The Polymers for Liquid Radioactive Waste Solidification: a Lost Chapter in the History of Engineering or a Step Forward? - 13529

Yury Pokhitonov
V.G. Khlopin Radium Institute, St. Petersburg, Russia
Dennis Kelley
Pacific Nuclear Solutions, Indianapolis, Indiana, USA

ABSTRACT

Ideas on the application of polymers for the liquid radioactive waste immobilization go a way back, and the first studies in the area were published 30-40 years ago. One should admit that regardless of the fairly large number of publications appeared in the past years currently the interest in this work came down greatly.
It was the successful assimilation and worldwide implementation of the LRW cementation technology caused a slump in the interest in polymers.
But today it's safe to say that the situation slowly changes, particularly due to the market appearance of the high-tech polymers manufactured by Nochar Company, and unique properties of these polymers gradually raise the demand in various countries.
The results of multiple experiments performed with the simulated solutions have passed the comprehensive tests with actual waste.
The economic effect from the implementation of the new technology is defined by the volume reduction of waste coming onto the repository, by the decline in the cost of transportation and of the repository construction on account of cutting down the construction volume.
Interesting results have been obtained during the search for the technical decisions that would allow using the polymer materials in the processing technology of the industrial toxic waste.
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.

INTRODUCTION

Research work aimed at locating materials for liquid radioactive waste (LRW) immobilization suitable for long-term controlled storage or disposal is under way at many research centers. There are numerous publications where various LRW solidification techniques including the use of polymers are reported.
The earliest studies of the application of polymers for incorporating LRW were published 30-40 years ago. However one should admit the polymers were not widely recognized as the materials for LRW immobilization ever since. Today just a few scattered instances of the limited practical use of polymers for this purpose are known.
The cause of depressed attention to polymer materials and their using in processes radwaste treatment is appearance and successful introduction in industrial scale another technological processes; first of all cementation and vitrification.
It seemed for several years that the polymers would remain just a chapter in the history of engineering and there were absolutely no prospects in the application of polymers.

Quite recently the new class of polymer materials has been developed and manufactured by the 'Nochar' Corporation of the U.S. Over the last 10-15 years the work associated with the application of those polymers for the liquid radioactive waste immobilization was in progress.
A number of tests were carried out with the U.S. Department of Energy at Hanford, Rocky Flats, Colorado, and Ohio sites, as well as with the Ministry of the Atomic Energy of Canada [1-4]. The experimental program has been accomplished in Sellafield, where the efficiency of 'Nochar' polymers for immobilizing liquid hydrocarbon waste has been demonstrated in the solid matrix that ensured the absence of liquid leaching under a slight compression [5]. Other examples of the successful application of polymers for immobilizing different RW types are given in references [6-10].
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.
It should been noted that in future the application of 'Nochar' polymers is not going to be limited to the exclusive use in the atomic industry.
The unique properties of these materials and the possibility of solidifying solutions of any composition allow the use of the polymers in the industrial chemical (non-radioactive) waste processing [10].
The goal of the planned work was to choose immobilization conditions for the solutions that would provide further isolation in the solid product form.
It is the high-tech polymers by Nochar Company that were used in our work and the primary goal was to develop a unique technology for solidifying aqueous, organic, and mixed radioactive waste.

RESULTS OF EXPERIMENTS AND DISCUSSION

The main advantages of waste processing by means of isolating it within the polymer matrix are as follows:
1. The possibility to conduct the waste immobilization process directly in containers as well as the possibility of the urgent radioactive waste localization in case of emergency at different enterprises of nuclear-chemical branches of industry.
2. The proposed technology does not require any special development of the equipment or additional supply of energy.
3. Cutting down the number of technological operations as compared to the conventional methods and lots of room for varying the characteristics of the solution composition.
In the beginning of work, we were well aware that the suggested solutions should be as simple and inexpensive as possible from the industrial scale implementation standpoint. And at that any considerable increase in volume of the produced material (waste form) subject to the long-term storage or disposal must not occur.
In the programs prepared, we expected to obtain answers to the three seemingly simple questions as follows.
1. Are the polymers offered by Nochar Company really versatile to the extent they could be used to solidify solutions of any composition?
2. It has been also not least important to establish how far the choice of the polymer mass to the solution mass ratio at the solidification stage was justified.

And the last: how the already solidified products would behave in the course of the following hold-up in the atmosphere of air or drying. (During the analysis of literature we did not find any data on this subject in the published papers.)
At the planning stage of work we also have taken into account the obvious requirements to look for the utmost simple and inexpensive decisions from the industrial implementation standpoint.
(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 [11].
The large volume of experimental studies with the simulated solutions performed at the Frumkin's Institute of Physical Chemistry and Electrochemistry RAS.
The main attention in this work was paid to the study of the waste solidification process with polymers in the presence of solid porous material additives and sorbents. In the work they used silica gel of different grade; zeolites; volcanic rocks, namely, slag, sand, pumice, glass, tufa; diatomites and some others.
The performed experiments allowed to reveal a number of the interesting process peculiarities when solidifying aqueous solutions with polymer materials.
The appearance of one of the most successful samples after solidifying the solution is given in Fig.1.

Fig.1. Final condition of the product from Sample No.385 – after solidifying the simulated solution with polymer No.960 and the additives of bentonite and silica sol solution of SiO_2 concentration of 95 g/L

In the figure one can clearly see that the process of water removal occurred uniformly, without destruction of the sample. The density of the obtained pellet was 1.19 g/cm^3.
The results of multiple experiments performed with the simulated solutions have passed the comprehensive tests with actual waste.
For the experiments we used the waste of the decontamination facility where all drains from the radiochemical building are collected and the research waste generated in the labs of the Institute.
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 nowhere near full list of waste used in our experiments and specific activity thereof is given in Table I.

TABLE I. Experimental results on solidifying technological products at the decontamination facility.

The name of the product	Specific activity
A sample of the aqueous solution – the evaporator cube residue	$Av_{\Sigma\alpha}$, - $2.5\cdot10^6$ Bq/l, $Av_{\Sigma\beta}$, - $1.1\cdot10^7$ Bq/l
A sample of the aqueous solution from the evaporator	$A_{\Sigma\alpha}$, - $7.5\cdot10^4$ Bq/l $A_{\Sigma\beta}$, - $1.1\cdot10^7$ Bq/l
An organic precipitate from the LRW collector tank	$Av_{\Sigma\alpha}$, - $6.6\cdot10^6$ Bq/l, $Av_{\Sigma\beta}$, - $1.1\cdot10^7$ Bq/l
'Hot' vacuum oil	Analysis was not assayed
Liquid GS-8 scintillator with water and tritium	Analysis was not assayed
Perlite slurry	Am-241 - Bq/l, $A_{\Sigma\beta}$, - $1.1\cdot10^4$ Bq/l
Drains of organic liquids. (Water phase is presented. According manual observation it's something 3 -10%)	$A_{\Sigma\beta}$, $3.6\times10^{6-}$Bq/L
Acidic drains. (HNO_3 concentration more than 3 mole/L.	$A_{\Sigma\beta}$ $0.4\times10^{6-}$Bq/L
Neutralized LRW solution, strongly salt. (The salt concentration more than 100 g/L).	Analysis was not assayed

During these sets of experiments with the aid of Nochar polymers solidification was successful enough and the high values of acidity and the salt concentration do not interfere with the process. Here we will give merely one example of the results obtained in solidifying actual waste (see Fig.2).

A B

Fig.2. The appearance of the sample after solidifying the evaporator cube residue. The total α-activity was $2.5\cdot10^6$ Bq/kg; the total β-activity was $7.3\cdot10^7$ Bq/kg.
A – polymer No.960 was used, the polymer mass to the mass of the liquid ratio was S/L =1/5.
B – the mixture of polymers was used, 95% of polymer No.960 and 10% of polymer No.910.
The mass of the polymers to the mass of the liquid ratio was S/L =1/5.

The not least important was to find out how the solidified products would behave with respect to water? In other words, it was necessary to obtain the data on the chemical stability thereof.
In the experiments on solidifying various samples of the actual waste the variation of the solidified sample mass during the following hold-up in the atmosphere of air was monitored.
The study of the solidified waste dewatering process is of interest on the two reasons.
First, it is necessary to know clearly what kind of a material and of what moisture content is obtained before it is moved to the long-term storage and what measures are needed for its final incapsulation.

In the same time, if the mass of solid waste is reduced in the process of drying, why don't we repeat the solidification procedure with one more portion of LRW and, hence, reduce the volume of solid waste moved to the repository?
In the properties the "aqueous solution-polymer" systems are very similar to the class of lyophobic sols. Under certain conditions the latter are transformed into jelly-like mass, named jelly or gel. Dewatering of a gel occurs by means of evaporation of water at the ambient temperature or under heating. If the solvent is separated from a gel, the latter preserves its initial shape and volume and is capable to absorb some liquid of other similar to the porous solids capable of absorbing various liquids.
(We faced this very phenomenon when trying to determine the chemical stability of the solidified samples. In all cases absorption of the aqueous solution in a rather big quantity was observed.)
In the next series of experiments, we decided to repeat operation of adding solution several times. (After the water was removed, next portion of the feed waste was added.)
In these experiments there were taken the specimens of solutions which compositions are shown in the Table II.

TABLE II. The results of analyzing of solution from process vessel – LRW collector.

Radionuclide	Cs-137	Ce-144	Co-60	Ba-133	Eu-152	Mn-54
Content in spectrum, %	69.0	7.8	2.7	17.2	3.2	≤ 0.1
$A_{\Sigma\beta} - 1.1 \cdot 10^{-6}$ Ku/l, $A_{\Sigma\alpha} - 2.7 \cdot 10^{-7}$ Ku/l, uranium content 7 mg/l, HNO_3 - 0.07 mole/l						

(It might be well to point out immediately that the content of salts (nitrates), corrosion products (iron, nickel), and organic components in those solutions was not assayed. According to the most approximate estimate, organic substance content reaches from 0.5 to 3.0 weight % (including hydrocarbon diluents, water-soluble complex-forming agents applied for analytical purposes.)
When carrying out the experiments, the following technique was applied.
In view of the fact that solutions included organic admixtures, polymer No. 960 and mixtures of polymers No960 and No910 were used in the work.
Experiments were conducted in polyethylene cups of 100 ml in volume. A charge of polymer in amount of 10 g was placed into the cup and after that 50 ml of radioactive waste solution were poured there. Solidified compositions obtained after solution mixing with polymer were subjected to air curing at a room temperature.
Partial evaporation of water and volatile organic compositions took place in the course of solidifying. The degree of evaporation was determined by periodic weighting.
When evaporation was completed, fresh portions of LAW solution were added into the polymer cups with solidified samples with the purpose to include maximum amount of solution into the polymer matrix.
Test realization conditions are shown in the Table III.
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.

The given approach has no analogs in the world practice and even now we can speak about the principally new concept in the LRW handling area.

TABLE III.
Conditions to conduct waste solidification experiments.

Cycle No. (solidification procedure and air drying)	Volume of solution and the proportion between polymer masses and liquid (S:L).	Sample's solution mass loss after solidification and airing (air drying).			Reduction factor reached with respect to initial solution volume.
		After 10 days, %	After 24 days %	After 56 days, %	
Series experiments # 1. Polymer # 960.					
1-st cycle.	Volume of solution – 50 ml, polymer mass 10 g. (S:L =1:5)	43.7	84,7	93.2	≈ 5.0
2-nd cycle		35.0	47.8	64.0	≈ 10.0
Series experiments # 2. Mixture of polymers # 960 (95%) and # 910 (5%)					
1-st cycle.	Volume of solution – 50 ml, polymer mass 10 g.	43.6	82.4	93,0	≈ 5.0
2-nd cycle		33.4	42.2	61.9	≈ 10.0
Series experiments # 3. Mixture of polymers # 960 (90%) and # 910 (19%)					
1-st cycle.	Volume of solution – 50 ml, polymer mass 10 g.	40.8	81.4	92.8	≈ 5.0
2-nd cycle		34.1	47.9	65.0	≈ 10.0

The assessment process could help to visualize the economic effect from the implementation of the proposed technology gained from the reduction of the waste volume transferred to the repository.
Prospects of using the solidified material with polymer No.960 as a solid waste for disposal are greatly affected by the results of leach rate studies.
We have performed the experiments simulating the solid waste cementation procedure accepted at LSK 'Radon'.
Polymer No.960 and LRW were mixed at the ratio of 1/10, 60 ml of LRW and 6 g of the polymer, respectively. LRW characteristics were as follows: $A_{\beta}= 1.8\cdot10^{7}$ Bq/L, $A_{\alpha} = 3.6\cdot10^{5}$ Bq/L, $A_{Cs\text{-}137} = 9.5\cdot10^{6}$ Bq/L, $A_{Am\text{-}241} = 2.5\cdot10^{5}$ Bq/L, dry residue = 59 g/L, pH = 12.6, COD = 160 mgO/L.
Preliminarily solidified compound was put into a bag made of polyethylene film 0.1 mm thick and sealed tight. (Surface square area of the bag containing the compound was 80 cm^2, its weight was 66 g. The bag was secured in the center of the mould and grouted. The grout was prepared from the M400 Portland cement and sand taken at the cement/sand ratio of 1/2.)
Volume of the resulting cylinder was 850 cm^3 and its surface square area was 480 cm^2. After 5 days of holding the hardened monolith was put for leaching into a 2000 mL beaker filled with

distilled water. On the 1st, 3rd, 7th day and further in the certain time intervals the monolith was weighted and the leachate was examined using a gamma-spectrometer to determine the content of Cs-137 and Am-241.
It is seen from results obtained the Cs-137 leach rate from both samples is several orders of magnitude less than the value of $1 \cdot 10^{-3}$ g/cm^2/day required by GOST R 51883-2002; moreover, the Cs-137 leach rate in the second run is two orders of magnitude lower than in the first one.
During work a great attention was paid to the experiments on solidifying the actual organic waste.
One possible option for liquid organic waste handling is the long-term storage in special designed repositories. This technical solution may cause a number of problems, both environmental and economical. In the course of the storage organic waste may decompose yielding radiolytic gases and hence, assume a fire hazard.
That is why the storage of large quantities of organic liquids, such as extractants and solvents, in the laboratories of the Institute is unacceptable.
The experiments were run using the actual waste currently stored in the Radiochemical Building. Polymer No.910 was used for the organic waste solidification.
All organic solutions solidified with the aid of the polymers were prepared to transportation as the solid waste. The additional isolation procedure comprised mixing the solidified compositions with the cement grout. The solidified waste was placed into polypropylene containers and filled by the cement grout. The containers were covered with lids and put into polyethylene bags.

Fig. 3. Containers with solidified organic waste packed for transportation.

One more promising area of the possible application of polymers should be pointed out, the economic assessment of it being hard to make. It is the application of polymer materials as the assets for the emergency damage control when the advantages of the polymers become obvious.
From our standpoint this area demands very thorough and weighted approach and deserves the special consideration.

CONCLUSIONS

In our opinion, one of the main goals of the work has been achieved, namely, demonstration of the possibility to localize the liquid radioactive waste of different composition and activity level by means of solidifying it into the polymer materials.

From the data given in the paper it can be concluded that the third generation of the high-tech polymers offered by the 'Nochar' company has sufficiently broad spectrum of applications in the atomic industry on account of a number of advantages inherent to those materials.
As an outcome of 3-year work the new technical decision on the polymer materials application in the LRW solidification technology has been proposed.
LRW solidified in the polymer matrix are 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.
The given approach has no analogs in the world practice and even now we can speak about the principally new concept in the LRW handling area. Based on the results of the studies the patent claim titled 'Technique for Liquid Radioactive Waste Immobilization' authored by Yury Pokhitonov and Dennis Kelly has been submitted.
The economic effect from the implementation of the proposed technology is going to be received first of all on account of the volume reduction of waste coming into the repository and the lower costs of the transportation and the repository itself due to a severe cut of the construction volumes needed for the disposal of the same amount of radionuclides.
According obtained results we also can mentioned another possible application of polymers namely to use the polymers in cases of origination and elimination of accidental conditions, when it is necessary to reduce concentration of radioactive aerosols in air and prevent their spread in the environment.
Interesting results have been obtained in the course of experiments conducted to look for technical decisions that would allow the polymer materials application in the industrial toxic waste processing technology. The accumulation of the toxic waste in the environment presents as severe hazard as the radioactive waste.
It is worth to mention here that the polymers have been never used anywhere for the toxic chemical waste processing.
From our standpoint, it might be interesting to use and develop the results of the studies obtained in the following areas:

♦ The application of polymer materials for localizing radioactive and toxic waste in case of emergency;

♦ The development of a technology for the synthesis of polymer-based materials for immobilizing radionuclides by means of the deposition of protective coatings. This approach is advantageous in the possibility to obtain the leach-proof products along with the minimum increase of the solid waste volume transferred to the repository;

♦ The conditioning (solidification) of liquid organic radioactive waste followed by the thermal destruction thereof leading to the volume reduction of waste transferred to the repository;

♦ The necessary condition for the successful sharing of the experience in the application of polymers is the technical and economical assessment of different options available for the LRW solidification. The assessment process could help to visualize the economic effect from the implementation of the proposed technology gained from the reduction of the waste volume transferred to the repository.

Along with that it is difficult today to forecast all possible areas of the polymer application in future.

Further studies in the indicated areas would let to develop the principally new approaches that will play an important part in making the demand for polymers including the enterprises of the American and Russian atomic industry as well.

REFERENCES

1. Nochar® Inc., Indianapolis, Indiana – Technical Product literature "Nochar PetroBond® Absorbent Polymer Oil Solidification Agent".
2. Dennis Campbell, Richard Govers, Charles Pietsch. ALARA and cost savings success with highly contaminated liquid and liquid mixed waste solidification using Nochar® petrobond® polymer technology. EPRI/ISOE International ALARA Symposium, 2005.
3. "Nochar Petrobond Absorbent Polymer, Tritiated Oil Solidification", Innovative Technology Summary Report, DOE/EM-0598, U.S. Department of Energy, September, 2001.
4. "Deployment of Nochar Petrobond Technology to Solidify TRU Oil at Rocky Flats", Rocky Flats, Colorado, Environmental Technology Site, PRO-1582-POP/PQP, United States Department of Energy, Office of Environmental Management, October 23, 2001.
5. Helen Cassidy, Dennis Kelley. Oil immobilization program at Sellafield: an innovative approach. Waste Management Conference, 25 Feb – 25 March 1, 2007, Tucson, Arizona, USA.
6. KELLEY D., CAMPBELL D. 'Proven Technologies for the Treatment of Complex Radioactive Liquid Waste Streams; U.S. Department of Energy and International Case Studies', 29th International Symposium on the Scientific Basis for Nuclear Waste Management MRS 2005
7. Yuri Pokhitonov, Vadim Starchenko, Dennis Kelley, Ward Brunkow, "Application of High Technology Polymers for the Immobilization and Solidification of Complex Radwaste Types", Waste Management Conference, 25 Feb – 1 March, 2003, Tucson, Arizona, USA.
8. Dennis Kelley, Dennis Cambell, Yuri Pokhitonov, et al. "Innovative Technology for Liquid Radwaste Treatment for Use in Newly Designed Applications", 10th International Conference on Environmental Remediation and Radioactive Waste Management, ICEM '05, 4–8 September, 2005, Glasgow, Scotland, UK.
9. Bao Liangin, Lin Meiqiong, Dennis Kelley, "China's Scientific Investigation for Liquid Waste Treatment Solutions", 15th Pacific Basin Nuclear Conference, 15–20 October, 2006, Sydney, Australia.
10. Pokhitonov Yu., Kelley D., Nechaev A., Chugunov A., Pokhitonov A. Prospects on Immobilization of Liquid Radwastes and Industrial Wastes with the Use of High Technology Polymers. "15th Pacific Basin Nuclear Conference, 15–20 October, 2006, Sydney, Australia.
11. Yuri Pokhitonov, Vasiliy Babain, Vladislav Kamachev, Dennis Kelley, "Russia: Results and Prospects of Liquid Solidification Experiments at ROSATOM Sites", Waste Management Conference, 28 Feb – 3 March, 2011, Phoenix, Arizona, USA.