AVANTECH'S ADVANCED PFAS POLYMERIZATION (*AP2*) TECHNOLOGY DEVELOPMENT

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1.0 ABSTRACT

AVANTech completed bench-scale testing of a variety of solidification technologies to allow for the safe and efficient disposal of highly concentrated PFAS waste. The testing of AVANTech's Advanced PFAS Polymerization (AP2) technology primarily focused on epoxy polymer solidification of PFAS-contaminated Ion Exchange resins. Similar technologies have previously been successfully developed and employed for nuclear waste applications. Parameters such as percent resin loading, moisture levels, additives, and encapsulation methods were evaluated to determine the best formulation for immobilization of PFAS-contaminated resin. This formulation was found to be both effective at preventing leaching from the monolith and extremely physically stable. The resulting solidification technology is ready for the next step in development – on-site field demonstrations.

2.0 INTRODUCTION

Per- and polyfluoroalkyl substances (PFAS) are a group of pervasive chemicals that are manmade and used for a variety of purposes, including consumer products and firefighting foams. Due to their wide use and inability to degrade, PFAS waste is abundant. Wastes exist in liquid (wastewater and firefighting foam), gas (emissions), and solid (PFAS-absorbing media) forms. As more data is collected on the negative health effects of exposure to PFAS, states have begun regulating some of the more common and well-known chains, like PFOS and PFOA.

One of the more common disposal methods currently is incineration. However, there is a great deal of uncertainty surrounding the potential emissions and incomplete breaking of PFAS chains. Because of this uncertainty, a temporary moratorium on PFAS incineration for the Department of Defense was established by the National Defense Authorization Act for FY22 until the Secretary of Defense implements the latest EPA guidance [Ref. 1]. Other emerging technologies seek to fully destroy the molecule, but they are still in development.

Another solution is to immobilize the PFAS-containing materials. Challenges include the large amount of space and materials needed to immobilize products like foam or soil, since the actual concentration of PFAS is so low, as well as determining the correct formulation to prevent leaching when so much about the leaching potential of PFAS is still unknown. AVANTech seeks to address both of these challenges. By concentrating PFAS on media, such as granular activated carbon (GAC) or ion exchange (IX) resin, the volume for disposal is greatly reduced. This in turn reduces the materials and space required for disposal in a landfill. Additionally, this report details testing that was performed to determine the best way to immobilize spent PFAS media by evaluating several different parameters, formulations, and methods.

AVANTech is highly experienced in contaminant removal and isolation, particularly in the nuclear industry. Nuclear containment challenges are similar to PFAS removal and isolation challenges. In both applications, selective media is used to remove contaminants to very low levels, and waste containment must be specially designed to minimize leaching potential. AVANTech's experience with polymer immobilization of spent nuclear media provides a basis for immobilization of spent PFAS media.

3.0 METHODS AND RESULTS

Several parameters were evaluated to determine the best formulation and method for immobilization of spent media.

3.1 Materials

The ion exchange media used in all immobilization testing was a macroporous, perchlorate (also PFAS) selective resin with the ability to reduce PFAS to 1-5 ppt. Its ability to capture high levels of PFAS made it an appropriate choice for leaching tests on immobilization methods.

Monoliths were created by curing polymer/media mixtures in cylindrical plastic containers approximately 1.5 inches diameter by 2 inches high. Curing was achieved either by oven or by sitting out in the lab for approximately 24-hours.

3.2 Methods

The Toxicity Characteristic Leaching Procedure (TCLP), developed by the EPA [Ref. 2], is designed to determine the mobility (i.e. leaching) of both organic and inorganic analytes present in liquid, solid, and multiphasic wastes. The procedure uses acetic acid as the buffer solution. AVANTech modified aspects of the procedure for the scoping tests described in this report. After monoliths or loose resin were submerged in the buffer solution for 18 hours, a sample of the solution was extracted and sent to a lab for analysis by Liquid Chromatography/Tandem Mass Spectrometry (LC/MS/MS).

Due to cost and turnaround times for PFAS-selective laboratory testing by LC/MS/MS, conductivity tests were performed at AVANTech to assess the characteristics being evaluated prior to PFAS-selective testing. Hydroxide-form anion resin was loaded with sodium chloride (NaCl) by soaking in a 10% solution. Resin/polymer monoliths were left in tap water for a few days, during which time daily conductivity measurements of the water were taken. This measurement indicated how much salt had leached from the immobilized resin. It was assumed that the amount of leached salt would be similar to the amount of leached PFAS. Results of conductivity tests are reported as µS/cm, while results of TCLP tests using LC/MS/MS analysis are reported as ng/L PFAS.

3.3 Polymer Scoping

Many epoxy polymers were tested for their ability to cure as a neat monolith and remain intact when loaded with resin and immersed in acetic acid. Only two polymers passed these tests, and they were used throughout immobilization testing. For comparison, Figure 1 shows a successful polymer, and Figure 2 shows a failed polymer. The other polymers likely failed due to the poor reaction with the epoxy and water inside the waste. Ion Exchange resin typically has roughly 40% moisture as part of the manufacturing process, even when it is dry to the touch. Special care had to be taken to find an epoxy that was suitable for this application.

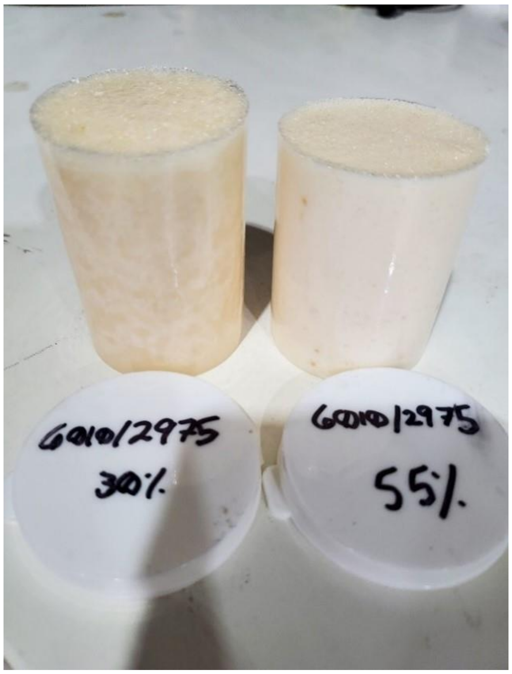

Figure 1

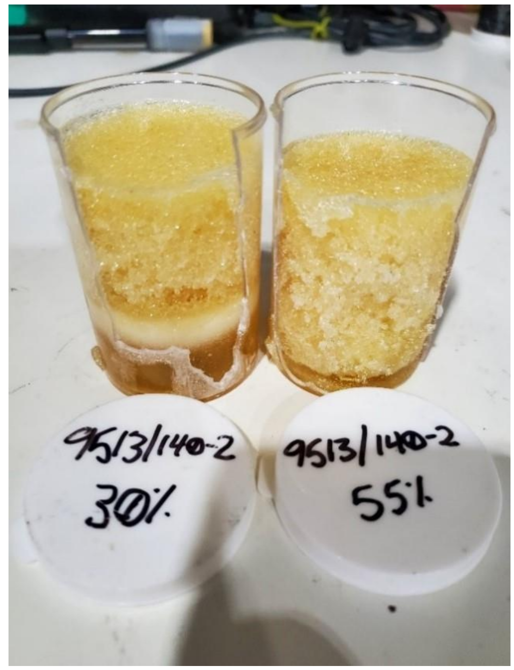

Figure 2

3.4 Percent Loading Test

Dewatered resin was used to determine the maximum percent loading of resin within the monolith. The more resin that can be encapsulated, the lower cost of polymer, transportation to disposal site, and space at disposal site. Samples were made, and percent loadings ranged from 50% to 75% by weight. Resulting monoliths are shown in Figure 3. Visual observation reveals that the optimal loading range is 55%-65%, with 60% being the best.

Figure 3

3.5 Moisture and Additive Tests

Three moisture levels of resin were evaluated in the polymer monolith. This test would help determine the optimal state of the resin for the most effective immobilization. Each sample had 50% resin loading. The three levels of moisture evaluated were dry, dewatered, and wet resin. Dry resin was used straight from the container. Dewatered resin was soaked in city water, and excess water was removed with a vacuum. Wet resin was also soaked in city water but was only drained of excess water (no vacuum). The samples are shown in Figure 4. No difference was observed between the dewatered resin and the dry resin, but the wet resin sample had resin accumulated on the top of the monolith.

Figure 4

A subsequent test on the moisture level was conducted to further understand how the mass of dried vs. dewatered resin impacts leaching. Dewatered resin was dried in an oven at 280°F to determine the proportional amount of dried resin to dewatered resin. Four monoliths, listed in Table 1, were subjected to a conductivity test.

Table 1

Monolith	Resin Moisture	Amount	Additive
1	Dewatered (Control)	72 g	None
2	Dried	54 g	None
3	Dried	72 g	None
4	Dried	72 g	Yes – Absorbent Powder

Monolith 4 fell apart during the test, likely contributing to the high conductivity. Each monolith contained the same mass of polymer. Results are shown in Figure 5.

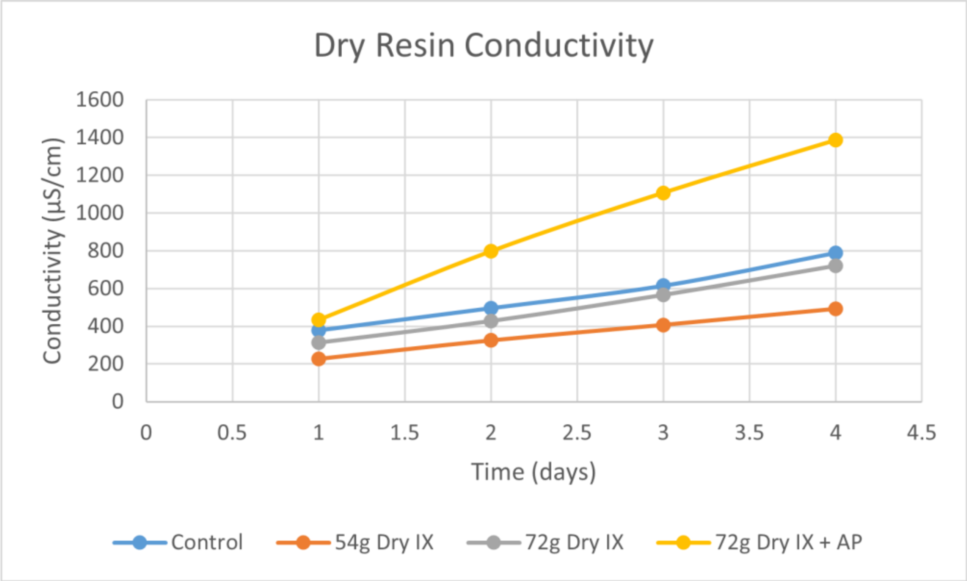

Figure 5

Conductivity tests were performed on the monoliths with a variety of additives to determine if they would further stabilize the spent media to minimize leaching better than the polymer alone. Table 2 lists each additive tested and the resulting conductivity. Additives include different types of polyacrylamide flocculant polymers (Floc), Absorbent Powder (AP), and super absorbent polymer (SOCO and WL770) at various percentages by weight. Resin was loaded with NaCl, rinsed with two bed volumes of tap water, and dewatered before being combined with polymer and cured by ambient air for 24 hours. Polymer was loaded with resin at 60wt%. Figure 6 shows the conductivity trend over several days for the best performing additives.

Table 2

Additive	Amount	End Conductivity (µS/cm)
Floc #5	1% diluted to 0.2% aqueous solution	1186
Floc #1	1% diluted to 0.2% aqueous solution	779
Floc #35	1% diluted to 0.2% aqueous solution	1127
No Floc	N/A	1106
Floc #6	1% diluted to 0.2% aqueous solution	1155
Floc #1 + AP	2% + 1.5%	2843
Dilute Floc #1 + AP	0.3% + 1.5%	1520
SOCO #1	5%	1483
SOCO #2	5%	1150
WL770	5%	1159
WL770	1%	765
AP	1.5%	579

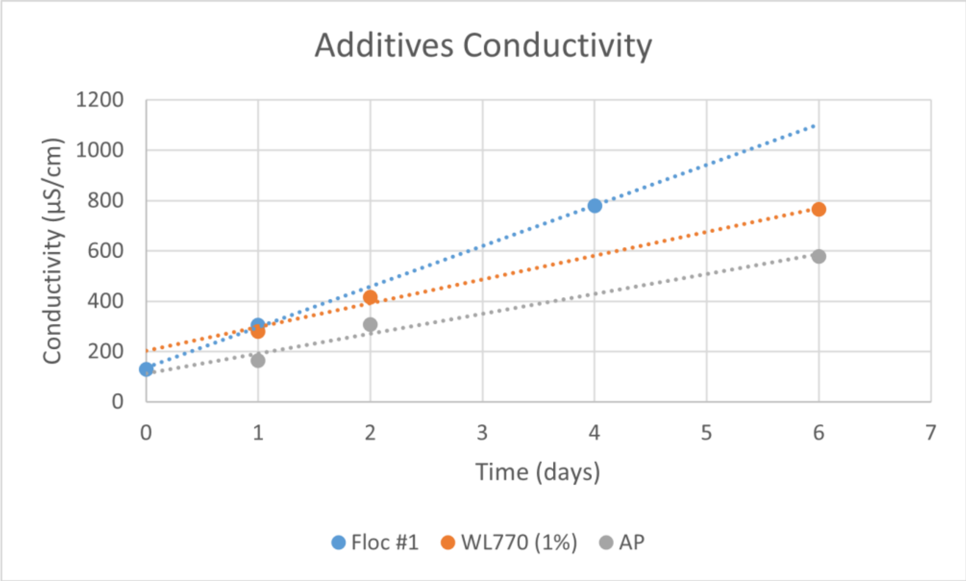

Figure 6

3.6 Encapsulation Method Test

Up to this point, only microencapsulated resin monoliths had been evaluated. When resin is microencapsulated, it is homogeneously mixed with polymer on all surfaces and within the monolith. While this method immobilizes the PFAS-spent resin to a degree, the outer surfaces of the monolith leave resin beads exposed. During leaching tests, PFAS could potentially leach from those beads.

Macroencapsulation adds an outer layer of neat polymer to the microencapsulated monolith. With this extra layer on all sides, no resin beads are exposed, and leaching can be drastically reduced or even eliminated. Macroencapsulation involves coating the container with polymer just prior to adding the resin/polymer mixture and allowing the mixture to cure with the polymer coating.

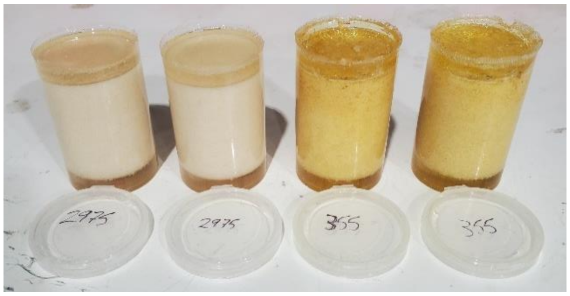

Figure 7

To test the leach rate of macroencapsulated resin, the container was lined with the same polymer as was to be mixed with the resin. Two samples each of two polymer formulations were tested. Resin was loaded at 50 wt% after being dewatered. After the container was filled with the polymer/resin mixture, it was topped off with the same polymer to create a full encapsulation.

3.7 Cementitious Grout Comparison

The use of cementitious grout is a traditional method employed for immobilizing spent resin produced in the nuclear fuel cycle. In order to best compare cement immobilization to polymer immobilization, the most robust cement formulation had to be determined. AVANTech prepared seven grout recipes in a similar manner to the polymer monoliths and tested their compressive strength and anti-leaching capabilities. All samples passed a minimum compressive strength test of greater than 700 psi, and the conductivity leaching results are listed in Table 3 [Ref. 3].

Table 3

Grout Recipe	Conductivity Leaching Result (µS/cm)
1	1931
2	829
3	2193
4	503
5	459
6	672
7	442

Grout recipe #7, which was comprised of Portland cement and ground blast furnace slag, showed the lowest leaching, so it was selected for further testing against the macroencapsulated polymer monolith. GEL Engineering, LLC performed a full TCLP on the monoliths, and results are shown in Figure 8.

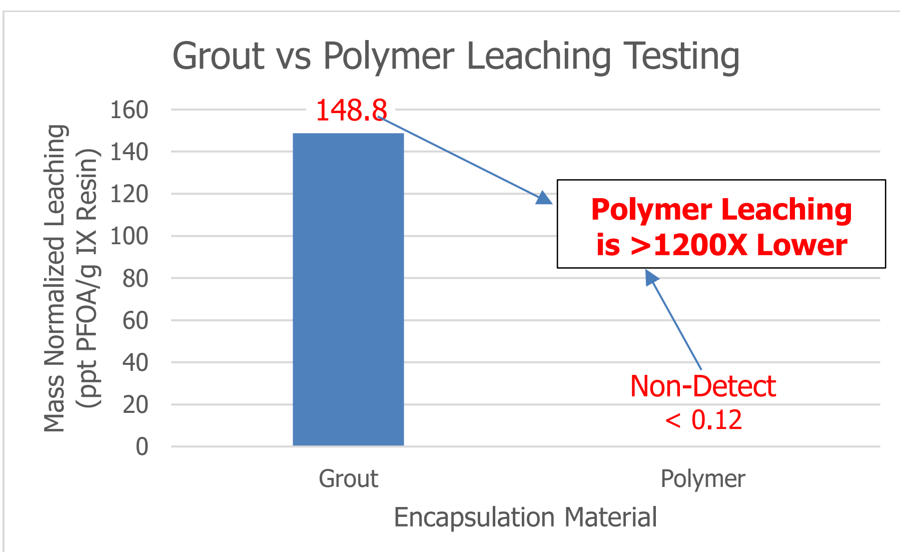

Figure 8

In a different testing experiment, the polymerized IX was compared against grout in an underwater test for longevity. The difference in stability is equally as stark as the difference in leachability.

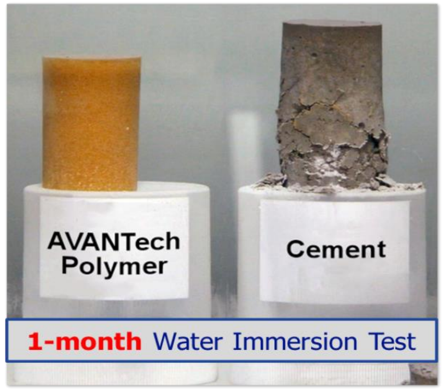

Figure 9

4.0 CONCLUSION

Several tests were performed to evaluate various characteristics of polymer monoliths for the immobilization of spent PFAS resin. Results show AVANTech's polymer choice can successfully encapsulate media and minimize leaching. Macroencapsulation prevents leaching to a much greater degree than traditional immobilization using cementitious grout.

5.0 WASTE CONTAINER

Waste containers can be any shape and size to best suit the needs of the user. The optimal container would include dewatering laterals and would be coated on the inside with neat polymer prior to addition of microencapsulated media. This macroencapsulation has shown to be stronger than both microencapsulation and cement, and it eliminates PFAS leaching. It is guaranteed to pass waste leaching requirements.

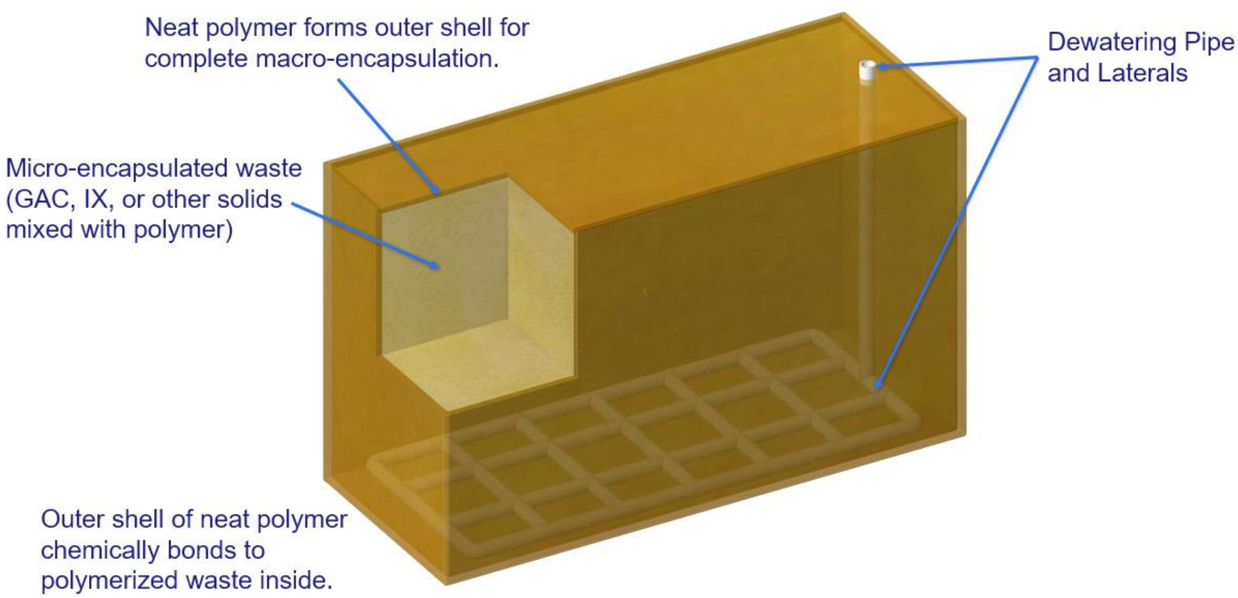

Figure 10

6.0 REFERENCES

1. "S.1605 – 117th Congress (2021-2022): National Defense Authorization Act for Fiscal Year 2022." *Congress.gov*, Library of Congress, 27 December 2021, https://www.congress.gov/bill/117th-congress/senate-bill/1605.

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3. ECS-21302-20210913, "Cementitious Grout Recipe Selection for Anionic IX Resin," *AVANTech, LLC*. September 2021.