Hanford's Supplemental Treatment Project: Full-Scale Integrated Testing of In-Container-Vitrification and a 10,000-Liter Dryer

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ABSTRACT

The GeoMelt®[1] In-Container Vitrification™ (ICV™)[2] process was selected by the U.S. Department of Energy (DOE) in 2004 for further evaluation as the supplemental treatment technology for Hanford's low-activity waste (LAW). Also referred to as "bulk vitrification," this process combines glass forming minerals, LAW, and chemical amendments; dries the mixture; and then vitrifies the material in a refractory-lined steel container. AMEC Nuclear Ltd. (AMEC) is adapting its GeoMelt ICV™ technology for this application with technical and analytical support from Pacific Northwest National Laboratory (PNNL). The DVBS project is funded by the DOE Office of River Protection and administered by CH2M HILL Hanford Group, Inc.

The Demonstration Bulk Vitrification Project (DBVS) was initiated to engineer, construct, and operate a full-scale bulk vitrification pilot-plant to treat up to 750,000 liters of LAW from Waste Tank 241-S-109 at the DOE Hanford Site.

Since the beginning of the DBVS project in 2004, testing has used laboratory, crucible-scale, and engineering-scale equipment to help establish process limitations of selected glass formulations and identify operational issues. Full-scale testing has provided critical design verification of the ICV™ process before operating the Hanford pilot-plant.

In 2007, the project's fifth full-scale test, called FS-38D, (also known as the Integrated Dryer Melter Test, or IDMT,) was performed. This test had three primary objectives:

1) Demonstrate the simultaneous and integrated operation of the ICV™ melter with a 10,000-liter dryer,
2) Demonstrate the effectiveness of a new feed reformulation and change in process methodology towards reducing the production and migration of molten ionic salts (MIS), and,
3) Demonstrate that an acceptable glass product is produced under these conditions.

Testing was performed from August 8 to 17, 2007. Process and analytical results demonstrated that the primary test objectives, along with a dozen supporting objectives, were successfully met.

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[1] GeoMelt® is a registered trademark of Geosafe Corporation.
[2] In-Container Vitrification™ (ICV™) is a trademark of AMEC Inc.

Glass performance exceeded all disposal performance criteria. A previous issue with MIS containment was successfully resolved in FS-38D, and the ICV™ melter was integrated with a full-scale, 10,000-liter dryer.

This paper describes the rationale for performing the test, the purpose and outcome of scale-up tests preceding it, and the performance and outcome of FS-38D.

INTRODUCTION

The U.S. Department of Energy Office of River Protection (DOE-ORP), through its Hanford tank farm operator CH2M HILL Hanford Group Inc., contracted with AMEC's GeoMelt Division, to develop and demonstrate its bulk vitrification process using its ICV™ technology. This project, named the Demonstration Bulk Vitrification System (DBVS), is being used to evaluate the process for supplemental treatment for a large portion of the Hanford Site low activity waste (LAW). Over 200 million liters of liquid waste is stored in Hanford's underground waste tanks and must be disposed of, per a "Tri-Party" agreement between the DOE, the U.S. Environmental Protection Agency, and the Washington State Department of Ecology. Approximately 160 million liters of this is LAW, and some of this waste will be treated at the Hanford Waste Treatment and Immobilization Plant (WTP), which is currently being constructed by Bechtel Inc.; however, the majority of the LAW portion of the waste must be disposed of using supplemental treatment because of the current processing capacity in the WTP design.

The DBVS project follows a graded approach in applying the GeoMelt vitrification process towards the eventual treatment of nuclear waste. Laboratory and crucible testing first determines acceptable glass formulation(s), followed by engineering-scale ICV™ testing, which confirms glass formulation and some operational characteristics using a one-sixth linear-scale melter. Finally, full-scale ICV™ testing demonstrates the actual operational response and glass performance of DBVS-scale equipment.

With the GeoMelt® ICV™ technology, liquid waste to be treated is mixed with glass formers and other additives, dried, and then fed into a refractory-lined metal box to undergo a joule-heating-treatment process. The waste mixture is heated to at least 1250°C, effectively destroying any organics, decomposing salts, and melting and homogenizing the constituents. When the contents are completely processed, joule heating is discontinued and the molten material is allowed to cool and solidify within the refractory-lined container. The melt container also serves as the shipping and disposal vessel. The glass block immobilizes any radioactive or Resource Conservation and Recovery Act or Toxic Substance Control Act hazardous constituents that might remain. Off-gasses generated during processing are contained within a sealed container and off-gas lid that is maintained at below-atmospheric pressure. These off-gasses are drawn through a treatment system that removes particulates and scrubs condensable gases (e.g., water vapor) and non-condensable gases (e.g., NO_x) from the flow stream. The treated off-gas flow is then safely released to the atmosphere.

Each of the full-scale tests performed since the project's inception in 2004 has employed a "bottom-up" GeoMelt® process where melting begins at the bottom of the container and then progresses using a feed-while-melt (FWM) process. FWM refers to the capability to continue to add waste and glass formers to the ICV™ container during the entire melting process. In this "bottom-up" melting process, a conductive "starter path" is arranged just above a bottom refractory liner surface, with two graphite electrodes set at opposite ends of the container, in contact with the starter path. A mixture of glass formers and waste material is spread on top of the starter path, and power is then applied to the electrodes, causing the starter path material to melt via joule heating. This heat propagates upward and outward, eventually melting the surrounding glass former and waste mixture. Additional glass former/waste material is periodically fed onto the surface of, and incorporated into, the melt pool. FWM continues and the volume of the melt increases until the container is filled. Because it continually compensates for the volume reduction inherent in a melting process, the FWM technique maximizes waste loading by production of a full box of vitrified waste. Treatment by GeoMelt® vitrification, interim storage, transport, and final long-term disposal is achieved entirely within the same ICV™ container.

TEST RATIONALE

Since project inception, design and operational improvements have been identified from each test and have been incorporated into planning and execution of each successive test. For example, the first full scale test, FS-38A, had refractory design problems that were subsequently corrected and validated in follow-on tests FS-38A-1 and FS-38B [1].

Full-scale test FS-38C was performed in May 2006. To better replicate the waste to be treated at the DBVS facility, a more prototypical “S-109” simulant, spiked with Re, was used in FS-38C rather than the previously used “six-tank composite” simulant. (Re serves as a non-radioactive surrogate for radioactive Tc, which is present in Hanford tank waste.) In addition, based on results from the earlier tests, FS-38C was operated with a large volume of feed mixture above the molten glass to act as a cold cap and improve contaminant retention in the glass.

The test successfully processed the full load of simulated waste material, and the thick cold cap operating methodology resulted in high single pass Re and SO_3 retentions in glass of 70.9-wt% and 95-wt%, respectively. However, the thick cold cap, combined with the change to S-109 simulant, also significantly increased the quantity of molten ionic salt (MIS) migration compared to what had previously been seen.

Previous work [2] explained 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. The feed being a mixture of LAW and glass forming solids, and the LAW being a mixture of salts, predominantly nitrates. As the feed temperature increases during an ICV™ melt, a single MIS phase that incorporates some B_2O_3 is formed from the LAW 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 just under 200°C, is fully developed by 450°C, and is nearly fully incorporated into a glass-forming phase by 800°C. The cast refractory liner (CRB), in direct contact with the feed, contains fine open pores that adsorb the free MIS and are capable, provided that an ample supply of MIS is available, to transfer, via capillary action, the MIS through the CRB wall and deposit it on its outer surface. The low viscosity of molten salts, which is close to that of water at ambient temperature, aids MIS penetration into the CRB. Because Tc is carried to the CRB by MIS, decreasing MIS migration into the CRB proportionally decreases the concentration of the soluble Tc in the refractory lining.

Fig. 1 shows the FS-38C outer refractory panel surface after partial disassembly. The clumped sand deposits that were fused together from the penetration and subsequent thermal decomposition of large quantities of MIS can be seen. Because of the undesirable concentration of Tc and other unwanted radioactive species, steps were taken after 38C to minimize its production. This phenomenon and the results of 38C are discussed in WM-7236, "Hanford Bulk Vitrification Technology Status" [3]. The FS-38C results led to a focused effort to reduce MIS migration while allowing the continued use of a cold cap in the ICV™ process.

Fig. 1 Full Scale Test 38C Refractory with MIS Deposits

Project reviews performed by external industry expert panels recommended that the various full-scale process equipment needed for the Hanford pilot-plant should be jointly tested, before commencing radioactive waste operations, where practicable. Specific hardware items that were identified as critical system components, in addition to the ICV™ melter, and that were readily available for testing in FS-38D, included a 10,000-liter dryer/mixer and subsystems and an off-gas particulate filter, referred to as a sintered metal fiber filter (SMFF).

Qualification testing of the dryer and subsystems was performed immediately before FS-38D to ensure operational readiness and to optimize dryer process methodology. The results from this dryer qualification testing are provided in the DOE report, RPP-RPT-32739, *DBVS Full Scale Dryer Qualification Test Report* [4].

LABORATORY AND CRUCIBLE-SCALE TESTING

Laboratory and crucible-scale experiments showed that the following methods could decrease MIS penetration into the CRB individually or in combination:

- Chemically react the low melting salts with a carbon source before melting,
- Limit the quantity of salt-containing feed staged above the melt surface, and
- Use glass-forming minerals of a smaller particle size to increase the overall specific surface area.

These tests demonstrated that a carbon source, such as cellulose, added to the feed material would react with and destroy a large portion of the nitrate and nitrite salts present in the feed during the normal ICV™ joule heating process. This reaction, occurring at relatively low temperatures (~200°C), prevents the concentration of a significant fraction of potential MIS, minimizing MIS contact with the ICV™ CRB. In addition, the particle size of the glass forming minerals was reduced, which was shown in crucible testing to minimize the segregation of the glass formers and MIS early in the melting process. Finally, the quantity of unprocessed feed material placed above the molten glass (cold cap) was significantly reduced, further limiting the probability of MIS formation at the CRB-melt interface.

Detailed results of this laboratory and crucible testing effort are discussed in a related paper, WM-8275, *Method to Reduce Molten Salt Penetration into Bulk Vitrification Refractory Materials* [5].

ENGINEERING-SCALE TESTING

Follow-on engineering-scale tests were also performed and successfully demonstrated that these three methods were effective in reducing the presence of MIS. Successful results from these efforts were evidenced by a four-fold reduction in sodium-penetration distance into the CRB by MIS in an engineering-scale test (ES-31F), as compared to a baseline engineering-scale test (ES-31J) [6]. Baseline test ES-31J simulated test conditions seen in the previous full-scale test 38C where an abundance of the problematic MIS was seen. A photograph of the engineering-scale melter at the GeoMelt Horn Rapids Test Site in Richland, WA is shown in Fig. 2

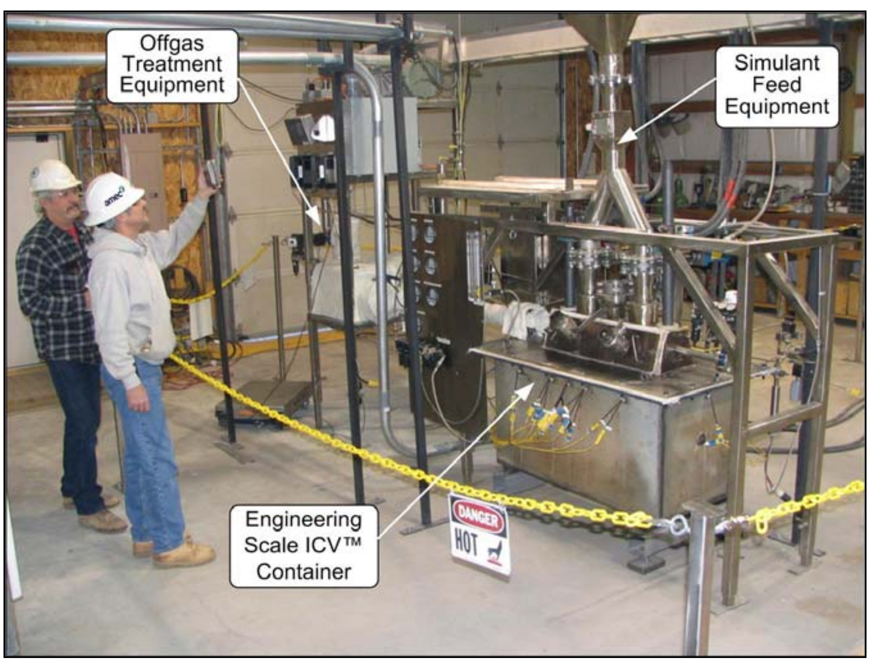

Fig. 2 GeoMelt® engineering-scale ICV™ equipment.

FULL-SCALE TESTING

FS-38D was performed from August 8 to August 17 and ran for approximately 210 hours. All of the planned 56 metric tons of waste-feed simulant material, along with almost 2 metric tons of non-simulant clean glass batch material, was melted, producing 44 metric tons of vitrified glass product. Each of the MIS reduction techniques developed in crucible-scale testing and validated in engineering-scale testing were applied in FS-38D, with the same goal of significantly reducing the MIS penetration and deposits in the CRB—as compared to those seen during FS-38C post-melt sampling and analyses. In addition, the 10,000-liter full-scale dryer intended for eventual use at the DBVS facility at Hanford was tested for the first time during FS-38D. A photograph of the FS-38D full-scale equipment at the GeoMelt Horn Rapids Test site in Richland, WA, is shown in Fig. 3 and Fig. 4.

FS-38D TEST RESULTS

Three primary objectives were determined for FS-38D. Each of the primary objectives was successfully met. Twenty more supplemental, or fact-finding, objectives were also identified for FS-38D. Twelve of these supplemental objectives were fully met, five were partially met, and three were not met. The three objectives that were not met had a cause directly or indirectly related to a suboptimal (powdery) dryer feed product. This powdery feed transported poorly, congested the dry waste transfer and off-gas systems, and prolonged the FWM process in the ICV™ container. These results suggest additional effort is required with the waste dryer system to optimize the physical properties of the dryer feed product.

Table 1 lists the primary objectives and success criteria as outlined in the test plan [7] and includes a column that summarizes the status of each objective against its success criteria. The test and analytical results, as reported in the final test report [8], demonstrate how the three major test objectives were met.

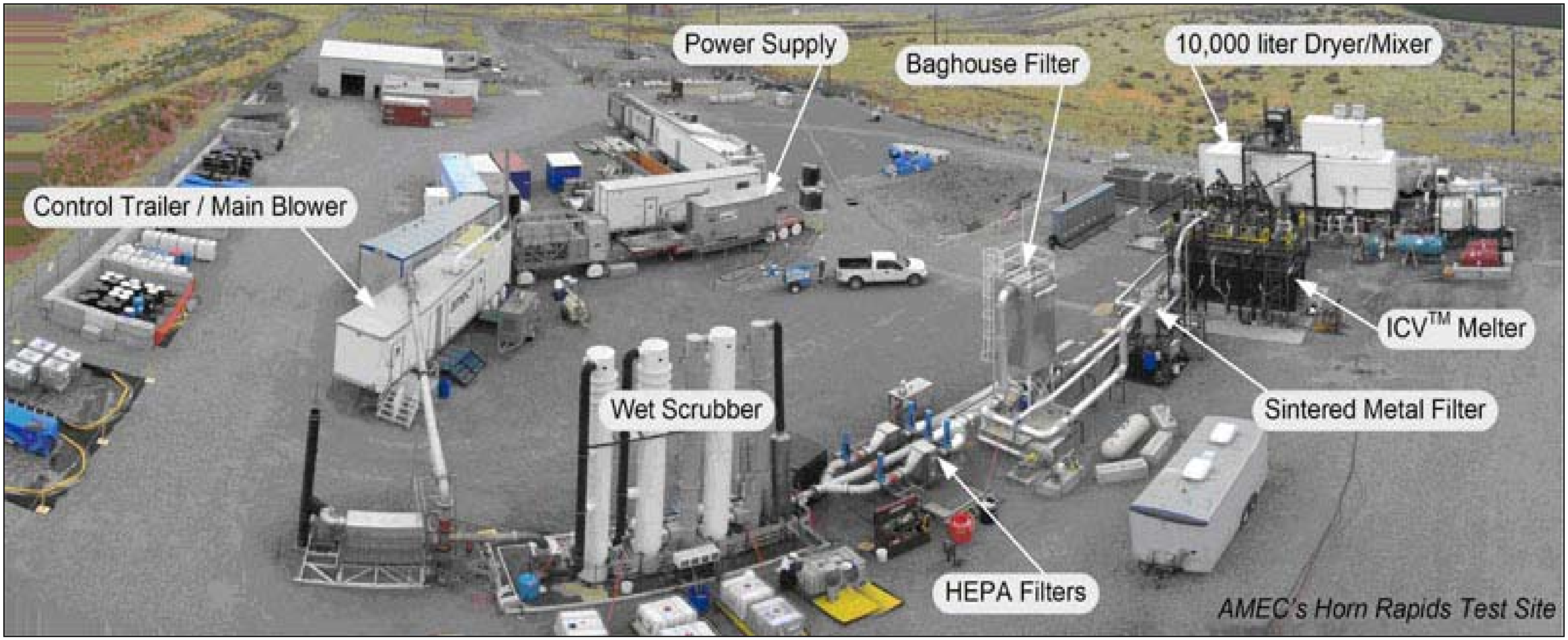

Fig. 3 GeoMelt® full-scale ICV™ equipment.

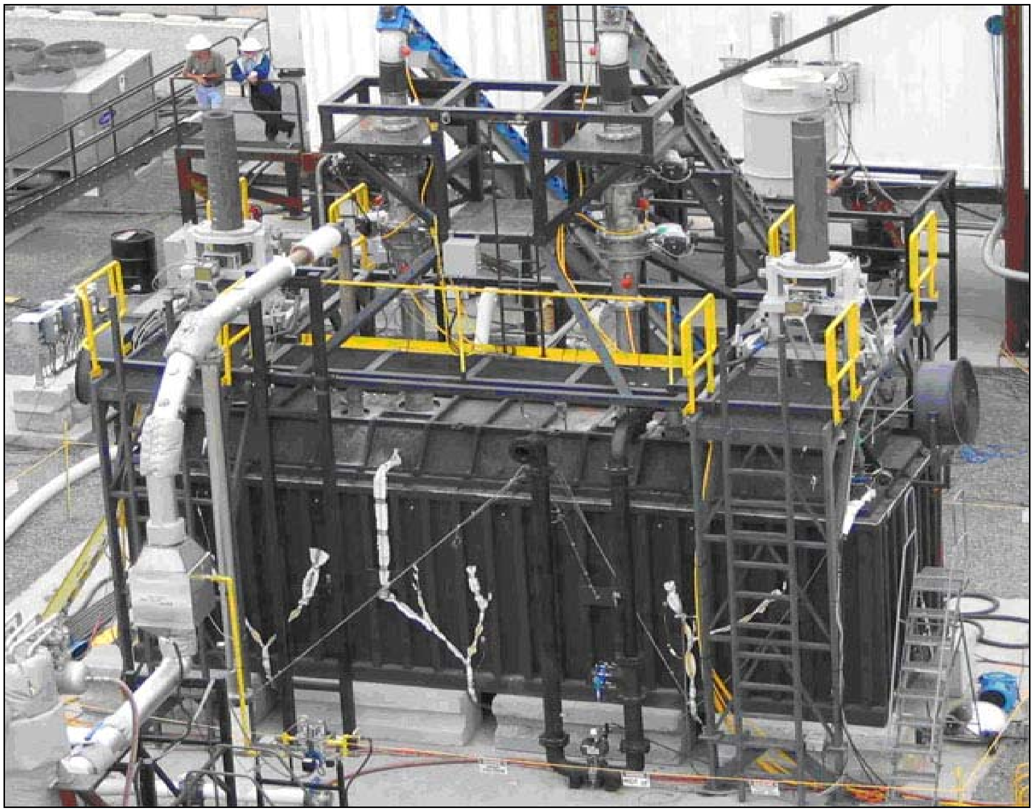

Fig. 4 GeoMelt® full-scale ICV™ melter.

Table 1 FS-38D objectives, success criteria, and status

Objective	Success Criteria	Status
1. Demonstrate integrated dryer and melt system operations.	Complete at least 20 feed discharge cycles from the 10,000-liter dryer to the ICV™.	**Objective Met**—30 feed discharge cycles completed.
2. Demonstrate resolution to the Molten Ionic Salt (MIS) issue.	Estimated Tc mass in CRB and sand does not exceed 3.7 % of total mass based on surrogate Re mass fed to melter. This will be demonstrated by the following: a) Initial field observations reveal no apparent clumped sand due to MIS. b) Initial field observations (confirmed by preliminary semi-quantitative sample analysis) show no MIS penetration beyond 50% of the depth into the CRB. c) Final Re analytical results are as defined in Appendix A.	a) **Objective Met**—No clumped sand observed. b) **Objective Met**—Scanning electron microscopy analyses showed that MIS penetration was <15% of wall thickness c) **Objective Met**—Estimated Tc mass in CRB and sand relative to total mass based on surrogate Re mass fed to melter = 0.03%
3. Demonstrate acceptable glass product.	Meet or exceed Waste Treatment Plant glass performance specifications [19] by: Vapor Hydration Test (VHT) (< 50 g/(m2 d) and Product Consistency Test (PCT) (< 2 g/m2)	Objective Met—Analyses results include: VHT—0.29 g/(m2 d) PCT—r_B = 0.166 g/m2 PCT—r_{Na} = 0.256 g/m2

Objective 1—Before the test, a feed discharge cycle was defined as 2.5% of the total planned feed. Twenty-five percent of the feed was produced during dryer tests conducted before melt operations. The plan was to produce the remaining 75% of the feed during melter operations, but an additional contingency batch that amounted to 12.5% of the total feed volume was available if dryer problems delayed the completion of the melt.

The dryer and melter were well integrated, and the dryer supplied the melter with all the feed necessary, including the 75% of the feed required during melter operations. Thirty feed cycles were completed: ten more than the minimum necessary to successfully meet the objective.

Objective 2—This objective involved demonstrating a resolution to the MIS issue. The quantitative measure was that the estimated Tc mass (based on results for the Re surrogate) was less than 3.7% of total mass added to the box. Qualitative measures of MIS penetration were also specified. Fig. 5 shows that, in contrast to the FS-38C refractory liner in Fig. 1, the FS-38D box had no clumped sand next to the CRB panels, indicating that the first qualitative measure was met.

Fig. 5 FS-38D refractory liner external skin after test completion.

The second qualitative (and subsequent semi-quantitative) measure specified that the MIS penetration depth into the CRB wall needed to be less than 50%. The MIS penetration depth was determined first visually, then through scanning electron microscope-energy dispersive spectroscopy analysis of the sodium levels in CRB wall cross sections. Fig. 6 shows that, in contrast to the FS-38C test, the sodium penetration was confined to a depth that was significantly less than 50% of the CRB wall thickness.

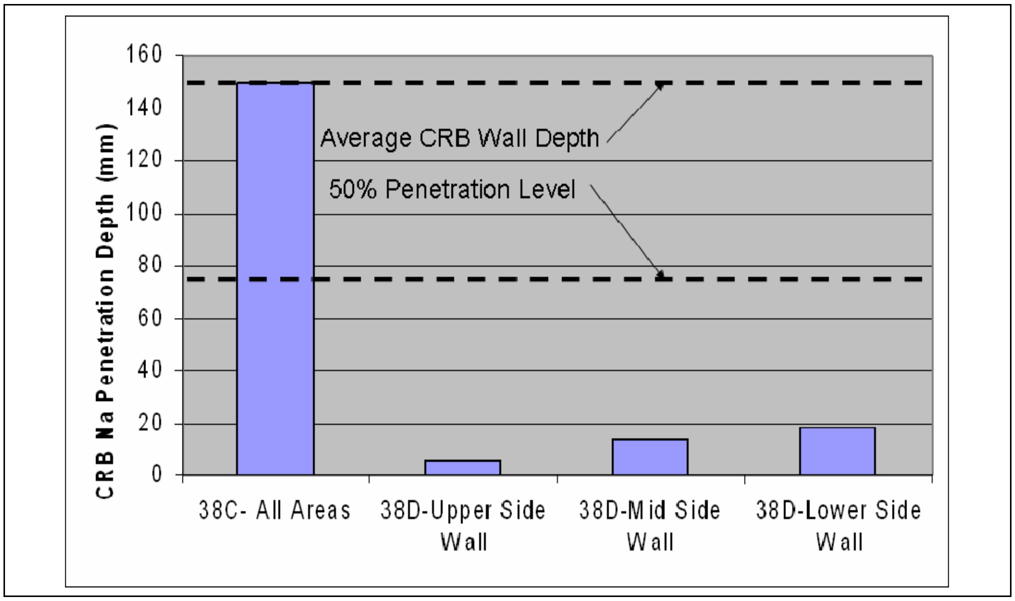

Fig. 6 Sodium penetration depths into the CRB.

The final measure for Objective 2 specified that the estimated Tc mass in the refractory liner had to be less than 3.7% of the total added to the ICV™ box. This estimate is determined by measuring the Re (Tc surrogate) concentration at 28 locations in the CRB and 5 locations in the refractory sand and extrapolating these values to calculate a total mass of Re in the CRB and sand layers. The total amount in these two layers is compared to the total amount of Re added to the box to generate a percent of total value. Estimated Tc levels are then determined by multiplying the Re levels by the Tc/Re mobility ratio (0.17) (determined from previous engineering-scale tests that were spiked with both Tc and Re [9].) Table 2 shows that the calculated amount of Re in the CRB and sand, of all 28 CRBs and all 5 sand locations, was very low, and the estimated total amount of Tc was over 120 times better than the 3.7% acceptance criterion.

Table 2. Calculated Re and estimated Tc quantities in the CRB.

Location	Calculated Re[a] (Wt% of total Re fed)	Estimated Tc (Wt% of total Tc fed)
CRB	0.12	0.02
Sand	0.04	0.01
Total	0.16	0.03

[a]No Re background level was applied to give a conservatively high calculated value. The Wt% of total feed is based on the formulated quantity of Re added to the ICV™ box.

Objective 3—The final objective was to verify that the changes made to the feed to address the MIS issue did not negatively affect the durability of the glass. The VHT results are more than 170 times better than the acceptance criterion, and the PCT results are almost eight times better than the acceptance criterion, demonstrating that objective 3 was easily met.

CONCLUSIONS

FS-38D successfully processed the total simulant feed volume and cover glass batch, and all of the primary objectives were met. The MIS phenomenon observed in previous testing was resolved; confirmed both visually and by analytical results that indicate estimated Tc levels in the refractory liner more than 120 times lower than the acceptance criteria. The glass durability was once again confirmed with the VHT and PCT results being 170 times and 8 times better than the acceptance criteria, respectively.

Although the addition of the full-scale dryer and subsystems made FS-38D the most complex of the Full Scale 38 Series tests to date, all equipment were operated safely and correctly, and modifications to the process were successfully demonstrated.

PATH FORWARD

FS-38D was successful, and the primary objectives were met; however, future testing should address a few specific areas for improvement, namely: 1) a full-scale dryer methodology should be developed that produces a more transportable feed product, and 2) the dry-waste transfer system and off-gas treatment system should be enhanced to allow for remote mechanical particulate cleaning during operations.

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