Progress of the Hanford Bulk Vitrification Project
ICV™ Testing Program

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ABSTRACT

In June 2004, the Bulk Vitrification Project was initiated with the intent to engineer, construct and operate a full-scale bulk vitrification pilot-plant to treat low-activity tank waste from Hanford tank 241-S-109. The project, managed by CH2M HILL Hanford Group, Inc., and performed by AMEC Earth and Environmental, Inc. (AMEC), will develop and operate a full-scale demonstration facility to exhibit the effectiveness of the bulk vitrification process under actual operating conditions.

Since project initiation, testing has been undertaken using crucible-scale, $1/6^{th}$ linear (engineering) scale, and full-scale vitrification equipment. Crucible-scale testing, coupled with engineering-scale testing, helps establish process limitations of selected glass formulations. Full-scale testing provides critical design verification of the In Container Vitrification (ICV)™[1] process both prior to and during operation of the demonstration facility.

Beginning in late 2004, several full-scale tests have been performed at AMEC's test site, located adjacent to the U.S. Department of Energy's Hanford Site, in Richland, WA. Early testing involved verification of melt startup methodology, followed by subsequent full-melt testing to validate critical design parameters and demonstrate the "Bottom-Up, Feed While Melt" process.

As testing has progressed, design improvements have been identified and incorporated into each successive test. Full scale testing at AMEC's test site is currently scheduled to complete in 2006, with continued full-scale operational testing at the demonstration facility on the Hanford Site starting in 2007.

Additional engineering scale testing will validate recommended glass formulations that have been provided by the Pacific Northwest National Laboratory (PNNL). This testing is expected to continue through 2006.

This paper discusses the progress of the full-scale and engineering scale testing performed to date. Crucible-scale testing, a critical step in developing acceptable glass formulations, along with follow-on glass performance tests, is being performed for AMEC by PNNL, and is discussed in detail by PNNL in a separate, related paper.

INTRODUCTION

More than 200 million liters (53 million gallons) of highly radioactive and hazardous waste is stored at the U.S. Department of Energy's Hanford Site, in southeastern Washington State. The U.S. Department of Energy (DOE) has committed to retrieving this waste and partitioning the less radioactive component, referred to as low-activity waste (LAW), from the highly radioactive constituents. The Waste Treatment Plant (WTP), currently under construction, is not currently designed with the capacity to treat the majority of the LAW within the timeframe agreed to between DOE, the Washington State Department of Ecology and the U.S. Environmental Protection Agency. This agreement, called the Tri-Party Agreement, specifies that pretreatment and immobilization of all Hanford waste be completed by the year 2028.

Several supplemental treatment technologies were evaluated by the DOE's Office of River Protection (ORP) and its prime contractor at Hanford, CH2M Hill Hanford Group, Inc. AMEC's bulk vitrification process, referred to as In-Container Vitrification (ICV)™, was selected for further evaluation. This project is referred to as the Demonstration Bulk Vitrification System (DBVS). An overall status, direction and detailed description of the DBVS program were summarized by Thompson, et al. [1]

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[1] ™ In-Container Vitrification (ICV) is a trademark of AMEC.

ICV™ PROCESS DESCRIPTION

The ICV™ process involves batch treatment of wastes in a refractory-lined, steel container. Commercially available containers can be used including drums, standard waste boxes, and roll-off boxes. Contaminated soil and wastes are placed in the container, an offgas collection lid fitted to the container and the waste treated. When the melt has solidified, the container of vitrified waste is transported to the disposal site. Capital and operating expenses are minimized compared to other alternatives because the ICV™ container and its simple lining system serve as the melter vessel as well as the shipping and disposal container. In some applications, the glass block can be removed from the container and the container reused.

Liquid wastes can be treated with the ICV™ process by first absorbing them on soil or other suitable materials. Solid wastes or bulky contaminated items can be treated by placing them in the ICV™ container and surrounding them with soil. The soil placed around the wastes could also be contaminated soil.

The ICV™ process is best suited for waste treatment applications where the wastes are accessible and movable and where in-situ treatment is considered undesirable. ICV™ is ideally suited to situations where there is a desire to dispose of the vitrified product in a designated area, such as a licensed landfill or burial ground. ICV™ waste feed can be pretreated, blended, or sorted as desired to optimize the process.

Unlike conventional melters that require scale-up and sparging (bubblers) to achieve the desired LAW treatment rates, the ICV™ process does not have to be scaled-up. It has been demonstrated at full-scale in processing simulated LAW during the FY 2003 Bulk Vitrification project. The GeoMelt®[2] technology has been proven in several configurations and has been used on a commercial basis to successfully treat a wide range of contaminants from organo-chlorines to mixed transuranic wastes.

DBVS FACILITY PROCESS DESCRIPTION

An illustration of the DBVS plant highlighting some of the main components is provided in Fig. 1. A simplified process flow diagram for the DBVS pilot plant is shown in Fig. 2.

Liquid waste from Hanford Tank 241-S-109 will be retrieved, conditioned to remove solids, and then pumped to a series of waste receipt tanks at the DBVS pilot plant.

The liquid waste is then pumped to a vacuum-type paddle dryer where it is mixed with soil and sufficiently dried. The vapor that evolves from the drying process is condensed and pumped to holding tanks for later transfer to a separate liquid waste effluent treatment system. After the soil and LAW are mixed and dried, ZrO_2 and B_2O_3 are added to the mixture to enhance the durability of the resulting glass. Each container of glass results in the treatment of approximately 13,000 gallons of liquid LAW.

Melt containers are prepared in the Container Preparation Building. This preparation includes lining the interior of the box with insulation sand and refractory materials, installation of instrumentation, and placement of an electrically-conductive starter path [consisting of graphite and soil (or glass frit.)] The starter path mixture is positioned atop the base cast refractory panels (CRB) and covered with protective glass sheets. Solid graphite electrodes and the container lid are lastly installed and the full assembled container is moved into the Melt Station.

Final connections to the container are made in the Melt Station and include electrode power cabling, simulant and soil feed chute connections, internal camera hookup, inlet and outlet offgas piping, and instrumentation cabling.

Once preparations are completed, three batches from the mixer-dryer are transferred to feed hoppers located above the container and conveyed into the melt container, directly onto the starter path layer. Melting is then initiated via current flow through the starter path. Continued application of power causes the surrounding mixture of soil and

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[2] ® GeoMelt is a registered trademark of Geosafe Corporation

waste to melt. When the waste mixture is molten, it becomes the primary conductor of the current. During operations, a total of five additional dryer loads of the waste and soil mixture are conveyed into the container.
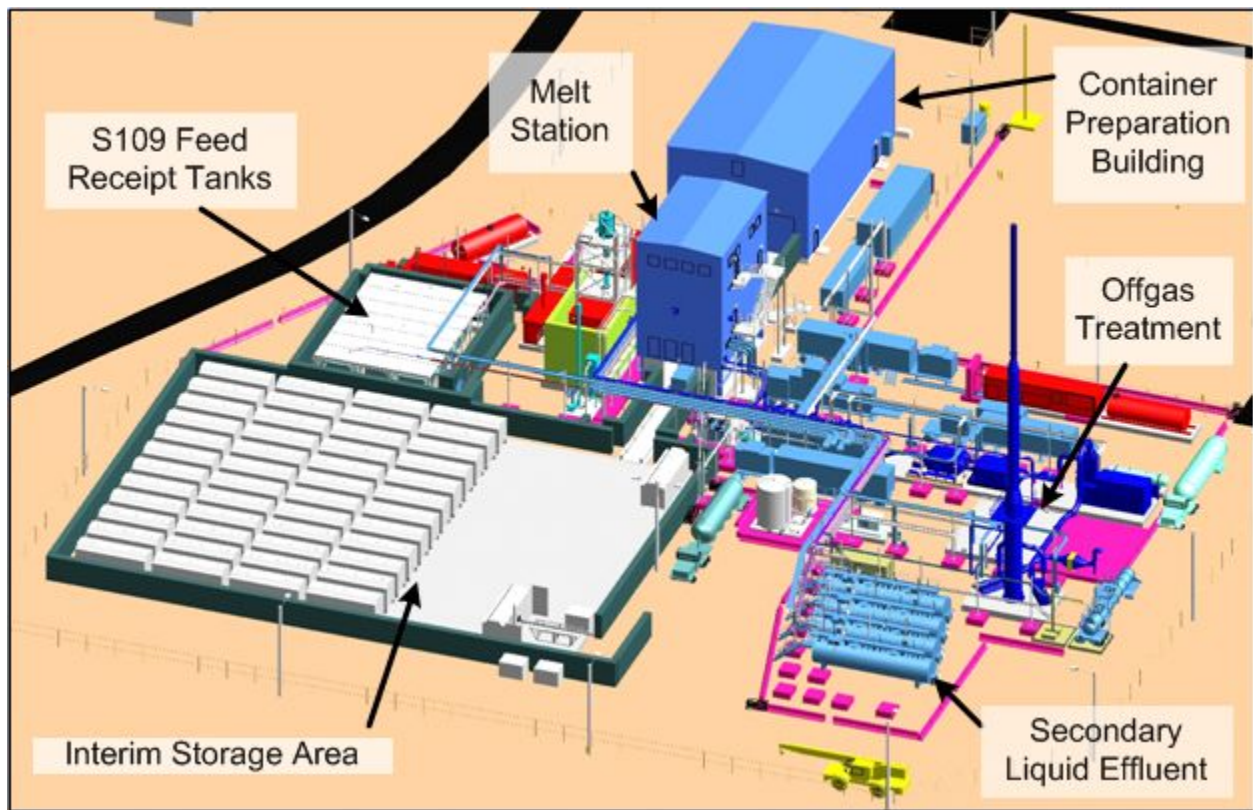

Fig. 1. Model of DBVS pilot facility at the Hanford Site

Offgases are collected and treated during the melting operations under vacuum by a downstream fan. The primary elements of the offgas treatment include particulate filtration, wet scrubbing, activated carbon (for residual radioactive iodine removal), and NO_x removal via selective catalytic reduction. Treated offgas is finally discharged through a stack to atmosphere.

After all eight dryer loads of the waste and soil mixture has been fed to the ICV^{TM} container, and sufficient electrical energy has been applied to ensure complete processing, power to the melt is terminated and the molten glass product is allowed to solidify within the container. Clean soil is then added to the top of the glass block to fill the void space in the container and provide radiological shielding. The container is then disconnected and moved from the Melt Station to the Box Storage Area for cooling, eventual glass sampling, and storage.
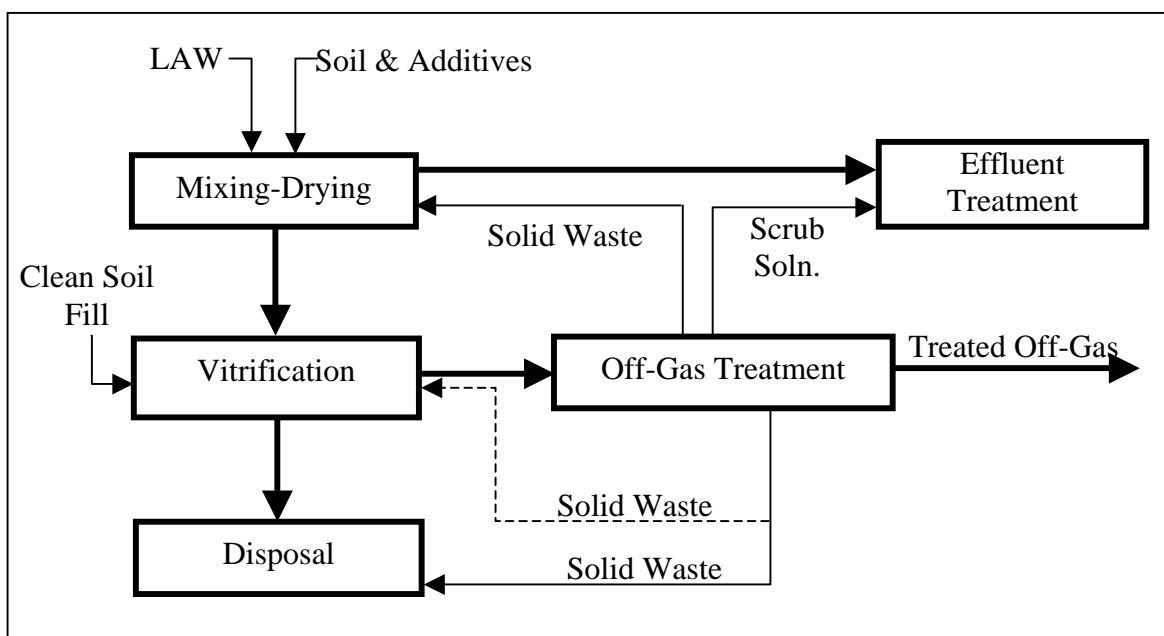
Fig. 2. Simplified process flow diagram for the DBVS plant

DBVS TESTING METHODOLOGY

Although containerized vitrification has been successfully practiced in the past, application to this Hanford tank waste stream requires execution of a thorough testing program. A three-step methodology is used:

1. Crucible or Bench scale - Typically performed first, these relatively quick and inexpensive experiments allow for multiple exploratory tests.

2. Engineering scale - Based on crucible scale results, these more involved engineering scale tests can then be performed to validate the crucible results (e.g., specific glass formulation response, refractory performance, etc.) in a more prototypical, $1/6^{th}$ scale environment.

3. Full scale - This testing provides final validation of glass formulations, engineering design, and, procedural operations.

CRUCIBLE SCALE TESTING

Preliminary Glass Formulations

Crucible testing is performed for AMEC by PNNL. Glass fabrication is performed according to standard PNNL procedures for glass batching and melting. Each crucible test involves production of 400 g of glass melted in a Pt crucible using a two step melting process: the first melting of raw materials batch, and the second melting of the glass from the first melting after quenching and grinding.

The resultant glass may be cooled by one of two methods, quenched or slow cooled. Slow cooling heat treatments are designed according to the slowest cooling profile the glass experiences in the full size bulk vitrification block. Slow cooling demonstrates whether or not a molten glass will exhibit undesirable or unacceptable characteristics such as crystallization or phase separation. Some of these characteristics may exclude a particular glass formulation from meeting Waste Acceptance Criteria for disposal.

This test matrix for this project included crucible testing on glass compositions for Hanford Tank 241-S-109 LAW and the Six-Tank Composite waste. Four phases of preliminary crucible testing were performed:

- Phase 1 - A 16-glass study designed to obtain a glass suitable for demonstration of the ICV^{TM} process on the simulated Six-Tank Composite LAW. The study was designed by varying the ratios of soil to LAW and by adding various concentrations of B_2O_3 and ZrO_2 additives.

- Phase 2 - A 5-glass study designed with systematic increases in waste loading and constant B_2O_3 and ZrO_2 concentrations. In addition, an actual radioactive Six-Tank Composite LAW glass was fabricated and tested to validate the use of simulants to represent the bulk glass properties.

- Phase 3 - (Series 20 test matrix) - A 12-glass study designed by varying one component at a time while keeping the remaining components in constant proportion (components consisted of soil, additive glass formers, and simulated waste).

- Phase 4 - (Series 21 test matrix) - A 16-glass study using a statistical design to optimally represent the composition region expected by the treatment of Hanford tank 241-S-109 LAW with local soil using B_2O_3 and ZrO_2 as additives.

The glasses were tested for phase assemblage, vapor hydration test (VHT) response, product consistency test (PCT) response, and toxicity characterization leaching procedure (TCLP) response of both quenched and slow cooled samples.[3] The detailed results from the initial testing and simulant glasses are discussed in Kim et al. 2003 [2]. The detailed results from the Phase I and Phase II matrices are discussed in Series 21 Test Report by Kim, et al. [3].

The results of these 49 glasses were evaluated to determine the composition region appropriate for meeting all the various glass-property constraints while processing the Hanford tank 241-S-109 LAW with Hanford soil, B_2O_3, and ZrO_2. The results of the evaluation are briefly described by Mahoney and Vienna [4]. The wastes evaluated represent the range of possible wastes to be treated by ICV^{TM} over the complete tank waste treatment mission.

Crucible Testing – Optimized Glass Formulations (Series 22/23)

Based on the evaluation of the results of the 49 preliminary crucible tests, a second matrix set of 40 additional crucible melts were performed to further optimize glass formulations. Similar to the preliminary crucible test glass matrices, PCT, TCLP, VHT, and PCT analysis will be performed.

These tests will generate sufficient data to define the acceptable glass composition region for processing various Hanford LAWs with local soil and additives using the baseline formulation derived from preliminary crucible testing. Results from this test matrix will refine the estimates of waste loading and formulate glasses for testing at engineering scale. There are two primary objectives of this testing:

1) Optimize the formulation for DBVS testing (i.e., minimize the cost of waste treatment by lowering the additive costs and/or increasing the acceptable waste loading) and,

2) Develop glass formulations and identify the acceptable glass composition region for wastes representing the suite of likely feed materials for the production facility.

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[3] Not all tests were performed on all glasses.

ENGINEERING SCALE TESTING

Engineering Scale Testing - Process Improvement (Re/Tc-99 Spike) (Series 31 and 32)

In FY 2003 and 2004, qualitative and quantitative engineering-scale tests were performed to advance the Bottom-Up, Feed While Melt techniques that maximize waste loading and to improve the Tc-99 immobilization performance in the waste package. These tests provided sufficient data to allow full scale, non-radioactive, simulant testing to go forward at AMEC's test site in Richland, WA.

This test matrix consisted of non-radioactive tests using a six tank composite LAW simulant and one test that had a simulant based on Hanford tank 241-S-109. The matrix also contained radioactive tests, one with Tc-99 spiked simulants and another test that used a six tank composite simulant that was mixed with 5.8% actual radioactive LAW from tank 241-AW-101.

Engineering Scale Test 31A used the Six-Tank Composite simulant with rhenium (Re) as a surrogate for Tc-99. The objective of this test was to demonstrate improved performance using the Bottom-Up, Feed While Melt technique over the previous (FY 2003) top-down engineering scale tests. This test was designed to be quantitative in nature in that a mass balance was performed to determine the post-melt disposition of Re. Key outcomes of this test were the significant reduction in bubbles/foaming within the final glass matrix as compared with the earlier top-down method. The retention of rhenium in the glass was determined to be 73%, which is very good considering the volatility of Re and the elevated temperatures in the melt cavity and plenum space. Approximately 1.5% of the batched rhenium was found in the pore spaces of the refractory liner and 0.85% was found at the glass surface. The 1.5% was well below the 7.4% found in the sand layer used in the top down melting method. The 0.85% at the glass surface prompted the use of a clean glass batch addition after all feed was added in subsequent ES tests.

Engineering scale test 31B used the 241-S-109 (S-109) tank simulant and was spiked with Re as a surrogate for Tc-99. This test showed that the S-109 tank simulant processed in a similar fashion to the Six-Tank Composite. A non-simulant bearing, clean glass batch, added after the simulant feed, reduced the soluble concentrations of Re at the surface to 0.02% of the batched Re. The refractory liner Re concentrations of 0.77% were about half that seen in the 31A test.

Engineering Scale Tests 31C, D and E used six tank composite simulant and Re as a surrogate for Tc-99. The purpose for these engineering scale tests was to advance the ICV™ container package performance by maximizing the incorporation of trace elements (e.g., Tc-99) in the glass product and minimizing the deposition of the trace elements in the cast refractory, interior container surfaces or the offgas assembly. Re concentrations were evaluated at four locations for each test; (1) high-efficiency particulate air (HEPA) filters, (2) offgas piping, (3) inside lid surfaces, and (4) refractory block.

ES-31C used a cast refractory block (CRB) that was glazed with pre-fired glaze materials in an attempt to reduce the Re vapor penetration into the refractory. Half of the CRB had a sodium silicate glaze and the other half had a ferrofrit glaze. This CRB had the highest Re levels in the refractory material of any quantitative test. Permeation data of the refractory showed that exposing the refractory to high temperatures during the glaze pre-firing increased the permeability. Additional data also indicated that molten salt penetration rather than vapor penetration was the primary mechanism for Re mobilization into the CRB. The poor performance of pre-fired glazes is thought to be a combination of rapid corrosion of the thin glaze by molten salt and the increased permeability of the pre-fired CRB. However, this test also had the highest power per mass of material treated than any other ES test which may have contributed to the higher Re levels.

Engineering Scale Test ES-31D used a de-nitrated six tank composite simulant and resulted in the lowest Re levels within the pore spaces of the refractory liner experienced of any FY 2004 test. This is likely the result of the lack of nitrate salts in the feed material, and therefore less molten salts and lower transport of Re to the refractory. Re deposits were higher on the inside lid surfaces and may be related to the lower lid skin temperatures causing a higher condensation of Re salts. This test was useful in helping to determine the mechanism for Re transport into the refractory but there are no plans for de-nitrating waste feeds for the Bulk Vitrification process.

Engineering Scale Test ES-31E used the six tank composite simulant. The major difference between this test and other FY 2004 tests was the incorporation of refractory tiles cast into to the inner walls of the CRB. This tiled refractory provided only marginal improvement in Re deposition within the cast refractory and may be the result of poor bonding of the tiles to the cast refractory.

Engineering Scale Tests 32A and 32B were radioactive tests that included Tc-99 spikes. These tests showed how Tc-99 behaved during processing and allowed engineering scale Tc-99/Re migration factors to be calculated that will be used to help extrapolate potential levels of Tc-99 in the full scale system from non-radioactive Re spiked tests. Both tests used six tank composite simulant but 32B also had 5.8 wt% radioactive tank waste from tank 241-AW-101 mixed with Six-Tank Composite simulant. Both tests also used a clean glass batch addition after adding all the Tc-99 spiked feed. These tests showed that Re was a good (conservative) migration surrogate for Tc-99 in that it tended to be present in the offgas HEPA filter and CRB in concentrations higher than those found for Tc-99. The average Tc-99/Re migration ratio calculated from these two tests for materials that mobilized into the CRB was 0.17 indicating that for every unit of Re present in the CRB, only 0.17 units of Tc-99 would be expected. The 32B test also showed that an addition of 5.8 wt% actual tank waste had no impact on the how the waste processed. The clean glass batch layer also kept soluble concentrations of Tc-99 at the surface to less than 0.03% of the batched Tc-99. These tests also indicated that soluble Tc-99 in the CRB ranged from 0.17 to 0.37 wt% of the batched Tc-99 with about 50% or more of the Tc-99 captured in glass. With planned recycle of Tc-99 containing offgas particulate, a 50% once through retention would allow most of the Tc-99 to be captured in the final glass waste form. The acceptability of the 0.3% Tc-99 levels in engineering scale CRB is pending final performance assessment analysis. Full scale tests with the lower surface area to volume ration are anticipated to have higher once through retentions and lower soluble quantities of Tc-99 in the refractory.

Engineering Scale Testing - Feed Envelope Verification (Series 33)

A total of five additional engineering scale tests (A-E) are planned to be performed at AMEC's test site. Unlike previous Series 31 and 32 tests that were designed to validate the ICV™ methodology, these Series 33 tests will be used to verify that waste feed variations and chemicals of concern will not result in processing problems, volatility, and unacceptable product quality. These tests will also help ensure that the full-scale tests with actual waste at the DBVS facility will produce acceptable waste forms.

To date, one of these engineering scale tests (33A) has been completed, with glass analyses pending. The remaining four tests and associated analyses are expected to be completed by the end of FY 2007.

A photo of the typical engineering scale test equipment used at AMEC's test site is shown in Fig. 3.

Fig. 3. Engineering scale test apparatus

The baseline Bulk Vitrification process includes a mixer/dryer to convert the liquid waste into a dried, blended feed for the ICV™ step. PNNL will prepare simulant feed for the Series 33 tests using a 22 liter steam-jacketed vacuum dryer that is a scale model of the full-scale dryer to be used in the DBVS plant.

In addition to preparing feed for these tests, the performance of the dryer for ICV™ feed preparation will be investigated. ICV™ feed preparation includes blending liquid LAW with Hanford soil, and drying the mixture to a suitable dryness, consistency, and particle size for transport to the ICV™ container for subsequent melting.

The dryer is designed to be operated in a batch mode. Pre-measured amounts of waste solution, soil, and amendments are added to the dryer. Steam is supplied to the dryer jacket to heat the dryer contents and evaporate water. The rotating mixer in the dryer is operated to blend the waste, soil, and glass formers, and to aid in drying and producing a granular flowable product. The vacuum system pulls a vacuum on the dryer to remove evaporated water[4]. At the end of a dryer batch cycle, the vacuum system is isolated and the dryer discharge valve is opened to remove the dried product, which is then staged as feed to the ICV™ melter.

The engineering-scale tests will be performed with Hanford Tank 241-S-109 LAW simulant as a baseline feed material, using the Bottom-Up, Feed While Melt approach. Variations to the baseline feed composition and the specific objectives and measurements for each test will be determined from the analysis of the Optimized Glass Formulation (Series 22/23) crucible test results.

FULL SCALE TESTING

Prior to operations at the DBVS facility on the Hanford Site, full scale testing in a controlled non-radioactive environment was needed. The following section describes full scale testing, both completed and planned. A photograph of AMEC's testing area, where these full scale tests are performed, is shown in Fig. 4. Additional test equipment, not shown below, includes trailer-mounted electrical transformers, a cooling system, and air compressor equipment.
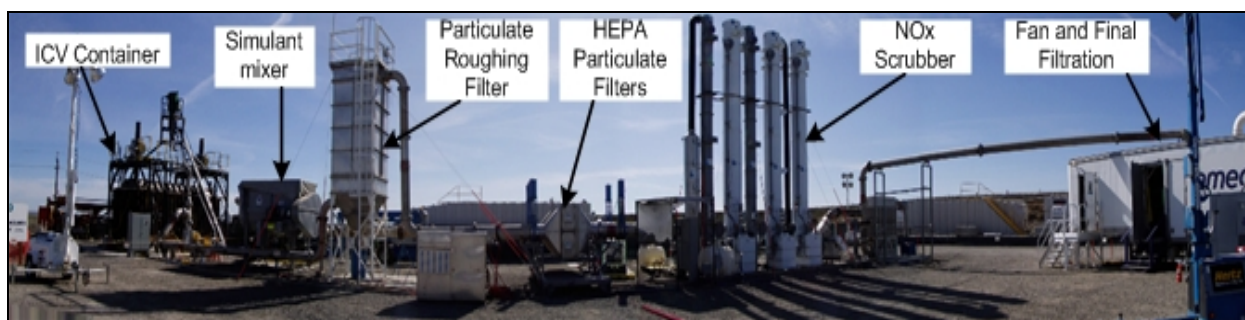

Fig. 4. AMEC's full scale testing area

Full Scale - Starter Path Testing

In 2003, prior to DBVS, AMEC had successfully demonstrated a full scale top-down process in which the melt is initiated at the top of the waste batch and progressively proceeds downward until the entire box contents are processed. For DBVS, a bottom-up method was proposed which involved placing the starter path at the base of the material to be melted. During a melt, whether top-down or bottom-up, transition occurs when the surrounding material is incorporated into the melt and becomes the primary conductor of electrical current. Fig. 5 illustrates an idealized electrical resistance change plot during startup.

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[4] Water can be evaporated at a lower temperature under vacuum than at atmospheric pressure, thereby reducing the chance of decomposing components of the waste, primarily nitrates and nitrites, during drying.
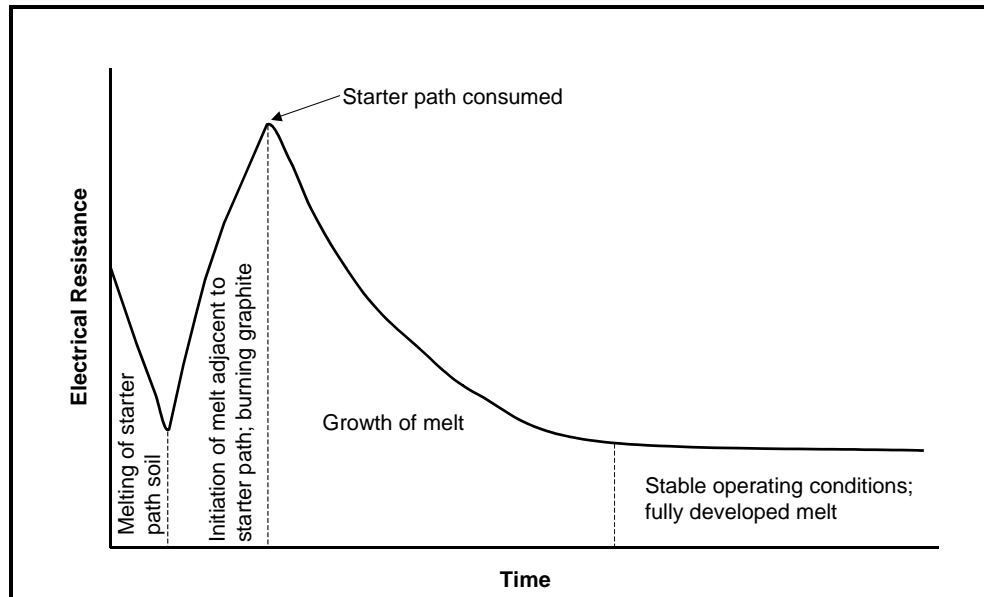
Fig. 5. Idealized test startup electrical resistance vs. time plot

The Bottom-Up, Feed While Melt method has several advantages over the top down method. One is the protection of personnel from radiation exposure. Assembly of the ICV™ container is performed in a clean, non-radiation area, followed by air-pallet transfer of the container into a melting station where remaining connections (electrode cables, wiring, etc) are made. Radioactive feed material can then be fed into the container (onto the pre-staged starter path) and melting can commence. No further personnel interaction with the ICV™ container is needed until melting is completed. With the top down method, a starter path would need to be placed onto a radioactive waste feel pile, potentially exposing operations personnel to radiation and contamination. Also, with the Feed While Melt method, additional feed material can be added during the melt process, compensating for volume reduction that occurs during melting of the waste materials. This feed addition maximizes the space available in the ICV™ container.

Previous engineering scale tests have validated the Bottom-Up, Feed While Melt technique. However, limited full scale testing was needed to demonstrate that a large scale melt could be successfully initiated and progress through the transition phase, and continue until full power applied in a steady state condition. The testing provided information on starter path improvements for subsequent DBVS tests and allowed for operator training and equipment checkout prior to testing with NO_x generating simulant. This limited testing was proposed and accomplished during full scale Starter Path Tests (SPT) 1 and 2.

Both SPT1 and SPT2 were successfully completed in January, 2005. The first test was performed primarily to validate the new starter path configuration and was designed to run just long enough to reach full power level, or 650 kW. For this test, a 12 inch layer of Hanford (non-radioactive) soil was used and placed directly above the starter path.

The second test, SPT2, was designed to validate the results from SPT1 but used the equivalent of three dryer loads (i.e., maximum start-up load) of soil cover over the starter path, and was allowed to run longer.

Results from these two starter path tests successfully demonstrated the full scale, Bottom-Up, Feed While Melt startup technique for DBVS. A photo of the full scale ICV™ container used for the starter path tests and subsequent full scale tests is shown in Fig. 6.
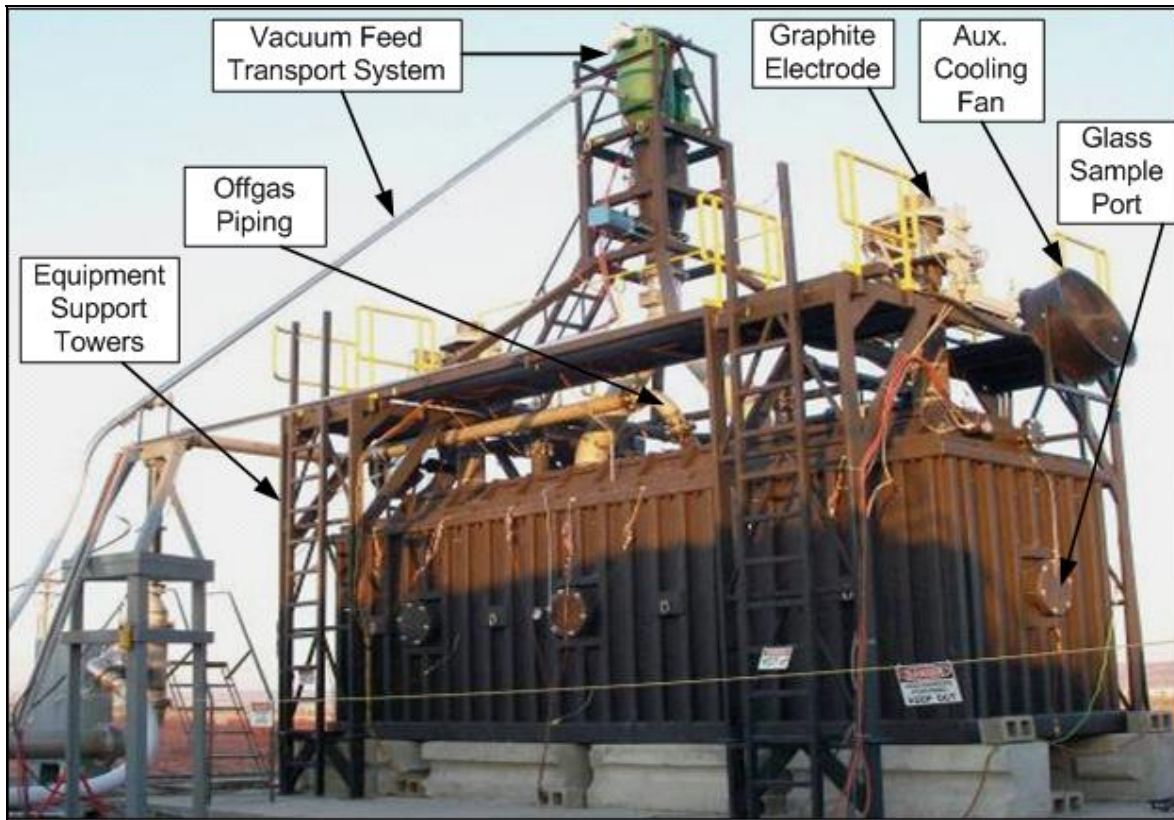
Fig. 6. Full scale ICV^{TM} test assembly at AMEC's site in Richland, WA

Full Scale - Test 38A

Test 38A was the first of two planned full scale tests that would be performed under test conditions similar to the future DBVS facility. This test was to run for 139 hours to vitrify a full box load consisting of eight dryer feed batches, producing 44 metric tons of vitrified material. This first test would use a non-nitrate simulant for the first six batches and a partial nitrate-based LAW simulant for the last two batches. The non-nitrate simulant was a mixture of sodium bicarbonate, common soil, ZrO_2, and B_2O_3. Nitrate-bearing LAW simulant produces potentially hazardous oxides of nitrogen (NO_x) gasses, and using a non-nitrate simulant in the first six batches allowed personnel to gain operational familiarity with the processing equipment prior to bringing the NO_x scrubber on line. The offgas heat transfer properties of the sodium bicarbonate simulant closely match the characteristics of the LAW simulant, providing fairly prototypic heating conditions in the ICV^{TM} container and offgas equipment.

Power was applied to the melt container on March 7, 2005 and continued for approximately 3-1/2 days. On March 11, a small quantity of molten metal and glass leaked through the box, near a thermocouple penetration, and onto the concrete pad below the ICV^{TM} container. Power to the melt was discontinued and the leak sealed itself seconds later.

Approximately 33 metric tons of the planned 44 metric tons were processed during the test. A post-melt investigation of the container and its contents revealed several main causes for the breach:

1) The structural support design under the glass contact refractory panels was found to be insufficient. This support consisted of silica sand and compressible insulating boards. Significant deformation of the insulating boards during the test resulted in settling of the glass-contact refractory panels. This settling caused cracking and movement of the joints between panels which allowed molten glass and metal to travel outside the panels and into the insulating boards, sand, and ultimately to the outer steel liner.

2)   The thermal design was inadequate in that excessive thermal insulation (insulating board) allowed the vitrified material to remain molten, rather than allowing it to freeze, once it passed outside the glass contact refractory.

3)   As a result of the above items, metal precipitate (approximately 300 kg) in the molten glass was able to leak through cracks in the bottom refractory panels and create an electrical pathway to the steel box. Electrical current was then able to pass preferentially from one electrode to the other through this lower resistance pathway. The "shorting" effect caused localized heating at the box steel liner, ultimately resulting in melting of the steel liner at one spot. Stainless steel sheath thermocouples located in the area most likely aided in the electrical shorting process.

As a result of these findings, the following changes were made to the container design:

1)   A rigid support base consisting of refractory block runners were placed under the bottom refractory panels.

2)   Finite element thermal analysis was performed to identify the optimal insulation thickness which would allow molten glass or metal to freeze within the sand refractory layer, but would still keep the metal skin temperature below design temperature limits. This analysis revealed that no insulating boards were needed, but instead could be substituted with additional silica sand.

3)   The glass contact refractory panels were redesigned with an improved joint and wall geometry to reduce potential cracking and with the addition of sumps in the bottom panels. These sumps effectively collect any reduced metal precipitate from the melt, which is denser than the molten metal, into a location away from the electrodes and away from the panel joints.

4)   Thermocouples monitoring the interior of the container and that were previously grounded to the container wall would be electrically isolated during future melts.

Although the breach of the steel container was unfortunate and unexpected, it did serve to validate the critical need for full scale "cold" (i.e., non-radioactive) testing. This approach allowed for discovery of required design changes in an environment where unexpected events can be accommodated much more easily than in a "hot" operating facility.

Full Scale - Test 38A1

As a result of the findings in Test 38A, a repeat of the test was proposed and adopted as new scope for the project. This test, called 38A-1, had the same objectives as 38A, in addition to incorporation of the new design and operational changes identified from 38A.

Testing commenced on August 2, 2005 and continued through August 10, 2005. All eight feed batches were loaded and melted in the ICV™ container, producing a vitrified glass block weighing 44 metric tons. Total test duration ran longer than planned, by approximately two days, due to offgas equipment malfunctions.

Real-time temperature monitoring of the ICV™ container during the test validated pre-test thermal model predictions. Cast refractory, insulating sand and box skin temperatures remained within 100° C of predicted values during steady state conditions. Some higher than expected temperatures were observed in one area of the box lid later in the test, but an increase in air flow through the ICV™ air plenum and a temporary reduction in melt power brought the temperature back to an acceptable level. Thermocouples placed under the bottom glass-contact refractory panels indicated the presence of glass outside the refractory panels in specific areas. Temperature readings from adjacent thermocouples in the sand and on the box skin indicated that the molten glass froze prior to reaching the designated freeze plane, as designed.

Post melt box investigation was performed approximately two weeks later. To accommodate this process, a complete destructive dismantling of the vitrified container was conducted. The photograph in Fig. 7 shows this process after the steel skin had been cut away and approximately 25% of the glass contact refractory and the vitrified glass had been removed.

Examination of the refractory showed virtually no glass leakage through the side refractory panels. As expected, some glass leakage was found under the base panels. This appeared to have originated through an opening in a joint

between two base panels. This opening was attributed to inadequate application or adherence of a mortar compound used between the panels, and not to panel shifting. The leak was confined to an area immediately adjacent to the refractory panels and did not travel beyond the designed freeze plane – the zone in which the glass solidifies and will no longer flow. The freeze plane was calculated to lie in the silica sand layer, up to halfway between the cast refractory panel and the outer steel box skin.

As with Test 38A, significant quantities (approximately 250 kg) of metal (primarily Fe) precipitated out of the molten glass. For this test, however, the molten metal collected, as designed, in the new sumps formed into the base refractory panels. No metal precipitate was found in the glass that had leaked outside the refractory panels. No evidence of panel settling was observed, as had previously occurred in Test 38A.

The quantity of metal precipitate found in the sumps is a potential concern for DBVS operations. Technetium has been shown in previous vitrification testing to preferentially migrate to the metal phase in comparison to the vitrified glass at a ratio of approximately 100:1. This is problematic because the heavier metal settles outside the vitrified glass and therefore is not encapsulated in the protective glass matrix. The metal does not have the long term durability that Bulk Vitrification glass has, and therefore may more readily release the Tc-99 into the surrounding soil where the containers are to be disposed. An investigation into this metal precipitate phenomena was initiated with the goal of eliminating the cause of the formation during the next full scale test, Test 38B. Test data were analyzed and several items were identified as possible causes for the metal precipitate.

One item that was identified as a potential cause for metal precipitate was excessively high melt temperatures, especially in the early stages of the test. The reduction of Fe oxide to Fe metal increases with increasing melt temperature. The ideal glass temperature for Bulk Vitrification is between 1300 and 1350° C. However, accurate measurement, and thus control, of the molten glass temperature at key locations during the test is difficult, if not impossible. A three-dimensional analysis using the Tempest[5] code was performed, with the goal of predicting melt temperatures at various times at specific power input levels. An accurate correlation between power and melt temperature would allow operators to control the melt temperature with some degree of accuracy. The results from the Tempest model indicated that a slower power ramp up and a lower maximum power were needed to maintain the molten glass at the desired temperature.

A second item identified as a causal agent for iron precipitation was the high Fe oxide content in the feed mixture. Soil found in the Hanford region ranges from approximately 3 to 10% Fe content. Soil used for these large scale tests has approximately 6% Fe content which, when mixed with the other constituents, provided a simulant containing 4.6% Fe. Acceptable glass formulations previously developed by PNNL have included an overall Fe content as low as 4%, but not lower. Use of a glass formulation lower than 4% would require additional glass development and analysis for durability. It was therefore decided for the next full scale test to use a simulant containing the minimum 4% Fe content.

A third causal agent was the presence of excessive carbon in the melt. For the Fe reduction reaction to occur the presence of carbon is required; therefore any decrease in carbon would theoretically decrease the chance to precipitate free Fe. Elemental carbon is present both in the two electrodes used to transfer power to the melt, and in the starter path used as the initiating current pathway. A reduction in the electrode size was evaluated but dismissed since decreasing the electrode diameter increases the current density on the surface. This effectively increases the temperature on the electrode surface which was considered to be the greater factor in Fe reduction. A decrease in the starter path volume was evaluated and resulted in the recommendation to decrease the volume to one-fourth the original quantity.

A fourth item identified was the longer than planned duration of the test. Power was originally planned to be applied for 139 hours, but because of equipment malfunction, was applied for almost two days longer. Applying joule heating to the melt beyond the prescribed time unnecessarily promotes Fe phase separation.

The fifth item identified as promoting elemental Fe reduction was the non-nitrate simulant. A sodium bicarbonate-based simulant produces a more chemically reducing environment than a nitrate-based simulant. Because a nitrate based LAW simulant was planned for all eight batches of the next full scale melt, the impacts of a nitrate simulant could be quantified at that time.

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[5] TEMPEST, developed by DOE at PNNL, is a time-dependant three dimensional, finite volume, computational code used for fluid dynamics, heat transfer, and other applications.

Overall, Test A-1 was considered a success in that several process improvements were identified, new design improvements, such as the refractory and insulation were validated and the full quantity of simulant was successfully processed.

Fig. 7. Post-melt ICV$^{\text{TM}}$ container examination and dismantling

Full Scale - Test 38B

Test 38B was designed to demonstrate the ability of the Bulk Vitrification to process a full nitrate-based LAW simulant using the Bottom-Up, Feed While Melt approach. In addition, an array of constituents of potential concern (COPCs) were added to the melt. These components included heavy metals such as Cd, Cr, Pb, etc., and spikes of non-radioactive Cs, I, and Re to serve as simulants for Cs-137, I-129, and Tc-99. The COPCs were included in the simulant feed to support "determination of equivalent treatment" (DET) discussions with state and federal regulators. Post melt glass analysis of these components will determine if the COPCs were sufficiently sequestered within the glass matrix. Sampling of the refractory, offgas piping, and other locations, will demonstrate the fate of the COPCs from the test.

Test 38B was performed from November 15, 2005 to November 22, 2005. Slightly more than five of the planned eight batches of LAW simulant were fed to the box, resulting in a 67% full box, or just less than 30 metric tons of vitrified material.

The test was terminated prior to loading the entire feed contents, due primarily to environmental conditions effecting feed equipment and offgas processing equipment, with temperatures near or below freezing, and humidity levels near or at 100% for the entire test.

Hygroscopic feed materials reacted with the moisture-rich ambient air, leading to repeated plugs in the pneumatic feed transport system. Typical feeding operations involve mixing the various simulant constituents in a plow blade

mixer. The homogeneous mixture is then dropped into a staging hopper where the pneumatic transport system then vacuums it into a vessel above the ICV™ container, periodically dumping it into the ICV™ container via connecting feed chutes. During previous full scale tests, mixing times typically ranged from 30 to 60 minutes. During this test, feed line clogging occurred unless mixing (and consequently drying) was allowed to run for up to four hours. This additional processing time significantly delayed feed addition, and subsequently extended melt duration.

Offgas equipment problems were attributed primarily to excessive condensation in the offgas line as well as temperature related chemical feeding problems to the NO_x scrubber unit. Water and nitric acid condensation in the early stages of the melt, produced by low offgas temperatures, caused wetting and prematurely high differential pressures in the particulate filters, which then caused reduced flow through the offgas line, further compounding the problem. Additionally, the large quantities of nitric acid condensate in the offgas line created a chemical imbalance in the first stages of the NO_x scrubbing unit, causing further delays.

Reduced flow through the offgas lines effectively reduced the ICV™ plenum vacuum. Early in the test, high concentrations of NO_x were produced in the ICV™ container and on several occasions were of sufficient magnitude to overcome the vacuum in the plenum, triggering a positive pressure condition. Visible quantities of NO_x were seen escaping from the plenum into the air above the ICV™ container for several seconds during these positive pressure events. After the initial load of three staged dryer batches had been sufficiently processed, this phenomenon discontinued, even after additional feed was added to the container. Once the melt had progressed to the point where plenum temperatures were high enough to eliminate offgas line condensation, downstream filtration equipment problems were minimized.

On day seven of the test, a high pressure condition was observed across one of the reaction columns in the NO_x scrubber. Attempts at troubleshooting were unsuccessful and due to the need to allow sufficient time for processing the NO_x-producing simulant already in the container, additional feeding was discontinued and power to the melt was terminated.

Although not all of the simulant load was fed and processed, the test is considered a success in that several previously unknown design issues were identified. First, the DBVS facility similarly uses a pneumatic transport system for delivering the dried waste material. The air supply to this transport system is not currently conditioned to remove moisture. As a result of this test, design changes will incorporate conditioning of the feed system air supply. Secondly, the DBVS design does not currently include a pre-heater in the offgas line. This testing showed that some method for ensuring the offgas temperature from the box remains above the dew point of water, and that of nitric acid, needs to be incorporated.

The increased NO_x generation that was observed early in the test has been evaluated and is postulated to have occurred for two primary reasons. First, nitrate compounds melt at approximately 300° C and begin to decompose at about 550° C. Thus, a large insulated pile of simulant above the molten glass zone will not begin to process until these temperatures are reached and will begin to process rather rapidly as these temperatures are reached. In addition, the sticky nature of the simulant appears to promote bridging and probably prevented the simulant from processing into the melt pool in a steady continuous fashion. Instead, the simulant may have sloughed into the melt pool in large chunks, causing sudden concentrated NO_x levels in the offgas stream. Future testing will consider reducing this pre-staged feed pile to eliminate the sudden NO_x surges.

Changes proposed after Test 38A-1 were incorporated and were successful. For example, previous full-scale tests experienced relatively erratic voltage and current swings during the startup transition period. A secondary benefit of the reduced starter path volume and slower power ramp up rate appears to have all but eliminated the erratic power swings, allowing for easier process control. In addition, the slower power ramp rate and reduced maximum power level enabled the optimal melt temperature of approximately 1350° C to be maintained, as desired. This was evidenced by readings from an in-melt thermocouple tree that continued to operate throughout the melt.

Finally, post-melt examination of the ICV™ container provided additional positive results. Less than half as much glass as in the previous test was observed to have migrated into the sand refractory insulating zone and less than 1 kg of metal precipitate was found to have separated from the glass matrix and collect near the base panel surface. This equates to a 250-fold reduction in metal precipitate, confirming that steps taken to reduce the precipitate were successful. Post-melt sampling has been completed but laboratory analysis is still pending.

FULL SCALE TESTING - PATH FORWARD

As a result of the 38B post-melt evaluation, a repeat full scale test (38C) has been proposed. This additional "cold" test would incorporate the findings from 38B and would be the final test prior to non-radioactive and radioactive testing at the DBVS facility on the Hanford Site.

CONCLUSION

AMEC's ICV™ Testing Program continues, with its teaming partners CH2M HILL and PNNL, to optimize engineering design and glass product for the DBVS facility in order to eventually process and dispose of a large fraction of the LAW at Hanford.

Crucible, Engineering Scale and Full Scale testing has provided the critical opportunity to validate glass performance, processing parameters and hardware design in a safe, controlled environment. Testing has identified a number of design improvements that are being incorporated into the Hanford DBVS pilot design.

Because of its value and simplicity, the quality of the resulting glass product, and the testing results of this project, Bulk Vitrification will continue to refine its design. Engineering, procurement and planning for continued construction at Hanford are underway as testing progresses on this project.

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