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PERSPECTIVES OF USING POLYMER MATERIALS FOR LIQUID RADIOACTIVE SOLUTIONS TREATMENT PURPOSES

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The article provides an overview of published data on the use of polymer materials for liquid radioactive waste management purposes. It presents the data on the use of polymer materials by Nochar company and the results of experiments carried out in V.G. Khlopin Radium Institute. The possibility for waste immobilization directly in the containers and in emergency cases is seen as the main advantage of Nochar's polymer materials.

Keywords: *liquid radioactive waste (LRW), liquid radioactive waste treatment methods, LRW immobilization, polymer materials.*

Introduction

Safe management of radioactive waste (RW) has always remained an important task that have been addressed during the development of nuclear power. Any scenarios of this process should take into account the need of reducing the RW amounts and, consequently, the cost of its disposal. Among numerous types of liquid radioactive waste (LRW) the most relevant are those produced:

- from nuclear power generation at nuclear power plants and during the processing of spent nuclear fuel;
- during operation and decommissioning of nuclear fuel cycle facilities, ships of the naval and civil fleets with nuclear power units.

The ultimate goal for managing any category of waste (not only radioactive), which is seen as an axiom, is to ensure maximum reduction of waste volume to be sent for storage in purpose-designed facilities, while minimizing the release of contaminants into the environment. From this perspective, management of liquid radioactive waste is believed to be most challenging as its volume and total activity significantly exceeds the one of SRW with the mobility of biologically hazardous components posing the greatest threat in case of its unauthorized contact with the ecosystem.

The very first studies on the use of polymer materials for RW immobilization purposes were published some 30—40 years ago. But after cementing and vitrification techniques were implemented at an industrial scale, interest in polymer materials sharply decreased. Nevertheless, with the advent of new products on the market, including polymer materials from Nochar (USA), a number of successful studies were conducted to investigate the potential of immobilizing LRW of various compositions.

Polymer materials can be used without any pretreatment of the waste subject to processing which is seen as their main advantage. The simplicity of the process enabling LRW solidification using polymers in the event of emergency spills is another important advantage worth noting.

Experience in the use of polymer materials for LRW solidification

As previously noted, successful industry-wide introduction of cementing technologies used to treat low-level and intermediate-level LRW is seen as the main reason why very little attention started to be paid to polymer materials. As for HLW, vitrification technology became a mainstream and was successfully implemented at radiochemical plants for nuclear fuel processing.

Over the past decades, the requirements imposed on the materials used for waste disposal purposes have increased drastically. It seems quite clear that any organic polymer material is in many ways inferior to glass and even to cement considering such indicators as chemical and radiation resistance.

Given the above, an obvious question arises: whether we should consider polymer materials only as a chapter of history or these still, at some point, can compete with well-known and well-developed technologies.

The use of polymer compositions in waste processing technology was first described in detail in IAEA technical review [1]

At the earliest stages in the development of relevant technologies, it was proposed to use a number of compositions based on epoxy resins, polyethylene, styrene divinylbenzene and methyl methacrylate [1].

The so-called CEA process was developed by researchers from the Kadarash Nuclear Research Center to isolate spent ion-exchange resins and concentrates from evaporators by applying epoxy resin with diamino-diphenol methane as a hardener [1, 2]. Epoxy resins are rarely used alone, since to obtain the desired properties, introduction of several additives is usually required. Hardeners required for the production of thermosetting compounds should be selected carefully, as they can significantly affect the properties of the product and the immobilization rate.

A number of technological processes developed for RW immobilization purposes imply the use of polyester resins [3—5]. To manufacture unsaturated polyester resins the following main ingredients are used: linear polyester resins, crosslinked monomers and inhibitors (hydroquinone, quinone and t-butyl catechin) enabling to slow down the cross-linking process during transportation and storage. Common crosslinking monomers include styrene, vinyl toluene, methyl methacrylate, alpha-methyl styrene and diallyl phthalate. Polyester polymers may be characterized by a wide range of physical properties. Polymers can be brittle and rigid, hard or soft and ductile.

Polymer-based RW immobilization process (wastewater solidification) was developed by Ontario Hydro (Canada) suggesting the formation of a water-oil emulsion of wastewater and a polymer. The emulsion is immobilized using combinations of catalysts and activators. The process results in disperse system formation involving spherical particles of liquid (small droplets) engrossed into a solid matrix of hardened binder [5]. This immobilization process was chosen as a waste treatment method by a number NPP operators [1, 6].

Urea-formaldehyde resin (UF resin) being a water emulsion of urea and formaldehyde completely miscible with water but not miscible with non-polar solvents, was used as another polymer material. When a catalyst is added, cross-linking occurs due to the condensation process. During the polymerization, the polymer matrix captures the by-water. When a UF resin is used for LRW solidification purposes, a catalyst should be added in a form of a weak acid or acid salt (phosphoric acid, sodium bisulfate) to adjust the pH of the mixture involving an aqueous solution and a polymer so that the pH would be equal to 1—2.

UF resins do not chemically react with the waste: they polymerize into a microstructure similar to cells the voids of which contain the waste, so the volume of the product obtained makes for the sum of the waste and resins volumes. UF resins can be used to isolate various RW (dehydrated sediments from filters or spent ion-exchange materials from demineralization facilities) [1, 7].

In Russia, the so-called ECOR, organosilicon elastomer [8], was proposed as a polymer for LRW solidification purposes. ECOR's properties are different from those of other known elastomers with two possible versions available (foam elastomer and solid compound). However, no examples providing for the industrial use of polymer materials to process LRW from nuclear power plants were found in Russia.

More recently, a new type of polymer materials was developed. These are now produced by Nochar in the US. Later, high-tech third-generation polymers were tested to study their suitability for LRW solidification purposes [9]. The first stage of the program was mainly focused on tritium-contaminated oils [10]. Tests aimed at study the immobilization of different LRW types, including genuine RW, were conducted for many of the Nochar manufactured polymer materials [11—14].

Results of the experiments conducted at JSC Radium Institute

Over 15 years ago, Radium Institute (Russia) and Pacific World Trade (the US) launched a series of research on the use of polymers to immobilize LRW of various types.

Answers to two simple questions were supposed to be given as the result of the experimental research:

1. Is it true that the versatility of the polymers produced by Nochar is sufficient enough to ensure their application for the immobilization of any aqueous solutions irrespective of their composition?

2. It was essential to investigate the behavior of already immobilized products during further exposure to air (drying) and upon entering in contact with water.

A quite wide range of solutions was tested: from alkaline solutions to concentrated nitric acid solutions, including those having high salt content. Polymer No. 960 and polymer mixtures No. 960 and No. 910 (if organic impurities were present in the solutions) were used in the experiment. The experimental results obtained using model solutions were tested on genuine waste. Thus, waste from the decontamination workshop and waste from the working premises of the Radium Institute were used in the tests. Table 1 presents a list of the wastes used in the experiments and their specific activities which obviously is far from being a complete one. Figures 1 and 2 show the waste samples after waste immobilization.

Table 1. List of waste used in the experiments

Product name	Specific activity, MBq/l
Aqueous solution (still residue) from evaporator	$A_{\Sigma\alpha}$ – 2.5, $A_{\Sigma\beta}$ – 73
Aqueous solution from evaporator	$A_{\Sigma\alpha}$ – 0. 075, $A_{\Sigma\beta}$ – 11
Bottom sediment from LRW storage tank	$A_{\Sigma\alpha}$ – 6.6, $A_{\Sigma\beta}$ – 11
Spent liquid scintillator (JC-8) containing tritium water	Analysis was not performed
Pearlite pulp	$A_{\Sigma\beta}$ – 0.011
Organic discharges (water phase content from 3 to 10 %)	$A_{\Sigma\beta}$ – 3.6
Acid discharges, HNO_3 concentration – 2–3 mol/l	$A_{\Sigma\beta}$ – 0.4
Neutralized highly saline solution, (salt concentration – more than 100 g/l)	Analysis was not performed

Under all the experiments performed, immobilization was implemented successfully demonstrating that, indeed, the use of polymers in the solidification process is not disrupted by high acidity and concentration of salts in the solution.

It should be noted that porous materials and sorbents (slag, sand, pumice, tuff and others) can be used as additives during LRW solidification [15]. Figure 2 shows the two samples after the immobilization of a model solution.

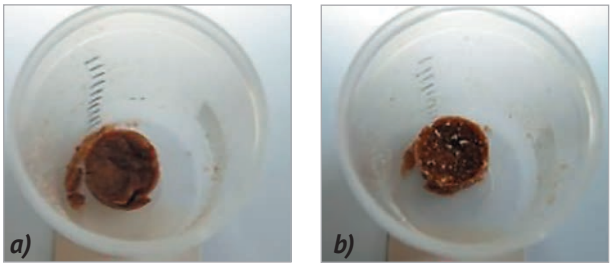

Figure 1. Samples after the solidification of bottom residue from evaporator: a) polymer No. 960 was used, the ratio of polymer mass to liquid mass (T:L) accounted for 1:5; b) a mixture of polymers was used (No. 960 – 90%, No. 910 – 10%), the ratio T:L = 1:5

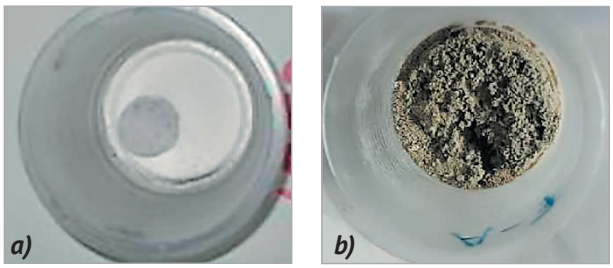

Figure 2. Samples after the solidification of solutions (polymer No. 960) with added silica (a) and zeolite (b); ratio T:L = 1:5

It was demonstrated that addition of silica resulted in a uniform dehydration not causing sample destruction. Density of the obtained pellet amounted to 1.19 g/cm^3.

However, a serious problem was faced when we tried to determine the chemical stability of the obtained products: the immobilized (dried) samples absorbed water again.

Attempts were made to increase the chemical stability of immobilized materials by applying a mixture of polymer and cement in different ratios, but these experiments failed.

Thus, along with a number of advantages, polymer materials do not allow to obtain a product complying with the requirements set for the treatment of waste prior to its long-term storage and (or) disposal.

The following experiments simulating SRW cementing process and aimed at obtaining an immobilized product suitable for final isolation were carried out at LSC Radon. Polymer No. 960 and LRW were mixed at a ratio of 1:10 (LRW composition: $A_{\Sigma\alpha}$ — $3{,}6\cdot10^5$ Bq/l, $A_{\Sigma\beta}$ — $9{,}5\cdot10^6$ Bq/l, salt content = 59 g/l, pH = 12.6, COD = 160 mgO/l). Immobilized compound was sealed into polyethylene and poured with a cement solution. After a 5-day exposure, the monolith was placed in a container with water with the leakage rate being measured. The rate of ^{137}Cs leaching from the samples amounted to $2{,}6\cdot10^{-8}$ — $3{,}7\cdot10^{-9}$ g/cm^2·day, which is several

Table 2. Concentration factor when re-adding a new portion of the solution [15]

Cycle No. (solidification and air drying)	Solution volume and the T:L ratio during solidification	Weight loss for the sample after solidification and air drying, %		Attained concentration factor with respect to the initial volume of the solution
		After 10 days	After 56 days	
Polymer No 960				
Cycle No 1	Solution volume – 50 ml, polymer weight – 10 g (T:L = 1:5)	43.7	93.2	≈5.0
Cycle No 2		35.0	64.0	≈10.0
Mixture of № 960 (95%) and № 910 (5%) polymers				
Cycle No 1	Solution volume – 50 ml, polymer weight – 10 g (T:L= 1:5)	43.6	93.0	≈5.0
Cycle No 2		33.4	61.9	≈10.0

orders of magnitude lower than the requirements set in relevant provisions of GOST R 51883-2002.

In the experiments, alterations in the mass of immobilized samples were monitored during their exposure to air. The interest in studying the dehydration (drying) of immobilized waste was due to two reasons. First, it was necessary to get a clear understanding of the type of the material (its moisture content) to be produced, and secondly, what measures should be taken to ensure its final isolation.

At the same time, if a reduction in SRW mass is revealed during drying, why then it is impossible to repeat the solidification operations for following LRW portions, thus, reducing the amount of SRW sent for storage?

Table 2 summarizes the experimental setting during the tests on LRW mass reduction by adding a new portion of the solution to already solidified and dried composition.

The number of operations required for the inclusion of LLW- and ILW-based solutions seems to be quite large. Salinity and activity are believed to be the only limiting factors determining the maximum volume of a solution that can be introduced into a polymer.

The economic effect resulting from the introduction of the proposed technology is mainly associated with a volume reduction of the waste subject to storage and a decrease in the cost of its transportation [16].

The research performed involved a number of experiments to study the entrainment of radioactive aerosols during the solidified samples drying. A sample of polymer was placed inside a glass with a portion of the solution poured into it ($A_{уд.\beta}$ — $1.5 \cdot 10^8$ Bq/l; $A_{уд.\alpha}$ — $1.3 \cdot 10^6$ Bq/l, salinity 27.0 g/l). Then the glass was covered by a filter. After 1, 3, 7, 15, 30 days, weighing was performed and the beta and alpha activity of the filter was measured. The degree of entrainment was determined to be a percentage of the initial radionuclide content in the portion of LRW handed over for solidification. The experiments showed that presence of a polymer can significantly reduce the concentration of radioactive aerosols in the air. Relevant entrainment was estimated as follows (in % of the initial activity in the sample): $1.3 \cdot 10^{-4}$—$1.5 \cdot 10^{-5}$ for alpha-emitting radionuclides; $5.0 \cdot 10^{-4}$—$6.4 \cdot 10^{-6}$ for beta-emitting, for ^{241}Am — not more than $8.9 \cdot 10^{-3}$ %.

Since many of the results obtained turned out to be equal to the level of measurement error, it was decided to perform some experiments enabling to evaluate aerosol entrainment not by means of filter analysis, but directly by determining the activity of the vapor phase condensate released from the solidified samples during drying. The solidified sample was dried at a temperature of 95 °C. The tested solution had the following characteristics: total α-activity — $5.7 \cdot 10^6$ Bq/l, β- activity — $4.5 \cdot 10^6$ Bq/l, pH — 9.9, salt content of about 100 g/l.

The experiment lasted 9 days, and in all the samples taken, the activity was not higher than the detection sensitivity limit: ^{137}Cs — 0.5 Bq/l and ^{241}Am — 2.8 Bq/l.

One promising area suggesting the use of polymer materials should be mentioned here, namely, as a mean applied in the elimination of emergencies when it's necessary to reduce the content of radioactive aerosols in the air and prevent their spread in the premises and the environment [17]. We believe that this area requires a very careful and balanced approach to be applied and deserves some particular attention.

The proposed materials and technologies can be also used at the stage of NPP decommissioning, when standard LRW processing systems (for example, evaporators) are no longer operational. In this case, the use of polymer materials seems to be a promising method for secondary LRW solidification.

To conclude let's note that the use of polymers is not limited exclusively to the nuclear industry. Their potential in immobilizing solutions of various compositions, including water-organic solutions

and various types of bottom sediments, enables their use in the processing of chemical (non-radioactive) waste.

Today it's quite difficult to predict all possible areas of polymer material future applications, but one can assume the potential of industrial waste processing (including galvanic waste, highly toxic substances and many others) can play a crucial role in addressing the challenges associated with monitoring and environmental protection.

Conclusion

Many research centers are searching for materials providing a matrix for LRW inclusion to address relevant challenges associated with its long-term controlled storage and/or disposal. However, it's believed that no single technology applied alone can solve all the problems associated with the processing of all LRW types generated at different sites. That is why we should not forget about the advantages of polymers that can be successfully used in those cases when traditional technologies turn out to be less efficient and more costly.

LRW processing by means of its containment inside a polymer matrix allows to avoid the storage of liquid hazardous products at different sites. The proposed technology does not require special equipment or energy supply.

Further efforts should be focused on production of chemically resistant compounds suitable for disposal and not requiring their additional isolation.

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