Experience of Non-Technological Waste Solidification with Polymers at Radium Institute - 13530

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ABSTRACT

In the run of scientific and production activities in Radium Institute there are generated the liquid radioactive wastes (LRW) of the most various compositions, which are partially processed (with the use of cementation technology) as accumulated and removed to the special-purpose enterprise ("Radon") for a long-term storage.
The process of cementation has wide practical application including the use for a long time at Radium Institute for solidification of aqueous solutions.
One of the problems appearing at laboratory waste processing consists in a presence of organic substances in aqueous solutions and high acid concentration.
Solidification of such waste (water-organic) also runs into a number of serious difficulties due to organic liquid and cement incompatibility.
In this connection, development of advanced technologies with using high-tech polymers seems to be quite justified.

INTRODUCTION

One of the key conditions for successful development of nuclear engineering in the nearest future is solving the problem of safe management and removal from the biosphere of all generated radioactive wastes.
Among liquid radwaste generated at NPPs, radiochemical plants and research centers, there are aqueous solutions of different level of specific activity and various in composition including, organic products, spent extractants, diluents, and oils.
In addition, it's clear as day that owing to a great diversity of compositions and activity levels, these wastes cannot be processed when using a single method, a universal one is needed.
The cementation is the most widely spread technique for radioactive waste conditioning. This method is economically efficient for immobilizing various waste types into the safe solid waste form suitable for the long-term storage.
On the minus side of the cementation one could mention the need for preliminary neutralization of acidic solutions and the problems appeared when cementing organic and mixed aqueous-organic solutions.
One of the problems appearing at laboratory waste processing consists in a presence of organic substances in aqueous solutions, and concentration of those substances can vary within wide range (0.1 - 10.0 g/l). Organic products can present in a form of solution or in a form of emulsion in aqueous solution.
It should also be mentioned that the solutions of such compositions (thanks to organic liquids, first of all) do not meet the requirements put forth by Radon enterprise and cannot be transferred there for further processing and long-term storage. In addition, processing of such solutions in laboratory space is associated with a great number of technical and financial problems.

Just because of this fact, there was proposed the idea to use polymer materials for solidification of Radium Institute's LRW directly at the site that will make it possible to give up in future the procedures of waste storage and transportation in liquid form [1, 2].
Besides the selection of the most effective LRW solidification technology, the experiments on the agenda are aimed at the solution of one more problem, namely, the removal of RW from the building that would allow the extension of the safe service life of the hot cells and the equipment for the period of up to the year 2020.

RESULTS OF EXPERIMENTS AND DISCUSSION

The ultimate goal of handling waste of any category is the maximum reduction of the volume of waste subject to the special storage under the condition of the minimum release of that waste into the environment. Therefore, the most serious issue is associated with the liquid radioactive waste handling, the volume and gross activity of which considerably exceed those of the solid radioactive waste.
The following performance criterions were selected for the methods, developed in our work:
- The materials, used in operation, should ensure strong fixation in a polymer matrix of all radionuclides, occurring in the solutions;
- The composition and the amount of reactants to be used should not hamper further waste processing and increase significantly their volume.

It is the high-tech polymers by Nochar Company that were used in our work.
At the first stage of work the large volume of experimental studies with the simulated solutions has been performed. (The variety of solutions used in the runs was sufficiently wide, ranging from alkali solutions to the concentrated nitric acid solutions with the high salt bearing.)
According to the data obtained the conclusion has been made that, indeed, the solidification process with the aid of Nochar polymers was successful enough and the high values of acidity and the salt concentration do not interfere with the process.
And at the next runs all experiments were performed with actual waste.
The set of experiments was carried out in department of decontamination (Gatchina). For these preliminary experiments we took several aliquots of LRW (aqueous solution) with high salt content (35.8 g/l). Composition of aliquots was the following: $Av_{\Sigma\alpha}$, - $2.5 \cdot 10^6$ Bq/l, $Av_{\Sigma\beta}$, - $7.3 \cdot 10^7$ Bq/l, pH-12.7, Cs-137 – $3.0 \cdot 10^6$ Bq/l, Am-241 – $2.1 \cdot 10^6$ Bq/l, Ce-144 – $1.0 \cdot 10^6$ Bq/l, Eu-154 – $4.7 \cdot 10^5$ Bq/l.
For the solidification of aqueous radioactive waste we used polymer No.960 and in certain cases we also used polymer No.910 intended for solidifying waste containing organic compound contaminants. The ratio, the mass of polymer (S) to the volume of solution (L) was in the range of 1:5. All samples of LRW were solidified successfully.
Composition of waste, conditions of solidification and the results of the next experiments are presented in Table I.
The standard test solutions were mixed with polymers at different proportions. (In the case of experiments with perlite slurry samples, grout washing were carried out before and water excess was decanted. We took away the solution excess from the pulp with only one reason to decrease the volume of solid substance after solidification.

TABLE I. Results of experiments on the solidification of solutions in department of decontamination.

Conditions of solidification					Results
Weight of polymer, g		Volume of solution, ml	Ratio, S:L	Characteristic of wastes.	
No 960	No 910				
-	5	25	1:5	Test sample of water solution with organic impurities from evaporator (evaporator system). $Av_{\Sigma\alpha}$, - $2.5\cdot10^6$ Bq/l, $Av_{\Sigma\beta}$, - $1.1\cdot10^7$ Bq/l	Solution has been solidified successfully.
0.25	4.75	25	1:5	Organic residue from LRW store holder. $Av_{\Sigma\alpha}$, - $6.6\cdot10^6$ Bq/l, $Av_{\Sigma\beta}$, - $1.1\cdot10^7$ Bq/l	Strong swelling during the stage of solution mixing. Solution has been solidified successfully
5	-	10	1:2	Perlite slurry (Am-241 - Bq/l, $A_{\Sigma\beta}$, - $1,1\cdot10^4$ Bq/l)	Solution has been solidified successfully

One of the source of liquid organic radioactive wastes is scintillation liquids wich are used in radiochemical analysis.
Spent scintillating solution (ZhS-8/LS-8) containing water with tritium was used in our experiments. (Experiments on liquid waste solidification were conducted in the plastic cups of 150 ml in volume, preliminary subjected to volume calibration by each 10 ml.)
The following conditions were selected for experiments on solidification of spent scintillating solution. There was used the mixture of polymers No. 910 (80%) and No. 960 (20%), and polymer to liquid mass ratio (S:L) was 1:2.
Stable weight of the sample was fixed after 14-day ageing. The mixture has lost its wet appearance, but is not changed in whole: it still looks friable; no any change of volume is detected. Sample appearance after solidification of spent scintillating solution is shown in the Fig. 1.

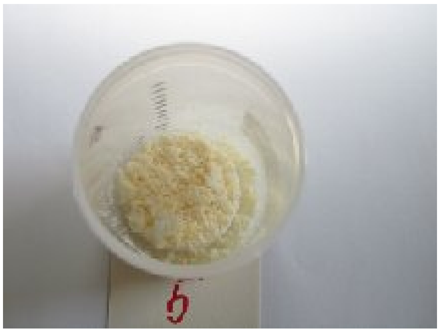

Fig. 1. Sample appearance after solidification of spent scintillating solution and after of air storage at a room temperature during 1 month.

A number of experiments have been conducted and the appearance of several samples after solidification of some products is shown in Figs. 2-3.

Fig. 2. Sample appearance after solidification of the residue from waste tank. There was used the mixture of polymer No. 910 (20%) and No. 960 (80%), and proportion between polymer masses and liquid (S:L) was 1:3. Total specific α-activity - $6.61 \cdot 10^6$ Bq/kg, total specific β-activity - $1.3 \cdot 10^8$ Bq/kg.

Fig. 3. Sample appearance after solidification of the vacuum oil. There was used No. 960 polymer, and proportion between polymer masses and liquid (S:L) was 1:5.

In addition to utilization of liquid wastes which have been accumulated in the Institute's laboratories, there exists one more acute problem which should be solved in the nearest time.

When a period of waste storing in process devices collecting LRW is sufficiently long, then sooner or later there will be registered accumulation of sediments on the bottom of process device.

When it is necessary to carry out decontamination of the capacitance equipment (for example, with the purpose of its further disassembly), there will appear the necessity of sludge (sediments) removal and at that it will be required to solve sufficiently complicated technical problem consisting in clearing of those capacities. But, as a rule, the level of bottom deposits (sediments, sludge) activity exceeds well that of solutions which were collected or stored in capacities mentioned. Sludge can also include various kind organic products, and this causes additional difficulties, when trying to dissolve or remove such products from process vessels.

Treatment of bottom sediments (sludge) with nitric acid solution represents the easiest and traditional method applied to solve the problem of decontamination of LRW collector capacities. At that, the procedures of sediment dissolving would be conducted repeatedly, and this course to accumulation of secondary waste which should also be withdrawn (utilized).

The use of polymer materials with the purpose to solidify solutions generated in the run of decontamination is also of interest in this case. The mentioned approach will allow the possibility to abandon the necessity to store additional volumes of LRW (secondary waste generated at decontamination) in Institute's territory and reduce total volume of waste to be transported to Radon.
Besides the experiments described above, the studies were under way with the other actual waste of the Radium Institute, namely, the liquid scintillator, drains of organic liquids of different origin, acidic drains.
Those experiments were aimed at the preparation of the regulations for solidifying all types of the low- and intermediate-level radioactive waste originated in the Radium Institute laboratories followed by the conversion thereof into the solid waste category.
Implementation of the proposed activities would allow to abandon the liquid waste storage at the Institute site and to reduce the total waste volume transferred to the special enterprise 'RADON'.
The tests are conducted according to the following technique. The experiments are run in polyethylene cans of the volume big enough to contain 5 L of LRW. The LRW solutions are poured into the cans followed by the polymer No.910 and 960 additives necessary for solidification.
After the mixing procedure is complete, the solidified compositions are held in the air at the room temperature. Characteristics of the LRW solutions used in the runs and the experimental conditions are given in Table II.

TABLE II. The experimental conditions of LRW solutions solidification with using of polymers.

The LRW composition	Solidification conditions	
	The mass of polymers	The S/L ratio
The scintillator liquid. Total β-activity $5.9\times10^{6-}$ Bq/L, including Cs-137 - 2.1×10^{6}Bq/L, Eu-154, 2.6×10^{6} Bq/L.	Total mass 0.25 kg Polymer No960 – 0.05 kg Polymer No910 – 0.2 kg	1:2
Drains of organic liquids. Total β-activity $3.6\times10^{6-}$Bq/L. (Water phase is presented. According manual observation it's something 3 -10%)	Total mass 0.25 kg Polymer No960 – 0.05 kg Polymer No910 – 0.2 kg	1:3
Acidic drains. (HNO_3 concentration more than 3 mole/L. Total β-activity $0.4\times10^{6-}$Bq/L.	Total mass 0,66 kg Polymer No960 – 0.6 kg Polymer No910 – 0.06 kg	1:4
Neutralized LRW solution, strongly salt. (The salt concentration more than 100 g/L).	Total mass 0,66 kg Polymer No960 – 0.6 kg Polymer No910 – 0.06 kg	1:4

According to the separate program the experiments were under way on solidifying the actual radiochemical lab waste using polymers and porous materials.
The composition of the solution used in the runs was as follows: uranium – 3 g/L, technetium – 144 mg/L, molybdenum – 2.6 g/L, zirconium – 150 mg/L magnesium – 3.2 g/L, plutonium – 5 mg/L, neptunium 40 mg/, value of PH quantity – 5.1.

The difference between this series of runs and those performed earlier is the application of porous materials intended to be used as a final solid waste form for the long-term safe storage or disposal.

As a result of the laboratory studies performed an absolutely new decision on the application of the polymers in the LRW solidification technology has been suggested.

The LRW solidified in the polymer matrix is held up in the atmosphere of air at the room or elevated temperature; after the water is removed, next portions of the waste solution are added. After several 'solidification-drying' operations the ultimate isolation of the solid waste is made in the container followed by the transportation to the repository [3].

Apart from the experiments mentioned above a large series of experiments was run with the other liquid waste arisen from the research under way at the laboratories of the Radium Institute.

A distinction of this type of waste is the great variety and instability in the composition even in one given laboratory. It should be noted that in a whole number of cases we are dealing with the mixed waste. It might be liquids of the organic nature with the aqueous phase present or the opposite when we have aqueous solutions contaminated by the organic contaminants. According to an approximate estimate the organic phase content in the laboratory drains (the research waste) may be as high as 15-20% by volume.

The preliminary conditioning and partitioning of such waste for the following cementation does not make sense on account of a rather low waste volume amounted from tens thru hundreds of liters in one given laboratory.

From the other hand, the LRW storage on the working premises for an indefinite time length may not be considered as an acceptable decision on the safety reasons and taking into account the possible emergencies.

Therefore the application of polymer materials is seen as the most acceptable option for handling the waste in question.

An appropriate selection of the polymer mix composition may provide a possibility to solidify all liquid laboratory drains and convert them into the solid waste category. No special equipment is needed to perform those operations.

The solidification process could be conducted directly in tanks, the latter playing the part of the transportation containers for the following removal of waste from the territory of the Institute.

CONCLUSIONS

It was shown in all cases the polymers can be effectively applied to LLW and ILW aqueous and organic waste.

Among their advantages at least two should be mentioned as the most important ones.

First, the apparent advantage of polymer materials is the possibility of solidifying solutions with rather high acidity and high salt bearing. It is an option for localization of waste of practically any composition including organic liquids and mixtures of aqueous and organic solutions.

Second, the application of polymers provides a possibility to reduce the solidified waste volume coming into the repository. Depending upon the RW salt bearing and activity the achieved waste volume reduction factor could be as high as 5 thru 10.

From the point of view of maximum ecological safety assurance under minimum volumes of the approved secondary RW, waste fractioning consisting in radionuclide isolation in a small volume of specific collectors seems to be the most efficient method of LRW management.

Polymer materials could be used also at the NPP decommissioning phase. Here those materials might be used both for solidifying various solutions generated as a result of the equipment and premises decontamination and for immobilizing precipitates, spent sorbents, and sludge.
One more promising area of the possible application of polymers should be pointed out. It is the application of polymer materials as the assets for the emergency damage control when the advantages of the polymers become obvious.
It's also interesting in future to examine the possibility to stock of polymers at different nuclear sites including research centers with the purpose of using it in the cases of incidents.

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