

**Non-Traditional In Situ Vitrification—
A Technology Demonstration at Los Alamos National Laboratory**

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ABSTRACT

The Department of Energy (DOE) Subsurface Contamination Focus Area (SCFA) sponsored a technology demonstration of non-traditional in situ vitrification (NTISV) at Los Alamos National Laboratory (LANL). The project team for this demonstration included MSE Technology Applications, Inc., Geosafe Corporation^a, and LANL.

The technology demonstration involved the performance of two large-scale test melts. The first, referred to as the “cold” test, was performed on a simulated absorption bed that contained surrogate contaminants. The cold test was conducted in April 1999. The second demonstration, referred to as the “hot” test, took place at LANL’s Material Disposal Area (MDA) V in April 2000. The hot test was conducted on a portion of an absorption bed that received radionuclide- and metal-contaminated wastewater from a laundry facility and a research laboratory from the mid-1940s to the early 1960s.

This paper presents the results of drilling and sampling following the hot test at LANL’s MDA V. The objectives of the sample collection were to characterize the vitrified mass and the effects of the hot test on the surrounding bedrock. Glass samples were analyzed for total radionuclide and metal content by standard EPA methods, and leachable radionuclide and metal content using Toxicity Characteristic Leaching Procedure (TCLP) and Product Consistency Test (PCT) methods. Based on the monitoring and analytical results, the following conclusions have been drawn:

- Borehole materials from three locations within the vitrified monolith indicate the total depth of the melt is 6 m (20 ft) below ground surface (bgs) and the thickness of the melt is approximately 3 m (10 ft); final electrode depths at the conclusion of the demonstration indicated an average melt depth of 8 m (26 ft) bgs at the electrode locations.
- Radioactive contaminants have been uniformly distributed throughout the melt at concentrations more than an order of magnitude lower than maximum pre-melt concentrations.
- Volatile contaminants have not been forced into surrounding rock as a result of the melting process.
- Data obtained from TCLP and PCT leach tests indicates that the resulting glass is durable and resistant to leaching.

INTRODUCTION

The DOE's SCFA sponsored an evaluation of NTISV technology as a potential remedy for treatment of radioactively contaminated absorption beds at LANL's MDA V. The NTISV technology chosen for the demonstration was the GeoMelt subsurface planar in situ vitrification (ISV) technology. This demonstration was done in conjunction with MSE Technology Applications, Inc.; Geosafe Corporation; and LANL. Funding for this project was provided through the DOE National Energy Technology Laboratory at the Western Environmental Technology Office under DOE Contract Number DE-AC22-96EW96405. LANL, as the host site, provided additional funding and site support for the demonstration.

Site History

TA-21 was used for plutonium research and metal production from 1945 to 1978. MDA V is a disposal area in TA-21 that consists of three cobble- and gravel-filled absorption beds constructed to dispose of wastewater. The absorption beds received effluent from a laundry facility from 1945 to 1961 and a waste treatment research laboratory from 1950 to 1953. The laundry facility was used to launder protective coveralls worn during research and production, and generated 23 million liters (6 million gallons) of radioactively contaminated wastewater annually. The absorption beds received nearly 379 million liters (100 million gallons) of effluent over the operating life of the laundry facility, and were observed to have overflowed as early as 1946. The absorption beds and the volcanic rock (Bandelier tuff) below them contain various radioactive and inorganic contaminants. The primary contaminants of concern are radionuclides, and include plutonium-239 and -238, americium-241, and uranium-234, -235, and -238.

In Situ Vitrification Process Description

In situ vitrification is a thermal treatment process that uses heat generated from electrical power to melt contaminated soil or rock to permanently destroy, remove, and/or immobilize contaminants. Melting is accomplished by passing electrical current between electrodes that have been inserted in the contaminated media. Temperatures up to 2000°C can be achieved during vitrification. The process promotes convective mixing of the molten material. Once electrical power is terminated, the molten mass cools and hardens into a vitreous monolith with physical, chemical, and weathering properties superior to the products produced by other solidification/stabilization technologies (1).

During the vitrification process, contaminants are treated in various ways. The high temperatures generated during the process destroy any organic contaminants present in the waste zone. Metals and radionuclides are uniformly distributed in the melt due to convective mixing, and are immobilized in the resulting product. Volatile constituents that are driven off during heating are collected under the off-gas hood covering the treatment area, and are drawn to an off-gas treatment system.

With conventional ISV technology, horizontally oriented melts originate at the surface and propagate in a downward and lateral progression through the treatment zone. Initiating the melting process at the surface limits the treatment depth, and makes the technology inefficient

for subsurface contamination because of the volume of uncontaminated material that needs to be melted before reaching the target depth for treatment. In addition, large horizontal melts can hinder the escape of gases generated beneath the melt, potentially resulting in the escape of gases through the melt and rapid expulsion of molten material.

In contrast, the GeoMelt subsurface planar ISV (or NTISV) process involves one or more vertically oriented planar melts established in the subsurface between pairs of electrodes. The planar melts can be initiated at the desired depth and separation within the subsurface, allowing for optimal treatment of the contaminated zone. If more than one pair of electrodes are used, they can be positioned so that individual planar melts coalesce as melting progresses. By the time the melts have grown sufficiently to merge and form a single melt, all volatile materials (primarily water) in the vicinity of the developing melts will have been safely removed from the treatment zone and captured by the off-gas recovery system.

Technology Demonstration Description

The NTISV project involved the performance of two large-scale demonstration melts. The first, referred to as the “cold” test, was performed in a simulated absorption bed that contained no radioactive contamination. The simulated absorption bed was designed and constructed to represent the actual MDA V absorption beds as closely as possible, including the use of similar construction materials (i.e., cobbles, gravel, and sand). The cold test also involved the use of surrogate chemicals for radionuclides of interest. The results of the cold test have been previously reported (2).

The second demonstration, referred to as the “hot” test, was performed within a portion of absorption bed 1 at MDA V (Fig. 1). Effluent from the laundry and research laboratory resulted in the contamination of MDA V, primarily by radionuclides. Samples from within the absorption bed indicated up to 2640 pCi/g of plutonium-239 (3). This paper focuses on the monitoring and analytical results obtained from the hot test.

The primary objective of both demonstrations was to gather performance data so that the NTISV technology could be evaluated for various applications at LANL and throughout the DOE Complex. Additional objectives of the NTISV technology demonstration include:

- demonstrate the ability to safely and successfully install planar starter paths significantly below grade within the Bandelier tuff formation,
- demonstrate the ability to homogenize and stabilize the contaminants or surrogate contaminants,
- confirm that the desired treatment volumes have been processed and that mobile contaminants have not been driven into the surrounding tuff,
- use process performance information from the cold test to optimize the processing configuration, operational parameters, and cost effectiveness of the hot test, and
- characterize the vitrified products by performing geochemical analyses to determine the degree of homogeneity, as well as product quality (TCLP & PCT) leach tests.

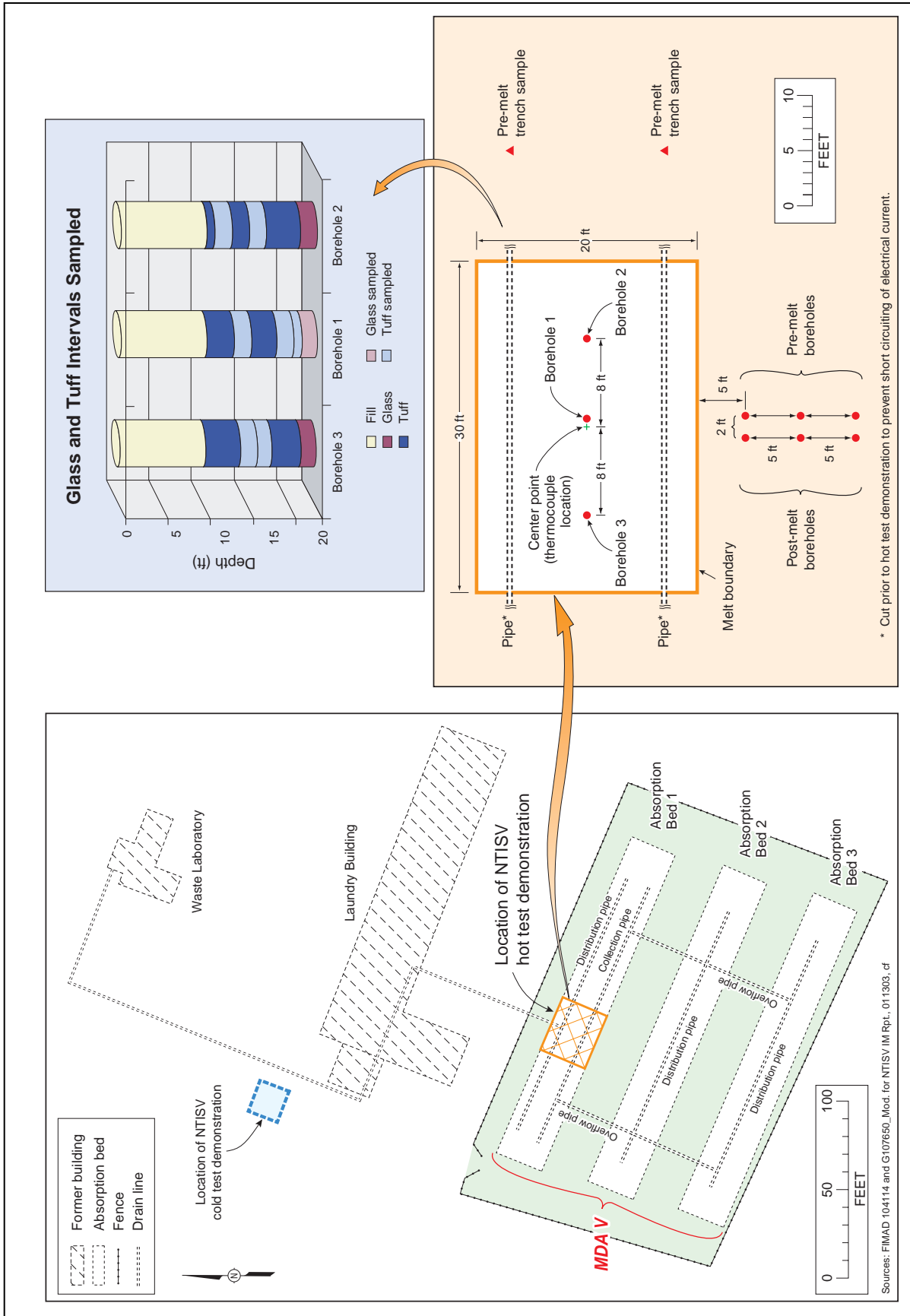


Figure 1. Layout of MDA V, locations of samples collected, and subsurface sample intervals

HOT DEMONSTRATION

The hot demonstration was conducted in the spring of 2000. Site preparation included cutting pipes in absorption bed 1 to prevent short-circuiting of the electrical current, adding a layer of clean fill to the site, and fracturing the native Bandelier tuff to prevent bridging above the subsidence crater during melting. Following site preparation, electrodes were placed in the subsurface and graphite-based starter-path material was injected to form two vertically oriented planes of starter material between each of two pairs of electrodes.

Power was turned on to the melt on April 4, 2000. No subsidence of the overburden was observed during the first several days of melting, indicating that the overburden had bridged rather than collapsing down into the melt. Power was turned off for 11 days to allow operations that would collapse the bridging. This was achieved by means of a vibratory hammer attachment on a backhoe. The power was then restarted, and the expected subsidence was observed. As overburden was slowly incorporated into the melt from above, additional overburden material (coarse gravel) was periodically added to maintain a good insulating cover over the melts. The melting was concluded on April 28, 2000. At that time, the dimensions of the melt were estimated to be 6 m by 9 m by 4.5 m deep (20 ft by 30 ft by 15 ft deep). This estimate was obtained using data from the electrode depths, subsidence volume, and seismic tomography. The top of the melt was estimated to be 2.4 m (8 ft) bgs (4).

MONITORING AND SAMPLING ACTIVITIES

Monitoring and sampling was conducted throughout the demonstration, both before and after the vitrification process, to fully characterize the NTISV technology. The following types of samples were collected (see Fig. 1):

- Prior to the hot test, trench samples were collected across absorption bed 1 at various depths to determine the types and concentrations of contaminants prior to treatment.
- Prior to the hot test, three boreholes were drilled and sampled adjacent to the targeted treatment area to characterize conditions in the surrounding tuff prior to vitrification.
- Following the hot test, three boreholes were drilled and sampled as close as possible to the pre-melt boreholes to evaluate potential contaminant migration during the melt process.
- Following the hot test, a borehole was drilled down to the top of the melt, in the approximate center, to install a thermocouple and monitor the cooling rate of the melt surface.
- Approximately two years after the hot test, three boreholes were drilled through the vitrified mass to collect a total of seven samples of the glass for complete characterization. Also at this time, one sample of tuff was collected from beneath the glass monolith to confirm that the desired treatment volume had been processed and that mobile contaminants had not been driven into the surrounding tuff.

Coring of the glass monolith took place during May and June of 2002. It took approximately 3 weeks to penetrate the glass in three locations and collect seven discrete samples. A hollow-stem auger rig with a diamond coring bit was used to collect the majority of the samples. The glass was extremely hard. Consequently, several diamond bits were destroyed during the drilling

effort. For two of the seven sample intervals, coring was very difficult and a tri-cone bit was used, yielding chip samples rather than core. Figure 2 shows a photograph of some glass core collected during June 2002.



Fig. 2. Glass core from the NTISV hot test demonstration at MDA V. Note transitional tuff/glass material collected from the top of the melt (approximately 3 m [10 ft] bgs) on the table.

Three boreholes were drilled in the footprint of the vitrified monolith. The boreholes were drilled along the long axis of the melt (approximately 9 m [30 ft] long). The first borehole was drilled near the center of the melt; the other two were located 2.4 m [8 ft] to either side of the center borehole. Each borehole was drilled from grade through the bottom surface of the vitrified monolith. Borehole logs generated during the drilling effort indicate that the top of the melt ranges in depth from 2.90 m to 3.35 m (9.5 ft to 11 ft) bgs; the bottom of the melt ranges in depth from 5.39 m to 6.49 m (17.7 to 21.3 ft bgs). Based on borehole log data and the four electrode depth measurements taken at the conclusion of the test (6.34, 7.92, 8.53, and 8.96 m [28.0, 20.8, 26.0, and 29.4 ft] bgs) (5), melt thickness is variable across the monolith footprint. It is typical for melt depth to be greatest near the electrodes; however, no boreholes were drilled in the immediate vicinity of the electrodes.

MONITORING AND ANALYTICAL RESULTS

Pre- and Post-Melt Tuff Sampling Results

Pre- and post-melt tuff samples were collected adjacent to the hot test demonstration area to evaluate potential contaminant migration during the melt process and assess the effectiveness of the melt in vitrifying the area of concern. Three pre-melt boreholes were drilled next to the targeted treatment area early in 2000. Following completion of the hot test, a post-melt borehole was drilled 0.6 m (2 ft) away from each pre-melt sampling location, for a total of three. Analytical results for samples collected from the same depth intervals in the pre-melt and post-melt boreholes were compared to determine if the vitrification process forced contaminants into

the tuff adjacent to the absorption beds. Most of the contaminants of concern at MDA V are not volatile, and would therefore not likely mobilize during the heating process. One exception is tritium, which would be closely associated with moisture in the absorption beds. Tritium levels in the absorption beds prior to vitrification ranged from 7 to 28 pCi/g. Pre- and post-melt data for tritium in tuff adjacent to the absorption bed are shown in Figure 3. These data do not indicate migration of tritium from the absorption bed materials into the adjacent tuff as a result of the vitrification process.

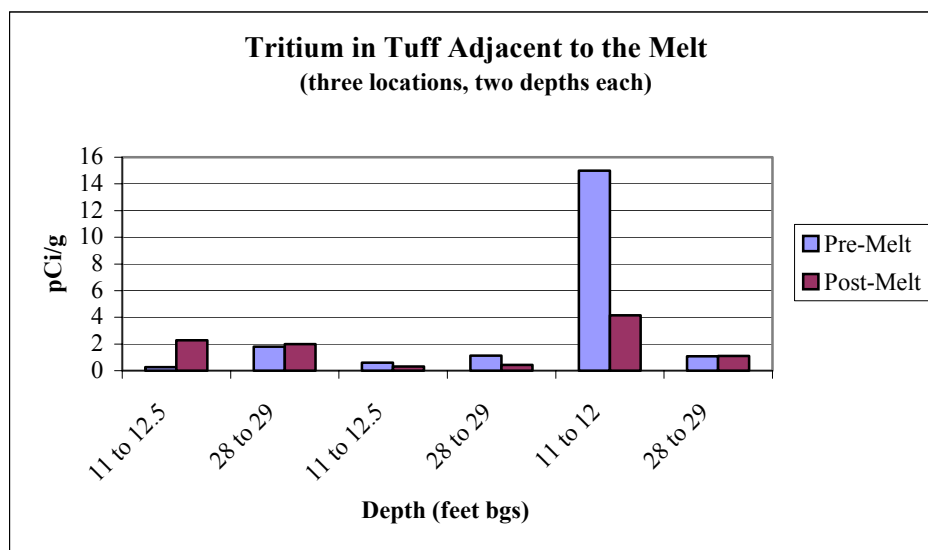


Fig. 3. Tritium results for pre- and post-melt tuff samples collected adjacent to the targeted treatment area.

In addition to the pre- and post-melt tuff samples collected adjacent to the demonstration area (described above), one sample was collected from the tuff beneath the melt (21 to 23 ft bgs) in June 2002. This sample had no detectable tritium. Mercury, a volatile metal that was found in the absorption bed at concentrations ranging from 0.2 to 8 mg/kg, likewise was not detected. These data further support the conclusion that contamination has not migrated into surrounding tuff as a result of the NTISV hot test demonstration.

Only four radionuclides were detected in the tuff sample from beneath the melt: plutonium-238, and uranium-234, -235, and -238. The isotopes of uranium are naturally occurring, and were detected at levels that have been defined as background for the upper unit of the Bandelier tuff (6). Plutonium-238 was detected at 0.0364 pCi/g, compared to a maximum of 17.2 pCi/g in the absorption bed materials prior to vitrification. With the exception of arsenic, metal concentrations measured in this sample are below the background 95% upper tolerance limit (UTL) defined for the upper unit of the Bandelier tuff (6). Arsenic is, however, less than the maximum value observed in background samples of the Bandelier tuff. The radionuclide and metal data for the sample collected beneath the tuff, along with published background UTL values for the Bandelier tuff, are presented in Table 1. Lack of significant contamination in this sample suggest that the hot test demonstration was successful in treating the vertical extent of contamination resulting from the absorption beds at MDA V.

Table I. Analytical Results for Tuff Underlying the Glass Monolith (21 to 23 ft bgs)

Inorganics (mg/kg)			
Analyte	Sample Detection Limit	Sample Result	Background Value (UTL)
Aluminum	4.90	88.7	7340
Antimony	0.370	ND	NC
Arsenic	0.490	3.21	2.79
Barium	0.490	ND	46
Beryllium	0.037	0.109	1.21
Cadmium	0.490	ND	1.63
Calcium	9.80	529	2200
Chromium	0.490	ND	7.14
Cobalt	0.490	ND	NC
Copper	0.490	0.51 (J)	4.66
Iron	4.90	540 (J)	14,500
Lead	0.490	ND	11.2
Magnesium	2.00	34.7	1690
Manganese	0.980	86.9	482
Mercury	0.0099	ND	NC
Nickel	0.370	0.393	6.58
Potassium	9.80	49.1	3500
Selenium	0.490	ND	NC
Silver	0.180	1 (J)	NC
Sodium	9.80	87.1	2770
Thallium	0.092	ND	1.10
Vanadium	0.490	ND	17.0
Zinc	0.490	8.49	63.5
Radionuclides (pCi/g)			
Analyte	Minimum Detectable Activity	Sample Result	Background Value (UTL)
Americium-241	0.062	ND	NA
Cesium-134	0.042	ND	NA
Cesium-137	0.046	ND	NA
Cobalt-60	0.05	ND	NA
Europium-152	0.12	ND	NA
Plutonium-238	0.013	0.0364	NA
Plutonium-239	0.021	ND	NA
Ruthenium-106	0.45	ND	NA
Sodium-22	0.062	ND	NA
Strontium-90	0.3	ND	NA
Tritium	2.3	ND	NA
Uranium-234	0.086	1.29	1.98
Uranium-235	0.054	0.0571	0.09
Uranium-238	0.053	0.87	1.93

ND = analyte not detected
 (J) = sample result is estimated
 NC = background not calculated
 NA = radionuclide is not naturally occurring

Temperature Monitoring of the Melt Surface

Following vitrification at MDA V, a thermocouple was installed in a borehole drilled to the surface of the melt in the approximate center of the melt footprint. Surface temperatures were measured and recorded monthly for two years to determine cooling rates and predict when successful coring of the melt body could be conducted. Due to the insulating properties of the surrounding Bandelier tuff, the melt took two years to return to near-ambient temperatures. Figure 4 shows the measured cooling curve for the top surface of the vitrified mass (approximately 3 m [10 ft] bgs). These data were in turn used as input in a heat diffusion model to predict when ambient temperatures would be reached within the vitrified mass. Results of the heat diffusion modeling indicated that the internal temperature of the glass monolith would reach 40°C during the summer of 2002. Temperatures measured within the boreholes during drilling activities in June 2002 showed very good agreement with the modeling results.

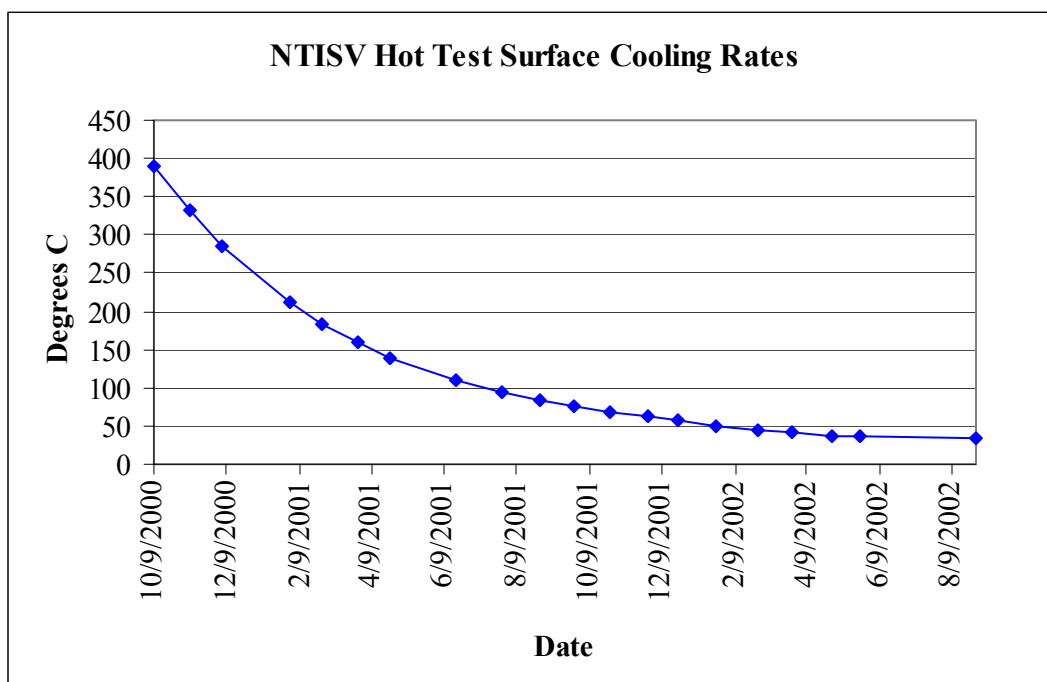


Fig. 4. Cooling curve for the surface of the glass monolith at MDA

Glass Sampling Results

Samples of glass were collected from seven different depth intervals distributed throughout the melt in three separate boreholes during May and June 2002 (see Fig. 1). All seven of these samples were submitted for analysis of metals and radionuclides by standard EPA methods, TCLP metals, and PCT. The PCT is an ASTM method used to evaluate the chemical durability of radioactive waste glass (7).

Comparison of the distribution of contaminants within the absorption beds prior to treatment and the glass samples following treatment show that contaminants have been homogenized within the melt due to convective mixing developed during the vitrification process. In particular,

concentrations of radionuclides show a remarkable uniformity within the glass. Figure 5 shows the range of contaminant values in the treatment area before and after vitrification for the most prevalent radionuclides. The range of concentrations observed in the post-melt samples is much narrower than that of the pre-melt absorption bed samples. In addition, the maximum concentrations of radionuclides measured in the post-melt samples are roughly an order of magnitude less than those measured in the pre-melt samples.

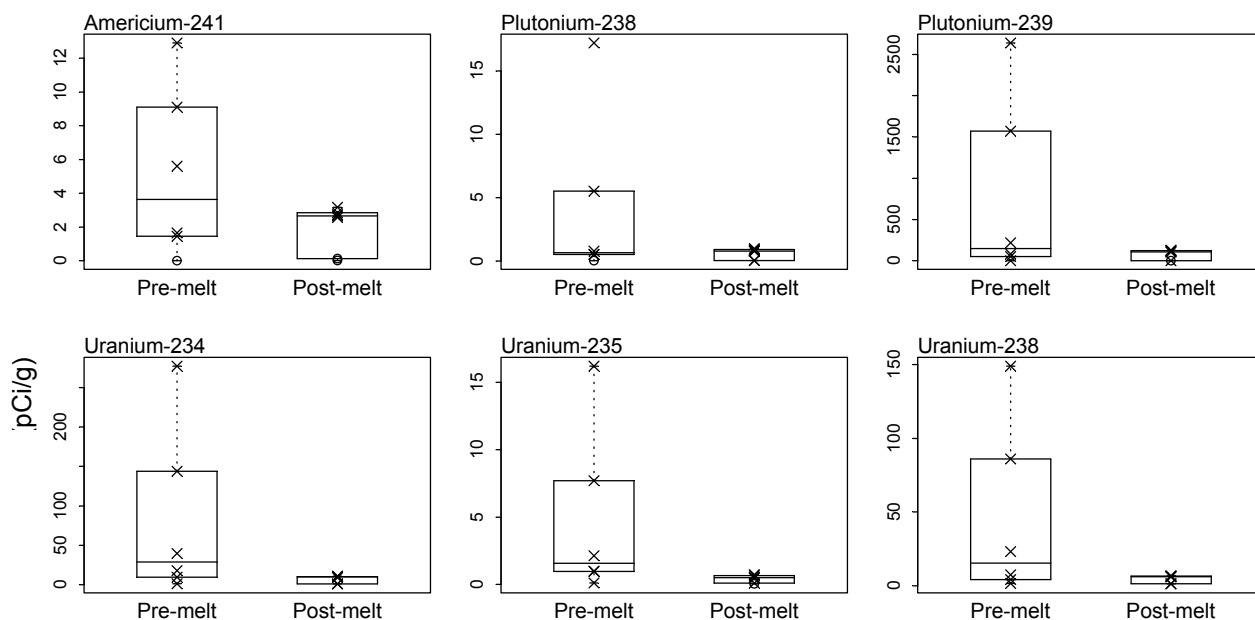


Fig. 5. Box and whisker plots showing the comparison of radionuclides in absorption bed materials (pre-melt) and in glass following vitrification (post-melt). The box area of the plot is the region between the 25th percentile and the 75th percentile of the data. The horizontal line within the box represents the median (50th percentile) of the data. Individual detections are represented by Xs and non-detected data, reported as the detection limit, are represented by Os.

TCLP data were evaluated to determine the potential for metals to leach from the glass. Of the eight TCLP metals evaluated (As, Ba, Cd, Cr, Pb, Hg, Se, and Ag), only barium was consistently detected in the TCLP leachate. The barium concentration in the leachate ranged from 22 to 45 ppb, roughly three orders of magnitude below the EPA's Uniform Treatment Standard (UTS) of 21,000 ppb for this analyte. In two samples, low levels of chromium were detected. These two samples coincide with the depth intervals that were drilled with a tri-cone bit. The chromium detects (55 and 67 ppb) are thought to be an artifact of the drilling method. These values are an order of magnitude below the UTS of 600 ppb for chromium.

Of the eight TCLP metals, only chromium and silver were present in the glass at concentrations that would have the potential to exceed their UTS, applying the "rule of 20." However, the concentration of these analytes in the leachate was non-detect for silver (which corresponds to a level four orders of magnitude below the UTS), and one order of magnitude below the UTS limit

for chromium. These results are consistent with all previous TCLP studies of the GeoMelt vitrified materials, demonstrating that the product is durable and resistant to leaching.

All seven samples collected from within the glass were subjected to the PCT procedure. Each sample was analyzed in triplicate (i.e., three splits of each of the seven samples were leached and analyzed). Concentrations of the major radioactive elements of concern (e.g., americium, plutonium, and uranium-234, -235, and 238) were generally below the detection limits in the PCT leachate. Uranium-234 and -238 were detected at low concentrations in three of the seven samples. However, none of the detects were reproduced in the corresponding duplicate or triplicate samples. Of those samples with detectable levels of uranium-234 and -238, the concentration found in the PCT leachate was two to three orders of magnitude lower than the concentration present in the vitrified product.

CONCLUSIONS

Based on the monitoring and analytical results we have to date, the following conclusions have been drawn:

- Borehole materials from three locations within the vitrified monolith indicate the total depth of the melt is 6 m (20 ft) bgs and the thickness of the melt is approximately 3 m (10 ft); final electrode depths at the conclusion of the demonstration indicated an average melt depth of 8 m (26 ft) bgs at the electrode locations.
- Radioactive contaminants have been uniformly distributed throughout the melt at concentrations more than an order of magnitude lower than maximum pre-melt concentrations.
- Volatile contaminants have not been forced into the surrounding rock as a result of the melting process.
- The resulting glass is durable and resistant to leaching. TCLP results indicate concentrations of the key heavy metals in the leachate are typically several orders of magnitude below the EPA UTS values. The PCT data indicate similar results. Concentrations of the radioactive elements present in the PCT leachate were typically below detection limits. Only uranium-234 and uranium-238 were detected at low concentrations in a few of the samples analyzed, and the data were not reproducible in the corresponding duplicate and triplicate samples.

FOOTNOTES

^aAMEC Earth & Environmental, Inc. now holds the exclusive, worldwide rights to the GeoMelt technology.

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