Proven Technologies for the Solidification of Complex Liquid Radioactive Waste (LRW): Global Case Studies of Applications and Disposal Options-17084

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ABSTRACT

Legacy radioactive waste streams from the Cold War still exist and newly generated waste streams from nuclear power plants and research institutes go untreated and expose environmental hazards at many nuclear sites. The nature of the waste is extremely diverse, depending upon the source or the process from which it originated. The most problematic waste streams include complex liquids such as organic (tri-butyl-phosphate TBP) solutions contaminated with Pu and U isotopes, mixed sludge types, high acid radioactive waste, tritium contaminated organic and aqueous streams, etc. Technological, environmental and economic challenges exist for the treatment and disposal of such waste streams.

A proven technology that has been applied to LRW on a global basis provides a low-cost solution to legacy streams and small volume, highly complex LRW frequently found during decommissioning at nuclear power plants and weapons sites. The engineered polymer technology from Nochar, USA, is capable of solidifying standard and highly complex LLW and ILW waste streams for interim or final storage, or for incineration.

INTRODUCTION

This paper examines several global case studies, describing specific waste problems and treatment processes utilized at nuclear sites. The case studies are intended to illustrate the variety of liquid waste streams that are present at nuclear sites and describe the conditions that may regulate a pathway for waste acceptance in each country. Projects are profiled in the U.K., France, Romania, Russia, U.S.A., Kazakhstan, China and Slovenia.

CASE STUDY NO. 1: UNITED KINGDOM – HARWELL AND SELLAFIELD SITES

In 2014, the Harwell Remote Handled-ILW Storage Tubes Water Recovery project commenced in three facilities known as the “tube stores” (Fig. 1). The legacy stores (7 meters in depth) contain contaminated ILW water which requires immobilization to meet the Geological Disposal Facilities, Letter of Compliance. Under Magnox management, a team was created to assess the problem and propose solutions. Nochar’s N960 polymer was selected to solidify the ILW water through perforated bags, followed by an encapsulation process with cement (Fig.2) Final disposal is in 500 liter drums. This is a long-term decommissioning project which continues today. [1]

Fig. 1.

Fig. 2.

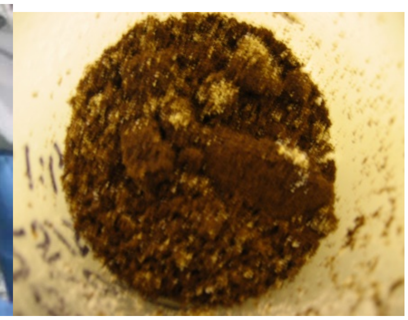


Fig. 3.

Fig. 1. Tube Stores at Harwell Currently Undergoing Decommissioning
Fig. 2. ILW Water Solidified with N960, and Encapsulated in Cement at Harwell Site
Fig. 3. Legacy Oil Sludge Solidification at Sellafield

The Sellafield Decommissioning Characterization & Clearance group commenced an oil immobilization test program in 2006 with more than 90 oil sludge types in the oil waste storage facility. All oil sludge forms were uncharacterized and the experiments were undertaken on a small scale using 200 mL of oil. Polymers N910 and N960 were applied to the oil and sludge forms at a 1.5 and 2 (liquid) to 1 (polymer) ratio (Fig. 3).   Following solidification, a test program was conducted to encapsulate the waste form into an acceptable cement grout matrix for final disposal. [2]

CASE STUDY NO. 2: FRANCE – CADARACHE LOR (LIQUIDES ORGANIQUES RADIOACTIFS) WASTE STREAMS

STMI-AREVA carried out a study to pre-treat waste streams to obtain an agreement with the French regulator, ANDRA, for final disposal. Two radioactive scintillation cocktails were legacy streams produced at Cadarache and stored in the Cellule de REconditionnement et d'Echantillonage des futs de Solvants radioactifs (CEREES) cell and held in the ICPE 312 facility. The two streams were composed of organic compounds including xylene and TBP. Water content was about 80%. Radiological contaminants included: Pu-238, Pu-239, Pu-240, Am-241, Cs-137 and H-3.

Polymers N910 and N960 were combined with the streams to form a solidified matrix. Sample LOR 75 is shown in Fig. 4 & 5. The results indicate that the solidification matrix appears suitable for a final acceptance at the ANDRA storage site. Additional test programs are currently underway by STMI-AREVA to validate the findings in this extensive research project. [3]

Fig. 4. Fig.5.

Fig. 4. LOR 75 Sample of Legacy TBP, Xylene and Water

Fig. 5. Sample Solidified with N910 and N960, Dry Waste Form

CASE STUDY NO. 3: ROMANIA – CERNAVODA NUCLEAR POWER PLANT

Since 2008, MATE-FIN Co., based in Bucharest, has been providing a variety of technical services to Cernavoda nuclear power plant including the treatment and packaging of low level organic waste. A series of organic waste streams have been generated by the CANDU 6 reactors that require treatment and disposal. These streams include spent oil with tritium, spent solvents, liquid scintillation cocktails (LSC), flammable solids (solid-organic liquid mixture) and sludge. Polymer N910 is used to permanently solidify the hydrocarbon based liquids. N960 is used to immobilize any aqueous liquids with tritium. The solidification ratio is 2.5:1.

Large scale solidification production is conducted in steel drums, by combining the tritiated oil with the polymers, then mixing with an electric mixer. Mixing is a slow, ten-minute process (Fig. 6 & 7). Over 30 metric tons of oil have been solidified and shipped to Studsvik, Sweden for incineration. The N910 polymer is also applied to flammable solids (textiles, clothes, plastic materials) that are contaminated with tritiated oil. The solids are layered with the polymer for absorption of the flammable liquids (Fig. 8). Solidified waste is then removed from the solid materials and packaged in polyethylene bags. [4 & 5]



Fig. 6. Fig. 7. Fig. 8.

Fig. 6. Oil with Tritium Mixed with N910 and N960, with Slow Speed Mixer
Fig. 7. Ten Minute Mixing Process, Solidification Completed, Ready for Disposal
Fig. 8. Treatment of Solid Materials Contaminated with Oil and Tritium, Solidified with Polymers

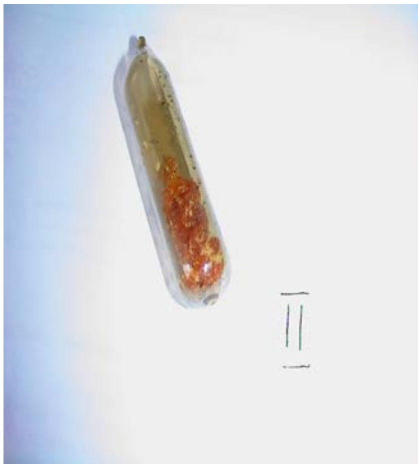
CASE STUDY NO. 4: RUSSIA – KRI GATCHYNA AND MINING CHEMICAL COMBINE (MCC) - KRASNOYARSK

The Khlopin Radium Institute, St. Petersburg, and the U.S. Department of Energy partnered under a three-year program to conduct experimental work with Nochar polymers. Tests included radiation and thermal stability using a Cobalt 60 gamma source irradiator, evaporation utilizing heat to evaluate the polymer's absorption capacity, gas generation on ILW waste forms, fire and safety, and cement encapsulation for final disposal. Over 250 real waste streams including a variety of organic and aqueous solutions were solidified with an emphasis on sodium nitrate solutions and high salt content solutions.

Irradiation tests (high dose) proved the polymers stability with one test duration of 103 days for a total exposure of 27 million gray (Fig. 9). Gas generation tests verified that the polymers are not gas generators. In addition, experiments proved that the polymers maintain stability when combined with sodium nitrate solutions. In real applications, ILW waste was solidified at Gatchyna and packaged in a thick polyethylene bag, then encapsulated in cement (Fig. 10). The cement form was then packaged in polyethylene drums for final disposal at the RADON Sosnovy Bor site, located west of St. Petersburg (Fig. 11).

Nochar polymer technology is the first foreign absorbent technology to be formally certified by ROSATOM, for use at Russian sites.

An extensive test program at the Mining Chemical Combine (MCC) near Krasnoyarsk, located in central Siberia, was sponsored by the U.S. Department of Energy in 2009-2010. This experimental program evaluated the application of the polymers with a solution of TBP in hexachlorobutadiene (HCBD), a highly toxic waste stream. At a 5:1 ratio (N910), the solution was solidified (Fig. 12) and was capped by paraffin wax to prohibit gas emission (Fig. 13). [6 & 7]



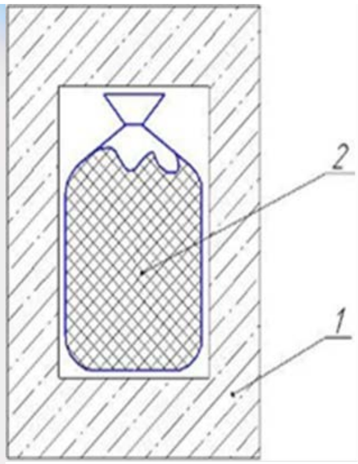


Fig. 9. Fig. 10. Fig. 11.

Fig. 9. Cobalt 60 Gamma Source, Irradition of Solidified Sample at 770,000 Gray at 30 Day’s Exposure

Fig. 10. Solidified Mass in Polyethylene Bag (2), Encapsulated in Cement (1)

Fig. 11. Packaging for Final Storage at RADON SosNovvy Bor Site, Russia

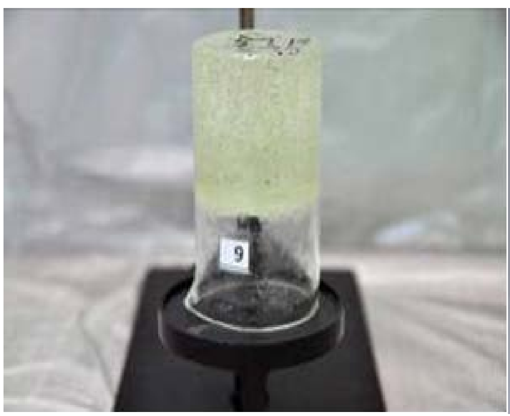


Fig. 12. Fig. 13.

Fig. 12. TBP in HCBD Solution Solidified with N910

Fig. 13. Solidified TBP-HCBD (Yellowish Color), Capped with Paraffin Wax

CASE STUDY NO. 5: UNITED STATES – DOE ROCKY FLATS

Rocky Flats Technology Site was one of the first DOE nuclear weapons site to undergo full decommissioning, with a final closure date of 2006. Critical to meeting the closure timeline was the treatment and removal of “orphan” liquid waste streams. These streams had no existing approved pathway for treatment or final disposal.

In 2000, the OASIS treatment system (cementation) failed to meet DOE criteria for transport and final disposal which caused Rocky Flats to seek an alternative waste treatment process for the orphan waste streams. Nochar’s polymers were selected for application to the several thousand liters of transuranic (TRU) waste forms which included concentrations of plutonium. Three waste streams were treated:

- Methanol based solution with organic contaminants such as cyclohexane
- Mixed organic waste consisting of Freon, carbon tetrachloride and trichloroethylene
- Spent pump oil

Special formula polymer N990 was applied to the organic waste stream (Fig. 14). N960 polymer was used with the aqueous waste.
All solidified waste was packaged in carbon steel 55 gallon drums and delivered to the Waste Isolation Pilot Plant (WIPP) for final storage (Fig.15). Cost savings to DOE for this project exceeded $ 10 million. [8]


Fig. 14.


Fig. 15.

Fig. 14. Spent Pump Oil with Pu, Solidified in N990 Polymer in Hot Cell
Fig. 15. Packaging in Drums for Final Disposal at WIPP

CASE STUDY NO. 6: KAZAKHSTAN, BN-350 FAST BREEDER REACTOR

The Mangystau Atomic Energy Combine (MAEC-Kazatomprom) located along the Caspian Sea closed operations in 1999. The BN-350 reactor was decommissioned with completion in 2010. Remaining on site are 3,217 cubic meters of liquid waste. Total activity of Cs-137 is 9,618 Ci. A test program to validate the effectiveness of the polymers was undertaken in 2014. Four waste streams were tested: machine oil, sodium hydroxide, and two saline solutions with high salt content. Solidification on all four waste streams was achieved by using Nochar's N910 polymer for oil and N960 polymer for the other streams. The solidification ratios were between 2:1 and 3:1 (liquid:polymer by weight). (Fig. 16, 17)

In addition to the solidification program, DOE and Kazakh scientists created an inexpensive method to dispose of the solid mass by encapsulating the machine oil / N910 into an inorganic filler and molecular sulfur material. After heating the entire mass in a short time, the mixture hardened and a solid waste form was generated.

The organic waste content in the final form can reach up to 60 wt. % at a compressive strength of about 100 kg/cm^2 (Fig.18). If a harder form is required, then the waste content can be decreased to 25-30%, and the compressive strength will increase to 300 kg/cm^2. [9 & 10]

Fig. 16. Fig. 17 Fig. 18

Fig. 16. Sodium Hydroxide Sample with N960 Polymer, Ready for Mixing
Fig. 17. Solidified Sample after Five Minutes, Solidification Ratio 3:1
Fig. 18. Samples of Sulfur Composite Waste Form, Volume of Oil Used for Each Form – 30 ml

CASE STUDY NO. 7: CHINA INSTITUTE OF ATOMIC ENERGY, CHINA

China Institute of Atomic Energy (CIAE), Beijing, conducted a formal test program in 2005 with Nochar polymers, resulting in one of China's first technical papers published and presented at global waste treatment conferences. The test program included oil, nitric acid at 0 pH, tri-butyl-phosphate (TBP), alkaline at 14 pH and resin beads saturated in water (Fig. 19). Following solidification, the samples underwent extensive irradiation and compression testing (Fig. 20). An IR spectra-graph test was conducted on N910 and N960 polymers because it is widely believed that polymers will degrade over time from the effects of radiation. The test demonstrated the polymers stability under Cobalt 60 gamma source irradiation, and there was no degradation.

A test program was conducted in 2007 at the China Academy of Engineering Physics (Institute # 9) in Minyang, Sichuan, on an oil with tritium waste stream. Additional test work at Institute # 9 is underway today.

One full scale production treatment project was successfully completed in 2008.

Two new test programs for applications at nuclear power plants will commence in 2017 with the Research Academy of Guangdong Nuclear Corporation and China Power Investment Corporation, Chongqing. The programs will validate the solidification process for nuclear power plant waste streams and study the possible disposal routes. These tests are required by the Chinese regulators to meet final disposal requirements at # 404 repository in Gansu province. [11]


Fig 19. Fig. 20

Fig. 19. Cation Resin Beads Solidified with N960 Polymer Creating a Dry Mass

Fig. 20. Irradiation of Solidified Oil Sample at 700,000 Gray

CASE STUDY NO. 8: SLOVENIA, AGENCY FOR RADWASTE MANAGEMENT (ARAO)

In 2013 the Agency for Radioactive Waste Management, ARAO, Slovenia's radioactive waste management regulator and operator of the waste treatment facility, the Central Storage Facility (CSF), commenced a full production solidification project with legacy institutional waste collected from 2004-2008. The waste stream was an accumulation of scintillation fluids that were combined into containers from several waste generators. The mixed waste streams posed a specific problem for ARAO, as the mixed streams were not uniform in composition.

The scintillation fluids were a combination of toluene, acetonitrile, water and a high percentage of ethanol and methanol plus tritium. Each drum of mixed waste contained varying percentages of the fluids.

The first phase of the project involved a test program to determine the correct polymer formula and solidification ratio. Three Nochar polymers were applied, N935 for light alcohols, N910 for organic toluene, and N960 for aqueous streams. When blended into a homogeneous stream, the scintillation fluid became a milky white color. The waste stream included tritium. Because of the waste stream complexity, a 1:1 solidification ratio resulted in a good solid mass and safe for interim disposal. The challenge for the waste treatment team was determining the polymer formulas prior to the addition of each waste from many containers. The solidification process was limited to small batches to ensure that each batch was successfully solidified with no loose liquid (Fig. 21). The waste was put into thick polyethylene bags for storage at CSF. The project was completed in late 2015.


Fig, 21. Solidification of Organic-Methanol-Ethanol with Tritium

CONCLUSIONS

Complex LLW and ILW waste streams are generated during operations, reprocessing and research, many times with no government approved method for final disposal. These orphan waste streams can be problematic especially during decommissioning. Small volumes can pose economic challenges as well. Global nuclear sites continue to search for reliable and proven technologies that can address these problems and find economical solutions.

The polymer technologies as described in this paper offer a solution to nuclear sites that require a treatment process to deal with complex organic waste streams. The polymers offer a variety of waste disposal options including direct loading into steel drums, encapsulation in cement or another inorganic materials formula or incineration. Each country is bound by its own waste acceptance criteria and the polymer technology presents a variety of options to meet those criteria.

The polymers capture and immobilize tritium (heavy water) which is a problematic component in many waste streams.

Through bench testing each waste stream, solidification ratios can be determined and safely applied to waste streams, thereby making the process manageable and low cost. Many small volume waste streams are not characterized due to poor record keeping and it is not cost effective to characterize each stream. The polymers offer flexibility in their capacity to solidify uncharacterized streams.

Given the scope and level of interaction at several major nuclear sites, the polymers have demonstrated their ability to effectively solidify complex LLW and ILW waste streams and meet the conditions and requirements of government regulators.

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