

**In Situ Solidification and Encapsulation of Commercial Nuclear Power Plant,
DOE and DOD Wastes**

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ABSTRACT

This paper looks at applications of Advanced Polymer Solidification (APST[™]) for stabilization of ion exchange media, as well as application of the related Vinyl Ester Resin In Situ (VERIT[™]) process for encapsulation of filters, irradiated hardware and other large-scale objects. The documented uses include projects at US commercial nuclear sites and DOE/DOD facilities, and extensive work in the UK for impregnation of filters for waste form stabilization.

We detail ongoing enhancements to the process, including modification of liner internals for better containment of fines during solidification, and improved fill head configuration to reduce the tendency of sluiced resin beads to adhere to the underside of the fill head. We also report on experience with stabilization of (n,p) Energy, Inc.'s PRC-01 and Purolite's 501P resins.

Updates are provided on the tensile creep analysis testing being conducted to permit application of the APST[™] system for encapsulation, and on the continued full-scale application of the technology at Diablo Canyon Power Plant (DCPP). Finally, we offer a brief analysis of the potential impact that loss of access to the Barnwell, SC facility will have on future treatment and on-site storage of Class B and C wastes.

INTRODUCTION

Historically, the requirements and fee structure of the Barnwell, SC disposal site favored use of High Integrity Containers (HIC) versus 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 NRC-approved HICs 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 (followed by retrieval for shipping and ultimate disposal) of Class B and C wastes, new considerations come into play. These include the costs and personnel exposure associated with inspecting and rewatering waste stored in HICs.

With these considerations in mind, Diversified Technologies Services, Inc. (DTS) developed the APSTTM technology to solidify a wide range of media used in the nuclear industry. DCPD has undertaken to evaluate the use of the APSTTM to prepare resin and filter media wastes for interim on-site storage.

APSTTM Background

In the 1990's, because of DTS' work with the NRC-approved Vinyl Ester Styrene (VES, aka DOW Process) and Vinyl Ester Resin In Situ (VERITM) 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 instances of interference of the KAPL media with the VES process were noted. As a result, DTS began to explore the use of a different polymerizing initiator to solidify the resin and activated carbon, which eliminated the need for pretreatment preconditioning of the resins and carbon media. Following extensive bench-scale and mock-up testing conducted 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.

Contemporary to the KAPL work, DCPD was exploring process alternatives in preparation for meeting disposal requirements at the proposed Ward Valley site (which required all waste to be solidified), as well as on-site storage, if Ward Valley development was discontinued and access to Barnwell, SC was lost.

Adopting the Naval work to media solidification at DCPD was straightforward, though formulations were modified to provide a more aggressive cure schedule. The application methods developed for the VES product were equally appropriate for the AP. To meet burial waste acceptance criteria for the new waste form, the full gamut of waste form testing was required.

In 1999, DCPD and DTS conducted a full-scale cold solidification test that included representative activated carbon, organic ion exchange resin and ion-specific exchangers. 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 South Carolina Department of Health and Environmental Control (DHEC) in January 2002. In February 2002, the solidification process and waste form were approved for disposal at Barnwell. In May 2003, INEEL issued a report confirming that the AP waste form met the NRC's Waste Form requirements. The Conference of Radiation Control Program Directors (CRCPD) reviewed the INEEL report, and its 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 commercially available modified epoxy binder that is chemically cured, through addition of epoxy hardeners, to form a hard, stable monolith.

To lower its viscosity and assure optimum flow through the waste media, AP is blended with diluent 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 waste media that has been initially dewatered. Figure 1 illustrates a typical solidification setup.

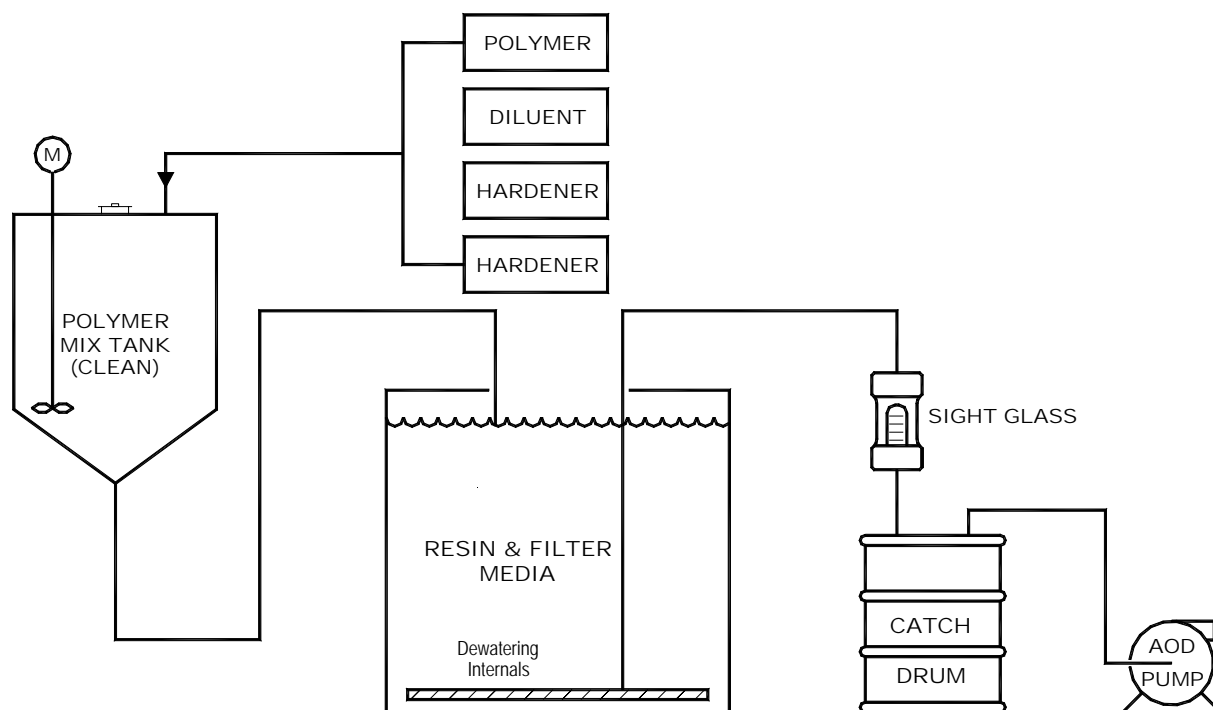


Fig. 1. APS™ simplified process flow diagram

When the AP has formed a cap on top of the waste media, the same AOD pump used in the initial gross dewatering is activated, and a combination of gravity and vacuum draws the AP

down through the waste media. 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, forming a liquid-free, hard, freestanding monolith inside the container. This process enables virtually 100% waste loading, since the polymer binder fills the voids within the waste media.

Typically, about two weeks is required to set up and sluice the resin to the solidification container, complete the Process Control Program (PCP) specimen solidification, and conduct the full-scale AP solidification. The additional exposure from handling PCP specimen samples is minimal (≈ 5 mRm).

DCPP Experience with APS™

Since the demise of the Ward Valley disposal site, DCPP's primary interest in waste form has been in looking ahead to potential loss of access to the Barnwell site, which is scheduled to refuse waste from non-Atlantic Compact members in July 2008. DCPP has no space reserved at Barnwell for Class B and C wastes after June 2006.

Table I below summarizes the AP solidification campaigns conducted at DCPP.

Table I. Summary of AP solidification campaigns.

Campaign	Liner	Contents	Comments
2002	88 cf (2.5m ³)	Resin	Loss of vacuum during polymer transfer resulted in partial solidification. Remediated liner was buried in Barnwell.
2003	88 cf (2.5m ³)	Resin	Redundant vacuum sources provided. Slower cure formulation resulted in successful solidification of 74 cf (2.1m ³). Liner buried in Barnwell.
2003	98 cf (2.77m ³)	Resin	70 cf (2.0m ³) solidified. Liner buried in Barnwell. DHEC pre-notification requirement dropped, and liners up to 200 cf acceptable.
2004	98 cf (2.77m ³)	Resin	81 cf (2.3m ³) solidified. Liner buried in Barnwell.
2005	98 cf (2.77m ³)	Resin	83 cf (2.35m ³) solidified and buried at Barnwell. Some beads from a new high-capacity cation resin adhere to underside of fill head.
2005	98 cf (2.77m ³)	Resin	70 cf (2.0m ³) of resin solidified to determine full scale swelling of PRC-01 resin. New fill head with flushing system used

Impact of High-Capacity and Filtration Resins

To extend the life of resin beds and thereby reduce the volume of waste generation, US nuclear power plants are using high-capacity cation resins. Several plants have loaded beds with IRN-99 cation resin.

During transfers of high-activity beds with IRN-99, DCPP noted that the resin appeared to clump, and took a long time to transfer. The first batch containing IRN-99, transferred to a waste container in January 2005, looked more like a dry sandblast spray than wet slurry. When the fill head was removed from the container, resin beads were stuck to the underside of the fill head. For the next solidification, a fill head modified with fittings to facilitate flushing was used. No

beads were seen on the fill head for that batch, but it must be noted that much less resin was sent to the container.

Many US PWR plants are adding a layer of resin to their shutdown clean up beds to provide filtration of submicron particulate. PRC-01 media from (n,p) Energy, Inc. and 501P from Purolite have been used for this application.

To obtain a side-by-side comparison, DCPD is using PRC-01 in Unit 1 and 501P in Unit 2. A 9% volume increase noted during the cold PCP tests of PRC-01 prompted DCPD to send DTS a PCP sample consisting of expended radioactive resin, so that DTS could verify that APS™ could solidify PRC-01. This sample was successfully solidified, but again, sample swelling was seen.

It was thought that an 80 cf (2.27m³) batch of resin with 20 cf of PRC 0-1 was inventoried in the DCPD storage tank. To allow for potential swelling during solidification, it was intended that the first full-scale batch containing PRC 0-1 be short-loaded with 70 cf (1.98m³) of resin. As it turned out, only 69 cf (1.95m³) was available to be sluiced out of the storage tank. During the subsequent full-scale solidification of that resin, no swelling was seen. This lack of swelling might well have been the result of resin commingling, whereby the PRC-01 was reduced to 15 to 20% of the resin mixture. This blending down of the PRC-01 is typical of what would occur at operating plants, as multiple resin batches are combined.

The next load out batch at DCPD, expected in February 2006, will also contain 501P and any residual PRC-01 that might have remained in the tank. This batch should provide further information on full-scale waste form swelling from PRC-01.

In sum, the resin commingling apparently mutes PRC-01 swelling during solidification, making this a non-issue for normal waste solidification processing. Nonetheless, if solidification of concentrated PRC-01 is contemplated, swelling should be anticipated and watched for.

Other APS™ Users

In late 2004, British Nuclear Fuels Limited's (BNFL's) Magnox division conducted encapsulation testing of large-scale objects using the APS™ process. Of particular interest was the reaction, or lack thereof, with the Magnox fuel cladding.

When encapsulated with cementitious grout, the cladding material reacts with a robust off gassing. Because the APS™ was found to be non-reactive with the metals, it is an ideal encapsulant for this waste. In early 2005, BNFL ordered a full-scale APS™ solidification system for production testing.

Storage and Retrieval Considerations

DCPD identified the following considerations and issues associated with long-term storage of waste, followed by retrieval and preparation for shipping and ultimate disposal. In each area, a comparison can be made between the performance and characteristics of the APS™ technology and that of dewatered waste in HICs. The items below summarize the relative advantages and disadvantages of polymer-solidified versus dewatered media in a HIC for long-term storage, pending future access to a burial site.

Process Control Program

HIC: No added exposure from PCP.

APS: Solidification of PCP with 10R/hr resin resulted in 5 mRem exposure.

Fire Protection

HIC: DCPD fire protection staff requires that all polyethylene HICs be placed in metal overpacks, increasing storage and container costs.

APS: This process can be performed in metal containers. Because the solidified media will not support combustion, no overpack is required, and no fire load is added to the storage facility.

Freestanding Water Limitations

HIC: DCPD's dewatering test report is only valid for 90 days. HICs in storage for more than 90 days must be revalidated for Freestanding Water (FSW) before shipment for disposal.

APS: This process expels any FSW and solidifies solids to a hard, freestanding monolith that does not require redewatering or revalidation.

Waste Reprocessing (Redewatering)

HIC: DCPD arranged for its HIC supplier to install a separate dewatering verification tube, fitted with a stone filter, at the bottom of the HIC. A connecting tube attached to the verification tube allowed testing for FSW. This preplanning resulted in reduced labor and exposure for revalidation, versus reinstallation of the dewatering fill head.

However, of the four HICs placed in storage for a twelve-month period when Barnwell was closed, three failed the FSW criteria when removed from storage. This verification testing and redewatering was found to be labor- and dose-intensive, requiring one week and a projected 420 mrem to process each HIC.

Should dewatering internals fail or plug during the storage period, transfer of the waste to a new container would be required, with the accompanying additional labor and exposure.

APS: Dewatering revalidation is not required. No FSW can remain in the monolith, because all the interstitial void spaces are filled with solidified polymer, and the monolith is rock hard. Any moisture present is likely to be chemically bound water. Even if isolated micro-droplets of FSW did exist, they could not migrate to the external surface of the package to accumulate as FSW.

Container Capping

HIC: Although some HICs can be capped remotely, the small HICs that fit in the storage building at DCPD did not have that feature. Exposure during dewatering revalidation

resulted from capping HICs prior to storage, removing the lid for redewatering, and recapping the HICs.

APS: This process can be conducted on waste in steel liners. These liners can be remotely capped with available drum cappers with virtually no dose.

Condensation inside Container during Storage

An empty sealed steel liner with a passive vent, placed in storage at DCPD for several years, was found to contain about 1" (2.54 cm) of water when removed from storage.

HIC: Condensation has been a source of excess water for HICs in storage. HICs will require dewatering verification after storage.

APS: Several methods can be used to mitigate or preclude moisture accumulation. First, the freeboard of the solidified liner is limited, so "breathing" of the liner is minimized. Since the waste is solidified and non-dispersible, the liner can be stored without a lid. A desiccant can then be dusted on top of the solidified monolith to absorb any trace condensation that does form.

Another alternative is injection of lightweight, high-expansion foam through the lid to displace air from the freeboard, thus precluding liner breathing and the associated condensation, and allowing the liner to be permanently sealed before it is placed in storage.

Final Waste Form

HIC: The CRCPD, including the states of South Carolina (Barnwell), Utah (Envirocare), Washington (Richland) and Texas (WCS), has agreed to grandfather all waste forms and containers currently in use that have an NRC-approved Topical Report, as well as those approved by SC DHEC for burial at Barnwell (such as poly HICs placed in a concrete overpack), though poly HICs alone are not approved.

APS: The AP waste form, one of the first of two waste forms submitted to INEEL for testing, was found to comply with the waste form test criteria (NRC criteria). This Test Report was submitted to the CRCPD, and approved for stabilizing Class B and C wastes. This approval for disposal at current and future sites is important for Utility planning, to ensure that waste does not require reprocessing or repackaging after storage.

Continued Improvements

APSTTM solidification, like all processes, benefits from continued evaluation of equipment, and improvement to procedures. The following have been completed or are currently being implemented:

- Modification to the fill head for flushing the underside, to remove hitchhiking beads.
- Modification of dewatering/solidification internals to mitigate particulate migration during initial dewatering.

- Installation of continuous level indication in the binder mix tank to permit continuous monitoring of the polymer transfer process.
- Verification of proper solidification of PRC-01 resin from (n,p) Energy, Inc. used for shutdown cleanup, with particular attention to the amount of resin swelling.
- Specimen solidification (completed) of Purolite 501P resin used for shutdown cleanup (no swelling observed with rock-hard monolith).
- APSTTM encapsulation waste form testing (completed) to permit filter encapsulation in the same container as radioactive spent resin.
- Submittal to the DOE –Idaho and the CRCPD for a national approval is planned for March, 2006. (Filter encapsulation with the VERITM polymer process already has NRC approval, but often requires chemical pretreatment of the resin to ensure non-interference with solidification. Because APSTTM can solidify resin without pretreatment, radioactive resins can be used to encapsulate solid objects, with no generation of secondary waste.)
- Specimen solidification of media such as high-capacity cation resin, to ensure efficacy of the solidification process.

CONCLUSION

The efficacy of the APSTTM process has been demonstrated at DCPD. APSTTM equipment, formulae and procedures have been refined over several solidification campaigns. The new types of resin being used to reduce Class B and C waste generation can be solidified with APSTTM.

APSTTM will also be tested for full-scale encapsulation of Magnox fuel cladding in the UK. Testing of APSTTM for the encapsulation of solid objects such as cartridge filters has been completed, and submittal for national approval in the US is planned for 2006.

While dewatering is the lowest-cost approach for immediate disposal, if access to the Barnwell burial site is limited in the future, DCPD concludes that the higher initial cost of solidification is justified by the advantages of decreased material handling, reduced labor requirements, and the lower exposure associated with not having to revalidate the dewatered status of HICs when waste is removed from on-site storage and prepared for ultimate disposal. Ancillary benefits, such as a less-dispersible waste form, reduced fire hazard, and perhaps lower-cost containers also accrue to APSTTM.

REFERENCES

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