New Developments in Advanced Stabilization Technologies including the Advanced Microwave System and Modular Vitrification System - 10279

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ABSTRACT

Novel developments and applications in Advanced Stabilization Technologies (AST) have been made possible by utilizing a custom designed, pilot-scale Advanced Microwave System (AMS™) and by a developing pilot-scale Modular Vitrification System (MVS™). This research is on-going at Materials and Chemistry Laboratory (MCL), our nuclear licensed facility in Oak Ridge, Tennessee, and induction melting pilot facility in Rolla, Missouri. The AMS™ consists of a 500 liter microwave vacuum vessel, 3 kW microwave power supply with circulator, directional coupler with stub tuner, and microwave compatible vacuum chamber with rotating table. A 6 kW power supply supplies 3 kW of microwave power (220 V, 35 A, 60 Hz, single phase) to the system. Partial or full vacuum can be maintained on the system, or purge gas or instrument air can be utilized. Material melt temperatures are monitored at the remote control panel by both a K-type thermocouple (through the front port) and an infrared pyrometer (through the top-mounted germanium window). A color, closed circuit television (CCTV) system monitors the internal conditions of the vessel along with safety view windows. The waveguide, fed by the power supply and the circulation water, consists of a circulator, directional coupler, four stub tuner and E-plane bend into the rear microwave window of the 500 liter vacuum chamber.

Testing has included independent microwave melting and pyrolysis volume reduction (VR) studies on organic resins, inorganic media (proprietary Ion Specific Media, ISM) and inorganic sludges. Further tests have involved a novel Modular Vitrification System (MVS™), currently at the pilot-scale. The MVS™ is a modular inductive melter which utilizes the normal stainless steel module as the melt and final waste form container and a graphite internal liner susceptor crucible with an external inductive heating coil. In the former, total pyrolysis can be achieved at lower temperatures in the 750-850 °C, while in the vitrification application, temperatures are 1150-1550 °C.

INTRODUCTION

Other solidification/stabilization technologies can offer some volume reduction to varying degrees depending on the additives and volumes required. Such as, standard solidification (1: 1.4-2), polymer encapsulation systems (1:1), thermal resin compaction (4:1 max.), and steam reforming (~5:1). To date, researchers have been able to achieve up to 7.6:1 volume reduction, VR, on inorganic sludges (e.g., carbonates) utilizing a microwave System [1]. While the volume reduction of inorganic sludges is limited by the nature of the material (i.e., totally inorganic and not able to undergo pyrolysis), organic sludges or organic resins can undergo much higher VR's when totally pyrolyzed. Tests are currently underway to determine the optimal VR achievable with such material. Unlike organic materials, we have developed several inorganic Ion Specific Media (ISM) to be suitable for microwave or vitrification melting. The VR, in the case of the modified herschelite, is achieved by the nearly total collapse of the leafy matrix, while the modified porous glass microspheres, in turn, act as a frit material in the melt [2].

To date, five types of organic resins (including various anion, cation, mixed-bed and powdex ion exchange resins) and two inorganic media (including a modified herschelite in a granular as well as fines form) have been tested to assure adequate coupling energies for a melt or pyrolysis. Coupling energy is defined as the energy input into the microwave chamber vs that energy reflected (i.e. the absorbed energy available for heating the material). Initial scoping tests were done in 7.0 cm^3 quartz tubes, surrounded by a high temperature insulating material, heating the media with 700 Watts at a set time at 2450 Mhz from an initial temperature of 21.1 °C (70 °F) to a final temperature after heating for 2 minutes. Actual coupling energies were not determined here as the simple proof of heating was an adequate determination to determine the media as a candidate for high temperature microwave treatment. For total pyrolysis, or vitrification, the energy and subsequent temperatures are much higher. In addition to coupling energies and optimal melt temperatures, current testing is focusing on the optimal depth of penetration of the microwave energy into the matrices.

In the case of the microwave vitrification system, a "starter" material (e.g. silicon carbide, SiC) can be added to the first layer of material until coupling occurs and the melt is self-sustaining. It has been found not to be necessary to add it to all the feed as part of the frit. Solid SiC on the crucible walls, or as a coated or thermally treated, internal probe, can also accomplish this phenomena.

This paper will also make a comparison of the new Modular Vitrification System (MVS™) with current market leading technologies (e.g. joule-heated melters, cold-crucible inductive melters , CCIM, plasma torch, or 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 vitrification system, the MVS™, there is nothing in the melt zone other than processed waste (e.g. no discharge valve, susceptors, 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 liner geometry or electrode distances to contend with. Further, higher melt temperatures are achievable allowing for better waste loading, glass quality and leach resistance [3,4,5 and 6]. 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) approach which involves vitrifying a 2-inch melt zone at a time as the module is filled. The MVS™ can handle either solid or slurry feeds (e.g., 40 wt. %) 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 a moving coil approach, or more simply by moving the current up the continuous coil (by way of electronic shunts.)

SYSTEM DESCRIPTIONS AND EXPERIMENTAL RESULTS

Advanced Microwave System (AMS™)

The AMS™ consists of a 500 liter microwave vacuum vessel, a 3 kW microwave power supply with circulator, directional coupler with stub tuner, and microwave compatible vacuum chamber with rotating table. See Figure 1. 3 kW of microwave energy can be supplied to the system (220 V, 35 A, single phase) at 2450 MHz. Partial, or full vacuum, can be maintained on the system, or purge gas/instrument air can be utilized. Material melt temperatures are monitored, as well as controlled at the remote control panel, by both a K-type thermocouple (through the front port) and a infrared pyrometer (through the top-mounted germanium window). The waveguide, fed by the power supplies and the circulation water, consists of a circulator, directional coupler, four stub tuner and E-plane bend into the rear microwave window of the vacuum chamber. See Figure 1 for a photo of the pilot system.

Figure 1. Pilot Advanced Microwave System (AMS™)

Initial AMS™ tests were done in 3-inch diameter quartz tubes, surrounded by a high temperature insulating material (See Figure 2a), heating the media with 700 Watts at a set time at 2450 Mhz. Temperatures ranged from 700 to >900 degrees C during these tests. Figure 2b shows the processing of a modified Herschelite (a specialized, highly Cs selective media) [2] at temperature, illustrating the melt zone with the insulator material removed. The final, volume-reduced, cooled melt is shown in Figure 2c. Similar runs were carried out on organic resins (cation, anion and mixed-bed) as well, to determine the VR resulting from total pyrolysis by microwave. Figure 2d illustrates such a run on cation resin at 900 °C. The resulting product is a pure carbon powder.

(a) Insulation setup (b) Final temperature

(c) Final Herschelite product (d) Final resin product

Figure 2. Advanced Microwave System set up and operation.

<u>Modular Vitrification System (MVS™)</u>

The MVS™ technology is a 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 3 for an overview of inductive heating. Advantages here include:

- Coupling with graphite insert; <u>no</u> 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 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.

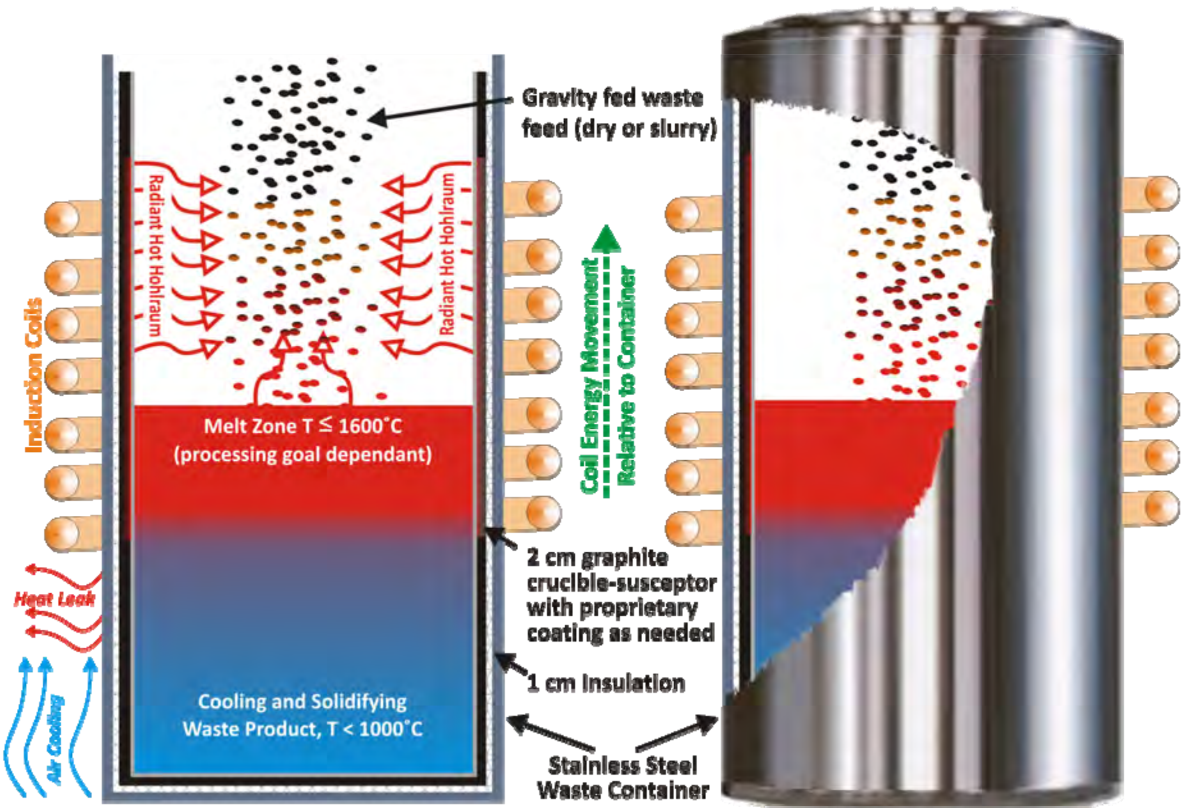

Figure 3. MVS™ Technology Overview – Inductive Heating

In the MVS™, the waste and frit, if utilized, are melted inside the final disposal canister itself, which has been modified to include the MVS™ internal liners. The canister serves a dual role as waste shipping/disposal container and secondary containment. The internal liners consist of the graphite crucible, a fiber wound graphite insulator and, sometimes a Grafoil® (Registered Trademark of Graftech) layer for heat dispersion or reflection. Virtually any disposal canister can be so modified to include the MVS™ liners. 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™ module is stainless steel, a relatively low frequency inductive coil is used. This low frequency (30-60 Hz) is unique to the MVS™ modular technology because it ensures that the

AC inductive field penetrates the stainless shell to heat the graphite. The outside coil is cooled by water coils, while the stainless shell is air cooled by knife jets.

The MVS™ uses a proprietary heating methodology that offers many benefits. It is called the Hot Hohlraum Melting (HHM) method. 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 hohlraum (a form of black body radiation), which serves to heat a shallow layer of molten waste (~ 2 inches in a ≤ 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 vitrified product as uniform as the waste feed.

The key advantages of the Hot Hohlraum 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 (3 and 4). [Similar studies on-going for Tc 99 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™ internal liners is offset by avoided costs for storage and disposal of disposal canisters, due to higher waste loadings (3,4,5 and 6) 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™ 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™ 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™ melter means that the MVS™ 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™ 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 Hohlraum melting method is used with the MVS™. This method ensures a homogeneous vitrified product, delivers a productive processing rate, and virtually eliminates deleterious waste foaming. The Hot Hohlraum Melting (HHM) method 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™ 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) and technetium (Tc-99), 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 volatized elements with the molten waste. However, the cold cap, required here, is not a real cap in the sense that it does not cover the entire surface of the melt pool. This can encourage the volatilization of both Cs and Tc. 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 up to 60% of the Tc-99 in the off-gas, which must then be handled in the secondary waste treatment system.

In contrast, within the MVS™ module, Tc-99 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 and Tc where the off-gas condensates are being analyzed for carry over. While 100% Cs retention has been demonstrated in past pilot runs [3 and 4], the retention of Tc-99 still needs to be confirmed.

Current on-going pilot tests involve inductive scoping studies on Hanford surrogate AN-104 in a) borosilicate glass, b) iron phosphate glass, and c) a proprietary surrogate from a pretreatment process. Once the 6-inch diameter graphite crucible tests are completed, along with the parametric modeling on-going at Graftech, the Hot Cell Pilot Unit will be shaken down and tested at MO-SCI in Rolla, Missouri. It is currently proposed that this same scale unit will then be commissioned in actual hotcell work at the 222S Labs at Hanford on actual waste.

Elimination of the above problems experienced in existing joule melters enables the MVS™ 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. This, of course, assumes that the final waste form has not been compromised [5 and 6]. 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 bench-scale vitrification of AZ-101 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.

Small-scale melts were performed with target waste loadings ranging from 35 to 78 percent following the heating profile described above. In addition, the small-scale melts were repeated using the same heating profile; however, the duplicate melts were given a prescribed cooling profile. This profile included a 1 °C per minute ramp from 1450 °C to 600 °C with a 24 hour dwell at 600 °C followed by a rapid cool down (in the crucible) to room temperature on a steel plate. The TCLP was performed on small-scale and small-scale duplicate samples with target waste loadings of 45, 50, 55, 60, and 65 percent.

The TCLP was performed on the large-scale glassy samples. The analytical results were compared to the Universal Treatment Standard (UTS) limits. From the small-scale data, cadmium was identified as the limiting element of concern. The TCLP cadmium results of the large-scale melts and small-scale melts versus waste loading were reported [5 and 6].

The toxicity characteristic of the glasses was dependent on waste loading, as indicated by the increase in cadmium release over the entire range. In general, the results indicate that an increase in waste loading increases the cadmium leach rate. All resulting glasses met the UTS limit for all analytes with one exception. The large-scale 66% waste loading exceeded the cadmium UTS limit.

In an MVS™ 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™ 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™ 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™ would offer distinct advantages in regard to safety, cost and schedule performance (See Table 1). 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 with tanks.

One of the most important features of the MVS™ is its modularity and ability to readily adapt to a wide variety of vitrification needs and feeds. The MVS™ 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.

The MVS™ has been tested at both bench-and pilot-scale, using graphite crucibles at inside diameters up to 5 inches and operating at temperatures of up to 1550 degrees C (approximately 400 degrees C hotter than conventional joule melters) and on both solid and slurry feeds (40-50 wt. %). Loadings of simulated waste up to 68% in borosilicate glass have been achieved. PCT and TCLP performance (leaching tests) have been excellent for a wide range of Hanford waste compositions. Over 100 pilot runs have been completed, with some 30 experimental runs for DOE on Hanford surrogates, and performance requirements were met [3,4,5 and 6].

SUMMARY AND CONCLUSIONS

While the MVS™ 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™ 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.

Possible issues encountered for current approaches are outlined in Table I, while itemizing the key advantages of the MVS™ over these conventional technologies. A summary of the MVS™ approach *vs* these alternative methodologies is further outlined. Finally, a comparison of the MVS™ with the four primary conventional approaches regarding the nine criteria predominate in vitrification safety case design concerns is also presented in Table I.

Evaluation of MVS™ Against Competing Vitrification Approaches

Metric	Kurion	Joule-Heated	CCIM	Plasma	Bulk Vit
Containment	**Double - Single use crucible + waste container**	Ceramic	Water cooled, precision fabricated, crucible	Ceramic	Ceramic & Sand
Components in process zone	**n/a**	Electrodes, Thermocouples	Starter susceptors	Torches, Thermocouples	Electrodes, Thermocouples
Molten Pouring	**n/a**	Yes	Yes or Ladle Pour	Yes or Ladle Pour	**n/a**
Heating hot spots	**n/a**	Yes – line source	Yes – line source	Yes – point source(s)	Yes – line source
Material additions that affect Off-gas or Melt Chemistry	**n/a**	**n/a**	Yes – sacrificial susceptor for starter path	Yes – torch gases	Yes – sacrificial susceptor for starter path
Coupling with waste-glass	**n/a**	Yes	Yes	**n/a**	Yes
Maintenance and disposal of contaminated melter equipment	**n/a**	Refractory, valve, electrodes, thermocouples	Crucible, valve	Refractory, valve, Torches, thermocouples	**n/a**
Special method to raise temperature to initiate glass conductivity	**n/a**	Yes – Heaters	Yes – Sacrificial susceptor ring or chain	**n/a**	Yes – Sacrificial susceptor path
Active melter component challenges	**n/a**	Arcing between electrodes and thermocouples, metal slag, valve reliability, pour controls	Arcing between susceptor and walls, arcing between wall segments, coolant failures, valve reliability, pour controls	Management of hot gas, valve reliability, pour controls, management of Torch gases	Arcing between electrodes and thermocouples, metal slag

Table I. MVS™ Mitigates Safety Case Design Concerns

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