Hanford Bulk Vitrification Technology Status

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ABSTRACT

Research and testing was initiated in 2003 to support the selection of a supplemental treatment technology for Hanford low-activity wastes (LAWs). AMEC's bulk vitrification process was chosen for full-scale demonstration, and the Demonstration Bulk Vitrification System (DBVS) project was started in 2004. Also known as In-Container Vitrification™ (ICV™), the bulk vitrification process combines soil, liquid LAW, and additives (B_2O_3 and ZrO_2); dries the mixture; and then vitrifies the material in a batch feed-while-melt process within a disposable, refractory-lined steel container. The DBVS project was initiated with the intent to engineer, construct, and operate a full-scale bulk vitrification pilot-plant to treat LAW from Tank 241-S-109 at the U.S. Department of Energy (DOE) Hanford Site.

Since the beginning of the selection process in 2003, testing has utilized crucible-scale, engineering-scale, and full-scale bulk 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 ICV™ process both before and during operation of the demonstration facility.

Initial testing focused on development and validation of the melt container and the glass formulation. Subsequent testing was focused on improvements to the baseline configuration. Challenges have been identified and met as part of the parallel testing and design process. A 100% design package for the pilot plant is complete and has been submitted to DOE for review.

Additional testing will be performed to support both the DBVS project and LAW treatment for the full Hanford mission. In the near term, this includes testing some key equipment components such as the waste feed mixer-dryer and other integrated subsystems, as well as waste form process improvements. Additional testing will be conducted to verify that the system is adaptive to changing feed streams.

This paper discusses the progress of the bulk vitrification system from its inception to its current state-of-the-art. Specific attention will be given to the testing and process design improvements that have been completed over the last year. These include the completion of full-scale ICV™ Test FS38C as well as process improvements to the feeding method, temperature control, and molten ionic salt separation control.

AMEC is adapting its ICV™ technology for this application with technical and analytical support from Pacific Northwest National Laboratory (PNNL) and design support from DMJN H&N. CH2M HILL Hanford Group, Inc. is the Prime Contractor for the DOE Office of River Protection for the DBVS contract.

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 (DOE's) Hanford Site in southeastern Washington State. In accordance with the Tank Waste Remediation System Environmental Impact Statement DOE has decided to retrieve this waste and partition 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 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 must be completed by the year 2028.

Several supplemental treatment technologies were evaluated by 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). Thompson et al. [1] summarized the overall status, direction, and description of the DVBS program, and Witwer et al. [2] updated this summary in 2006.

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 off-gas collection lid is fitted to the container, and the waste is 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.

The DBVS process includes a mixer/dryer pretreatment step prior to vitrification. Feed preparation includes blending liquid LAW with Hanford soil and other additives (B_2O_3 and ZrO_2), and drying the mixture to a suitable dryness, consistency, and particle size for transport to the ICV™ container

An off-gas treatment system (OGTS) collects particulate and gasses liberated from the melt. A negative differential pressure is applied to the plenum space above the melt and draws the effluent airstream through several stages of filtration and scrubbing. The complexity of the OGTS increases from crucible-scale to full-scale. The crucible and engineering-scale systems use HEPA filtration only. The full-scale system employs two stages of HEPA filtration, and two stages of scrubbing (first Oxidation/Reduction, then tandem-nozzle venturi scrubbers). On many tests, especially full-scale, off-gas sampling is conducted to ensure air emissions are within regulatory constraints and to complete mass balance calculations.

CRUCIBLE SCALE TESTING

Preliminary Glass Formulations

Pacific Northwest National Laboratory (PNNL) has conducted crucible testing for the project. Each crucible test involves producing 400-g of glass melted in a Pt crucible using a two-step melting process: the first involves melting raw materials, and the second melts the quenched and ground glass from the first melt. The resultant glass may be cooled by one of two methods, quenched (as-melted) 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 a molten glass will exhibit undesirable or unacceptable characteristics through crystallization or phase separation. Some of these characteristics may exclude a particular glass formulation from meeting waste acceptance criteria for disposal.

The test matrix initially included testing on glass compositions for a six-tank composite waste simulant used in the 2003 supplemental treatment selection process. After the selection process, Hanford Tank 241-S-109 (S-109) was selected as the feed tank for DBVS operations, and the test matrix was expanded to include glass compositions for simulants based on S-109 information. Table 1 shows that the main difference in the two simulants is that S-109 has a higher nitrate and lower hydroxide and sulfate concentrations.

Table 1. Comparison of S-109 and Six-Tank Waste Simulants

Species	Moles/Mole of Na	
	S-109	Six Tank Composite
Al	0.0088	0.0143
Ca	0.0002	0.0000
Cl	0.0014	0.0088
Cr	0.0028	0.0021
F	0.0011	0.0063
Fe	0.0009	0.0000
K	0.0008	0.0029
P	0.0109	0.0098
SO_3	0.0074	0.0180
NO_3	0.8241	0.5070
NO_2	0.0123	0.0848
CO_3	0.0338	0.0953
OH	0.0666	0.1479
Organic C	0.0050	0.0573

Glasses from the test matrix 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.[1] Kim et al. [3] discuss the detailed results from the initial testing of simulant glasses. Mahoney and Vienna [4] summarize the results from the expanded test matrix. The glass crucible testing to date has shown that all the various glass-property constraints while processing the Hanford Tank 241-S-109 LAW with Hanford soil, B_2O_3, and ZrO_2 are met as long as the final glass composition falls within the following constraints:

- $17 \leq Na_2O \leq 22$ mass%
- $3 \leq B_2O_3 \leq 5$ mass%
- $8 \leq Al_2O_3 \leq 12.5$ mass%
- $5.5 \leq ZrO_2 \leq 8$ mass%; $6.4 \leq ZrO_2 \leq 8$ mass% if $Al_2O_3 \geq 9.5$ mass%
- $40 \leq SiO_2 \leq 48.5$ mass%.

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

Optimized Glass Formulations

Future 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 full-scale DBVS operations (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.

ENGINEERING-SCALE TESTING

Qualitative and quantitative engineering-scale tests were performed as a quick and economical means to provide early data to support later full-scale, non-radioactive simulant testing. These tests were conducted at AMEC's test site in Richland, WA. Fig. 1 shows the typical engineering-scale test equipment used.

Fig. 1. Engineering-scale test apparatus.

A series of seven engineering-scale tests used various feed types including six-tank composite and S-109 simulants with rhenium (Re) as a surrogate for ^{99}Tc. The objectives of the tests were to:

1. Demonstrate improved performance using the bottom-up, feed-while-melt technique over the previous (FY 2003) top-down engineering scale tests.
2. Evaluate the use of Re as a surrogate for the radioactive ^{99}Tc isotope.
3. Determine the post-melt fate and disposition of Re.

4. Advance the container package performance by maximizing the incorporation of trace elements (e.g., ^{99}Tc) in the glass product and minimizing the deposition of the trace elements in the cast refractory, interior container surfaces, or the offgas assembly.

Key outcomes of the engineering-scale tests completed between 2003 and 2005 include:

1. S-109 tank simulant processed in a similar fashion to the six-tank composite.
2. Re was a good (conservative) surrogate for ^{99}Tc in that it tended to be present in the offgas high-efficiency particulate air filter and cast refractory block (CRB) in concentrations higher than those found for ^{99}Tc from radioactive engineering-scale tests. The average ^{99}Tc/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 ^{99}Tc would be expected.
3. Soluble ^{99}Tc in the CRB ranged from 0.17 to 0.37 wt% of the batched ^{99}Tc with about 50% or more of the ^{99}Tc captured in glass. With planned recycle of ^{99}Tc containing offgas particulate, a 50% once-through retention would allow most of the ^{99}Tc to be captured in the final glass waste form.
4. Permeation data of the refractory showed that exposing the refractory to high temperatures during an experimental pre-firing glaze increased permeability. The 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.
5. Using de-nitrated six-tank composite feed simulant resulted in very low Re levels within the pore spaces of the refractory liner as compared to other tests, which is likely the result of the lack of nitrate salts in the feed material, and therefore there were less molten salts and lower transport of Re to the refractory.
6. A non-simulant bearing, clean glass batch, added after the simulant feed, reduced the soluble concentrations of Re at the glass surface.
7. Bottom-up melting resulted in a significant reduction in bubbles/foaming within the final glass matrix as compared with the earlier top-down method.

FULL-SCALE TESTING

Before operations at the DBVS facility on the Hanford Site, full-scale testing in a controlled non-radioactive environment was needed. The following section describes the full-scale testing conducted through FY 2006. Fig. 2 shows AMEC's testing area where these full-scale tests are performed.

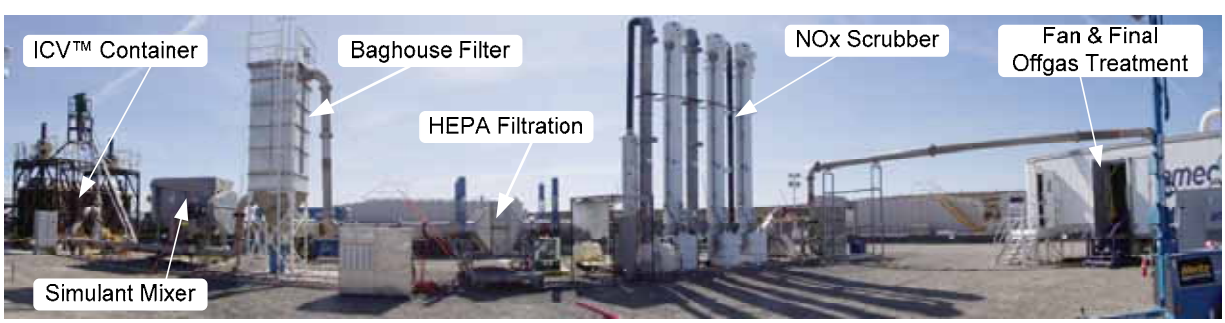

Fig. 2. AMEC's full-scale testing area.

REVIEW OF PRIOR FULL-SCALE TESTS

Starter Path Testing

In 2003, AMEC successfully demonstrated a full-scale, top-down process in which the melt was initiated at the top of the waste batch and propagated downward until the entire contents in the box were processed. For DBVS, a bottom-up melting method was used which involved initiating the melt at the base of the material to be processed and propagating the melt upward

Two full-scale starter path tests successfully demonstrated the bottom-up, feed while melt startup technique for DBVS. Fig. 3 shows the full-scale ICV™ container used for the starter path tests and subsequent full-scale tests.

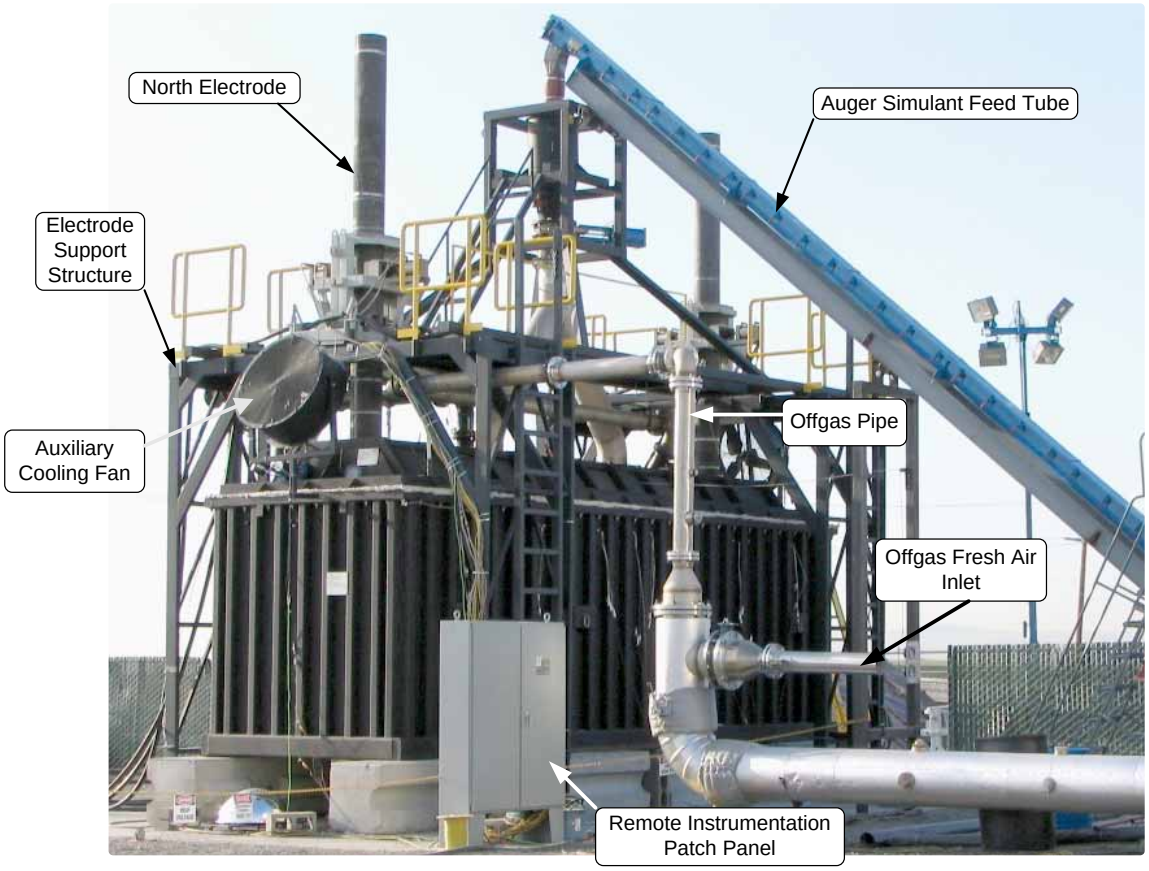

Fig. 3. Full-scale ICV™ test assembly at AMEC's site in Richland, WA.

Test 38A

Test 38A took place in March 2005 and was the first full-scale test performed. The main objective for the test was to determine how the refractory liner would perform during a 139-hour melting test that processed enough feed to produce 44 metric tons of glass. The six-tank waste simulant was used for these tests to tie back to earlier engineering-scale test results. However, the nitrate and nitrite components in the six-tank composite simulant were replaced with sodium bicarbonate for the first seven (out of eight) feed batches to minimize the need for NOx treatment in this first test. Refractory containment problems and metal precipitate formation in Test 38A revealed the need for a redesign of the refractory materials and geometries. AMEC staff consulted with industry refractory experts to complete the redesign. Validation of the thermal performance of the new design was done using 3-D thermal modeling. The thermal modeling also correlated key refractory temperatures to an optimal

molten glass temperature. Test 38A was valuable to the testing program in that it identified refractory design and operational weaknesses of the full-scale ICV™, which were subsequently corrected.

Fig. 4. Post-melt ICV™ container examination and dismantling.

Test 38A1

As a result of the findings from Test 38A, a repeat test was performed using the new refractory design. This test, called Test 38A1, had the original 38A objectives and would verify the new refractory design and operational changes. Testing was performed in August 2005. As was planned for Test 38A, the first $^{7}/_{8}$th of the simulant feed was sodium-bicarbonate based and the last $^{1}/_{8}$th was the six-tank composite (nitrate based) simulant. All of the planned waste simulant was processed in the ICV™ container, producing a vitrified glass block weighing 44 metric tons. Real-time temperature monitoring of the ICV™ container during the test validated pre-test thermal model predictions. A post melt box investigation was performed after the glass block had cooled, as shown in Fig. 4. Examination of the refractory showed that some glass leaked through the bottom refractory panels, but froze in the sand layer at the freeze plane as designed, and virtually no glass leaked through the side refractory panels. This melt also showed good incorporation of the zirconium; whereas, 38A resulted in a basal layer deposit that was not homogenously incorporated with the glass monolith.

A lesser quantity of metal, relative to 38A, precipitated out of the molten glass in 38A-1. The quantity of metal precipitate found in the sumps is a potential concern for DBVS operations. Technetium has been shown in previous engineering-scale vitrification tests to reduce and combine with the Fe metal phase, resulting in Tc concentrations in the metal phase that are roughly 100 times greater than those in the vitrified glass. This is problematic because the heavier metal phase settles to the bottom of the vitrified glass and therefore is not encapsulated in the durable glass matrix. The metal does not have

the long-term durability that bulk vitrification glass has, and therefore may more readily release the ^{99}Tc into the surrounding soil where the containers are to be disposed. An investigation into this metal precipitate phenomena indicated that several key contributors could be managed to minimize or eliminate the metal formation. These included an excessively high melt temperature, high iron oxide content in the soil, and excessive carbon content in the melt (from the starter path.) The use of the non-oxidizing carbonate waste simulant was also a probable contributor to the reduction of Fe oxides to Fe metal. Process and chemistry changes were made to minimize these contributors for future testing.

Test 38A1 showed that a full box of glass could be produced, and the baseline design was established for further refractory improvements in subsequent boxes.

Test 38B

Test 38B was performed in November, 2005, to validate process and chemistry changes recommended after Test 38A1. The maximum melt temperature was controlled to less than 1350°C, and the size of the starter path was further reduced. This test used the six-tank composite simulant (see Table 1) with the nitrate and nitrite materials to allow for a direct correlation to earlier engineering-scale tests. Improvements were made to the side refractory panel joints to further improve glass containment. The test ran for 168 hours but was terminated with only $^{2}/_{3}^{rd}$ the planned simulant load added. Offgas treatment system problems, aggravated by inclement weather and high condensate levels in the offgas stream, forced early termination of the test. In addition, feed delivery delays to the melt resulted in the early melt-off of unprocessed feed on the melt surface, allowing the molten glass to be covered by only a thin layer of feed (cold cap) during much of the run, rather than a pile of feed material which is the norm. A consequence of this small cold cap was that Re (used as a surrogate for Tc) retention in the melt was only 38%.

Post-melt examination of the Test 38B container and glass showed that improved refractory sealing methods resulted in less glass migration into the refractory-sand insulating zone. Lower melt temperatures and less available carbon from a smaller starter path resulted in a 250-fold reduction in the quantity of metal phase precipitate. One consequence of the lower melt temperature was that the ZrO_2 glass former did not incorporate as well as seen in Test 38A1. Zircon ($ZrSiO_4$) was recommended for subsequent tests to provide better ZrO_2 incorporation.

Test 38B showed that Fe metal precipitation could be significantly reduced in nitrate feeds by reducing the starter path size and controlling the melt temperature. The test also showed that the melt should be operated with a cold cap to improve contaminant retention, and that ZrO_2 would not completely dissolve at the lower operating temperatures. Process and equipment changes were identified to prevent a reoccurrence of the problems experienced in Test 38B.

FY 2006 FULL-SCALE TEST 38C

Full-scale test 38C was performed in May 2006. To replicate the waste to be treated at the DBVS facility, S-109 simulant was used in 38C rather than the six-tank composite simulant previously used. A Re spike was added to the simulant to act as a Tc surrogate. Based on earlier test results, Test 38C was operated with a significant cold cap (simulant waste pile) above the molten glass to improve contaminant retention in the glass. Additional refractory improvements, specifically on the floor panel joints, and the use of zircon ($ZrSiO_4$) in place of ZrO_2 were implemented. Based on the reduced quantity of Fe metal seen in 38B, the maximum melt temperature was again controlled to less than 1350°C, and the reduced size starter path was used. The offgas treatment system and simulant feed equipment problems encountered in 38B were resolved before initiating Test 38C. The pneumatic feed transport system, which was impeded by simulant clogging in Test 38B, was supplemented by an auger-style feed system in Test 38C. Fifty-six metric tons of feed material, along with 2 metric tons of

clean cover material were melted, producing 44 metric tons of vitrified product. The results of the test are described in the sections below.

Glass Performance

The entire 44 metric tons of glass were processed as planned. The 38C glass passed all the regulatory limits for VHT, PCT, and TCLP, similar to glasses from previous ICV™ tests. The VHT response of the glass sample was < 0.27 g/(m^2·d) compared to the limit of 50 g/(m^2·d). The PCT response of the glass was nearly an order of magnitude below the regulatory limit of 2 g/m^2 for normalized release of boron and sodium. The TCLP response of the glass was more than an order of magnitude below the universal treatment standard (UTS) limits for Ba and Cr.

Fe Precipitation Control

Post-test examination of the 38C glass block found only 536 grams of iron precipitate that contained less than 0.04 wt% of the total Re added to the melt. These results again confirmed that Fe precipitation could be significantly reduced by minimizing the starter path size and controlling the melt temperature.

ZrO_2 Incorporation

The use of zircon increased the dissolution of the zirconia into the glass. A few deposits of undissolved zircon on the floor of the CRB were only 1 to 3 mm thick compared to a 20- to 25-mm-thick layer covering most of the CRB floor in 38B. The 1 to 3-mm deposits of undissolved zircon represented a small fraction of the overall zircon added with the feed, and had little, if any, impact on glass quality.

Refractory Performance

Although the refractory base design used in 38A1 and 38B had contained molten glass within a designed freeze plane in the refractory sand, a need for improvement was identified and implemented during 38C. The base panel joints were redesigned to include the addition of a refractory sealing plug to better contain molten glass within the cast refractory panels.

In general, the ICV™ refractory liner system worked well and produced the desired temperatures at key locations around the melt. However, one location developed elevated skin temperatures because molten ionic salt (MIS) leaked through the refractory liner followed by a leakage of molten glass. (See the following section for further description of MIS.) Although MIS leakage was observed at several locations around the CRB during ICV™ dismantling, this particular MIS leak point was aggravated by localized heating induced by a short circuit through one or both of two in-melt thermowells. The short-circuiting thermal wells were removed during the test, eliminating the localized resistive heating effect, and allowed the skin temperatures to drop to normal levels. The glass in the leak area then froze in the sand layer just outside the refractory wall, effectively stopping any further glass leakage and allowing the test to complete. ICV™ post-test dismantling and investigation revealed that aside from the one leak area caused by the short circuit, glass movement beyond the CRB panels was minimal (less than 20 kg) and was the best performing refractory design tested to date. The base panel refractory modification was successful at eliminating virtually all glass leakage.

Cold Cap Performance

The use of the simulant cold cap resulted in high single pass Re and SO_3 retentions in glass of 70.9 wt% and 95 wt%, respectively. However, the presence of significant quantities of MIS outside the CRB

panels is thought to be related to the use of a large cold cap during all but the end of melting operations. The main problem with MIS outside of the CRB panels is that radionuclides present in the waste are also initially in the form of salts and are concentrated in the MIS. If the MIS migrates to cooler regions of the ICV™, the salts do not decompose, or only partially decompose, forming glasses with poor durability. These salts and low-durability glasses are susceptible to leaching after disposal. In addition to the cold cap, the significant quantities of MIS in 38C are also thought to be related to the higher concentration of low melting nitrates in the S-109 simulant.

The large cold cap used in 38C was an attempt to improve contaminant retention in the glass. However, the low-melting nitrate salts are extremely fluid in comparison to molten glass, with a viscosity similar to water at ambient temperature. It was postulated that a substantial quantity of MIS existed in the cold-cap regions where the temperatures were above the melting points of the salts but below the nitrate decomposition temperature. The low-viscosity MIS penetrated pores and micro cracks in the CRB, even though molten glass did not penetrate at those locations.

PNNL had identified MIS migration as the predominant mechanism for movement of Tc into the CRB [5,6] and had efforts underway to look at methods to minimize the levels of MIS penetration. The results from 38C showed that using S-109 simulant in combination with a large cold cap to improve contaminant retention could significantly increase the quantity of MIS migration. The 38C results led to an accelerated effort to devise methods to reduce MIS migration to allow the continued use of cold caps in the bulk vitrification process.

Efforts to Control MIS Migration

Previous work [5,6] described how a substantial portion of a well-dispersed and very-minute component (Tc) can segregate from a large volume of feed and migrate into a porous refractory wall that is contacted by that feed for a relatively short time at a relatively low temperature. As discussed previously, the feed used in these tests is a mixture of an LAW simulant, soil (Hanford soil), and additives, currently ZrO_2 and B_2O_3, that improve glass durability. The LAW simulant is a mixture of salts, predominantly nitrates. As the feed temperature increases during the melting process, a single MIS phase that incorporates some B_2O_3 is formed from the LAW simulant salts. The MIS wets the grains of feed solids, spreading over and bridging them, and fills some of the space between the grains. The MIS begins to form at a temperature as low as 150°C, is fully developed by 450°C, and is nearly fully incorporated into a glass-forming phase by 800°C. By 300°C, the amount of MIS is sufficient to allow migration. The CRB contains fine open pores that adsorb the free MIS and are capable, provided that an ample supply of MIS is available, to transfer the MIS through the refractory wall and deposit it on its outer surface. The low viscosity of molten salts, which is close to that of water, facilitates MIS penetration into the CRB.

Because Tc is carried to the CRB by MIS, decreasing MIS migration into the CRB would proportionally decrease the concentration of the soluble Tc in the refractory lining. Several methods for controlling MIS migration were explored but focused mainly on methods to decrease the MIS mobility within the BV feed. Decreasing MIS mobility was achieved by (a) increasing the specific surface area of solids and (a) adding organic carbon to the feed. Using solids with fine grains or grinding the existing solids (soil) reduces migration by bonding free MIS to solid grains by capillary forces. Additions of organic carbon decrease the amount of MIS in the feed by destroying its main components, nitrates and nitrites, at temperatures below 300°C.

Material and Procedures

The CRB material used for the DBVS project to date is Vibrocast 60PC,[2] a 60% alumina, mullite-based, low-cement castable designed to provide minimum porosity. The particle density of the Vibrocast CRB is 3145 kg/m^3, the bulk density is 2579 ± 76 kg/m^3, and the porosity is 17 to 21%. The loss on ignition is ~1.9 mass% at 550°C and 2.2 mass% at 1200°C.

The standard glass feed composition used was based on a mixture of additives (Hanford soil,[3] ZrO_2, and B_2O_3) with LAW simulant. Two kinds of simulants were used: a six-tank composite and S-109 simulant (see Table 1). Early tests were conducted with the six-tank composite simulant, but later tests shifted to the S-109 simulant when 38C results indicated that MIS migration might be worse with the S-109 material. Feeds were prepared for laboratory experiments by adding solid ingredients to liquid simulants and drying the mixture. The feed preparation processes for this and previous tests to mix and dry the simulant and glass formers were not prototypical.

Modified feeds were prepared with fine-grain ingredients (silica flour, diatomaceous earth, kaolin, bentonite, and fly ash) or ground soil. The fine-grain materials partly replaced the soil in feed formulated to maintain glass properties in specified limits. Grinding was performed in a laboratory-scale tungsten carbide mill in 20-g batches. As Fig. 5 shows, grinding the soil for 2 min decreased the sizes of nearly all particles. Increasing the grinding time to 5 min showed some further size reduction but also indicated that there was a practical limit to the particle size reduction that could be obtained in the carbide mill.

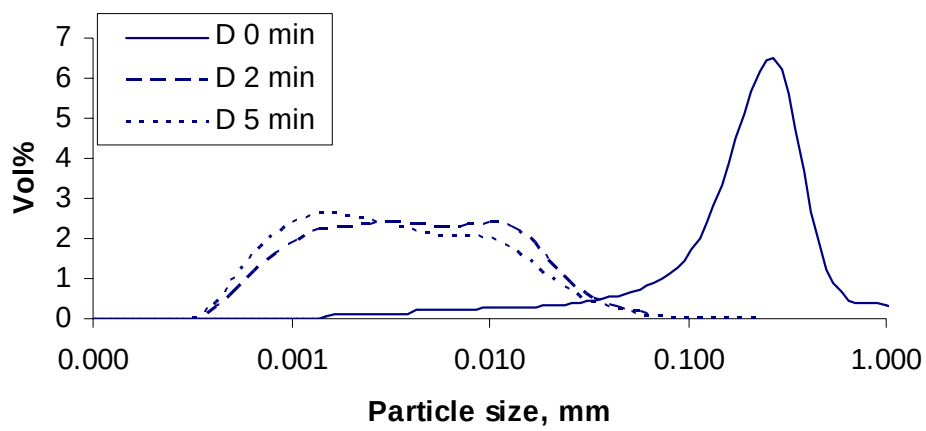

Fig. 5. Comparison of particle size distribution of Hanford soil as received and ground for 2 and 5 min; samples were deagglomerated

Hanford soil samples were also sent to Praxair Specialty Ceramics (PSC), in Woodinville, WA, to develop a soil-grinding process that could be scaled up to produce the larger quantities of ground soil necessary for larger scale experiments. The specific surface areas of all the tested soils were measured by the Brunauer, Emmett, and Teller (BET) technique (a method for measuring surface areas). The as-received Hanford soil had a surface area of 5.74 m^2/g; 2-min grinding in a tungsten carbide mill increased it to 9.75 m^2/g and 5-min grinding to 10.78 m^2/g. The Praxair methods included plate grinding and ball milling that produced a soil with a surface area of 8.00 m^2/g and a longer ball milling process that produced a surface area of 8.80 m^2/g.

[2] E. J. Bartell Co., Spokane, Washington
[3] HRTS05 soil from AMEC's Horn Rapids Test Site, Richland, Washington

To test the MIS migration into the CRB, 2×2 cm rods were placed axially in Pt crucibles filled with feed. Silica crucibles were also used as model refractories. The porous silica crucible walls are more uniform in composition, structure, and porosity than the CRB, allowing an easy detection of migrated MIS in sectioned samples. Small silica crucibles with the wall thickness of 3 to 5-mm were used for scoping tests. Systematic studies were performed in medium-sized crucibles with the wall thickness of ~9 mm.

Both Pt crucibles and silica crucibles were heated at 5°C/min to a temperature below 700°C (usually at 500 or 550°C) and held for 1 hour (feeds with six-tank composite simulant) or 30 min (feeds with S-109 simulant). Then CRB rods were removed from the feed, and feed was removed from the silica crucibles. The CRB rods and silica crucibles were weighed before and after heating. The removed rods and empty crucibles were then heated at 5°C/min to 1200°C (feeds with six-tank composite simulant) or 1000°C (feeds with S-109 simulant) to allow the MIS to fully react with the crucible material and thus to avoid the uncertainty regarding the degree to which MIS was decomposed during the first heating. The rods and crucibles were then weighed and sectioned for further examination.

Laboratory Results

The volume fraction of MIS in the feed is large; for the six-tank LAW simulant, MIS makes 41.6 vol% of the condensed phase (excluding void) and can be as high as 46 vol% if all the B_2O_3 is dissolved in the MIS. Some of the MIS is immobilized through absorption by the solid grains, but a large fraction is free to migrate in the space between grains. The mobile part can be decreased by increasing the surface area available for adsorption or by destroying nitrates and nitrites before the MIS migrates to the CRB.

Scoping tests with unaltered and modified feeds indicated that (1) the MIS mobility within the unaltered feed is high, allowing a continuous supply of MIS from the bulk feed to the crucible wall, (2) the first MIS that penetrates the refractory, starting at 300°C, is composed of low-temperature eutectics, (3) while MIS decomposition continues in the feed with increasing time and temperature, very little MIS reacts with the silica refractory at temperatures below 550°C, and (4) the depth of MIS penetration increases sharply within the temperature interval from 300°C to 400°C, progressing at a slower rate at higher temperatures.

Additions of kaolin, bentonite, and fly ash had little impact on MIS migration. Diatomaceous earth slightly decreased MIS migration into silica crucibles but caused a substantial vertical drainage of MIS in the feed and slowed feed-conversion reactions. Diatomaceous earth probably holds MIS inside the fractal-like silica particles that react with MIS at a slower rate than the soil does.

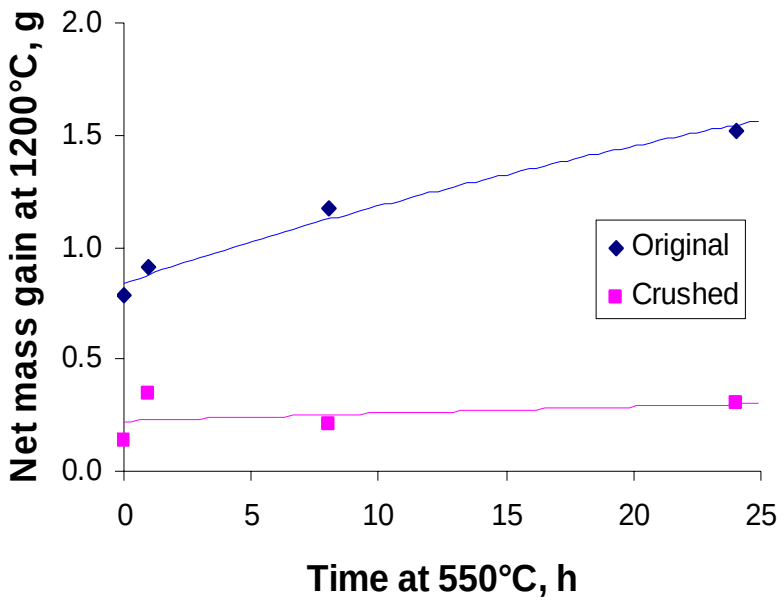

Fig. 6. Effect of 550°C heat-treatment time on MIS migration to CRB from original and ground feed prepared using six tank composite simulant; the lines represent a square-root fit (the y-intercept represents the amount of MIS migrated before the temperature reached 550°C)

The most successful attempt to keep MIS in the feed and limit its penetration into the CRB was achieved by grinding the Hanford soil. Mixing as-received soil with soil ground for 2 min decreased the depth of penetration of MIS into silica crucibles by 25% with 15% addition of ground soil and by 50% with a 37% addition of ground soil. Using 100% ground soil resulted in an 85% decrease.

Fig. 6 shows that the reduction in MIS mobility with ground soil is a long-term effect that lasts for more than 24 hours. This figure plots the net mass increase of CRB rods heat-treated at 1200°C as a function of CRB rod exposure time to feeds at 550°C. The net mass increase was obtained by correcting for the CRB loss on ignition and is an indication of the quantity of MIS that penetrates into the CRB while heating to and holding at 550°C. When the feed was ground, the total amount of MIS in the CRB samples decreased by an order of magnitude and did not significantly increase with time, suggesting that only a small fraction of free MIS was present in the ground feed.

Based on the results from 38C, the waste simulant in the MIS migration tests was changed from the six-tank composite to S-109. The feeds prepared with the S-109 simulant showed faster drainage and more extensive migration than feeds with six-tank composite simulant. This is probably due to the higher nitrate, lower hydroxide, and lower organic carbon fraction in the S-109 (see Table 1). However, the general relationship between MIS migration and the soil surface area remained the same, and feeds prepared with finer soils showed less penetration. **Error! Reference source not found.** shows that the relationship between the soil surface area and the amount of MIS penetration is linear.

Extrapolation of the line in Fig. 7 yields zero MIS migration at the specific surface area of 12.6 m^2/g. The fraction of MIS that is free to migrate is given by $f = 1 - a/a_0$, where a is the specific surface area of the soil, and $a_0 = 12.6$ m^2/g is for the surface area of the soil necessary to prevent MIS migration. At $a < a_0$, MIS migration will stop if a sufficient fraction of the nitrate and nitrite salts are destroyed before they start to migrate at a temperature around 300°C.

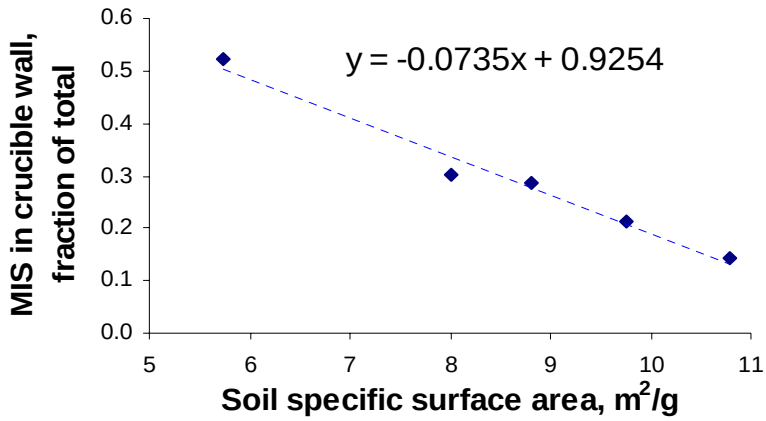

Fig. 7. Effect of soil specific surface area (by BET) on the fraction of MIS lost from S-109 feed to crucible walls

Fig. 8 shows the amount of free MIS that would be expected for soils with different surface areas. This figure also shows that the nitrate and nitrite salts represent 85% of the S-109 MIS, indicating that destroying these components of the MIS at low enough temperatures could eliminate migration. Nitrate destruction can be achieved at temperatures below 300°C by adding appropriate carbon sources to the feed.

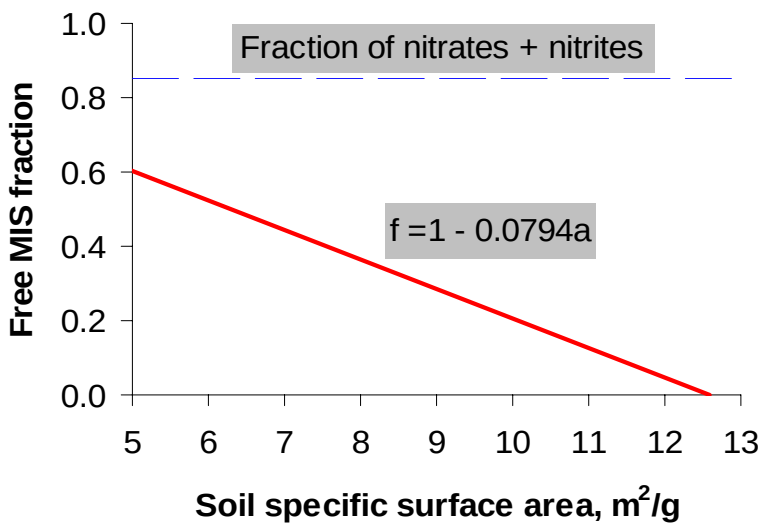

Fig. 8. Fraction of MIS that is free to migrate as a function of the surface area of soil

The next step in the ongoing work is to determine the type and quantity of carbon source that will not prematurely react during bulk vitrification feed-preparation operations in the vacuum dryer where inside wall temperatures can reach as high as 120 °C but will destroy the nitrates before they migrate at temperatures above 300°C. The carbon source must not interfere with drying operations or transporting the dry feed from the dryer to the ICV box, and must not promote precipitation of reduced iron in the melt,. Candidate materials at this point include sucrose, starch, and cellulose. Other activities include looking at the tradeoffs associated with grinding the Hanford soil to produce the higher surface areas versus purchasing glass-forming minerals with the required high-surface area.

Engineering Design Status and Near-term Testing Plans

In FY 2006, the design of the full-scale DBVS pilot plant to be constructed at Hanford was completed. DBVS site development has been initiated with the completion of structural foundation and the installation of underground utility infrastructures. Long-lead equipment procurements have been initiated, and in some cases, equipment has been received, ready for installation at the DBVS site.

In FY 2007, laboratory MIS migration reduction tests, three engineering-scale tests (ES-30J, ES-30K and ES-31F), and a single full-scale test (FS-38D) will be performed. These tests are intended to determine and demonstrate process changes to control MIS migration.

The objective of the laboratory MIS migration reduction tests is to select the high surface additives and the carbon source that trade off the degree of MIS penetration with the impact on the current design of the DBVS facility.

The objective of the first engineering-scale test (ES-30J) is to evaluate the performance of a newly modified refractory liner that more closely matches the full scale refractory design, and reproduce the MIS migration phenomena observed during Test 38C. This first "baseline" test will be followed by a second test (ES-30K) which is intended to mitigate the MIS migration phenomena, using a modified feed formulation that incorporates high-surface-area glass formers and/or additional carbon sources. The third test (ES-31F) will incorporate a cold cap control scheme to optimize the size of the cold cap and further reduce MIS availability while still maintaining contaminant retention. A thermal imaging system will be used to monitor the cold cap progression and will be evaluated to determine its applicability to full scale testing. These tests will provide sufficient test data to support a decision to perform a full-scale test using the modified feed formulation and the cold cap control.

Upon successful completion of ES-31F, a full-scale test (FS-38D) will be conducted at AMEC's test facility in FY 2007. A primary test objective is the demonstration of the feed modifications tested on engineering-scale to mitigate the MIS migration into the refractory. Another primary objective of this test will be to integrate the DBVS mixer dryer to the rest of the ICV™ operation. This integration will demonstrate the viability of the dryer and for the first time at full-scale produce prototypic feed for the ICV™ container. In addition, sintered metal particulate filters, the first component in the DBVS offgas treatment system, and the dried waste and glass former conveyance systems will also be incorporated and tested.

CONCLUSION

The DBVS ICV™ testing program continues, with its teaming partners CH2M HILL, AMEC, PNNL, and DMJM H&N, to optimize engineering design and glass product for the DBVS facility with the goal to eventually process and dispose of a large fraction of the LAW at Hanford.

Crucible, engineering-scale, and full-scale testing has and will continue to provide critical validation of glass performance, processing parameters, and hardware design in a safe, controlled environment.

Testing has identified a number of design changes that have been incorporated to improve the DBVS design and challenges are being addressed with further testing. Using a combination of high-surface-area feed solids and organic carbon (sucrose, starch, or cellulose) appears to be a promising method to significantly decrease MIS migration through the CRB.

DOE continues to support the DBVS project and is promoting further refinement of its design via crucible, engineering, and full-scale testing and analysis scheduled for FY 2007.

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