *b* — manganese

formation of oxidized manganese compounds is also typical for this system.

According to the SEM data, visually, the surface of zeolite with 10% ferrum has a relatively inhomogeneous rough structure with aggregated plates, 2-3 μm in size, and a small fraction over 100 nm in size (Fig. 2, *a*). Ozonation of drain water in the presence of zeolite leads to an increase in the roughness of its surface. Fig. 2, *b* shows the SEM image of zeolite after ozonation in the presence of 10% manganese. Aggregated zeolite particles are better crystallized compared to the sample formed in the presence of ferrum. The size of the aggregates is 3-4 μm , the content of the monometric fraction is insignificant.

According to EDS data, the elemental composition of the zeolite sample — 10% ferrum in-

cludes the main structure-forming elements of clinoptilolite — oxygen, silicon, aluminum, as well as a small amount of exchangeable more mobile alkaline — potassium and sodium, alkaline earth metals — calcium and magnesium, and ferrum. The analysis of the spectra (Table 2) shows that the main chemical elements that make up the zeolite are distributed quite evenly in a relatively narrow range, in particular, the mass% of sodium varies between 1.28-1.63; potassium — 2.81-4.63; magnesium — 0.42-0.61; aluminum — 4.98-7.85; calcium — 0.97-1.75. At the same time, the distribution of ferrum is uneven — 3.44-6.88 and 23.16 wt.%, giving reason to believe that the formation of ferrum-containing phases (goethite) occurs in the form of individual phase particles. A similar assumption can be made in relation to silicon, but in this case such a distribution is less pronounced due to its inclusion in the composition of zeolite minerals. At the same time, the Si/Al ratio slightly increases compared to the original zeolite due to a decrease in the aluminum concentration (Table 2).

Analysis of the EMF spectra of zeolite with 10% manganese is characterized by a uniform distribution of rock-forming elements (zeolite), in particular, the mass% of sodium varies between 1.15-2.19; magnesium — 0.27-0.57; potas-

Table 2. The elements' containing in nature zeolite of Sokyrnytsky deposit (Zt_0) and after ozonation of drain waters with salts of iron (Zt_{Fe}) and manganese (Zt_{Mn}) additions (by EDS data)

Element	Zt_{Fe}			Zt_{Mn}					Zt_0	
	(*1)	(*2)	(*3)	(*1)	(*2)	(*3)	(*4)	(*5)	(*1)	(*2)
O	42.92	42.29	46.85	46.13	47.27	35.49	48.53	44.60	49.37	53.50
Na	1.63	1.28	1.61	1.55	1.15	2.19	1.43	2.03	1.12	1.37
Mg	0.61	0.42	—	0.38	0.27	0.57	0.54	0.54	0.67	0.30
Al	7.85	4.98	6.57	4.57	2.53	2.88	6.45	7.28	8.19	6.85
Si	37.81	24.09	32.10	19.56	10.02	6.81	37.48	35.63	34.73	32.86
S	—	—	—	—	—	1.68	—	—	—	—
Cl	—	—	—	—	—	1.93	—	0.70	—	—
K	4.63	2.81	3.74	3.25	1.38	1.43	3.73	4.31	2.38	2.50
Ca	1.30	0.97	1.75	1.79	3.71	2.78	0.46	1.04	1.66	1.67
Mn	—	—	—	—	—	34.82	—	0.96	0.44	—
Fe	3.44	23.16	6.88	1.68	0.39	—	1.38	2.91	1.44	1.96
Co	—	—	—	0.52	0.41	1.84	—	—	—	—
Sr	—	—	—	20.57	32.87	1.77	—	—	—	—
Σ	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Si/Al	4.81	4.83	4.88	4.28	3.96	2.36	5.81	4.89	4.24	4.80

* Containing of elements in one of the points of investigation.

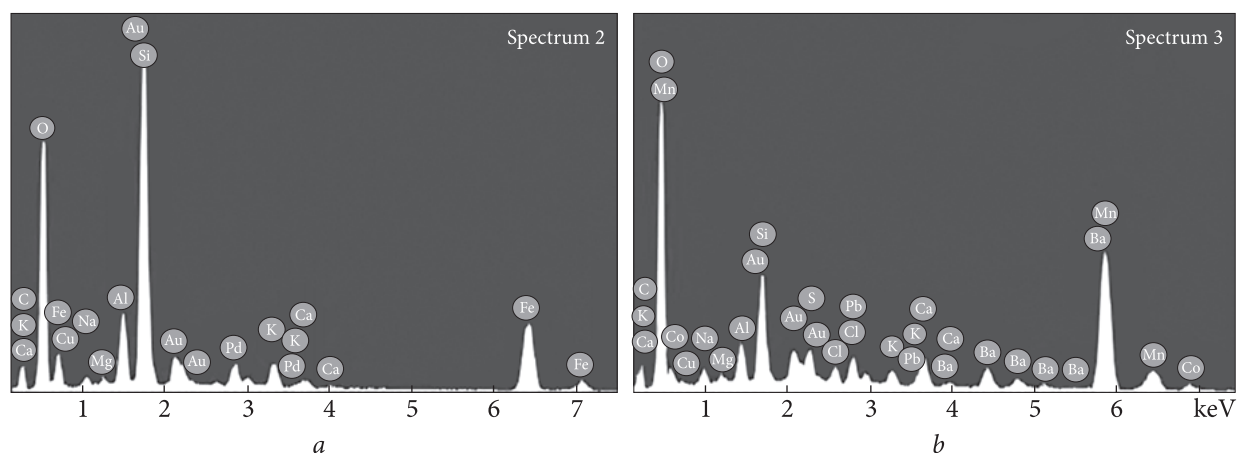


Fig. 3. Energy-dispersion spectra of zeolite, ozonized with additions (10%): *a* — iron (point 1), *b* — manganese (point 3)

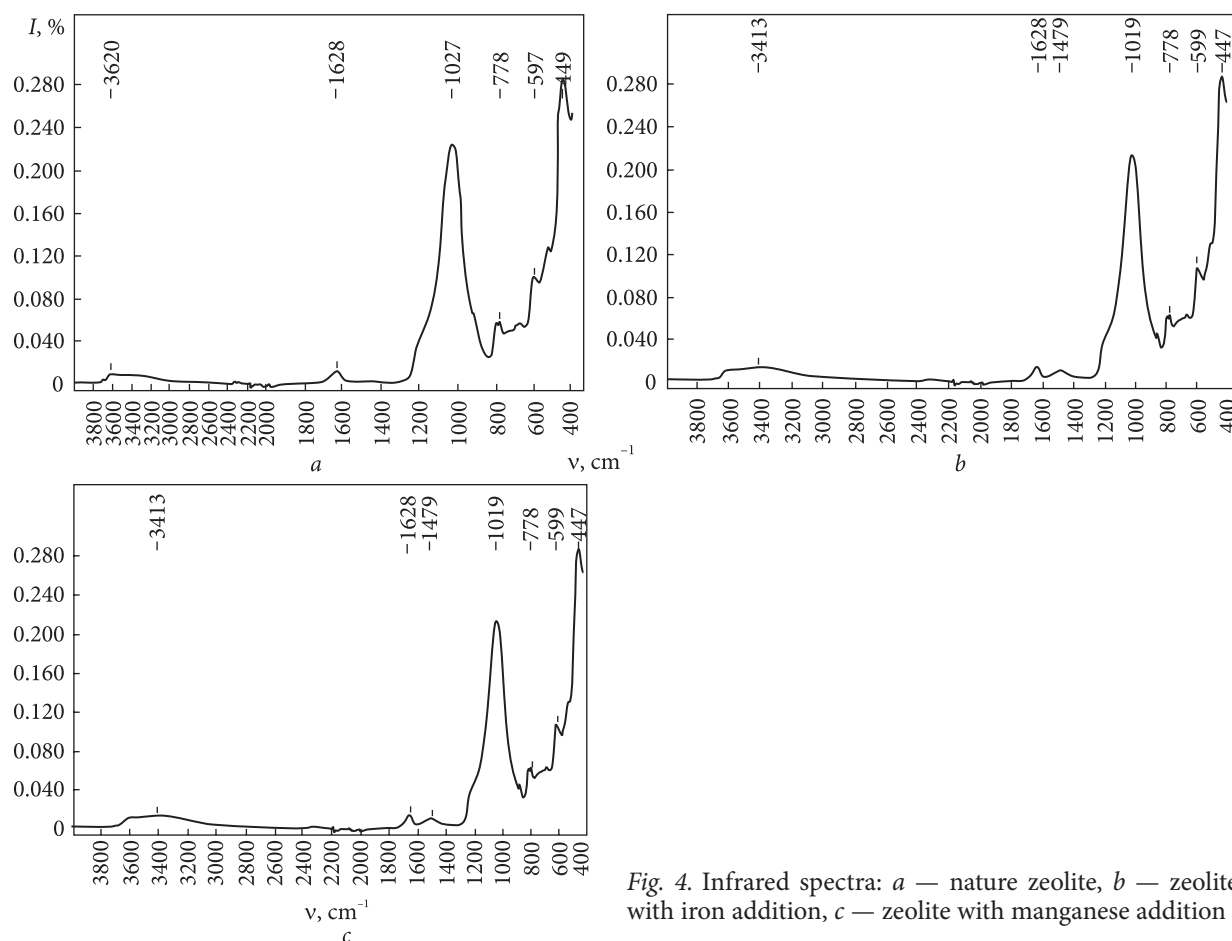


Fig. 4. Infrared spectra: *a* — nature zeolite, *b* — zeolite with iron addition, *c* — zeolite with manganese addition

sium — 1.38-4.31; aluminum — 2.53-7.28 and ferrum — 0.39-2.91.

At the same time, the distribution of silicon is uneven 6.81-10.02; 19.56 and 35.63-37.48, which indicates the formation of individual quartz particles. The high manganese content (34.82 wt.%) in only one spectrum gives grounds for asser-

ting the formation of an individual manganese-containing phase. Sulfur, chlorine, cobalt and strontium can be considered impurity elements, which can be attributed to the components of drain water with which the zeolite came into contact during ozonation. Fig. 3, *a* shows the EDS spectrum of zeolite-ferrum (10%). The

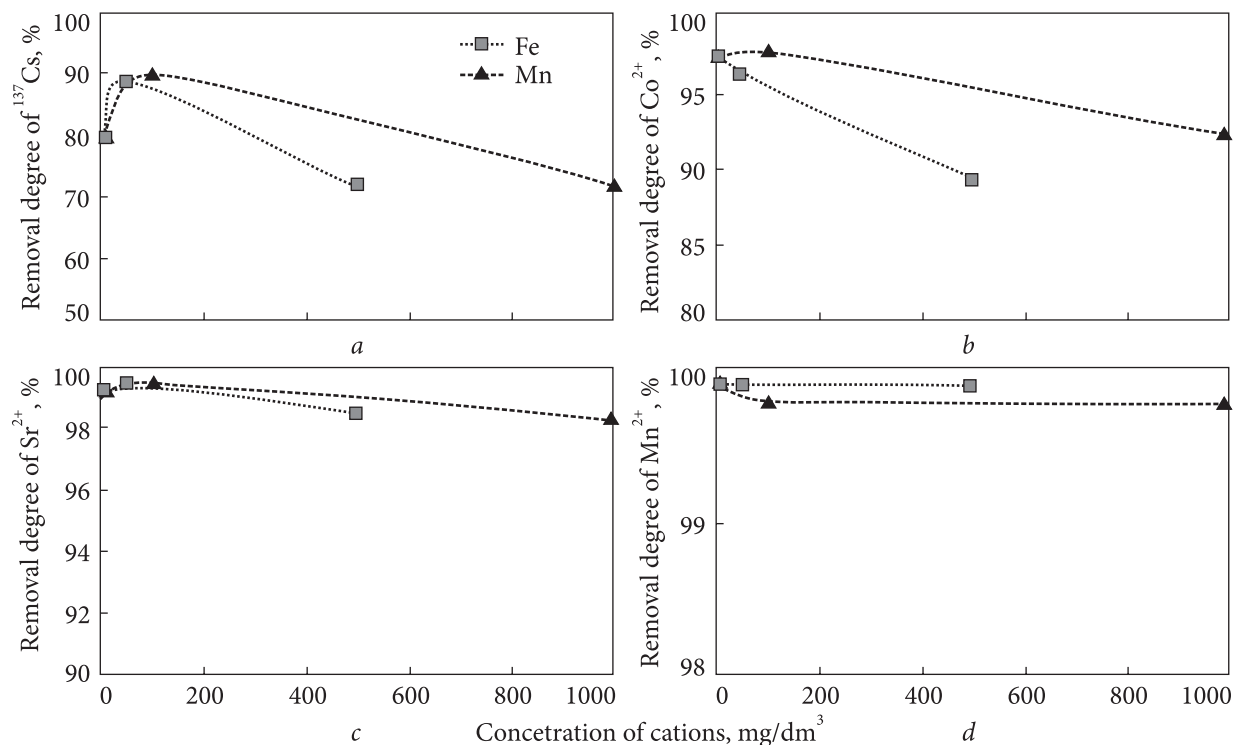


Fig. 5. Radionuclides removal degree received during ozonation process with zeolite depending on the initial concentration of Fe, Mn and Ca in the simulated NPP trap water solution

presence of gold and palladium reflexes is due to sputtering of the sample with precious metals. The most intense are reflexes of silicon (quartz) and ferrum (goethite).

The elements that make up the zeolite itself are weakly expressed. Fig. 3, *b* shows the spectrum of zeolite obtained after ozonation in the presence of manganese. In this case, the sample with manganese particles was selected (spectrum 3, Table 2), therefore the most intense reflexes belong to manganese and oxygen. The intensity of silicon is lower, and the rock-forming elements of zeolite are at the background level.

Fig. 4 shows IR spectra in the region of 4000-400 cm⁻¹ of natural zeolite (Z_0) and zeolites after ozonation of drain water in the presence of iron ($Z_{t_{Fe}}$) and manganese ($Z_{t_{Mn}}$) salts. The spectra of the samples are typical of clinoptilolites 2, [14] and remain well resolved. Water molecules in the zeolite framework are bound to exchangeable cations, and changes in the IR spectra are due to the content of exchangeable cations and their redistribution — migration from large planes to small ones, which leads to a change in the width and intensity of almost all absorption bands. In the region of 4000-3000 cm⁻¹, a

band with a maximum at 3620 cm⁻¹ is observed, which is characteristic of the oscillation of the bridging Brønsted OH group in the Si(OH)Al fragment, and a blurred band with a maximum in the range of 3400-3415 cm⁻¹ is characteristic for molecular water [8].

In the range of deformation vibrations of H₂O molecules for a sample of natural zeolite (Z_0), a band of average intensity at 1628 cm⁻¹ is observed. For zeolites after ozonation of drain water in the presence of iron ($Z_{t_{Fe}}$) and manganese ($Z_{t_{Mn}}$) salts, two bands are recorded in this range at 1636 and 1433 cm⁻¹ and 1628 and 1479 cm⁻¹, respectively. The bands at 1433 cm⁻¹ and 1479 cm⁻¹ can be attributed to the deformation vibrations of H-O-H and Me(Fe/Mn)-O-H bonds. An intense broad band with a maximum at 981, 1019, 1027 cm⁻¹ refers to asymmetric and symmetric stretching vibrations of the Si-O-Al bonds of clinoptilolite, as well as quartz. In the region of 800-400 cm⁻¹ there are bands that correspond to valence symmetric vibrations of the T-O-T structural fragment (where T is an Al or Si atom) of clinoptilolite. The obtained results are in good agreement with the work [9].

Absorption of radionuclides can occur by two mechanisms. The ion exchange mechanism consists in the exchange of ions that are in the pores of the crystal lattice of clinoptilolite for ions of radionuclides from solutions. Another mechanism is chemisorption. During chemisorption, stable inner- and outer-sphere complexes are formed, and radionuclide ions form chemical bonds with the functional groups of the clinoptilolite framework [3]. As a rule, during the sorption of radionuclide ions, both types of complexes exist at the same time. The interaction of exchangeable clinoptilolite cations with radionuclides in solution is determined by the strength of the bond between the cation and the clinoptilolite crystal lattice: the weaker this bond is, the more energetic the interaction is.

The degree of sorption of ^{137}Cs (Fig. 5, *a*) by the zeolite of the Sokyrnytsky deposit during the ozonation process of the model solution of the NPP drain water of the normal concentration of competing cations in the drain water (Fe^{2+} — 5 mg/dm³; Mn^{2+} — 10 mg/dm³; Ca^{2+} — 5 mg/dm³) is about 80%. Increasing the concentration of Fe^{2+} cations to 50 mg/dm³ leads to an increase in cesium sorption by 8.5% (up to 88.5%), and increasing the concentration of Fe^{2+} to 500 mg/dm³ leads to a significant decrease of this indicator to 72%. The increase in the concentration of Mn^{2+} cations in the initial solution to 100 mg/dm³ leads to an increase in the extraction efficiency of ^{137}Cs to 90%, and at 1000 mg/dm³, the degree of cesium extraction decreases to 72%. An increase in the concentration of Ca^{2+} cations in the initial solution to 50 mg/dm³ or more leads to a decrease in the degree of ^{137}Cs extraction to 75%.

The degree of extraction of cobalt (Fig. 5, *b*) by zeolite during ozonation of a model solution of drain water with the initial concentration of competing cations is 97.5%. Increasing the concentration of Fe^{2+} cations in the model solution to 50 mg/dm³ leads to a slight decrease in cobalt sorption to 96.2%, and increasing Fe^{2+} to 500 mg/dm³ reduces the degree of cobalt extraction to 89.2%. An increase in the concentration of Mn^{2+} cations in the initial solution to 100 mg/dm³ leads to a slight increase in the degree of its extraction to 97.7%, and at a concentration of Mn^{2+} cations of 1000 mg/dm³, the degree of cobalt extraction is 92.2%. In-

creasing the concentration of Ca^{2+} cations in the initial solution to 50 mg/dm³ and 500 mg/dm³ reduces the degree of cobalt extraction to 87.6 and 87.3%, respectively.

The efficiency of strontium removal (Fig. 5, *c*) in the process of ozonation of the solution practically does not depend on the concentration of competing cations in the solution and varies between 98-99.4%.

A similar situation is also characteristic of manganese (Fig. 5, *d*), the degree of sorption of which, depending on the concentration of competing cations, ranged from 99.7 to 99.9%.

Therefore, the values of the degrees of ^{137}Cs and cobalt extraction from the model solution of NPP effluents in the ozonation process in the presence of natural zeolite remain high when the concentration of competing cations in the solution increases to: Fe^{2+} — 50 mg/dm³; Mn^{2+} — 100 mg/dm³. When the concentration of Ca^{2+} cations is increased to 50 mg/dm³, there is a significant decrease in the degree of sorption of cesium and cobalt. The degree of extraction of strontium and manganese practically does not depend on the initial concentration of cations in the initial solution, at least up to: Fe^{2+} — 500 mg/dm³; Mn^{2+} — 1000 mg/dm³; Ca^{2+} — 500 mg/dm³.

Thus, for effective sorption extraction of dose-forming radionuclides by zeolite in the process of ozonation of a model solution of NPP effluent, it is quite permissible to increase the concentration of competing cations in the initial solution to: Fe^{2+} — 50 mg/dm³; Mn^{2+} — 100 mg/dm³, which practically does not affect the degree of sorption of radionuclides. Though, it is not desirable to increase the concentration of Ca^{2+} even up to 50 mg/dm³.

Conclusions. The following results were obtained from a complex study of the process of simultaneous oxidative decomposition by ozone of organic components of model drain waters of nuclear power plants and sorption interaction of the main dose-forming radionuclides of drain waters with natural zeolites of the Sokyrnytsky deposit in the presence of sorption-reagent compounds — salts of ferrum(II) and manganese(II).

The phase composition of zeolite in the ozonation process in the presence of ferrum salts is represented by the main rock-forming mineral clinoptilolite and the secondary mineral — quartz. The main ferrum-containing phase on

the zeolite surface is goethite. Secondary phases include Fe(II)-Fe(III) layered double hydroxides (Green Rust) and lepidocrocite, but their relative content is insignificant.

For zeolites after ozonation of drain water with the addition of manganese (II) salts, the main phases are also clinoptilolite and quartz. Manganese-containing phases on the zeolite surface are represented by hausmannite Mn_3O_4 , manganese(II) oxide, and manganese oxyhydroxide $MnO(OH)_2$. Ferrum- and manganese-containing phases deposited in the ozonation process on the surface of the zeolite are mostly weakly crystallized or amorphized structures.

In both cases, ozonation conditions in the presence of sorption-reagent compounds — salts of ferrum(II) and manganese(II) do not lead to the destruction of the clinoptilolite framework.

The degree of extraction of the investigated radionuclide imitators in the process of ozonation of a model solution of drain water in the presence of natural zeolite of the Sokyrnytsky

deposit, which is the main sorbent compared to iron- and manganese-containing compounds on its surface, was determined as follows:

The maximum degree of sorption of ^{137}Cs by zeolite is up to 90% when the concentration of Fe^{2+} is increased to 50 mg/dm^3 or Mn^{2+} to 100 mg/dm^3 , the degree of cobalt sorption is 97.5% at the initial typical concentration of competing cations ($Fe^{2+} — 5\text{ mg/dm}^3$; $Mn^{2+} — 10\text{ mg/dm}^3$) and when the Mn^{2+} concentration increases to 100 mg/dm^3 . The maximum degree of extraction of Sr^{2+} and Mn^{2+} is 99.4% and 99.9%, respectively.

For effective extraction of ^{137}Cs and Co^{2+} by zeolite in the ozonation process, an increase in the concentration of competing Fe^{2+} cations is permissible — 50 mg/dm^3 ; $Mn^{2+} — 100\text{ mg/dm}^3$ in solutions of drain waters.

The efficiency of extraction of Sr^{2+} and Mn^{2+} practically does not depend on the concentration of competing cations (Fe^{2+} , Mn^{2+}) in drain water solutions.

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ХІМІЧНИЙ І МІНЕРАЛЬНИЙ СКЛАД ПРИРОДНИХ ЦЕОЛІТІВ ТА ЇХНІ СОРБЦІЙНІ ВЛАСТИВОСТІ У ПРОЦЕСІ ОЗОНУВАННЯ ЗІ СТИЧНОЮ ВОДОЮ АЕС

Розкрито закономірності сукупного процесу озонолітичної деструкції органічних компонентів модельних трапних вод атомних електричних станцій і сорбції імітаторів основних дозоутворювальних радіонуклідів (Cs — ізотопною міткою ^{137}Cs ; стабільних ізотопів солей Co, Sr, Mn) трапних вод природним цеолітом Сокириницького родовища і сорбційноактивних сполук — солей феруму (II) і мангану (II). Хімічний склад головних елементів цеоліту після озонування трапних вод із додаванням солей феруму і мангану практично не відрізняється від складу природного цеоліту. Його фазовий склад у процесі озонування за присутності солей феруму представлений основним породоутворювальним мінералом клиноптилолітом і другорядним мінералом — кварцом. Головною ферумвмісною фазою на поверхні цеоліту є гетит. До другорядних фаз належать Fe(II)-Fe(III) шаруваті подвійні гідроксиди (*Green Rust*) і лепідокрокіт, але їх відносний вміст незначний. Для цеолітів після озонування трапних вод із додаванням солей як феруму, так і мангану (II) головними фазами є клиноптилоліт і кварц. Манганвмісні фази на поверхні цеоліту представлені гаусманітом Mn_3O_4 , оксидом мангану(II) і оксигідроксидом мангану $\text{MnO}(\text{OH})_2$. Ферум- і манганвмісні фази, осаджені в процесі озонування на поверхню цеоліту, характеризуються переважно слабо окристалізованою або аморфізованою структурою. Основним сорбентом дозоутворювальних радіонуклідів трапних вод є цеоліт, а не ферум- і манганвмісні сполуки, які утворились на його поверхні під час озонолізу. Максимальний ступінь сорбції ^{137}Cs цеолітом складає до 90 % за збільшення концентрації Fe^{2+} до 50 мг/дм³ або Mn^{2+} до 100 мг/дм³, ступінь сорбції кобальту — 97,5 % за вихідної типової концентрації катіонів (Fe^{2+} — 5 мг/дм³; Mn^{2+} — 10 мг/дм³), що конкурують, та за збільшення концентрації Mn^{2+} до 100 мг/дм³. Максимальний ступінь вилучення Sr^{2+} та Mn^{2+} становить 99,4 % та 99,9 % відповідно. Для ефективного вилучення ^{137}Cs і Co^{2+} цеолітом у процесі озонування припустимим є збільшення концентрації катіонів Fe^{2+} — 50 мг/дм³; Mn^{2+} — 100 мг/дм³, що конкурують, у розчинах трапних вод, а ефективність вилучення Sr^{2+} та Mn^{2+} практично не залежить від концентрації катіонів Fe^{2+} і Mn^{2+} у розчинах трапних вод.

Ключові слова: трапні води АЕС, озонування, хіміко-мінеральний склад, сорбція, цеоліт.