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Proven Technologies for the Treatment of Complex Radioactive Liquid Waste Streams; U.S. Department of Energy and International Case Studies

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Abstract – *Radioactive liquid waste streams, particularly organic waste, have been difficult to treat by absorption and encapsulation processes in the past, due to eventual leaching and instability in the matrix of the final mass. Previous usage of polymers and other sorbent materials for liquid solidification in the 1980's and 1990's proved to be unsafe and unreliable on a worldwide basis. The U.S. DOE recognized the unreliable methods of liquid waste treatment in the 1990's and decided to seek out more reliable means of solidification.*

As a result of a research and development program initiated and sponsored by the U.S. Department of Energy commencing in 1997, a commercially available absorbent technology was improved and applied to radioactive liquid waste streams. Today the technology provides a safe manner in which to treat liquid waste and enables safe transport to storage or repository sites. Additionally, the technology is flexible in its use for short and intermediate storage, final burial in a repository or incineration. Through extensive scientific research and direct field applications over the last eight years in the U.S. and internationally, the Nochar polymer technology has demonstrated cost effectiveness and reliability for the solidification of low, intermediate and high level waste products.

Nochar's Petrobond and Acidbond are a group of 3rd generation polymers designed to solidify organics, sludges, acids, alkaline and aqueous radioactive waste into a solid matrix. Unlike standard sorbents, which work by "adsorption" (surface collection), the polymers "absorb" the liquid waste creating a low volumetric increase in the process. The final waste form results in a durable matrix which prevents leaching, while locking up metals, even in a high mega rad environment.

This paper examines several case studies and projects that illustrate Nochar's solidification technology for use on simple and complex waste streams.

I. INTRODUCTION

As a result of a research and development program initiated and sponsored by the U.S. Department of Energy commencing in 1997, a commercially available absorbent technology was improved and applied to radioactive liquid waste streams. Today the technology provides a safe manner in which to treat liquid waste and enables safe transport to storage or repository sites. Additionally, the technology is flexible in its use for short and intermediate storage, final burial in a repository or incineration. Through extensive scientific research and direct field applications over the last eight years in the U.S. and internationally, the Nochar polymer technology has demonstrated cost effectiveness and reliability for the solidification of low, intermediate and high level waste products.

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The following case studies illustrate these points.

II. CASE STUDIES

II.A. Case Study 1: U.S. Department of Energy: Mound, Ohio (DOE-MEMP)

In 1997, the U.S. Department of Energy (DOE) approached Nochar regarding its solidification technology used for commercial oil spill control and other liquid spill applications. Following an extensive three year test program involving 43 tests, DOE determined that Nochar's technology would be suitable for actual test work at the Mound, Ohio site. In 1999, tests were conducted on tritiated mixed waste oil and the tests required for final disposal at DOE's Nevada Test Site repository passed intense examination. In 2000, full scale solidification of tritiated vacuum pump oil commenced under the EM-50 program. Nochar's absorbent technology became the baseline technology for the treatment of Mound's LLW and MLLW oils. Over the three year project term, 100,000 curies of radioactive waste were solidified and shipped to NTS for final burial. This includes a container of oil with 2,200 curie per liter. PCB oil was also treated by a special Nochar polymer blend.

Solidified waste was packaged in special polyethylene containers with a standard steel drum overpack.

Extensive TCLP (leach) testing was conducted on the waste to ensure full solidification with no liquid release and to evaluate the stability of heavy metals. No mixing was required for the treatment of the oil which also provided a new production methodology, meeting ALARA safety standards. DOE estimated the cost savings due to the use of Nochar exceeded $ 1 million.

Picture 1: Polyethylene Drum for Tritiated Oil

Table 1: Mound Solidified Mixed Waste Oil TCLP (leach) Analysis - Severn Trent Labs

Analyze	Physical Form	Result	Units	Reg Limit (mg/L)	Dilution	Method	SW-486
Mercury	Solid	.00092	mg/L	*0.2	4	TCLP Metals	EPA 7470
Arsenic	Solid	ND	mg/L	5	4	TCLP Metals	EPA 6010
Barium	Solid	ND	mg/L	100	4	TCLP Metals	EPA 6010
Cadmium	Solid	0.014	mg/L	1	4	TCLP Metals	EPA 6010
Chromium	Solid	0.0047	mg/L	5	4	TCLP Metals	EPA 6010
Copper	Solid	0.12	mg/L		4	TCLP Metals	EPA 6010
Lead	Solid	0.29	mg/L	5	4	TCLP Metals	EPA 6010
Selenium	Solid	ND	mg/L	1	4	TCLP Metals	EPA 6010
Silver	Solid	ND	mg/L	5	4	TCLP Metals	EPA 6010
Zinc	Solid	0.071	mg/L	NA	4	TCLP Metals	EPA 6010

Note: baseline values for untreated mixed waste oil were comparable to bench test I and II non-treated oil.
Worst case metals analysis was approximately 7.2 mg/L - Mercury.
***** Current Nevada Test Site (NTS) LDRs for Hg limit it to 0.025 mg/L.

II.B. Case Study 2: U.S. Department of Energy: Rocky Flats, Colorado (DOE - REFTS)

Rocky Flats Environmental Technology Site (REFTS) was one of the first major nuclear weapons sites in the DOE complex that has been declared a full closure site. The final closing date is scheduled for 2006. A key effort to meet this deadline was to treat and remove all "orphan" waste streams. Orphan wastes are those with no existing solution for treatment or final disposal.

In 2000, the OASIS treatment system (cementation) failed to meet the DOE criteria for shipment and disposal at Waste Isolation Pilot Plant (WIPP), DOE's ILW repository. The polymer technology was evaluated for the treatment of transuranic (TRU) waste and was selected for the solidification of several thousand liters of TRU contaminated organic liquid, oil and acid waste with concentrations of plutonium. Three TRU oil waste streams were selected for treatment:

- methanol based waste with various organic contaminants such as cyclohexane
- mixed organic waste consisting of freon, carbon tetrachloride and trichoroethylene
- contaminated used pump oil

Picture 2: Bench Test of TRU Oil in Rocky Flats Glove Box

The challenge was to create a stable waste product without hydrogen or flammable organic gas generation which is prohibited by WIPP. Extensive test work was conducted on the waste compositions and it was determined by DOE that the use of polymers would be the baseline treatment for the stabilization and solidification of TRU waste. Headspace gas sampling and TCLP tests (EPA # 1311) were conducted on the actual waste. The Nochar process met all WIPP criteria for transportation and final disposal.

Today, all waste forms have been shipped to WIPP for final disposal. Cost savings based on DOE estimates from the solidification program exceeded $ 10 million.

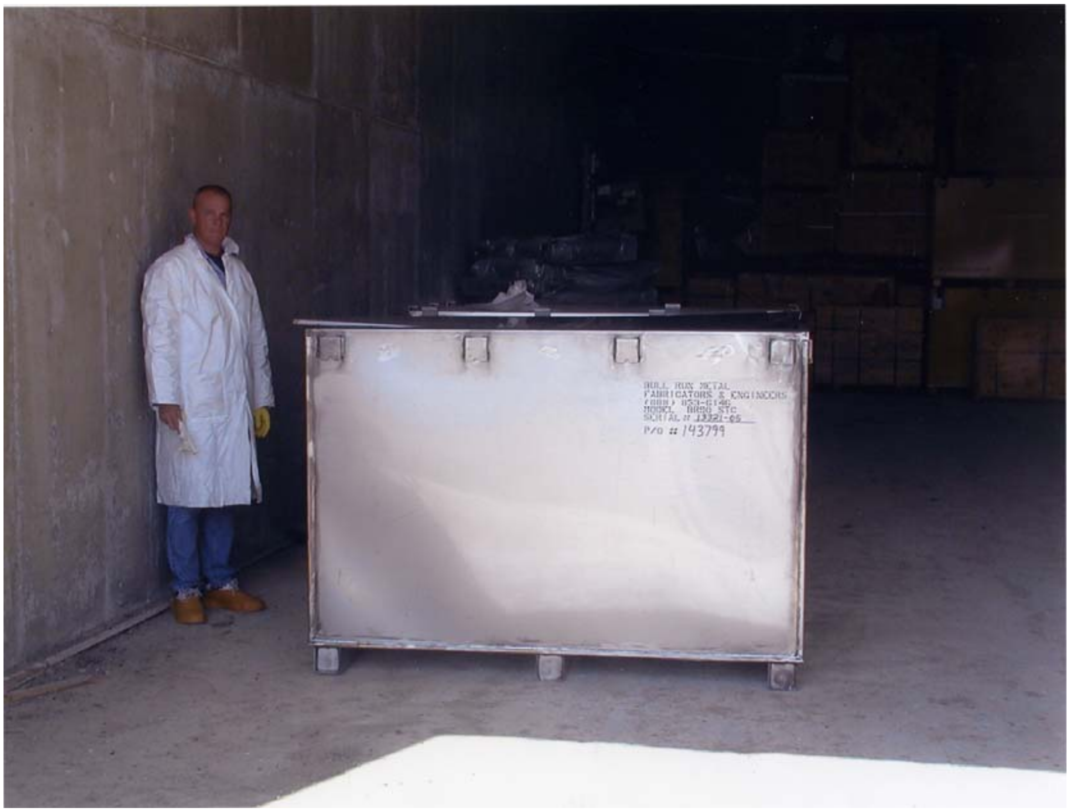
II.C. Case Study 3: U.S. Department of Energy: Savannah River (SRS)

Legacy waste from DOE Savannah River (SRS) had been incinerated in previous years; however, with very high costs to incinerate plus associated environmental issues, DOE sought alternative solutions for its TBP (tri-butyl phosphate - "purex") waste, located at the Canyon F facility.

Following an extensive three year test program that included TCLP, thermal stability, vibration, irradiation and pressure tests, DOE concluded that the N910 polymer would be used to solidify 120,000 liters of purex in Phase 1. SRS's purex consists of 80% N-pariffin / 20% TBP, plus a small amount of water. Irradiation tests were conducted at SRS using a Cobalt 60, gamma source on N910 and on the purex solidification. Total exposure was 90,000,000 rad with little or no breakdown of the polymer and no liquid release. DOE's conclusion is that the solidified mass will remain stable for several thousand years.

The purex is moved by tanker truck from SRS to Waste Control Specialists (WCS-Texas) for treatment and packaging. For this waste stream, a pan mixing machine is used to combine the purex with the N910. The mixing procedure is simple, safe and effective. For each batch operation, approximately 3,500 gallons of purex is combined with 8,260 pounds of N910 for the prescribed 3:1 bonding ratio. The total mix time for one batch is 4-6 hours. The waste is mixed and dropped from the mixer directly into the B-25 box. The waste is transported to the Nevada Test Site for final disposal. For Phase 1 of this project, it is estimated that DOE will save $ 42 million by using N910. In Phase 2, additional amounts of purex will be solidified in 2005 / 2006.

Picture 3: Final Packaging of Purex in Stainless Steel B-25 Box



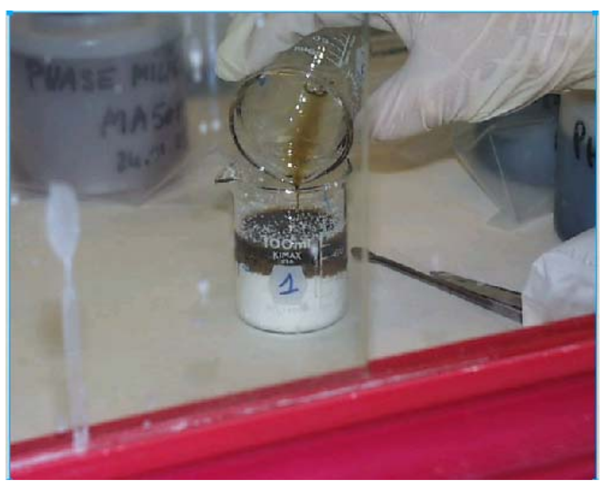
II.D. Case Study 4: France

In January, 2003, representatives from Societe des Techniques in Milieu Ionisant (STMI) and Pacific World Trade conducted laboratory tests outside of Paris on a four phase organic - aqueous legacy waste steam. The waste was a collection of various waste streams that had been generated over a 20 year period and held in a tank. STMI provided a waste characterization which was essential for the test program. The four phase waste stream consisted of:

- Phase 1: top phase, heavy, thick organic material with 2% water content
- Phase 2: medium phase, 83% water with a small amount of hydrocarbon solvents
- Phase 3: residue phase, thick organic hydrocarbon sludge resulting from evaporation
- Phase 4: bottom phase, dark colored sludge with approximately 48% water content

The purpose of the test program was to identify the appropriate polymer formulas for complete solidification of the total waste stream emulsified and the four individual phases. Polymer formulas were created according to the composition of each waste stream. A 2:1 (liquid : Nochar) solidification ratio was the target. No mixing was required for Phase 3; however, light mixing was necessary for the aqueous waste.

Picture 4: Solidification of Phase 2



Picture 5: Filter Test of Phase 2

Immediately following each test, the solidified mass was put into a paint filter "drop test" to check for free liquids. After 2-3 hours, each solidified mass was placed on absorbent paper and pressed by hand to check for liquid release. Four of the five masses were completely dry after 3 hours. Phase 4, the bottom phase, had a small wet area indicating that additional drying time was necessary.

This particular waste stream included a small percentage of alcohol. A large amount of alcohol presents difficulty for polymer absorption; however, in this case the polymers are able to solidify alcohol along with the aqueous and organic waste.

Conclusions of the test program are:

- All tests indicated very little, if any, volume increase in the solidified mass
- 4 of 5 masses dried quickly, within a few hours
- Some compression of the mass is possible at the 2:1 bonding ratio, with no likelihood of leaching
- Over time the masses will harden and decrease in volume
- Final forms of the masses were solid, dry with no presence of free liquid

Due to regulatory policy for final disposal, STMI proceeded to conduct further tests to check the feasibility of encapsulating the solidified Nochar organic mass into a unified cement matrix. Phase 2, the organic waste, was mixed with cement at a 30% organic to 70% cement proportion. This "dual solidification" form passed an 80 BAR compression test, as required.

II.E. Case Study 5: Russia

The Cold War era created a massive build-up of nuclear weapon stockpiles in the former Soviet Union and United States. The primary objective during this period was the development of nuclear technologies for weapons, space and power with inadequate attention paid to the impact of radioactive waste on the environment. As a result, significant amounts of liquid radwaste have existed since the 1950's. The Russian government seeks new technologies from internal sources and from the West that will provide high performance, long-term stability, safe for transport and for permanent disposal at a reasonable cost.

In an attempt to address some of the environmental issues, the V.G. Khlopin Radium Institute, St. Petersburg, and Pacific World Trade have conducted over 50 tests with waste solutions from Khlopin-Gatchina and RADON-Sosnovy Bor in northern Russia over the last four years. The waste streams tested have included sludge residues from decontaminating solutions, several forms of TBP from the extraction facility for spent fuel processing, and spent extractant solutions of many compositions with heavy metal content.

The purpose of this test program was to:

- Verify that high technology polymers can solidify radwaste products that vary in composition and in specific activity
- Determine exact bonding ratios per each waste stream for efficiency and economic considerations
- Consider the various applications for the use of polymers

Experiments on the solidification of products generated during the operation of the extraction facility were (various combinations of polymers were used):

Table 2: Test Results of Extractant Waste

Test No.	Composition of Waste	Results
4283	Uranium extractant	Solidified, no free liquid; used for Leach Test
7201	Plutonium extractant	Solidified
6509	Cesium extractant	Solidified
7219	Neptunium extractant	Solidified
7218	Extractant Saturated with Neptunium	Solidified

The solidified products were evaluated over a number of months with positive results, good stability and no leaching.

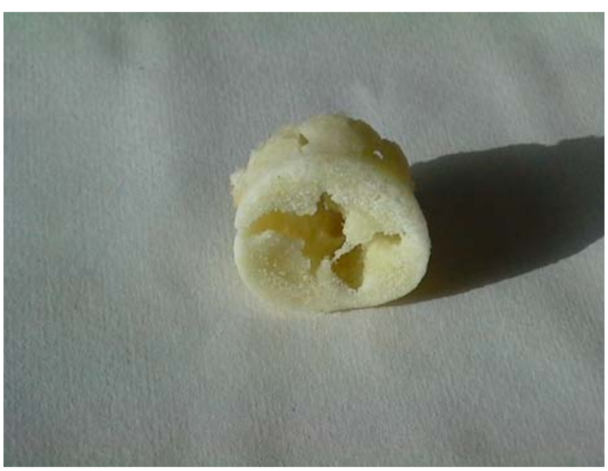
As a result of this work, new applications have been considered for the polymers. In 2004 an extensive program was initiated by the V.G. Khlopin Radium Institute to evaluate the application of polymers in a newly designed Yttrium-90 generator. While using extraction technology division of strontium-90 and yttrium-90 (yttrium-90 generator), two types of waste are formed that require treatment; a nitric acid containing strontium-90 and an exhaust extractant (mixture of di-2 ethyl, hexyl phosphoric acid in a hydrocarbon diluent. The treatment process requires solidification immediately following the two year life of the generator.

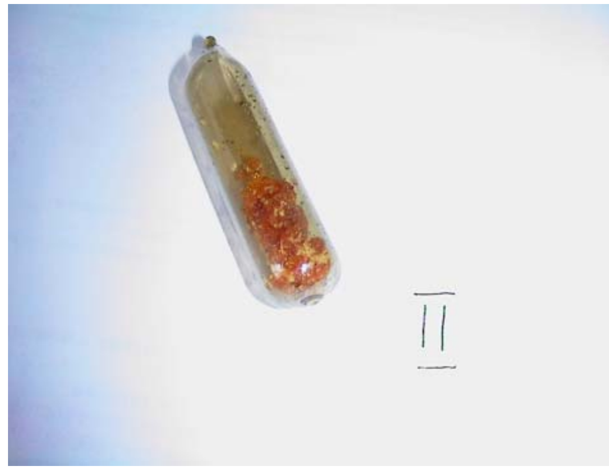
Two primary experiments were conducted; to determine the bonding formula and ratio that did not require mixing and to irradiate the sample to determine stability for long-term storage of the ILW. The results of the tests proved:

- The optimum bonding ratio is 4:1 using a combination of N910 and N960 polymers
- Stability of the mass is conclusive; mass is reduced in volume and there is no leaching

The irradiation testing was conducted with a Cobalt 60 gamma source. After 30 days or 77,000,000 rad, the sample was removed for inspection. The sample was hard, no liquid present. The ampoule was then placed into the irradiator for an additional 73 days of exposure. Following a total of 103 days of exposure, 270,000,000 rad, the sample became brittle and broke into two parts. The dose rate was 30 x 24 x 3600 x 30 (30 rad per second). The conclusion is that the polymer technology can withstand extreme doses of activity and remain stable over a very long period of time.

Picture 6: Organic / Nitric Solidification





Picture 7: Irradiated Sample at 77,000,000 Rad

As a result of the test program, Nochar's process will be used in the Yttrium-90 generator as a single step process for solidification of the complex waste stream.

II.F. Case Study 6: Canada

In 2001 a program was initiated by Atomic Energy of Canada to treat 12,000 liters of radioactive organic liquid as a result of operations conducted at Whiteshell Laboratory, Manitoba, Canada. The contaminated liquid consisted of a mixture of used WR-1 reactor coolant (HB-40), xylene rinse solution, dielectric (EDM) fluid, vacuum pump oil and water. The organic sludge was above the allowable activity limit (15 Bq/ml) for incineration at the Whiteshell organic incinerator, so an alternative treatment was required.

Bench tests were conducted on site and a polymer formula was created for solidification. Full production of waste was completed in 2002. A simple paddle mixing machine was required for the final process. The waste was packaged in B-25 boxes and stored in the Whiteshell above-ground facility. The use of Nochar eliminated the need to move the sludge across international borders for treatment and disposal. According to AECL, the total cost savings was $ 250,000.

III. CONCLUSIONS

Based on the results of the work completed in the U.S. DOE complex and in international markets, we can conclude that the polymer technology provides waste generators with a cost effective and high performance option for the treatment of liquid waste. The technology can solidify the most complex waste streams and offers various options to regulatory authorities for disposal: short or medium-term storage, final disposal and incineration.

To meet some international regulatory requirements, further work is necessary in the area of solidification / cement encapsulation, compression and activity leach in water conditions. As the polymer technology is relatively new to prospective users, additional test work may be required to validate its use in certain countries.

The technology has multiple applications in the nuclear sector, provides for an environmentally safe process and encourages safe transport to storage facilities.

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