RUSSIA: RESULTS AND PROSPECTS OF LIQUID SOLIDIFICATION EXPERIMENTS AT ROSATOM SITES

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

ABSTRACT

Ongoing experimental work has been underway at selected nuclear sites in the Russian State Atomic Energy Corporation (ROSATOM) during the past two years to determine the effectiveness, reliability, application and acceptability of high technology polymers for liquid radioactive waste solidification. The long term project is funded by the U.S. Department of Energy's Initiatives for Proliferation Prevention (IPP) program. IPP was established in 1994 as a non-proliferation program of DOE / National Nuclear Security Administration and receives its funding each year through Congressional appropriation. The objectives of IPP are:

- To engage former Soviet nuclear weapons scientists, engineers and technicians, currently or formerly involved with weapons of mass destruction, in peaceful and sustainable commercial activities.
- To identify non-military, commercial applications for former Soviet institute technologies through cooperative projects among former Soviet weapons scientists, U.S. national laboratories and U.S. industry
- To create new technology sources and to provide business opportunities for U.S. companies, while offering commercial opportunities and meaningful employment for former weapons scientists.

Argonne National Laboratory provides management oversight for this project. More than 60 former weapons scientists are engaged in this project.

With the project moving toward its conclusion in 2012, the emphasis is now on expanding the experimental work to include the sub-sites of Seversk (SGCHE), Zheleznogorsk (GKhK) located in Siberia and Gatchyna (KRI) and applying the polymer technology to actual problematic waste streams as well as to evaluate the prospects for new applications, beyond their current use in the nuclear waste treatment field. Work to date includes over the solidification of over 100 waste streams for the purpose of evaluating all aspects of the polymer's effectiveness with LLW and ILW complex waste. Waste stream compositions include oil, aqueous, acidic and basic solutions with heavy metals, oil sludge, spent extractants, decontamination solutions, salt sludge, TBP and other complex waste streams. Extensive irradiation evaluation (up to 270 million rad), stability and leach studies, evaporation and absorption capacity tests and gas generation experimentation on tri-butyl phosphate (TBP) waste have been examined.

The extensive evaluation of the polymer technology by the lead group, V.G. Khlopin Radium Institute, has resulted in significant discussion about its possible use within the ROSATOM network. At present the focus of work is with its application to legacy LLW and ILW waste streams that exist in a variety of sectors that include power plants, research institutes, weapons complex, site and submarine decommissioning and many others. As is the case in most countries, new waste treatment technologies first must be verified by the waste generator, and secondly, approved for use by the government regulators responsible for final storage. The polymer technology is the first foreign sorbent product to enter Russia for radioactive waste treatment so it must receive ROSATOM certification by undergoing irradiation, fire / safety and health / safety testing. Experimental work to date has validated the effectiveness of the polymer technology and today the project team is evaluating criteria for final acceptance of the waste form by ROSATOM.

The paper will illustrate results of the various experiments that include irradiation of actual solidified samples, gas generation of irradiated samples, chemical stability (cesium leach rate) and thermal stability (Fig.2), oil and aqueous waste stream solidification examples, and volume reduction test data that will determine cost benefits to the waste generator. Throughout the course of this work, it is apparent that the polymer technology is selective in nature; however, it can have broad applicability to problematic waste streams. One such application is the separation and selective recovery of trans-plutonium elements and rare earth elements from standard solutions.

1. INTRODUCTION

Liquid solidification test programs have been underway at three ROSATOM sites since 2009 under the Initiatives for Proliferation Prevention program. The research tests have investigated the stability and capacity of polymers for use with standard and complex waste streams. Additional research work has been conducted by the Institute of Physical and Electro-Chemistry, Moscow, to determine a suitable waste form for storage. The first series of tests focused on absorption capacity, evaporation, irradiation and stability, thermal stress analysis, compression and gas generation of organic and aqueous waste. Results from these tests have validated the polymer's ability to fully absorb liquid waste without liquid release and degradation.

For the polymers to be used on a large scale within the ROSATOM network, proper certification and licenses are required for importation, distribution, use and disposal. In 2010 formal certification began with the Scientific Technical Center of Nuclear Radioactive Safety, an agency of ROSTEHNADZOR, the Russian technical supervisory authority in ROSATOM. The first series of tests conducted by V.G. Khlopin Radium Institute have generated data required by the Scientific Technical Center. Documentation required for certification includes irradiation analysis, human health and safety, fire and explosion and suitability for final storage.

Test data and analysis is summarized from three ROSATOM sites: V.G. Khlopin Radium Institute (KRI), Siberian Chemical Combine (SGCHE), and Mining Chemical Combine (GKHK).

2. EXPERIMENTS: V.G. KHLOPIN RADIUM INSTITUTE

Hundreds of experiments of been conducted at KRI over recent years using simulant and real solutions. This section will illustrate several pertinent experiments involving solidification ratios, evaporation, heat-stability, irradiation and gas generation.

Selective waste streams are shown in Figure 1, with waste composition, volume of waste applied to two types of polymer and the result. N960 polymer is applied to aqueous waste and N910 polymer is applied to organic waste. Polymers are blended to capture the mixed waste. Ratios vary from less than 1: 1 (liquid: polymer) to 5: 1, with successful results.

	Characteristic (composition) of wastes	**Conditions of solidification**			**Results**
		Volume of waste used, ml	**Amount of # 960 used, g**	**Amount of # 910 used, g**	
4232	Sludge residue from the bottom of the apparatus (aqueous phase). U-80g., $NaNO_3$~200g, HNO_3-0,8 M/I	6	8	0,5	Successfully solidified
4231	Sludge residue from the top of the apparatus (occurrence of organic phase is probable). U-80g., $NaNO_3$~200g, HNO_3-0,8 M/I. Very thick black liquid.	6	8	0,5	Successfully solidified
4237	LL decontaminating solution with low amounts of organic substances, U-153 g/l, $NaNO_3$~100-150g, $HNO_3$2,5 M/I	12	8	0,5	Successfully solidified
4238	LL decontaminating solution with low amounts of organic substances. U-153 g/l, $NaNO_3$~100-150g, $HNO_3$2,5 M/I	20	4	2	Successfully solidified
4125	U-20 g, $NaNO_3$40g, $HNO_3$1,2 M/I. There was a precipitate in the solution.	15	16	0,5	Successfully solidified
4283	Uranium re-extracts. U-70g, HNO_3-0,07 M/I.	20	4	1	Successfully solidified

Figure 1. Solidification formulas and bonding ratios

Figures 2 and 3 represent solidifications of ILW solutions in a hot cell environment.

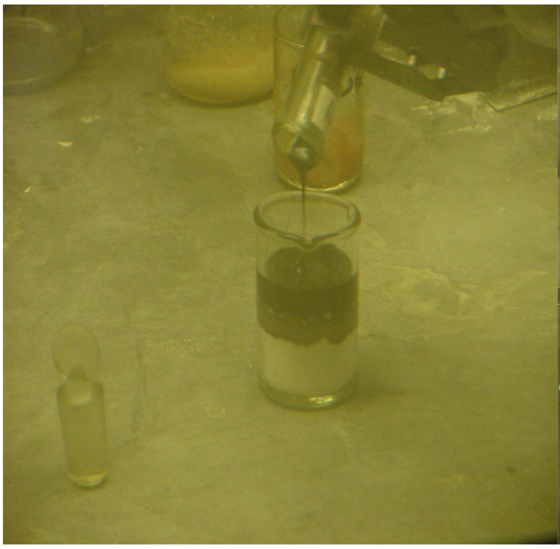

Figure 2. Organic sludge

Figure 3. Nitric acid with plutonium

Differential thermal analysis experiments were carried out as KRI studied thermal stability of the polymers, see Figure 4. Additional DTA tests were conducted using 1.0M HNO_3 solutions with similar results. It can be concluded from these experiments that the polymers possess rather high thermal stability with decomposition occurring at 300C.

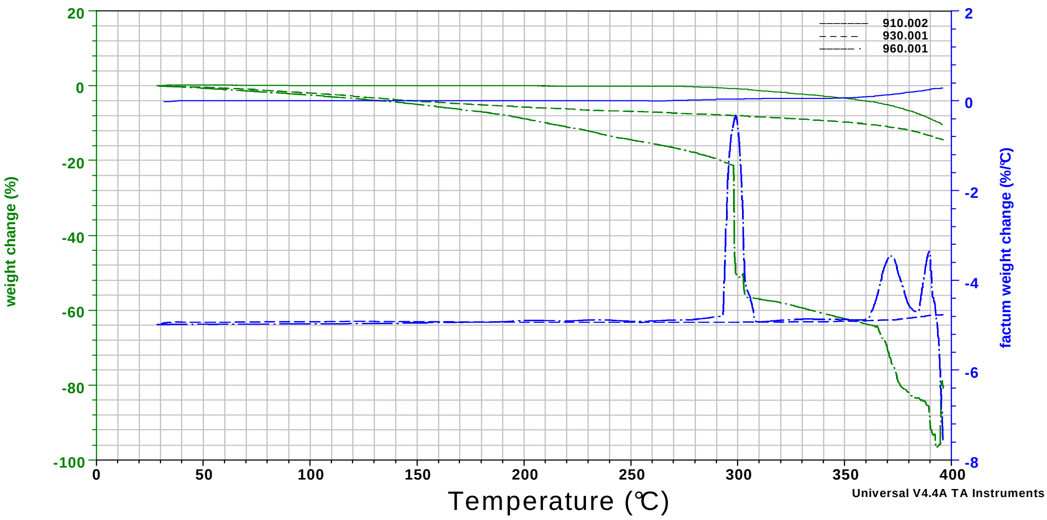

Figure 4. DTA – curves for polymers, N910, N930 and N960

Extensive irradiation testing using a Cobalt 60 gamma irradiator has been conducted at KRI to determine polymer stability. Recent experiments have focused on extreme irradiation conditions, 270 million rad (30 rad per second for 30 days + 73 days) on a nitric / organic solution. The result is shown in Figure 5, as the solidified sample is hard, brittle with no liquid release. Gas generation tests have been conducted on the polymers, solidified samples with nitric acid and samples with oil and TBP. Results have shown that there is no gas release from the polymers under irradiation. A very small percentage, less than 1%, of hydrogen gas was detected from the oil / TBP sample and no gas generation was detected from the nitric sample. All tests were conducted with glass ampoules, as seen in Figure 6.

Figure 5. Irradiation experiment on nitric organic solution

Figure 6. Irradiation test of N960 to determine gas generation

There is strong interest in Russia with respect to the polymer's absorption capacity. Experiments have been conducted to determine the polymer's ability to absorb various aqueous waste solutions, then place the solidified forms in the open air for 3-8 weeks and calculate the amount of water evaporation. Considerable weight loss occurs over time with evaporation.

Figure 7. Potassium dichromate sample

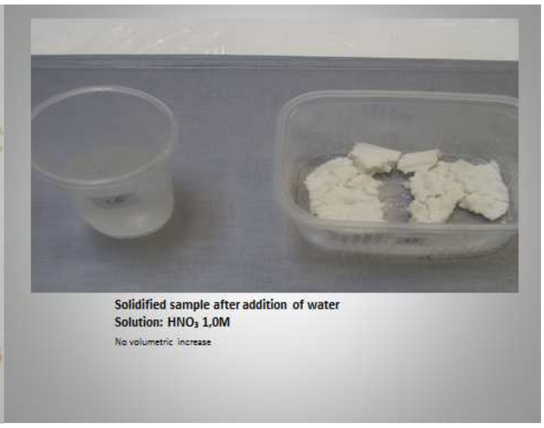

Figure 8. Absorption capacity

Figure 7, shows a solidified waste form of potassium dichromate that has been left in open air for 60 days. The weight loss from evaporation is shown in Figure 9. The advantage of weight loss in the solidified sample provides for increased absorption capacity of the polymer, which in turn, allows the polymer to be re-used in a secondary application by adding waste, thus reducing the total volume of liquid waste for storage. Figure 8 shows the results of solidified material after a secondary application of water. If applied in certain circumstances, economic advantages will be demonstrated for final storage of the waste.

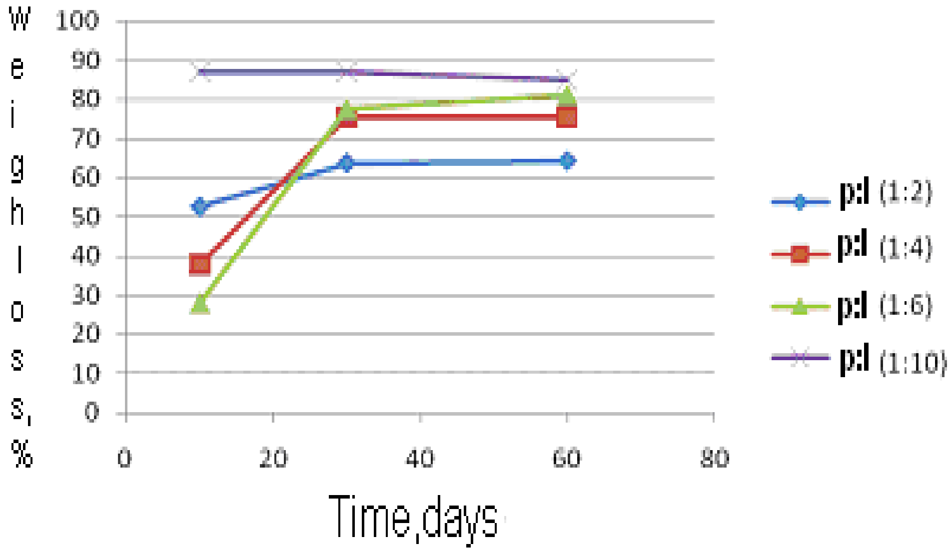

Figure 9. Weight loss of solidified samples with 4 polymer formulas

2.2 EXPERIMENTS: SIBERIAN CHEMICAL COMBINE

The Siberian Chemical Combine was established in 1949 and is located in Seversk, formally known as Tomsk-7. SGCHE is one of the principal nuclear materials production sites in the ROSATOM complex with uranium processing facilities, plutonium production reactors (recently closed), a spent fuel reprocessing plant, a uranium enrichment plant and a variety of other processing and storage facilities.

Four waste streams were tested at SGCHE, iron-containing sludge, insoluble natural uranium concentrate condensed residues, and two types of liquid organics. Spent ion exchange resins were solidified using a resin-in-oil process. Figure 10 shows a solidified sample of S957 resin saturated in uranium in oil. The result is a strongly secured bonding of the resin grains.

Figure 10. Solidified sample of resin saturated in uranium

This chart shows results of solidification tests, indicating the type of liquid waste, pre-treatment of the waste, the solidification ratio of liquid to polymer and the results.

#	RW appearance.	Pretreatment of the RW	The liquid phase mass / solid phase mass (polymer) ratio, (S/L)	Notes
1	Insoluble residues from the natural uranium concentrate digestion.	Dilution by distilled water with the solid/liquid ratio of S/L=1/3.	5:1	Solidified mass of the closely stick together brown colored granules with the surface inclusions of precipitate particles. Specific activity of 5200 Bq/kg. (Fig. 3)
2	VM-1c vacuum oil.	No pretreatment.	2:1	Solidified mass of the closely stick together white-yellow colored granules with the density less than that of water (≤1 kg/dm^3). (≤1 кг/дм^3) (Fig. 4.)
3	Spent VM-1c vacuum oil.	No pretreatment.	2:1	Solidified mass of the closely stick together dark-grey colored granules with the surface inclusions of precipitate particles and the density less than that of water (≤1 kg/dm^3). Specific α-activity of 181 Bq/kg. (Fig. 5.)

4	Spent VM-4 vacuum oil.	No pretreatment.	4:1	Specific α-activity of 181 Bq/kg. Solidified mass of the closely stick together dark-grey colored granules with the surface inclusions of precipitate particles and the density less than that of water (≤1 kg/dm^3). Specific α-activity of 250 Bq/kg.
5	S957 resin containing 250 mg/g of uranium.	Resin suspension in vacuum oil VM-1c. S/L =1:4	2:1	Loose mix of the polymer granules and resin granules. (Fig. 6.)
6	S957 resin containing 250 mg/g of uranium.	Resin suspension in vacuum oil VM-1c. S/L =1:6	7,5:1	Gel-like mass with the strongly secured resin granules. (Fig. 7.)

Figure. 11 Test results on four waste streams

Figure 12 represents a sample of insoluble residue from the natural condensed uranium concentrate, drying under normal room temperature. Figure 13 is a sample of solidified VM-4 vacuum pump oil at a 4:1 bonding ratio.

Figure. 12

Figure. 13

2.3 EXPERIMENTS: MINING AND CHEMICAL COMBINE (GKHK)

The Mining and Chemical Combine was established in 1950 and is located in Zheleznogorsk, formally known as Krasnoyarsk-26. GKhK’s primary task for ROSATOM was to produce plutonium for nuclear weapons. The three plutonium production reactors have been shut down, with the last one closing in 2010.

Tests have been conducted on a heavy TBP diluent, hexachlorobutadiene (HCBD), a major component of TBP. Tests using N910 polymer were conducted at 5:1 and 7:1 ratios. The solidified form was homogeneous with a glass or crystallized appearance. Some air bubbles were present and were most likely formed during the mixing process.

A large scale test will be conducted in the 3rd quarter to determine the appropriate mix rate and final form. Conditions for final storage are under evaluation, with temperatures reaching -40C, it is necessary to consider effects on the solidified material. The polymers have passed "freeze-thaw" tests in the U.S., so it is not believed that extreme cold will not cause degradation of the polymers.

2.4 SMALL SCALE SOLIFICATION PROJECT: KHLOPIN RADIUM INSTITUTE-GAYCHYNA

The Khlopin Radium Institute was established in 1922 to conduct research and development for the nuclear industry that included analytical laboratory services, design nuclear accident response procedures, study environmental consequences of nuclear testing and produce isotopes. KRI has an experimental facility in Gatchyna as well as facilities in Sosnovyy Bor.

The Radiochemistry Department of KRI has accumulated an inventory of liquid organic radioactive waste stored in Gatchyna. The total inventory is more than 300 liters and can be identified as follows:

- TBP solutions in kerosene and other hydrocarbons
- Chlorinated cobalt dicarbollide (ChCoDiC) in different solvents
- Solutions of unknown composition with storage time of 7-10 years

The purpose of solidification of this waste is to permit safe removal of LRW from the building so that the safe service life of the hot cells and other equipment can be extended to 2020.

Phase 1 of this program is the solidification of bench scale volumes (.05-2.0 liter) from different waste batches. Polymer formulas of N910 and N960 were applied to mixed waste of organic and aqueous solutions. In addition, samples using polymers and porous materials were applied to the waste. The combination of materials resulted in a "brick-like" mass. See Figure ----

Figure 14. **Samples of lab waste using polymer and porous materials**

The Institute of Nuclear Physics, also located at Gatchyna, is conducting ongoing tests on aqueous waste forms. A solidification ratio of 5:1 was applied to aqueous waste of 20 grams of sodium nitrate at 9 pH. The solidified material was dried in a 50 degree Celsius temperature oven for a period of 12-13 days. The solidification process was repeated. See Figure -- .The purpose of this work is to find a safe solidified form that stretches the polymer capacity and results in economic savings for final storage.

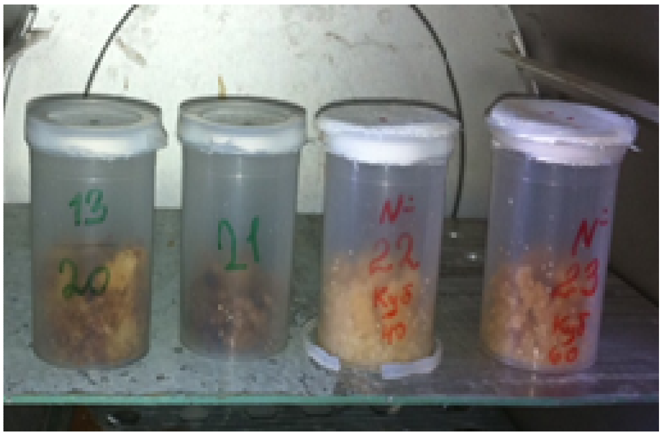

Figure 15. Solidified aqueous waste samples

Cesium 137, americium and strontium were added to the solution to check whether there were any activity changes over time. Through the evaporation process, no cesium or americium were emitted through a filter. The final solidified product can be incinerated, resulting in a 3% ash residue. Future work will continue with this process and a larger scale test program will be initiated in September.

CONCLUSIONS

The IPP program has allowed the U.S. industrial partner to work with various ROSATOM sites and conduct extensive solidification experiments for the purpose of validating the polymer solidification technology and for offering possible solutions t the ROSATOM sites for problematic waste streams. Thus far, the test work has confirmed the following findings:

- The polymers can be effectively applied to LLW and ILW organic and aqueous waste streams. No polymer degradation has been detected in any irradiation and thermal stability tests.
- Aqueous polymer, when combined with cement, can damage cement during the encapsulation process. Additives to the solidification will solve this problem, further investigations are underway.
- Polymers provide a waste treatment solution for specific, problematic waste streams such as TBP.
- Through evaporation techniques, the polymers can re-absorb aqueous waste, thus reducing the final volume of waste and creating economic advantages for final storage.
- New applications for the polymers are being discovered through this program such as combining spent ion exchange resins in oil. Applications to super critical fluids and lower heat incineration are under test and evaluation with promising results.
- Solidification ratios achieved through testing demonstrate the economic advantages of the polymer technology.
- Further investigations ar required to determine the appropriate final form of the waste for long term storage. Final conclusions of this work will be forthcoming in the 4th Q., 2011.

As a result of this experimental work, it is expected that formulas, applications and inventions derived will be suitable for use in global markets.

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