RADIATION RESISTANCE OF ORGANIC COMPOUNDS FOR LRW SOLIDIFICATION

Ostashkina E. E., Savkin A. E.

FSUE RADON, Moscow, Russia

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Experiments were carried out to determine the radiation resistance of a bitumen compound produced based on genuine still residue from the Kalinin NPP using bitumen grades BND 60/90 and BND 90/130, polymer compounds based on spent ion exchange resins and spent inorganic sorbents. It was found that at an irradiation dose of $1 \cdot 10^6$ Gy, the volume of the bitumen compound increases to no more than 10 vol.%, which complies with the NP-019-15 requirements. The polymer compound based on spent ion-exchange resins from the testing of a pilot plant for resin conditioning directly in a disposal container by dewatering and impregnation with an epoxy binder meets the requirements of NP-019-15 not only as regards the radiation resistance, but also according to all quality indicators. The polymer compound based on Russian epoxy resins can be considered promising for the solidification of spent inorganic sorbents with a specific activity of up to 10^{11} Bq/kg.

Keywords: *radioactive waste, bitumen compound, polymer compound, ion-exchange resin, inorganic sorbent, radiation resistance.*

Introduction

Such methods as cementation, bituminization, vitrification and inclusion into a polymer matrix are currently used to immobilize liquid radioactive waste (LRW) in Russia. These methods should result in products with their quality indicators meeting those established in NP-019-15 [1] and NP-093-14 provisions [2]. Most important quality indicators are water stability, mechanical strength, frost resistance, water resistance, thermal and radiation resistance.

LRW solidification methods resulting in inorganic compounds (vitrification, cementation) and their properties are quite extensively discussed in the literature [3—6]. A large number of publications discusses LRW bituminization [7—9]. In recent years, published was a number of studies focused on the incorporation of heterogeneous LRW into a polymer compound [10, 11]. However, these literature sources usually provide no information on their radiation resistance.

While this indicator does not raise any doubts in case of inorganic compounds due to their nature, for bitumen and polymer binder-based organic compounds it largely governs the safety of their long-term storage/disposal. If the radiation resistance of an organic compound is not adequate, then during further storage, its structure changes, thus, decreasing all quality indicators, which can cause serious damage to the environment.

FSUE RADON has developed a method allowing to measure the radiation resistance of a bitumen compound. Based on it, the radiation resistance has been measured for:

- bitumen-salt compound (BSC) based on still residues from Kalinin NPP;
- polymer compound based on spent ion-exchange resins (IER);
- polymer compound based on spent inorganic sorbents.

Experimental part

Radiation resistance of a bitumen-salt compound

Radiation resistance of materials is their ability to retain their properties under radiation effects. Radiation resistance of a bitumen compound is characterized by a change in the bitumen compound sample volume (vol.%) after being irradiated to a dose of $1 \cdot 10^6$ Gy. In accordance with NP-019-15 requirements [1], the increase in the compound volume after its irradiation with the above dose should be less than 10 vol.%.

BSC samples were irradiated using an RKhM-gamma-20 unit (Figure 1).

Figure 1. External appearance of the PXM-gamma-20 unit

At the time of the study, the gamma radiation dose rate in the process chamber of this unit amounted to 2 Gy/s.

Gravimetric method was used to measure the change in the volume of the bitumen compound samples. This method implied the use of a volume meter that measured the mass of distilled water displaced by this sample after its complete immersion in accordance with GOST 12730.1 [12].

The volume meter is a cylindrical vessel with its capacity allowing to test 20—100 cm^3 samples. A tube with an inner diameter of 8—10 mm and a bent end was welded into it.

The reservoir for the BSC sample preparation was selected at the initial stage of the study. Tested were the following items:

- disposable medical container;
- disposable paper cup;
- glass beaker or weighing bottle.

After being properly treated and cooled, the BSC samples could be easily removed from the disposable medical containers and paper cups. However, due to irradiation, they started to change their shape due high temperature ranging from +40 to +45 °C. The samples in paper cups did not change their shape. However at post-irradiation stage, the paper became porous, which introduced a large error into the volume measurements; therefore, a thermally and chemically resistant 100 ml glass beaker or bottle was chosen as a reservoir for the BSC sample.

Empty glass bottles were irradiated to 10^6 Gy. Their volume did not change (ΔV was less than 1 vol.%). To identify the dependence between the volume changes and the absorbed dose, the BSC samples were not removed from the reservoirs.

The following materials were used for BSC production:

- still residue from Kalinin NPP (generated in 1996) with the following characteristics:
  a) total salt content — 540 g/dm^3;
  b) borate ion content — 130 g/dm^3;
  c) COD — 6 140 mg O_2/dm^3;
  d) pH — 11.3;
  e) specific activity of ^{137}Cs — $1.4 \cdot 10^7$ Bq/dm^3;
  f) specific activity of ^{60}Co — $3.1 \cdot 10^3$ Bq/dm^3;
- bitumen of BND 60/90 and BND 90/130 grades.

BSC samples were treated in the following way: a metal container with bitumen was placed on a heating laboratory plate and heated to a temperature of +105 — +110 °C. Stirring was done with a spatula and the temperature was monitored using a mercury thermometer. When the indicated temperature was reached, the calculated amount of the still residue from Kalinin NPP was added to the molten bitumen in small portions (2—3 ml each) with periodic stirring with a spatula. After the entire amount of still residue was added, hot BSC was poured into glass bottles. The salinity for all BSC samples amounted to 50 wt.%.

After such treatment, the BSC samples were cooled in a fume hood for two hours and then irradiated to $1 \cdot 10^5$ Gy, $5 \cdot 10^5$ Gy, $1 \cdot 10^6$ Gy, $4 \cdot 10^6$ Gy. For each grade of bitumen, each irradiation dose was applied to two parallel BSC samples.

Figure 2 presents the workstation used to measure the BSC sample volume.

Figure 2. Workstation for BSC sample measurements

The change in the volume of SBC samples at the post-irradiation stage (ΔV, vol. % of the initial sample volume), was calculated based on the below expression (1):

$$\Delta V = \frac{(V_2 - V_1)}{(V_1 - V_0)} \cdot 100, \qquad (1)$$

where V_2 is the volume of the bottle with the BSC sample at the post-irradiation stage, cm^3; V_1 is the volume of the bottle with the BSC sample before irradiation, cm^3; V_0 is the volume of an empty bottle for the BSC sample, cm^3.

Tables 1 and 2 summarize the measured radiation resistance of BSC samples, i. e., changes in their volume depending on the radiation dose (ΔV, vol. %).

Table 1. Changes in the volume of BSC samples based on BND 60/90 bitumen

Irradiation dose, Gy	Change in the sample volume, vol. %
$1.08 \cdot 10^5$	0.2
$5.00 \cdot 10^5$	4.3
$1.00 \cdot 10^6$	8.1
$4.00 \cdot 10^6$	12.3

Table 2. Changes in the volume of BSC samples based on BND 90/130 bitumen

Irradiation dose, Gy	Change in the sample volume, vol. %
$1.08 \cdot 10^5$	0.2
$5.00 \cdot 10^5$	4.4
$1.00 \cdot 10^6$	7.8
$4.00 \cdot 10^6$	11.9

Figures 3 and 4 present the appearance of the samples given different radiation doses. Horizontal marks on the bottles correspond to the pre-irradiation volume of the BSC samples.

Figure 3. Appearance of BSC samples at an exposure dose of $1 \cdot 10^6$ Gy

Figure 4. Appearance of BSC samples at an exposure dose of $4 \cdot 10^6$ Gy

The studies showed that the volume of BSC samples increases by more than 10 vol. % for both grades of bitumen at a gamma irradiation dose of some $3 \cdot 10^6$ Gy.

Thus, the resulting BSC based on the still residue from Kalinin NPP and BND 60/90 and BND 90/130 bitumen meets the NP-019-15 requirements [1].

Radiation resistance of polymer compounds based on ion-exchange resins

FSUE RADON has developed and manufactured a pilot industrial air conditioning unit IOS. Tests involving this unit were performed providing the dehydration and inclusion of 7.5 m^3 of spent IER with a specific 137Cs activity of $2 \cdot 10^6$ Bq/kg into a polymer binder and its packaging into KMZ-RADON and NZK-150-1.5P type containers with a metal insert.

Epoxy resin Etal-247 and hardener Etal-45M produced by JSC ENPC EPITAL were used as polymer binder components. After the impregnation of the dehydrated IER in containers was completed, compound samples were taken to identify their quality indicators. Before that, the samples were kept for 28 days to provide their hardening.

In keeping with NP-019-15 [1] provisions, radiation resistance of polymer compounds is governed by the inalterability of their structure and water resistance at an irradiation dose of 10^4 Gy.

Radiation resistance of the samples made of solidified IER-based polymer compound was specified via their irradiation up to a total absorbed dose of $1 \cdot 10^4$ and $1 \cdot 10^6$ Gy and evaluated according to relevant changes in their compressive strength and water resistance due to such irradiation.

The average compressive strength for the polymer compound samples at pre- and post-irradiation stages amounted to 22 MPa. In NP-019 15 provisions, no requirements are imposed on the polymer compound strength. In comparison with the cement compound, with the strength requirements imposing a limit of 4.9 MPa, this indicator turned out to be much higher for the obtained samples of the IER-based polymer compound.

At the pre-irradiation stage, water resistance (leaching rate) of polymer compound samples according to ^{137}Cs radionuclide amounted to $4.21 \cdot 10^{-5}$ g/(cm^2·day) on the 28th day of exposure in water. NP-019-15 provisions [1] state that this parameter should fall within the range between $1 \cdot 10^{-2}$ and $1 \cdot 10^{-3}$ g /(cm^2·day).

The leaching rate identified for polymer compound samples after their irradiation to $1 \cdot 10^4$ and $1 \cdot 10^6$ Gy, was found to be falling within the range between $1 \cdot 10^{-6}$ and $1 \cdot 10^{-5}$ g/(cm^2·day) in both cases.

Thermal resistance tests involving the polymer compound samples held at a temperature of 100 °C for three days showed that their structure did not change. On the 28th day of exposure in water, the leaching rate after such temperature treatment amounted to $2.21 \cdot 10^{-5}$ g/(cm^2·day). Provisions of NP-019-15 [1] discussing the thermal stability state that no changes in the structure and water resistance should occur due to the storage of material at temperatures ranging from 0 to 100 °C.

Therefore, the tests involving actual spent IERs from FSUE RADON showed that their conditioning product would meet all the requirements stated in NP-019-15 provisions [1], including those associated with the radiation resistance.

Radiation resistance of a polymer compound based on inorganic sorbents

Inorganic sorbents are widely used to provide the selective treatment of various LRW types from radionuclides. These include both natural (clinoptilolite, vermiculite) and synthetic (titanates, zirconium phosphates and hydroxides, ferrocyanides, etc.) sorbents. The specific activity of spent sorbents can amount to 10^{10} Bq/kg, and sometimes, for example, in emergency situations, it can be even higher. Thus, at Fukushima NPP, the specific activity of spent clinoptilolite amounts to 10^{11} Bq/kg.

Usually, spent sorbents are emplaced into filter-containers, in which, after being washed and dehydrated, they are handed over for disposal. This practice is in place at Kola NPP, where the still bottom is subject to ion-selective treatment with ferrocyanide sorbent. However, in this case, all protective functions are assigned to the container material, which, taking into account the high specific activity of the sorbent, cannot be considered as being safe for the environment; therefore, a method suggesting the incorporation of spent sorbent into polymer matrix was tested.

Natural clinoptilolite, namely its 1—3 mm fraction, was used as a sorbent. The compound was obtained by mixing the ETAL-247 epoxy resin and the ETAL-45M hardener with pre-soaked and then dehydrated clinoptilolite, the content of which in the compound amounted to 60 wt.%.

Preliminary calculations showed that if the specific ^{137}Cs activity of the spent sorbent was 10^{10} Bq/kg, the irradiation dose until complete decay would be about 10^6 Gy, and if the sorbent activity was 10^{11} Bq/kg, the radiation dose would be equal to 10^7 Gy.

The radiation resistance was also measured solidified samples of clinoptilolite-based polymer compound via their irradiation to a total absorbed dose of 10^6 and $1.3 \cdot 10^7$ Gy followed by the evaluation of the irradiation-driven changes in their compressive strength.

At the pre-irradiation stage, the average indicator for the two samples amounted to 31 MPa, after being irradiated to a dose of 10^6 Gy and $1.3 \cdot 10^7$ Gy, it exceeded 50 MPa (i. e., the threshold set for the testing unit). Figure 5 shows the samples at different irradiation doses. Horizontal marks on the

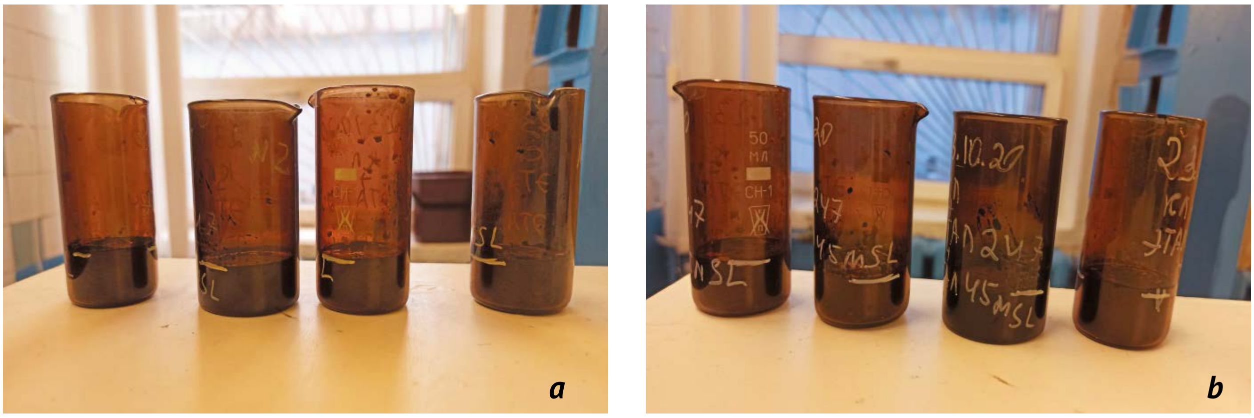

Figure 5. Appearance of a compound based on clinoptilolite at the post-irradiation stage: a) irradiated at a dose of 10^6 Gy, b) irradiated at a dose of $1.3{\cdot}10^7$ Gy

weighing bottles correspond to the volume of the compound at the pre-irradiation stage.

As can be seen from Figure 5, no change is observed in the volume of polymer clinoptilolite-based compound samples during their irradiation. Thus, Russian epoxy resins can be used effectively to immobilize spent inorganic sorbents.

Conclusions

1. Experiments were performed to determine the radiation resistance of bitumen compounds produced based on genuine still residues from Kalinin NPP using BND 60/90 and BND 90/130 bitumen, polymer compounds based on spent ion-exchange resins and inorganic sorbents.

2. It was found that at an irradiation dose of $1{\cdot}10^6$ Gy, the volume of bitumen compound increases to less than 10 vol.%, which meets the requirements of NP-019-15 provisions.

3. A polymer compound based on spent ion-exchange resins generated from tests of a pilot-production unit providing their conditioning by dehydration and impregnation with an epoxy binder directly in a disposal container meets the N-019-15 requirements not only in terms of the radiation resistance, but also considering all relevant quality indicators.

4. A polymer compound based on Russian epoxy resins can be considered as a promising material that can be used to immobilize spent inorganic sorbents with a specific activity of up to 10^{11} Bq/kg.

References

1. NP-019-15. *Federal'nyye normy i pravila v oblasti ispol'zovaniya atomnoy energii «Sbor, pererabotka, khraneniye i konditsionirovaniye zhidkikh radioaktivnykh otkhodov. Trebovaniya bezopasnosti»* [Federal Norms and Rules in the Field of Atomic Energy Use Regarding the Collection, Processing, Storage and Conditioning of Liquid Radioactive Waste. Safety Requirements].

2. 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 Regarding the Radioactive Waste Acceptance Criteria for Disposal].

3. Nikiforov A. S., Kulichenko V. V., Zhikharev M. I. *Obezvrezhivaniye zhidkikh radioaktivnykh otkhodov* [Liquid Radioactive Waste Treatment]. Moscow, Energoatomizdat Publ., 1985.

4. Roux R, Jouan A. Cold crucible melter for vitrification of low to high activity waste / ICEM'99 (Proc. 7th Int. Conf. on Radioactive Waste Management and Environmental Remediation, Nagoya, 1999), American Society of Mechanical Engineers, New York, 1999.

5. Improved cement solidification of low and intermediate level radioactive wastes. Technical Reports Series No. 350. 1993. 110 p.

6. Varlakov A. P. Nauchnoye obosnovaniye unifitsirovannoy tekhnologii tsementirovaniya radioaktivnykh otkhodov [Feasibility Study of a Unified Technology for Radioactive Waste Cementation]. Dr. techn. sci. diss. Abstr. Moscow, 2011. 51 p.

7. Sadovnikov J. Bituminization of liquid radioactive wastes at nuclear plants in the USSR / Paper presented at the Summer MTG of the American Institute of Chemical Engineers, Denver, CO. 1988.

8. Davydov V. I., Kostin V. V., Savin L. N., Bryukhanov A. G., Simonov V. I., Dobrygin P. G., Kulikov V. A. Ustanovki otverzhdeniya zhidkikh otkhodov nizkogo i srednego urovnya aktivnosti [Installations for the solidification of liquid low- and intermediate-level waste]. *Atomnaya Energiya — Atomic energy,* 1995, vol. 79, no. 6, pp. 429—433.

9. Bituminization processes to condition radioactive wastes. Technical Reports Series No. 352. 1993. 96 p.

10. Savkin A. E., Ostashkina E. E., Pavlova G. Yu., Karlina O. K. Opytnaya pererabotka otrabotavshikh ionoobmennykh smol [Experimental processing of spent ion-exchange resins]. *Voprosy atomnoy nauki i tekhniki. Series: Materialovedeniye i novyye materialy — Issues of nuclear science and technology. Materials science and new materials,* 2016, no. 3 (86), pp. 40—49.
11. Ostashkina E. E., Savkin A. E. Nauchno-tekhnologicheskoye obosnovaniye vybora sposoba konditsionirovaniya otrabotavshikh radioaktivnykh ionoobmennykh smol [Feasibility study for a decision-making on a conditioning method for spent radioactive ion-exchange resins]. *Voprosy atomnoy nauki i tekhniki. Series: Materialovedeniye i novyye materialy — Issues of nuclear science and technology. Materials science and new materials,* 2020, no. 3 (104), pp. 40—53.
12. GOST 12730.1-78. *Betony. Metod opredeleniya plotnosti* [Concrete. Density Determination Method].

Information about the authors

Ostashkina Elizaveta Evgenyevna, project chief, FSUE "RADON" (2/14, 7-th Rostov lane, Moscow, 119121, Russia), e-mail: EEOstashkina@radon.ru.
Savkin Alexander Evgenevich, Ph. D., expert, FSUE "RADON" (2/14, 7-th Rostov lane, Moscow, 119121, Russia), e-mail: AESavkin@radon.ru.

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