



## **OVERVIEW OF GEOMELT PROCESSING OF SPENT FUEL COMPONENTS AND SLUDGES**

The GeoMelt® technology has been demonstrated on several occasions to be an effective approach for treating spent fuel components, sludges and other processing wastes. Due to convective flow patterns that are established within the melt uranium, plutonium and most fission products are oxidized and effectively mixed homogeneously throughout the melt. Cladding components are also oxidized and incorporated into the glass waste form. Appendix A presents a discussion of GeoMelt waste form homogeneity and criticality concerns when treating actinides. Below are examples of projects focusing on spent fuel and sludge treatment applications.

### **GEOMELT® ICV DEMONSTRATION FOR HANFORD 'K' BASIN SLUDGE**

GeoMelt® ICV™ process was successfully demonstrated for the U.S. Department of Energy for application to the treatment of Hanford's K-Basin sludge through a series of laboratory and full-scale tests of both radioactive and non-radioactive simulants.

Laboratory crucible melts of non-radioactive K Basin Sludge Simulant, containing misch metal as a uranium surrogate, provided initial information used in the design of a non-radioactive engineering-scale Bulk Vitrification demonstration, completed November 20, 2003. This testing with K Basin sludge clearly demonstrated that U is fully oxidized during melting. Radioactive samples were analyzed using a series of tests (Ignitability, Corrosivity, Pyrophoricity, and Spontaneous Combustion) to determine if vitrified K Basin sludge would be acceptable for disposal at the Waste Isolation Pilot Plant (WIPP). The results of this testing indicated full satisfaction of WIPP disposal requirements.

At the time of this earlier testing, the chosen disposition path for disposal of a vitrified K Basin sludge was as contact handled (CH) TRU. Preliminary dose calculations based on several geometries suitable for Standard Waste Box (SWB) containment and varying waste loadings (ranging from 22 to 40 weight %) provided the basis for the engineering-scale test which was performed within the scope of the Bulk Vitrification project. The dose rate calculations performed indicated the surface dose rate would be less than the WIPP CH waste acceptance criteria of 200-mrem/hr for a SWB containing up to 18.5-kgs of vitrified K Basin sludge in ~46-kgs of glass.

The ICV demonstration was completed using approximately 17 kg of K Basin Sludge Simulant, at approximately 39 weight % waste loading (quantities driven by the goal of producing a contact handled package). Processing was achieved without difficulty and without special modification of existing equipment. Figure depicts the vitrification of sludge simulant used during testing. The demonstration was completed in approximately 15 hours, and resulted in a cylindrical vitrified monolith approximately 12 inches in diameter, and 7.5 inches in height. These dimensions match one target geometry specified by dose calculations, and indicate that ICV of actual K Basin sludge can yield waste packages suitable for WIPP disposal as contact-handled transuranic waste. Samples from the test were analyzed with a series of tests (Ignitability, Corrosivity, Pyrophoricity, and Spontaneous Combustion) to determine if vitrified K Basin sludge would be acceptable for disposal at the Waste Isolation Pilot Plant (WIPP). The results of this testing indicated acceptable satisfaction of WIPP disposal requirements.

IMPACT has been selected to perform additional testing for the DOE for treating the K-Basin sludge. This work is currently on-going.



**Figure 1 - Processing of K Basin Sludge Simulant**

## SELLAFIELD THERMAL TREATMENT DEVELOPMENT

Treatment of UK Sellafield Nuclear waste simulant, using the GeoMelt vitrification technology, was performed at the GeoMelt Horn Rapids Test Site in Richland during the first half of 2009.

GeoMelt demonstrated its vitrification technology in response to a request from the Sellafield Limited (SL) Thermal Treatment Development Programme. SL is attempting to gain confidence in the potential of GeoMelt ICV to treat a range of waste forms, and provide a potential alternative approach to the SL baseline techniques, such as grout encapsulation.

Two separate tests were chosen for demonstration, and each was performed in a climate controlled facility at the HRTS. The tests were performed using a small scale (200-litre) GeoMelt ICV melter. This treatment system typically consists of four main subcomponents; a melt power supply transformer, the melt container and hood assembly, the off-gas treatment system (OGTS), and the supervisory control and data acquisition (SCADA) system. For this trial, an additional simulant feed assembly, to provide delivery of the liquid simulant and dry frit during the melt process, was included. Figure 2 shows some of the testing equipment as assembled inside the small scale testing facility at Impacts Horn Rapids Test Site (HRTS).



**Figure 2 - 200-liter GeoMelt® Vitrification Equipment inside the Horn Rapids Test Site**

Testing incorporated ASME NQA-1 controls via a project-specific quality assurance plan (PQAP) and Health and Safety controls were administered using a site-specific Health and Safety Plan (HASP).

Each test was designed to treat two unique SL simulated waste streams, addressing a total of four SL waste streams. Test 1 demonstrated the successful treatment of plutonium contaminated materials (PCM) and SIXEP Magnox sludge simulants, using the GeoMelt process to treat wastes staged and treated bottom up followed by feed while melting processing of feed materials. For Test 2, simulated waste streams of ion exchange media and pile fuel cladding silo waste were treated using a traditional top-down GeoMelt approach. The five Trial-specific process objectives listed in the Specification were completed, namely:

- Ensure radioactive (surrogates) and chemo toxic elements are immobilized and hazardous materials are pacified.
- Minimize non-active additives.
- Maximize volume reduction.
- Minimize secondary wastes that require other processing.
- Meet the RWMD product compliance requirements.

Follow-on testing with the GeoMelt system, in the United Kingdom, at a permitted radioactive facility is currently in the planning stage.

### **Sellafield Thermal Treatment – GeoMelt Phase Two Demonstration**

In response to a request by Sellafield, Ltd (SL) in June of 2011, Kurion demonstrated its GeoMelt® ICV™ Vitrification Technology towards treating high metal wastes. SL has the requirement to support

the proposition of directly converting a container (skip/box/drum) of raw solid ILW into an immobilised waste form such that the waste form is suitable for interim storage at Sellafield and subsequent disposal at the Geological Disposal Facility (GDF). Potential SL feed streams for a future treatment facility include sludges, ion-exchange media, sand, Plutonium Contaminated Material (PCM), concrete, uranium, fuel cladding, soils, metals, and decommissioning wastes. Key strategic objectives for this work scope included passivation and stabilisation of the raw waste, immobilisation of radiological and chemo toxic species in the raw waste, and production of an inert and durable product

The goal of testing was to replicate and treat the high metal wastes arising from solid ILW material. A simulant containing 23wt% stainless steel, 26% carbon steel, 9% aluminium, 5% magnesium, 28% cerium/lanthanum mix, and 9% grout/organics was used. Glass forming minerals and non-radioactive surrogates were also included in the simulant to mimic species of interest, including Pu, Cs, Tc, Sr, and Ru. The GeoMelt system located at AMEC's Birchwood facility was used for this demonstration. A 500 litre stainless steel ICV vessel with an inner refractory liner contained the waste surrogates and process off-gas containment was provided by an integrated offgas treatment system. A photo of the ICV vessel is shown in Figure 3.

Testing was performed on June 3, 2011 and was successfully completed in approximately 16 hours. Other than two brief periods when the treatment rate was heightened, processing occurred a relatively steady pace. Although a high concentration and variety of metals and organics were processed, the materials were processed completely, producing a stable two-phase glass/metal product. The 95 litres of staged material was reduced to about 41 litres, providing a 57% overall feed to glass/metal volume reduction, with a final mass of 138 kg. A photo of the resulting two phase product is shown in Figure 4.

Analytical results demonstrate that the glass was homogeneous and had excellent leach characteristics, as demonstrated via PCT testing, performing well below US DOE glass leach limits, and was shown to be on par with other GeoMelt glass results. Of the mass of material recovered, 89.4% to 100% of the tracer metals were retained within the ICV product.

Strontium, caesium, and europium were primarily retained in the glass, while ruthenium and rhenium were primarily retained in the metal phase. Based on the completion of the key strategic objectives and other secondary considerations, the test results confirmed the ability of the GeoMelt process to treat one of the more diverse and problematic waste streams currently stored at the Sellafield Site.



**Figure 3 - GeoMelt Demonstration System ICV Vessel**



**Figure 4 - Two phase glass/metal product**

## ROCKY FLATS

The Rocky Flats Environmental Technology Site is a DOE environmental cleanup site located near Denver, Colorado. Historically, components for nuclear weapons were produced at Rocky Flats, using various radioactive and hazardous materials, including Pu, U, and Be. Nearly 40 yr of nuclear weapons production left a legacy of contaminated facilities, soils, and ground water. As part of DOE's cleanup of Rocky Flats, ~30 tons of depleted uranium, soil, and other wastes were removed from a disposal area known as Trench 1. A significant amount of this waste was characterized as a mixture of radioactive waste and PCBs, other VOCs, and metals. Because no disposal facility accepts this type of mixed waste, alternatives for treating the waste before disposal are being evaluated. The ICV process was chosen to demonstrate the treatment and stabilization of Trench 1 mixed waste.

About 21,500 lb of waste (~65% soil, 30% depleted uranium chips and turnings, and 5% steel drum fragments) were treated. The waste was shipped in six B-12 containers to the Waste Control Specialists, LLC, facility near Andrews, Texas. All the containers held LLW, and several of them had levels of PCBs, cadmium, and other VOCs that exceeded land disposal requirements.



The Rocky Flats mixed waste was vitrified in two melts. Each melt was completed in ~3 days with no operational difficulties. The tests resulted in monolithic blocks ~80 ft<sup>3</sup> in size, indicating that the waste volume was reduced more than 50% during treatment. The vitrified product was removed from the container after each melt for sampling and packaging for land disposal. Figure 5 shows one of the vitrified waste forms being removed from the box and sand liner. Refractory and insulation materials were recycled between melts, thus minimizing the generation of secondary waste.

Table 1 summarizes analytical results of the vitrified product from the Rocky Flats demonstration. The table shows reduced radionuclide concentrations in the vitrified product, which is a result of the homogenous form of the vitrified product. The previtrified waste was not homogenous. The analytical results indicate destruction of PCBs, trichloroethylene (TCE), and tetrachloroethylene (PCE). No detectable concentrations of organic contaminants were found in the resulting glass, including PCBs or VOCs. Cadmium, from container X09800, was treated in Melt 1. The analytical results indicate that leachable concentrations of cadmium were reduced by a factor of 70.

<b>Table 1. Analytical Results from ICV Treatment of Rocky Flats Trench 1 Waste</b>									
	<b>Melt 1 Waste Inventory</b>			<b>Melt 1 Vitrified Product</b>	<b>Melt 2 Waste Inventory</b>			<b>Melt 2 Vitrified Product</b>	<b>Regulatory Limits</b>
	<b>X09800</b>	<b>X09824</b>	<b>X09826</b>		<b>X09804</b>	<b>X09809</b>	<b>X09810</b>		
<b>Radionuclides, pCi/g</b>									
Uranium-238	96,200	199,000	199,000	19,180	1,830	42,300	133,000	59,000	330,000*
Uranium-235	1,590	2,010	2,210	216	33.6	766	2,050	371	1,900*
<b>PCBs, mg/kg</b>									
Aroclor® 1254	5.8	NA	NA	NA	1.3	10	130	ND	10**
<b>VOCs, mg/kg</b>									
TCE	ND	400	ND	ND					
PCE	0.46	3,000	0.059	ND	0.88	0.22	0.31	ND	6.0**
<b>TCLP Metals, mg/L</b>									
Cadmium	26.74	NA	ND	0.398 <sup>^</sup>					0.11**
*Maximum allowable average radionuclide concentrations from Envirocare of Utah, License UT 2300249, amendment 13. **Universal Treatment Standards: U.S. EPA Land Disposal Restrictions, 40 CFR 268.48. <sup>^</sup> Preliminary result. NA – not analyzed; ND – not detected above laboratory reporting limits; Aroclor® is a registered trademark of the Monsanto Company.									



**Figure 5 - Removing vitrified product from the ICV™ Container. The exterior of the vitrified product is composed of high-temperature siliceous liner material that anneals to the block during melting. The block retains the symmetry of the container.**

## GEOMELT PLANAR-ISV REMEDIATION OF BURIED DRUMS CONTAINING DEPLETED URANIUM CHIPS AND OIL WASTES

A test was performed on August 30, 1999 to demonstrate the efficacy of using the GeoMelt® Planar-ISV™ process to remediate the drummed depleted uranium (DU) chips and oil wastes present at the Hanford 618-4 Burial Ground. This is waste containing radioactive, RCRA, and TSCA contaminants. A 1-gal canister containing approximately 1.4 liters of oil and 0.9-kg of DU chips was processed in this test. This, together with the geometry of the target treatment zone, resulted in a 3.2-wt% DU waste loading for this test. Figure 6 shows the test setup used for this demonstration.

The soil/waste matrix was processed without complication in just under 8 hours of operation. A 128-kg vitrified monolith was generated. The test consumed approximately 96-kWh electrical energy to produce this block. Therefore, the specific energy consumption for this test was 0.75-kWh/kg. This is considerably lower than the nominal 1-kWh/kg required in conventional, top-down ISV applications, despite the significant quantity of volatile, liquid materials processed in this test. This lower specific



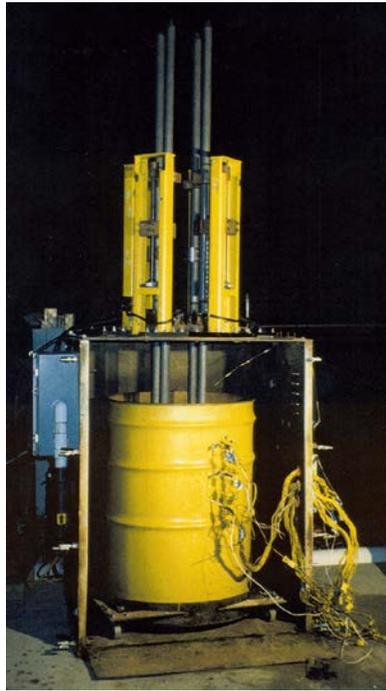
energy consumption is a direct result of the thermal efficiencies afforded by the subsurface, Planar-ISV approach to processing.

Off-gas samples taken during the course of the test indicated low concentrations of volatile materials present in the flow. These samples were taken upstream of the thermal oxidizer employed for this test. The temperature and residence times set for the thermal oxidizer insured that these low concentrations were effectively destroyed in the process.

Airborne radiological samples obtained during the test, as well as radiological surveys performed after the test, indicated that the radioactive material was essentially completely contained within the treatment zone. Direct surveys of the ISV equipment and piping indicated no detectable levels of radiation above background on any surface. Moreover, the InsulWool blanket placed over the treatment zone, as well as the HEPA filter media used in the test, also indicated only background radiation levels.

Samples of the vitrified product were subjected to the Toxicity Characteristic Leaching Procedure (TCLP) to assess its quality and durability as a waste form. The leachate generated from this test was analyzed to determine the concentration of RCRA metals contained therein. The results indicated that, with the exception of barium, the concentrations of all analytes were below the detection limit for that element (i.e. – in the 0.1 to 50 parts per billion range). These results included hazardous elements such as arsenic, cadmium, chromium, lead, and mercury. The most stringent EPA Universal Treatment Standard (UTS) limits for these elements ranged from 18× to 250× higher than the detection limits listed. The barium concentration present in the leachate was also very low – less than ¼ the allowable level for the most stringent EPA UTS for this element. Finally, the TCLP results indicated that the PCB concentrations in the glass were at or below the detection limit of 61-ppb. These results indicate that the PCBs present in the oil were effectively remediated by the Planar-ISV process.

All of the objectives set for this treatability test were met. The test clearly demonstrated that oil and potentially pyrophoric uranium wastes could be readily processed using the GeoMelt Planar-ISV process. In addition, the vitrified product generated readily met the standards for transfer of the waste form to the ERDF. Finally, the data and experience gained from this investigation will prove useful for evaluation and remedial design of large-scale applications of the Planar-ISV at the Hanford 618-4 Burial Ground. Moreover, this information will be useful for evaluations of using this process throughout the DOE Weapons Complex to remediate similar waste sites.



**Figure 6 - Geosafe Engineering-Scale ISV System Test Container and Electrode Feeder Assemblies**



## APPENDIX A

### GeoMelt Homogeneity and Criticality

# Evaluation of Homogeneity in GeoMelt Glass

## Homogeneity of GeoMelt® Vitrified Product

The GeoMelt waste treatment and immobilization process is a well-established, commercially proven vitrification technology that is performed on in-situ wastes associated with contaminated land and on ex-situ wastes using refractory-lined containers. This process is used for radioactive and hazardous wastes. One notable feature of the GeoMelt technology is the homogenization effect of convective currents within the molten material undergoing vitrification.

This paper provides two project specific examples of homogeneity of the GeoMelt vitrified wasteform and explains the mode of homogenization using computer modeling results.

### Case 1: Plutonium Plate Test

In 1995 a pilot-scale GeoMelt demonstration involving plutonium and uranium was completed at the Taranaki area of the Maralinga Nuclear Test Range, South Australia. This work was performed for the Australian Commonwealth Department of Primary Industries and Energy as part of a feasibility study which led to the selection and application of the GeoMelt technology for the treatment of 13 large plutonium-contaminated debris pits. This work was completed in 1999.

The plutonium plate test was configured in a manner to represent the actual plutonium-contaminated debris pits found at Taranaki. This demonstration involved the melting of a point source of plutonium and uranium oxides and was carried out to demonstrate the homogenizing effects of the GeoMelt process.

To simulate a highly localized source of contaminated material, 2.27 kg (5 lb) of sand was mixed with 1,048.9 g of uranium oxide. This mixture was placed in a plastic bag and positioned in the center of the test pit directly adjacent to a small steel plate containing 0.44 g of plutonium, as characterized by the Australian Radiation Laboratory (ARL). This plate was debris from historic plutonium dispersion testing.

Following melt operations, the resulting monolith was core drilled and excavated. Figure 1 shows a piece of the vitreous and crystalline material from the block. A total of 25 product samples were obtained from the monolith in order to evaluate the geochemical effect of convective mixing (Figure 2).

Radiochemistry and gamma-ray spectroscopy of vitrified product samples indicated an even distribution of activity of  $^{238}\text{U}$ ,  $^{239/240}\text{Pu}$ , and  $^{241}\text{Am}$  throughout the monolith,

demonstrating the homogenization effects of the GeoMelt process (Figure 3).



Figure 1. Vitrified product from the Maralinga Phase 2 Plutonium Plate Test

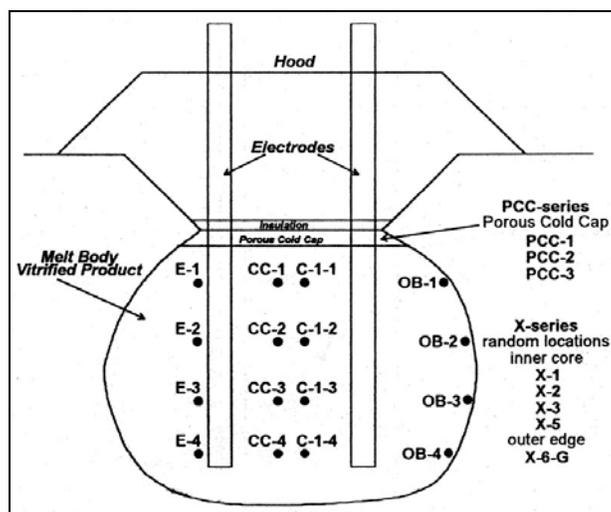


Figure 2. Maralinga Phase 2 Plutonium Plate Test Glass Sample Locations

The radiochemical and spectrographic analysis of the glass monolith and the top cold cap layer which forms as gasses vent to the surface to be captured by the GeoMelt off-gas treatment system demonstrate the homogeneity of the glass. These results also demonstrate the homogenization effect of the GeoMelt process. What was once a point source of concentrated plutonium and uranium ended up evenly distributed throughout the glass monolith by the GeoMelt process.

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# Evaluation of Homogeneity in GeoMelt Glass

Figure 4 visually displays the radionuclide homogenization typical of GeoMelt vitrified waste forms. The photograph is an alpha-track etch image showing alpha particle impact points (light color) illustrating the relatively uniform concentration of alpha activity (from Pu-239 decay) of a sample obtained from the plutonium plate test glass core.

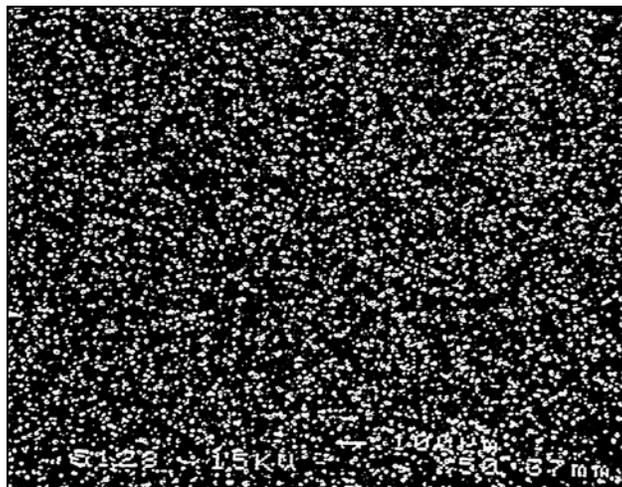


Figure 4. Alpha Track Etch Image of the Maralinga Phase 2 Plutonium Plate Test Glass

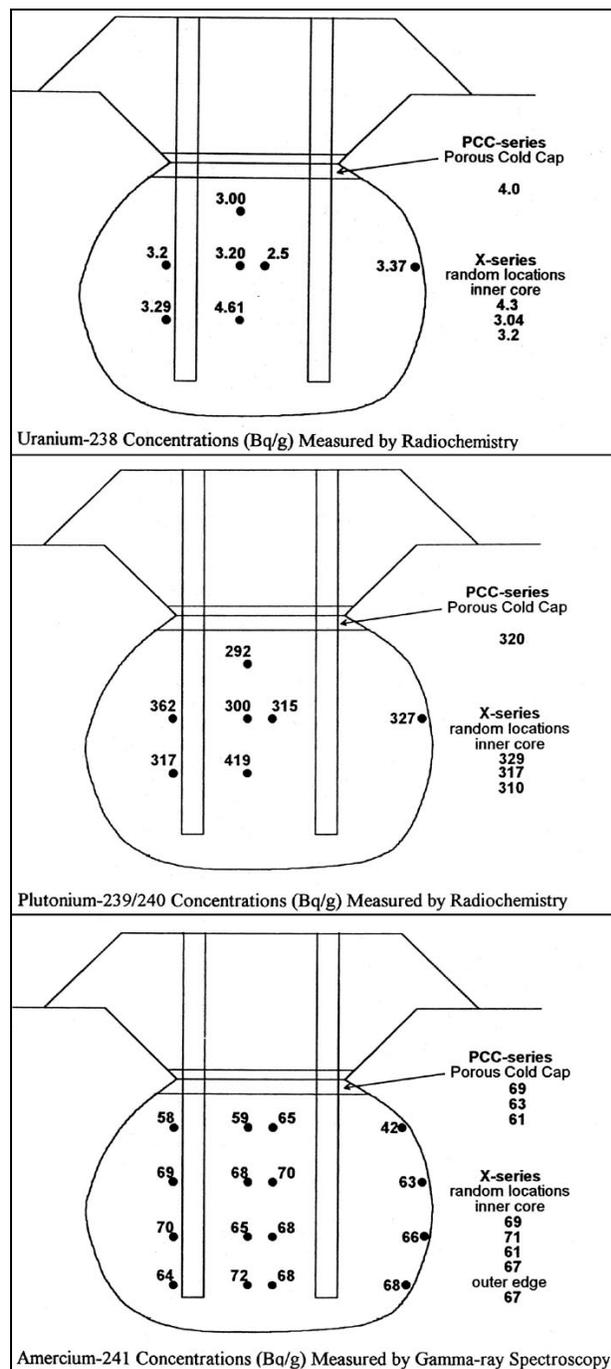


Figure 3.  $^{238}\text{U}$ ,  $^{239/240}\text{Pu}$ , and  $^{241}\text{Am}$  concentrations in the Maralinga Phase 2 Plutonium Plate Test Monolith

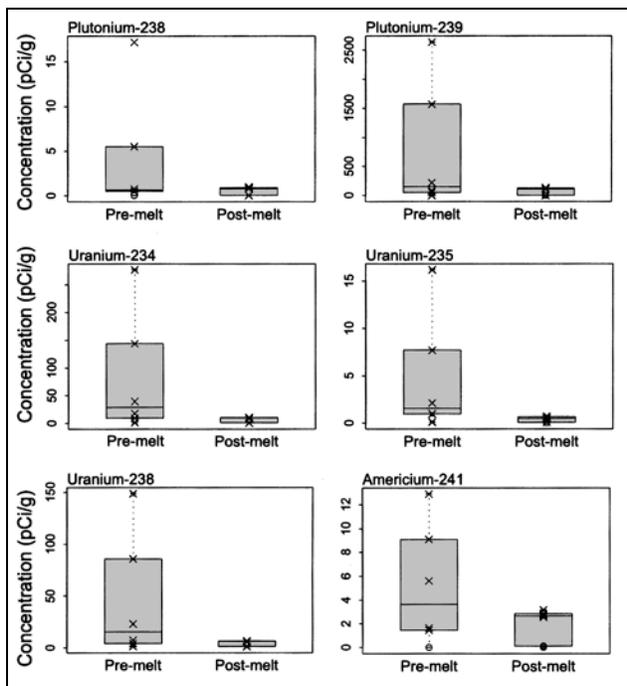
## Case 2: Los Alamos National Laboratory

In 2000, a series of GeoMelt Subsurface Planar Vitrification (SPV)<sup>™</sup> demonstrations were completed at Los Alamos National Laboratory (LANL). The purpose of these demonstrations, which included non-radioactive and radioactive testing, was to determine the effectiveness of the GeoMelt technology for the remediation of Material Disposal Area (MDA) V. The radioactive demonstration was performed in an absorption bed, a gravel-lined subsurface structure used to dispose radioactive wastewater into the ground. One of the primary objectives for the radioactive demonstration was to determine the homogeneity of the post-melt vitrified product. The melt resulted in a vitrified mass weighing approximately 600 tons.

Figure 5 shows pre-melt absorption bed and post-melt glass radionuclide contaminant analytical results. The shaded box area is the region between the 25<sup>th</sup> and 75<sup>th</sup> percentiles of the data and the horizontal line is the 50<sup>th</sup> percentile. Crosses indicate detections and open circles represent non-detected data, reported as the detection limit. Figure 5 indicates that not only is there a general reduction in radionuclide concentrations in post-melt glass (maximum measured concentrations are approximately one order of magnitude less in the post-melt glass than in the pre-melt absorption bed samples), but that the radionuclide content is much more homogenous, as a result of convective mixing during vitrification. Glass samples were obtained from 3 boreholes at depths ranging from 11 to 21 feet (Figure 6). Figure 7 shows a typical core sample of homogenous black glass from the radioactive demonstration.

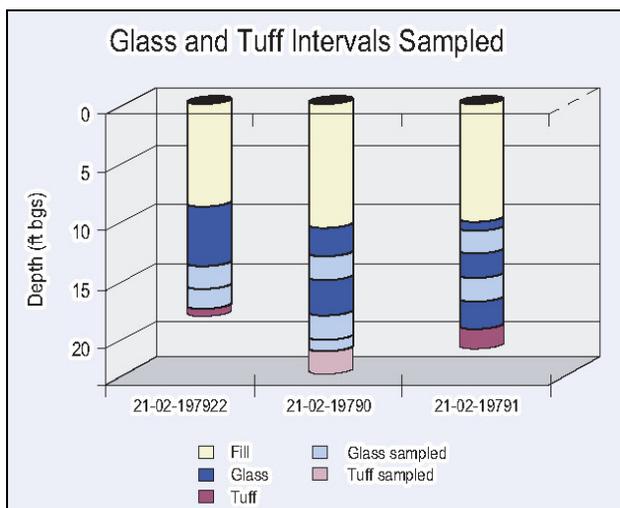
<sup>™</sup> Subsurface Planar Vitrification (SPV) is a trademark of Veolia

# Evaluation of Homogeneity in GeoMelt Glass



**Figure 5. Comparison of Pre-melt Absorption Bed and Post Melt Vitrified Product Radionuclide Concentrations**

The glass samples were analyzed by X-ray diffraction (XRF) to give bulk compositional data, and by scanning electron microscopy (SEM) for imaging coupled with electron microprobe and wavelength dispersive x-ray analysis for phase identification. All of these analyses indicated chemical homogeneity between various macroscopic samples and homogeneity at the microscopic level.



**Figure 6. LANL Sample Locations**



**Figure 7. LANL Radioactive Demonstration Vitrified Product Typical Core Sample**

## Computer Modeling

The GeoMelt process has been modeled numerous times for a variety of applications. Most frequently modeling has been performed with the TEMPEST computer code which is used to analyze and illustrate three-dimensional time-dependent fluid flow and heat transfer. This code was modified to solve electric field equations for multi-phase electrical systems in order to model GeoMelt and other joule heating applications. Plots of temperature and velocity vector fields are illustrated on Figures 8 and 9, given as examples of previous GeoMelt computer model outputs. These outputs represent two-dimensional snapshots in time during full-scale (Figure 8) and engineering-scale (Figure 9) GeoMelt operations. These models illustrate the convective currents resulting from temperature gradients caused by heat loss through the melt surface and edges. The flow patterns are divergent and sinking at the melt periphery and convergent and upwelling at the center. For a typical GeoMelt application there are four primary melt currents that converge and up-well at the melt core between the 4 electrodes. The molten material outboard of the electrodes is carried downward, then inward, then upward to complete the cycle. The result is significant mixing. This mixing results in dispersion of contaminants, including radionuclides.

# Evaluation of Homogeneity in GeoMelt Glass

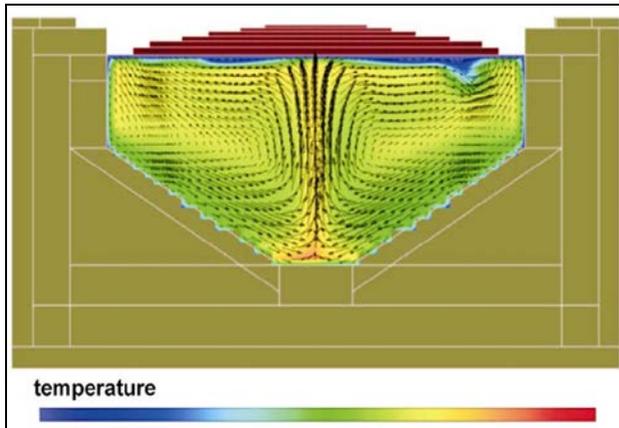


Figure 8. Full Scale GeoMelt SPV Heat Transfer Model Image

Figure 10 shows a real-world example of GeoMelt mixing preserved in the glass monolith. This melt was produced from a Pilot-Scale (i.e., 10-ton melt) In-Container Vitrification (ICV)<sup>™</sup> system that was treating asbestos waste. The blue material is the treated waste and the dark-blue/black material was from non-hazardous cover soil used in the treatment process. The cover material had melted and was being incorporated into the melt when the power was shut down. This incorporation was the result of convective cells that are seen in the computer modeling. In this case the flow pattern is easily seen the glass because of the markedly different color of the waste glass to cover soil glass, and the rapid cooling (owing to the relatively small melt size) which prevented full incorporation of the molten cover soil into the molten waste.

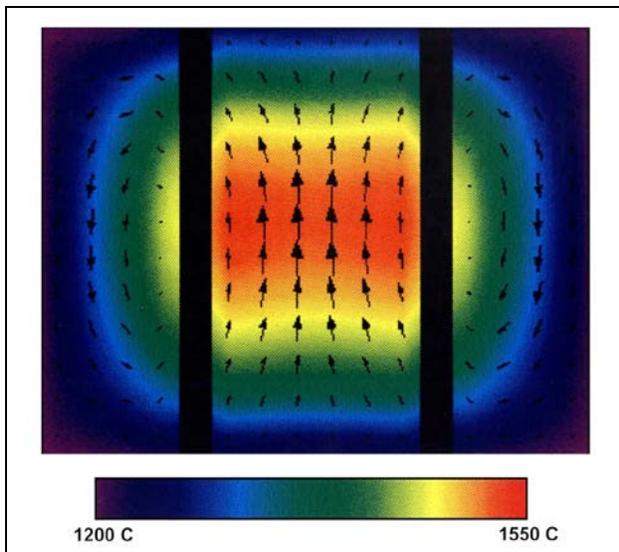


Figure 9. Engineering-Scale GeoMelt ICV Heat Transfer Model Image



Figure 10. Flow Pattern in GeoMelt ICV Glass Indicates Mixing

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