

FSUE RADON'S EXPERIENCE IN THE CONDITIONING OF SPENT RADIOACTIVE ION EXCHANGE RESINS FROM THE KALININ NPP

Ostashkina E. E., Savkin A. E., Slastennikov Yu. T.

Research and Production Complex – Sergiev Posad Branch of the Federal State Unitary Enterprise
Joint Ecological-Technological and Research Center for Disposal of Radioactive Waste and Environmental Protection,
Sergiev Posad, Moscow region, Russia

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The paper discusses the practice applied by FSUE Radon, namely, by the NPK – Sergiev Posad branch to the conditioning of spent ion exchange resins from the Kalinin NPP: they are immobilized within a polymer waste form using a purposely designed and manufactured pilot unit. Based on the laboratory and methodological capacities of the enterprises, the study demonstrates the compliance of the obtained polymer compound and the waste packages with relevant quality indicators and acceptance criteria provided for by the regulatory requirements.

Keywords: radioactive waste, quality indicators, acceptance criteria, polymer compound, spent ion exchange resins, test procedures.

Introduction

FSUE RADON has developed and commissioned a pilot plant designed to condition spent ion exchange resins (SIER): they are dehydrated and immobilized into polymer binders based on Russian-made epoxy resins by impregnation in a disposal container [1].

In 2019, trial conditioning of a SIER batch from a special waste treatment station operating at RADON site was implemented to check the performance of the unit and whether the final product would meet relevant regulatory requirements [2], [3]. The next step that would further promote this method is seen in demonstrating the reference nature of this installation through its testing at different enterprises, and more specifically the feasibility of its application in the processing of accumulated SIER inventories with different fractional compositions and specific activity levels. Another important goal

is seen in providing further transfer of conditioned waste to the National Operator, which requires the compliance assessment of the resulting product with relevant regulatory requirements. For this reason, the resulting polymer compound with SIER inclusions should be characterized by some quality indicators meeting both the NP-019-15 requirements [4] and the acceptance criteria for disposal set forth in the NP-093-14 [5].

In 2022, the following activities were implemented by RADON's Sergiev Posad branch to address the above tasks:

- the proposed conditioning method was tested at a pilot plant based on a SIER batch shipped from the Kalinin NPP;
- measurement techniques enabling the assessment of conditioned SIER compliance with relevant quality indicators and acceptance criteria set

forth in relevant regulations were developed and approved;

- necessary research was implemented to demonstrate the compliance of polymer compound with SIER inclusions from the Kalinin NPP with relevant quality indicators and acceptance criteria for disposal.

Experimental part

Characteristics of SIER from the Kalinin NPP

The proposed SIER conditioning method was tested at a pilot-production unit based on genuine radioactive waste (RW) from the Kalinin NPP. The first SIER batch had a total volume of 7.6 m³: the waste was shipped to site in primary packaging, i. e., 200-liter drums.

According to initial data on the SIER origin, these materials were used at SVO-5 facility to treat the water supplied from steam generators. At most NPP, such treatment systems are fitted with cation exchange filters utilized as mechanical filters; then the treated water is supplied to two recoverable filters filled with cation and anion exchangers.

SIER from the Kalinin NPP were subjected to granulometric analysis, which confirmed their origin and revealed three main types of resins, the characteristics of which are presented in Table 1.

Table 1. SIER particle size distribution

Particle fraction size, mm	Fraction content, %		
	Cation resin with mechanical impurities	Cation resin with no mechanical impurities	Mixture of cation resin and anion resin with no mechanical impurities
More than 1.25	0.5	0.2	2.8
From 0.9 to 1.25	2.1	12.8	9.4
From 0.63 to 0.9	21.4	64.7	54.1
From 0.315 to 0.63	59.4	18.5	28.8
From 0.16 to 0.315	7.1	0.9	2.8
From 0.08 to 0.16	5.9	0.2	0.6
Less than 0.08	3.6	2.8	1.4
Less than 0.315	16.6	3.9	4.8

Table 1 shows that the cation exchanger with mechanical impurities contained up to 16.6% of small particles (with a size of less than 0.315 mm). Thus, impregnation of this SIER type with a polymer binder could be somewhat complicated due to their large inventory.

Visual assessment showed that fractions with a particle size of less than 0.16 mm (black suspension) were free of SIER. Their chemical

composition was evaluated to select an appropriate treatment method, which was done based on the Kvant atomic adsorption device and a KFK-3M photo colorimeter. The following results were obtained, wt. %:

Fe₂O₃ — 77, Cr₂O₃ — 0,79, NiO — 2,5, SiO₂ — 13,3.

The above chemical composition indicates that these fractions were mainly represented by inorganic sludges of a corrosive origin, the presence of which is considered common for in-reactor aqueous solutions.

Gamma spectrometric measurements showed that according to its radionuclide composition SIER contained such basic radionuclides as cesium-137, cesium-134 and cobalt-60. The measured specific beta activity accounted for (2–4)·10⁵ Bq/kg.

SIER conditioning method and implementation of this process at a pilot-production unit

The method proposed for SIER conditioning at the pilot-production facility suggested that their pulp was dispensed into certified containers, the designs of which were able to provide in-container resin dehydration and impregnation with a polymer binder. The conditioning process involved the following key operations (Figure 1a):

- SIER supply via montjus and pulp thickening in the dispenser;
- container filling with condensed pulp from the dispenser unit using compressed air;
- in-container SIER dehydration by vacuuming;
- in-container SIER impregnation with a polymer binder.

SIER conditioning at the pilot-production unit provides for the use of two container designs: KMZ-RADON-IO5 and NZK-150-1.5P with an insert. The KMZ container and the NZK insert are similar in their designs involving a single common feature, which are the top and the bottom partitions with screen meshes (Figure 1b). At the container filling stage, the ion exchange resin is fed into the space between these partitions. SIER pulp loaded into it is dehydrated via free liquid filtering through the bottom partition into the bottom drainage cavity, which is further removed by vacuum. At the SIER impregnation stage, a polymer binder (a mixture of epoxy resin and hardener) is fed under the bottom partition until the container gets filled completely from its bottom to the top.

SIER from the Kalinin NPP containing no mechanical impurities were basically conditioned in a routine manner. In case of cation resin with some mechanical impurities SIER supply through the pipelines could be potentially hampered with some in-container dehydration and impregnation of the resin that could be expected as well.

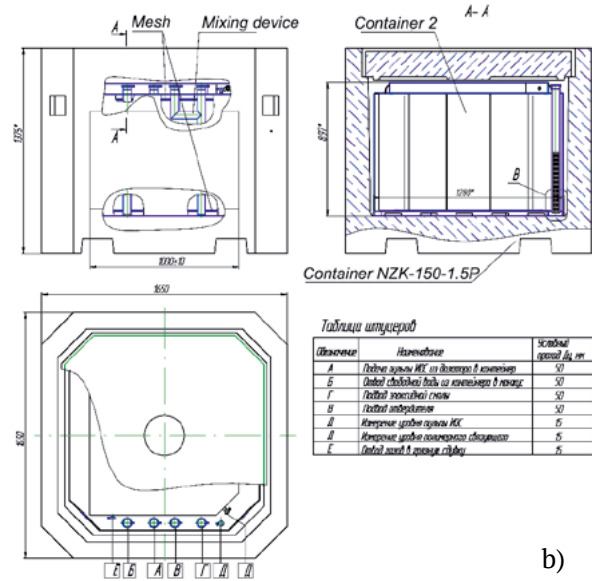
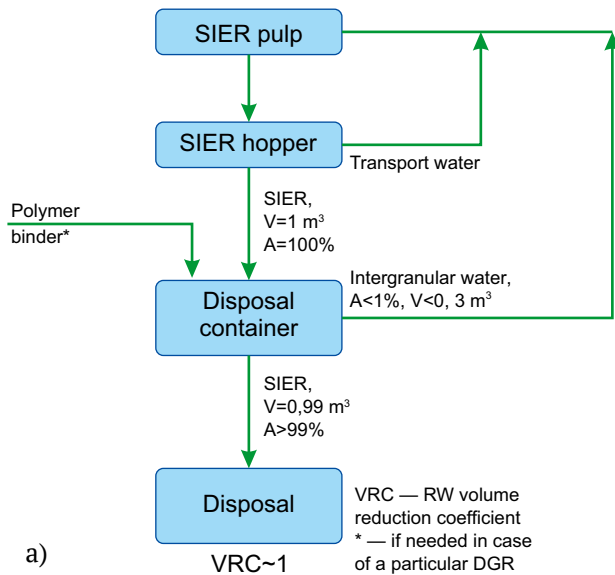


Figure 1. SIER dehydration and inclusion into a polymer binder: a) flowchart of the process; b) NZK-150-1.5P container with an insert

The SIER was purposely pretreated to provide its better fluidity: process water was poured into 200-liter drums previously used for its shipment to the site. The water was supplied through a metal pipe lowered to the drum bottom until it became visible above the resin layer. To acquire adequate fluidity level, the SIER pulp was exposed to water for several hours, then it was pumped by vacuuming from the drums into the montjus of the pilot-production unit and then into dispenser using compressed air. Table 2 presents the main impregnation parameters for the SIER containing no mechanical impurities.

Table 2. Impregnation of SIER containing no mechanical impurities

Impregnation parameter	Impregnation time, min					Completion of the process
	Onset of the process	5	10	12	14	
Epoxy resin consumption, m ³ /h	1.2	1.2	1.2	0.9	0.65	0.65
Hardener consumption, m ³ /h	0.8	0.8	0.8	0.6	0.42	0.42
Pressure in the container, atm	0.31	0.67	0.93	1.0	1.1	0.63

In 16 minutes since the launch of the impregnation process, the container was filled with a polymer binder and the pumps were turned off.

Upon completing the impregnation process, samples of the polymer compound with SIER inclusions were taken to measure its quality indicators. Figure 2 presents the external appearance of a filled container.

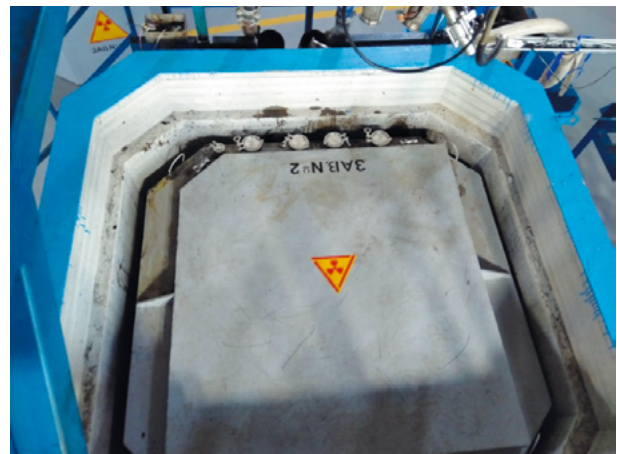


Figure 2. External appearance of NZK-150-1.5P container with an insert filled with SIER from the Kalinin NPP at the post-impregnation stage

Compared to SIER with no visible inclusions, it took much more time to dehydrate cation exchange resin containing some mechanical impurities in the container, which could be possibly explained by container's bottom mesh clogging with small fractions. Subsequent stabilization of the SIER impregnation process with a polymer binder has required the resin to be washed bottom-up inside the container with some technical water. Thus, the fraction of particles with a size of less than 0.315 mm in the resins dropped to 6.6% (Table 3), thereby enabling effective impregnation of the resin with a polymer binder, the results of which are presented in Table 4.

The time required for container filling with polymer binder accounted for 15 minutes.

Table 3. Granulometric composition of cation exchanger with mechanical impurities at the post-washing stage

Particle fraction size, mm	Fraction content, %
More than 1.25	0
From 0.9 to 1.25	4.9
From 0.63 to 0.9	41.7
From 0.315 to 0.63	46.9
From 0.16 to 0.315	6.6
From 0.08 to 0.16	0
Less than 0.08	0
Less than 0.315	6.6

Table 4. Impregnation of washed cation exchange resin with mechanical impurities

Impregnation parameter	Time, min					
	Onset of the process	2	4	10	15	Completion of the process, 21
Consumption of epoxy resin, m ³ /h	0.9	0.9	0.9	0.9	0.9	0
Consumption of hardener, m ³ /h	0.6	0.6	0.6	0.6	0.6	0
Pressure in the container P, at	0.30	0.51	0.61	0.62	0.78	0.33

Due to in-container SIER washing with water, its subsequent impregnation with a polymer binder could be implemented with no changes expected in polymer consumption along the process. In this case, the pressure at the container’s inlet did not exceed 0.78 at (0.078 MPa). Upon completing the impregnation process, the compound was sampled to measure its quality indicators.

The washing water was fed into a settling tank, in which, after the fine fraction separation process was completed, the sludge was cemented.

The following parameters were monitored along this process:

- mass ratio of hardener/epoxy resin — 0.6;
- the calculated SIER content in the polymer compound ranging from 59 to 71 wt. %;
- impregnation time — 11–15 minutes;
- container wall temperature during the impregnation process (no more than 40 °C).

Table 5 considers an example of a single container presenting the duration of the key stages constituting to the SIER conditioning process implemented at the RADON enterprise.

It should be noted that the performance indicators have been calculated with no account taken of any auxiliary operations, therefore, they actually appear to be somewhat lower amounting to ~0.5 m³/h.

Table 5. Duration of the key operations

No.	Name of the stage	Duration, min
1	Montjus filling	8
2	Dispenser filling	21
3	Container filling	8
4	SIER in-container dehydration	19
5	SIER impregnation with epoxy compound	11
Total time, min		67
Volume of dehydrated SIER, m ³		1.2
Dehydration and impregnation performance, m ³ /h		1.1

Compliance assessment of SIER-based polymer compound with regulatory requirements and preparation of relevant documentation

According to relevant recommendations [7], RW compliance with quality indicators and acceptance criteria for disposal should be demonstrated based on their characteristics and properties measured before, during and after the waste conditioning operations with the adequate reliability of the results obtained provided through the use of certified measurement techniques.

RADON enterprise has developed and has been implementing the measurement methods applicable to most of the required quality indicators and acceptance criteria. However, no adequate methods appeared to be in place to evaluate the quality indicators of a polymer compound with SIER inclusions and to confirm its compliance with the NP-019 provisions [4]. Thus, in 2022, the following missing measurement methods were developed [6]:

- MI-206-2022 (FR.1.28.2022.44467) Measurement technique for the free liquid content in ion exchange resin;
- MI-207-2022 (FR.1.28.2022.44463) Measurement technique. Polymer compound evaluation in terms of its quality indicators. Thermal and radiation resistance of a polymer compound generated from ion-exchange resin conditioning measured based on its mechanical strength level (compressive strength);
- MI-208-2022 (FR.1.28.2022.44465) Measurement technique. Polymer compound evaluation in terms of its quality indicators. Radiation resistance of a polymer compound generated from ion-exchange resin conditioning measured based on the volume change indicator;
- MI-209-2022 (FR.1.38.2022.44462) Measurement technique. Polymer compound evaluation in terms of its quality indicators. Water resistance (tritium and cesium-137 leaching rates), thermal and radiation resistance of a polymer compound generated from ion-exchange resin conditioning.

A series of tests focused on the fire hazard properties of a polymer compound with SIER inclusions was implemented in accordance with the GOST 12.1.044 by an accredited laboratory run by a specialized organization, namely, Federal State Budgetary Institution VNIPO EMERCOM of Russia (accreditation certificate No. TRPB.RU.INO2) [9].

Assessment of polymer compound with SIER inclusions from the Kalinin NPP for its compliance with quality indicators and acceptance criteria for disposal

Mechanical strength of the polymer compound samples was measured with the following results obtained from the tests:

- samples that have suffered no preliminary exposure — from 6.1 to 10.61 MPa;
- samples at the post-irradiation stage — from 6.58 to 11.50 MPa;
- samples subjected to thermal exposure — from 10.65 to 20.32 MPa.

As can be seen from the above results, the mechanical strength levels for all the polymer compounds sampled from all containers did exceed the standard one established for the cement compound at a level of 4.9 MPa.

Due to thermal and radiation exposure, this indicator was found to be higher for all the collected samples. Therefore, one can assume the stability of the polymer compound structure with SIER inclusions.

Thus, the indicated polymer compound was able to meet the requirements of the NP-019 [4] for thermal and radiation resistance and the NP-093 [5] for the mechanical strength level.

Irradiation has contributed to a decreased sample volume, which was observed in almost every studied case. This phenomenon may guarantee the container integrity during its long-term storage. In all cases, the observed changes in the sample volume did not exceed 5%. Thus, polymer SIER-based compound samples showed higher radiation resistance than the level specified in the regulatory requirements established for bitumen compounds [8]. Therefore, the observed volume changes have demonstrated their compliance with the NP-019 requirements [4] for radiation resistance.

Already on the first testing day, samples with SIER inclusions demonstrated their compliance with the NP-019 requirements [4] according to the ¹³⁷Cs leaching rate, as well as radiation and thermal resistance indicators. Polymer compound subjected to no thermal and radiation impacts demonstrated its compliance with the NP-019 requirements [3] according to the tritium leaching rate on the seventh day of testing. Upon completing relevant

thermal and radiation tests, this indicator did meet the regulatory requirements already on the first testing day.

Gas release from the polymer compound was measured as well: gas phase volume reached its maximum in the first 15 minutes since the onset of the sample hardening process. Since slight exothermic effect (up to 40 °C) was observed in the very beginning, this increase could most likely be explained by thermal expansion of the air remaining inside the laboratory installation. At the polymer compound sample storage stage, the observations revealed no increase in the gas phase volume.

Polar-2Ex gas analyzer was used to measure the content of harmful substances in the air. Subsequent analysis showed that the air contained solely some SIER element compounds (CO, NO_x, SO₂, H₂S, NH₃, CH₄). Their concentration in the gas phase did not exceed the threshold concentrations established for the workplace air.

Based on the above, the polymer compound with SIER inclusions was recognized as meeting the NP-093 requirements [5] considering the thresholds established for toxic gas, aerosol and sublimate releases, as well as the concentrations of chemical toxic substances.

Fire hazard properties of a polymer epoxy resin-based compound with SIER inclusions were evaluated according to the GOST 12.1.044-89 provisions [9]. The following indicators have been revealed for the tested samples:

- the average time needed for a sample to reach the maximum superheat level amounted to 189 seconds;
- ignition temperature — 355 °C;
- self-ignition temperature — 515 °C.

According to the RB-155 provisions (namely, clause 47) [7], a time period of over 0.5 minutes required to reach the maximum overheating level allows to consider such compound as not belonging to the category of solid flammable substances (materials).

Ignition and self-ignition temperatures established for the polymer compound samples evidence that these neither can get ignited in case of their exposure to air for 5 minutes nor get self-heated in case of air exposure as long as there's no external energy supply, i. e., that these samples should not be referred to the category of substances prone to spontaneous combustion.

The evaluated fire safety criteria showed that the polymer compound can be referred to the category of combustible material with an intermediate flammability level.

Consequently, the polymer compound with SIER inclusions meets the NP-093 requirements [5]

regarding the content of flammable and spontaneously combustible substances and the susceptibility to spontaneous ignition.

Conclusion

In 2022, RADON enterprise and more specifically its Sergiev Posad branch conditioned a total of 7.6 m³ of SIER from the Kalinin NPP.

To demonstrate the compliance of the polymer compound itself and the packages with such compound with relevant quality indicators and acceptance criteria for disposal, appropriate measurement techniques have been developed, approved and certified. As a result, the enterprise managed to prepare the entire set of documentation required to demonstrate the compliance of the polymer compound containing SIER inclusions with the requirements set forth in the NP-019 and the NP-093 provisions.

Polymer compound samples were taken from all containers with SIER delivered from the Kalinin NPP site and conditioned at the pilot-production unit. According to the study, the final product and the packages were found to be meeting relevant quality indicators and acceptance criteria for disposal.

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Information about the authors

Ostashkina Elizaveta Evgenyevna, leading process engineer, Research and Production Complex — Sergiev Posad Branch of the Federal State Unitary Enterprise Joint Ecological-Technological and Research Center

for Disposal of Radioactive Waste and Environmental Protection (5, Shemetovo village, ter. RADON, Sergiev Posad city district, Moscow region, 141335, Russia), e-mail: EEOstashkina@radon.ru.

Savkin Alexander Evgenevich, Ph. D., leading process engineer, Research and Production Complex – Sergiev Posad Branch of the Federal State Unitary Enterprise Joint Ecological-Technological and Research Center for Disposal of Radioactive Waste and Environmental Protection (5, Shemetovo village, ter. RADON, Sergiev Posad city district, Moscow region, 141335, Russia), e-mail: AESavkin@radon.ru.

Slastennikov Yuri Tovievich, lead engineer, Research and Production Complex – Sergiev Posad Branch of the Federal State Unitary Enterprise Joint Ecological-Technological and Research Center for Disposal of Radioactive Waste and Environmental Protection (5, Shemetovo village, ter. RADON, Sergiev Posad city district, Moscow region, 141335, Russia), e-mail: YTSlastennikov@radon.ru.

Bibliographic description

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