



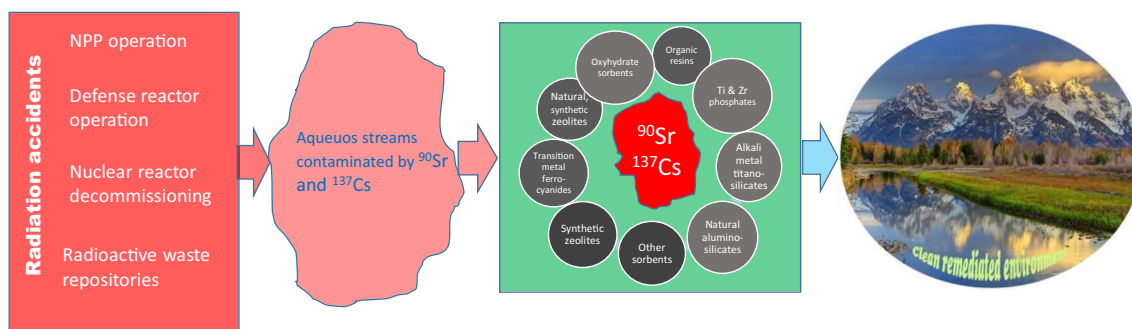
# Adsorption techniques for decontaminating liquid radioactive waste and radionuclide-contaminated natural water

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## Abstract

The paper reviews the adsorption methods used for decontaminating liquid radioactive waste (LRW) and radioactive-contaminated natural water of different origins from radionuclides. The primary attention is paid to the sorption of long-lived cesium and strontium radionuclides, which, besides the high radiotoxicity, in most cases define the overall activity of radioactive waste. A standard technique was developed for evaluating the efficiency of various sorption materials in relation to cesium and strontium radionuclides by determining the distribution coefficient ( $K_d$ ) values of tracer  $^{137}\text{Cs}$  and  $^{90}\text{Sr}$  radionuclides in solutions of sodium and calcium salts, the essential bulk components of LRW, and natural water. The results showed that natural aluminosilicate sorbents, zeolites, zirconium phosphate, and ferrocyanide sorbents could effectively remove  $^{137}\text{Cs}$  from low-salt solutions. The sorbent based on manganese (III, IV) oxyhydrate exhibited the highest selectivity to strontium. A correlation between the crystalline and porous structure of the sorbents and the selectivity to cesium and strontium radionuclides was shown. The results obtained provide an adequate choice of the most effective sorbents for the decontamination of radioactively contaminated natural water and technogenic liquid waste from cesium and strontium radionuclides.



**Keywords** Cesium and strontium radionuclides · Liquid radioactive waste · Radioactively contaminated natural water · Decontamination · Adsorption

## 1 Introduction

In the production and application of materials containing radioactive substances, the formation of liquid radioactive waste (LRW) of various chemical compositions and activity levels is inevitable. LRW presents the most severe potential environmental hazard due to its large volume and high total activity. Furthermore, in emergency and radiation accidents, an uncontrolled release and migration of radioactive substances occur, resulting in environmental contamination. For example, the enormous environmental damage resulted

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from the Chernobyl Nuclear Power Plant of the USSR, in 1986 [47] and Fukushima-1 Nuclear Power Plant of Japan, in 2011 [23] radiation accidents. Therefore, developing and upgrading techniques for decontaminating LRW and radioactively contaminated natural water is an important and challenging issue.

Among the physicochemical methods used for decontaminating aqueous solutions from toxic impurities, including radioactive, a high profile is adopted by sorption methods based on physical adsorption and ion exchange. Physical adsorption methods with various types of adsorbents, primarily active carbons, are mainly used at the initial stages of polluted water treatment to remove oil products, surfactants, uranium, and heavy metals [1, 9, 27, 42, 51].

Since radionuclides in aqueous solutions are basically simple or partially hydrolyzed aqua-ionic species, they can be removed by ion-exchange techniques using organic ion exchange resins and natural and synthetic inorganic sorbents of various types.

Organic ion exchange resins are commercially available products that possess high sorption, kinetic, and performance characteristics and are widely used to remove toxic components from waste effluents.

Strongly acidic sulfonic cation exchangers are most widely used in industrial practice. This type of ion exchanger is characterized by an increase in affinity with an increase in the charge and size of the adsorbed ion. However, in general, their selectivity, in particular to cesium and strontium radionuclides, in the presence of interfering cations is low, and they are used for decontamination of low salt-bearing solutions only [7, 22].

Medium acid phosphate cation exchangers, weak acid carboxyl cation exchangers, and chelate ion exchangers with iminodiacetate and phosphonic groups exhibit a high selectivity to uranium, thorium, and nonferrous metal ions, which makes it possible to use this type of ion exchangers to remove the above impurities against the background of the prevailing bulk amounts of alkali and alkaline earth metal ions [16, 25, 56].

Whereas radionuclides in the wastewater composition exist substantially as the cationic species, anion exchangers are sparingly used for removing radioactive elements. However, anion exchange resins are still employed to recover uranium from sulfuric acid and carbonate solutions, where uranium exists in the form of complex anionic species [11, 26].

Ion exchange resins are commercially produced by several companies, namely Dow Chemical (USA), Rohm&Haas (USA), Lanxess (Germany), Purolite (Great Britain). In Russia, the ion-exchange resins are manufactured at the LLC Production Association “TOKEM” (LLC PO “TOKEM”), Kemerovo, and JSC “Axion—Rare and Precious Metals” (JSC “ARDM”), Perm.

Because of limited selectivity and high cost, exhausting organic ion-exchange resins are subjected to regeneration with solutions of inorganic acids or salts and reused. The experience gained in the operation of ion-exchange plants and technical and economic calculations showed that the application of the ion exchange technique with organic ion exchangers is reasonable merely for the treatment of water containing no more than  $1 \text{ g dm}^{-3}$  of dissolved salts. The higher the salt content, the more frequent regeneration of ion exchangers is required generating significant volumes of secondary LRW.

To date, inorganic sorbents of various types are widely used to remove radioactive contaminants from LRW and natural water. Among them are natural aluminosilicates (clays) [18, 33, 39, 52]; zeolites of natural and artificial origin [8, 41, 45], oxyhydrate sorbents [21, 28, 55] titanium and zirconium phosphates [24, 54]; alkali metal titanates and titanosilicates [13, 20, 30, 40, 46, 50]; transition metal ferrocyanides [32, 36, 37], and other types of sorbents. These sorbents are primarily used to remove long-lived cesium and strontium radionuclides that most of the time define the total LRW radioactivity.

Inorganic sorbents exhibit increased selectivity to certain ions, high chemical, thermal resistance, and radiation stability, unlike the organic ion exchangers. The selectivity of inorganic sorbents is associated primarily with the so-called “zeolite” effect, which, in its turn, is explained by the close match between the adsorbed ion size and that of the entry windows in the sorbent's crystal lattice [10, 14, 29, 31].

The capability of inorganic sorption materials to the selective adsorption of cesium and strontium radionuclides is widely employed for the treatment of LRW and radioactive natural water of various compositions [2, 19, 30, 48] and for creating engineered geochemical barriers around the radioactive waste storage facilities [3, 4, 17].

Despite a significant number of works and reviews devoted to the sorption studies of cesium and strontium on various sorption materials, the sorption characteristics reported were determined under various experimental conditions, which does not allow an objective comparison of the sorbent efficiency for removing cesium and strontium from solutions.

In that regard, this work pursued the characterization studies of different types of sorption materials most effective for sorption of cesium and strontium radionuclides being the primary radioactive contaminants in the LRW and natural water composition. In addition, the primary attention was given to those commercially available and currently produced on an industrial or pilot-scale. In the last 5–10 years, no new types of sorbents have appeared, superior in selectivity to those known before.

The novelty of our work is the comparative testing of various types of sorbents for the sorption of cesium and

strontium radionuclides based on a standardized technique developed in our laboratory. This technique provides an objective comparison of the available sorbents' sorption characteristics for a particular application.

## 2 Experimental

The sorption-selective characteristics of different sorbent types were evaluated by determining distribution coefficients ( $K_d$ ) of tracer  $^{137}\text{Cs}$  and  $^{90}\text{Sr}$  radionuclides. The  $K_d$  value constitutes the main thermodynamic characteristic of the sorbent during the sorption of tracer amounts. In the range of tracer concentrations, the  $K_d$  value depends neither on the solid-to-liquid phase ratio nor the initial activity of the solution. This was reported in many publications on the sorption studies of sorbents' characteristics [12, 24, 55].

The experiments were run under batch conditions by mixing a 0.1 g weighed portion of the sorbent with a 20 cm<sup>3</sup> aliquot of a feed solution containing  $^{137}\text{Cs}$  and  $^{90}\text{Sr}$  for 24 h. Further, the sorbent was filtered off through a paper filter of a "blue tape" type with the pore size of 2–3 micron, and the filtrate was analyzed for the specific activity of the radionuclide under study.

$K_d$  values were calculated using the results of analyses according to the formula:

$$K_d = \frac{A_0 - A_f}{A_f} \times \frac{V_1}{m_s}, \quad (1)$$

where  $A_0$ ,  $A_f$  denoted the specific activity of the adsorbed radionuclide in the feed solution and filtrate, respectively, Bq dm<sup>-3</sup>;  $V_1$  is the the liquid phase volume, cm<sup>3</sup>;  $m_s$  is the sorbent mass, g.

Sorption of  $^{137}\text{Cs}$  was performed from an aqueous 0.1 mol dm<sup>-3</sup> NaNO<sub>3</sub> solution, pH=6.0;  $^{90}\text{Sr}$  was adsorbed from an aqueous 0.01 mol dm<sup>-3</sup> CaCl<sub>2</sub> solution, pH=6.0. The simulated feed solution for the experiments was prepared by introducing  $^{137}\text{Cs}$  and  $^{90}\text{Sr}$  tracers in  $\sim 10^5$  Bq dm<sup>-3</sup>.

The sorbents used in our work are listed below.

**Purolite C 100**—a gel-type strongly acidic sulfonic cation exchanger. Grain size—0.315–1.25 mm, manufactured by the "Purolite" Company, UK;

- *Bent-Ru*—bentonite clay, Belgorod region, Russia;
- *Bent-Gr*—bentonite clay, Milos Island, Greece;
- *Cl-UKR*—clinoptilolite of the Sokirnitsa deposit, Ukraine;
- *Cl-RUS*—clinoptilolite of the Kholinsky deposit, Chita Region, Russia.

- *NaA*—sodium form of the type A zeolite, TU 2163-003-15285215-2006, manufactured by Ishimbay Specialized Chemical Plant of Catalysts (ISCPC), Bashkiria, Russia;
- *NaX*—sodium form of the type X zeolite, TU 2163-077-05766575-99, manufactured by Ishimbay Specialized Chemical Plant of Catalysts (ISCPC), Bashkiria, Russia;
- *Termoksid-3K*—spheric-shaped granulated zirconium oxyhydrate, manufactured by the JSC "Termoksid," Russia;

*MDM*—manganese (III, IV) oxide-based granulated sorbent, TU 2641-001-51255813-2007, manufactured by the Frumkin Institute of Physical Chemistry and Electrochemistry of the Russian Academy of Sciences (IPCE RAS), Moscow, Russia;

- *Termoksid-3A*—spheric-shaped granulated zirconium phosphate, manufactured by the JSC "Termoksid," Russia;
- *Termoksid-35*—spheric-shaped granulated nickel-potassium ferrocyanide on a zirconium oxyhydrate carrier, the ferrocyanide phase content is 28–32 wt%, manufactured by the JSC "Termoksid," Russia
- *FNS*—granulated nickel-potassium ferrocyanide on a silica gel carrier, the ferrocyanide phase content is 8–10 wt%, manufactured by the IPCE RAS, Moscow, Russia;
- *FND*—finely dispersed nickel-potassium ferrocyanide on a natural aluminosilicate carrier, the ferrocyanide phase content is 15–20 wt%, manufactured by the IPCE RAS, Moscow, Russia;
- *SRM-Sr*—granular sorption-reagent barium silicate-based material, granule size of 0.25–3.0 mm, the specific surface area of 326 m<sup>2</sup> g<sup>-1</sup>; manufactured at the Institute of Chemistry, Far Eastern Branch of the Russian Academy of Sciences, Vladivostok, Russia;
- *BAU*—granulated activated birch wood-based carbon. Granule size of 1.2–3.6 mm, 1.2–3.6 mm, bulk density—of 0.12 g cm<sup>-3</sup>, the specific surface area of 700–800 m<sup>2</sup> g<sup>-1</sup>; micropores' volume of 0.22–0.25 cm<sup>3</sup> g<sup>-1</sup>, mesopores' volume of 0.08–0.10 cm<sup>3</sup> g<sup>-1</sup>, macropores' volume of 1.35–1.45 cm<sup>3</sup> g<sup>-1</sup>, manufactured by the NPO "Sorbent," Russia;
- *NWC*—granulated activated coconut shell-based carbon. Granule size of 0.42–1.7 mm, bulk density of 0.18–0.52 g cm<sup>-3</sup>, the specific surface area of 350–400 m<sup>2</sup> g<sup>-1</sup>; the micropores' volume of 0.33–0.35 cm<sup>3</sup> g<sup>-1</sup>, mesopores' volume of 0.03–0.05 cm<sup>3</sup> g<sup>-1</sup>, macropores' volume of less than 0.01 cm<sup>3</sup> g<sup>-1</sup>, the adsorption capacity of 240 mg g<sup>-1</sup>, produced by NWC Carbon (India).

**Table 1** The distribution coefficient ( $K_d$ ) values for  $^{137}\text{Cs}$  and  $^{90}\text{Sr}$  on different sorbent types

Sorbent type	Brand name, designation	$K_d$ $^{137}\text{Cs}$ , $\text{cm}^3 \text{ g}^{-1}$ in $0.1 \text{ mol dm}^{-3} \text{ NaNO}_3$	$K_d$ $^{90}\text{Sr}$ , $\text{cm}^3 \text{ g}^{-1}$ in $0.01 \text{ mol dm}^{-3} \text{ CaCl}_2$
Sulfonic cation exchanger	Purolite C 100	450	290
Bentonite clay	Bent-Ru	9100	40
Bentonite clay	Bent-Gr	2300	35
Clinoptilolite	Cl-UKR	1600	70
Clinoptilolite	Cl-RUS	1800	65
Zeolite of type A	NaA	8900	350
Zeolite of type X	NaX	1800	320
Zirconium(IV) oxyhydrate	Termoksid-3K	150	210
Manganese (III, IV) oxyhydrate	MDM	290	5600
Zirconium phosphate	Termoksid-3A	1800	440
Nickel-potassium ferrocyanide	Termoksid-35	$1.2 \times 10^5$	35
Nickel-potassium ferrocyanide	FNS	$8.4 \times 10^4$	10
Nickel-potassium ferrocyanide	FND	$8.1 \times 10^4$	25
Barium silicate	SRM-Sr	< 10	185
Activated charcoal	BAU	440	< 5
Activated charcoal	NWC	470	< 5

The specific activity of  $^{137}\text{Cs}$  and  $^{90}\text{Sr}$  radionuclides in solutions was measured by a multipurpose  $\alpha$ - $\beta$ - $\gamma$  SKS-50 M spectrometer (Green Star Technologies, Moscow, Russia). The  $\gamma$ -channel was equipped with a CsI scintillation detector, an energy resolution of 8 keV, an efficiency of 0.08 counts per quantum, and a measurement error not higher than 10%. The measurement geometry was a glass beaker of 60 mm diameter and 20 mm height. The  $\beta$ -channel was equipped with a BDEB-70 scintillation detector, an energy range of 50–3500 keV, energy resolution of 15 keV, measurement error not higher than 10%. The measurement geometry was a stainless steel cup of 50 mm diameter and 3 mm height.

The internal structure of the granulated sorbents was analyzed by scanning electron microscopy and X-ray spectroscopic microanalysis using a JSM-V3 electron microscope (Japan) equipped with an EDX option “JEOL” (“Getac,” Germany).

The mineral composition of clays was determined by X-ray diffraction using an ULTIMA-IV diffractometer, Rigaku, Japan. The operating mode was 40 kV–40 mA, copper radiation, nickel filter, measurement range— $3$ – $65^\circ 2\theta$ , the new generation's DTex/Ultra semiconductor detector.

Morphological characteristics of clay minerals were studied using a TITAN 80–300 TEM/STEM transmission electron microscope.

A Quadrasorb SI/Kr setup was used to determine the specific surface area at liquid nitrogen temperature (77.35 K). The nitrogen of 99.999% purity was used for an adsorbate. The surface was calculated using the BET method, and several isotherm points in the P/Ps range from 0.05 to 0.30.

The samples were preliminarily dried in a vacuum unit at 100 °C for 5–24 h, depending on the properties of the initial samples.

### 3 Results and discussion

In Table 1, the distribution coefficient ( $K_d$ ) values for  $^{137}\text{Cs}$  and  $^{90}\text{Sr}$  radionuclides were given for various types of sorbents. The values were calculated as an average of 2–3 parallel experiments; the relative error in determining the  $K_d$  value did not exceed 10%.

The results presented in Table 1 showed that in an  $0.1 \text{ mol dm}^{-3} \text{ NaNO}_3$  low-salt-bearing solution, bentonite clays, natural and synthetic zeolites, zirconium phosphate, and ferrocyanide sorbents exhibited an increased selectivity to  $^{137}\text{Cs}$ , with a  $K_d$  of  $^{137}\text{Cs} > 10^3 \text{ cm}^3 \text{ g}^{-1}$ . Conversely, sulfonic cation exchangers, oxyhydrate and charcoal sorbents showed relatively low selectivity to cesium.

As mentioned earlier, the selectivity of sorption on inorganic sorbents is associated with the so-called “zeolite” effect, when the complete sorption is observed if the sizes of the entrance windows in the crystal structure of the sorbents and absorbed ions are close.

As shown in Table 1, bentonite clays are effective for the selective sorption of cesium. Sorption characteristics of this type of clay are associated mainly with minerals of the smectite group (illite, montmorillonite) in their composition [44]. The selectivity of sorption, in this case, is associated with the possibility of replacing cations in the interlayer space

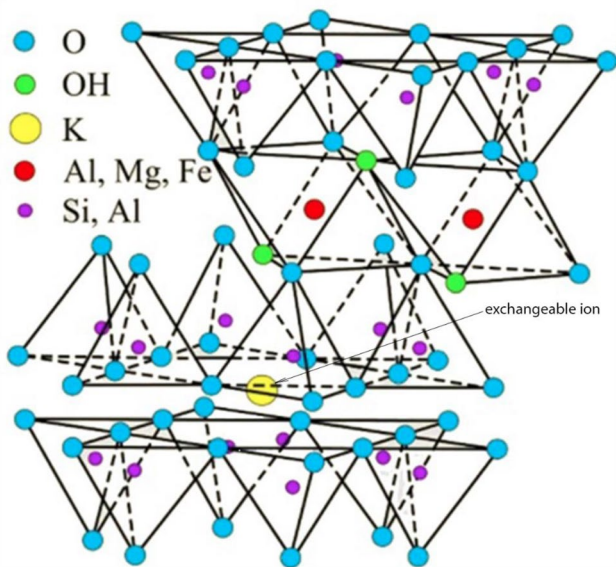


Fig. 1 Crystal structure of illite

with  $\text{Sr}^{2+}$ ,  $\text{Ba}^{2+}$ ,  $\text{Rb}^+$ , or  $\text{Cs}^+$  ones, having the ion radius in the range from 1.75 to 2.02 Å (Fig. 1) [43].

Sorption of cesium on clay minerals occurs by the ion exchange mechanism. Ion exchange on clay minerals occurs due to the exchange of mobile ions in the interplanar layers of clays for ions in the liquid phase. The exchangeable ions can be  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ , and  $\text{Mg}^{2+}$ . As an example, Fig. 1 shows the illite mineral, where the exchanging ion is  $\text{K}^+$ . In Fig. 1, it is indicated by arrow.

Ions in the interlayer space of clay minerals can be  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ , and  $\text{Mg}^{2+}$ . The selectivity series for alkali metals during sorption on bentonite clays is as follows:  $\text{Cs}^+ < \text{Rb}^+ < \text{K}^+ < \text{Na}^+$ , which indicates a high selectivity of the material in question to cesium ions [12].

In the sorption on clays, the surface structure is of great importance. For example, bentonite clay particles (Bent–Ru sorbent) are mainly hexagonal-shaped, with the predominant size in the range of 10–100 nm (Fig. 2). The block structure of illite particles contributes to the formation of a rather large specific surface area of  $22 \pm 1 \text{ m}^2 \text{ g}^{-1}$ , defining the high degree of radionuclide sorption from aqueous solutions [35].

The zeolite effect manifests itself to the greatest extent during the sorption of cesium on transition metal ferrocyanide-based sorbents.

Divalent transition metal ferrocyanides are formed due to the interaction between a soluble transition metal salt and alkali metal (sodium, potassium) ferrocyanides. Depending on the ratio of the reacting components, precipitates of mixed transition metal ferrocyanides of the general formula of  $\text{Me}^{\text{I}}_{4-2x}\text{M}^{\text{II}}_x[\text{Fe}(\text{CN})_6]$  are formed, where Me(I) denotes Na or K, and M(II) is the divalent transition metal ion, namely, Cu, Ni, Co, Zn, etc. The tendency of alkali metal

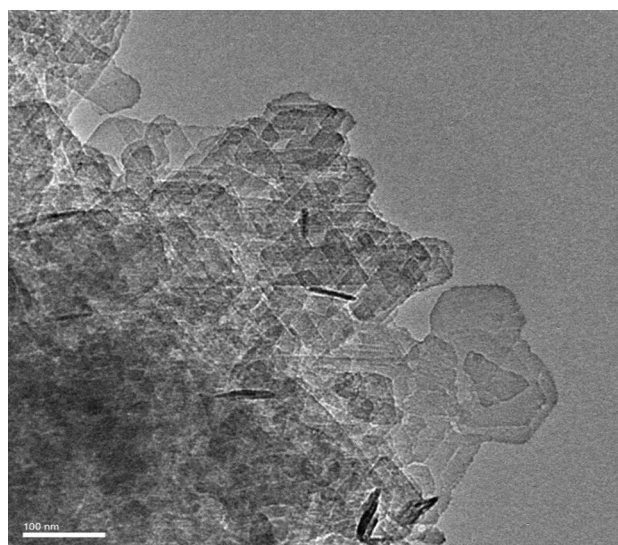


Fig. 2 A micrograph of the bentonite clay particles

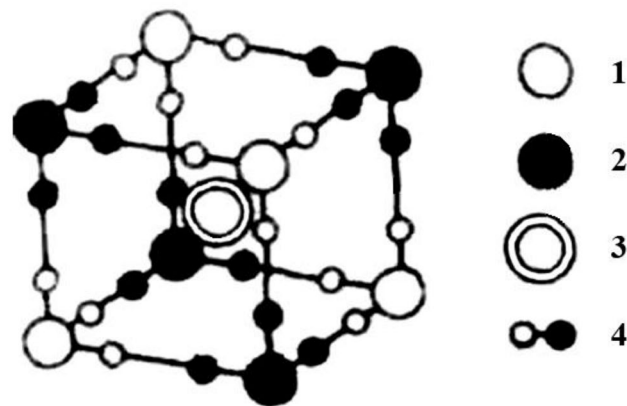


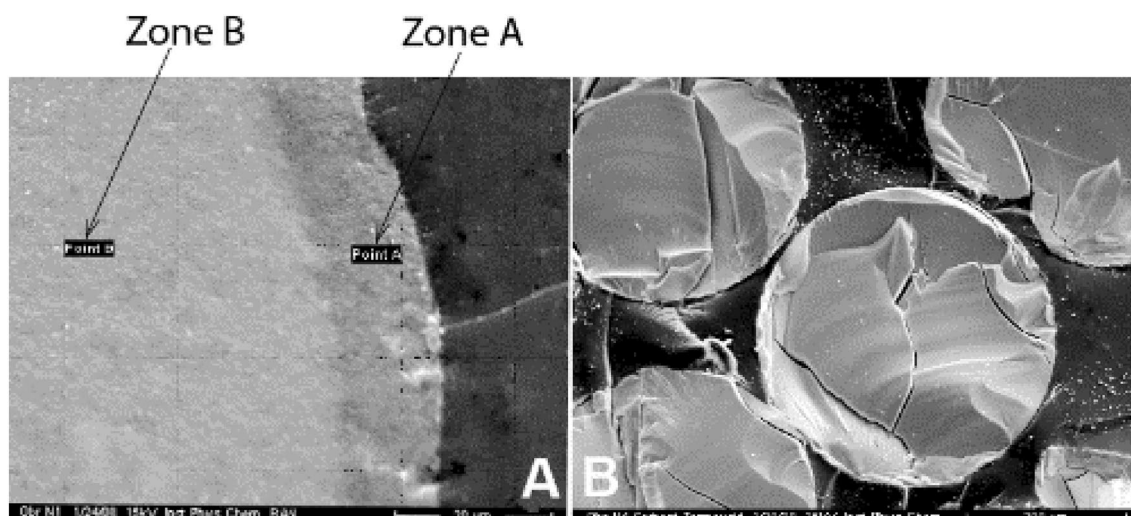
Fig. 3 A crystal structure model of mixed ferrocyanides. 1—Me (II); 2—Fe (II); 3—Me (I); 4—C-N

ions to enter the composition of transition metal ferrocyanides increases with an increase in the ionic radius of an alkali metal [53].

Mixed transition metal ferrocyanides have a face-centered cubic lattice consisting of a poly-anion framework that contains equal amounts of M(II) and Fe(II) transition metal ions located at the lattice sites. In an octahedral arrangement around the iron atoms, CN- groups oriented in the direction of the transition metal atoms make bridges. Some transition metal ions M(II) and alkali metal ions Me(I) are located in the center of the cubic lattice octants (Fig. 3, [53]).

The ion-exchange properties of ferrocyanides are attributed to their ability for an equivalent replacement of mobile alkali metal cations located in the center of the lattice.

The entrance windows' size in the lattice of mixed transition metal ferrocyanides ranges from 3.3 thru 3.5 Å, which



**Fig. 4** Micrographs of FNS (A) and Termoksid-35 (B) sorbent granules' cross-sections

is very close to the size of the cesium ion ( $r_i = 1.65\text{\AA}$ ). When a  $\text{Cs}^+$  ion enters the lattice, the close coincidence of sizes leads to a strong dispersion interaction and, accordingly, the high selectivity to cesium. The selectivity series for mixed transition metal ferrocyanides is the following:  $\text{Cs}^+ < \text{Rb}^+ \ll \text{K}^+ \ll \text{Na}^+$  [34].

A fine-crystalline nature of mixed ferrocyanide precipitates does not enable their application for cesium sorption in a flow mode. Therefore, several methods were used to obtain granular sorbents. The first one consists in depositing a layer of transition metal ferrocyanide precipitate on a porous inorganic matrix with a high specific surface area (silica gel, aluminosilicate). In particular, the FNS sorbent, nickel-potassium ferrocyanide, deposited on the surface of large-pore silica gel belongs to this group. The second granulation method is based on the sol–gel process and includes fabricating a spheric gel of the corresponding metal oxyhydrate followed by sequential treatment of it with solutions of a transition metal salt and potassium ferrocyanide. According to this technology, the nickel-potassium ferrocyanide-based Termoksid-35 sorbent and zirconium oxyhydrate-based Termoksid-3K sorbent is produced [49].

Figure 4 shows micrographs of FNS (A) and Termoksid-35 (B) sorbent granule cross-sections taken by scanning electron microscopy.

The photographs show that for the FNS sorbent, the nickel ferrocyanide phase is mainly concentrated on the external surface of the carrier granule.

An uneven distribution of the nickel ferrocyanide phase in the FSS sorbent, was confirmed by the elemental analysis of this sorbent's composition on the surface (zone A) and in the center of the granule (zone B). The molar ratios of Si/Fe in zones A and B are 48.6 and 59.4, and Si/Ni are 41.1 and 60.9, respectively, which indicates that the nickel

ferrocyanide phase is mainly concentrated on the external surface of the granule. In photo 4, the boundary of the nickel-potassium ferrocyanide layer is clearly visible.

In the Termoksid-35 sorbent, the ferrocyanide phase is uniformly distributed over the entire volume of the granule. In the case of the Termoxide 35 sorbent, the ratios of the sorbent matrix component (Zr) to the sorption phase components (Fe, Ni) over the entire volume of the granule remain almost constant, which indicates the uniform distribution of nickel ferrocyanide in the sorbent phase.

The low-temperature nitrogen adsorption method was used to determine the porous structure of the FNS and Termoksid-35 sorbents. Adsorption isotherms and pore size distribution for FNS and Termoksid-35 sorbents are shown in Figs. 5, 6, and 7, 8, respectively.

Unfortunately, characteristics of the analytical instruments available did not allow us to determine pores with a size below 2 nm. Again, micro- and mesopores in the sorbent are responsible only for the transport of absorbed ions to the phase boundary. The ion exchange itself occurs due to the replacement of mobile ions of the crystal lattice by the ions in the liquid phase. As mentioned above, the size of the entrance windows in transition metal ferrocyanides is 3.3–3.5 Å (0.33–0.35 nm), which is a good match to the size of the cesium ion (0.35 nm).

Characteristics of the porous structure for ferrocyanide sorbents under study, calculated from the adsorption isotherms, are given in Table 2.

The results presented in Table 2 showed that the FNS sorbent largely inherited the macroporous structure of the initial silica gel carrier used for the synthesis. The specific volume of macropores in the FNS sorbent was almost three times as high as in the Termoksid-35 sorbent. Moreover, the presence of macropores in the composition of the FNS

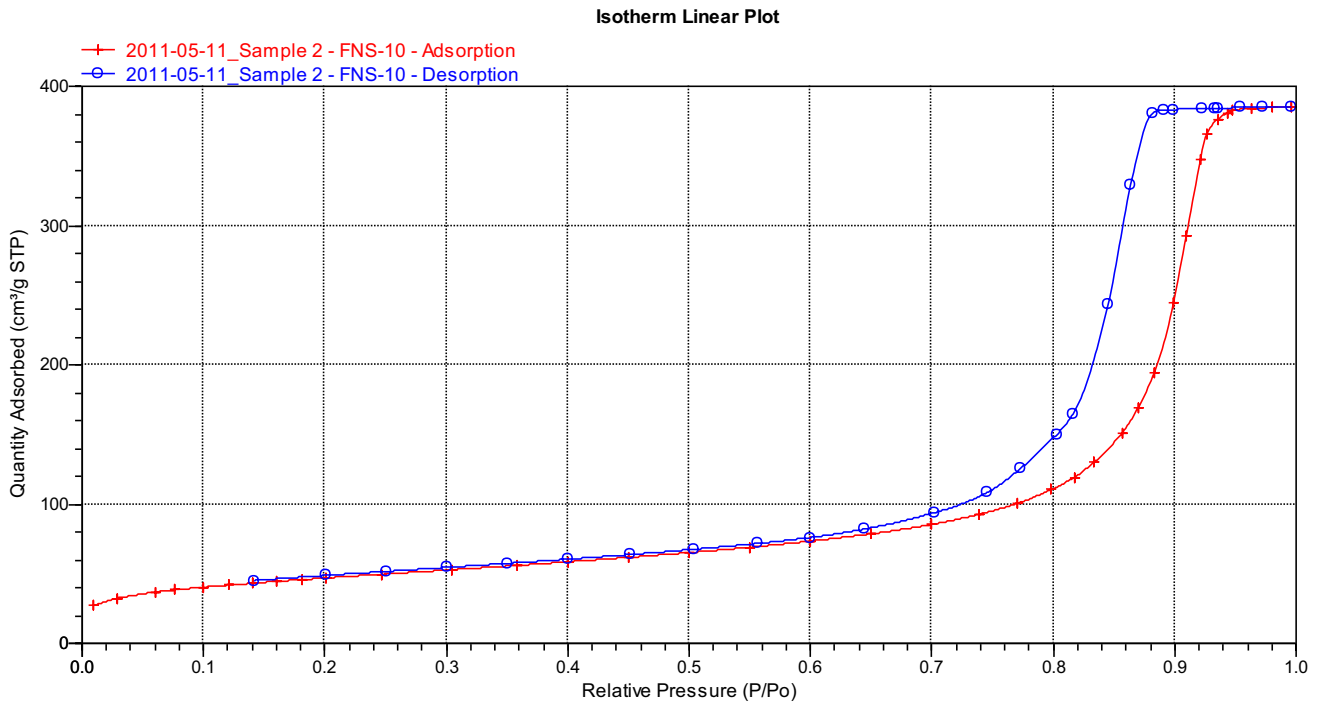


Fig. 5 An adsorption isotherm of nitrogen on the FNS sorbent

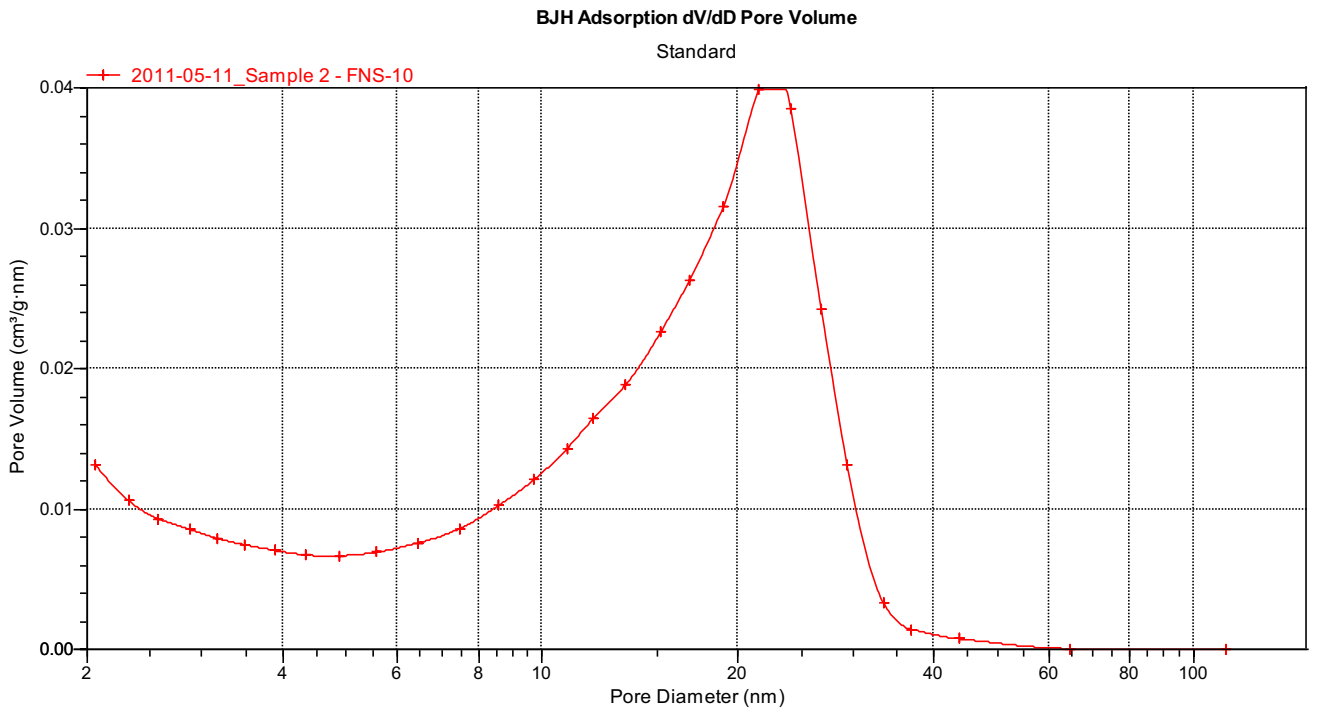
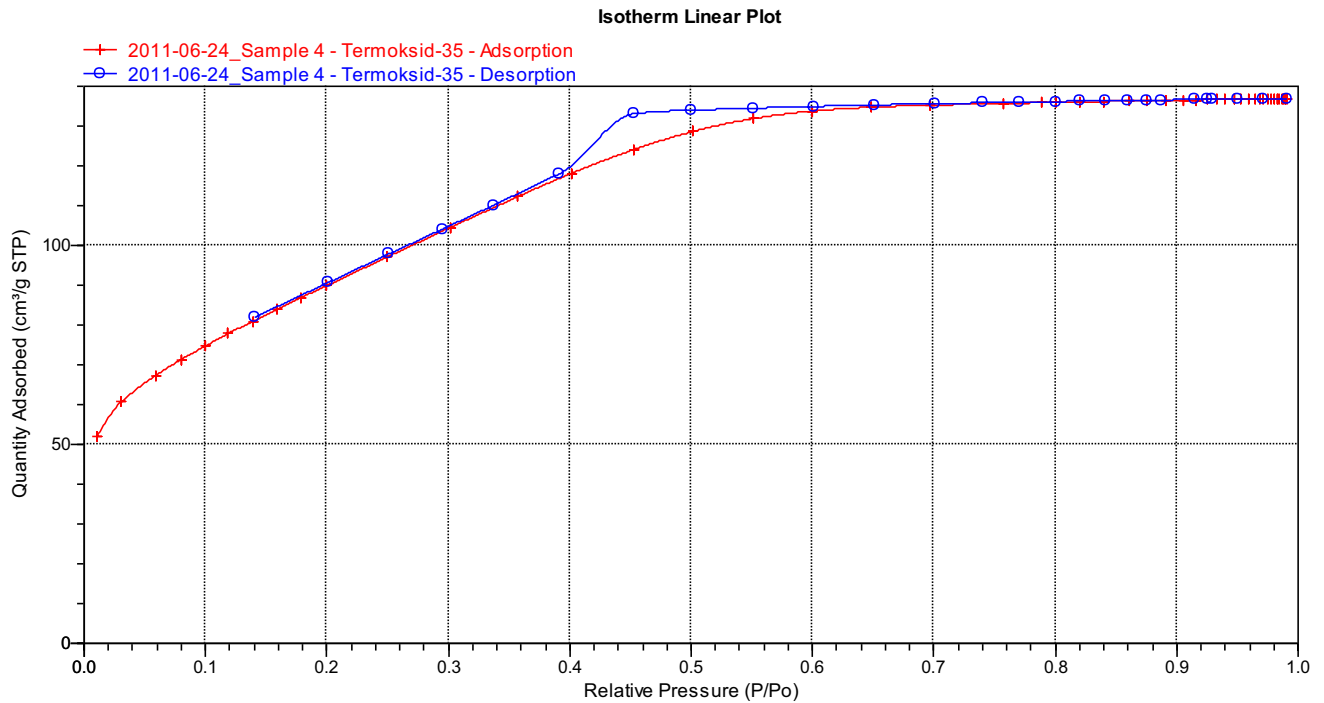


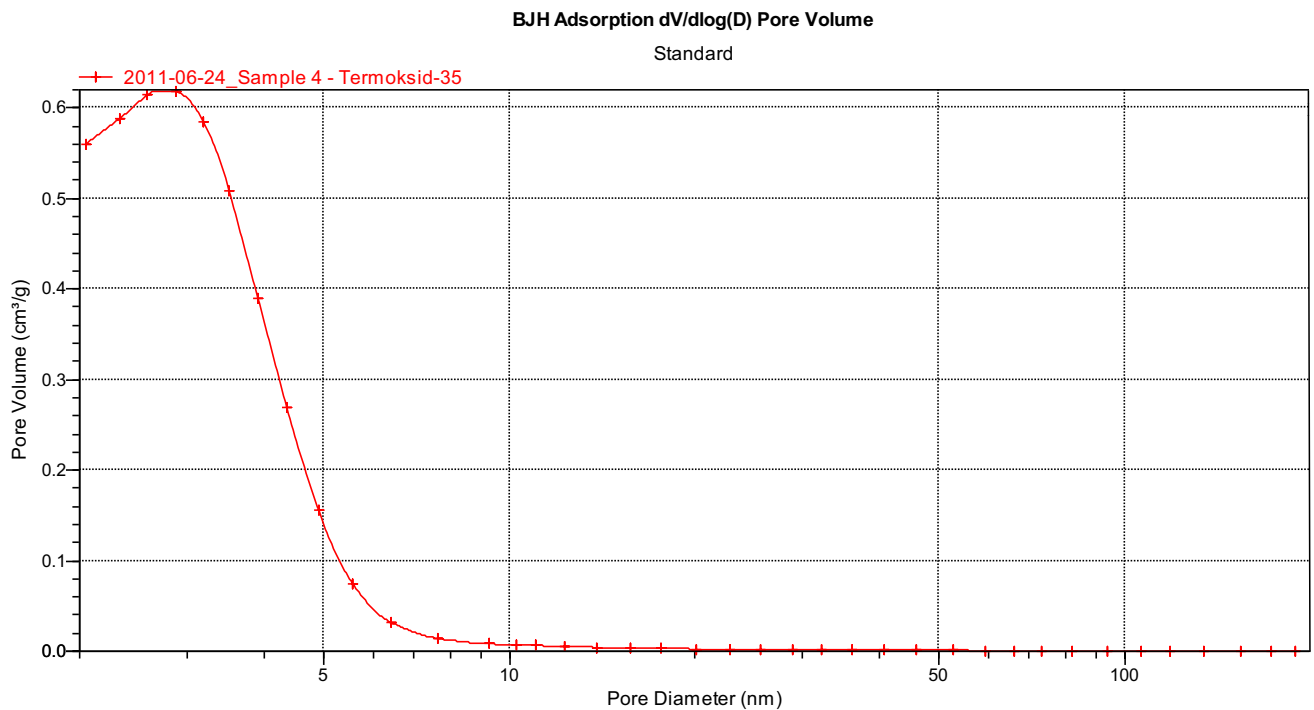
Fig. 6 A pore size distribution for the FNS sorbent

sorbent provided for higher kinetic characteristics during the sorption of cesium. The half-time of exchange during the sorption of tracer  $^{137}\text{Cs}$  was  $200 \pm 20$  and  $120 \pm 10$  s [38],

and the internal diffusion coefficient values of  $^{137}\text{Cs}$  were  $(3.3 \pm 0.8) \times 10^{-12}$  and  $(7.8 \pm 1.5) \times 10^{-12} \text{ m}^2 \text{ s}^{-1}$ , on FNS and Termoksid-35 sorbents, respectively.



**Fig. 7** An adsorption isotherm of nitrogen on the Termoksid-35 sorbent



**Fig. 8** A pore size distribution for the Termoksid-35 sorbent

During the sorption of <sup>90</sup>Sr in the presence of calcium ions, maximum selectivity was observed on the manganese (III, IV) oxyhydrate-based MDM sorbent. On the other

studied sorbents, strontium sorption was much less efficient because of the competition from calcium ions. In the MDM sorbent, the best match was observed between the sizes of



**Table 2** Characteristics of the porous structure for FNS and Termoksid-35 sorbents

No.	Characteristics	Unit of measurement	Value of the characteristic	
			FNS	Termoksid-35
1	Type of the adsorption isotherm according to IUPAC	–	IV	IV
2	Specific surface area, by BET	m <sup>2</sup> g <sup>-1</sup>	167 ± 2	328 ± 4
3	Specific volume of pores below 300 nm in diameter	cm <sup>3</sup> g <sup>-1</sup>	0.60 ± 0.01	0.21 ± 0.01
4	Specific volume of micropores	cm <sup>3</sup> g <sup>-1</sup>	0.04 ± 0.01	0.08 ± 0.01
5	Prevailing pore diameter	nm	23 ± 1	2.8 ± 0.3

**Table 3** The distribution coefficient ( $K_d$ ) values of <sup>137</sup>Cs and <sup>90</sup>Sr during sorption from river water on various sorbents

Sorbent name	Bent-Ru	Cl-UKR	Purolite C 100	NaA	MDM	FNS
$K_d$ <sup>137</sup> Cs, cm <sup>3</sup> g <sup>-1</sup>	2.5 × 10 <sup>4</sup>	1.8 × 10 <sup>4</sup>	1650	8500	–	2.4 × 10 <sup>4</sup>
$K_d$ <sup>90</sup> Sr, cm <sup>3</sup> g <sup>-1</sup>	330	580	1880	4400	8600	–

the sorbent crystal lattice's entrance windows (2.850 Å) and the diameter of the Sr<sup>2+</sup> ion (2.40 Å). For comparison, the diameter of the Ca<sup>2+</sup> ion is 2.08 Å.

The sorption selectivity to <sup>90</sup>Sr in the presence of calcium ions on the MDM sorbent is also related to the “zeolite” effect. The MDM sorbent possesses a hexagonal symmetry birnessite-like structure with the crystal lattice parameters of  $a = 2.850$  and  $C = 7.05\text{--}7.16$  Å [15]. The strong effect of calcium ions on strontium sorption was related to the relatively small difference in the ionic radii of Ca<sup>2+</sup> and Sr<sup>2+</sup> ions of 1.04 and 1.20 Å, respectively. The porous structure of the MDM sorbent is represented by mesopores with a predominant pore diameter of 6–8 nm and a specific surface area of 220–240 m<sup>2</sup> g.

The results obtained allowed us to propose the most effective types of sorbents for removing cesium and strontium radionuclides from radioactively contaminated natural water and technogenic liquid waste.

In case of radiation accidents, low salt-bearing fresh and groundwater become contaminated with cesium and strontium radionuclides. The tests on removing <sup>137</sup>Cs and <sup>90</sup>Sr radionuclides from the water of Moscow River, Russia, were run to determine the efficiency of various sorbents studied for decontaminating this type of natural water. The chemical composition of river water was, mg dm<sup>-3</sup>: Na<sup>+</sup>—6–8; K<sup>+</sup>—4–5; Mg<sup>2+</sup>—15–17; Ca<sup>2+</sup>—52–56; Cl<sup>-</sup>—6–8; SO<sub>4</sub><sup>2-</sup>—36–38; HCO<sub>3</sub><sup>-</sup>—200–205; total salt content of 310–330; total hardness of 3.6–3.8 mg-eqv dm<sup>-3</sup>; pH = 7.6–7.8. Before the runs, the trace amounts of <sup>137</sup>Cs and <sup>90</sup>Sr radionuclides were added in about 10<sup>5</sup> Bq dm<sup>-3</sup> to obtain a simulated feed solution. The  $K_d$  values of <sup>137</sup>Cs and <sup>90</sup>Sr from river water on various sorbents were given in Table 3.

The results in Table 3 illustrated that inexpensive natural sorbents, namely bentonite clays, clinoptilolite, and diatomite, could decontaminate low salt-bearing natural water

from <sup>137</sup>Cs rather effectively. Moreover, those sorbents in their sorption capacity were not inferior to much more expensive synthetic sorbents.

However, the efficiency of natural sorbents for decontamination from strontium significantly decreases because of the intense competition with foreign ions, primarily calcium. In this case, the most reasonable is the application of the manganese (III, IV) oxyhydrate-based MDM sorbent and the synthetic zeolite of A-type.

After the Fukushima-1 Nuclear Power Plant accident, the issue of decontaminating seawater from <sup>137</sup>Cs and <sup>90</sup>Sr radionuclides has acquired particular importance. The main difficulty in seawater processing was its high salt bearing of up to 35 g dm<sup>-3</sup>. The tests aimed to determine the set of sorbents most effective for solving the issue were performed on the sorption of <sup>137</sup>Cs and <sup>90</sup>Sr from a simulated seawater of the following composition, g dm<sup>-3</sup>: Na<sup>+</sup>—10.29; K<sup>+</sup>—0.38; Mg<sup>2+</sup>—1.23; Ca<sup>2+</sup>—0.39; Sr<sup>2+</sup>—0.0074; Cl 18.51; SO<sub>4</sub><sup>2-</sup>—2.59; HCO<sub>3</sub><sup>-</sup>—0.123; Br<sup>-</sup>—0.064; H<sub>3</sub>BO<sub>3</sub>—0.024, total salt content—34.0; pH = 7.8 [6]. Prior to the experiments, the <sup>137</sup>Cs and <sup>90</sup>Sr radionuclide tracers were added to the feed solution in about 10<sup>5</sup> Bq dm<sup>-3</sup>. The  $K_d$  values of <sup>137</sup>Cs and <sup>90</sup>Sr from seawater on various sorbents were given in Table 4.

The results obtained during the sorption of <sup>137</sup>Cs from seawater showed that applying natural sorbents for the purpose was much less practical than synthetic inorganic sorbents, the ferrocyanide sorbents being the most effective.

For the decontamination of seawater from <sup>90</sup>Sr, it appeared most reasonable to use the barium silicate-based sorption-reagent material SRM-Sr; under the conditions given, it exhibited the maximum efficiency in removing <sup>90</sup>Sr [5].

**Table 4** The distribution coefficient ( $K_d$ ) values of  $^{137}\text{Cs}$  and  $^{90}\text{Sr}$  during sorption from seawater on various sorbents

Sorbent name	Bent-Ru	Cl-UKR	NaA	MDM	FNS	SRM-Sr
$K_d$ $^{137}\text{Cs}$ , $\text{cm}^3 \text{g}^{-1}$	3500	1700	280	< 10	$1.1 \times 10^4$	< 10
$K_d$ $^{90}\text{Sr}$ , $\text{cm}^3 \text{g}^{-1}$	< 10	< 10	< 10	590	< 10	$4.0 \times 10^4$

## 4 Conclusions

This work was to perform a comparative study of the adsorption characteristics of various sorption materials concerning cesium and strontium radionuclides. These fission products represent the most significant hazard to humans and the environment because of their half-life of about 30 years and high radiotoxicity. For our study, we have developed a standard technique for determining the distribution coefficients ( $K_d$ ) of tracer  $^{137}\text{Cs}$  and  $^{90}\text{Sr}$  radionuclides in solutions of sodium and calcium salts being the main bulk components of LRW and groundwater.

As a result, we found bentonite clays and natural and synthetic zeolites to be the best choice for decontaminating low-salt solutions (groundwater) from cesium radionuclides. High salt-bearing solutions (seawater) were the most effectively decontaminated from cesium with ferrocyanide sorbents. For removing strontium from groundwater, the manganese (III, IV) oxyhydrate-based MDM sorbent showed the best results, and for seawater, the barium silicate-based SRM-Sr sorbent was the most effective.

In summary, our technique provides a tool for the reasonable choice of the most effective sorbents for decontaminating groundwater and LRW from highly toxic cesium and strontium radionuclides.

**Author contributions** VVM: the idea, supervision, conceptualization, methodology, data analysis, writing—original draft. NAN: investigation, literature search, data analysis, writing—original draft. VOK: investigation, literature search. EAK: resources, writing—review and editing.

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## Declarations

**Conflict of interest** The authors have no relevant financial or non-financial interests to disclose. The authors have no competing interests to declare that are relevant to the content of this article. All authors certify that they have no affiliations with or involvement in any organization or entity with any financial interest or non-financial interest in the subject matter or materials discussed in this manuscript. The authors have no financial or proprietary interests in any material discussed in this article.

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