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INNOVATIVE TECHNOLOGY FOR RADWASTE TREATMENT FOR NEW APPLICATIONS

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ABSTRACT

Radioactive liquid waste products are created during many stages of the nuclear power cycle. Liquid waste is generated from the ore extraction process through to nuclear power plant decommissioning. Effective treatment of waste from the initial stage to the final stage has been a challenge for nuclear nations. This is particularly true for the more complex waste streams with organic, acid, alkaline, aqueous and metallic compositions. Today the nuclear community is keenly aware of safeguards that are necessary to protect and secure liquid waste. Innovative technologies are being developed to solidify these waste streams, to provide methods for safe transport and disposal, and to lessen the risk of accidents.

With wide diversity of liquid compositions and activity levels, it is important to note that many of these products cannot be treated with existing, commonly used techniques. Additionally, as new generators of waste are designed and utilized, there is a need to consider new and safer methods for the treatment of waste.

One solution to this problem is to apply proven, low cost polymers to absorb liquid compositions soon after production. The polymers may be combined to create a formula specifically designed to permanently solidify a waste stream in a simple one-step process. Principal advantages for using high tech polymers for treatment are high chemical and radiation stability after solidification without leaching.

The purpose of the presented research is to:

- determine the optimum bonding ratio for the complex waste stream;
- evaluate the immobilization and stability process from polymer solidification after gamma irradiation (Cobalt 60 source).

Conditions of the experiments and the test results are analyzed and evaluated in this paper.

INTRODUCTION

Many difficult to treat waste streams have been put aside in temporary storage because few dependable, low cost solutions are available. Consequently, legacy waste remains untreated and new nuclear powered equipment in production and under design will require more effective techniques for waste treatment. Through scientific research we seek new ways of treatment utilizing flexible technologies and advanced equipment designs to address the radwaste production, as it is generated.

For example, during the process of extraction division of strontium -90 and yttrium -90, (Yttrium -90 generator), the amount of acidic and organic radioactive waste is small, perhaps several liters per year. However, medical centers using generators of radioisotopes very often do not process the waste product, which results in an accumulation of untreated liquid waste. In addition, during the manufacture of isotopes, standard industrial equipment and technologies for waste treatment (evaporation, extraction and sorption) are not cost effective.

In 2003 the V.G. Khlopin Radium Institute (St. Petersburg, Russia) and Pacific World Trade (Indianapolis, USA) began an extensive research program to determine the effectiveness and performance of polymers for the solidification of complex waste streams in newly designed applications. Furthermore, testing was conducted to prove the stability of polymers under conditions of LLW, ILW and HLW solidification. The research program, continuing through 2004, has provided us with conclusive results.

EXPERIMENTAL RESULTS AND ANALYSIS

The purpose of the research program is to determine the optimum conditions for solidification of the waste stream.

An important aspect of the work is to analyze the immobilization and stability process from polymer solidification after gamma irradiation (Cobalt 60 source) and to confirm that polymers can be applied in the treatment of high toxic liquid waste generated by medical centers.

The case study examines the application of radwaste treatment from the Yttrium -90 generator used in nuclear medicine. The Yttrium -90 generator design is innovative and addresses the issue of safety features for the treatment of HLW liquids.

While using extraction technology division of strontium -90 and yttrium -90 (yttrium -90 generator) two species of waste are formed that require treatment, in this case immediately following the two year life of the generator.

The first solution is nitric acid containing strontium -90. The second solution is exhaust extractant (mixture of di-2 ethyl, hexyl phosphoric acid - $(C_8H_{17}\text{-}O)_2P(O)OH$) in hydrocarbon diluent, dodecane). With regard to the small volume of waste and the circumstances of the generator location, the treatment method of cementation is not suitable for organic solutions solidification. The decision to use polymer technology was accepted based on the experiment test results and economic factors.

Polymers used in the experiments are manufactured by Nochar, Inc., USA. Nochar polymers have been applied extensively to solidify various waste streams in the U.S. and international nuclear sectors. The polymers have wide ranging capability and have been thoroughly tested for leaching, stability (75-90 million rad, gamma, cobalt source), compression and many other tests conducted by the U.S. DOE. Radwaste compositions treated by Nochar include LLW-HLW tritiated oil, TRU acid and TRU oil, TBP-purex, extremely high alkaline (14.2 pH) and aqueous compositions, and various complex extractants that include heavy metals, solvents, scintillation fluid**,** etc. [Ref. 3-4]

To conduct the experiments the necessary items included glass beakers, polymers, solutions and a weight scale. The polymer formula is based on the chemical composition of the waste stream as one or more polymers may be combined. A solidification ratio can be determined based on the net weight of the liquid and polymers, or by volume of liquid and weight of the polymer, as noted in Table 1. The model solution is nitric acid -0.5-5.0 M/l. Water is also tested. Polymers N960 and N910 were blended at a 70/30% ratio. The blending of two polymers was determined by the actual waste stream composition of nitric acid and the hydrocarbon diluent.

During the tests the polymers were stretched or taken to their full capacity. This is a recommended procedure in order to consider the limits of the solidification and to consider cost factors for actual application of the polymers.

A distinguishing feature of the experiments was the absence of any mixing of the polymer to the nitric acid solution.

Fig. 1 Polymers in beaker

Table 1

#	Conditions		Results
	Weight of polymer, g	Volume of a solution, sm^3	
X	7.1	55 (0.5 M HNO_3)	After 15-17 hours, no free liquid is present.
1	6	50 (0.5 M HNO_3)	After 1 hour, jelly-like mass formed, no liquid.
2	12	50 (0.5 M HNO_3)	After 7-10 minutes, no free liquid. Excess polymer at bottom of beaker.
3	3	25 H_2O	After 7-10 minutes, no free liquid. Excess polymer at bottom of beaker.
4	6	25 H_2O	After 1 hour, jelly-like mass, weak structure. Free liquid present.
5	3	25 (5 M HNO_3)	After 1 hour, jelly-like mass, weak structure. Free liquid present.
6	6	25 (5 M HNO_3)	After 1 hour, mass, no free liquid.
7	3	25 (0.5 M HNO_3)	After 1 hours, jelly-like mass, free liquid present
8	15	50 (0.5 M HNO_3)	After 7-10 minutes in upper part of beaker, loose jelly-like mass is present. After 20-25 minutes, sample is jelly mass, no free liquid. Excess polymer at bottom of beaker.

Notes: Solution was added in separate portions during each test without mixing. (15 ml + 15 ml + 15 ml + 10 ml). After the initial solidification, the first addition of solution was made. The second and third additions of solution were made after 1 and 2.5 hours after the experiments began. The last addition (10 ml) was made the following day, approximately 15-17 hours later.

The final examination was carried out after 3 months aging. (Samples aged in open air at room temperature.) The appreciable reduction of volume was noted. The appearance of the sample after aging during 3 months is submitted in:

Fig. 2 Solidification Sample

The following polymers - 910, 941 and 930 were used in next experiments to solidify extractant (dodecane + di-2 ethyl, hexyl phosphoric acid 0.25 M).

The conditions of experiments on solidification of exhaust extractant and the results obtained are presented in Table 2. (All experiments were carried out without mixing.)

Table 2

#	Conditions		Results	Notes. Fig. #
	Mass (g) and # of the polymers.	Mass of liquid (extractant) added, sm^3		
201	3 ***941***	10 + 10	After 5-20 seconds, no free liquid is present. Excess polymer at bottom of beaker. After 10 minutes 10 ml more have added. Solidification has not taken place.	Pic # 201 The appearance of the sample after aging during 15 days.
202	3 ***910***	10 + 10 + 10	After 5-20 seconds, no free liquid is present. Excess polymer at bottom of beaker. After 10 minutes 10 ml more have added. Solidification was successful. After 20 minutes 10 ml more have added. Solidification was going slowly.	
203	3 ***910***	20	After 3-5 seconds, no free liquid is present.	Pic # 203 The appearance of the sample after aging during 15 days.
Next experiments.				
205	2 ***910***	30	Solidification was not successful, free liquid present.	
206	2 ***910***	20	Solidification was not successful, free liquid present.	
207	2 ***910***	12	After 2 minutes, jelly-like mass, weak structure. Only after 5 days, no free liquid is present.	Pic # 207 The appearance of the sample after aging during 15 days.
208	2 ***930***	12	After 2 minutes, jelly-like mass, but no free liquid is present.	Pic # 208 The appearance of the sample after aging during 15 days.
Next experiments. (Last week.)				
210	2	8	After 2-4 seconds, no free liquid is present.	

	910			
211	2 ***910***	10	After 2-4 seconds, no free liquid is present.	

As a result of the experiments carried out it was shown, that an optimum ratio of weight of polymer to weight of a solution of extractant is 1:4 -1:5.

For solidification it is possible to use all polymers tested, however, 910 is preferable.

IRRADIATION / STABILITY OF POLYMER AND SOLUTION

Given that the HLW solidification materials will be placed in large term storage and the activity level will be rather significant, experiments were conducted on the radiation stability.

The conditions of experiments and results are presented in Table 3.

Table 3

#	**Weight of polymer, g**	**Volume of a solution, sm^3**	**Irradiation. External Dose, RAD**	**Results of samples inspection. Irradiation / Stability of Polymer.**
1	6	50 (0.5 M HNO_3)	$4.3x10^7$	In ampoule, liquid appears.
2	12	50 (0.5 M HNO_3)	$1x10^8$	Sample is solid, no free liquid is present.
3	3	25 H_2O	$3.4x10^7$	Bi-phase system. Free polymer & frozen Transparent phase.
4	6	25 H_2O	$3.4x10^7$	
6	6	25 (5 M HNO_3)	$3.4x10^7$	In ampoule, liquid appears.

Fig. 3 Solid, no free liquid (#2 in Table 3)

As a result of the experiments carried out it was shown the samples investigated have remained their properties after gamma irradiation (cobalt 60 source) up to radiation dose 10^8 rad.

CONCLUSIONS

Each nation has its own set of requirements for the treatment and disposal of waste containing radionuclides; the essential ones being safety and economic. Historical biases also play a part in determining a nation's requirements. Continuous investigation for new but proven and safe technologies for liquid waste treatment is the object of all countries, especially those with long-term and final storage facilities.

Based on the results of this research work, we can make several significant conclusions regarding the use of high tech polymers to solidify liquid waste.

Complex streams that include organic waste and that vary in specific activity can be solidified with no leaching and with long-term stability. Experiments indicate that 25-30% by weight of the polymer to liquid can achieve satisfactory results for the solidification of radwaste from an yttrium -90 generator. The polymer to liquid bonding ratio is attractive for economic considerations. For this waste stream no mixing was required which eliminates many handling and safety issues. For each waste stream it is important to carry out the investigation of the chemical composition and to determine the correct polymer formula in order to maximize the efficiency of the final solidification.

The samples show that they have adequate stability to remain in storage indefinitely, prior to transport to a long-term or final storage facility. This feature of the polymer technology provides new opportunities for producers of low – high level waste to safely store and transport the packaged waste without the possibility of leaching.

Furthermore, we can conclude that the final form of the waste solidification has no relationship to its ability to remain stable. The critical factor with solidification is its ability to remain stable, without leaching, for a very long or indefinite time. The hardness of the solid mass is not relevant to realizing the final objective.

The successful results of the research program allow the yttrium -90 generator designer to create a prototype that includes the polymer as an integral part of the generator system, thus enabling the generator to treat the waste as it is produced. In our judgment this is a revolutionary application and one that will be carefully considered by the nuclear community in the future.

Not only can the polymers be used to treat existing legacy waste or newly produced waste, but it can also be considered for use at nuclear plants in the case of emergencies. Polymers applied directly to closed vessels could prevent liquid waste from spreading into the environment and endangering people.

We can also suggest that the polymers may be used in factories that produce toxic waste products, such as chemical plants. However, we do acknowledge that polymers cannot solve all liquid waste problems.

The authors recommend that the efforts of joint collaboration and research in this field be continued in Russia and the United States so that new solutions for environmental safety may be found and advanced worldwide.

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