EXPERIMENTAL STUDY AIMED AT DECREASING THE ACTIVITY OF SPENT ION-EXCHANGE RESINS

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High-level decontamination is seen as a method providing the reprocessing of ion-exchange resins: they are treated with specifically selected solutions to achieve high degree of radionuclide elution. In 2021, Research Manufacturing Technological Bureau Onega launched an experimental study aimed at reducing the activity of spent ion-exchange resins unloaded from ships undergoing maintenance. Under the study, a few experiments were performed to select appropriate regenerating solutions, optimal methods for spent ion-exchange resin processing and treatment of regenerating solutions on sorbents of NZpS and TsMPA types. Based on the study, a method was proposed with an appropriate processing flowchart developed to manage spent ion-exchange resins at the ship repair site Zvezdochka.

Keywords: *radioactive waste, intermediate-level waste, ion-exchange resins, regeneration, effluent.*

Operation and maintenance of ship nuclear power units involves spent ion-exchange resin unloading from the coolant treatment systems of the steam generators.

Over 250 traps with a capacity of 0.3 m^3 filled with spent intermediate-level ion-exchange resins that have been unloaded from the filters are currently stored in long-term solid radioactive waste (SRW) storage facilities of the ship repairing center Zvezdochka awaiting conditioning in accordance with waste acceptance criteria and further transfer for disposal [1].

The waste management methods applied at the Zvezdochka site do not meet the requirements imposed by the current legal framework in radioactive waste (RW) management. In particular, provisions of the Federal Law of July 11, 2011 No. 190-FZ [2] state that all RW shall be disposed of or emplaced into long-term storage facilities provided their prior conditioning in accordance with waste acceptance criteria and packaging into certified containers. Moreover, protection of present and future generations as a principle laid down in the provisions of the Fundamental Safety Principles [3] as applied to RW should be implemented, namely, "Radioactive waste must be managed in such a way as to avoid imposing an undue burden on future generations; that is, the generations that produce the waste have to seek and apply safe, practicable and environmentally acceptable solutions for its long-term management …".

Compared to other RW types, the processing of spent ion-exchange resins is considered as the most challenging and costly process. No mass-produced process units are yet available for these purposes. High-level decontamination, i. e., IER regeneration by special solutions providing high degree of radionuclide elution is one of the methods applied.

Literature sources evidence that aqueous solutions of salts, namely, the salts of alkali and alkaline earth metals of various concentrations provide most effective high-level IER decontamination

when used as regenerating solutions [4], [5], [6]. Another option provides for the transfer of the radionuclides sorbed on an ion-exchange resin into a solution of acidic sodium salts and further treatment of the decontamination solution from cesium radionuclides based on a composite ferrocyanide sorbent [7]. Under another method, ion-exchange resins can be decontaminated with a decontaminating solution followed by subsequent decontamination of this solution from radionuclides [8].

In 2021, RMTB Onega developed a plan for an experiment seeking to reduce the activity of spent intermediate-level ion-exchange resins (by washing) [9] being unloaded from the ships undergoing maintenance at the Zvezdochka site. Relevant experimental study has been successfully completed, i. e., Experiment Seeking to Reduce the Activity of Spent Ion Exchange Resins Being Unloaded from the Ships Undergoing Maintenance [10].

The study was seeking to test the method proposed to reduce the activity of spent intermediate-level ion-exchange resins by washing them with regenerating aqueous solutions of sodium nitrate and calcium nitrate with their concentrations ranging from 0.5 M to 3.0 M at an increment of 0.5 and their subsequent decontamination from radionuclides using sorption-selective filters.

Under the study, washed was the spent intermediate-level ion-exchange resin from a receiver tank (trap) [11] stored in a long-term storage facility for SRW at the Zvezdochka site.

A series of experiments were performed in laboratory conditions to identify the optimal concentration of regenerating sodium nitrate and calcium nitrate solutions. For this purpose, aliquots of the spent intermediate-level ion-exchange resin were loaded into chromatographic columns and washed with freshly prepared aqueous solutions of these salts at concentrations of 0.5 M, 1.0 M, 1.5 M, 2.0 M, 2.5 M, 3.0 M. After that the specific activity of the regenerated ion-exchange resin and the radionuclide composition of the spent regenerating solution (eluate) were measured. Optimal concentrations of the regenerating solutions calculated based on the radiometric and spectrometric measurements amounted to 1.0 M and 0.5 M for sodium nitrate and calcium nitrate respectively.

According to the experimental plan [9], the following methods were proposed to reduce the activity of the spent intermediate-level ion-exchange resin (by washing):

- cyclic treatment with regenerating solutions (at least three cycles);
- exposure to regenerating solutions for 60, 120, 180, 240, 300, 360 minutes;
- step-by-step treatment with the regenerating solutions:
  a) 1.0 M sodium nitrate, then 0.5 M calcium nitrate;
  b) 0.5 M calcium nitrate, then 1.0 M sodium nitrate;
- treatment with a mixture of regenerating solutions involving 1.0 M sodium nitrate and 0.5 M calcium nitrate at a volume ratio of 1 : 1.

The specific activity of the regenerated ion-exchange resin and the radionuclide composition of the eluate was measured at each treatment stage. The average fraction of radionuclides that did pass into the eluate was calculated based on the radiometric and spectrometric measurements (Table 1).

Table 1. Average fraction of radionuclides that passed into the eluate

Method of spent ion-exchange resin treatment	Concentration and chemical composition of the regenerating solution	Average fraction of radionuclides that passed into the eluate, %	
		^{137}Cs	^{90}Sr
1 – single-component	1.0 M sodium nitrate	97	58
2 – single-component	0.5 M calcium nitrate	95	30
3 – two-component (successively)	1.0 M sodium nitrate followed by 0.5 M calcium nitrate	99	81
4 – two-component (successively)	0.5 M calcium nitrate followed by 1.0 M sodium nitrate	99	85
5 – two-component (simultaneously)	1.0 M sodium nitrate and 0.5 M calcium nitrate at a volume ratio of 1:1	97	60

At the next stage, a series of experiments were performed to select the optimal IER treatment method based on regenerating solutions of 1.0 M sodium nitrate and 0.5 M calcium nitrate.

The following conclusions could be drawn based on this study:

- after being washed with the regenerating solutions the spent intermediate-level ion-exchange resin could be referred to the low-level waste category;
- after being washed with a regenerating solution of 0.5 M calcium nitrate, the decrease in the activity of spent ion-exchange resin was found to be higher than in case of its washing with the 1.0 M sodium nitrate. However, 0.5 M calcium nitrate when applied as a regenerating solution to wash the spent ion-exchange resin could trigger the generation of sparingly soluble precipitates complicating the treatment process;
- regenerating solutions with higher concentrations may increase considerably the salinity level, thereby contributing to sediment precipitation,

which, in turn, would further complicate the process of the spent regenerating solution treatment;
- cyclic treatment, as well as spent ion-exchange resin exposure to regenerating solutions of 1.0 M sodium nitrate and 0.5 M calcium nitrate provided no significant increase in the proportion of radionuclides passing into the solution as compared to washings with no cyclic processing and exposure in place;
- most effective treatment was achieved when the spent ion-exchange resin was washed with regenerating solutions of 0.5 M calcium nitrate and 1.0 M sodium nitrate, followed by their decontamination using the on NZhS- and TsMPA-type sorbents and reuse for IER washing purposes.

Table 2 presents the specific activity of the spent ion-exchange resin before and after being treated with regenerating solutions.

Table 2. Specific activity of spent ion exchange resin before and after its treatment with regenerating solutions

Type of ion-exchange resin	Specific activity of beta-emitters ($A\beta_{sp}$), Bq/kg	Specific activity of alpha-emitters ($A\alpha_{sp}$), Bq/kg
1. Original spent ion exchange resin	$8.1 \cdot 10^7$	$8.6 \cdot 10^2$
2. Spent ion exchange resin after being washed with 1.0 M sodium nitrate regenerating solution	$3.9 \cdot 10^6$	$5.0 \cdot 10^2$
3. Spent ion exchange resin after being washed with a 0.5 M calcium nitrate regenerating solution	$1.9 \cdot 10^6$	$2.8 \cdot 10^2$

Based on this experiment, as well as subsequent R&D, a method was proposed to treat the spent radioactive ion-exchange resins [12]. This treatment method after being refined to account for all necessary equipment available at the Zvezdochka site includes the following operations:
- 310 liters of spent intermediate-level ion-exchange resin are loaded into a receiver tank (trap) [11];
- regenerating solution is mixed in a tank;
- regenerating solution is supplied to the receiver tank (trap) [11] filled with spent intermediate-level ion-exchange resin;
- the spent intermediate-level ion-exchange resin is washed in the receiver tank (trap) [11] with the regenerating solutions: first with 0.5 M calcium nitrate, then with 1.0 M sodium nitrate;
- hot air is supplied to the receiver tank (trap) [11] to provide ion-exchange resin dehydration;
- the spent regenerating solution is supplied from the receiver tank (trap) [11] to the settling unit providing its separation from the generated precipitates;
- the clarified spent regenerating solution is supplied from the settling unit to the sorption filters of NZhS and TsMPA types;
- the regenerating solution is treated from radionuclides on sorption filters;
- the decontaminated regenerating solution is returned to the tank and can be used again in the processing of spent ion-exchange resin in a receiver tank (trap) [11];
- spent ion-exchange resin is unloaded from the receiver tank (trap) [11] into B31A2-216.5 drums or certified NZK-150-1.5P(IOS) containers for its subsequent management.

After being washed and dried, the spent intermediate-level ion-exchange resin can be referred to the RW Class 4 according to the Government Decree of the Russian Federation of October 19, 2012 No. 1069 [13].

The resulted precipitate is sent for processing (drying) and conditioning according to the process flowchart adopted at the enterprise.

The regenerating solution after being treated from radionuclides on sorption filters is reused until it can be categorized as liquid radioactive waste according to the radiation-process analysis. After that, the solution is sent for processing and conditioning in accordance with the process flow chart adopted at the enterprise. Spent selective sorbents of the sorption filters are also sent for processing (drying) and conditioning according to the process flowchart adopted at the enterprise.

The receiver tank (trap) [11] is returnable, i. e., after the spent ion-exchange resin is washed, it is decontaminated (if necessary) [11] and shipped to a nuclear facility, where it is loaded again with spent intermediate-level ion exchange resin.

Having successfully completed the R&D, RMTB Onega has finalized the designs of a unit fitted with a receiver tank (trap) that would be operated to reduce the activity of spent ion-exchange resins at the Zvezdochka site [11].

The dried low-level ion-exchange resin would be further managed at the Zvezdochka site according to the following flowchart:
- the dehydrated low-level ion-exchange resin is loaded into B31A2-216.5 drums, in which it is ultimately dried (if the content of free liquid in the ion-exchange resin exceeds 3%) according to [14], [15];
- the dried low-level ion-exchange resin is loaded into a certified NZK-150-1.5P(IOS) container (if the content of free liquid in the ion-exchange resin does not exceed 3 %);
- parameters of the certified NZK-150-1.5P(IOS) container loaded with dried low-level ion-exchange

resin are measured to check their compliance with the waste acceptance criteria [16];
- the containers are handed over to NO RAO for long-term storage and disposal.

After being washed in a receiver tank (trap), 1.4 m^3 of dried low-level ion-exchange resin is generated from 2.17 m^3 of spent intermediate-level ion-exchange resin [11].

In accordance with the NP-093-14 requirements [17], no prior immobilization is required in case of RW Class 4 disposal.

The studies and calculations presented in the article [18] show that the resulting ion-exchange resin, the free liquid content in which does not exceed 3%, can be stored in certified NZK-150-1.5P(IOS) containers for 300 years with no radionuclide releases expected to occur outside the container walls.

A single certified NZK-150-1.5P(IOS) container is required to condition 1.4 m3 of dried low-level ion-exchange resin.

Table 3 presents the costs calculated for the dried spent low-level ion-exchange resin (RW Class 4 as per the RW classification system according to the disposal route) when the waste is conditioned and shipped by NO RAO.

Table 3. Conditioning and transportation costs calculated for RW Class

Items	Cost, RUB
Purchase unit cost per certified NZK-150-1.5P(IOS) container	184,400.00
Transportation unit cost per certified NZK-150-1.5P(IOS) container loaded with Class 4 RW from the Zvezdochka site (Severodvinsk, Arkhangelsk Region) when shipped to the NO RAO site	145,861.00
The tariff accounting for the transfer and disposal of a single certified NZK-150-1.5P(IOS) container with Class 4 RW	175,745.52
Total:	506,006.52

Note: the disposal cost is set according to the NO RAO tariffs established for RW Class 4 as of 2023.

Thus, the above method proposed for spent intermediate-level ion-exchange resin management at the Zvezdochka enterprise is believed to reduce the specific activity to the level of low-level waste preventing the overexposure of personnel engaged in the waste management process and to reduce the inventory of spent intermediate-level ion-exchange resins stored at the RW storage facilities of the enterprise. Thereby, the radiation situation may improve both at the enterprise site and in the region as a whole reducing the negative environmental impact produced by the harmful substances.

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