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Sorption of the Main Dose-forming Radionuclides of Nuclear Power Plants Drain Water on Natural Bentonite in the Process of their Co-ozonation

Keywords:

NPP drain water,
ozonolysis,
sorption,
dose-forming radionuclides,
bentonite

The article presents the general pattern of the combined process of oxidative decomposition of organic components of simulated nuclear power plant (NPP) drain water and sorption interaction of the imitators of main dose-forming radionuclides (Cs — radiolabel for ^{137}Cs ; stable isotopes of Co, Sr, Mn salts) on natural bentonites from the Cherkasy deposit in presence of sorption-reagent compounds — iron (II) and manganese (II) salts. Hydroxides, oxyhydroxides and oxides of Fe and Mn formed during ozonation are predominantly localized on the surface of bentonite. The chemical composition of the main elements of bentonite after drain water ozonation with the addition of iron and manganese salts remains almost the same as that of natural bentonite. The phase composition of bentonite is presented by the main rock-forming mineral montmorillonite and secondary mineral quartz. The iron-containing phases of the ozonised bentonite are Fe(II)-Fe(III) layered double hydroxides (Green Rust), goethite $\alpha\text{-FeOOH}$ and magnetite Fe_3O_4 , and the manganese-containing phases are hausmannite Mn_3O_4 , manganese oxide (II) and manganese oxyhydroxide $\text{MnO}(\text{OH})_2$. The iron- and manganese-containing phases deposited on the bentonite surface during ozonation are predominantly weakly crystallized or amorphized structures. At the concentration of salts of iron (50 mg/dm^3) and manganese (100 mg/dm^3) in the drain water, the specific surface area of bentonites with the formed layer of iron and manganese hydroxides, (oxy)hydroxides and oxides increases compared to natural bentonite ($34.2\text{ m}^2/\text{g}$) and equals to 55 and $51\text{ m}^2/\text{g}$, respectively. The degree of radionuclide removal during ozonation of the simulated solution with the initial concentration of cations (Fe^{2+} — 5 mg/dm^3 ; Mn^{2+} — 10 mg/dm^3 ; Ca^{2+} — 5 mg/dm^3) in the presence of natural bentonite is ^{137}Cs — $78\% \pm 2\%$, Sr^{2+} — $97.55\% \pm 1\%$, Co^{2+} — $96.5\% \pm 1\%$, Mn^{2+} — $99.7\% \pm 0.5\%$. To preserve the efficiency of ^{137}Cs and Co^{2+} radionuclide removal, the initial concentration of cations in the solution can be increased to the following values: Fe^{2+} — 50 mg/dm^3 , Mn^{2+} — 100 mg/dm^3 , Ca^{2+} — 50 mg/dm^3 , and to: Fe^{2+} — 500 mg/dm^3 , Mn^{2+} — $1,000\text{ mg/dm}^3$, Ca^{2+} — 500 mg/dm^3 for Sr^{2+} and Mn^{2+} removal.

Introduction

Treatment and conditioning of liquid radioactive waste (LRW) from nuclear power plants (NPPs) is one

of the main environmental problems. Today, to reduce the LRW volume, a special drain water treatment technology is applied at the Ukrainian NPPs. The LRW come from various sources and are collected in settling tanks

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and decanters with the volume of several thousand litres [1]. In the collection tanks, an alkaline ($\text{pH} > 10$) environment is maintained. The drain water treatment consists of the following main operations: receiving and pre-treatment of the water, evaporation and distillate purification, delivery of VAT residue and salt melt for long-term storage at NPP storage facilities. The drain water pre-treatment and purification are the key processes in this list. The main sources of drain water are routine washing of the internal surfaces of the equipment and pipelines of the first and second NPP circuits, and cleaning of special laundries and showers with decontamination solutions such as solutions with organic complexing agents — ethylenediaminetetraacetic (EDTA) and oxalic ($\text{H}_2\text{C}_2\text{O}_4$) acids [2]. Radionuclides, for example, ^{60}Co and ^{54}Mn form stable soluble complexes with these acids, which makes their efficient sorption extraction impossible. The initial destruction of organometallic complexes of cobalt, manganese and iron as the corrosion products of the NPP circuit metal equipment that is located in the zone of high neutron flux density and γ -irradiation can significantly simplify the further treatment of the drain water from the nuclear power plants.

According to the oxidative-sedimentary sorption technology [3–5] that envisages destruction of the drain water organic compounds by oxidative methods at the initial stages is the first choice among the available technological schemes of the LRW treatment. The application of this technology makes it possible to concentrate radionuclides in a small volume of the final radioactive product with subsequent conditioning of the secondary waste for long-term storage and disposal.

Ozonation is considered to be one of the efficient and relatively simple oxidative methods of destruction of oxalates, EDTA and other organic compounds in aqueous solutions [6]. To increase the adsorption activity of clay sorbents used for decontamination of the radiation-contaminated aqueous media, various sorption-reagent compounds, for example, iron, aluminium, manganese and other salts are added [7, 8]. Thus, in order to increase the efficiency of the combined oxidative-sedimentary sorption method for the drain water decontamination, a procedure for simultaneous oxidative decomposition of organic compounds by ozone and sorption of the decomposition products and radionuclides on natural sorbents should be developed.

The aim of the work is to identify the laws of sorption of the imitators of dose-forming radionuclides of nuclear power plant drain water on natural bentonite of the Cherkasy deposit during the drain water ozo-

nation in the presence of sorption-reagent compounds of iron and manganese.

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 $3\text{--}7\text{ g/dm}^3$ (rarely up to 15 g/dm^3) [9]. 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 ^{137}Cs and ^{90}Sr — uranium fuel fission products, and ^{60}Co and ^{54}Mn — activation products of the circuit equipment. ^{137}Cs and ^{90}Sr are present in the ionic forms, while ^{60}Co and ^{54}Mn 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 ^{137}Cs and salts of stable elements of Sr, Co, Mn as chemical analogues of the related radionuclides were added to the initial solution. Initial activity of ^{137}Cs in model solution of LRW was $85,600\text{ Bq/dm}^3$. Initial pH of model solution was 12 units.

To produce the concentrations of Fe^{2+} (50 and 500 mg/dm^3), Mn^{2+} (100 and $1,000\text{ mg/dm}^3$) and Ca^{2+} (50 and 500 mg/dm^3) ions in the initial solution, iron (II) and manganese (II) sulphates, and calcium chloride were used respectively.

Bentonite samples. In our study, we used Dashukivka bentonite of the Cherkasy deposit (II layer). The main

Table 1. Composition of the initial simulated drain water solution

Chemical compounds	Concentration, mg/dm^3
H_3BO_3	1,700
KNO_3	1,000
Na_2SO_4	2,000
NaCl	1,450
NaOH (45 %)	1,450
CoSO_4	132
$\text{MnSO}_4 \cdot \text{H}_2\text{O}$	30.77
$\text{Sr}(\text{NO}_3)_2$	120.5
CsNO_3	73.3
$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$	25
The CaCl_2	13.9
EDTA	100
$\text{H}_2\text{C}_2\text{O}_4$	40
Lotos-M	350
Mineralization	7,035.47

rock-forming mineral of bentonite is montmorillonite (65–70 %), the secondary mineral — quartz (20–25 %). Also, the bentonite samples contain accessory minerals — calcite (3–5 %), kaolinite (3–5 %), feldspar (3 %) and hydromica (5 %) [10]. The chemical composition of bentonite (wt. %) is as follows: SiO_2 — 68.02, $\text{FeO}+\text{Fe}_2\text{O}_3$ — 6.86, Al_2O_3 — 19.45, MgO — 2.42, CaO — 1.45, Na_2O — 0.27, etc. Particle size analysis shows that the fraction <0.001 mm makes ~83.5 %. The specific surface area of bentonite is $34.2 \text{ m}^2/\text{g}$ (BET method, employed gaseous adsorbate — nitrogen).

Ozonation conditions. Ozonation of the simulated drain water solutions was performed by ozone-air mixture, which was produced in an ozone generator and fed into the column with the simulated drain water solution through the dispersant [11]. 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. In the process of ozonation was controlled of pH on initial level (11–12 units) by NaOH. After ozonation, the simulated solution was filtered with a vacuum pump through a membrane filter. Then ^{137}Cs activity and residual concentration of Sr^{2+} , Co^{2+} , Mn^{2+} were determined.

Research methods

Specific surface area. The specific surface area of the fine bentonite fractions was determined by BET method employing argon (GOST 23401-90) as adsorbate gas. The samples were dehydrated at $T = 120^\circ\text{C}$ for 1 hour.

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 $9 \cdot 10^{-3}$ 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 — 0.05–0.1 degrees, exposure — 4 seconds, 2θ diffraction angles — from 15 to 90° . Patterns were collected at standard temperature. Identification was performed according to the ASTM file [12].

Atomic adsorption spectroscopy. To determine 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

After ozonation of the simulated solution with the addition of iron salt, the bentonite structure is represented by dense 1 to 4 μm platelets of various forms, often with clear contours (Fig. 1a, 1b). According to EDS analysis data (Fig. 1c, 1d), the main elements of the bentonite are (wt. %): silicon 24.9–29.75, aluminum 7.64–8.51, oxygen 41.59–46.09, magnesium 1.27–1.32 and titanium 0.38–0.64. The qualitative composition of this bentonite is practically the same as of natural bentonite [10].

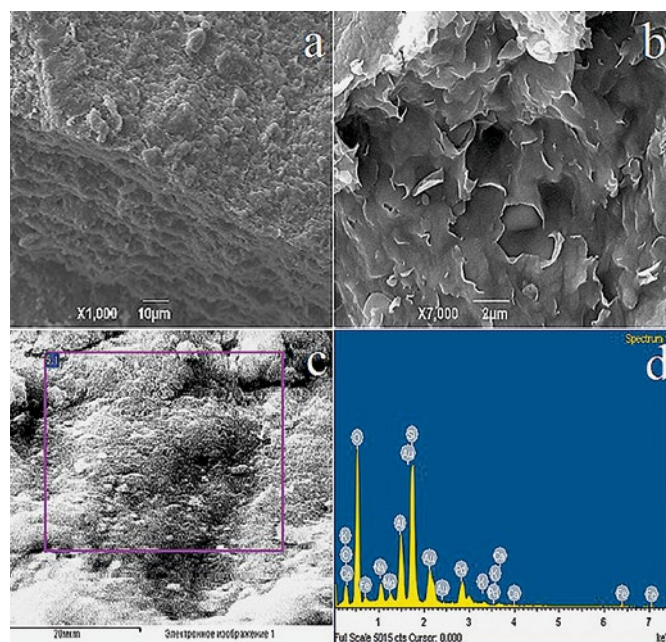


Fig. 1. SEM images of bentonite (a, b, c) and EDS spectrum (d) after ozonation of the simulated drain water solution in the presence of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$

At the same time, the concentration of other elements changes (wt. %) [10]: sodium 2.55–2.8 (0.20), chlorine 0.74–0.81 (0), potassium 1.71–1.72 (0.98), calcium 5.15–6.23 (0.54), iron 7.29–8.23 (5.33). This difference is explained by the complex processes that accompany ozonation — occlusion, co-precipitation, leaching, adsorption, etc. In the typical image of the EDS spectrum

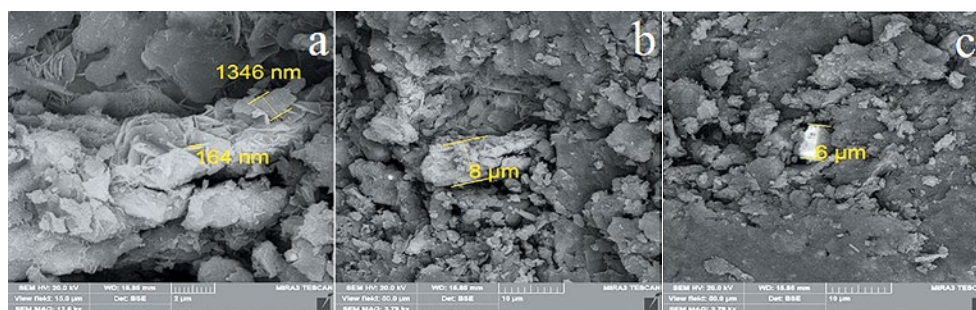


Fig. 2. SEM images of bentonite after contact with manganese-containing solution: a — size of individual crystals; b — size of aggregates; c — crystal of manganese oxide

there are reflexes of gold and palladium — the components of the sputtered alloy. SEM images of bentonite sometimes show single white crystals containing barium and sulphur. No individual phase of iron oxides was detected.

The average size of bentonite platelets after ozonation with the addition of manganese salt is 1.3 μm , and a platelet thickness is 164 nm (Fig. 2a). The bentonite particles form microaggregates of various configurations, about 8 μm in size (Fig. 2b). The manganese-containing phase is presented by individual 6 μm particles (Fig. 2c). Bentonite contains the following elements (wt. %): O — 46.06, Na — 2.63, Mg — 1.54, Al — 8.04, Si — 26.97, Cl — 0.87, K — 1.50, Ca — 4.63, Ti — 0.54, Mn — 1.31 and Fe — 5.91. Manganese is part of an individual phase, amounting to 60.6 wt. %. The content of other components of the manganese-containing phase, except oxygen (24.06 wt. %), is insignificant, which may indicate the formation of manganese oxide phases.

Fig. 3 presents EDS spectra of manganese-containing bentonite (Fig. 3a) and manganese oxide (Fig. 3b).

According to X-ray diffraction data, the diffraction pattern of bentonite with the addition of Fe salt (Fig. 4a) shows the reflexes of the main rock-forming mineral — montmorillonite (#00-012-0204; #000030009). The secondary mineral is quartz (#01-089-8937). Iron-bearing

phases are presented by Fe(II)Fe(III) layered double hydroxides (GreenRust) (#13-92), goethite (#8-97) and magnetite (#19-029). The diffractogram of bentonite with the addition of Mn salt (Fig. 4b) shows the reflexes of montmorillonite and quartz. Manganese-bearing phases are presented by hausmannite Mn_3O_4 (#4-0731), manganese oxide (II) (#12-720) and manganese oxyhydroxide $\text{MnO}(\text{OH})_2$ (#15-604).

At the diffraction patterns of the both samples at 2Θ angle 20–30°, a halo is observed, which indicates the presence of amorphous phases in the sediments. Iron and manganese hydroxides, deposited during ozonation of the studied samples, are weakly crystallized or amorphized structures.

Sorption, coagulation and other surface processes using mainly oxidative methods and alkalizing reagents are at the core of the purification of man-made aqueous solutions from heavy metal cations and radionuclides. The sorption processes depend on many factors, such as aqueous medium characteristics (pH, Eh, ionic strength of the solution, aquaforms of elements, radionuclides) and sorbent features (structure, specific surface and associated pores).

Ozonation of drain water with the addition of Fe^{2+} and Mn^{2+} salts, and bentonite can be considered as an example of sorption-reagent interaction, i. e. the activity

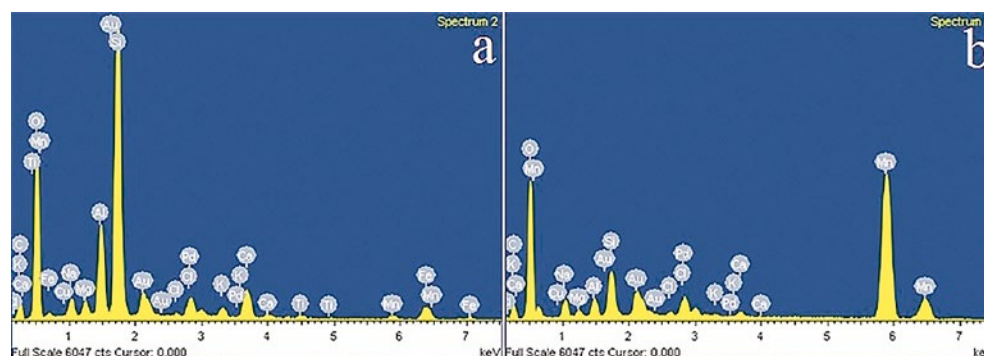


Fig. 3. EDS spectra of bentonite after ozonation of the simulated drain water solution in the presence of $\text{MnSO}_4 \cdot \text{H}_2\text{O}$: a — bentonite; b — manganese oxide

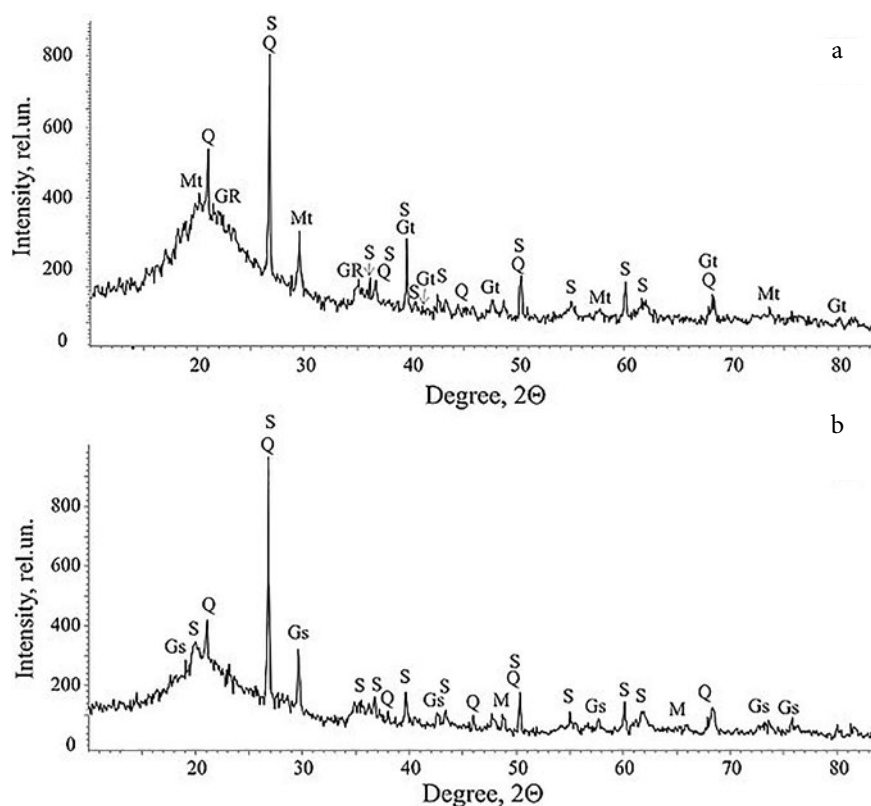


Fig. 4. Diffractograms of montmorillonite samples with additions (10 %): a — iron; b — manganese.
 Legend: S — montmorillonite (smectite); Q — quartz; GR — Fe(II)-Fe(III) layered double hydroxides;
 Gt — goethite; Gs — hausmannite; Mt — magnetite; M — manganese oxyhydroxide

of sorbents increases as a result of the chemical reaction of the sorbent with the solution to be purified [13]. As a result, hydroxides, oxyhydroxides and oxides of Fe and Mn are mainly formed on the surface of montmorillonite, which leads to the surface stabilization and reduction of solubility of the mineral. Two types of montmorillonite modified with Fe(III) [8] may be present in an alkaline environment. If the concentration of Fe(III) in the solution is relatively low, intercalation and adsorption of iron proceed, which results in formation of montmorillonite that contains Fe(III) localized mainly in the interlayer space of the mineral. When the concentration of Fe(III) is relatively high, iron compounds are formed. They are localised not only in the interlayer space but also on the active centres of the surface.

The adsorption capacity of bentonite (the main adsorbing agent in the system) can be explained by its specific structure and inhomogeneity of the bentonite surface, and especially, the presence of adsorption centres of various nature — exchange cations, oxygen atoms and hydroxyl groups on the basal faces of particles; coordinatively unsaturated ions Mg^{2+} , Al^{3+} , Fe^{3+} , Si^{4+} ; exchange cations and hydroxyl groups on the faces and edges

of crystals and the formation of hydrogen bonds with active positively charged complexes of montmorillonite particles. The selectivity of adsorption of bentonites is mainly explained by the presence of micro- and mesopores (secondary pores) between the adjacent platelets. The radius of the pores is 5–9 nm [14]. Montmorillonite belongs to microporous sorbents with the pore size that may change during adsorption. Depending on the electronic and geometric structure, the montmorillonite lattice in the process of adsorption of polar substances expands by 0.3–1.2 nm and one or several hydroxylated layers of the adsorbed substance are formed in the interpacket space. This gives grounds for expansion of the range of sorption of different cations (radionuclides) on bentonites leading to formation of layers of iron (oxy) hydroxides and manganese compounds (adsorbents associated with bentonite) on its surface. At the same time, the surface layers may block the active adsorption centres of bentonite.

At the concentration of salts of iron (50 mg/dm^3) and manganese (100 mg/dm^3) in the drain water, the specific surface area of bentonites with the formed layer of iron (III) (oxy)hydroxides and manganese com-

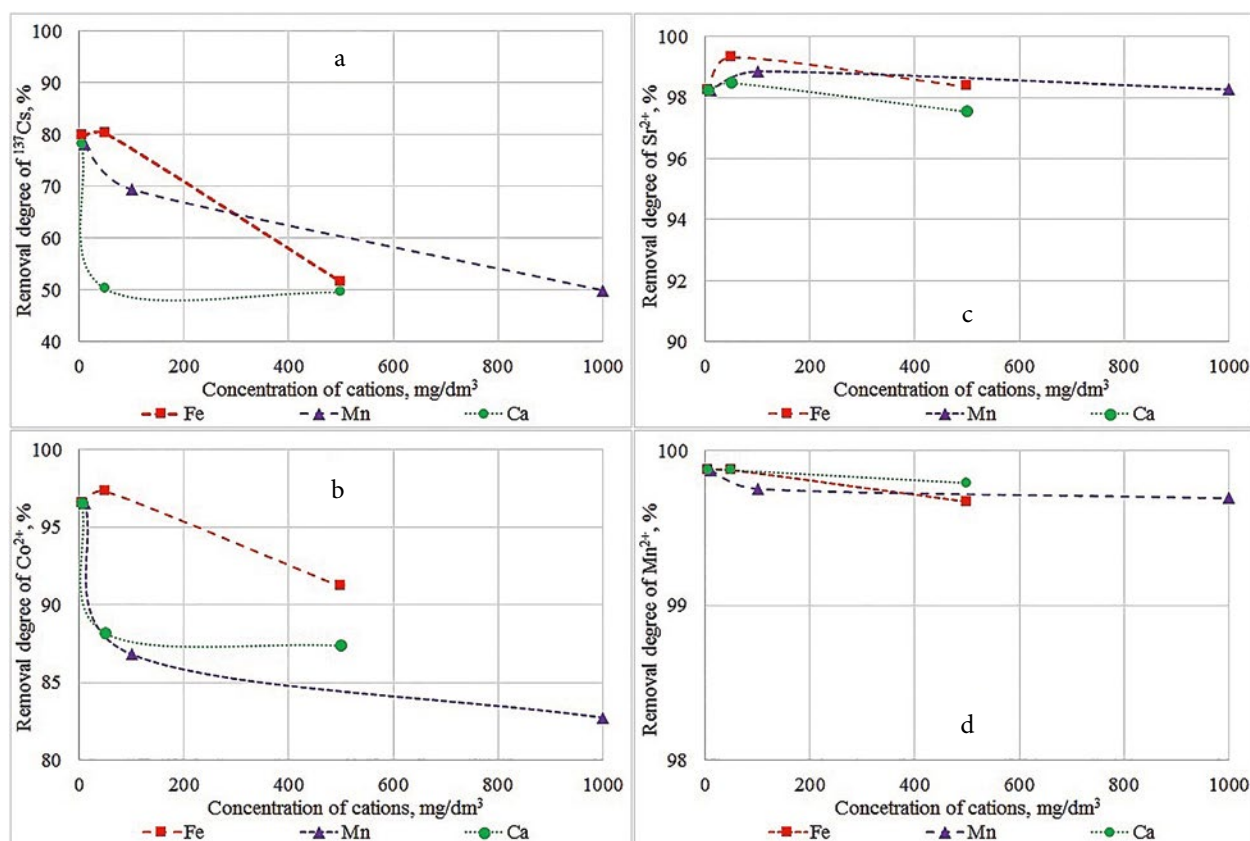


Fig. 5. Degree of radionuclide removal during ozonation with bentonite depending on the initial concentration of Fe, Mn and Ca in the simulated NPP drain water solution

pounds increases and are equal to 55 and 51 m²/g, respectively, exceeding the similar values for the natural bentonite (34.2 m²/g) [15]. The improving of the sorption properties of composite sorbents based on bentonite modified with ferrihydrite and goethite is illustrated in a number of papers, for example [16]. The presence of ions of variable valency (Fe(II)/Fe(III); Mn(II)/Mn(III)/Mn(IV)) that increases the oxidative degradation of organic compounds in the solution due to the Fenton effect [17, 18], can also increase the sorption properties of the sorbents.

It is shown [19] that a mixture of bentonite and magnetite (2 : 1) adsorbs 75 % of ¹³⁷Cs from NaNO₃ solution with ionic strength 0.04M at pH = 10.5. When the ionic strength of the solution increases to 0.14, adsorption decreases to 60 %. Bentonite is a more efficient sorbent for ¹³⁷Cs removal compared to magnetite, so sorption of caesium occurs mainly on bentonite. Compared to ¹³⁷Cs, 70 % of Sr²⁺ is adsorbed on bentonite at pH = 9.0 and ionic strength of the solution is 0.14.

Freshly precipitated oxides and oxyhydroxides of Fe and Mn have a high sorption capacity of ¹³⁷Cs and Sr²⁺ at pH 8–10. The mechanism of ¹³⁷Cs sorption is simi-

lar to the surface adsorption, which is practically independent of the pH of the medium. Simultaneously with surface adsorption, chemisorption occurs leading to the formation of ferrites. In mixed iron-manganese oxides and oxyhydroxides, ¹³⁷Cs sorption increases with increasing of the Mn : Fe ratio. That is, Mn oxides and oxyhydroxides have higher ¹³⁷Cs selectivity and show a high ¹³⁷Cs content regardless of pH due to the surface adsorption. Iron hydroxides have increased sorption capacity of Sr²⁺ in an alkaline environment leading to the formation of ferrites [20].

On the other hand, sorbents based on crystallized manganese dioxide are Sr²⁺ selective. That is caused by steric factors: the size of the hydrated ¹³⁷Cs and Sr²⁺ cations and the diameter of macro- and micropores [21].

The degree of ¹³⁷Cs removal (Fig. 5a) during ozonation of the simulated drain water solution with typical for NPP drain water concentration of competing cations (Fe²⁺ — 5 mg/dm³; Mn²⁺ — 10 mg/dm³; Ca²⁺ — 5 mg/dm³) in the presence of natural bentonite from the Cherkasy deposit is 78 ± 2 %. Increase in the concentration of Fe²⁺ ions to 50 mg/dm³ causes increase in caesium adsorption by only a few percent (up to 80.3 ± 1.5 %), and increase

Table 2. Distribution coefficients of radionuclides in the system: bentonite / simulated drain water solution

№	Initial concentrations of cations, mg/dm ³			Distribution coefficients of radionuclides, Kd, dm ³ /kg			
	Fe ²⁺	Mn ²⁺	Ca ²⁺	¹³⁷ Cs	Sr ²⁺	Co ²⁺	Mn ²⁺
1	5	10	5	355	5,592	2,774	81,900
2	50	10	5	407	14,700	3,576	81,900
3	500	10	5	185	6,067	1,036	30,270
4	5	100	5	352	8,780	658	40,900
5	5	1,000	5	176	5,742	479	32,700
6	5	10	50	101	6,527	745	81,900
7	5	10	500	98	3,973	691	48,135

in the concentration of Fe²⁺ to 500 mg/dm³ results in a sharp decrease in caesium removal to $51.5 \pm 3\%$. Increase in the concentration of Mn²⁺ in the initial solution to 100 mg/dm³ leads to a decrease in the degree of extraction of ¹³⁷Cs to $69.4 \pm 2.5\%$, and at 1,000 mg/dm³ the degree of caesium removal decreases to $49.8 \pm 3\%$. Increase of the concentration of Ca²⁺ ions in the initial solution to 50 mg/dm³ and more leads to a decrease in the degree of removal of ¹³⁷Cs to $50 \pm 3\%$.

The degree of Co²⁺ removal from a solution with a typical concentration of cations (Fe²⁺ — 5 mg/dm³; Mn²⁺ — 10 mg/dm³; Ca²⁺ — 5 mg/dm³) during ozonation is 96.5 % (Fig. 5b). Increase in the initial concentration of Fe²⁺ cations in the simulated solution to 50 mg/dm³ leads to a slight increase in Co²⁺ sorption to $97.3 \pm 0.5\%$, while increase of Fe²⁺ to 500 mg/dm³ reduces the degree of Co²⁺ removal to $91.2 \pm 0.5\%$. Increase in the Mn²⁺ concentration in the initial solution to 100 mg/dm³ leads to a decrease in the degree of Co²⁺ removal to $86.8 \pm 1\%$, and at the initial concentration of Mn²⁺ 1 000 mg/dm³, the degree of Co²⁺ removal is $82.7 \pm 1\%$. Increase in Ca²⁺ ion concentration in the initial solution to 50 mg/dm³ and up to 500 mg/dm³ reduces the degree of Co²⁺ removal to 88.2 and $87.4 \pm 1\%$, respectively.

The degree of Sr²⁺ removal (Fig. 5c) during ozonation of the drain water solutions with different concentrations of competing cations varies from 97.55 to $99.3 \pm 0.5\%$, i. e., it is almost independent of the changes in the concentration. A similar situation is observed for Mn²⁺ (Fig. 5d). The degree of Mn²⁺ adsorption, depending on the concentration of competing cations, varies from 99.7 to $99.9 \pm 0.1\%$.

Thus, the degree of ¹³⁷Cs and Co²⁺ removal from the simulated NPP drain water solution during ozonation in the presence of bentonite remains high with increase of concentration of competing cations to: Fe²⁺ — 50 mg/dm³; Mn²⁺ — 100 mg/dm³; Ca²⁺ — 50 mg/dm³. The degree of Sr²⁺ and Mn²⁺ removal is practically in-

dependent of the initial concentration of cations in case the concentration increases at least to: Fe²⁺ — 500 mg/dm³; Mn²⁺ — 1 000 mg/dm³; Ca²⁺ — 500 mg/dm³.

Based on the results of the experimental study, the radionuclide distribution coefficients under pseudo-equilibrium conditions in the sorbent / solution system (Table 2) during ozonation of the simulated NPP drain water solution in the presence of natural bentonite of the Cherkasy deposit were calculated. For all studied radionuclide imitators, the highest distribution coefficients were determined at the initial concentration of cations in the simulated drain water solution and at increase of their initial concentration to: Fe²⁺ — 50 mg/dm³; Mn²⁺ — 100 mg/dm³; Ca²⁺ — 50 mg/dm³. Based on the calculated distribution coefficients, Sr²⁺ and Mn²⁺ are most efficiently removed from the simulated drain water solution, removal of Co²⁺ is less efficient, and the lowest distribution coefficients were determined for ¹³⁷Cs [16].

Thus, for the effective removal of radionuclides in the process of ozonation of the simulated NPP drain water solution with bentonite, increase in the concentration of competing cations in the initial solution to Fe²⁺ — 50 mg/dm³; Mn²⁺ — 100 mg/dm³; Ca²⁺ — 50 mg/dm³ is reasonable.

Conclusions

The following results of the integrated study of the combined process of oxidative decomposition of organic components of the simulated NPP drain water by ozone and sorption interaction of the main dose-forming radionuclides with natural bentonites of the Cherkasy deposit in the presence of sorption-reagent compounds — iron (II) and manganese (II) salts have been received.

1. Compared to natural bentonite, the concentration of the main elements of the bentonite used in drain water ozonation with the addition of salts is practically unchanged. The phase composition of bentonite is pre-

sented by the main rock-forming mineral montmorillonite and secondary mineral quartz. Iron-containing phases are Fe(II)-Fe(III) layered double hydroxides, goethite and magnetite, and manganese-containing phases — hausmannite, manganese oxide (II) and manganese oxyhydroxide. During ozonation, iron- and manganese-containing phases were mainly deposited on the bentonite surface. They are weakly crystallized or amorphized structures.

2. At the concentration of salts of iron (50 mg/dm³) and manganese (100 mg/dm³) in the drain water, the specific surface area of bentonite after formation of iron and manganese compounds on the bentonite surface increases and equals to 55 and 51 m²/g, respectively, which exceeds the similar values for natural bentonite (34.2 m²/g).

3. The degree of radionuclide (¹³⁷Cs) and chemical analogues (stable isotopes of Sr, Co and Mn) removal from the simulated solution with typical for NPP drain water concentration of competing cations (Fe²⁺ — 5 mg/dm³; Mn²⁺ — 10 mg/dm³; Ca²⁺ — 5 mg/dm³) during ozonation of the simulated drain water solution in the presence of natural bentonite of the Cherkasy deposit is as follows: ¹³⁷Cs — 78 ± 2 %, Sr²⁺ — 97.55 ± 0.5 %, Co²⁺ — 96.5 ± 0.5 %, Mn²⁺ — 99.7 ± 0.1 %. From the point of view of the efficiency of ¹³⁷Cs and Co²⁺ removal, the initial concentration of competing cations in the solution can be increased to: Fe²⁺ — 50 mg/dm³, Mn²⁺ — 100 mg/dm³, Ca²⁺ — 50 mg/dm³, and to: Fe²⁺ — 500 mg/dm³, Mn²⁺ — 1,000 mg/dm³, Ca²⁺ — 500 mg/dm³ for Sr²⁺ and Mn²⁺ removal.

4. The increase in the concentrations of competing cations in the simulated solution has insignificant effect on the degree of radionuclide adsorption. At relatively high concentrations, the sorption efficiency decreases. Thus, bentonite is the main adsorbent, while the sorption-reagent compounds — salts of iron (II), manganese (II) and calcium (II) play a minor role in the sorption processes and can block active sorption centres of bentonite at high concentrations.

5. The distribution coefficients of the radionuclides in the system bentonite / simulated NPP drain water solution during the ozonation process were calculated based on the experimentally obtained sorption rates. The highest radionuclide distribution coefficients were found at the initial concentrations of competing cations (Fe²⁺ — 5 mg/dm³; Mn²⁺ — 10 mg/dm³; Ca²⁺ — 5 mg/dm³) and at their increase to: Fe²⁺ — 50 mg/dm³, Mn²⁺ — 100 mg/dm³, Ca²⁺ — 50 mg/dm³ in the simulated solution.

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Сорбція основних дозоутворюючих радіонуклідів трапних вод АЕС природним бентонітом у процесі їх сумісного озонування

У статті розкрито закономірності сукупного процесу озонолітичної деструкції органічних компонентів модельних трапних вод атомних електричних станцій та сорбції імітаторів основних дозоутворюючих радіонуклідів (Cs — ізотопною міткою ^{137}Cs ; солей стабільних ізотопів Co , Sr , Mn) трапних вод природним бентонітом Черкаського родовища за присутності сорбційно-реагентних сполук — солей феруму (II) і мангану (II). Хімічний склад головних елементів бентоніту після озонування трапних вод із додаванням солей феруму і мангану практично не відрізняється від складу природного. Фазовий склад бентоніту представлений основним породотвірним мінералом монтморилонітом і другорядним мінералом — кварцем. Ферумовмісні фази озонованого бентоніту представлені Fe(II)-Fe(III) шаруватими подвійними гідроксидами (Green Rust), гетитом $\alpha\text{-FeOOH}$ і магнетитом Fe_3O_4 , а мангановмісні фази — гаусманітом Mn_3O_4 , оксидом мангану(II) і оксигідроксидом мангану MnO(OH)_2 . Ферумо- і мангановмісні фази, осажені в процесі озонування на поверхню бентоніту являють собою переважно слабо окристалізовані або аморфізовані структури. Величина питомої поверхні бентонітів з шаром гідроксидів, оксигідроксидів і оксидів феруму і мангану збільшується порівняно з природним ($34,2 \text{ м}^2/\text{г}$) і дорівнює, відповідно, 55 і $51 \text{ м}^2/\text{г}$ при концентрації солей феруму $50 \text{ мг}/\text{дм}^3$

і мангану 100 мг/дм³ у трапних водах. Ступені вилучення радіонуклідів (¹³⁷Cs) та їхніх хімічних аналогів (стабільних ізотопів Со, Sr, Mn) у процесі озонування модельного розчину із вихідною концентрацією катіонів (Fe²⁺ — 5 мг/дм³; Mn²⁺ — 10 мг/дм³; Ca²⁺ — 5 мг/дм³) за присутності природного бентоніту складає: ¹³⁷Cs — 78 ± 2 %; Sr²⁺ — 98 ± 1 %; Со²⁺ — 97 ± 1 %; Mn²⁺ — 99 ± 0.5 %. Для збереження ефективності

вилучення радіонуклідів ¹³⁷Cs і Со²⁺ припустимим є збільшення вихідної концентрації катіонів розчину до: Fe²⁺ — 50 мг/дм³; Mn²⁺ — 100 мг/дм³; Ca²⁺ — 50 мг/дм³, а при вилученні Sr²⁺ і Mn²⁺ до: Fe²⁺ — 500 мг/дм³; Mn²⁺ — 1 000 мг/дм³; Ca²⁺ — 500 мг/дм³.

Ключові слова: трапні води АЕС, озоноліз, сорбція, дозоутворюючі радіонукліди трапних вод, бентоніт.

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