METHODOLOGICAL SUPPORT FOR MONITORING COMPLIANCE WITH QUALITY INDICATORS OF A POLYMER COMPOUND BASED ON RADIOACTIVE SPENT RESINS

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NPK Sergiev Posad branch of FSUE RADON has developed a methodological support enabling quality control of polymer compounds with inclusions of spent ion-exchange resins produced by a pilot plant. Polymer compound quality indicators calculated based on a statistical data set indicate its compliance with regulatory requirements.

Keywords: *radioactive waste, quality indicators, acceptance criteria, polymer compound, spent ion exchange resins, methodological support.*

Introduction

A pilot plant providing spent ion exchange resin (SIER) conditioning has been developed and assembled at FSUE RADON. The conditioning method involves SIER dehydration and its incorporation into a polymer binder based on epoxy resins produced in Russia by impregnation in a disposal container [1], [2].

Compliance of the resulting product with relevant regulatory requirements is seen as a must when it comes to the application of different radioactive waste (RW) conditioning methods, as well as providing further RW transfer to the National Operator. For this reason, the quality indicators of the polymer compound with SIER included into it shall meet the requirements set forth in NP-019-15 [3], as well as the acceptance criteria for disposal discussed in NP-093-14 provisions [4].

According to the recommendations provided in RB-155 [5], RW compliance with relevant quality indicators and acceptance criteria for disposal shall be demonstrated based on such an approach that would help to identify RW characteristics and properties before, during and after waste conditioning, whereas the reliability of the results obtained shall be provided by the application of certified measurement techniques.

NPK Sergiev Posad branch of FSUE RADON has a sufficient variety of such methods that can be used to check the compliance with the regulatory limits set for the cement compounds. Nevertheless, no such methods have yet been developed by the enterprise for the polymer compounds.

To demonstrate the compliance with the regulatory requirements specified for SIER conditioning at the pilot plant, a methodological support system has been developed to monitor the compliance of the obtained polymer compound with relevant quality indicators.

Experimental part

According to the regulatory requirements at the first stage of the project, the methods developed had to address the following tasks:
- to measure the free liquid contained in the SIER;
- to calculate thermal and radiation resistance of a polymer compound with SIER inclusions based on mechanical strength indicator (ultimate compressive strength);
- to calculate the radiation resistance of polymer compounds in terms of their volume changes;
- to calculate water resistance (leaching rate of tritium and cesium-137 radionuclides), thermal and radiation resistance of the polymer compound (according to this indicator).

To provide a statistical data array, polymer compound samples with inclusions of SIER from the special water treatment plant (SVO) operated by FSUE RADON, as well as those with SIER from the Kursk NPP were collected: their content in the polymer compound amounted to 60 % wt., whereas the hardener/epoxy weight ratio was equal to 0.7. Table 1 summarizes the data from radiometric and spectrometric evaluations focused on the applied SIER.

Epoxy resin Etal-247 and hardener Etal-45M produced by JSC ENPC EPITAL were used as components of the polymer binder.

10 basic elements were selected during the development of each measurement technique. To collect statistical data, two (three) parallel measurements were implemented for each element by two operators. In total, more than 900 measurements of various indicators have been performed.

Applied methods and equipment

The content of free liquid in the ion exchange resin was measured with an account taken of the following moisture bonding forms:
- chemical (hydrate, moisture of complex compounds);
- physical and chemical (adsorption and osmotic moisture);
- physical and mechanical (moisture of microcapillaries);
- surface moisture and macrocapillary moisture.

The free liquid in the ion-exchange resin may refer to surface moisture and macrocapillary moisture. It could be removed from the material mechanically (centrifugation, pressing, vacuum treatment).

The technique has been developed with an account taken of a method used to measure the content of free (unbound) liquid in the SIER based on the calculated amount (mass) of water removed from the material. This process involved vacuum treatment provided by a pump, a flask with a tube and a Buchner funnel.

According to NP-019 provisions [3], radiation and thermal resistance of materials depends on their ability to maintain their structure and properties (strength, water resistance, volume) under temperature and radiation impacts.

According to RB-155 [5], the structural stability of conditioned waste forms depends on their ability to maintain their mechanical properties under expected storage and (or) disposal conditions. Mechanical strength (ultimate compressive strength) is considered such an indicator for a polymer compound. According to RB-155 requirements, radiation resistance of a polymer compound is characterized by a change in the volume of its sample driven by its irradiation (%).

Given the circumstances indicated above, changes in the following indicators were considered during the development of relevant methods to calculate the radiation and thermal stability of a polymer compound:
- mechanical strength (ultimate compressive strength);
- volume of the compound sample;
- water resistance (leaching rate for tritium and cesium-137 radionuclides).

Polymer compound specimens with SIER inclusions were subjected to temperature testing implemented in the MK-53 climate chamber with the RHM-gamma-20 unit that provided their irradiation.

IR-5047-50S tensile testing machine was used to measure their mechanical strength.

Volumetric changes in polymer compound samples were measured by the gravimetric method using a volumetric meter. This device measures the

Table 1. SIER testing results used for statistical data collection purposes

SIER type	Specific activity, Bq/kg					
	α-activity according to Pu standard	β-activity according to ^{9}0Sr + ^{90}Y standard	^{137}Cs	^{60}Co	^{94}Nb	^{90}Sr
SIER from Kursk NPP	$4.9 \cdot 10^4$	$2.85 \cdot 10^7$	$4.3 \cdot 10^7$	$2.8 \cdot 10^6$	$6.6 \cdot 10^5$	$2.95 \cdot 10^6$
Anion resin from RADON	-	$5.3 \cdot 10^3$	$3.3 \cdot 10^2$	$1.1 \cdot 10^4$	–	–
Cation resin from RADON	-	$1.3 \cdot 10^6$	$1.0 \cdot 10^6$	$1.1 \cdot 10^4$	–	–

mass of distilled water displaced by the sample being completely immersed into it [6]. It is a cylindrical vessel, the size of which is sufficient to test the samples with their size that may be ranging from 20 to 100 cm^3. The vessel is equipped with a tube that has a curved bottom tip. Its inner diameter may range from 8 to 10 mm.

The change in the volume of the polymer compound samples due to their irradiation (ΔV, %), expressed as a percentage of the initial volume, was calculated based on the following expression:

$$\Delta V = \frac{(V_0 - V_1)}{V_0} \cdot 100, \quad (1)$$

where V_0 is the volume of the polymer compound sample before its irradiation, cm^3; V_1 is the volume of the polymer compound sample after its irradiation, cm^3.

The water resistance of a polymer compound (leaching rate for tritium and cesium-137) is characterized by the release rate of radionuclides into the aquatic environment upon their contact with the latter. The leaching rate of tritium and cesium-137 radionuclides from the polymer compound was evaluated taking into account GOST R 52126 requirements [7]. In this case, the samples were exposed to a certain volume of distilled water. During the measurements, at certain intervals, the distilled water that had come into contact with the sample was replaced with a new portion of water. When exposed to water, the activity of radionuclides that passed into the water over a given time interval was measured with the leaching rate of radionuclides from the sample (R, g/(cm^2·day) measured over a given time interval according to the following expression:

$$R = \frac{a}{\bar{A}_0 \cdot S \cdot \tau}, \quad (2)$$

where α is the activity of the aqueous contact solution sampled after the nth leaching period, Bq; $\bar{A}_0$ is the specific activity of the polymer compound sample, Bq/g; S is the open surface area of the compound sample, cm^2; τ is the duration of the leaching period, days.

Water being in contact with the polymer compound sample was replaced after 1, 3, 7, 10, 14, 21, 28 days.

Mechanical strength, volume and water resistance of the polymer compound samples were measured with no preliminary treatment of the samples heated at temperatures ranging from 0 to 130 °C for 2—7 hours depending on the sample thickness and subjected to radiation exposure of $1 \cdot 10^4$ and $1 \cdot 10^6$ Gy.

Results

Statistical data was collected under the methodological support development process. Various indicators of polymer compound samples were measured and their compliance with relevant regulatory requirements was evaluated.

Their mechanical strength with no thermal and radiation effects involved was found to be ranging from 17.78 to 20.87 MPa. These indicators were found to be ranging from 20.24 to 22.84 MPa after the thermal tests had been performed, whereas the radiation exposure was found to be ranging from 16.45 to 24.81 MPa. Thus, changes in the mechanical strength caused by thermal and radiation exposure did not exceed 25 %. Since the regulatory framework provides no requirements for the mechanical strength of polymer compounds, these were compared with the cement compounds, the standard strength for which amounted to 4.9 MPa. The tests showed that this indicator for the obtained SIER-based polymer compound samples turned out to be much higher.

Changes in the volume of such samples exposed to irradiation at a dose of 1×10^4 Gy was found to be ranging from 1.12 to 1.78 %, whereas an exposure dose of 1×10^6 Gy resulted in a volume change of 3.68—4.21 %. Standard radiation resistance for the bitumen compound of 10 % was used as a guideline to calculate this indicator.

Even considering excessive radiation exposure at a dose of $1 \cdot 10^6$ Gy, the radiation resistance indicator calculated for SIER-based polymer compound samples did not exceed the regulatory limits set for bitumen compounds.

The rate of ^{137}Cs leaching from the polymer compound being subject neither to any thermal nor radiation effects was ranging from $1.0 \cdot 10^{-5}$ to $8.0 \cdot 10^{-4}$ g/(cm^2·day) already in the first testing day. However, after the thermal tests were completed, this indicator was found to be ranging from $1.0 \cdot 10^{-4}$ to $1.0 \cdot 10^{-3}$ g/(cm^2·day). After the radiation exposure test, the leaching rate exceeded $1.5 \cdot 10^{-4}$ g/(cm^2·day). All the ranges calculated for cesium-137 leaching rates, both before and after thermal and radiation exposure tests, did meet the requirements set forth in NP-019-15 [3].

The rate of tritium leaching from polymer compound not subject to any thermal and radiation effects reached the level set forth in NP-019-15 [3] on the seventh day of testing ranging from $9.6 \cdot 10^{-3}$ to $9.9 \cdot 10^{-3}$ g/(cm^2·day). Following the thermal tests, this indicator reached the regulatory level already on the first day and was ranging from $3.53 \cdot 10^{-3}$ to $4.05 \cdot 10^{-3}$ g/(cm^2·day). Following radiation exposure, it was found to be ranging from $2.34 \cdot 10^{-3}$ to $6.25 \cdot 10^{-3}$ g/(cm^2·day).

Table 2. Error characteristics relevant for polymer compound quality control methods

Name of the method		Accuracy indicator (bound of the measurement error), $\pm\delta_l$, rel. units, no more than	Intermediate precision limit, R_l, rel. units, no more than
Free liquid content measurement		0.06	0.08
Evaluation of thermal and radiation resistance based on mechanical strength indicators		0.25	0.34
Evaluation of radiation resistance based on volumetric changes	Dose of $1\cdot10^6$ Gy	0.37	0.53
	Dose of $1\cdot10^4$ Gy	0.12	0.17
Evaluation of tritium and cesium-137 leaching rate, thermal and radiation strength evaluation		0.13	0.45

Table 2 presents measurement error characteristics and in-process monitoring standards for all the developed methods.

Thus, NPK-Sergiev Posad branch run by FSUE RADON has developed a methodological support system. It was designed to monitor the compliance of polymer compounds with SIER inclusions produced by the pilot unit with relevant quality indicators.

The following methods have been developed:

- MI-206-2022 Measurement technique. Measurement of free liquid content in ion exchange resins;
- MI-207-2022 Measurement technique. Evaluation of quality indicators for polymer compounds. Thermal and radiation resistance of polymer compounds resulted from ion-exchange resin conditioning measured based on the mechanical strength (compressive strength);
- MI-208-2022 Measurement technique. Evaluation of quality indicators for polymer compounds. Radiation resistance of polymer compounds resulted from ion-exchange resin conditioning measured based on the volume changes;
- MI-209-2022 Measurement technique. Evaluation of quality indicators for polymer compounds. Water resistance (leaching rate of tritium and cesium-137 radionuclides), thermal and radiation resistance of a polymer compounds resulted from ion-exchange resin conditioning.

A set of statistical data was acquired, relevant errors were calculated and the developed methods were certified. The certificates were issued by the FSUE RADON's metrological service having appropriate accreditation for measurement uniformity provided under the activities (rendering services) for the certification of measurement techniques (methods). It was assigned with an ID number RA.RU.311520 in the register of accredited persons.

Theoretical and experimental studies of the developed certification programs provided a basis for such certification. The methods were introduced to the federal information fund providing the uniformity of measurements.

The quality indicators of the polymer compound identified during the statistical data acquisition indicate its compliance with regulatory requirements for quality indicators and waste acceptance criteria for disposal.

References

1. Ostashkina Ye. Ye., Savkin A. Ye., Slastennikov Yu. T. Opytno-promyshlennoe konditsionirovanie otrabotavshikh ionoobmennykh smol [Pilot Industrial Conditioning of Spent Ion Exchange Resins]. *Proc. of the IAEA International Conference on Radioactive Waste Management: Solutions for a Sustainable Future.* Austria, Vienna, November 1—5, 2021.
2. Ostashkina Ye. Ye., Savkin A. Ye., Slastennikov Yu. T., Sumenko A. V. Opytno-promyshlennoe konditsionirovanie otrabotavshikh ionoobmennykh smol [Pilot Industrial Conditioning of Spent Ion Exchange Resins]. *Sbornik dokladov chetvertogo nauchnotekhnicheskogo seminara "Problemy pererabotki i kondicionirovaniya radioaktivnyh othodov" [Proc. of the fourth scientific and technical seminar "Problems of Radioactive Waste Processing and Conditioning".* Saint-Petersburg, June 14—18, 2021.
3. NP-019-15. *Sbor, pererabotka, khraneniye i konditsionirovaniye zhidkikh radioaktivnykh otkhodov. Trebovaniya bezopasnosti* [Collection, Processing, Storage and Conditioning of Liquid Radioactive Waste. Safety Requirements].
4. NP-093-14. *Federal'nyye normy i pravila v oblasti ispol'zovaniya atomnoy energii. Kriterii priyemlemosti radioaktivnykh otkhodov dlya zakhoroneniya* [Federal Norms and Rules in the Field of Atomic Energy Use. Radioactive Waste Acceptance Criteria for Disposal].
5. RB-155-20. *Rukovodstvo po bezopasnosti pri ispol'zovanii atomnoy energii. Rekomendatsii po poryadku, ob"yemu, metodam i sredstvam kontrolya radioaktivnykh otkhodov v tselyakh podtverzhdeniya ikh sootvetstviya kriteriyam priyemlemosti dlya zakhoroneniya* [Safety Guidelines for Atomic Energy Use. Recommendations on the Procedure, Scope,

Methods and Means of Radioactive Waste Control to Confirm their Compliance with the Acceptance Criteria for Disposal].

6. Ostashkina E. E., Savkin A. E. Radiatsionnaya stoikost' organicheskikh kompaundov dlya otverzhdeniya zhidkikh radioaktivnykh otkhodov [Radiation resistance of organic compounds for LRW solidification]. *Radioaktivnye otkhody — Radioactive Waste,* 2021, no. 3 (16), pp. 44—50. DOI: 10.25283/2587-9707-2021-3-44-50.

7. GOST R 52126-2003. *Otkhody radioaktivnyye. Opredeleniye khimicheskoy ustoychivosti otverzhdennykh vysokoaktivnykh otkhodov metodom dlitel'nogo vyshchelachivaniya* [Radioactive waste. Chemical Stability of Solidified High-level Waste and its Evaluation by the Long-term Leaching Method].

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