SPENT ION EXCHANGE RESIN CONDITIONING TECHNOLOGY BASED ON THERMAL VACUUM DRYING METHOD

Sorokin V. T.[1], Prohorov N. A.[1], Pavlov D. I.[2]

[1]JSC ATOMPROEKT, Saint-Petersburg, Russia
[2]Saint-Petersburg branch of JSC FCNIVT SNPO ELERON — VNIPIET, Saint-Petersburg, Russia

Article received on April 04, 2021

The article deals with the issues associated with the conditioning of intermediate- and low-level spent ion exchange resins (SIER) by thermal vacuum drying method to obtain packages that would meet the acceptance criteria set for near-surface disposal.
The paper describes an experimental installation and the industrial technology of SIER dehumidification. For air conditioning of intermediate-level SIER, it proposes the use of certified reinforced concrete containers. As it comes to the conditioning of low–level SIER, it proposes plastic containers being similar in their designs to the metal ones. The paper also evaluates the compliance of SIER packages with relevant safety requirements.

Keywords: *radioactive waste, spent ion exchange resins, drying, reinforced concrete container, disposal.*

Introduction

Operation of water purification and liquid radioactive waste (LRW) treatment facilities at Russian nuclear facilities has resulted in over 30,000 m^3 of SIER accumulated to date. NPPs and other nuclear facilities in Russia are not fitted with any industrial facilities providing SIER processing and conditioning.

Application of SIER bituminization and cementing methods can increase the RW volume by 2—5 times.

Complex gas purification systems are required in case of SIER processing by thermal methods at high temperatures which also results in big amounts of secondary radioactive waste (RW).

SIER inclusion into polymeric materials is currently considered as a most promising processing method, nevertheless, requiring some additional research and feasibility demonstration.

Back in 2009, the authors of this publication proposed a conditioning method with SIER drying followed by its emplacement into reinforced concrete containers suggesting no matrix inclusion [1, 2].

This proposal is based on the estimated SIER properties and performed R&D and meets relevant regulatory requirements.

Analysis of SIER properties

Dried SIER is a solid granular material that can be considered as a form suitable for long-term storage and disposal, since it meets the general acceptance criteria for RW Class 3 and 4 classes, i. e., it does not contain substances:

- in powder form with high dispersibility;
- chemically unstable and strong oxidizing agents;

- corrosive substances;
- poisonous, pathogenic and infectious substances;
- biologically active substances;
- flammable and explosive substances;
- substances capable of detonation or explosive decomposition;
- substances capable of an exothermic interaction with water accompanied by an explosion;
- substances containing or capable of generating toxic gases, vapors or fumes.

It is important to note that radionuclides are firmly fixed in the structure of ion-exchange resins. Therefore, their treatment with strong acids and alkalis is required for their decontamination.

The moisture content of dried SIER (intergranular moisture content) intended for disposal should be less than 3%, which is provided by preliminary drying.

Table 1 shows the calculated radionuclide SIER composition assumed in the designs of the Novovoronezh NPP-2.

Table 1. Calculated volumetric activity of spent ion-exchange resins, Bq/m³ (Bq/g)

Nuclide	Intermediate-level SIER	Low-level SIER
^{89}Sr	$3.14 \cdot 10^8$ ($0.43 \cdot 10^3$)	$5.74 \cdot 10^5$ ($0.80 \cdot 10^0$)
^{90}Sr	$1.70 \cdot 10^8$ ($0.23 \cdot 10^3$)	$5.59 \cdot 10^5$ ($0.77 \cdot 10^0$)
^{134}Cs	$8.90 \cdot 10^{10}$ ($1.20 \cdot 10^5$)	$1.04 \cdot 10^3$ ($0.14 \cdot 10^{-2}$)
^{137}Cs	$1.38 \cdot 10^{11}$ ($1.92 \cdot 10^5$)	$1.62 \cdot 10^3$ ($0.23 \cdot 10^{-2}$)
^{58}Co	$2.88 \cdot 10^9$ ($0.40 \cdot 10^4$)	$2.24 \cdot 10^3$ ($0.31 \cdot 10^{-2}$)
^{60}Co	$7.81 \cdot 10^9$ ($1.08 \cdot 10^4$)	$5.30 \cdot 10^3$ ($0.74 \cdot 10^{-2}$)
^{144}Ce	$8.19 \cdot 10^8$ ($1.14 \cdot 10^3$)	$4.60 \cdot 10^5$ ($0.64 \cdot 10^0$)
^{144}Pr	$8.19 \cdot 10^8$ ($1.14 \cdot 10^3$)	$4.60 \cdot 10^5$ ($0.64 \cdot 10^0$)
TOTAL	$2.43 \cdot 10^{11}$ ($3.12 \cdot 10^5$)	$3.11 \cdot 10^6$ ($2.85 \cdot 10^0$)

The table shows that intermediate-level SIER belong to RW Class 3 according to the classification adopted by the Decree of the Government of the Russian Federation No. 1069 of October 12, 2012. Thus, if a SIER package meets the requirements established for the packages of this class, it can be disposed of in a near-surface disposal facility for radioactive waste (RWDF).

Low-level SIER are categorized as very low-level waste of RW Class 4 and can be disposed of in near-surface RWDF suggesting no emplacement into protective containers as provided for by the requirements [3].

Regulatory requirements for SIER packaging

In accordance with [4], RW of Class 3 not being included into the waste form matrix (such as non-recyclable solid RW, non-fragmented contaminated equipment, compressed RW, fragmented metal RW, dehydrated ion-exchange resins, salt melt) can be disposed of if the RW package meets the requirements established by federal norms and rules and the RW acceptance criteria for disposal set forth for a particular RWDF.

RW of Class 4 can be disposed of with no prior immobilization and (or) in unpackaged form given that such RW disposal method is provided for in the RWDF design and the disposed RW meets general acceptance criteria established by federal rules and norms for unpackaged RW of Class 4, as well as the RW acceptance criteria for disposal set forth for a particular RWDF.

Table 2 summarizes the main requirements established for RW packages of Class 3 and 4.

Table 2. Basic requirements for RW packages of Class 3 and 4

Requirements	RW class	
	3	4
Absorbed dose rate at the surface of a RW package	Not more than 2 mSv/h *	Not more than 0.05 mSv/h **
Mechanical strength	Not lower than the required value set forth in the transportation rules for A-type packaging	According to the values set forth in container conformity certificates
Containment capacity of the RW package	Service life of a package under disposal conditions should be not less than 100 years	N/a
Rate of radionuclide release from the package	No more than $1 \cdot 10^{-2}$/year for tritium; no more than $1 \cdot 10^{-3}$/year for beta- and gamma-emitting radionuclides; no more than $1 \cdot 10^{-4}$/year for alpha-emitting radionuclides	No more than $1 \cdot 10^{-4}$/year for alpha-emitting radionuclides
Container filling with radioactive or matrix material	Not less than 80%	Not less than 80% (excluding Big-Bag-type packages)

* Not more than 10 mSv/h under a special permit approved by the management of the operating organization and agreed upon with the national authority responsible for the conditioned waste disposal.

** Not more than 2 mSv/h under a special permit approved by the management of the operating organization and agreed upon with the national authority responsible for the conditioned waste disposal.

Description of the SIER drying flowchart

Thermal vacuum drying method was developed to form SIER packages of class 3 being considered suitable for disposal in a near-surface RWDF. This method provides complete removal of free liquid and partial removal of intragranular chemically bound liquid at a drying temperature ranging from 80 °C to 100 °C [5]. This avoids thermal degradation of resin, whereas the gaseous waste does not require any treatment from toxic products. Figure 1 presents relevant flowchart.

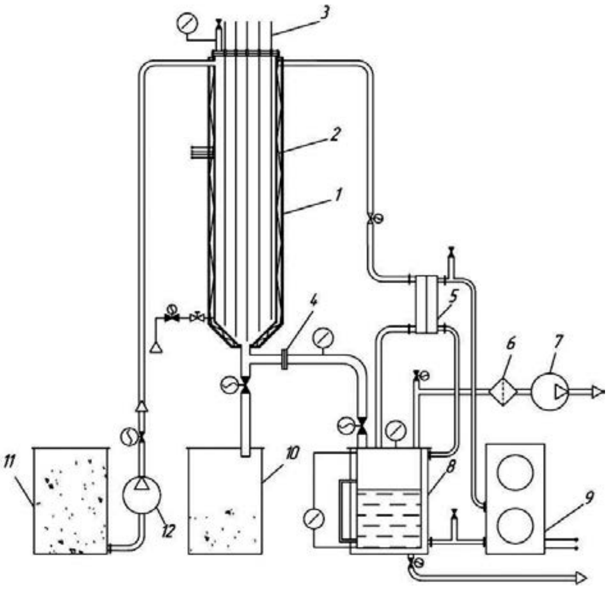

Figure 1. Process flow diagram for a SIER thermal vacuum drying unit:

1 — thermal reactor, 2 — external heaters, 3 — internal heaters, 4 — drainage device, 5 — condenser, 6 — aerosol filter, 7 — vacuum pump, 8 — condensate collector, 9 — chiller, 10 — dry SIER collector, 11 — slurry tank, 12 — impeller pump

To test the modes of SIER thermal vacuum drying, a full-scale pilot demonstration unit was developed and manufactured. In terms of its capacity and performance it meets the requirements set forth for industrial units. The unit is equipped with temperature sensors providing control over the drying process and the electrical power of the heaters in an automatic mode. Figure 2 presents a photograph of the unit.

Main technical characteristics of the unit:

- resin loading capacity — 0.1 m^3;
- overall dimensions — 2,050 × 1,580 × 3,500 mm;
- operating weight — 900 kg;
- installed electric power of the heaters — 10 kW;
- drying temperature — 80 °C — 100 °C;
- absolute pressure in the unit sufficient for the drying process — 4—6 kPa.

Figure 2. Pilot demonstration SIER drying unit

The SIER drying depth can reach a residual value of up to 30 % of the bound (intragranular) water. In this case, free moisture is completely absent. The dried product is poured freely from the installation into a container, as shown in Figure 3.

Figure 3. Pouring the dried product out of the resin dryer

The SIER volume to be processed by the installation at a time was set to 0.1 m^3 providing a processing capacity of 12.5—25 dm^3/h considering the initial resin. This volume can be taken as a baseline for further development of industrial units.

For example, for one WWER-1200 NPP unit, an installation of such a capacity is more than sufficient, since it is able to reprocess the annually generated SIER volume of 25 m^3 per 1,000—2,000 hours.

Dried SIER conditioning

Different modifications (designs) of reinforced concrete non-returnable shielded containers with different structural material densities and wall thicknesses (NZK-150-1.5P; NZK-150-1.5P (V); NZK-RADON) fitted with different metal or polymer inserts can be used for dried Class 3 SIER conditioning purposes. These containers should be sealed with a lid to prevent spilling during emergency depressurization of the protective container.

Table 3 presents the characteristics of the recommended reinforced concrete containers selected with due account of SIER radionuclide composition and activity based on the calculated dose rates at a distance of 1 m from the package surface.

Table 4 summarizes the main characteristics of metal and polymer inserts provided for in NZK-150-1.5P designs for Class 3 SIER.

Table 3. Characteristics of reinforced concrete containers

Name	Dimensions, mm	Wall thickness, mm	Concrete density, t/m^3	Container weight, t	Useful container capacity, m^3
NZK-150-1,5P	1,650×1,650×1,375	150	2.4–2.6	4.5	1.5
NZK -150-1,5P(V)	1,650×1,650×1,375	150	4.5	8.9	1.4
NZK -RADON	1,650×1,650×1,340	105	2.4–2.6	4.0	1.9

Table 4. Main characteristics of metal and polymer SIER inserts

Parameter	Parameter value	
	Metal (Sm-1,3)	BPS-1,3*
Height, mm	900	970 (without neck – 910)
Width, mm	1,290	1,290
Length, mm	1,290	1,290
Wall thickness, mm	6	8
Full volume, m^3	1.3	1.35
Net weight, no more, kg	360	60**
Gross weight, no more, kg	1,400	1,140
Material	St3 steel	Radiation resistant polyethylene / polypropylene **

*VPS - polymer SIER insert.
** Data to be specified during the development of design documentation.

More detailed characteristics of reinforced concrete containers and metal inserts are presented in a catalog [6].

Figure 4 shows a reinforced concrete container NZK-150-1.5P fitted with 2 types of inserts: of a metal type (Sm-1.3 commercially produced by the industry) and of a polymer type (VPS-1.3 currently being at the design development stage).

If the pretreatment of SIER Class 3 and 4 is performed separately, then it seems reasonable to use metal or polymer containers to package dried low-level SIER, which significantly facilitates their handling during further storage, transportation and disposal.

Figure 4. NZK-150-1.5P container and its inserts:
on the left – metal type Sm-1.3,
on the right – polymer type VPS-1.3

Figure 5. Containers for low-level SIER:
left - KRAD-1.36 container, right - KPS-1.4 container

The NZK container on the right is shown in section without a protective cap. In the upper part of the VPS-1.3 insert, there is a throat for SIER supply.

Figure 5 shows a metal container KRAD-1.36 and a polymer container KPS-1.4 for low-level SIER, the designs of which are currently being developed with the technical specifications being refined.

Lids of polymer containers can be sealed using an adhesive or by thermal welding.

Figure 6 presents sketches of the KPS-1.4 polymer container for Class 4 SIER and the VPS-1.3 polymer insert for the NZK-150-1.5P reinforced

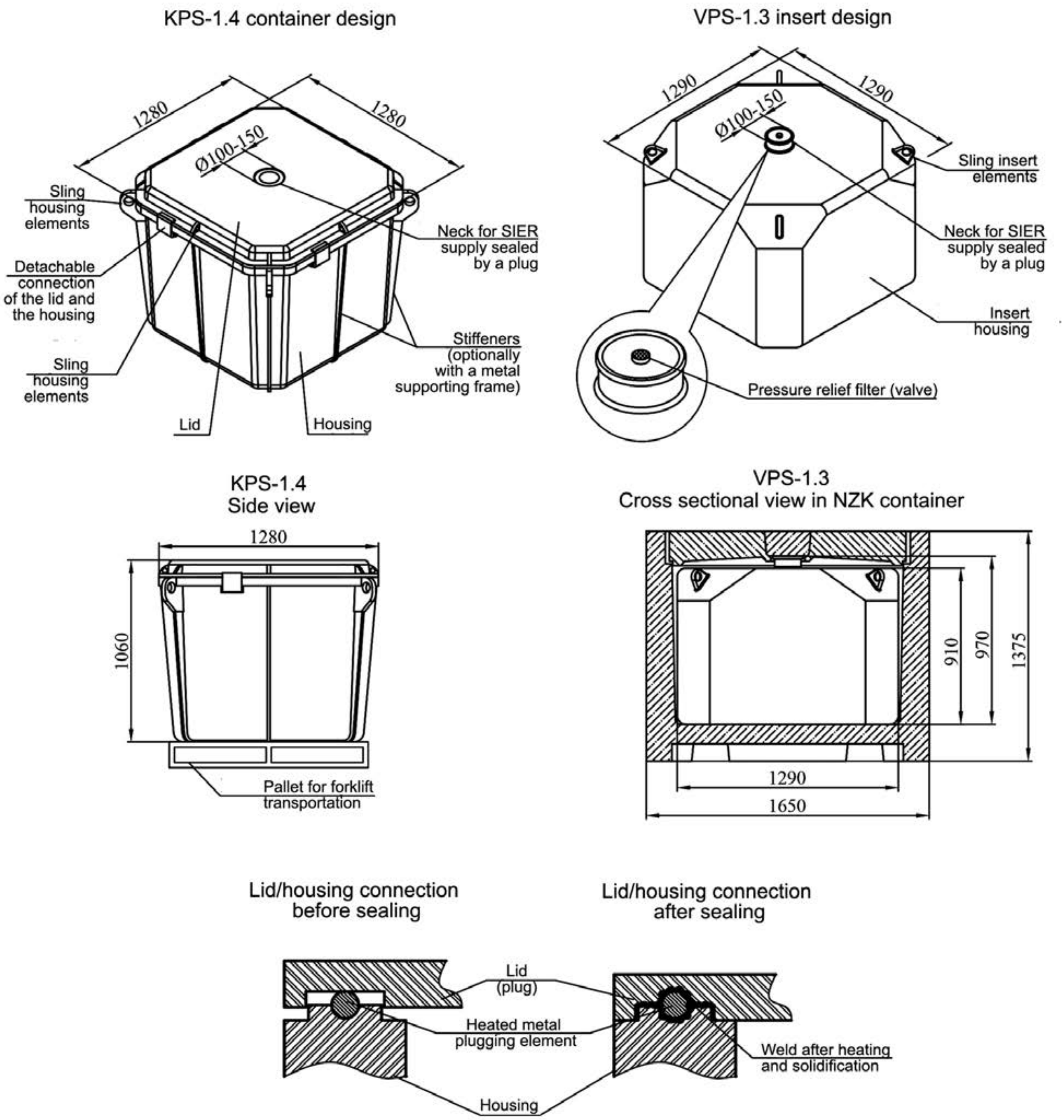

Figure 6. Designs of a polymer container for SIER Class 4 and VPS-1.3 polymer insert for the reinforced concrete NZK-150-1.5P container intended for SIER Class 3 packaging

concrete container intended for SIER Class 3. To seal an insert or a container, thermal welding of caps (plugs) was proposed: the metal insert constituting to the container structure and the insert along the perimeter of the "lid (plug) — body" connection is heated; when the embedded element is heated, the lid (plug) material and the body melts providing permanent connection upon their solidification. An electrical network or a remote unit (in case of the induction heating method) can be used for heating.

A ceramic filter (or a valve) is to be installed into the plug closing the neck of the insert for intermediate-level SIER providing the release of gaseous products generated due to the decomposition of Class 3 SIER and preventing the water from entering the polymer insert.

Table 5 shows the characteristics of containers for low-level SIER.

Table 5. Characteristics of containers for low-level SIER

Parameters	KRAD-1.36 characteristics	KPS-1.4 characteristics*
Empty weight, kg	280	80
Loaded weight, kg	Up to 1,400	Up to 1,200
Loading volume, m^3	1.4	1.4
Dimensions, mm	1,280×1,280×1,057	1,280×1,280×1,060
Wall thickness, mm	4	5
Sealing method	bolted-type connection	thermal welding
Service life, years	30	50
Number of tiers when stacked	7	7
Classification according to NP-053-14	type 2 (IP-2)	type 2 (IP-2)

* Data are being refined along with the development of design documentation.

Assessing the compliance of SIER packages with safety requirements

Summarized below is the assessment of the initial data and the performed calculations.

The NZK-150-1.5P container with a metal or polymer insert proposed for the intermediate-level SIER packaging meets all regulatory requirements set forth for RW Class 3 packages.

As regards 137Cs, the total activity of intermediate-level SIER in the NZK-150-1.5P package with a 1.3 m^3 metal insert accounts for $2.92 \cdot 10^{11}$ Bq, which meets the requirements set forth for type A packaging.

The dose rate on the package surface and at a distance of 1 m from it accounts for less than 2 mSv/h and 100 μSv/h respectively [7].

The service life of the certified reinforced concrete NZK-150-1.5P container amounts to more than 100 years.

During the long-term storage of intermediate-level SIER, their degradation can possibly occur due to the radiation effect from the radionuclides accumulated in the waste.

The calculations showed that for a resin with a specific activity of ~$3 \cdot 10^{11}$ Bq/m^3, the absorbed dose after 300 years of storage will be equal to some $3.7 \cdot 10^5$ Gy.

Chlorine ions, sulfate ions, and hydrogen ions account for the degradation products of the irradiated cation exchanger, while those of the irradiated anion exchanger involve methylamine, dimethylamine, trimethylamine, and ammonia.

Based on the data from [8] and considering a storage time of some 300 years, the calculated yield of degradation will be as follows:

- sulfates — 6.8 kg;
- chlorides — 1.7 kg;
- hydrogen ions — 0.19 kg;
- trimethylamine — 25 kg;
- dimethylamine — 8.5 kg;
- methylamine — 4.4 kg;
- ammonia — 2.4 kg.

To produce reinforced concrete NZK-150-1.5P containers, concrete of a high-water resistance grade W20 is used, thus, avoiding any water from entering the container for several hundred years even considering a humid environment. Dried resin emplaced into a polymer insert and sealed by a lid with a ceramic filter is seen as an additional barrier allowing to keep the SIER dry.

The total amount of gases generated over 300 years of storage will amount to some 40 kg, i. e., the average release rate will amount to 14.5 mg/h. The gases formed in the polymer matrix escaping through the ceramic filter will enter the free volume of the NZK-150-1.5P container and therefrom diffuse through its walls both by the concentration mechanism due to the concentration difference and by the filtration mechanism due to the growing pressure inside the container.

According to [9], resistance to air permeability of a 100-mm thick concrete layer would amount to 19,620 $m^2 \cdot h \cdot Pa/kg$. Accordingly, the permeability will amount to $5.1 \cdot 10^{-5}$ $kg/m^2 \cdot h \cdot Pa$. The wall thickness of the NZK container is 150 mm, therefore, the total wall area of the container is approximately 7.6 m^2. Even if the pressure inside the container is 1 Pa higher than the pressure in the container storage room, the rate of evacuated gases removal will be equal to:

$$(5.1 \cdot 10^{-5}/1.5) \times 7.6 = 25.9 \cdot 10^{-5}\ kg/h = 260\ mg/h.$$

The above air permeability of the reinforced concrete container appears to be much higher than the rate of gas generation due to SIER radiolysis.

When the resin is dry, the radionuclide release outside the container is practically excluded due to low diffusion coefficients in dry concrete [10].

If some water manages to enter the container, ammonia and amines formed during the decomposition of the anion exchanger will interact with water to form compounds of the methyl ammonium hydroxide type, which exhibit basic properties and are not corrosive.

Gases considered as being insoluble in water (hydrogen, trace amounts of nitrogen, carbon monoxide) will diffuse through the walls of the container. During container saturation with water, the concentration of sulfates, chlorides and other compounds will be ten times less than the one assumed to consider the solution aggressive to concrete.

Computational and experimental studies presented [11] suggest that the service life of concrete produced based on Portland cement at W20 will amount to 370 years considering the impact of a sulfate ion solution with a concentration of 5 g/l (Table 6). During this time, its performance will not decrease. In our case, this concentration will be achieved in 300 years.

Table 6. Service life of a Portland cement-based concrete of the Voskresensk plant

Sulfate ion concentration, mg/l	Service life of concrete, years		
	W/C=0.4 W8–W10	W/C=0.32 >W20	W/C=0.29 >W20
5,000	100	145	370
12,000	25	40	35
50,000	7	6	8

Studies focused on the diffusion permeability have shown that the radionuclides contained in the SIER will not escape the walls of the reinforced concrete container for over 300 years. Figure 7 shows the results of calculated ^{137}Cs diffusion in the concrete of a container wall.

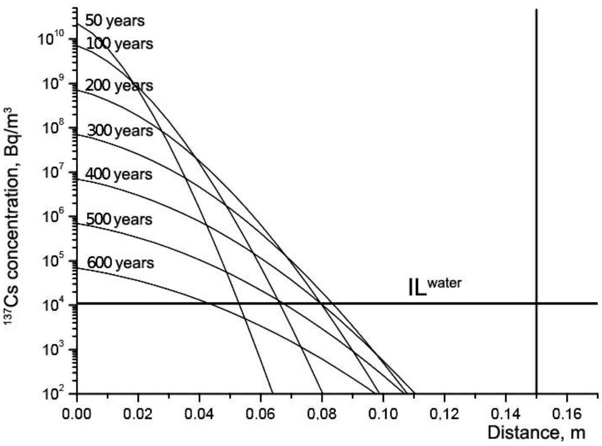

Figure 7. ^{137}Cs concentration in the pore moisture of a container wall

The horizontal line in the figure corresponds to the intervention level in water specified for ^{137}Cs — $1.1 \cdot 10^4$ Bq/m^3.

Due to the minor activity of low-level SIER, radiation effects during their storage and disposal could be neglected, which provided the opportunities for container sealing. The choice of an optimal method under such resin management option should be governed only by relevant cost considerations.

Conclusion

The method proposed for SIER conditioning suggesting its thermal vacuum drying and packaging into containers according to the RW class is considered as the simplest design option requiring no matrix material and providing no increase in the volume of the disposed waste. Assuming the application of reinforced concrete NZK-150-1.5P containers with polymer inserts, packages with dried intermediate-level SIER would meet modern waste acceptance criteria for disposal in near-surface disposal facilities.

Polymer containers complying with the requirements set forth for RW Class 4 packaging can be recommended for drained low-level SIER storage and disposal.

References

1. Sorokin V. T., Demin A. V., Prokhorov N. A. et al. Hranenie otrabotavshih ionoobmennyh smol niskogo i srednego urovnya aktivnosti v kontejnerah tipa NSK bes vklyucheniya v matricu [Storage of low- and intermediate-level spent ion-exchange resins in NZK-type containers with no matrix inclusion]. *Yadernaya i radiatsionnaya besopasnost — Nuclear and radiation safety,* 2009, no. 4, pp. 19—21.

2. Babkin D. N., Prokhorov N. A., Sorokin V. T. et al. Technologiya pererabotki i chraneniya otrabotavshih ionoobmennyh smol dlya AEhS novogo pokoleniya [Spent ion-exchange resins processing and storage technology for the new generation of nuclear power plants]. *Atomnaya ehnergiya — Atomic energy,* 2011, vol. 111, iss. 4, pp. 214—219.

3. SP 2.6.6.2572. *Obespechenie radiatsionnoj pri obrashchenii c promyshlennymi otchodami atomnych snantsiy, soderzhashchimi technogennye radionuklidy* [Radiation safety during the management of industrial waste from nuclear power plants containing technogenic radionuclides].

4. NP-093-14. *Federalnye normy i pravila v oblasti ispolsovaniya atomnoj ehnergii "Kriterii priemlemosti radioaktivnych otkhodov dlya zachoroneniya"* [Federal

norms and rules in the field of atomic energy use Radioactive Waste Acceptance Criteria for disposal].

5. Babkin D. N., Demin A. V., Iroshnikov V. V et al. *Ustanovka dlya termicheskoj pererabotki radioaktivnoj smoly. Patent na poleznuyu model* [Installation for radioactive ion-exchange resin thermal processing of. Utility model patent] No. 121396, 2012.

6. Oborudovanie dlya obrashcheniya s radioaktivnymi otkhodami na predpriyatiyakh GK Rosatom. Katalog AO 345 MZ [Equipment for radioactive waste management at the enterprises of the State Corporation Rosatom. JSC 345 MZ catalog], 2021.

7. Gataulin R. M., Davidenko N. N., Sviridov N. V. et al. *Kontejnery dlya ralioaktivnykh otkhodov nizkogo i srednego urovnya aktivnosti* [Containers for low and intermediate level waste]. Moscow, Logos Publ., 2012. 256 p.

8. Tulupov P. E. *Stojkost ionoobmennykh materialov* [Resistance of ion exchange materials]. Moscow, Khimiya Publ., 1984. 232 p.

9. STO 00044807-001-2006. *Teplozashchitnye svojstva ograzhdayushch komstruktsij sdamij* [Heat-shielding properties of building envelopes]. Rossijskoe odshchestvo inzhenerov-stroitelej [Russian Community of Civil Engineers], 2006.

10. Ivanov I. A., Shatkov V. M., Sorokin V. T. et al. Diffusiya radionuklodov v tsementosoderzhashchikh materialakh [Diffusion of radionuclides in cement-containing materials]. *Radiokhimiya — Radiochemistry,* 1994, vol. 36, iss. 2, pp. 183—185.

11. Rozental N. K. *Rjrrozionnayz stojkost tsementnikh betonov nizkoj i osobonizkoj pronitsaemosti* [Corrosion resistance of low and extra low permeability cement concretes]. Moscow, FGUP TsPP Publ., 2006. 520 p.

Information about the authors

Sorokin Valery Trofimovich, Ph.D, Chief Technology, JSC “ATOMPROEKT” (82-A, Savushkina St., St. Petersburg, 197183, Russia), e-mail: vsorokin@atomproekt.com.

Prohorov Nikolai Alexandrovich, PhD, Head of the Department of Chemical Technologies, JSC “ATOMPROEKT” (82-A, Savushkina St., St. Petersburg, 197183, Russia), e-mail: prokhorov@atomproekt.com.

Pavlov Dmitriy Igorevich, Team Leader of Saint-Petersburg branch of JSC “FCNIVT “SNPO “ELERON” — “VNIPIET” (55, Dibunovskaya St., St. Petersburg, 197183, Russia), e-mail: dipavlov@eleron.ru.

Bibliographic description

Sorokin V. T., Prohorov N. A., Pavlov D. I. Spent Ion Exchange Resin Conditioning Technology Based on Thermal Vacuum Drying Method. *Radioactive Waste,* 2021, no. 2 (15), pp. 39—48. DOI: 10.25283/2587-9707-2021-2-39-48. (In Russian).