

**Recent Developments in a Transformative Technology for the Treatment of Nuclear Waste:  
Modular Vitrification System – 11396**

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**ABSTRACT**

Proper management of certain radionuclides is necessary for clean, safe and secure radioactive waste management, both at commercial Nuclear Power Plants (NPPs) and at Department of Energy Environmental Management sites. Typically, risk-informed methodologies are used to define the appropriate final waste form. A monolithic, leach resistant, glassed-based product is the preferred waste form for a number of waste streams, including, but not limited to, the Department of Energy Hanford and Savannah River Sites as well as many international nuclear waste sites. The incumbent technologies to produce a glass-based monolithic waste form are extremely large and costly centralized facilities that are designed to pre-treat and adapt the waste feed so that it is compatible with long lasting (~5 years lifetime) melters. Attempts to develop in-can, single use melters have failed in the past due to detrimental estimated cost/performance ratio mostly caused by sluggish throughputs.

We herein describe the design and performance capabilities, of the Modular Vitrification System (MVS<sup>®</sup>), together with the latest results of experimental tests. The MVS<sup>®</sup> is a heat treatment system in which nuclear waste can be processed directly inside the single-use, final disposal container. The MVS<sup>®</sup> single-use module consists of an outer canister, typically to be made of stainless steel specified by the client's site and by the waste acceptance criteria of waste repositories, and an inner induction susceptor/crucible, typically made out of graphite, which can be thermally insulated from the outer stainless canister. The inner crucible is inductively heated to the appropriate temperature, from ~800°C – low melting point glasses- to up to 1550°C, by an external low frequency, alternating current (AC), water-cooled induction coil. The very wide range of operating temperatures, the independence of melter to the chemistry of the waste and glass (e.g., conductivity) and the fact that parts exposed to high temperature molten glass are single-use, significantly decreases pre-treatment needs and permits making a wide range of vitrified products from borosilicate glass to iron phosphate glass. Moreover, technology development cycles and deployment are much faster and less costly on a single-use system designed to work for only a few hours at high temperatures in extreme conditions as compared to approximately 5 years for incumbent technologies.

We herein report proof of concept, scoping study results performed on a mock up 2.5 inch melt diameter system operating in the 10-19 kW range at 1200-1800 Hz. We introduce, as well, a higher fidelity 75 kW, 3 inch melt diameter lab-scale system, installed at our Pilot Facility in Rolla, MO, operating in the 1000-1800 Hz frequency range. The product glasses in the initial scoping studies met or exceeded DOE's Product Consistency Test (PCT), and the Environmental Protection Agency's Toxicity Characteristic Leaching Procedure (TCLP) requirements at waste loadings higher than current baselines. The MVS<sup>®</sup>

normalized throughput in metric tons of glass produced per square meter of molten surface per day (MTG/m<sup>2</sup>.d) matches incumbent melter performance. While the retention of Cesium (Cs-137) in the melt has been demonstrated, by off-gas analysis, other volatile isotopes of concern such as Technetium (Tc-99) and Iodine (I-129) surrogates will also be characterized. We conclude by outlining areas of future development and supplemental treatment applications.

## INTRODUCTION

### Modular Vitrification System (MVS<sup>®</sup>)

This paper will further outline potential advantages of the new Modular Vitrification System (MVS<sup>®</sup>) over current market leading technologies (e.g. joule-heated melters, JHM, cold-crucible induction melters, CCIM, plasma torch, and bulk vitrification systems). The benefits of this advanced stabilization technology include: simple “First Principles” design which eliminates complex and capital intensive refractory’s, water-cooled crucibles or refractory’s that could fail, leak volatiles, or require maintenance. In the case of this modular, supplemental vitrification system, the MVS<sup>®</sup>, there is nothing in the melt zone other than processed waste (e.g. no discharge valve, susceptor materials, refractory, thermocouples, unprocessed waste or sand). This allows reduced safety case design challenges, which when combined with the modular design, affords faster deployment and project acceleration. Scale up is simply by adding additional modules. The intent here is to utilize the client’s existing stainless steel (or other) canisters as the melt and final waste form storage container. Process control challenges are also mitigated since there is no linear geometry or electrode distances to contend with. Further, higher (or lower in the case of iron phosphate glasses) melt temperatures are achievable allowing for better waste loading, glass quality and leach resistance. The off-gas system can also be reduced in size and complexity utilizing this system, due to the use of a Hot Hohlraum (black body radiation from the susceptor walls above the melt zone) approach which involves vitrifying a 2-inch melt zone at a time as the module is filled. The MVS<sup>®</sup> can handle either solid or slurry feeds (e.g., 40 wt. % solids) unlike some melters. The lower portion of the module is cooling as the melt zone moves up the canister. This moving melt zone is accomplished by simply moving the current up the continuous coil (by way of segmented coils, electrically shunted.)

## OPERATION AND THEORY

The MVS<sup>®</sup> technology is a supplemental, modular vitrification system primarily designed as a radioactive waste immobilization/stabilization process. It can be used for both high-level waste (HLW) and low-level waste (LLW or LAW). The system is heated inductively and totally avoids the use of internal electrodes, or, for that matter, any materials within the melt itself. See Figure 1 for an overview of inductive heating. Advantages here include:

- Coupling with graphite insert; no waste/glass chemistry dependence
- Heating starts immediately; no in-mix sacrificial susceptors or starter heating required
- Non-intrusive melting; no in-mix electrodes, torches, or probes
- Homogeneous heating above surface via radiant Hot Hohlraum Method (HHM) and/or below via conductive heating; no hot spots
- Quiescent shallow melt pool mitigates volatilizing off-gases due to low ejection energy; no problematic cold cap to maintain
- Higher melt temperatures means higher glass quality and waste loading; no electrode limitations
- Lower melt temperature capability which adds the capability of other glass types (e.g., low melting iron phosphate glasses)

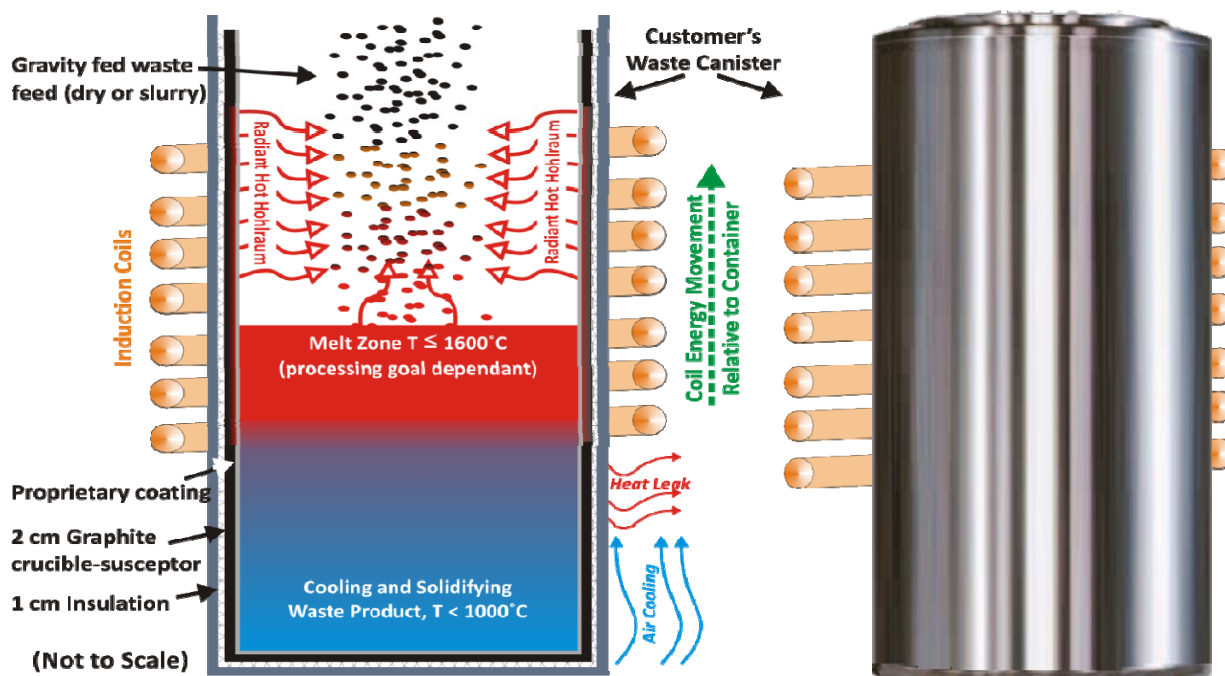


Figure 1. MVS<sup>®</sup> Technology Overview – Inductive Heating

In the MVS<sup>®</sup>, the waste and frit, if utilized, are melted inside the final disposal canister itself, which has been modified to include the MVS<sup>®</sup> internal susceptor liner. The internal liner consists of a graphite crucible. It can also include a fiber wound graphite insulator or a Grafoil<sup>®</sup> (Registered Trademark of Graftech) layer for heat dispersion or reflection. Virtually any disposal canister can be so modified to include the MVS<sup>®</sup> liner. When so modified, the disposal canister is referred to as a module. The melter and vitrified waste are disposed of together in the module, so there is no separate melter disposal, decontamination and decommissioning cost. If the outer canister of the MVS<sup>®</sup> module is stainless steel, a relatively low frequency inductive coil is used. This low frequency (decreasing with increasing crucible diameter) is unique to the MVS<sup>®</sup> modular technology because it ensures that the AC inductive field penetrates the stainless shell to heat the graphite. The outside induction coil is cooled by water coils, while the stainless shell is air cooled by air knife jets.

The MVS<sup>®</sup> uses a proprietary heating methodology that offers many benefits. It is called the Hot Hohraum Melting Method (HHM). It permits waste to be added to the module in liquid or solid form and melted as added. In this method, the walls of the crucible above the waste are heated to form a radiant hohraum (a form of black body radiation), which serves to heat a shallow layer of molten waste (~ 2 inches in a  $\leq 2$  foot diameter melt). Active cooling of the lower part of the module permits the molten layer of waste to be resident over a rising solidified waste product. This method ensures virtually no foaming during melting and a uniform vitrified product.

The key advantages of the Hot Hohraum Melt (HMM) method are:

- Very homogeneous melt: No spatial differentiation of solid feed waste and components are completely uniform along the module
- Rapid cooling and solidification of waste: Minimum time for crystallization and phase separation
- Minimum radial variation of properties: Melt surface at same temperature throughout

- Minimization of Cesium volatilization: Melt residence time is very short and quiescent. [Similar studies on-going for Tc-99 and I-129 retention.]
- Minimize module process time: Much faster than zonal melt (ZM) or uniform melt (UM) methods
- Minimize foaming: Gas rapidly evolves at the surface of the melt, not deep inside the filled module

The added cost of the MVS<sup>®</sup> internal liners is offset by avoided costs for storage and disposition of disposal canisters, due to higher waste loadings and by avoided costs for melter replacement and decontamination and disposal. Also, a faster processing rate often translates to added savings due to avoided waste upkeep and storage costs. The MVS<sup>®</sup> is a modular technology and will function with a single melting station or any number of additional stations to meet varying processing rates and completion schedules. With a modular, smaller melt system, problem or non-homogeneous tank wastes can also be addressed more readily.

The MVS<sup>®</sup> facility thus has three inherent features contributing to reliability and robustness: 1) The crucible in each module is exposed to high temperature molten glass only once for only a few hours; 2) One-time use of the MVS<sup>®</sup> melter means that the MVS<sup>®</sup> module widens the permissible waste feed chemistry envelope, with no concern for melt viscosity, electrode conductivity, crystallinity and noble metal settling; and 3) Failure of an MVS<sup>®</sup> melter will halt only the processing of a single module, which could be quickly removed and replaced with the next module.

As mentioned, the proprietary Hot Hohlräum melting method is used with the MVS<sup>®</sup>. This method ensures a homogeneous vitrified product, delivers a productive processing rate, and virtually eliminates deleterious waste foaming. The Hot Hohlräum Melting Method (HHM) relies on using a thermal radiative flux to melt the waste. This is distinctively different from thermal conduction and convection, as one might experience in heating the contents in a pot. In operation, the lined graphite susceptor within the MVS<sup>®</sup> becomes very hot in the section of graphite exposed to the inductive field. This section, in turn, radiates thermal energy in a localized area.

In the HHM method, the external induction coils are selectively energized to heat a segment of the graphite crucible above the melt surface. Unheated parts of the crucible are significantly cooler thus allowing the waste to solidify below the molten waste pool at the surface. In the HHM method, the heated segment of the graphite crucible rises as waste is added to the module. This can be accomplished by physically raising the induction coil, lowering the canister, or, in the current design, by electronically switching appropriate sections of the coil on and off using a shunt mechanism.

This HHM method further offers the means to enhance retention of volatile elements, like cesium (Cs-137), technetium (Tc-99) and iodine (I-129) within the vitrified product. Volatilization is typically a surface phenomenon, that is, the elements tend to volatilize at the surface of the melt. Traditional melters stir, bubble, or otherwise attempt to mix a molten pool. In such traditional melters, this typically involves a melter of a size equal to two or more meters in diameter. Additionally, the melting process usually is in a molten state over a relatively long period of time to achieve a homogeneous mixture. This mixing and convective process in such melters encourages volatilization by continuously surfacing elements amenable to volatilization across a large melter surface area. The cold cap of a frothy unmelted waste at the surface of the melt pool in traditional melters aids in trapping these volatilized elements with the molten waste, but can lead to entrainment in the off gas with subsequent plugging of off gas lines. Additionally, in the case of most traditional melters, a refractory is required. In particular, Tc-99 has a tendency to migrate through such a refractory and, thus, out the off gas. In this type of application, one can lose substantial amounts of the Tc-99 in the off gas, which must then be handled in the secondary waste treatment system.

In contrast, within the MVS<sup>®</sup> module, Tc-99 (or I-129) atoms must diffuse through a stagnant molten layer. The melt pool diameter is only the size of the canister, so the area of the surface is relatively small. Radiative heating predominates, convection is minimized, and no stirring or bubbling is involved. So, volatilized elements are not actively transported to the surface of the melt, thus resulting in a lower volatilization rate and lower off-gas issues. Pilot tests are on-going utilizing surrogates for Cs, Tc and I where the off-gas condensates are being analyzed for carry over. While 100% Cs retention has been demonstrated in past pilot runs, the retention of Tc-99 and I-129 still needs to be confirmed.

Current on-going scoping tests involve inductive studies on Hanford surrogate AN-104 in a) borosilicate glass, and b) iron phosphate glass. Now that the S.S. canister, with graphite crucible, tests are completed, along with on-going parametric modeling, the Hot Cell Pilot Unit (3-inch melter) is being shaken down and tested at the Pilot Facility in Rolla, Missouri. It is currently proposed that this same scale unit will then be commissioned in actual hot cell work at one of the DOE sites on actual waste.

Elimination of the above problems experienced in existing joule melters enables the MVS<sup>®</sup> to vitrify at much higher temperatures, typically 400 °C higher than a joule melter (i.e., up to 1550 °C). This, in turn, allows much more waste to be dissolved (loaded) in the glass, which means higher waste loadings per disposal canister. Such higher waste loadings enable major cost and schedule benefits by reducing the total volume of vitrified product to be disposed.

The objective of these small-scale crucible tests was to conduct scoping experiments to define the target composition and feed additives for the lab-scale vitrification of AN-104 simulant. These scoping tests were also meant to begin waste loading optimization, and to evaluate cooling as a function of crystallinity. The acceptance criteria for the bench-scale process (primarily TCLP, PCT and, to a lesser extent, degree of crystallinity) defined the selection process along with the goal of maximizing the waste loading.

In an MVS<sup>®</sup> module, the waste chemistry tolerance is much higher, since each module must operate only for a few days in comparison to years required for traditional melters. Thus, it can vitrify wastes that would destroy a traditional melter well short of its intended lifetime. The ability for the MVS<sup>®</sup> to easily vary its operating temperature enhances its tolerance for non-uniform waste chemistries wherein melting temperature can be expected to vary. The high melting temperature capability of the MVS<sup>®</sup> assures that it can vitrify waste compositions and concentrations that simply cannot be melted in traditional melters without chemical treatment and dilution.

Thus, for virtually all vitrification applications where the actual chemistry of the waste is uncertain, the MVS<sup>®</sup> would offer distinct advantages in regard to safety, cost and schedule performance. The Hanford wastes are a particularly apt example of this. At Hanford, there is expected a wide variability of waste chemistry, not only from tank to tank, but even within tanks.

One of the most important features of the MVS<sup>®</sup> is its modularity and ability to readily adapt to a wide variety of vitrification needs and feeds. The MVS<sup>®</sup> can be quickly set up and operate at a site at much lower cost than a conventional fixed melter, to vitrify a relatively small amount of waste, or large amount, as conditions warrant. One melting station can operate for months or years, as required, and then be quickly dismantled without leaving any radioactive equipment behind.

## **EXPERIMENTAL**

### **MVS<sup>®</sup> Scoping Studies: Phase I**

This report describes the results of two series of successful experiments wherein a low melting (950 °C) iron phosphate glass and a higher melting (1050 °C) borosilicate glass, both containing approximately 30

weight percent of a simulated Hanford LAW, were melted by induction melting. The goal of these two experiments was to evaluate and demonstrate the concept that such simulated nuclear waste could be melted by inductively heating a graphite crucible/susceptor that was surrounded by a stainless steel container. These were the first experiments where such simulated waste forms of both compositions were successively melted by inductive heating using the combination of a graphite crucible/susceptor surround by a stainless steel container. The key to the success of these two experiments was air cooling the outside of the stainless steel container which, in the first experimental series, reached a maximum temperature of 1162 °C during the melting of 800 gms of the borosilicate composition. Approximately 10 kW of power was sufficient to melt these glasses in the system used for these experiments. These two experiments, while limited in scope and scale, are believed to have provided evidence supporting the feasibility of the Modular Vitrification System (MVS<sup>®</sup>) for vitrifying nuclear waste.

This report describes the procedures and results obtained from two experiments which consisted of melting an iron phosphate glass that contained 30 weight percent of the simulated Hanford LAW waste, hereafter referred to as IP30LAW and a borosilicate glass that contained 29.3 weight percent (calculated) of simulated Hanford LAW (AN-104). This borosilicate glass is hereafter referred to as BS AN-104.

Both glasses were melted by induction heating using procedures and materials that were intended to model those that would likely be employed in the Modular Vitrification System (MVS<sup>®</sup>). These were the first small scale experiments where a simulated nuclear waste would be melted by induction heating in an arrangement consisting of a graphite crucible (susceptor) surrounded by a stainless steel container.

The primary objective of these first two experiments was to assess the feasibility of the MVS concept. Initially, the primary concern was whether the raw batch could be heated to a high enough temperature (melting) without distorting, oxidizing or melting the stainless steel container. Therefore, a low melting (950 °C) iron phosphate glass (IP30 LAW) was used for the first experiment and the stainless can was air cooled. Since this was the first experiment, no information was available to estimate the power level that would be needed, so 12 kW output was selected initially. At this power, the temperature reached an unintended value of 1190 °C. However, the iron phosphate batch was successfully melted and subsequent inspection of the air cooled stainless steel container showed it had not been damaged. The same air cooled stainless steel can was successfully reused to melt the higher melting BS AN-104 glass in the second induction melting experiment.

A description of the procedures using in these two induction melting experiments are described more fully in the following sections.

### **Batch Compositions Used**

The composition of the IP30LAW glass is given in Table I along with the composition of the simulated Hanford LAW. This glass was chosen in the present work since it has a low melting temperature, about 950°C, has been investigated previously and its chemical durability meets all current DOE requirements.

The composition and raw materials for the borosilicate glass batch were provided by our laboratory in Oak Ridge, see Table II. Since there was no data for this composition, a small amount of the raw materials was melted in a crucible to determine its minimum melting temperature which was found to be 1100 to 1150 °C. The oxide composition of the surrogate AN-104 waste and trim chemicals (glass forming chemicals) are given in Table I.

The dry raw materials for each composition were thoroughly mixed to insure that the batch was chemically homogeneous before melting.

**Table I: Weight Percent Composition of the Iron Phosphate and Borosilicate Glass Waste Form Compositions used for Induction Melting Experiments**

Oxides	Hanford LAW Simulant (wt%)	Iron Phosphate Waste Form with 30 wt% Law, IP30LAW (wt%)	AN-104 Surrogate (wt%)	Borosilicate Waste Form with 29.26 wt% AN-104 Surrogate (wt%)
Al <sub>2</sub> O <sub>3</sub>	4.40	1.30	27.48	8.04
B <sub>2</sub> O <sub>3</sub>				8.00
CaO				2.91
Cl	0.60	0.20	1.36	0.40
Cr <sub>2</sub> O <sub>3</sub>	0.40	0.10	0.26	0.08
F	1.60	0.50	0.10	0.03
Fe <sub>2</sub> O <sub>3</sub>		20.00		2.01
K <sub>2</sub> O			1.37	0.40
Li <sub>2</sub> O				3.00
MgO				3.35
Na <sub>2</sub> O	75.30	22.60	67.36	19.71
P <sub>2</sub> O <sub>5</sub>	7.70	52.20	0.58	0.17
SiO <sub>2</sub>	0.50	0.20		43.43
SO <sub>3</sub>	9.50	2.90	1.49	0.44
TiO <sub>2</sub>				1.00
ZnO				5.01
ZrO <sub>2</sub>				2.02
Total	100.00	100.00	100.00	100.00

**Table II. Composition and Raw Materials used for AN-104 Surrogate and Trim Chemicals for Borosilicate Glass---Second Induction Melting Experiment.**

Batch #1: AN-104 surrogate for Glass Making  
 Container 1A = Surrogate waste chemicals  
 Container 1B = Glass Trim chemicals

Compound	Surrogate Waste (g)		Glass Trim (g)	
	Target	Actual	Target	Actual
Al(OH)3	703.84	703.8		
NaCl	37.43	37.4		
Cd(NO3)2*4H2O	0	0		
Na2CrO4	11.28	11.3		
NaF	3.62	3.6		
K2CO3*1.5H2O	40.23	40.2		
Na2CO3*H2O	2147.73	2147.7		
Na2HPO4	36.77	36.7		
Na2SO4	44.30	44.3		
Fe2O3			114.80	114.8
B2O3			457.91	458.0
Ca(OH)2			219.87	219.9
Li2CO3			424.65	424.8
Mg(OH)2			277.21	277.5
SiO2			2484.24	2485.0
TiO2			57.26	57.3
ZnO			286.20	286.3
ZrO2			115.49	115.6
Sum	3025.21		4437.63	
	40.54%		59.46%	

Prepared by: *Jeff Holt* Date: 3/5/2010

## Induction melting experiments

### 1. Induction power supply

The induction power unit that was used in both experiments was manufactured by Inductotherm, Model VIP (Variable Induction Power). Figure 2 below shows the control console of the unit and the range in operating power, frequency and voltage for this unit. Typical operating conditions in both experiments were 8 to 12 kW power at a frequency of 1600 to 1800 hertz and voltage of 160 to 240 volts.



Figure 2. General view of the control panel of the induction power supply used for the glass melting experiments.

### 2. Crucible arrangement

The same arrangement of crucibles was used for both experiments. Figure 3 shows the physical components utilized and illustrates the dimensions of the crucibles. The ceramic safety crucible (10.70 inches in dia) function was to contain any liquid (glass or metal) from coming in contact with the induction furnace coils. Next is a thin (35 mil) stainless steel can (selected because it was assumed to be easier to cool than the thicker, Hanford, stainless steel canister used in the Phase II Scoping Studies), 6 inches in diameter and 9 inches tall. Finally, is the graphite crucible (3.75 inches in diameter and ~ 8 inches tall). Inside the graphite crucible was a ceramic tube (2.5 inches in diameter and 23 inches long). The dry, raw batch was charged periodically into the top of the ceramic tube.

Figure 3 below is a photograph of these individual components showing the ceramic safety crucible on the left, the stainless steel can in the middle the graphite crucible on the right and the ceramic melter tube in the front. The stainless steel can was air cooled on the outside during each melting experiment. The vertical stainless tube in the middle of the figure carried air to the short, vertical stainless steel tubes spaced at four locations around the perimeter of the can. Compressed air was blown on the outside of the stainless steel can through small holes in the vertical cooling tubes.





Figure 3. Ceramic safety crucible (left), stainless steel can (middle) and graphite crucible (right) and ceramic melter tube (in front) used in both induction melting experiments. The stainless can, graphite crucible, and ceramic melter tube were placed inside the large ceramic safety crucible.



Figure 4. Appearance of the outside surface of the stainless steel can after two induction melting experiments. The four short cooling tubes provided air cooling during the melting experiments. The can is in good shape and shows what is considered only minor oxidation. In the second scoping experiment where the borosilicate glass was melted, the can reached a maximum temperature of  $\sim 700\text{ }^{\circ}\text{C}$  and the maximum temperature of the graphite crucible/susceptor was  $1075^{\circ}\text{C}$ .

### 3. Preparation for Induction Melting Experiments

The procedures and apparatus used for melting the iron phosphate and borosilicate glass were basically the same, although there were some differences in the heating rate and maximum temperatures achieved. However, these small differences had no relevance to the outcome, so the following is a generic description of the techniques applicable to both induction melting experiments.

The melting experiments started by placing the ceramic safety crucible inside the induction coils. The next step was to place the graphite crucible/susceptor inside the stainless steel can and to fill the annular space between the outer surface of the graphite crucible and the inside of the stainless steel can with a fibrous insulating material as depicted by the red arrow in Figure 5.



Figure 5: Photo showing graphite crucible/stainless can assembly inside ceramic safety crucible. White fiber insulation (red arrow) is placed between graphite and stainless can to insulate the stainless can from the hot graphite crucible. Black arrow points to air cooling tube and the fountain pen placed on the safety crucible is scale marker.

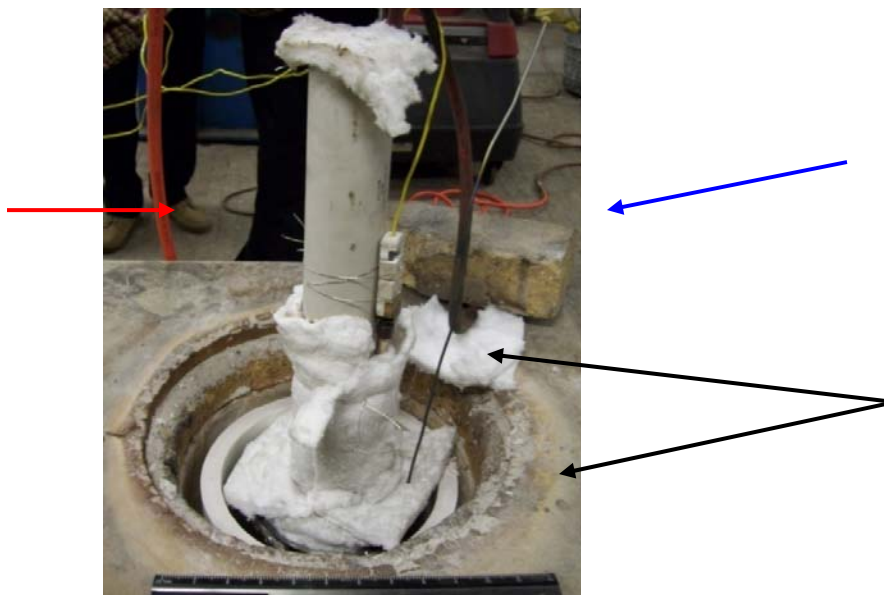


Figure 6. Photo of the components placed inside the induction coils and ready to start melting experiment.

As shown in Figure 6 above, the next step was to place the ceramic melter tube inside the graphite crucible and to place thermocouples (black arrows in Figure 6) close to the outside surface of the stainless can and the outside surface of the graphite crucible. The temperature at both locations was recorded continuously during the induction melting experiment. The blue arrow points to the gas line that was attached to a ceramic tube which delivered argon to the bottom of the assembly close to the graphite crucible to protect it from excessive oxidation at elevated temperature.

The red arrow in Figure 6 points to the air line that was connected to the stainless steel cooling tube in Figure 6 that delivered cooling air to the outside of the stainless can. The white material is Kaolin, a ceramic fiber insulation that was placed on the top of the stainless can and graphite crucible and wrapped

around the ceramic melter tube for the purpose of insulating the melting area and reducing heat losses. During melting, the open end of the ceramic melter tube was covered with a small piece of this insulation.

#### 4. Melting of the Borosilicate BS AN-104 composition

The same general procedures and equipment were used to melt the iron phosphate and borosilicate glass, but only the induction melting of the borosilicate glass is described in detail since it is considered of more importance. Prior to starting the induction unit, the insulation at the top of the ceramic melter tube was removed, a portion of the powdered batch was dropped into the tube and the insulation was replaced. The induction unit was then turned on at a low power of 8-10 kW to heat the components slowly and minimize thermal shock to the ceramic components. At 8 kW, the voltage was 160 volts and the frequency was 1700 Hz. After about 15 minutes at these settings the outside temperature of the stainless can was about 500 °C. Heating continued as the power was adjusted to 12 kW to maintain a heating rate of 15 to 25 °C/min. Hot graphite crucible (800 °C) is becoming visible through fiber insulation.

The following figures were taken during the melting of the BS AN-104 composition on March 18, 2010.

After about 25 minutes after heating started, the temperature of the can and graphite crucible were 800 °C and 510 °C, respectively. A glowing color was becoming visible through the insulation. The temperature inside the ceramic melter tube was 600 °C and the batch in contact with the melter tube was observed to be melting at this time. The power was reduced at this point. The temperature continued to gradually increase and additional batch was periodically dropped into the melter tube until all 800 gms of batch had been added (total of 14 separate additions).

One hour after starting, the temperature of the stainless can and the graphite crucible was 997 °C and 809 °C, respectively, and the power was again reduced, where it remained until the power was turned off. At 2.5 hours after starting, the temperature of the stainless can and graphite crucible was 1162 °C and 1075 °C, respectively, which was the maximum temperature used in this experiment.



Figure 7. Induction melting of borosilicate glass, BS AN-104, 2.5 hrs after start. Temperature of graphite crucible was 1075 °C. The melt was fluid with a consistency of honey.

After 2.5 hrs, the 800 grams of batch was totally melted so the furnace power was reduced to 5 kW to allow the furnace contents to cool. At 2.75 hrs the furnace power was turned off and the contents were allowed to cool to room temperature overnight.

The next morning the system was disassembled and the appearance of the ceramic safety crucible, the ceramic melter tube, graphite crucible and stainless can after removal from the induction furnace found all of the components were in good to excellent condition, especially the stainless steel.

The bottom portion of the melter tube was broken apart as shown in Figure 8 and revealed the dark borosilicate glass tightly bonded to the ceramic tube. The glass had obviously cracked during cooling but it appeared homogeneous and contained relatively few gas bubbles. It is estimated that the 800 gms of batch yielded approximately 560 gms of glass. There was no significant corrosion of the ceramic tube by the molten borosilicate glass.

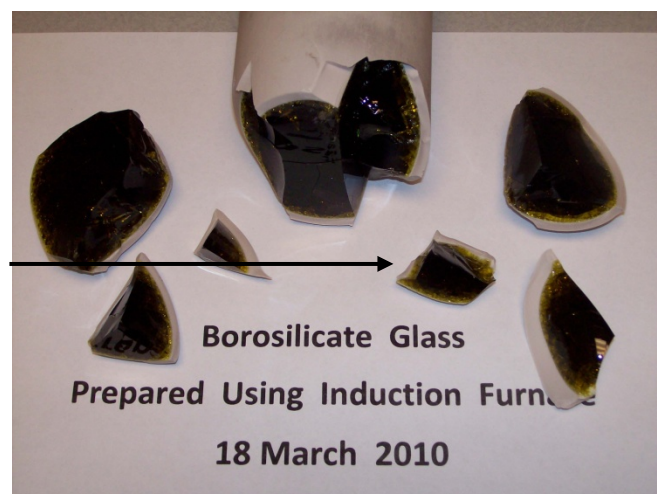


Figure 8. Broken end of the ceramic melter tube that contained dark borosilicate glass BS AN-104 after melting.

### **MVS<sup>®</sup> Scoping Studies: Phase II**

This section of the report describes the results of an experiment wherein about 1100 gms of a borosilicate composition, containing ~ 30 wt % of a simulated Hanford AN-104 LAW was successfully melted at 1080 °C by induction melting. The purpose of this experiment was to evaluate the performance of a thick wall (0.182 inches) stainless steel container, whose thickness is equivalent to that of a MVS<sup>®</sup> container that would be used in practice, in combination with a graphite crucible when this combination is heated in an induction furnace. The main objective was to determine if the BS AN-104 composition could be melted, using the thick wall stainless container, as it was in an earlier experiment where a thin wall (0.035 inch) stainless steel container was used. With the aid of additional forced air cooling, the performance of the thick wall stainless container was essentially the same as that of the thin wall container. The thick wall container did not limit the temperature reached in the graphite crucible (1313 °C max) and ~1100 gms of the BS AN-104 batch was melted in a ceramic tube at 1080 °C during the 5.5 hr experiment. The maximum temperature of the air cooled thick wall stainless container was 715 °C. The sidewalls and bottom of the thick wall stainless container were tarnished, but no excessive oxidation was observed and there was no measurable change in wall thickness. The maximum induction power used in the present experiment was 15 kW, compared to the 10 kW used in the earlier experiment where this borosilicate composition was melted using the thin wall stainless can. Based on the results from the present experiment, it is estimated that compositions with melting temperatures up to 1250 °C, and possibly higher, could be melted in containers of the present configuration.

The results of the two, laboratory scale, induction melting experiments conducted to date (thin and thick wall stainless container) using the BS AN-104 composition, provide a growing body of evidence showing that the Modular Vitrification System is a feasible concept for vitrifying nuclear waste.

This report describes results of the second time a borosilicate glass containing 29.3 weight percent (calculated) of a simulated Hanford LAW (AN-104) was melted in an induction melter. This borosilicate glass is hereafter referred to as BS AN-104. The experiment was conducted at the Missouri University of Science and Technology (MS&T), April 1, 2010.

In addition to gaining additional experience about the induction heating of a system composed of a graphite susceptor/crucible inside a stainless steel container, the primary objective of the experiment described herein was to melt the BS AN-104 composition, see Table I, in a thick wall (0.182 inches) stainless steel container with an OD of 6 9/16 inches and a height of 7 inches. This wall thickness is close to that of the stainless container which would be used in practice (e.g., Hanford).

## **Phase II Induction Melting Experiment**

1. Batch composition/raw materials: The composition and raw materials for the borosilicate glass batch was the same as in Phase I, see Table I. The dry raw materials for the surrogate waste and glass trim were thoroughly dry mixed prior to use to insure that the batch was chemically homogeneous before melting. The oxide composition of the surrogate AN-104 waste and trim chemicals (glass forming chemicals) are also given in Table I.

2. Induction power supply: The induction power supply used in this experiment was the same as used in the previous experiment on 19 March 2010, Inductotherm, Model VIP. Typical operating conditions in this experiment were 5 to 15 kW power at a frequency of 1600 to 1800 hertz and voltage of ~160 to 220 volts.

3. Crucible arrangement: The crucible arrangement used in this experiment was the same as that used in the previous experiment. Figure 9 below is a photograph of the four individual components showing the ceramic safety crucible on the left, the thick wall stainless steel container in the middle, the graphite crucible on the right and the ceramic melter tube in the front.

The thick wall stainless steel container was air cooled on the outside during the entire melting experiment. An additional air supply tube was used in this experiment. In addition, two additional short vertical stainless steel air cooling tubes were added and spaced at six locations around the perimeter of the container. Compressed air was blown continuously on the outside of the stainless steel container during the entire time the induction power unit was operating and when the assembly was cooling in the furnace at the completion of the experiment. Air was blown on the outside surface of the stainless container, both perpendicularly and tangentially, through small holes in the vertical cooling tubes.



Figure 9. Ceramic safety crucible (left), thick wall (0.182 inches) stainless steel container (middle), equipped with air cooling device, graphite crucible (right) and ceramic melter tube (in front). In the induction melting experiment the stainless container, graphite crucible, and ceramic melter tube were placed inside the large ceramic safety crucible.

4. Preparation for Induction Melting Experiment: The procedures and apparatus used for melting the BS AN-104 borosilicate glass were basically the same as those used in the previous two induction melting experiments. The one major difference in this experiment was that the thick wall stainless steel container was used in place of the thin wall stainless steel can used previously.

The melting experiment started by placing the ceramic safety crucible/stainless steel container/graphite crucible/ceramic melter tube inside the induction furnace coils as in Phase I. The annular space between the graphite crucible/susceptor and the stainless steel container was filled with a fibrous insulating material for the purpose of insulating the stainless steel container from the hot graphite crucible at higher temperatures.

Additional hoses were used to supply air to cool the outside of the stainless steel container. Two thermocouples were used to measure the temperature (approximately) of the inside surface of the stainless steel container and the temperature inside the graphite crucible/susceptor. The temperatures of these two thermocouples were measured / recorded continuously during the melting experiment.

To reduce heat losses, the opening at the top of the tall vertical melter tube was covered with a piece of refractory insulation during the experiment and additional refractory insulation was wrapped around the tube where it extends beyond the graphite crucible. A gas line connected to a refractory tube was used to deliver argon to the vicinity of the graphite crucible to create an argon rich atmosphere to reduce potential oxidation of the graphite crucible at high temperatures. A mirror was used to view the contents (batch/glass) inside the melter tube.

5. Melting of the Borosilicate BS AN-104 composition: Prior to starting the induction unit, the cooling air and argon gas was turned on and the insulation covering the top of the ceramic melter tube was removed. Approximately 125 gms of the dry, powdered batch was dropped into the melter tube and the insulation was replaced.

The induction unit was then turned on at an initial power of 5 kW to slowly heat the components and minimize thermal shock to the ceramic tube. Ten minutes later, the power was increased to 8 kW and the

temperature inside the stainless container was 130 °C. Twenty minutes later, the temperature inside the stainless container was 280 °C and the power was increased. Twenty minutes later, when the stainless container temperature was 415 °C, the power was again increased. Twenty minutes later, the power was increased a final time. The temperature inside the stainless container was 478 °C and a dull red color was noted in one area of the stainless steel container. An additional air cooling line was inserted adjacent to the stainless container in the area where it had a dull red color.

A plot was recorded of the “inside” surface temperature of the stainless steel container and the temperature inside the graphite crucible, as a function of time in minutes, starting when the induction power unit was turned on.

There are several noteworthy features of the thermal plot. Initially, the temperature of the stainless steel container is higher than the temperature inside the graphite crucible. This is to be expected since the thick wall stainless container is closer to the furnace induction coils and, therefore, is receiving a higher fraction of the electro-magnetic energy. Once the system was at temperature, the stainless remained some 600 °C lower than the graphite for the duration of the melt.

At approximately 100 min, the temperature inside the graphite crucible increases very rapidly from 630 °C to 1230 °C over a period of ~30 minutes, while the temperature of the stainless steel increases only slightly from ~600 °C to 675 °C. This sudden increase in temperature inside the graphite crucible indicates that more of the electro-magnetic energy is now being absorbed (better coupling to the electro-magnetic field) by the graphite due to a number of factors to be detailed in a subsequent report.

For the remainder of the experiment, the induction power was varied between 14 and 15 kW in order to maintain the stainless steel at a “constant” temperature. A decrease in temperature in the curves at ~ 315 minutes was simply due to the induction power being turned off. This portion of the curves gave an indication of the cooling rate in the assembly, with the cooling air turned on.

About 125 gms of the dry batch was placed in the ceramic melter tube before the induction power was turned on so that it would be gradually heated and form a bed for the subsequent additions of the batch. The second ~125 gm addition of batch occurred about two hrs after heating commenced and dry batch was added periodically (total of 9 times) over the time interval. The batch additions and small adjustments in induction power account for the larger fluctuations in temperature in the graphite temperature curve compared to that of the stainless counterpart. Of course, adding cold batch causes a temporary reduction in temperature.

After the last addition of dry batch, the top of the melter tube was closed and the batch was allowed to melt for approximately 1 hr. A total of ~ 1100 gms of dry batch was melted during this experiment. The molten glass was tested with a silica rod to show its chemical homogeneity and lack of gas bubbles. The depth of the melt on the ceramic tube was about 4.5 inches.



Figure 10. Appearance of the stainless container/graphite crucible/ melter tube assembly in the induction furnace when the temperatures were 1313 °C inside the graphite crucible, 714 °C on the inside of the stainless steel container, and 1080 °C inside the melter tube (measured by a thermocouple immersed in the melt).

The induction power was reduced from 15 kW to 10 kW about five hours after heating began to allow the system to cool somewhat before the induction unit was turned off 15 minutes later. The cooling air was left on as the system cooled overnight. The time for the entire experiment was 5.5 hrs.

The following morning the system was removed from the induction furnace, disassembled, examined and photographed. Special attention was given to examining the condition (oxidation) of the thick wall stainless steel container.

## SUMMARY AND CONCLUSIONS

### Phase I: CONCLUSIONS

Both induction melting experiments were considered a success in that the lower melting iron phosphate glass and the higher melting borosilicate glass were both successfully melted with no major problems. The system as used was clearly capable of melting a borosilicate glass composition containing roughly 29 weight percent of a Hanford LAW, which is a respectable waste loading, at temperatures as high as 1075° C. Air cooling the stainless steel can prevented it from melting and protected it from excessive oxidation. Likewise, the argon rich atmosphere provided good protection and prevented any major oxidation of the graphite crucible/susceptor.

There are still some unanswered questions, but the results of these two inductions, rather simple, melting experiments are believed to have provided results that demonstrate the concept of an Modular Vitrification System (MVS<sup>®</sup>) has considerable merit.

Several follow-on induction melting experiments followed on April 1, 2010. In these test runs, the thin walled stainless steel canister used in Phase I experiments 1 and 2 was replaced with a thicker wall, 3/16 inch, stainless steel container.

### Phase II: Examination of Components After Induction Melting Experiment

**Thick wall stainless steel container:** An important part of the present experiment was to determine the performance of the thick wall stainless steel container, especially if the oxidation could be prevented or



minimized by air cooling when the graphite crucible was at a temperature high enough to melt the BS AN-104 batch. The two views (front/back) of the stainless container in Figure 11 below show that, while the thick wall crucible became tarnished, any oxidation was minor and certainly not excessive. The average wall thickness, calculated from 15 measurements, at the completion of the experiment was 0.182 inches which, within experimental error, is the same as the thickness of the as-received container. In general, the tarnish/oxidation of the thick wall container is not appreciably different from that observed for the thin wall stainless container.

The temperature measured close to the inside wall of the stainless container shown below was in excess of 550 °C (dull red color) for 3.5 hrs and exceeded 715 °C for ~1 hr. During this time, the temperature inside the graphite crucible ranged from 575°C to a high of 1313 °C. The temperature of the outside surface of the stainless container was measured several times with an IR camera and was in the range of 530 to 570 °C max.



Figure 11. Two views, front side/back side, of the thick wall stainless steel container at the completion of the glass melting experiment. Non uniform tarnishing is evident, but oxidation is minimal or non-existent.

The appearance of the bottom of the air cooled thick wall stainless steel container at the completion of the experiment was considered of particular importance. There was some difference in the color, as there was a temperature gradient across the bottom during the experiment. The extent of the blue tarnish indicates that the bottom of the crucible was somewhat hotter than the sidewalls shown in Figure 11. A hotter bottom is not unexpected since it was cooled only indirectly and did not receive direct air impingement as did the side wall. Overall, however, the amount of tarnishing is small and, for practical purposes, is of little consequence.

**Condition of graphite crucible:** Appearance of the graphite crucible; after the first two melting experiments and after the completion of the present experiment showed little effect. The hot graphite crucible is semi-protected by an argon-rich atmosphere. After the second melting in Phase I, the re-used crucible still showed a weight loss of only 6.7%.

The slight oxidation of the graphite crucible in this experiment is not considered a serious problem. It can be minimized by increasing the amount of cooling air and improving its distribution over the sidewalls of the stainless container by increasing the number of vertical cooling tubes and increasing the air flow around the side wall, as well as assuring that the argon blanket is not diluted within the susceptor.

**BS AN-104 borosilicate glass produced:** Several pieces the glassy chunks are shown in Figure 12. The estimated weight of the glass produced is ~ 800 gms.

The glass had a dark color similar in appearance to the BS AN-104 glass melted previously and contained relatively few bubbles. A thermocouple immersed about 2 inches into the melt just before the induction power was turned off indicated a melt temperature of 1080 °C. At this time the temperature of the inside surface of the stainless container and inside the graphite susceptor was 715 °C and 1313 °C, respectively.



Figure 12. Chunks of the colored BS AN-104 glass that had been melted and let cool.

**Table III: Illustrates the successful glass product quality utilizing the standard testing procedures: PCT, TCLP and Crystallinity Test Results for the Borosilicate Glass**

Hanford Quality Assurance Test Matrix	MVS®		LAW Baseline	
<b>Glass Quality (lower is better)</b>				
Product Consistency Test (PCT) <i>ASTM C 1285-02</i>	Na	0.84 g/m <sup>2</sup>	Na	2 g/m <sup>2</sup> ‡
	Si	0.25 g/m <sup>2</sup>	Si	2 g/m <sup>2</sup> ‡
	B	0.34 g/m <sup>2</sup>	B	2 g/m <sup>2</sup> ‡
Toxicity Characteristic Leaching Procedure (TCLP) <i>EPA SW-846 Method 1311</i>	Cr	0.043ppm	Cr	5 ppm ‡
	Ba	0.15 ppm	Ba	100 ppm ‡
	6 others below detection levels			
Crystallinity by XRD	Totally amorphous		Totally amorphous ‡	
<b>Waste Loading (Key Performance Metric – higher is better)</b>				
Waste Loading (Na <sub>2</sub> O wt%).	19.7 %		15.7 % †	
<b>Throughput Flux Rate (metric tons of glass/(m<sup>2</sup>-day) – higher is better)</b>				
As tested	1.8 MTG/(m <sup>2</sup> -day)		1.5 MTG/(m <sup>2</sup> -day) *	

References:

‡ [Office of River Protection, Prime Contracts, BNI Contract, Statement of Work](#)

\* [DOE Office of River Protection Plan, ORP-11242 System Plan, Rev 4](#)

**Melt** \* From Dr. Pegg of Catholic University presentation at DOE's Next Generation Melter Workshop, D.C., March 2010

The main objective of this Phase II induction melting experiment was to evaluate the performance of the thick wall stainless steel container, especially from the standpoint as to whether it would limit the temperature that could be achieved by the graphite crucible/susceptor. With the aid of air cooling, the thick wall stainless container performed in a manner similar to that of the thin wall stainless steel can that had been successfully used in two previous melting experiments. The thick wall stainless container did not limit the temperature reached in the graphite crucible and approximately 800 gms (~1100 gms of

batch) of the borosilicate BS AN-104 glass was successfully melted at 1080 °C. In terms of these results, this experiment was considered a success.

Forced air cooling of the outside of the thick wall stainless steel container proved to be an effective way of the controlling and limiting the temperature of the container. Careful examination of the thick wall stainless steel container after the melting experiment did not reveal any excessive oxidation or other type of damage. Tarnished areas were visible, but in general, the appearance of the thick wall stainless steel container was essentially the same as that of the thin wall stainless steel container. There was no detectable change in the wall thickness of the thick wall stainless steel container after use.

The results obtained to date clearly demonstrate that the thick wall stainless container/graphite crucible/susceptor system, used in this experiment, is capable of melting compositions which melt at 1080 °C or below. While still not documented, it is considered likely that glass melting temperatures of 1250 °C (or possibly more) can be reached with improved air cooling of the stainless steel container and through optimization of the ratio of wall thicknesses of the stainless steel container and the graphite crucible. The present combination, as used, is clearly capable of melting a borosilicate glass composition containing ~ 29 weight percent of the Hanford AN-104 LAW.

The results of the three, laboratory-scale induction melting experiments conducted to date provide significant factual evidence of the feasibility of the Modular Vitrification System concept. These results also provide justification for continued experimental work to optimize the induction heating process, to determine the melting kinetics and melt thru-put, and to commence planning for scale up.

**Future Scale Up:** The scoping study system has now been scaled up to a 3-inch Lab-Scale MVS<sup>®</sup> and is undergoing start up at our Pilot Facility in Rolla, MO. This unit was sized and designed for use not only with surrogates, but also for Hot-Cell demonstrations on actual wastes.

With completion of the TRA in mid-July 2010, the Company focused on its design and fabrication of a high fidelity MVS<sup>®</sup> Lab Scale system suitable for extensive testing of a wide range of simulated wastes. System shake down occurred in November and glass production initiated in December 2010. The current Scoping Efficacy Tests will be supplanted by the new high fidelity Lab-Scale system with updates to the Hanford LAW TRA made as appropriate.

Starting in 2011 the company will be building successively larger systems to meet the TRA Bench-Scale and Engineering-Scale requirements for HLW, LAW and other waste processing opportunities. The Lab-Scale MVS<sup>®</sup> was designed to fit within typical hot cells for testing on actual wastes and application towards  $\geq$ TRL4 status in conjunction with the large systems.

While the MVS<sup>®</sup> technology has a long history of development and accomplishments, a great deal of development work is currently in the planning. This is especially the case for the very challenging Hanford Low Active Waste, LAW, potential application.

One paramount advantage of the MVS<sup>®</sup> technology is the dramatic reduction in pretreatment complexity and cost since the batch modular system can be tuned to make the glass match the incoming feed vs monolithic external melters where the feed must be tuned to match the glass and not harm the refractory.

Initial Lab-Scale testing at our pilot facility will involve both low melting and high melting glasses, such as iron phosphate and borosilicate formulas. Optimization of designs for the stainless canister and graphite susceptor, as learned from on-going parametric modeling, will be studied with this system. Also, of utmost importance, will be the studies of volatiles retention in the glass melts (e.g., Cs-137, Tc-99 and I-129).