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

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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 (SCC), Zheleznogorsk (MCC) 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 80 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 sites, 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, 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. Another application is the use of polymers at sites where radioactive liquids are accidently emitted from operations, thus causing the risk of environmental contamination.

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 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.

The description of experiments, test data and analysis is summarized from three ROSATOM sites: V.G. Khlopin Radium Institute (KRI), Siberian Chemical Combine (SCC), and Mining Chemical Combine (MCC).

Experiments: V.G. Khlopin Radium Institute

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

Examples of different waste streams with successful solidification are shown in Table 1.

In some cases two types of polymers have been used to form solidification of aqueous and organic waste. Polymer N960 is applied to aqueous waste and N910 polymer is applied to organic waste.

Ratios vary from less than 1:1 (liquid: polymer) to 5:1, with successful results.

Conditions of experiments.		Notes
Composition of solutions.	The proportion between polymer and liquid (P:L).	
Sludge residue from the bottom of the apparatus (aqueous phase). U-80g, $NaNO_3$~200g, HNO_3-0,8 M/I	1:0.7	Blend of polymers N960 (94%) and N910 (6%) were used
Sludge residue from the top of the apparatus (occurrence of organic phase is probable). U–80 g/l, $NaNO_3$ ~ 200 g/l, HNO_3-0,8 M/l.)	1:0.7	Blend of polymers N960 (94%) and N910 (6%) were used
LL decontaminating solution with low amounts of organic substances. U–153 g/l, $NaNO_3$ ~ 100-150 g/l, HNO_3-2,5 M/l.	1:1.4	Blend of polymers N960 (94%) and N910 (6%) were used
LL decontaminating solution with low amounts of organic substances. U–153 g/l, $NaNO_3$ ~ 100-150 g/l, HNO_3-2,5 M/l.	1:3.3	Blend of polymers N960 (66%) and N910 (34%) were used
Uranium solution, U–20 g/l, $NaNO_3$ –40 g/l, HNO_3-1,2 M/l. (There was a precipitate in the sample.)	1:1.1	Blend of polymers N960 (97%) and N910 (3%) were used
Uranium re-extracts. U-70g/l, HNO - 0,07 M/l.	1:4	Blend of polymers N960 (80%) and N910 (20%) were used
Organic sediments from the waste tank.	1:3	Blend of polymers N960 (80%) and N910 (20%) were used
The vat residue from evaporator.	1:3	Blend of polymers N960 (80%) and N910 (20%) were used
Water solution with organic impurities from evaporator	1:5	Polymer N960
Organic residue from LRW store holder.	1:5	Blend of polymers N960 (5%) and N910 (95%) were used
Pearlite pulp.	1:2	Polymer N960
Spent scintillating solution (ZhS-8/LS-8) containing water with tritium.	1:2	Blend of polymers N960 (80%) and N910 (20%) were used
The “dirty” vacuum oil.	1:5	Polymer N910

Table 1. Solutions combined with polymer to make solidification

In all cases after several hours loose liquid was not present. (Specific activity of these solutions was in the range -10^{-5} - 5 Cu/l.)

Figures 1 and 2 represent solidifications of ILW solutions in a hot cell experiments at KRI Gatchyna.

Samples appearance after solidification of the residue from waste tank and the vacuum oil represent in Figures 3 and 4.

Experimental studies at the Institute of Physical and Electrochemical Chemistry (Russian Academy of Sciences), Moscow, have been carried out with the primary focus on waste immobilization with polymers and additives of some inorganic materials in order to achieve a "hard" solidification. The addition of the porous materials in the liquid radioactive waste, along with radionuclide sorption, increases the rate of the water removal because of the developed surface and capillary effect. See Figures 5 and 6.

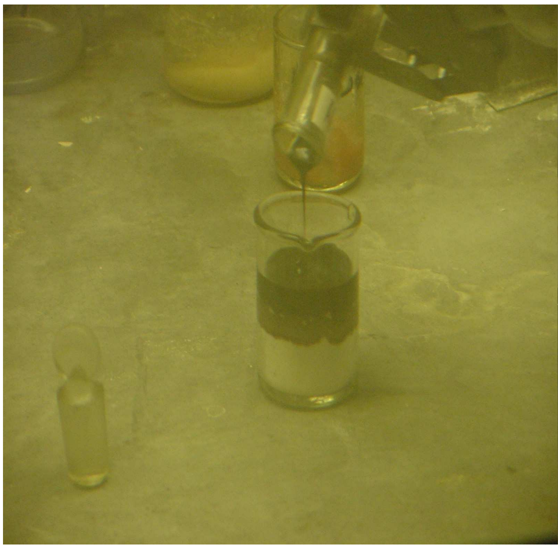

Figure 1. Organic sludge solidification

Figure 2. Nitric acid solution with plutonium.

Figure 3. **Sample appearance after solidification from waste tank organic residue**

Figure 4. **Sample appearance after solidification of vacuum oil**

Figure 5. **Specimen after solution solidification with zeolite included**

Figure 6. **Specimen after solution solidification with schungite included**

Differential thermal analysis experiments were carried out at KRI with samples of initial polymers and polymers after different solutions solidification. At the final stage additional tests have been carried out with the most dangerous compositions including nitric acid, high concentration of nitrates and organic substances. It can be concluded from these experiments that the polymers possess rather high thermal stability with decomposition occurring at 300C. See Figure 7.

According the last data obtained in Scientific Technical Center of Nuclear Radioactive Safety it was shown the immobilization processes with polymers using and storage of products after solidification is quite safe.

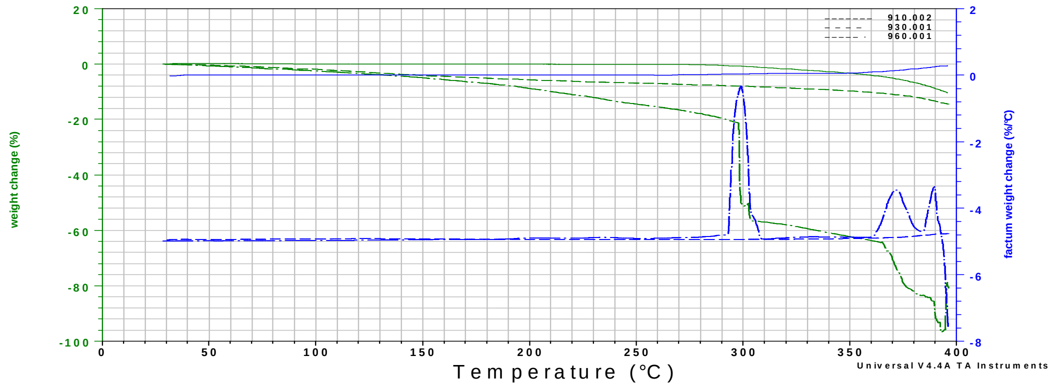

Figure 7. DTA – curves for polymers, N910, N930 and N960

There is another issue connected with the storage and disposal of waste when we use polymer materials, namely radiation stability. Given that the radwaste materials after solidification will be placed in large term storage and the activity level will be rather significant, experiments were conducted on the radiation stability using a Cobalt 60 gamma irradiator.

Figure 8. The appearance of specimen (polymer N910 +oil+TBP) after irradiation.

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 solidified, irradiated samples are hard, brittle with no liquid release. See Figure 8.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 samples after nitric acid solution immobilization. All tests were conducted with glass ampoules.

There is a 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.

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. If applied in certain circumstances, economic advantages will be demonstrated for final storage of the waste.

The Radiochemistry Department of KRI has accumulated an inventory of liquid organic radioactive waste stored in Gatchyna. The total inventory is more than 300 liter 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 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 9.

The Institute of Nuclear Physics, also located at Gatchyna, is conducting ongoing tests on aqueous waste forms. A solidification ratio of 5:1 (liquid: polymer) was applied to aqueous waste of 20 grams of sodium nitrate at 9pH. The solidified material was dried in a 50 degree Celsius temperature over for a period of 12-13 days. The solidification process was repeated. See Figure 8. 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.

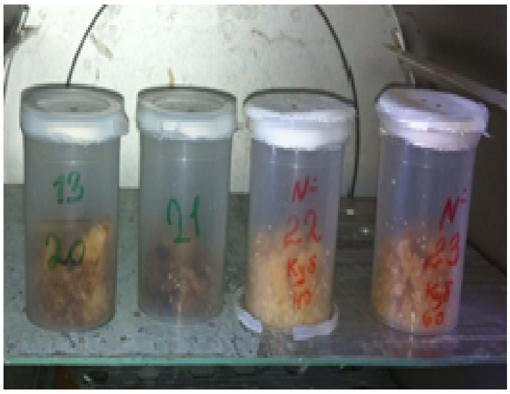

Figure 9. Solidified aqueous waste samples.

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 mitted 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.

Experiments: Siberian Chemical Combine

The Siberian Chemical Combine was established in 1949 and is located in Seversk, formally known as Tomsk-7. SCC 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 SCC, iron-containing sludge, insoluble natural uranium concentrate condensed residues, and two types of liquid organics.

Table 2 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**
Iron-containing precipitates from decontaminating LRW by coagulation	No pretreatment	5:1	Total water absorption; solidification ends (the polymer swelling complete) in 30 min. Solidified mass in the form of dark-brown colored granules densely stuck together with surfaced inclusions of the precipitate particles. During the holding period the solidified mass became more condensed, but the embedment was not observed
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
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 ($\leq$1 kg/dm^3)
Spent VM-1c vacuum oil	No pretreatment	2:1	Solidified mass of the closely stick together dark-grey colored granules with the surface inclusions of precipitate particles and the density less than that of water ($\leq$1 kg/dm^3). Specific α-activity of 181 Bq/kg
Spent VM-4 vacuum oil	No pretreatment	4:1	Specific α-activity of 181 Bq/kg Solidified mass of the closely stick together dark-grey colored granules with the surface inclusions of precipitate particles and the density less than that of water ($\leq$1 kg/dm^3)
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

Table 2**: Solidification examples**

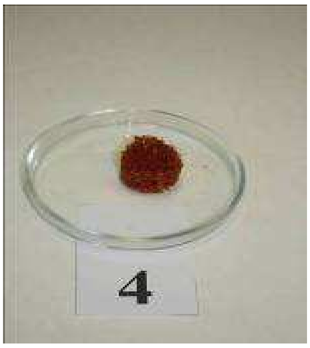

Figure 10. Solidified sample of the iron-containing precipitate from decontaminating LRW by coagulation.

Figure 11. A sample of the solidified S957 resin saturated with uranium.

Spent ion exchange resins were solidified using a resin-in-oil process. The result is a strongly secured bonding of the resin grains.

Experiments: Mining and Chemical Combine (MCC)

The Mining and Chemical Combine (MCC) was established in 1950 and is located in Zheleznogorsk, formally known as Krasnoyarsk-26. MCC's primary task for ROSATOM was to produce plutonium for nuclear weapons.

The modern extraction process flowchart applied to spent nuclear fuel reprocessing; tributylphosphate (TBP) in the mixture with an inert diluent agent (light or heavy) has wide application.

In the course of operation the decomposition products are accumulated as the result of radiation and hydrolytic damage. These products influence the extraction process behavior including hydrodynamic properties of the extractant.

A number of different manufacturing operations for treating the spent extractant were considered at MCC:

- TBP decomposition when TBP is heated with a concentrated solution of sodium hydroxide;
- Separation of the extraction mixture with the use of a concentrated solution of phosphoric acid and consequential thermal decomposition of TBP;
- Organic solution incineration;
- Disposal in the deep reservoir bed;

A significant disadvantage of the options considered is a rather high cost of treatment and secondary waste generation, including toxic liquids.

Of particular interest in the above-stated system is the high toxicity of HCBD and corrosiveness of the HCBD decomposition products. For this reason the treatment method under development shall be highly reliable with respect to immobilization of the solutions. Therefore, the main interest from a practical point of view for MCC is the issue related to the isolation of the spent extractant based on TBP solution in HCBD.

Several samples have been taken and analyzed. 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.

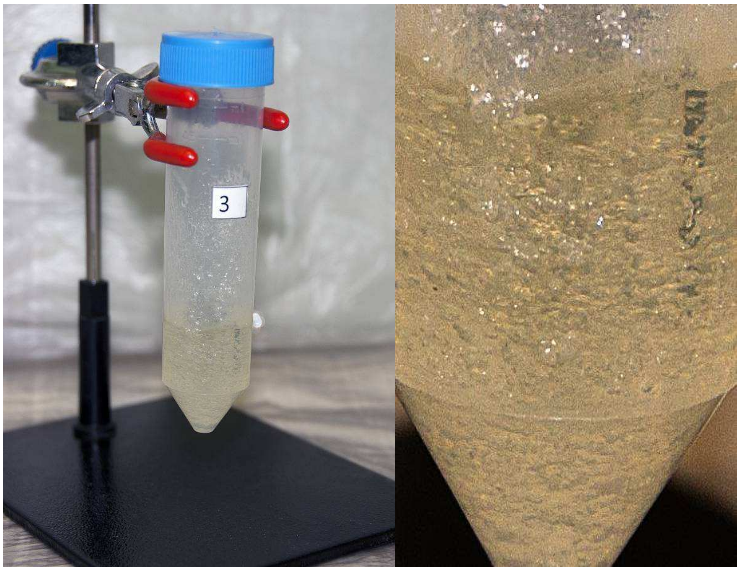

Figure 11. Appearance of specimen (polymer N910+ TBP in HCBD).

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 has been planned for the 3rd Q., 2011, 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.

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 to 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 irradiation tests and thermal stability is quite satisfactory.
- Aqueous polymer, when combined with cement, can damage cement during the encapsulation process. In some cases additives are needed during solidification to solve this problem, further investigations are underway.
- Polymers provide a waste treatment solution for specific, problematic waste streams such as TBP and mixed (water – organic bi-phase) sludge.
- 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 are required to determine the appropriate final form of the waste for long term storage. Final conclusions of this work will be forthcoming in the 4^{th} 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. Of particular interest may be the polymer’s use for emergency accidents at nuclear sites, to avoid environmental contamination.

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