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Nanofiltration Purification of Liquid Radioactive Waste

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Abstract—The paper presents the results of testing the purification of real liquid radioactive waste from radionuclides, bottom residues of the Kola and Beloyarsk nuclear power plants (NPP), as well as low-level wastewater from the radiochemical building of the Institute of Physical Chemistry and Electrochemistry RAS (IPCE RAS) using the method of nanofiltration (NF) using a polymer membrane manufactured by the Russian company "RM Nanotech." It has been shown that in the case of single-stage NF purification of bottoms of the Kola NPP, the coefficient of purification from ^{60}Co is 2.8, while no purification from ^{137}Cs practically occurs. When cleaning the bottom residues of the Beloyarsk NPP from ^{60}Co using a five-stage scheme, a coefficient of purification from ^{60}Co equal to 388 was obtained. The combination of nanofiltration purification and selective sorption of cesium on the ferrocyanide sorbent Temoksid-35 makes it possible to obtain a dry salt residue that is not related to radioactive waste. When using the method of nanofiltration for the treatment of low-level wastewater of the Institute of Physical Chemistry and Electrochemistry of the Russian Academy of Sciences, the degree of purification was, %: ^{137}Cs ~ 75; ^{90}Sr ~ 91; ^{241}Am ~ 99.5; ^{152}Eu ~ 91; ^{239}Pu ~ 99.5.

Keywords: nanofiltration, polymer membrane, liquid radioactive waste, bottoms of NPP, purification, cesium, cobalt

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INTRODUCTION

In the process of manufacturing and other activities related to the production and use of radioactive substances, the formation of radioactively contaminated materials that are not subject to further use—radioactive waste (RAW) of various aggregation states and activity levels—occurs. Among the generated radioactive waste, liquid radioactive waste (LRW) is of the greatest danger due to its large volume, high total activity, and also, in case of emergency, the possibility of rapid spread in the environment.

Among the methods of reprocessing LRW, membrane methods based on the reverse osmosis, micro-, ultra- and nanofiltration occupy a prominent place. These methods have a number of advantages relative to other purification techniques: membrane methods do not require large consumption of reagents, i.e., they are low-waste; when using them, high degrees of purification are achieved, and the existing membrane devices are quite compact and easy to use due to the possibility of complete automation of the purification process [1].

The nanofiltration (NF) method, unlike other baromembrane processes, includes, in addition to the diffusion and convective separation mechanism, also an electrostatic one, caused by the presence on the surface of the NF membrane of active charged functional groups that dissociate upon contact with the separated solution [2, 3]. In connection with this phenomenon, when using the nanofiltration process, it becomes possible to more effectively retain multiply charged ions compared to singly charged ones [4–6]. This feature of nanofiltration was used to purify natural and mine waters [7], as well as drinking water [8], from uranium. During the purification process, the NF membrane selectively removes 90–98% of uranium, while other trace elements are practically not retained with the membrane.

In our previous works [9–12], in experiments on model solutions, it was shown that the NF method is very effective for the retention of multiply charged ions of transition metals, uranium, thorium, radionuclides of strontium, cobalt, europium, plutonium, organic complexing agents and surfactants. The main feature

of the NF membrane is its low retention capacity for singly charged alkali metal ions, which makes it possible to separate the main inactive salt component of liquid radioactive waste of low and medium activity levels—sodium nitrate—from multiply charged active and inactive components [9, 10]. The results obtained on model solutions showed the high promise of the NF method for reprocessing of real low- and medium-level liquid radioactive waste.

This type of liquid radioactive waste includes, in particular, the bottom residues of nuclear power plant evaporators, which are high-salt solutions and pulps with a total salt content of up to 500 g/dm^3. The main salt component of NPP bottoms is sodium and potassium nitrates, as well as various organic compounds [13]. The main contribution to the total activity of bottom residues is made by radionuclides ^{137}Cs (90–95%) and ^{60}Co (5–10%). The main difficulty in reprocessing bottom residues is the removal of cobalt radionuclides, which are bound in these solutions into strong organic complexes. To purify bottom residues from ^{60}Co, the method of oxidative destruction of organic cobalt complexes with ozone is applied, followed by separation of the resulting precipitates containing radioactive cobalt on ceramic ultrafiltration membranes [14, 15]. This method is characterized by low productivity, complex hardware design, and the need to use highly toxic ozone.

This paper reports the results of experiments on the purification by nanofiltration of several types of real liquid radioactive waste: bottom residues from the Kola and Beloyarsk NPPs, as well as low-level wastewater from the radiochemical building of the Institute of Physical Chemistry and Electrochemistry RAS (IPCE RAS).

METHODOLOGICAL PART

In the experiments, we used a nanofiltration polymer membrane of NanoNF-1812 grade produced by the company "RM Nanotech" (Vladimir, Russia), with an effective filtration area of 0.3 m^2. The characteristics of the membrane and a description of the laboratory setup are given in [9–12].

The experiments were carried out according to the following procedure: the solution to be purified was placed in the initial container and, using a pump, it was passed through the NF module in circulation mode at a pressure on the membrane of 6.5–7.0 atm.

Samples of the filtrate and circulating solution were periodically taken to measure the activity. Based on the results obtained, the retention capacity (R, %) and the purification coefficient (K_{pur}) of the NF membrane for the corresponding radionuclide were calculated by equations:

$$R = (1 - A_f/A_0) \times 100\%,$$
$$K_{pur} = A_0/A_f,$$

where A_f, A_0 are activity of the radionuclide in the filtrate after the membrane and in the circulating solution, respectively.

The pH of solutions was measured using an Ecotest 2000 ion meter. The salt content was determined by measuring electrical conductivity by a Dist-4 salinity meter (Hanna, Germany). To prepare model solutions, distilled water and reagents (analytical or reagent grade) were utilized.

Specific activity was measured by direct radiometric method with the SKS-50M spectrometric complex (Green Star Technologies, Russia). The measurement time was selected to reach an error of no more than 15%.

RESULTS AND DISCUSSION

Treatment of Bottom Residues of the Kola NPP

The actual bottom residues of the Kola NPP, previously purified from ^{137}Cs using the Termoksid-35 ferrocyanide sorbent, were used as the initial solution. The salt content of the bottom residue was 180 g/dm^3, pH 12. The salt composition was represented mainly by sodium and potassium nitrates and borates. The specific activity of ^{60}Co and ^{137}Cs in the initial solution was 12200 and 490 Bq/dm^3, respectively. The results obtained are listed in Table 1.

The results in Table 1 demonstrate that when using NF, purification from ^{60}Co occurs by 65% (K_{pur} = 2.8), while no purification from ^{137}Cs occur, which corresponds to previously obtained data in [9]. The salt content of the filtrate decreased by no more than

Table 1. Results of purification of the bottom residue of the Kola NPP from ^{60}Co and ^{137}Cs using the nanofiltration method

Solution	Volume of solution, cm^3	Salt content, g/dm^3	Specific activity, Bq/dm^3	
			^{60}Co	^{137}Cs
Original	568	180	12200	490
Filtrate	165	160	4290	480
Concentrate	407	190	13100	608

Table 2. Results of purification of bottom residue from ^{60}Co using nanofiltration in a multi-stage mode

Steps nos.	Volume of solution, cm^3			Specific activity ^{60}Co, Bq/dm^3		K_{pur}	
	original	filtrate	concentrate	original	filtrate	on the step	general
1	2400	1965	435	4770	2270	2.10	2.10
2	1965	1530	435	2270	960	2.36	4.97
3	1530	1145	385	960	540	1.78	8.83
4	1145	765	380	540	57	9.47	83.7
5	765	370	395	57	12.3	4.63	387.8

12%, which corresponds to the data on the low retention capacity of NF for alkali metal salts.

To increase the degree of purification from ^{60}Co, a multi-stage purification method can be used, when the filtrate after NF is sent for repeated purification. Due to the limited volume of the actual bottoms of the Kola NPP, this technique was demonstrated by an example of cleaning the bottoms of the Beloyarsk NPP.

Treatment of Bottom Residues of the Beloyarsk NPP

For purification, we used real bottom residue from the Beloyarsk NPP. Composition of the bottom residue: salt content 102 g/dm^3, chemical oxygen demand (COD) 3.0 g O_2/dm^3, pH 11.4, ^{137}Cs 6200 Bq/dm^3, ^{60}Co 4770 Bq/dm^3.

The test procedure was as follows: The initial solution was placed in a 5-liter container and passed through the NF module using a pump, the filtrate was collected in a separate container, and the concentrate was returned to the initial container. When the volume of the starting solution required for the NF process was exhausted, its residues (concentrate) were poured into a separate container, and the resulting filtrate was again passed through the membrane. In this way, 5 consecutive purification cycles were carried out. Based on the resulting data, the purification coefficient (K_{pur}) from ^{60}Co were calculated. The results obtained are shown in Table 2.

The results obtained demonstrate that when carrying out a five-stage NF purification, a purification coefficient from ^{60}Co was more than 380. The observed sharp increase in the retention capacity at the 4th and 5th stages is apparently due to the fact that organic components are removed at the previous stages solution, which negatively affect the extraction of ^{60}Co. The possibility of effective retention of organic complexing substances and surfactants we detected during nanofiltration was reported in [11]. ^{137}Cs, which is present in the bottom residues in the form of singly charged Cs^+ ions, is practically not retained by the NF membrane.

The limited volume of real bottom residues from nuclear power plants did not allow complete simulating the actual technological purification process. In practice, membrane processes are carried out, as a rule, in a countercurrent mode, in which the filtrate, after purification at the first stage, enters the next purification stage, and the concentrate is returned to the previous stage. With this mode, a high degree of purification

Table 3. Radiochemical analysis of the dry residue of the still residue after sorption and nanofiltration purification

Radionuclide	A_i, Bq/kg	MSSA,[a] Bq/kg	A_i/MSSA$_i$
^{137}Cs	400	1.0×10^4	0.04
^{60}Co	2300	1.0×10^4	0.23
^{40}K	3570	1.0×10^5	0.04
^{22}Na	5540	1.0×10^4	0.55
Total	11810	–	0.86

[a] (MSSA) minimum significant specific activity (NRB-99/2009. Radiation safety standards).

Table 4. Retention capacity (R) for the treatment of low-level wastewater at the Institute of Physics and Chemistry of the Russian Academy of Sciences

Type of filter material	R, %				
	^{137}Cs	^{90}Sr	^{241}Am	^{152}Eu	^{239}Pu
NF	75 ± 7	90.8 ± 1.8	99.4 ± 0.1	91.2 ± 1.7	99.6 ± 0.5
MF	69 ± 6	12.7 ± 1.8	91.1 ± 1.8	89.5 ± 1.8	48.7 ± 1.0
Paper filter	7.4 ± 2.0	1.8 ± 0.5	13.4 ± 17	88.1 ± 2.4	1.2 ± 0.6

is reached with a minimum amount of concentrate (no more than 10–15% of the volume of the starting solution). This technique is standard and widely used in water and wastewater treatment engineering [1].

After five-stage purification, the filtrate was passed through the Termoksid-35 sorbent to remove ^{137}Cs, evaporated to dryness and dried at a temperature of 105°C for 16 h. The resulting dry residue was examined for radionuclide content. The results obtained are presented in Table 3.

According to NRB-99/2009, material for which ΣA_i/MSSA$_i$ < 1 does not belong to radioactive waste. Thus, the combination of sorption purification of the bottom residue from ^{137}Cs and NF purification from ^{60}Co makes it possible to reprocess the NPP bottom residues to produce a salt residue that does not belong to the category of radioactive waste.

Treatment of Low-Level Wastewater from the Radiochemical Building of IPCE RAS

Low-level liquid radioactive waste generated during work with radioactive substances in the radiochemical building of IPCE RAS are weakly alkaline solutions with a total salt content in the range of 0.25–0.5 g/dm^3. In addition to inorganic salts, wastewater contains impurities of organic substances (oxalates, complexones, surfactants, oils, etc.). The COD index, which characterizes the total content of oxidizable organic substances, usually varies in the range of 50–150 mg O_2/dm^3. The total alpha and beta activity of liquid radioactive waste is determined mainly by radionuclides ^{241}Am, ^{239}Pu, ^{137}Cs, ^{90}Sr/^{90}Y and, as a rule, is in the range of 10–30 and 25–150 Bq/dm^3, respectively.

To test the possibility of using the NF method for the purification of low-level liquid radioactive waste of the radiochemical building of IPCE RAS, an average sample of waste water was taken from a operating tank. Chemical composition of the sample: total salt content 0.25 g/dm^3, total hardness 2.5 mg-equiv./dm^3, COD 50 mg O_2/dm^3, pH 8.3; total alpha and beta activity 10 ± 1 and 25 ± 3 Bq/dm^3, respectively.

Due to the low specific activity of water during testing, indicator amounts of radionuclides ^{137}Cs, ^{90}Sr, ^{241}Am, ^{152}Eu, ^{239}Pu were added to it in an amount of 10^3–10^4 Bq/dm^3. After adding the labels, the sample was mixed and kept for 5 days to establish equilibrium in the system.

In the course the tests, 1 L of source water containing

the extracted radionuclide was passed through the NF membrane. After receiving 500 mL of filtrate, purification was stopped and the specific activity of the radionuclide in the filtrate was measured.

In order to compare the effectiveness of using a NF membrane, wastewater containing extractable radionuclides was filtered through a blue ribbon paper filter with a pore size of about 5 μm and through a ceramic microfiltration (MF) membrane with a pore size of 0.2 μm. The results obtained are presented in Table 4.

From these results it is clear that the NF method allows the effective purification of IPCE RAS low-level wastewater from all radionuclides present. The highest degree of purification (more than 99%) is detected for radionuclides ^{241}Am and ^{239}Pu, which under these conditions are in water in the form of colloidal and pseudocolloidal particles, effectively retained by the NF membrane. Noteworthy is the significant discrepancy between the retention rates of ^{152}Eu and ^{241}Am by the paper filter. This is apparently attributable to the different initial chemical state of radionuclides before they enter wastewater. Due to the fact that these and other radionuclides enter wastewater from various laboratories in different chemical and phase-dispersed states, their state in real wastewater is very complex and variable. As can be seen from results presented in Table 4, the nanofiltration method is effective for the removal of various radionuclides, especially those in colloidal form and in the form of multiply charged ions.

The relatively high degree of ^{137}Cs extraction (about 75%) is due to the presence in the water composition of coarse and fine particles of insoluble substances—aluminosilicates (clays), silicic acid, metal hydroxides and other impurities of inorganic and organic nature, on the surface of which effective sorption of cesium occurs with the formation pseudocolloids effectively retained by the NF membrane.

CONCLUSIONS

The possibility of using the nanofiltration method to remove radionuclides from several types of real liquid radioactive waste: bottom residues of the Kola and Beloyarsk NPPs, as well as low-level wastewater from the radiochemical building of IPCE RAS, was investigated.

During treatment of bottom residues from nuclear power plants, it was shown that it is possible to effectively extract the radionuclide ^{60}Co without using an expensive and complex engineering operation for ozonation. The combination of nanofiltration purification and selective sorption of cesium on the ferrocyanide sorbent Temoksid-35 made it possible to fabricate a purified product—a salt residue—that is not classified as radioactive waste.

The possibility of using nanofiltration for deep purification of liquid radioactive waste from radiochemical research centres was also demonstrated by an example of low-level wastewater from the radiochemical building of IPCE RAS. It was shown that the nanofiltration method makes it possible to deeply purify this type of liquid radioactive waste from strontium, cobalt, REE and TPE radionuclides to levels that meet the current applicable standards for discharge into an open sewer network.

Thus, the results obtained showed that the nanofiltration method is effective for removing radionuclides that are in colloidal form and in the form of multiply charged ions, which indicates the promise of using this method for reprocessing liquid radioactive waste of complex chemical and radionuclide composition.

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CONFLICT OF INTEREST

The authors declare no conflict of interest.

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