

**Polymer Solidification and Stabilization:
Adaptable Processes for Atypical Wastes**

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ABSTRACT

Vinyl Ester Styrene (VES) and Advanced Polymer Solidification (APS™) processes are used to solidify, stabilize, and immobilize radioactive, pyrophoric and hazardous wastes at US Department of Energy (DOE) and Department of Defense (DOD) sites, and commercial nuclear facilities.

A wide range of projects have been accomplished, including in situ immobilization of ion exchange resin and carbon filter media in decommissioned submarines; underwater solidification of zirconium and hafnium machining swarf; solidification of uranium chips; impregnation of depth filters; immobilization of mercury, lead and other hazardous wastes (including paint chips and blasting media); and in situ solidification of submerged demineralizers.

Discussion of the adaptability of the VES and APS™ processes is timely, given the decommissioning work at government sites, and efforts by commercial nuclear plants to reduce inventories of one-of-a-kind wastes.

INTRODUCTION

Historically, the requirements and fee structure of the Barnwell, South Carolina disposal site favored use of High Integrity Containers (HIC) in lieu of solidification to provide stability for Class B and C wastes. In 1993, Barnwell required that all Class B and C wastes be placed in concrete overpacks, even when packaged in HICs approved by the US Nuclear Regulatory Commission (NRC), or solidified in NRC-approved waste forms that provide stability without the need for an overpack. This drove waste generators to use polyethylene HICs, though other and improved stabilized waste forms were available. As a consequence, polymer-solidified waste forms have been relegated to special applications.

Today, as Utilities face potential long-term on-site storage of Class B and C wastes (followed by retrieval for shipping and ultimate disposal), new considerations come into play. These include the costs and personnel exposure associated with inspecting and re-dewatering waste stored in HICs.

With these considerations in mind, Diversified Technologies Services, Inc. (DTS) has developed solidification/stabilization methods for a wide range of radioactive and hazardous materials.

VES AND APS™ SOLIDIFICATION

The original Vinyl Ester Styrene (VES, a.k.a. DOW) process was formulated for solidification of liquids (e.g., evaporator bottoms) and resin slurries. It uses a high-energy mixer to form an emulsion. When non-aqueous solutions are involved, low-energy mixing can be used.

Follow-up work developed an in situ process that did not require mixing, but instead involved pulling the polymer down through the bed of bead resin or granular media, effectively filling the interstitial void space. Ancillary benefits of this in situ process were that waste volume was not increased, and less binder was needed.

In the 1990's, because of DTS' work with the NRC-approved VES and Vinyl Ester Resin In Situ (VERI™) processes, Knolls Atomic Power Laboratory (KAPL) engaged DTS to develop a process to in situ solidify ion exchange media and activated carbon in the process vessels in decommissioned submarines.

During the KAPL testing, some interference was noted between the KAPL media and the VES binder. Since pretreatment to totally exhaust the resin and carbon was impractical, DTS began to explore the use of a different polymerizing initiator that eliminated the need for pretreatment or preconditioning of the resins and carbon. Following extensive bench-scale and mock-up testing to develop optimum formulations and application methods, the first successful full-scale solidification was performed on vessels in a decommissioned submarine at Puget Sound Naval Shipyard. This formulation later became known as Advanced Polymer (AP).

Contemporary to the KAPL work, Diablo Canyon Power Plant (DCPP) was exploring process alternatives in preparation to meet storage requirements when access to the Barnwell site is lost. Adapting the KAPL work to media solidification at DCPP was straightforward, though formulations were modified to provide a more aggressive cure schedule. The in situ method of resin solidification at DCPP using VES worked equally well with the Advanced Polymer Solidification (APS™) formulations. To meet burial waste acceptance criteria for the new formulation, the full gamut of waste form testing was required.

In 1999, DCPP and DTS conducted a full-scale cold solidification test with activated carbon, organic ion exchange resin and ion-specific media. The resulting monolith was sectioned to check for voids, and core samples were sent to Idaho National Engineering and Environmental Laboratory (INEEL), where they were subjected to a variety of tests to determine whether the waste form met the stability requirements listed in the NRC Branch Technical Position on Waste Form, Rev. 1. Testing was done for: 1) compression, 2) thermal cycling, 3) irradiation, 4) biodegradation, 5) leaching, 6) immersion, 7) freestanding liquid, and 8) full-scale waste form.

The results of the waste form testing were submitted to the South Carolina Department of Health and Environmental Control (DHEC) in January 2002. That February, the solidification process and waste form were approved for Barnwell disposal. In May 2003, INEEL issued a report confirming that the APS™ waste form met the NRC's Waste Form requirements. The Conference of Radiation Control Program Directors (CRCPD) reviewed the INEEL report, and the E-5 Committee issued a letter of waste form approval for the APS™ process. This serves as a national approval in the US, replacing the now-defunct NRC Topical Report Program.

APS™ Process Description

The DTS APS™ process involves a chemical formulation similar to that described in Topical Report DNS-RSS-200-NP: The Dow Waste Solidification Process for Low-Level Radioactive Waste (Docket Number WM-82). The APS™ process uses a four-part modified epoxy binder that is chemically cured, through addition of hardeners, to form a hard, stable monolith.

To lower its viscosity and assure optimum flow through waste media, AP is blended with diluents in a mix tank. Two epoxy polymer hardeners are added and incorporated into the diluted polymer. The mix tank is then pressurized, and the AP allowed to flow into the freeboard of a liner filled with dewatered waste media.

When the AP has formed a cap on top of the waste media, a combination of gravity and vacuum draws the AP down through the bed. The advancing polymer, which is hydrophobic, drives any remaining interstitial water from the media as it flows down through the container, filling voids between the beads and grains. The polymer is then allowed to exotherm over 24 hours, and forms a liquid-free, hard, free-standing monolith inside the container. Since the polymer binder fills the voids within the waste media, this process yields virtually 100% waste loading,

UNIQUE POLYMER APPLICATIONS

While the VES and APS™ processes were initially intended to solidify evaporator bottoms, bead resin and activated carbon, further development has allowed them to address a wide range of unique waste materials. Processing goals range from rendering pyrophoric material non-flammable, to stabilizing material for long-term storage or disposal as Class B and C waste, to rendering toxic debris non-toxic. A sampling of VES and APS™ process applications follows.

Naval Reactor Facility Machining Swarf

The Naval Reactor Facility (NRF) in Idaho Falls had an inventory of zirconium and hafnium machining swarf stored in a spent fuel pool. This pyrophoric material represented a packing and disposal problem. While it was assumed that solidification with cement would render the zirconium non-pyrophoric, there was no test data to support this conclusion. Further, while the mechanical process of mixing the metal shavings with cement is straightforward, the need to provide a protective atmosphere of nitrogen or similar inert gas while removing the shavings from the pool and introducing them to the mixing process was not.

During investigation of alternative means of packaging or otherwise rendering the zirconium and hafnium non-flammable, NRF personnel contacted DTS about possible application of the polymer solidification process. Based on prior experience, DTS was confident that the solidification could take place underwater. This would eliminate the need for protective atmospheres and other material handling precautions. It would also be possible to introduce the polymer in situ (without mechanical mixing), which would greatly simplify the equipment needed and eliminate any increase in waste volume.

Though it was well established that the cured polymer is non-flammable, it was not known whether the solidified zirconium would also be rendered non-flammable – which was key for handling, packaging, transport and disposal.

DTS was awarded a contract to conduct testing ranging from bench-scale to full-scale. The full-scale testing consisted of solidification of both zirconium and hafnium in the actual disposal containers. This Proof of Concept Testing was conducted underwater to simulate the conditions at the NRF water pit.

After the solidified polymer/metal monolith was sectioned to expose its interior, pieces of it were subjected to 1100°C (2000°F) torch for 20 minutes. During this “torch test,” small flashes of metal burn-off from the surface of the monolith were evident, but diminished as the inventory of exposed metal was consumed. Thereafter, such sparks were infrequent, and the face of the monolith exposed to the torch became carbonized. When the torch was removed, a few flickers of flame were evident for one to two minutes, but then self-extinguished. Inspection of the monolith showed that the carbonized layer seemed to insulate the layers of polymer and metal directly beneath, thus protecting them from rapid oxidation (burning). Without the presence of a direct torch flame, the metal and polymer matrix would not support combustion.

This Proof of Concept Testing showed that the in situ injection method could be used to successfully solidify metals underwater in the disposal containers. The resulting product was resistant to high-temperature ignition sources, would not support combustion, and was quickly self-extinguishing. Based on this testing, a polymer solidification system was procured for full-scale solidification processing at the NRF site.

Puget Sound Naval Shipyard Submarine Decommissioning

Past practice during nuclear submarine decommissioning at Puget Sound Naval Shipyard (PSNS) involved sluicing carbon filter media and ion exchange resin from the submarine reactor. This sluice-out process was effective, but costly. Because of the high potential for spills, personnel exposure, and contamination, it required shutdown of the significant portion of the base that was devoted to decommissioning, packaging, transport and disposal. For those reasons, PSNS tasked KAPL to explore alternatives.

KAPL personnel, familiar with DTS' polymer solidification technology, contacted DTS to discuss possible alternatives. During discussion of the in situ process, it became apparent that a superior strategy would be to in situ solidify the carbon and resin beds in the submarine, rather than sluicing them out to receiving liners or HICs.

Since both the filter media and ion exchange resin beds are in the reactor compartment, the use of in situ solidification would mean that the compartment could be solidified intact, then cut out for transport to the Hanford disposal facility. The immobilized carbon and resin would ensure that there would be no dispersion of contaminated material in a handling or transport incident.

Examination of submarine piping confirmed that there was ingress and egress piping to the water processing room that could be cut and connected to the polymer solidification equipment. Extensive 10%-scale testing was undertaken to confirm efficacy of the injection process in the configuration in the submarine. The viscosity of the polymer mix needed to be low enough so that the mix would navigate the tortuous pipe runs, impregnate the vessels, and return (the excess) through tortuous return piping, all at relatively low temperatures.

Formulations and injection techniques were developed that successfully overcame these hurdles, yet two shortcomings remained. The first was that one of the raw polymer binder components was flammable. The second was that the binder, as it passed through the carbon and ion exchange vessels, was subject to alteration. Depending on the state of exhaustion of the carbon and resin material, promoter was sometimes stripped from the passing binder, resulting in extended cure intervals of unpredictable lengths. PSNS tasked DTS with finding an alternative formulation whose components were not flammable and whose binder would not interact with the carbon or resin during passage through the beds.

DCPP expressed a similar desire for a non-flammable, non-interactive formulation for solidification of ion exchange resin and, in conjunction with that Plant, DTS undertook a two-year campaign to develop a compliant formulation. Eventually, non-flammable binder components were identified and tested. Fortuitously, these new components used a different promoter system of a viscosity that would permit injection through process media, and appeared to be impervious to stripping by carbon and resin.

Extensive KAPL testing using the new formulation was now repeated, with good success. To support use at DCPP, the new polymer-solidified product was subjected to the extensive waste form testing stipulated by the NRC Branch Technical Position. This testing was conducted by INEEL, and the results submitted to the CRCPD E-5 Committee. Approval for Stabilization of Class B and C wastes was granted in May 2003.

While the DOE does not subscribe to either NRC or CRCPD approval, the test data generated for the CRCPD submittal was used as reference material for documenting the process and resulting waste form. Prior to E-5 Committee Approval, KAPL/PSNS reviewed and accepted this data. In early 2001, the purification piping and vessels of the first submarine reactor compartment were successfully in situ solidified and buried. Since then, DTS has continued to perform testing for KAPL on this and similar applications of the DTS polymer solidification technology.

Naval Reactor Facility Spent Fuel Pool Demineralizers

In 2005, NRF personnel contacted DTS about application of in situ process for immobilization of resin in demineralizers submerged under 7.6 meters (25 feet) of water in a water pit containing other classified or sensitive materials and equipment. As part of a cleanup campaign, the demins had to be removed from the pit. In order for this to be accomplished, the vessel pipe penetrations would have to be cut, which would result in loss of resin. Sluicing out the resin before the cutting was unattractive, as the two vessels had been out of service for more than 15 years, and the integrity of the piping system could not be assured. Establishing the radiation and contamination controls associated with the sluicing process was equally daunting.

DTS was asked to determine whether it was feasible to in situ solidify these demineralizers underwater. This would allow the vessel pipe penetrations to be cut without resin being lost to the water pit. The intact vessels would then be shipped for disposal.

Based on a study of piping access and mitigation of processing problems associated with commonality of piping, DTS confirmed that this approach was feasible. Subsequently, NRF issued a contract for a Proof of Concept Demonstration in March 2007, to be followed by the full-scale solidification at NRF.

Magnox Filter Solidification/Impregnation/Encapsulation

In 2002, Magnox Electric of the United Kingdom (UK) contracted with DTS to conduct testing of solidification of an annular filter. This filter consisted of concentric mesh-screen barriers, with the annular area between the screens filled with UOP-911 media to capture cesium and strontium. Though the accepted practice in the UK is to grout filters, in this case, the grout could not adequately penetrate the 7.5–10 cm (3”-4”) thick media-filled annulus ring. This would leave the media unsolidified and unstabilized.

DTS conducted solidification tests of a cold filter at its headquarters in Knoxville, Tennessee. After solidification, the filter in the surrounding disposal container was cut in half with a large-diameter concrete saw. Inspection of the sectioned monolith showed that the exchange media had been 100% impregnated, and all void areas internal to the filter had been filled. Thus, this solidification process effectively impregnated the filter media while forming an encapsulating barrier that would isolate the filter and filter contents from the storage and burial environment.



Fig. 1. Filter Canister with a 7.5–10 cm (3”-4”) inner annulus filled with UOP-911 media.

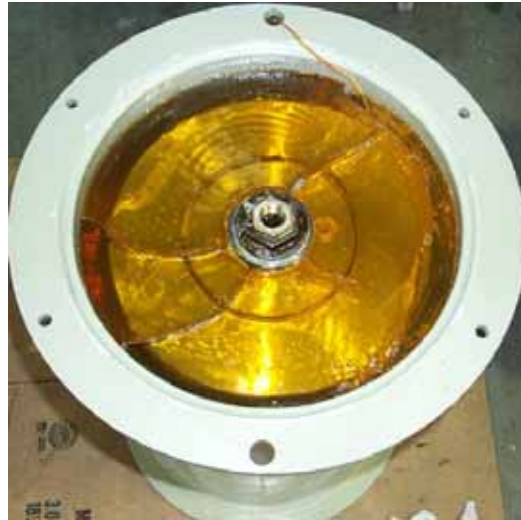


Fig. 2. Solidified and encapsulated filter in the transport and disposal container.



Fig. 3 Solidified package cut in half to show full impregnation of UOP-911 media.

GTCC and High-dose Decommissioning Wastes

In 2006, DTS processed several drums of sludge and water from a decommissioning project. This waste contained high concentrations of americium and other TRU material that rendered it greater than Class C (GTCC). Using the VES process, the solids and liquids were incorporated with a polymer binder mixture to form an emulsion. This polymer stabilization process, which resulted in a waste form covered by an NRC-approved Topical Report, converted a potential legacy waste into a readily disposable waste form that met the physical and radiological burial site requirements for burial at Barnwell.

In 2001, during the Maine Yankee Decommissioning Project, DTS developed an encapsulation container for high-dose residue from core internal segmenting. This DT-355 container was essentially a “vessel within a vessel.” The payload area of the inner vessel was filled with garnet cutting material and activated metal from the cutting kerf, and the gap between the inner vessel and the higher outer sidewall was poured full of polymer, thus forming a single continuous environmental barrier.



Fig. 4. DT-355 Encapsulation Container before closure cap is poured.

Calculations demonstrated that this several ton package would withstand the burial site required 1.8-meter (6-foot) free-fall to an unyielding surface, while maintaining the structural integrity and intact environmental barrier.

Over several weeks, as the activated metal fines accumulated, each disposal package was loaded underwater in order to mitigate dose rates and personnel exposure. Only the final dewatering and pouring of the cap occurred with the top out of the water. This unique package and polymer encapsulation process permitted disposal of high-dose activated metal fines and particles without the risks normally associated with handling and processing of this difficult-to-contain waste.

Paducah Uranium Chips

The DTS polymer solidification process has been used to stabilize natural and depleted pyrophoric uranium metal from machining operations. The waste consisted of uranium chunks, turnings, chips, and fines; plus large tramp material such as buckets, bottles, plastic bags, pieces of wood, a metal box, and assorted trash. This waste was contained in badly deteriorated 208-liter (55-gallon) metal drums that were over-packed in 322-liter (85-gallon) polyethylene drums. The waste was covered with varying amounts and combinations of water, soluble oil, machine coolant, antifreeze, grease, and dirt. Mixtures of these liquids had corroded the metal inner drums, and some liquids had leaked into the void between the metal drum and overpack.

The turnings, fines, and smaller pieces had mixed with dirt and/or grease, and had become sludge-like. Chunks and chips of uranium and pieces of tramp material were mixed throughout this sludge-like layer of material at the bottom of the drums: the result was a substance that was the consistency of wet coarsely ground cornmeal.

This uranium material was packaged under an argon atmosphere, and covered with oil. (The free oil was removed during the solidification process, but the remaining oil film on the metal was useful for reducing oxidation potential.) Unlike cement, polymer did not cause gaseous generation from high pH, and peak exotherm was more muted than with cement. Another key advantage of the polymer process is that it tolerates up to 10% petroleum oils and solvents. In this instance, the polymer binder, which was miscible with the oil film, could adhere directly to the metal surface. The resulting product was non-flammable, and suitable for storage without special environmental or flammability hazard precautions.

Savannah River Mixed Waste

Savannah River Plant (SRP) contracted with DTS to perform waste treatment tests on a variety of problem materials, including silver saddles (ceramic structures impregnated with silver for removal of iodine), as well as lead- and mercury-contaminated wastes. In each case, after in situ or mixing solidification, the resulting solidified product sequestered the offending agent(s) well enough to pass Toxicity Characteristic Leaching Procedure (TCLP) testing.

Diablo Canyon Lead Paint Chip, Blast Media and Chromated Resin

Over several years, DCPD has used the VES process to process paint chips and blast media contaminated with lead. It has also used the in situ process on chromated resins. In each case, the hazardous components were rendered immobile, and consistently passed TCLP testing.

SUMMARY

The VES and APS™ media and processes are highly adaptable to a wide range of waste forms, including liquids, slurries, bead and granular media; as well as metal fines, particles and larger pieces. With the ability to solidify/stabilize liquid wastes using high-speed mixing; wet sludges and solids by low-speed mixing; or bead and granular materials through in situ processing, these polymer will produce a stable, rock-hard product that has the ability to sequester many hazardous waste components and create Class B and C stabilized waste forms for disposal.

Technical assessment and approval of these solidification processes and final waste forms have been greatly simplified by exhaustive waste form testing, as well as multiple NRC and CRCPD waste form approvals.