LRW processing at nuclear facilities leads to generation of concentrates (highly saline LRW) and spent filtering materials, predominantly ion-exchange resins (IER). Virtually all storage capacities for such kind of waste are exhausted at nuclear facility sites in Russia. Approximately 30 thous. m³ of IER was accumulated at Russian NPP compared to 90 thous m³ of accumulated LRW. Large quantities of IER were also accumulated at Atomflot facilities. Considerable content of IER in the accumulated LRW makes their combined reprocessing virtually impossible. Specialized facilities need to be developed for IER reprocessing. There currently are no industrial process facilities for IER reprocessing in Russia.

Experimental part

A number of methods for processing and conditioning spent radioactive ion exchange resins (IER) were tested at FSUE "RADON". The technical applicability of the methods was assessed against the following criteria: conformance to the requirements of regulatory documents, specific activity of IER and availability of certified package, facility capacity. The following methods conform to the selected criteria: dewatering, embedding in polymer matrix and cementation. Feasibility study was performed for the selected technologies. A full scale pilot facility for IER dewatering and embedding in a matrix material directly inside the disposal container was constructed and tested using real IER specimen. Operational documentation for a pilot facility for IER conditioning directly inside the container was developed for subsequent introduction of process facilities at nuclear sites. The containers used may include modernized KMZ or NZK-150-1.5P containers based on the specific activity.

Keywords: ion-exchange resin, NPP, polymeric binder, dewatering, cementation.

A number of methods for processing and conditioning spent radioactive ion exchange resins (IER) used worldwide were tested at FSUE "RADON" [1, 2]. They included both destructive (pyrolysis, peroxide oxidation, supercritical water oxidation), and non-destructive methods (decontamination, drying, dewatering, embedding in matrix materials). Out of these technologies, dewatering and embedding in a polymer binder were carried out directly inside the container, which was a benchmark disposal container (Fig. 1).

Container had two partitions in lower and upper halves. The partitions were permeable for water, polymer binder, air and were impermeable for IER. Partition (mesh) cell dimensions were less than 0.1 mm. The lower partition was required for removal of transport (free) liquid from IER, while the top one was required to retain IER in container whilst it was impregnated by polymer binder. Only the lower partition was sufficient for IER dewatering, while dewatering and impregnation required presence of two partitions (Fig.1).

In IER dewatering process the free liquid was withdrawn by vacuum maintained below the lower partition in the container. In IER impregnation process the polymer binder components (epoxy resin, hardener) were mixed outside the container in a flow mixer and pumped to below the lower partition. Polymer binder then rose up and filled free space between IER particles. Once the polymer binder was detected above the container partition, the pumping was stopped.

The tested technologies were compared against the following criteria:
1. Compliance to the regulatory documentation (NP-095-14, NP-019-15) [3, 4].
The main requirements included:
• content of free liquid in the RW package should be less than 3% mass;
• the package shall maintain integrity in process of storage (disposal).

Implementation of drying only does not conform to the requirements of NP, as dried IER in storage may swell due to moisture absorption and lead to package failure [2].

2. Specific activity of IER and availability of certified package for disposal.

Specific activity of IER accumulated at Russian NPP lies in the range between $10^7$ and $10^8$ Bq/kg. Currently only KMZ and NZK containers are certified for storage and disposal of conditioned RW. For NZK-150-1.5P maximum RW activity for dose rate at the container surface to remain within 10 mGy/h [2, 3] is $1.6\cdot10^8$ Bq/kg ($^{137}$Cs — 50%, $^{60}$Co — 50%), and for KMZ — $1.6\cdot10^7$ Bq/kg. Therefore, technologies leading to considerable reduction of volume (pyrolysis, incineration, etc.) and, consequently, to increase of waste specific activity, could not be used due to the absence of a certified disposal package.

3. Installation capacity.

Calculations [2] show that capacity of an installation to be used at each of the NPP shall be at least 0.3 m$^3$/h in order to alleviate the problem of accumulated and generated IER at NPP of Russia. Such capacity can be achieved only for installations using dewatering, embedding in polymer binder and cementation technologies. Thermal installations have insufficient capacity.

Thus, comparison of tested technologies shows that only dewatering, embedding in polymer binder and cementation conform to all the assessment criteria.

Preliminary economic analysis demonstrated that in case of use of KMZ container as the disposal package for conditioned IER, for disposal cost of 40 thous. robles per m$^3$ (4 class RW), and for installation capacity of 0.3 m$^3$/h, the cost of IER processing would be, in thous. robles/m$^3$:
• for dewatering — 160;
• for dewatering and embedding in a polymer binder — 415;
• for cementation — 507.

NP-093 allows disposal of non-solidified 3 class RW (which includes dehydrated IER), although with a condition. RW allocated for disposal shall conform to the acceptance criteria for a specific disposal facility. These criteria may require RW solidification, as in the case of Saida Bay, where IER shall be solidified prior to acceptance for storage. Moreover, IAEA recommends solidifying IER prior to disposal.

Therefore, though there are evident economic advantages of using IER dewatering, pilot installations for both IER dewatering and embedding in a polymer binder need to be developed for subsequent introduction of process facilities at nuclear facilities.

FSUE “RADON” has developed, constructed and tested a pilot installation to demonstrate the technology of IER dewatering and polymer binding. The installation included both the equipment available at NPP (storage vessel, montejus for LRW transportation) and equipment required for IER conditioning (Fig. 2). IER sludge for the storage vessel 1 ($V = 5$ m$^3$) was injected using montejus 2 ($V = 1.2$ m$^3$) to the batcher 3 ($V = 1.3$ m$^3$). The sludge was densified in the process due to the difference in densities of IER and transport water. The batcher flow pipe (lower side pipeline) was used to inject specific amount of IER to the container. Once the batcher was filled with sludge, excess IER sludge was drained from the batcher through the overflow pipe. IER was then directed by gravitational flow to KMZ-RADON container of 4 type. The above operations were repeated until the container was filled. The container filling was monitored using the level meter installed inside the container. Container for IER dewatering and polymer binding had two partitions in the bottom and top parts of the container.

Once the container was filled with IER, the resin was dehydrated by vacuum applied by montejus 5
Processing, Conditioning and Transportation of RW

Fig. 2 – Pneumatic and hydraulic diagram of the experimental IER conditioning facility

1 – IER tank, 2 – montejus, 3 – batcher, 4 – container, 5 – montejus, 6 – polymer binder tank, 7 – hardener tank, 8 – peristaltic pump
through the pipe located below the bottom partition of the container. Water from montejus 1 was directed either to vessel 1 or to special sewage. After completion of IER dewatering, IER was impregnated with polymer binder in the container. This included pumping polymer resin from vessel 6 (V = 0.2 m³) and hardener from vessel 7 (V = 0.2 m³) by dosing pumps through two additional pipe mixer fittings located in the container. The mixer was a pipe (Du = 60 mm) with two fittings, filled with packing. The height of the packing layer was 2000 mm. Uniform IER impregnation with polymer binder was ensured by the flow rates of the polymer binder components, the structure of lower part of the container and bottom partition. The container was filled with polymer binder up to the moment of liquid detection in the open orifice of container lid. The container was then sent for intermediate storage for solidification of polymer binder and then to storage facility.

The installation for IER dewatering was tested on a mix of spent cationite and anionite unloaded from the water treatment system of building #14 of FSUE “RADON” (Table 1).

Table 1. Results of IER analysis

<table>
<thead>
<tr>
<th>IER type</th>
<th>Specific activity, Bq/kg</th>
<th>( ^{24} \text{Cl} )</th>
<th>( ^{137} \text{Cs} )</th>
<th>( ^{60} \text{Co} )</th>
<th>( ^{57} \text{Co} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anionite</td>
<td>3.0 E+4 1.1 E+4 2.2 E+1 5.6 4.0 E+4</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cationite</td>
<td>9.7 E+3 4.0 E+5 1.3 E+5 7.8 E+2 6.4 E+5</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Due to low specific activity of IER and in order to demonstrate the technology, the trial was carried out with removed container lid as described below. IER sludge from the water treatment system was transported to tank 1 and technical water was added to increase the flow capabilities (solid/liquid = 1/1 – 1/2). Then the following operations were performed:

1) filling of montejus 2 by sludge from tank 1 by vacuum maintained in montejus 2;
2) filling of batcher 3 by sludge from montejus 2 as a result of pressure maintained in montejus 2;
3) container 4 filling with sludge from batcher 3 by gravitational flow;
4) resin dewatering in container 4 by vacuum maintained in montejus 5;
5) drain of transport and interpore water from montejus 5 to special sewage system or tank 1.

Volume of each IER portion was 0.4 to 1.2 m³. The process of container filling with sludge and IER dewatering are shown in Fig. 3.

It can be seen that there was a somewhat non-uniform filling of the container with dehydrated IER. There was an incline of IER from the wall of the container, where the filling was performed, to the opposite wall. Therefore, the container filling with IER in the interval from 80 to 100% was performed using mechanical vibration of the container with an external vibrator. This provided virtually uniform distribution of dehydrated IER in the container.

The extent of container filling with IER sludge was controlled visually and by level meters.

IER was sampled after the completion of dewatering process in order to measure the content of free liquid. Duration of specific technological operations of IER dewatering in the container are shown in Table 2.

Table 2. Duration of technological operations in process of IER dewatering

<table>
<thead>
<tr>
<th>Technological operation</th>
<th>Duration, min</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 Filling of montejus 2</td>
<td>2</td>
<td>3.7</td>
<td>3.5</td>
<td>2.0</td>
<td></td>
</tr>
<tr>
<td>2 Filling of batcher 3</td>
<td>25*</td>
<td>5.0</td>
<td>4.0</td>
<td>2.0</td>
<td></td>
</tr>
<tr>
<td>3 Filling of container 4</td>
<td>4</td>
<td>6</td>
<td>8.3</td>
<td>2.0</td>
<td></td>
</tr>
<tr>
<td>4 IER dewatering in the container</td>
<td>2</td>
<td>2</td>
<td>6</td>
<td>2.0</td>
<td></td>
</tr>
<tr>
<td>Total cycle time</td>
<td>33</td>
<td>17</td>
<td>22</td>
<td>8</td>
<td></td>
</tr>
<tr>
<td>Dewatered IER volume, m³</td>
<td>0.4</td>
<td>0.84</td>
<td>1.2</td>
<td>0.4</td>
<td></td>
</tr>
<tr>
<td>Capacity, m³/h</td>
<td>0.73</td>
<td>3.0</td>
<td>3.3</td>
<td>3.0</td>
<td></td>
</tr>
</tbody>
</table>

* pipeline bend between montejus 2 and batcher 3

The free liquid volume was determined as follows. Specific volume (200 ml) sample of dehydrated IER was extracted from the container and transferred to conical funnel or Büchner funnel with Bunsen flask. “White tape” filtering paper was used as filtration partition. In process of free liquid determination in a Büchner funnel, Bunsen flask was vacuumed for 5—10 minutes. In process of free liquid determination in a conical funnel, it was put on top of a measuring cylinder and liquid accumulation over 30 minutes was observed.

4 IER samples were taken in process of container filling and dewatering (one sample after each cycle). No free liquid was found in any of the samples.

IER dewatering and impregnation tests inside the container utilized a polymer binder based on epoxy...
compound KDA and hardener ETAL-45M, which were selected based on laboratory experiments and tests at an experimental apparatus with a ~20 l container.

At the first stage the container with lid removed was filled with IER sludge and the sludge was dewatered. Given that the overall height of the container between the partitions was 110 mm, the resin level inside the container after its filling and dewatering reached 102 mm.

Flow rates of polymer binder components KDA/ETAL-45M were selected to have a ratio of 2/1 with respect to volume. KDA flow rate (maximum) was 1000 l/h, and ETAL-45M flow rate was 500 l/h. NP-25 pump was used for KDA injection, and NP-25 pump with frequency transformer was used for ETAL-45M injection.

Then impregnation of dehydrated IER in the container started (Fig. 4). After the pumps were engaged, the pressure at the inlet to the container settled at the value of 0.8 atm. within several minutes. For 45 minutes the process of components injection was stable. Pressure at the inlet to the container remained at the same value. In 45 minutes the polymer binder components were detected above the upper partition and the pumps were stopped. The container was left alone to allow time for epoxy compound solidification. Calculated IER content in the polymer compound was 60% mass.

Compound samples from the bottom of the container were taken via the sludge injection fitting in order to determine the radionuclide leaching rates and compression strength. After the storage time of 28 days the compression strength of all samples exceeded 50 MPa, and the leaching rate for 137Cs was less than 10⁻⁴ g/cm²·day.

In 16 hours after the stop of impregnation, the polymer compound in the container was solid and could not be depressed by sharp objects. The carried out calculations demonstrated that:
- the technology of IER conditioning directly inside the container could be implemented and the IER could be brought into compliance with the acceptance criteria for disposal of 4 class RW;
- the capacity of IER dewatering installation was ~ 3 m³/hour;
- the capacity of IER dewatering and polymer binding installation was ~ 0.5 m³/hour;
- there is a need to develop a number of technical solutions in order to ensure:
  - container vibration in process of filling with IER sludge to ensure uniform spreading of the contents along container cross-section;
  - presence of quick release connections at the container for injection of fluids (IER sludge, vacuum, etc.) in order to reduce the dose loads on the personnel.

Development of working design documentation

Operational design documentation for a pilot facility for IER conditioning directly in the container using dewatering and polymer binding methods was subsequently developed. The development goal was to construct a mobile facility with a capacity of up to 800 m³/year for IER reprocessing and conditioning at the sites of various nuclear facilities.

The facility could be disassembled and transported to customer sites, assembled at the site, connected to utilities, used to condition the IER, with subsequent transportation and handing over to the National Operator.

The facility has the following parameters:

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Specification</th>
</tr>
</thead>
<tbody>
<tr>
<td>Package for conditioned IER (dependent on specific activity)</td>
<td>NZK type container with a metal insert or KMZ container, supplemented by two partitions</td>
</tr>
<tr>
<td>facility capacity, m³/h</td>
<td>at least 0.4</td>
</tr>
<tr>
<td>content of free liquid in the dehydrated IER, % mass</td>
<td>&lt; 3</td>
</tr>
<tr>
<td>IER content in polymer compound, % mass</td>
<td>at least 60</td>
</tr>
<tr>
<td>operation mode</td>
<td>periodic</td>
</tr>
<tr>
<td>operational pressure, MPa</td>
<td>not more than 0.1</td>
</tr>
<tr>
<td>operational rarefaction, MPa</td>
<td>- 0.06, not more than</td>
</tr>
<tr>
<td>safety class</td>
<td>3Н</td>
</tr>
</tbody>
</table>

At the IER processing site the facility needs to be connected to the following utilities:
- IER injection;
- compressed air supply;
- vacuum;
- technical water feeding;
- decontaminating solution injection;
- blow-off;
- special sewage.

The trial installation includes the following assemblies and systems (Fig. 5):
- batcher A1 - 1 pc., V = 1.3 m³;
- container A2;
- montejuas A3, V = 1.3 m³;
The Development of Technology for Conditioning Spent Ion Exchange Resins

The vibrobench BB;
- fixer-tray for vibrobench;
- maintenance pad;
- leak collection tray;
- epoxy resin tank А5, \( V = 0.5 \) m\(^3\);
- hardener tank А6, \( V = 0.5 \) m\(^3\);
- batcher pump \( \text{НД} \) — 2 pcs.;
- pipeline and fittings;
- process control system.

The process control system implements the following functions:
- process control;
- manual control of electrically operated valves;
- manual turning on/off batcher pumps and their frequency transformers;
- manual turning on/off the vibrobench;
- video control of the IER sludge condition in the pipeline of IER return from the batcher А1 in case of its filling with IER;
- video control of container fittings leaktightness;
- indication of the valve positions and the conditions of pumps 7 and their frequency transformers;
- indication of the absence of rarefaction in blowoff pipelines.

The system has safeguards protecting against process failures and LRW spills.

The montejus is used to inject the IER sludge from the storage tank (Fig. 5) to the batcher А1 (\( V = 1.5 \) m\(^3\)). When the batcher is filled with IER, the excess sludge is returned to the collection tank via the upper pipeline. In this process the sludge is densified due to the difference in the densities of IER and water, and virtually all the transport water is removed, leaving only the interpore one. Batcher filling with densified sludge is controlled by a videocamera installed at the viewport of pipeline of IER removal from the filled batcher to the collection vessel, and a screen installed at the control panel. The batcher is considered to be filled with densified sludge when backflow of only IER and not water is observed.

The batcher overflow pipe is used to feed specific amount of IER to the container. Once the batcher is filled with sludge, excess IER sludge is drained

\[ \text{Fig. 5. Diagram of the pilot facility for IER conditioning} \]
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from the batcher through the overflow pipe to the collection tank. Then the densified IER sludge is injected to the container A2 (container 1 of KMZ type or container 2 of NZK type with metal insert). Filling of the container is done with periodic engagement of vibrobench B6. This is required for uniform spreading of IER sludge across container cross-section.

Once the container is filled with IER, which is determined (controlled) by the sludge level meter in the container, the sludge is dehydrated by vacuum applied in the montejus A3. Transport and inter-pore water pass through the lower partition, whilst IER remains in the container. The end of IER sludge dewatering process is detected by the readings of pressure sensor in montejus A3. Once all the water is extracted, rarefaction in montejus drops abruptly to zero.

Then polymer binder (epoxy resin and hardener) is injected to the container from vessels A5 and A6 up to the moment of triggering of the inclined polymer binder level sensor located at the sidewall of the container lid. Then the container with dehydrated and conditioned IER is sent to quality control section using forklift.

Water from montejus A3 is drained either to vessel provided at the facility, or to special sewage.

Each equipment element can be connected to technical water and decontamination solution supply to decontaminate the inside surfaces. Drain of spent solutions to special sewage is also provided. All release sources are connected to blowoff.

Development and implementation of the facility will provide resolution of the problem of IER accumulated at nuclear power facilities and other facilities using radioactive materials.

References


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Bibliographic description