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Cold Crucible Induction Melter (CCIM) Testing on Glass Ceramic and Ceramic Waste Forms

Fuel Cycle Research & Development

Prepared for
U.S. Department of Energy Office of Nuclear Energy
Materials Recovery and Waste Forms Development Campaign

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SUMMARY

The U.S. Department of Energy Office of Nuclear Energy's Fuel Cycle Research and Development (FCR&D) program is developing advanced high level waste (HLW) forms for the immobilization of the long-lived radionuclides resulting from future potential reprocessing of the used nuclear fuel from commercial reactors. One of the program's goals is to have orders of magnitude improvements in durability (compared to the reference borosilicate glass waste form for HLW), to facilitate lower costs including less expensive and complex processing, to lower storage costs and to provide for final disposal of the waste in a deep geological repository. Both glass ceramic and ceramic waste forms are being developed and evaluated as possible improvements to borosilicate glass to achieve these objectives.

The cold crucible induction melter (CCIM) melts material inductively by creating an eddy current inside the melt pool using a water-cooled, high-frequency electrical coil that surrounds the outer walls of the CCIM. The CCIM design is much less sensitive to the waste form chemistry than joule-heated melters (the reference used in the U.S. for processing borosilicate HLW glass), which allows feeds with more diversified chemistry and lessens the burden put on the pretreatment processes. The CCIM can also run at much higher temperatures to allow for processing alternative waste form chemistries such as those containing crystalline phases. Therefore, the CCIM technology is attractive for glass ceramic and ceramic waste form processing.

The CCIM Pilot Plant at the Idaho National Laboratory (INL) is being used for glass ceramic and ceramic waste form process demonstrations in support of the FCR&D program. In FY12, demonstration testing was conducted on a glass ceramic composition. This test campaign demonstrated the ability of the CCIM to:

- initiate and couple to a low electrical conductivity waste form (as compared to borosilicate glass)
- consistently feed a slurry of representative feed
- build a cold cap (even with a dilute feed) and break up the cold cap with an air bubbler
- start and stop several pours
- pour glass ceramic into receipt containers
- perform post-pouring thermal treatment on glass ceramics.

The testing also revealed some issues with the INL CCIM system including limitations with the pour spout design to allow for controlled pouring at higher temperatures and allow for pouring of glass ceramics containing some crystalline phases and limitations in operational frequencies to support processing lower electrical conductivity melts.

Additional testing on the glass ceramic waste form was conducted in FY13 and FY14. This testing saw limited success as no glass pours were made in the testing.

In FY14, testing was conducted on a titanate ceramic waste form composition. The composition tested was a formulation identified to melt at lower temperatures, however, was known to have limits with product quality (i.e. not result in the desired ceramic phase assemblage). This testing demonstrated that:

- initiation of the melt could be achieved using a supported titanium ring configuration
- the CCIM frequency could be adjusted to couple to the ceramic waste form composition with higher electrical conductivity that typical borosilicate glasses and the glass ceramic waste form
- dry ceramic batch material could be added to the ceramic waste form melt.

Limitations with the INL CCIM drain system design were again identified and precluded pouring of the ceramic waste form from the melter.

In FY15, melter modifications are being made to the INL system in an effort to improve processing of the glass ceramic and ceramic waste forms. The new melter has features that will provide more reliability, operability and maintainability as well as greatly facilitate the tapping and draining of high temperature waste forms. Modifications to the radiofrequency (RF) system will allow the CCIM to reach higher operating power levels.

A CCIM campaign is planned in FY15 on the glass ceramic waste form composition. The primary goal is to demonstrate sustained processing of this waste form. Future demonstration testing on the ceramic waste form is also planned.

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ACKNOWLEDGEMENTS

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1 INTRODUCTION

An objective of the Fuel Cycle Research and Development (FCR&D) Program is to make a U.S. fuel cycle more effective by the development of the next generation of radioactive waste management technologies. Fuel cycles that perform any separations of used nuclear fuel will generate wastes from both the separation processes and the fabrication of advanced fuels or targets containing reprocessed materials to be transmuted. Glass ceramics and ceramics waste forms are being developed for immobilization of high level waste (HLW) by the melt process as alternatives to borosilictate glass. The glass ceramic is being developed to double the waste loading relative to borosilicate glass, and may also result in an incremental increase in waste form performance. The ceramic waste form is being developed because of its superior durability relative to borosilicate glass. The ceramic waste form should have orders of magnitude improvements in durability (compared to reference borosilicate glass waste form HLW) which will reduce the reliance on engineered and natural barrier systems and thereby open new disposal options and lower cost disposal. In addition, developed advanced waste forms and processes should facilitate lower cost management to include less expensive and complex processing, lower storage and disposal costs, and be more flexible to wider ranges of disposal environments and fuel cycles. Glass ceramic and ceramic waste forms are being evaluated as possible improvements to borosilicate glass to achieve these goals; and concurrently the cold crucible induction melter (CCIM) technology is being advanced as a melting method to produce these advanced waste forms.

Glass ceramic waste forms take advantage of both crystalline and glassy phases where “troublesome” elements (e.g. those with low solubility in glass) and/or very long-lived radionuclides partition to highly durable ceramic phases with the remainder of the HLW elements residing in the glassy phase. The ceramic phases are tailored to create certain minerals (i.e. unique crystalline structures) that will very effectively host the radionuclides by binding them in their specific crystalline network yet, at the same time, do not adversely impact the residual glass network.

Ceramic (or crystalline) waste forms incorporate the radionuclides in the waste as part of the crystal structure in a crystalline, multiphase assembly. As such, ceramic forms are tailored to create certain minerals (i.e. unique crystalline structures) that will host the radionuclides by binding them in their specific crystalline networks.

The CCIM melts material inductively by creating eddy currents inside the melt pool using a water-cooled, high-frequency electrical coil that surrounds the outer walls of the CCIM. Spaced cooling in the melter wall tubes create a steep temperature gradient that exists near the walls. This results in a “frozen” material layer that forms along the inside walls of the CCIM and separate the walls from the molten material, thus, protecting the melter walls from corrosion. The CCIM design is much less sensitive to waste form chemistry than joule-heated melters (the reference melter technology used in the U.S. for processing borosilicate HLW glass), which allows feeds with more diversified chemistry and lessens the burden put on any pretreatment processes. As such, the CCIM runs at much higher temperatures as is necessary to allow for processing alternative waste form chemistries such as glass ceramics and ceramics.

Recent advancements with the CCIM and, moreover, deployment of the technology in waste vitrification plants in France and South Korea, provide impetus for evaluating the CCIM as an attractive means to process glass ceramic and ceramic waste forms to support future fuel cycle initiatives. Therefore, a key element of the advanced waste form technology development effort is to demonstrate processing of glass ceramic and ceramic waste forms in the CCIM. This report provides a summary of CCIM test campaigns on glass ceramic and ceramic waste forms conducted to date and development plans for the future.

2 OBJECTIVES

The overarching objective of the current efforts involving the CCIM Pilot Plant located at the Idaho National Laboratory (INL) is to demonstrate that glass ceramic and ceramic waste forms developed to immobilize HLW from advanced fuel cycles can be processed using the CCIM technology. This includes demonstrating that the melting process can be initiated through induction, melting can be sustained to reach "steady state" conditions, and the waste form product can be controllably tapped and poured from the melter into a receiving vessel.

Once CCIM process demonstration is achieved, a number of other objectives regarding glass ceramic and ceramic processing behavior and product quality are of interest. These include:

- performing mass balances to determine yield, constituent partitioning, and volatility to the off gas system
- determination of processing rates including surrogate waste feed rates and waste form production/pouring rates
- evaluation of melting behavior including cold cap coverage, foaming behavior, etc.
- demonstration of melter operations under normal and off-normal conditions including demonstrating stopping and starting of glass pouring, melter idling, etc.
- demonstration of pouring into different receipt container configurations including a 2 foot diameter canister (consistent with the reference container currently used for HLW vitrification in the U.S.)
- evaluation of different controlled cooling profiles including what would be representative of a U.S. HLW canister cooling under natural convection conditions in a production plant environment
- characterizing waste form products produced in the CCIM including phase assemblage determination, microstructure and relative durability and comparing these measurements to products produced at lab scale at both PNNL and SRNL.

3 COLD CRUCIBLE INDUCTION MELTER PLATFORM AT INL

The Idaho National Laboratory pilot scale CCIM Pilot Plant is located and operated in Bay West-1 (W-1) of INL's Idaho Engineering Demonstration Facility (IF-657). The INL CCIM platform is comprised of the following 8 systems as depicted in Figure 3-1:

- Radiofrequency (RF) generator power system
- Feed system
- Crucible system
- Molten product pouring system
- Crucible and generator cooling systems
- Off-gas system
- Process monitoring and control system
- Poured melt controlled cooling collection system.

The slurry feed system employs a feed tank equipped with a stirrer, sparger and recirculating loop. Slurry in the form of a liquid simulant HLW containing additives for waste form formation is fed to the melter using a recirculating pump that meters feed to the melter and recirculates excess feed to the feed tank. A hopper on the mid-level above the melter is deployed for feeding waste surrogate and frit in solid particulate form. The 267 mm inner diameter CCIM vessel is constructed from 304L stainless steel and consists of lower manifold, upper manifold, and cooling tubes. The cooling tubes are oriented vertically to form the crucible cylinder. The induction power system consists of a variable high frequency generator that can operate in frequency ranges from 200-400 kHz and 1.5-4 MHz to produce a maximum power of 75 kW (however, overpower interlocks limit the maximum power to 60 kW). A conductive metal (copper) Faraday cage encloses the melter and induction coil system to minimize worker exposure to electromagnetic radiation (Figure 3-2). Figure 3-3 provides a view of the INL CCIM melter in its Faraday protective metal cage. The molten glass is drained semi-continuously through a resistively heated bottom drain assembly. The off-gas system consists of a heated duct to the thermal reaction chamber, athermal reaction chamber, an off-gas quench section, a wet scrubber system, a wet electrostatic precipitator system, a charcoal bed column container, and an induced draft fan.

Due to the current objectives and nature of the of the CCIM processability testing for both glass ceramic and ceramic waste forms, the off gas system components are only sparsely operated. Future testing will assess the capabilities of these components to capture various off –gas constituents of the melt. The air permit for the CCIM Pilot Plant allows for unabated discharge of all CCIM gaseous effluents.

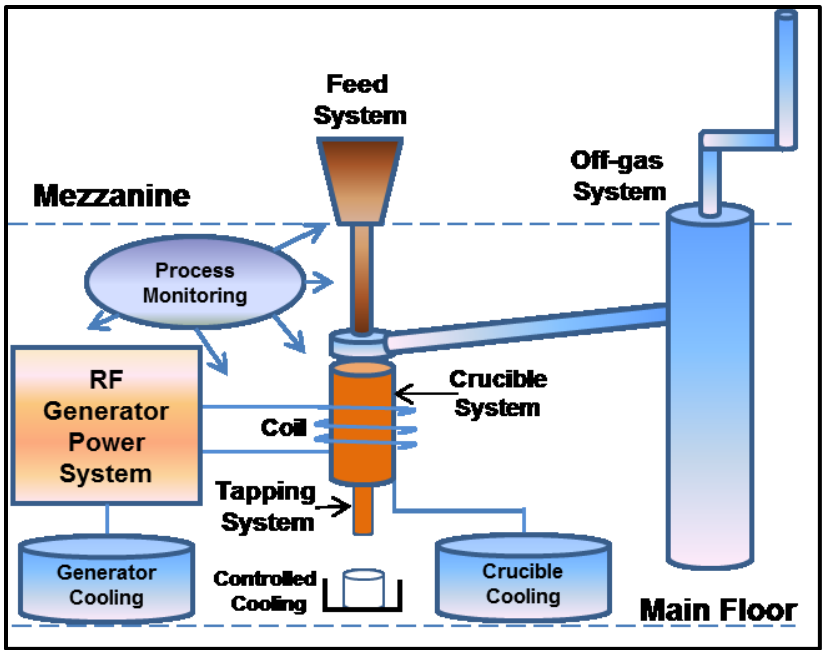

Figure 3-1. Simplified schematic diagram for the INL CCIM pilot scale platform.

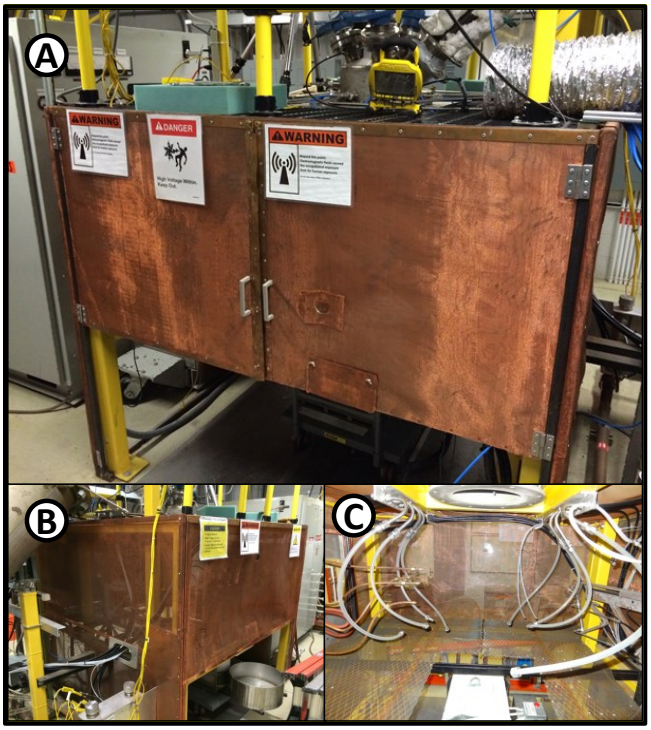

Figure 3-2. Photos of the CCIM Faraday Cage. (A) is the 'front' where the inside of the cage is accessed. (B) shows the opposite (back) side of the cage. (C) shows the inside of the cage with the crucible and induction coil removed.

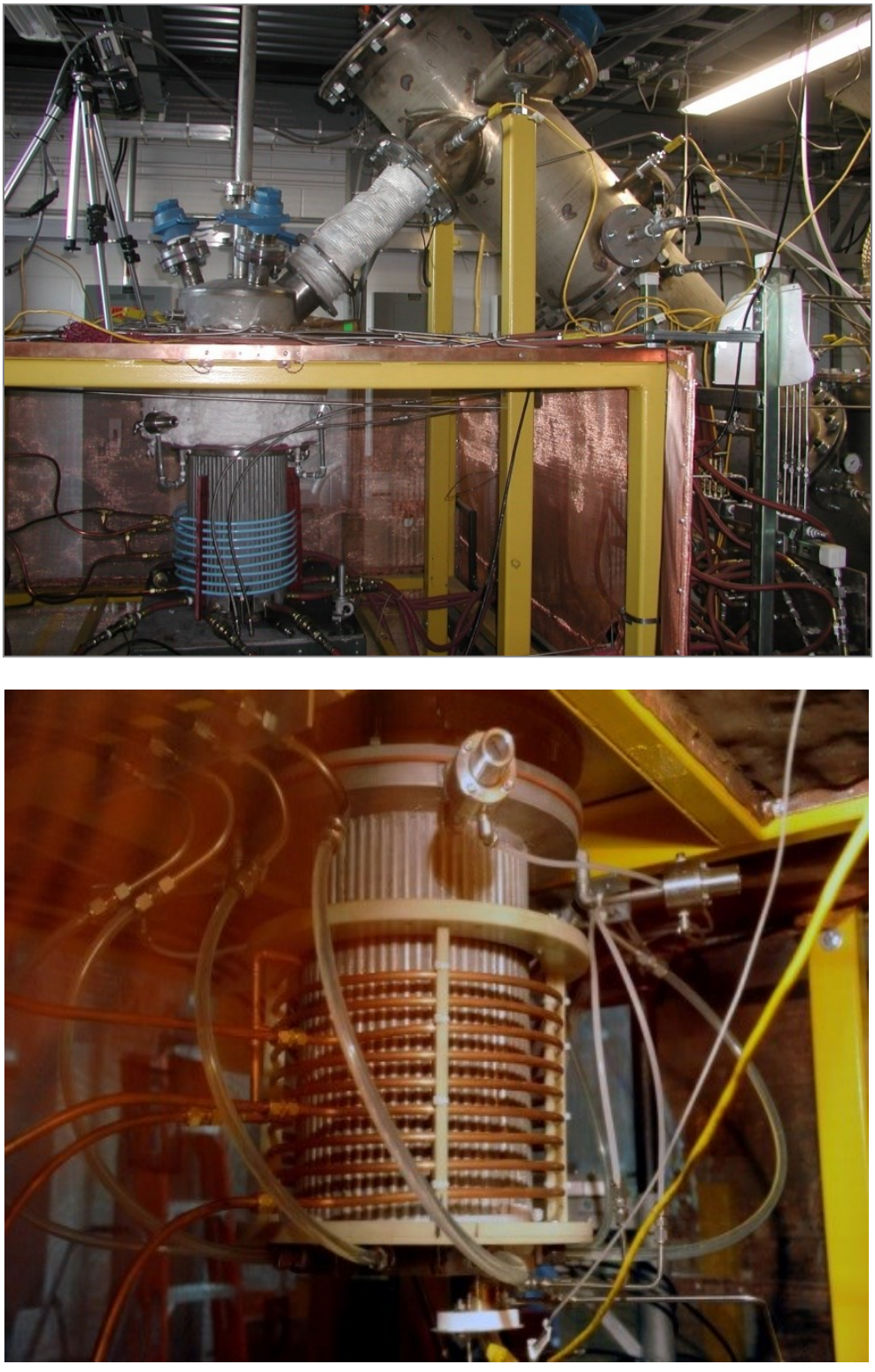

Figure 3-3. INL CCIM melter in the copper protective metal cage.

4 FY12 GLASS CERAMIC WASTE FORM TESTING

The FY12 CCIM demonstration campaign focused on a glass ceramic composition to immobilize a combined surrogate HLW stream consisting of transition, alkali, alkaline earth and lanthanide metals. The PNNL glass ceramic formulation developed at the laboratory scale targets the formation of the following three stable crystalline phases:

- powellite ($XMoO_4$) where X can be (Ca, Sr, Ba, and/or Ln (lanthanide))
- oxyapatite ($Y_x,Z_{(10-x)}Si_6O_{26}$ where Y is an alkaline earth, Z is Ln
- lanthanide borosilicate ($Ln_5BSi_2O_{13}$).

These three phases incorporate the specific waste components (e.g. Mo) that are above the solubility limit of a single-phase borosilicate glass. The glass ceramic is designed to be a single-phase melt, just like a borosilicate glass, and then crystallize the targeted crystalline phases upon slow cooling. To support melter testing, a data package was produced that provided property data for electrical conductivity, viscosity and crystallization behavior (Crum 2012). The glass ceramic composition selected for CCIM testing was designated as CS/LN/TM-Mo-6.25.

4.1 Objectives

A run plan was developed by INL to guide the testing and was contained in the testing logbook. The run plan included the test objectives, testing conditions, composition of the glass ceramic waste form, and sampling and analysis guidance. A sequence of key steps for the testing was also provided.

The overall test objective was to provide an initial demonstration of the processability of the glass ceramic composition using CCIM technology. Specific objectives for this initial glass ceramic surrogate test were as follows:

- demonstrate the ability to prepare and feed a nonradioactive slurry consisting of a combination of glass ceramic forming additives and the appropriate simulated HLW raffinate
- demonstrate the ability to melt the surrogate HLW composition and the appropriate glass ceramic chemical additives
- demonstrate the ability to intermittently tap and pour the molten glass ceramic mix from the melter
- demonstrate the ability to perform post drain waste form cooling for the glass ceramic waste form with a controlled system reflecting that of standard canisters cooling under natural conditions and under conditions that reflect faster than natural cooling conditions
- determine qualitatively if the specific glass ceramic waste form produced would fill a canister with a 2 foot diameter (U.S. standard diameter size for a HLW canister) without crystallizing before the glass flows to the canister outer walls
- evaluate the final microstructure and phase assemblage of selected glass ceramic samples
- obtain process data on an opportunistic basis to determine and assess processing rate, cold-cap coverage, foaming potential and volatility from the melt.

4.2 HLW Simulant Liquid CCIM Feed and Dry Surrogate HLW

The CCIM Pilot Plant waste form simulant (CS/LN/TM-Mo-6.25) was based on lab scale melting tests conducted at PNNL. Simulants were prepared with the proper waste form precursor additives by NOAH Technologies of San Antonio, TX in liquid form (for pilot plant melter feeding) and by MOSCI

Corporation of Missouri Rolla in amorphous solid oxide form (for initial crucible charging). Nd was used to represent both one of the many fission product lanthanides and any actinides (i.e. U, Pu, Np, Am, and Cm) that could still remain after solvent extraction.

To reduce costs, modifications were made to the CS/LN/TM-Mo-6.25 original surrogate (in both oxide and nitric acid form). Table 4-1 shows the PNNL targeted glass ceramic composition and the modified INL CCIM targeted glass ceramic composition. The calculated amount of additives required in the surrogate melter waste feed for the pilot scale CCIM test campaign are also shown. The first five chemicals listed in the table were the glass ceramic precursor additives (as determined by PNNL) and are not part of the surrogate HLW inventory expected from proposed future reprocessing.

Since cadmium, antimony, and selenium (Cd, Sb, and Se) were present at very low concentrations in the HLW surrogate, they were removed from the simulant to eliminate generating unnecessary RCRA hazardous waste. At these concentrations, these three elements would be expected to readily dissolve into the glass phase and their removal would have no effect on the formation of the desired glass ceramic phases. To the contrary, the noble metals in the surrogate waste are very insoluble in the glass and become nucleation sites for crystallization and subsequent ceramic phase formation. To be cost effective, the total noble metal content was reduced to 0.1 wt %. To reduce costs further, Ru represented all the noble metals in the waste composition. Although not optimal, it was thought that noble metal concentration at 0.1 wt % would provide sufficient nucleation sites for crystallization upon cooling while minimizing costs for the melter experiments. After the modifications were made to the PNNL targeted glass ceramic composition, the composition was renormalized to obtain the surrogate glass ceramic feed composition (both liquid and solid) for the melter test.

It should be noted that there was a low solids content in the nitric acid based feed. The initial solids loading in the feed was 186 g/L with a portion of the nitrate and carbonate additives further dissolving. Only minor attempts were made to concentrate the feed. In actual operations, concentration of the feed would likely be pursued through evaporation or calcination.

4.3 Initial Melting Observations

On June 20, 2012, the CCIM research team attempted to start the CCIM Pilot Plant by electrically inducing a current to the melter containing ~25kg of the HLW (dry oxide) particulate surrogate. The first attempt at initiation was conducted using the conventional method used in the INL CCIM test bed. That is, a conventional carbon steel serpentine ignition ring was placed into the feed bed. Additionally, a small amount of lithium was added to the surrogate HLW in an attempt to increase its conductivity to a level more compatible with the design frequency range of the RF Generator (which was established previously for melting glasses). The need for conductivity adjustments were not surprising since testing and analysis conducted by PNNL and reported in the data package revealed the conductivity to be approximately 10-20 S/m in the process temperature range corresponding to a melt temperature frequency too high for the RF generator's nominal design level. It should be further noted that electrical conductivity values described above were measured on a laboratory developed composition (GC-Mo-Li-6.25) and the simulant composition used in the testing was predicted to have even lower electrical conductivity (Table 4-2). Though a visible glow was present after ~30 minutes while operating at a voltage level of 8.7 kV, a melt did not progress through the whole bed resulting in unsuccessful ignition via inductive coupling. Figure 4-1 shows a photograph of the partially melted material after the unsuccessful first test.

Table 4-1. Modifications to the original PNNL targeted glass ceramic composition and additives/concentrations for preparing the CCIM surrogate waste (CS/LN/TM-6.25 Mo)

Oxide	PNNL targeted composition wt.%	Modifications	INL targeted composition wt.%	Additive	Mass additive kg
Al_2O_3	5.00%	keep	5.04%	Al_2O_3	3.73
B_2O_3	9.40%	keep	9.46%	B_2O_3	12.44
CaO	4.26%	keep	4.29%	$CaCO_3$	5.67
Na_2O	3.54%	keep	3.57%	Na_2CO_3	4.52
SiO_2	32.82%	keep	33.06%	SiO_2	24.46
MoO_3	6.25%	keep	6.29%	MoO_3	4.66
SrO	1.57%	keep	1.58%	$Sr(NO_3)_2$	2.39
BaO	3.53%	keep	3.55%	$Ba(NO_3)_2$	4.48
Rb_2O	0.68%	keep	0.68%	$RbNO_3$	0.80
Cs_2O	4.60%	keep	4.63%	$CsNO_3$	4.74
Y_2O_3	1.00%	keep	1.01%	$Y(NO_3)_3*6H_2O$	2.54
Ce_2O_3	4.96%	keep	4.99%	$Ce(NO_3)_3*6H_2O$	9.78
Eu_2O_3	0.27%	keep	0.28%	$Eu(NO_3)_3*6H_2O$	0.52
Gd_2O_3	0.26%	keep	0.26%	$Gd(NO_3)_3*5H_2O$	0.46
La_2O_3	2.53%	keep	2.55%	$La(NO_3)_3*6H_2O$	5.01
Nd_2O_3	8.38%	keep	8.44%	$Nd(NO_3)_3*6H_2O$	16.28
Pr_2O_3	2.32%	keep	2.33%	$Pr(NO_3)_3*6H_2O$	4.55
Sm_2O_3	1.72%	keep	1.73%	$Sm(NO_3)_3*6H_2O$	3.27
ZrO_2	4.77%	keep	4.81%	$ZrO(NO_3)_2*2H_2O$	7.72
PdO	0.03%	**remove**			
RhO_2	0.12%	**remove**			
RuO_2	0.32%	**reduce to 0.1%**	0.10%	$Ru(NO)(NO_3)_3$	0.18
Ag_2O	0.18%	keep	0.18%	$AgNO_3$	0.19
CdO	0.18%	**remove**			
Sb_2O_3	0.02%	**remove**			
SeO_2	0.13%	**remove**			
SnO_2	0.11%	keep	0.11%	SnO_2	0.08
TeO_2	1.05%	keep	1.06%	TeO_2	0.78
Sum	**100.00%**		**100.00%**		**119.24**
Waste loading	**44.98%**		**44.59%**		

Table 4-2. Predicted electrical conductivity values (S/m) for the Mo-Sci simulant and the GC-Mo-Li-6.25 lab-scale composition

Temperature, °C	Predicted σ, S/m	
	Mo-Sci Simulant	GC-Mo-Li-6.25
1350	11.82	17.44
1300	9.41	14.08
1250	7.39	11.21
1200	5.70	8.79
1150	4.32	6.77
1100	3.21	5.12
1050	2.33	3.79
950	1.13	1.93
850	0.49	0.87
750	0.18	0.34

Figure 4-1. The cooled torus (around the initiator ring) of the partially melted particulate (CS/TM/LN-6.025 Mo) HLW surrogate. Note the change in phase from crystalline to glassy to sintered material as the radial distance from the center of the torus. Also note the convective pattern of the cooled material demonstrating the high mixing achievable with induction melting.

4.4 Sustained Melting Observations

The design-basis frequency for operation of the INL CCIM was established at 2.0 MHz to align with typical electrical conductivity of 20 S/m for HLW borosilicate glasses. As mentioned, the electrical conductivity of the glass ceramic waste had a significantly lower electrical conductivity of 5-10 S/m. After two unsuccessful trials to initiate the melting process, successful coupling was achieved with a thick titanium ring as an initiator as opposed to the previously used serpentine wire. To support and assist the induction ignition of this resistive bed, conductive sodium carbonate was added in and around the titanium ring initiator on top of the bed and to a lesser extent throughout the bed. These changes enabled a melt ignition; however, high power levels (60-65 kW) were required to maintain the melt leading to inefficiencies in energy use and near automatic shutdown of the RF generator. Nonetheless, melting was sustained and the melt appeared to be well mixed at temperatures averaging 1250° C.

Once the starting bed was melting consistently for just under an hour, the CCIM Pilot Plant continued to operate with slurry feed rates between 1 and ~ 2kg/hr. At the higher feed rate an observable cold cap begin to appear above the melt. However, the feed rate of the liquid surrogate HLW with glass forming frit additives was not increased above its highest level and feeding lasted for only 45 minutes. Except for one time the cold cap never became considerably large enough to approach bridging and the air sparger easily broke up the cold cap. Additionally, the slurry feed was too dilute with nitric acid and water to allow for proper induction heating efficiency and as a consequence the inherent benefits of high waste throughput could not be obtained under these dilute feeding conditions. Future testing in FY15 will include concentration of the feed (e.g. 10M nitric acid instead of 5M) to accurately assess cold cap behavior, and liquid/slurry feed melting behavior and throughput.

4.5 Tapping and Pouring Observations

The drain and heater assemblies used for both the July 3, 2012 and July 10, 2012 glass ceramic CCIM test runs were constructed and operated in the same manner. The 900 watt rated cylindrical ceramic drain heater (Figure 4-2) is 6 inches long with a 2.31inch outside diameter and consisted of a round ceramic tube containing an internal heating element wire weaved along its interior.

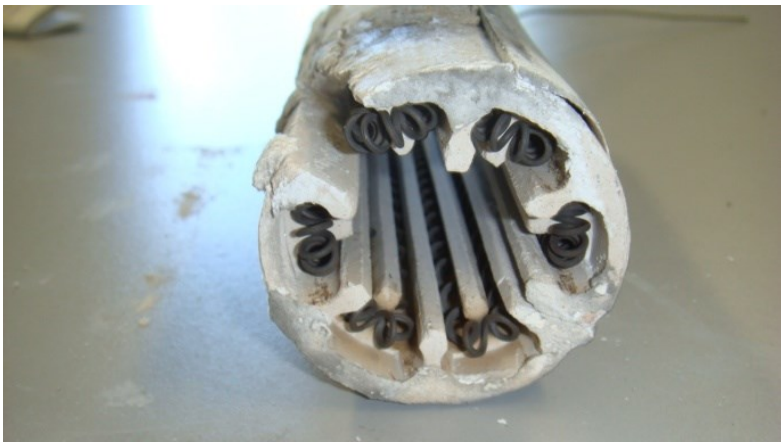

Figure 4-2. A front view of the clamshell-type ceramic (electrical resistance) heater. The heater gets inserted in the annulus between the CCIM's drain tube and shell as shown in Figure 4-4.

Before the first test run on July 3rd, the tubular ceramic drain heater was slid into the drain shell's annulus around the drain tube, as shown in Figure 4-3, and held in place by set screws. The complete drain

assembly was placed through and into the bottom cooled pie-shaped segmented plate of the CCIM crucible, and anchored with high temperature putty, as shown in Figure 4-4.

Figure 4-3. The drain shell and tube assembly removed from the melter without the heater in the annulus. Note the presence of solidified glass ceramic waste form in the drain tube.

Figure 4-4. The complete drain assembly installed in the bottom of the pilot plant crucible.

The drain shell and tube were constructed of Inconel 625 with the drain tube attached to a round Inconel plate welded to the top of drain shell. After installing the assembly in the bottom of the CCIM, the drain tube extended past the end of the shell by ~½ inches. The dimensions of the drain shell, tube, and plate are as follows:

- Drain Shell: 6.1” long x 2.5” OD x .065” wall
- Drain Tube: 6.6” long x .50” OD x .065” wall
- Drain Plate: 2.35” OD x .505 ID x .125” Thick

The July 1, 2012 test run began at 5:30 am and initiation of the melt was achieved with the titanium ring and a higher recommended lithium and potassium carbonate salt loading to improve conductivity. In preparation for melter tapping, at 11:30 am, the ceramic drain tube heater was turned on to 7.4 amps to initiate the first draining. The temperature of the drain heater, based on a specially placed TC, rose to 1100° C in 20 minutes. Draining of the CCIM started at 12:10 pm and lasted for approximately 6 minutes (Figure 4-5). During this time, the drain temperature ranged between 1100 and 1200° C as determined with a 2-color hand held pyrometer. During the end of the desired draining period the vacuum on the CCIM crucible was adjusted from 3" to 13" of water to determine if this would enhance slowing of the pour, and therefore, assist in stopping the pour. Once vacuum reached 13" there was a noticeable slowing of the draining process and drain stoppage was successful.

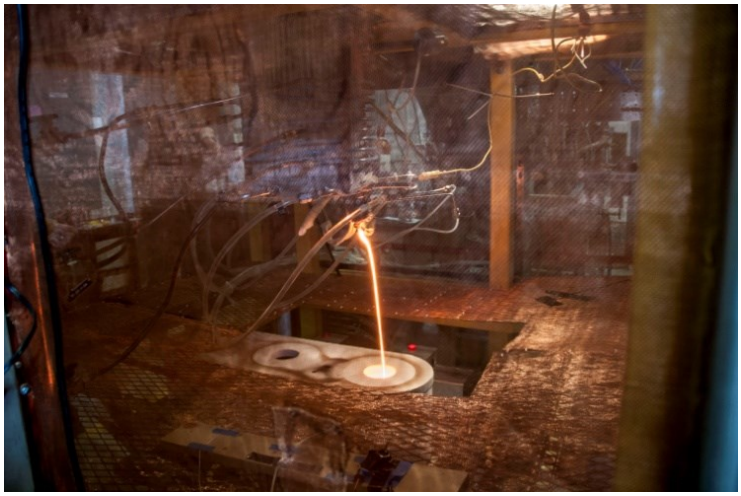

Figure 4-5. The first successful CCIM glass ceramic molten waste form tapping and draining into a temperature controlled graphite canister (surrounded by an insulated mantle). This particular pour was controlled cooled according to the canister centerline cooling profile for a standard U.S. HLW canister of 2 foot diameter.

After 6 minutes of draining, the temperature of the heater slowly started to decrease and the digital readout on the rheostat went to 0. The run was then shut down to investigate the unexpected heater failure.

Once the CCIM reached a safe temperature, an attempt to remove the entire resistive heater from the drain shell was made. Only the lower half of the heater could be removed from the shell because the upper half of the heater had adhered to the drain shell (Figure 4-6). Since this was not a normal occurrence (i.e. not observed during previous glass processing), the entire drain system had to be removed from the CCIM. When looking at the drain it was noted that the molten mass in the crucible had melted through the top part of the drain shell-made of the Inconel (melting temperature 1400 degrees C) as indicated in Figure 4-7 and more than likely shorted out the ceramic heater.

Figure 4-6. Drain shell outside surface after failure.

Figure 4-7. Drain shell showing the internally damaged ceramic heater

The July 1, 2012 run was conducted in the same manner as the earlier run but with a new drain shell and heater. The run began at 5:30 am. At 12:00 pm the heater was turned on to 7.4 amps to commence the pour for the "½ X" (i.e. cooled twice as slow as the canister centerline cooling profile) controlled cooled waste form. The temperature of the heater elevated to 1100° C in 20 minutes. By 1:00 pm the temperature reached 1250° C.

At 1:05 pm a small amount of glass appeared from the end of the drain tube but appeared to have solidified there. An attempt was made to break the glass off of the end of the drain tube but failed. It was determined that the problem was that the ½" portion of the drain tube that was exposed to the atmosphere was not getting hot enough to keep the flow progressing through the tube. Attempts were then made to insulate the end of the tube.

A small round doughnut shaped piece of insulation was then placed on the exposed portion of the drain tube. The temperature on the heater then increased to 1350° C and 45 minutes later the CCIM started to drain as indicated in Figure 4-8. The first drain was a "2X" controlled cooled graphite mold (i.e. cooled twice as fast as the canister centerline cooling profile) and lasted approximately 4 minutes. The second drain, which was allowed to cool under ambient conditions into a 4" graphite mold, also lasted approximately 4 minutes. The temperature during this last drain was 1200° C as determined with a hand held 2 –color pyrometer.

Figure 4-8. Third drain of the CCIM test run (ambient cooled). Consequently it was the fasted cooled of all three pours and the heating mantles for controlled cooling remained off.

At 3:19 pm, the drain was turned back on at 7.4 amps. At 4:43 pm, the draining started and then suddenly stopped. The heater temperature then started to decrease and the rheostat moved to 0. Once the CCIM reached a safe temperature, it was determined that, as in the first run, the molten mass in the crucible had melted through the top part of the drain shell and shorted out the heater.

4.6 Pouring into Containers and Controlled Cooling

During pouring events, glass ceramic from the melter was poured into specially designed canisters in heating mantles in an attempt to bound possible post-melt cooling conditions using controlled cooling schedules (i.e. to mimic producing glass ceramic waste forms in standard waste canisters of full and larger scale diameter) (Figure 4-9). Three pours were successfully made into the specially designed canisters. These pours occurred over two separate days (i.e. July 1 and July 3) and all three involved canisters 4 inches in diameter with 10 inch long graphite cylinder molds. The 3 canisters each contained separate single pours from the CCIM, which represented draining about 2.5 inches of height from the melter.

Figure 4-9. The three heating mantle containers for holding the graphite molds/canisters used for collecting pours from the CCIM. The system is located on rails below the melter so that is can be positioned for each CCIM pouring event without personnel access inside the Faraday cage.

For the collection of quantitative data during and after melter pours, each of the three cylinders were equipped with thermocouples to record temperature changes in the glass ceramic, both radially and axially, over the controlled cooling time period. The thermocouples were connected to a data recorder via leads to the existing CCIM Pilot Plant data acquisition system. For each of the pours, one of the radial thermocouples was used as the dynamic set point in a controlled slow cooling scheme with the heating mantles. The heating mantles were 8 inches in diameter and consisted of 2 halves in a clamshell arrangement. The mantles were specified to provide constant heating to temperatures as high as 1100° C. Slow controlled centerline cooling of glass ceramics in the cylindrical canisters occurred by connecting each of the heating mantles to a programmable controller to ensure the melt was slowly cooled according to the desired schedule. The last pour, which was to coincide with completion of the test run, was to consist of draining the remaining melter contents into a 2 foot diameter shallow canister. Due to drain failure this final pour was not completed.

The procedure used for the controlled cooling and observations concerning those pours are provided below:

- Preheated the first canister to ~1000° C after it was positioned under the crucible drain
- Tap the crucible drain by heating the drain tube and pour long enough to fill a canister assuming a 2.5" CCIM height drop to fill each canister. The pouring method used the drain heating methods outlined in the section below. As described in the section below pours took longer and required more heat due to solidification of some phases within the glassy matrix in the drain line resulting in a highly viscous material.
- De-energized the pour spout heaters and stopped the melt draining by using a wood handled rod equipped with a ½" metal ball at the end that was pre-cooled with tap water
- Covered the mantle

- Allowed the sample to cool naturally to about 980° C.
- Initiated the controlled cooling program to regulate the desired cooling rate automatically to the desired cooling schedule. For example, for the waste form specimen shown below in Figure 4-10, the cooling rate was set at ~ 9 ° C/hr resulting in cooling for about 2 days 17 hours according to the canister centerline cooling profile. During this time all 3 TCs were logged in space and time over the whole controlled cooling period. Additional cooling profiles and their associated cooled melt pours in the canisters are described in Figures 4-11 and 4-12.

Figure 4-10. The first "1X" glass ceramic pour in its 4 inch diameter graphite mold after cooling, solidification and removal from its cooled heating mantle. 1X indicates a rate of cooling reflecting the slowest possible cooling rate for a standard 2 foot diameter disposal canister (i.e. the canister centerline). Note the cut thermocouple leads extending from the top right of the canister.

Figure 4-11. The second "2X" glass ceramic pour in its 8 inch diameter heading mantle after cooling and solidification. 2X indicates a rate of cooling twice as fast (cooled in half the time as the waste form in Figure 4-10). Note: A malfunction occurred in this heating mantle resulting in overheating of the glass ceramic and oxidizing the graphite crucible. This surrogate waste sample material was not further analyzed since it was exposed to thermal conditions that would not be possible under full scale operations of a CCIM.

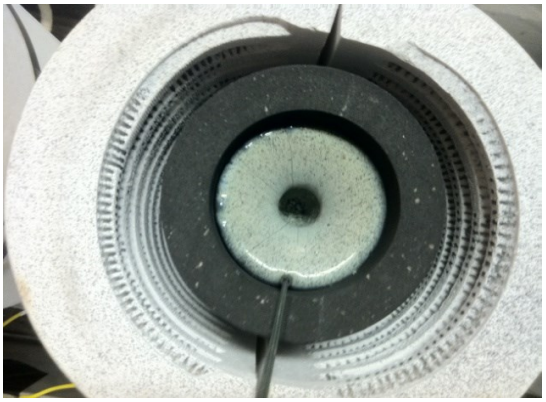

Figure 4-12. The third "room temperature" cooled glass ceramic pour in its 8 inch diameter heading mantle after cooling and solidification. For this pour the canister centerline cooling control system was not used and the mantle was off. As a result the rate of cooling was considerably faster. Note the glassy appearance consistent with fast cooling.

4.7 Summary of CCIM Operating Parameters

Table 4-3 provides a summary of the operating parameters for the CCIM testing. Overall, the melter operated for over 20 hours with three successful pouring events.

Table 4-3. Operating Parameters for the CCIM Testing with Composition CS/LN/TM-Mo-6.25

Parameter	Units	Full Cold Cap Test at the specified Operating Temperature
Melter Feed:		
Average loading on a mass basis in the final glass ceramic waste form	mass percent	45%
Melter feed rate	1-2kg/hr.	Highest rate achievable with a nearly complete cold cap
Duration	hrs.	≥20hrs
Melter:		
Induction power	60Kw or greater	Sufficient enough for a target glass Temperature of 1250-1350° C
Desired Induction Frequency based on pre-tested melt resistivity /conductance	Hz	5-6 MHz (only 2 MHz could be achieved due to lack of capacitance)
Melt Conductivity near the melt temperature	S/m	11.2 at 1250° C, 17.5 at 1350° C, 25.9 at 1450° C (based on lab-scale composition measurements)
Melt viscosity range near melt temperature	Pa·s	3.3 at 1250° C, 1.1 at 1350° C, 0.4 at 1450° C
Cold top coverage	%	~10 % to 100%
Target melt temperature	^{o}C	1250
Air bubbler rate for stirring of the melt	Standard liters per minute (slpm)	Used one time during the test run to break up the cold cap-successfully
Freeboard P	in. ofH_2O	-0.5'' to -13" of water

4.8 Analyses of Samples from CCIM Testing

The three cylinders that resulted from the CCIM test campaign were shipped to PNNL for analyses. Samples from the "1X" and "naturally cooled" canisters were obtained by coring both vertically and radially. The 2X cured waste form was not cored or analyzed as noted above. Optical microscopy, scanning electron microscopy coupled with energy dispersive spectroscopy (SEM/EDS) and x-ray diffraction (XRD) were used to analyze the core samples. The results of the analyses were reported by Crum, et al. (Crum 2014).

4.9 Conclusions from FY12 Testing

- The results of scaled CCIM testing successfully demonstrated the concept of processing a glass ceramic waste form in a CCIM and crystallizing the targeted phases according to varying cooling rates, including demonstrating the ability to:
    - initiate and couple to a low thermal conductivity waste form (as compared to borosilicate glass)
    - consistently feed a slurry of representative feed
    - build a cold cap (even with a dilute feed) and break up the cold cap with an air bubbler
    - start and stop several pours
    - pour glass ceramic into receipt containers
    - perform post-pouring thermal treatment on glass ceramics under different cooling schedules to attempt to make the appropriate glass ceramic surrogate HLW forms.

- The testing indicated the need for formulation and melter design improvements to facilitate processing, including
    - concentration of solids in the slurry HLW surrogate feed to increase production rate
    - improvement of pour spout design to allow for controlled pouring at higher temperatures and allow for pouring of glass ceramics containing some crystalline phases that require latent heat
    - providing for a wider range of operational frequencies to support processing lower electrical conductivity melts.

5 FY14 GLASS CERAMIC WASTE FORM TESTING

In FY14, additional attempts were made to process the glass ceramic waste form. These efforts built on the initial successes obtained in FY12 and further attempts conducted in FY13. The glass ceramic testing in FY14 was not successful. Attempts were made in May and August, 2014 to process the glass ceramic waste form and these efforts are briefly described below.

5.1 Objectives

For the May 2014 test, a run plan was developed by INL to guide the testing (Maio 2014a). A subsequent run plan was developed for the August 2014 testing (Maio 2014b). The overall objective of the testing was again to demonstrate processability of the glass ceramic composition in a sustained manner. Specific objectives of the testing were as follows:

- Completion of pours to determine the boundary on cooling rates where acceptable glass ceramic waste forms with targeted crystalline phases are formed. Controlled cooling in the graphite molds at 2, 3 and 4 times faster than centerline canister cooling profile for standard U.S. HLW canister was targeted.
- Completion of crucible pours to determine the effects of multiple pours (pours on top of pours in the same mold) on the formation of the glass ceramic. This type of pour was necessary to reflect conditions of canister filling for operations on a production scale where process abnormalities may result and starting and stopping of pouring.
- Observe the behavior of the molten glass ceramic waste form when it was poured into a pan with a standard disposal canister diameter. This test was important to visually observe if the molten waste can completely fill or nearly completely fill the total cross section of a standard U.S. canister diameter.

5.2 HLW Simulant CCIM Feed

The surrogate used in this test was again the CS/LN/TM-6.25Mo compositions (Table 4-1). This surrogate feed was also doped with lithium carbonate in an attempt to increase the electrical conductivity of the feed.

5.3 Melter Adjustments to Facilitate Processing

The high power requirement for the RF generator in the FY12 testing with the glass ceramic formulation was due to a mismatch between the resistivity of the waste form material and design frequency of the RF generator. The resistivity of the material to be melted, the frequency of the induced current and the diameter of the crucible must all be considered in a manner to efficiently deliver energy to the waste form material. In this case the design frequency (2.0 MHz) was not high enough (4-6 MHz would be likely required) to maintain the resistive melt at ~1300° C unless high power levels were maintained. This condition was unacceptable for sustained CCIM Pilot Plant operation.

The approach used to raise the frequency range of the RF generator to facilitate efficient coupling of the more resistant melt involved lowering the capacitance with the removal of an existing fixed capacitor and installation of a variable capacitor in the capacitance bank located between the RF generator chassis and

the crucible. Since this change in capacitance controlled the L-C circuit behavior characteristic of RF induction melters (as long as there are no changes in crucible diameter and inductance), calculations and follow on testing validated that frequencies of over 4 MHz were obtainable upon the completion of tuning experiments with the new capacitor. Even though this frequency was closer to optimum for the resistive melt, attempts to initiate and sustain the melt at higher frequency levels led to considerable interference of many instruments throughout the CCIM Pilot Plant; several of them critical for safe operation. Despite efforts to eliminate the interference (e.g. remounting and rewiring of instrument panels, removal of over 100 yards of unconnected and abandoned instrument wire in the overhead trays, etc.) the interference was not fully reduced to a safe level. Therefore, it was determined that the FY14 tests run would be operated near the design frequency (1.8 to 2.2 MHz) and operating time would be minimized at the high power levels to avoid the risk of the RF generator automatically shutting down due the high power interlocks. The new variable capacitor was replaced with the older design basis fixed capacitor. Also, in an effort to increase electrical conductivity, additional "salting" of the solid surrogate bed with sodium carbonate was conducted.

The drain heater failure and excessive drain material corrosion in the FY12 tests were due to the high melting point and crystalline nature of the waste form. The most immediate and least costly fix for the crucible drain assembly and its heater was to keep their same configurations, but implement the following modifications:

- Potting of the open area around the resistive heater's coiled wire elements (Figure 5-1). This may keep the elements from sagging and snapping after exposure to cycling and high amperage (i.e. high temperatures) for long time periods (> 30 min.). The potted heaters were tested over several slow heating cycles (100-1000° C) to verify their robustness and to precondition their resistive wire elements for both cycling and thermal shock.
- Increasing the pour tube diameter from 3/8 to 1/2 inch
- Replacing the existing exhaust blower with one of greater vacuum and less flow to ensure drain pour control
- Addition of a nitrogen purge to the top end of the drain assembly's sheath exposed to the 1300° C plus molten environment in the crucible.

Figure 5-1. Tube shell heater with potted coils around a Hastelloy drain tube with a wider ½" diameter.

Another operational change pertinent to this test was targeted at improving melt initiation with the glass ceramic waste feed. Starting with FY13 testing, the starting bed material consisted of the NOAH Corporation liquid feed melted at low temperature (900-1000° C) to form a partially melted batch material instead of the MOSCI Corporation vitreous feed material. This starting material contained more crystalline material and was, thus, more difficult to melt. Despite attempts in FY13 to "salt" the bed, locate and remove non-desired induction sources and trying a variety of initiator rings and wires of various shapes, partial ignition was only achieved on one occasion. To improve the likelihood of ignition of the surrogate feed in the FY14 tests, the material was reground to about 0.8 mm or less. Additionally, an induction ring of high resistance (i.e., titanium) targeting a square wave pattern was used. This special pattern was designed to maximize heat generation and distribution in the optimum torus region of the crucible's cross section.

FY2013 testing also revealed that when long induction ring ignition times are required, RF generator power cannot couple fast enough to the surrogate; eventually electrically stressing components in the generator's chassis. As before this is a consequence of the induction ring not conducting enough heat to support the latent heat to melt the glass ceramic batch material. The inability to obtain "load" in less than an hour for the RF generator led to burnout of two switches (the existing switch and its replacement) that control use of the lower or upper induction coils surrounding the crucible. For the FY14 testing, the switch was not replaced. Instead, a single 6 turn induction coil was utilized for surrogate bed initiation and melting. This coil was compressed to provide for an increase in power density of ~40 % to the surrogate bed as shown in Figure 5-2 .

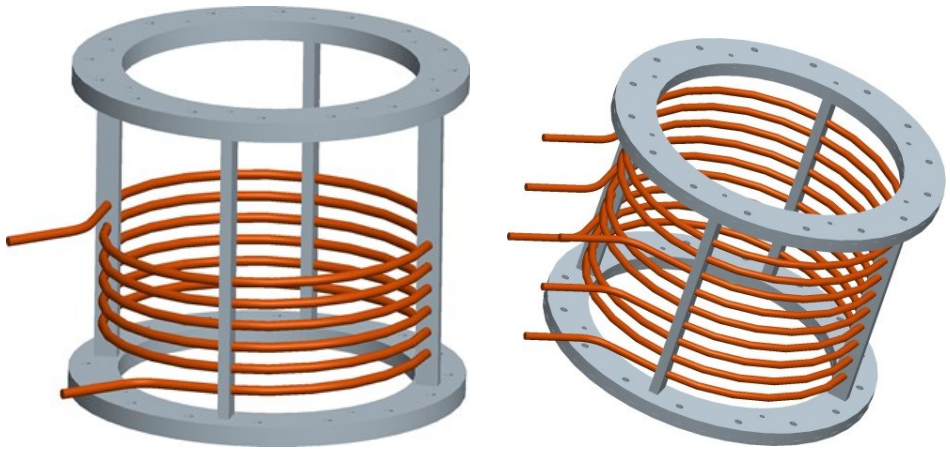

Figure 5-2. The specified compressed 6 turn CCIM single induction coil on the left compared to the previously used 6 turn coil on the right. The previous coil used a 3-3-3 coil design to allow switching of a 6 turn coil between upper and lower parts of the crucible.

5.4 Melting Observations

Sustained operations could not be achieved for the glass ceramic composition even with the changes identified in Section 5.3. On May 7 and May 8, 2014, the test run was initiated. Initial ignition of the melt was successful with the use of a new induction starter ring. Unlike previous tests with both glass and glass ceramic waste forms in the CCIM Pilot Plant, this starter ring was placed in the bed vertically as opposed to horizontally. In addition the effective length of the starter ring was considerably increased by bending the ~1.6 mm dia. titanium wire into 44 vertical waves with a wave length of ~1.8 cm and amplitude of ~2.8 cm. This resulted in an effective resistive heating distance of over 2.6 meters within a

ring diameter of ~24.13 cm. Since the crucible's diameter is ~26.4 cm, the vertical wave ring was located at or very near the electrical skin depth of the induction melter. In this position the induced magnetic field sees a continuous circumference of 76 cm for maximizing the length for inducing current while providing maximum resistance heating over the full 2.6 meters. As a result, ring temperatures achieved after start-up of the RF generator were a minimum of at least 20% higher than temperatures achieved with horizontal initiator rings. As shown in Figure 5-3, a pre-test of this ring in air without the crucible and any surrogate dry solid oxide HLW gave a temperature of 1100° C via a pyrometer; which was 200° C higher than any other horizontal ring tested regardless of its material type, size, or configuration.

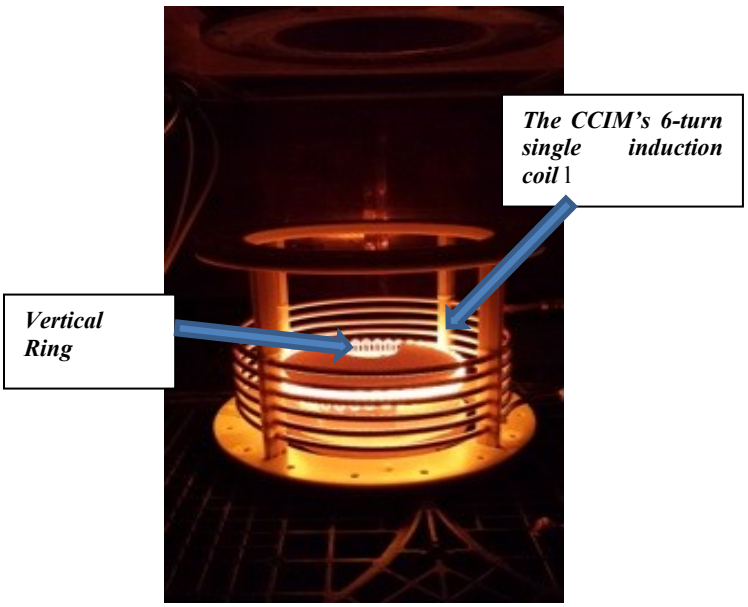

Figure 5-3. Test of the new vertical initiator ring design prior to the FY14 glass ceramic tests.

After being automatically shut down by an RF generator interlock due to a non-damaging spark from a frame screw to the main induction coil, the system was easily restarted and achieved center line temperatures up to 1100° C. This indicated that coupling with the melt was achieved. During initiation, heat-up and initial coupling, the temperature of the surrogate feed material increased over 850° C in a thirty minute period consistent with rates observed for amorphous materials. However, the melt stalled out at ~1100° C before the whole waste volume became molten indicating insufficient power and loss of HLW surrogate conductivity as the melt grew.

A restart of the test was attempted in August 2014. The test bed from the May 2014 test was reground because it was thought that this pre-melted material may assist in melt initiation under the assumption that the pre-melted, fused test bed material would be more conductive than the starting materials. The restart incorporated complete "salting" of the surrogate (as opposed to just around the ring area) with $NaCO_3$ to increase conductivity. This involved mixing 400 g of $NaCO_3$ with 20 kg of starting material. The power level of the RF generator was also allowed to increase (but still remain below 10 kV). However, even with these provisions, this attempt was also unsuccessful.

6 FY14 CERAMIC WASTE FORM TESTING

The FY14 CCIM test campaign on ceramic waste forms was aimed at demonstrating melting and pouring of the ceramic. A multi-phase ceramic waste form is being developed at the Savannah River National Laboratory (SRNL) for treatment of waste streams generated by advanced fuel reprocessing. As previously mentioned, the envisioned waste stream contains a mixture of transition, alkali, alkaline earth, and lanthanide metals. Ceramic waste forms are tailored (engineered) to incorporate waste components as part of their crystal structure based on knowledge from naturally found minerals containing radioactive and non-radioactive species similar to the radionuclides of concern in wastes from fuel reprocessing.

The multi-phase ceramics were designed to crystallize upon immediate cooling from the melt. Compositions were designed based on combinations of the surrogate waste and additives to target desired hollandite, perovskite, and pyrochlore phases upon melting. Elements with a +3 or +2 valance form perovskite ($(A^{+2})TiO_3$) and pyrochlore ($(A^{+3})2Ti_2O_7$) type phases. Zirconium (+4 valence) partitions to a zirconolite ($CaZrTi_2O_7$) phase. Cs and Rb elements partition to a hollandite structure based on the general formula
$Ba_xCs_yM_zTi_{48-z}O_{16}$ where $z = 2x+y$ for trivalent cations and $z = x+y/2$ for divalent cations for charge compensation (Amoroso 2014a). To support melter testing, a data package was produced that provided property data for electrical conductivity, viscosity and crystallization behavior (Amoroso 2014a).

6.1 Objectives

A run plan was developed for the FY14 ceramic waste form CCIM testing (Maio 2014c). The overarching objective of the FY14 CCIM testing for the ceramic waste form was to demonstrate that the compositions could be melted using the CCIM and poured from the CCIM into a receiving container. Specific objectives were as follows:

- Demonstrating successful melt initiation involving a refractory material (melting temperature up to 1700° C) using a resistive power starter ring.
- Demonstrating successful coupling to the melt after melt initiation. The ceramic composition has significantly higher electrical conductivity (~100-130 S/m) than the glass ceramic composition (5-10 S/m). Therefore, RF generator coupling is expected to be less arduous for the ceramic than the glass ceramic. However, "re-strapping" the RF generator for the lower frequencies needed to match the higher conductivity of the ceramic as well as designing, fabricating and installing a new coil around the new crucible to increase inductance was required; but unfortunately this approach was found to be applicable and designed only for entirely metal melts.
- Demonstrating successful tapping and pouring of the ceramic waste form and pouring into 4" diameter graphite molds that are controlled cooled under pre-heat conditions to evaluate microstructural changes.
- Observe the behavior of the molten ceramic waste forms poured into a pan representing the diameter of a standard U.S. HLW disposal canister.

6.2 HLW Ceramic Simulant Composition

Compositions designated as Fe-MP and CAF-5% TM-MP were selected for the CCIM testing. The Fe-MP composition was an early developed composition and was known to melt at lower temperatures (i.e. 1425° C) but may suffer from improper phase assemblage and resulting poor product quality (Brinkman 2012, Brinkman 2013). The Fe-MP composition was expected to be adequate for processing in the CCIM

as currently configured at INL. Therefore, the Fe-MP composition was used for testing in FY14. The CAF-5%TM-MP composition was formulated based on a baseline Cr/Al/Fe-based hollandite composition but with 5% addition of transition metal (TM) elements in an effort to enhance melt-ability for processing in the CCIM (Amoroso 2014b). The Fe-MP and CAF-5%TM-MP compositions in oxides are provided in Table 6-1 (Maio 2014c).

Non-radioactive, dry surrogates (consisting of oxides and carbonates) of the two multi-phase ceramic compositions were prepared by MOSCI Corporation (Rolla, MO). The surrogate contained representatives of the alkaline and alkaline earth fission products; mainly cesium and strontium, the lanthanide fission products and the transition metal fission products. The surrogate also contained the correct amount of oxide precursors required to produce the desired ceramic phase assemblages.

Table 6-1. Target Oxide Concentrations (wt %) in Ceramic Waste Forms

Component	Fe-MP	CAF-5%TM-MP
Al_2O_3	0.00	1.25
CaO	1.37	1.75
CdO	0.11	0.11
Cr_2O_3	0.00	6.23
Eu_2O_3	0.17	0.17
Fe_2O_3	15.13	6.55
Gd_2O_3	0.16	0.16
SrO	0.97	0.96
TiO_2	48.65	49.48
ZrO2	2.96	3.06
BaO*	12.63	12.57
Ce_2O_3	3.07	3.03
Cs_2O	2.85	2.81
La_2O_3	1.57	1.55
MoO_3	0.84	0.83
Nd_2O_3	5.18	5.11
Pr_2O_3	1.43	1.41
SeO_2	0.08	0.08
SnO_2	0.07	0.07
Sm_2O_3	1.07	1.05
TeO_2	0.65	0.67
Y_2O_3	0.62	0.64
Rb_2O	0.42	0.43
Total	100.0	99.97
Precursor Additives	75.60	75.55
Waste Oxides	24.40	24.42

Red font depicts ceramic precursor additives

* BaO is present in the waste and added as a ceramic precursor

6.3 Melter Adjustments to Facilitate Processing

As mentioned, the conductivity of the ceramic waste form is between ~100-130 S/m at the planned melt temperatures (~1450-1550° C). Because frequency is inversely proportional to melt conductivity, the optimal operating induction frequency to process the ceramic is 395 kHz. The move to lower frequency required two system modifications prior to the FY14 ceramic waste form test: 1) the fabrication of a new primary inductor (e.g., the coil around the CCIM) and 2) the addition of an impedance matching network to the existing radio frequency (RF) generator. The fabrication of a new inductor required determining the number of turns to attain the desired inductive reactance and specification of coil spacing compatible with electrical arcing issues. Fortunately, the INL CCIM Pilot Plant's RF frequency generator was designed for lower frequency operation and the impedance matching network was already installed in the existing RF generator system. The RF system manufacturer instructions were used to "re-strap" the network to accommodate operation at 395 kHz. However, unfortunately the lower frequency impedance coupling was found to be only acceptable to metal melts not glass or crystalline melts. This required operating with the traditional L-C circuit for frequency generation and, as such the lowest frequency obtainable was 1.2 MHz requiring potentially operating at high power levels.

6.4 Melting Observations – September 2014 Test

On September 30, 2014, the first attempt to melt the ceramic waste form composition was made. The test was started using a titanium vertical induction wire ring (8.4" diameter) bent in waves as previously done for the two previous FY13/FY14 glass ceramic tests. The wire initiating ring was 0.08 inches thick and bent into 38 waves of amplitude ¾" to 1". This particular titanium wire ring configuration provides the greatest length of induced current resistance and therefore provides heat over a greater volume of the initial cold crucible charge. The ring was placed at ~5.5" above the bottom of the crucible upon 9 kg of packed and tamped powdered oxide/carbonate surrogate. The ceramic feed batch was of lower density compared to pre-melted materials used in previous testing so crucible loading was meticulous and required considerable tamping to ensure sufficient mass was placed in the crucible. Another 4 kg of the ceramic waste form surrogate was added on top of the initiation ring for a total height of ~7.5 inches in the crucible (Figure 6-1). Another 13 kg of surrogate batch was then placed in the feed hopper on the mezzanine level of the pilot plant directly above the crucible. In addition, prior to installing the drain tube for this test, it was filled with low melting phosphate glass to facilitate tapping of the CCIM. The RF generator was powered up and operated at the lowest frequency tunable (~1.2 MHz) to initiate a melt by first inducing a resistive joule -heated current in the titanium wire ring.

Figure 6-1. Pre-test fill of the Fe-MP batch material in the CCIM (note: total crucible height is about 14").

The overall test met with partial success in that a melt was initiated, but only in the lower 2-3" of the crucible (in a region known as the marsh). After loss of the initial wire ring, two more attempts to initiate the Fe-MP surrogate melt were made with incrementally heavier starter rings with limited success. It appeared that the first wire ring, as specified above, achieved very high temperatures very quickly as desired due to the high insulation of the packed powder Fe-MP starting bed. However, based on visible observations, it was assumed the relatively high carbonate content (>20%) of the Fe-MP surrogate quickly formed a small melt around the ring which caused a failure (break) in one or more locations of the initiator rings. The break then created a type of junction of which the low melting carbonate material occupied, in turn causing a superheated area that quickly oxidized the ring.

For the heaviest starter ring (8.5" OD, 7.5"ID. ¼" thick), the annulus of influence was sustainable and did not consume the ring as quickly as the first two. However, the very hot annulus region of influence (created by the melting carbonate salt below the hot ring) melted its way down through the packed powder material until it fell below the direct influence of the induction coil. Once it passed the last turn of the induction coil, coupling with the RF generator was lost and temperature decreased. It was noted that appreciable melting took place in the marsh area. Evidence of this melting was based in part on quick rises in CCIM cooling water temperature and observation (even through the frozen shell) of a red melt glow between the cooling stays.

On the following day, October 1, 2014, the CCIM team removed the crucible for inspection of its contents. The results of this post melt examination are described through Figures 6-2 to 6-4 and associated captions. Additionally, the results indicate consistency with the instrument data and associated observations made during the attempted melt the previous day. No remnant of the third titanium ring was found.

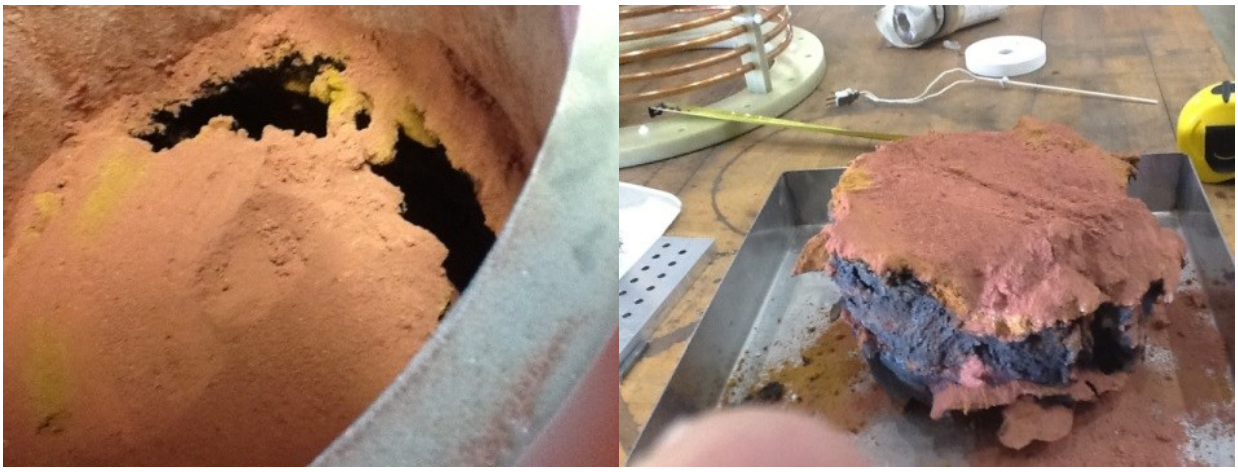

Figure 6-2. Left Side: The bridge at the top of the bed of the partial melt after initiation with the last heaviest titanium ring. The bridge was formed as anticipated since ~1kg of Fe-MP surrogate was added to the bed as insulation after the placement of the last ring. The partially melted ~8.5" diameter core (Right Side) resided about 1 inch below the bridge. Note the complete melt of the outer surface as the ring melted down the length of the crucible.

Figure 6-3. Shard of cold melt removed just below the core section shown in Figure 6-2 .The thin dark rim is consistent with high temperature melting in the annulus location of the third titanium ring. The yellow region indicates the extent of insufficient (for coupling) radial heat conduction in one location as a result of the ring being mobile. The remaining reddish area is the compacted original Fe-MP surrogate.

Figure 6-4. Four shards of melted material taken from the marsh that possess sufficient dark melt volume to assume that ceramic phases were produced.

6.5 Melting Observations – October 2014 Test

Prior to conducting the second CCIM test campaign with the Fe-MP ceramic waste form composition several preparations were made in attempt to improve the likelihood of success. Due to the very high temperatures required to process the ceramic waste form, the cleaned crucible was first coated on the outside with a thicker than normal heat resistant putty and then wrapped tightly with special resistant heat tape (Figure 6-5). This unique preparation was required based on the observed warping of the lower portion of the crucible as a consequence of reaching higher than average temperatures (>1550° C) for sustained periods during both the ceramic test conducted in September and the glass ceramic test conducted in May.

Figure 6-5. The crucible showing high temperature putty and heat wrapping prior to installation in the CCIM Pilot Plant.

Just prior to the test, three small 4 inch tall alumina crucibles (each weighing 300 g) with 2.438” OD and 2.188” ID were inverted and placed at the bottom of the crucible - each spaced apart by ~120 degrees (Figure 6-6). Each small alumina crucible was packed with ~350 g of the starting charge containing the Fe-FP surrogate. The intent of the alumina crucibles were to provide an initiation ring support to avoid the initiation ring sinking phenomena experienced during the test conducted in September. This resulted in the ring dropping below the influence of the induction coil once isolated local melting occurred only below the initiation ring and thereby terminating sustained heating. Following placement of the three small crucibles, 3.2 kg of fresh Fe-MP powered surrogate was tamped and packed in around the crucibles. Fresh powdered surrogate and reground partially melted Fe-MP surrogate from the previous test was then added and tamped to give a total charge to the melter of ~13.5 kg. The reground bed was added as additional support for the titanium initiation ring in an attempt to further immobilize the ring. The last step involved even placement of a 1/4” thick titanium initiation ring (7” ID and 8” OD) upon the three alumina crucibles. This charge provided a total height of 6 inches from the bottom of the CCIM, leaving a shallow bed compared to previous melt tests involving glass and glass ceramic waste forms. As such, the 6 turn induction coil was placed outside the crucible low enough to cover the marsh area of the melter. This was to ensure initiation ring to coil coupling in the unfortunate event that the ring sunk to the bottom as had occurred previously.

Figure 6-6. Left to Right, Top to Bottom. Six photos showing the progression of placement of the three small alumina initiation ring support crucibles, charging of the "Fe-MP" surrogate and titanium ring installment inside the CCIM.

After the crucible was re-bolted inside the Faraday cage, preoperational checks were completed on the morning of October 30th and the test run was initiated at ~9:00 am. Temperature rise observed within 30 minutes of increasing the RF generator voltage from 5.0 to 8.0 KV (based on melter centerline type K thermocouple readings near the surface of the surrogate) coupled with corresponding slow but steady slight rises in plate current indicated early coupling of the titanium induction ring. However, at ~9:45 am, the RF generator tripped from an apparent arching as observed by a spark. Upon evaluation, inspection revealed that a grounding strip needed to be repositioned if RF generator operation at the anticipated high power levels (up to over 60 kW) was to be continued. After this repositioning the RF generator was restarted at ~10:30am.

Over the next 3 hours, plate current began to rise at the desired rate (from 3.1 to 5.9 amps) as well as the value of the type K thermocouple. As indicated by tabulated log book data of key power and current values as well as higher trending of screen temperatures as logged by the Lab View data acquisition system, it became evident that complete coupling and full resistive heating of the of titanium ring had occurred. Consequently the surrogate was starting to heat up by conduction from the ring. This indicated that the partially melted waste surrogate was coupling to the RF field despite the high frequency (1.4 MHz). This also indicated that the ring was staying in place sufficient enough to not only just melt the surrogate below, but ensure even surrogate heating and avoid undesirable sinking of the ring as observed in the previous test.

At ~1:30pm the temperature of the surrogate rose above 1400° C requiring the use of the type B thermocouple to obtain higher and accurate temperature readings. Clearly at this point a full sustainable melt was now successfully achieved with temperatures rising up to over 1600° C over the next 45 minutes (Figure 6-7). Also at approximately 1:30 pm fresh surrogate was fed intermittently at a 5.5 kg/hr. (from the hopper on the upper mezzanine level) over the next 40 minutes. The primary purpose of fresh surrogate feeding for this particular test was to build melter head to ensure melt draining at an acceptable rate.

Since continuing to operate at or above the design power level of 60 kW increased the risk of tripping the

RF generator, at ~2:15 pm the decision to tap the melter and pour was made; despite the feeding of only an additional ~3 kg of fresh surrogate. After terminating the nitrogen cooling purge to the drain system and gradually increasing the amperage on the tube heater, it took another two minutes for the low melting phosphate glass plug to melt and discharge from the drain tube (Figure 6-8). Immediately following this event the leads to the tube heater burned out from high thermal exposure precluding pouring of the melt and causing the surrogate ceramic to crystallize to a solid in the drain tube. As a final effort to re-initiate the pour, cooling water to the drain system was decreased; however, pressure from the cooling water boiling caused a leak in the cooling tubing which subsequently triggered an RF generator shut down. At ~2:30 pm the test was officially terminated and the cooling water to the stays of the crucible was increased for an hour to cool the melt quickly and potentially provide samples from the melt for analysis that exhibited varying cooling rates.

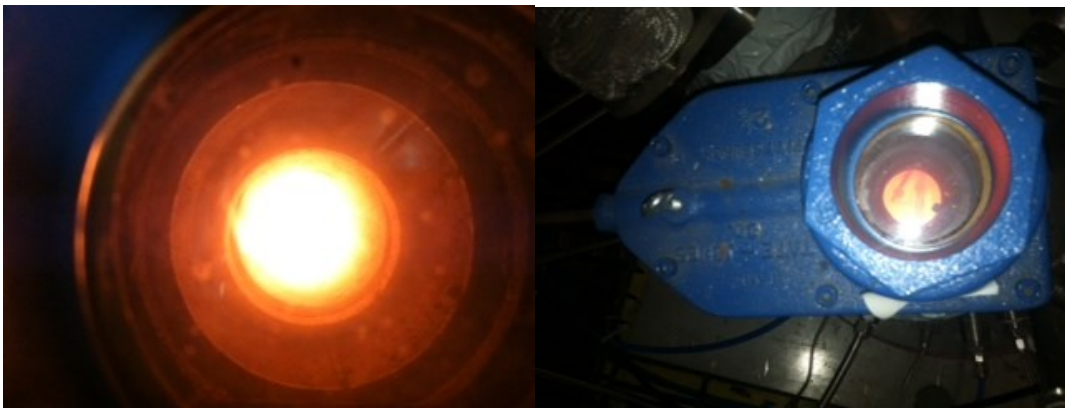

Figure 6-7. Visual indication of complete melt initiation and sustainability via the two view ports installed on the head dome on top of the melter.

Figure 6-8. The presence of a portion of the drain's tube phosphate glass plug (contained in the graphite canister collection system) removed during attempted melt tapping and pouring prior to drain heater failure.

After the crucible and its contents were allowed to cool, the crucible was removed for inspection. As shown in the left photo of Figure 6-9, the cooled melt densified to a depth of ~3" above the bottom of the crucible in contrast to the ~6" at the onset of the test. Seven core samples were then taken in the locations noted in the far right photo of Figure 6-9. Each core was 1 inch in diameter and varied in length from 1-1/8" to 2". These cores were shipped to SRNL for analyses. One specific core taken from the center of the

cooled melt is shown in Figure 6-10. Post melt analysis revealed no indication of the original titanium initiation ring, but half of one of the small alumina support crucibles was found indicating that it floated to the top. The drain of the crucible was also removed and inspected. The drain tube was also sent to SRNL for analysis. Despite nitrogen and water cooling to the drain system during melting, prevalent material damage occurred during tapping as shown and described in Figures 6-11 and 6-12. However, as indicated in Figure 6-11, it appeared that ceramic waste form material entered the drain tube.

Figure 6-9. Left to right, the cooled and partially densified surrogate HLW/SYNROC melt occupying ~3”on the bottom of the crucible, a ~1-1/2” shard of the solid surrogate, core sample locations.

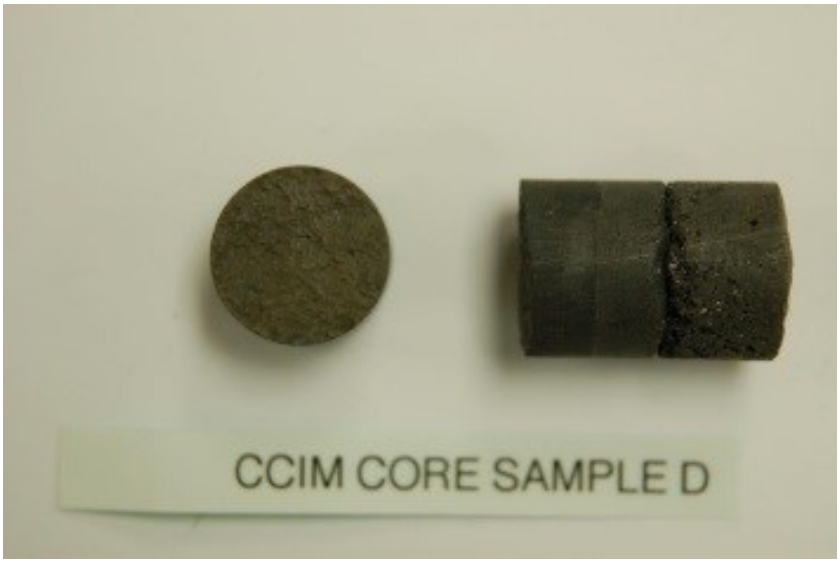

Figure 6-10. Photographs of center Core Sample.

Figure 6-11. The Inconel drain tube and its corresponding shell after the test. The left photo shows where unwanted melt entered outside the tube and penetrated the shell. Note the difference in material condition on the outside of the shell that is in the melt and the condition where the shell is protected by the crucible's bottom plate. The right photo shows the top end of the drain indicating that some ceramic waste form did enter the tube for draining. The screwdriver in the right photo shows where the melt corroded through the shell cap.

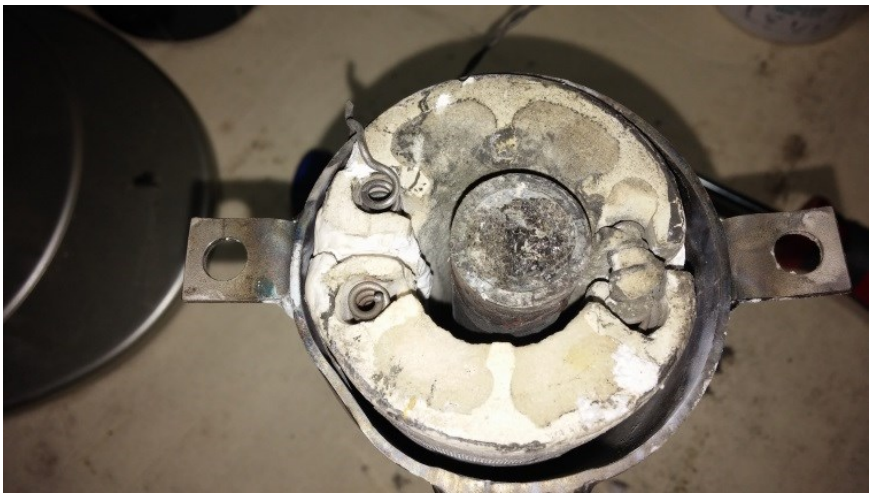

Figure 6-12. The bottom of the drain tube showing damage to the annulus tube heater. It appears that the material at the end of the tube is part of the original phosphate glass plug and not cooled ceramic waste form material.

6.6 Analyses of Samples from CCIM Testing

The core samples will be analyzed at SRNL to determine the homogeneity of the melt, its microstructure, the presence of specific ceramic phases (e.g. zirconolite, pervoskite, and hollandite) and the partitioning of key surrogate HLW components between the ceramic phases. A measure of relative durability will be made to compare to lab produced samples. These results will be provided later this fiscal year in a report.

6.7 Conclusion from FY14 Test

Although pouring was not achieved during the ceramic CCIM test, it was apparent that a sustained melt was achieved. This testing demonstrated that:

- initiation of the melt could be achieved using a supported titanium ring configuration and higher frequencies than optimum
- the CCIM frequency could be adjusted to couple to the ceramic waste form composition with higher electrical conductivity that typical borosilicate glasses and the glass ceramic waste form, yet maximum power levels were required
- dry ceramic batch material could be added to the ceramic waste form melt
- limitations in the INL CCIM drain system design continue to preclude pouring of high melt temperature materials.

7 PATH FORWARD

7.1 Melter Modifications

Using separate non-FCRD funding obtained through INL's program development program, the CCIM team completed the engineering design, fabrication and assembly of a new crucible melter. As shown in Figure 7-1, the new melter has features that will provide more reliability, operability and maintainability as well as greatly facilitate the tapping and draining of high temperature surrogate HLW forms such as those containing all or some crystalline phases.

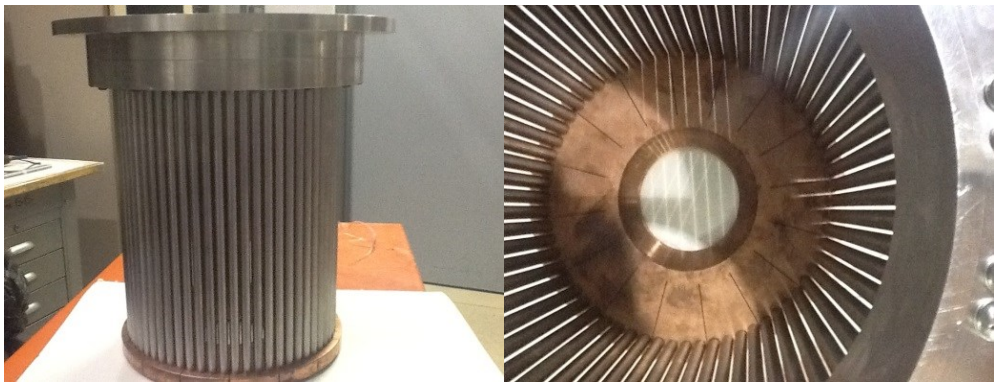

Figure 7-1. New melter design showing integrated copper plate in the bottom of the melter.

The new melter is also equipped with a unique tapping/melt pouring design. One key feature of the design is the use of a replaceable conical sleeve (Figure 7-2) for the drain hole that will be flush with both the top and bottom end of the copper base in the melter. The conical sleeve (which can be constructed of graphite or platinum) will be surrounded by boron nitride insulation to ensure heating of the sleeve while maintaining cooling of the base. Another feature is a remotely operated arm with a cooling plate attached to the end of the arm. The purpose of the arm and plate will be to ensure cooling of the drain opening during periods of no tapping (Figure 7.3).

Figure 7-2. Replaceable conical sleeves to facilitate melt pouring to be placed and tested in the melter's bottom copper plate as shown in Figure 7.1. Examples in figure fabricated from graphite.

Figure 7-3. Full side view of the new CCIM design with the remote arm drain plugging and cooling device.

The new melter design will improve operability and maintainability by utilizing a single water inlet and outlet for crucible cooling and employing O-rings for each individual tube in the construction. The new melter design will undergo acceptance testing in the spring of 2015. Part of the acceptance testing will include demonstration of operations using previously processed borosilicate glass.

The operation of the RF generator is also being modified with the addition of current sensors to allow for power level up to 70 kW. This will facilitate processing of the glass ceramic waste form composition since high frequencies cannot be met. Higher power compensates for the lack of operating at ideal frequencies and lowers the risk of melter electrical tripping during sustained melting and insufficient melt initiation with the starter rings.

Finally, modifications are being made to the off-gas system to enhance off-gas testing and analysis. A NO_X monitor is also being added to support testing with high nitrate concentration feeds as will be necessary to demonstrate the high inherent throughputs of the CCIM technology with slurry feeds.

7.2 FY15 Glass Ceramic Waste Form Testing

A glass ceramic CCIM campaign will be conducted in FY15. It is expected that modifications to the CCIM will improve melting performance and allow for achieving the objectives outlines in sections 4.1 and 5.1. Additional objectives for the FY15 testing include the following:

- performing an extended duration run (up to 50 hours) to achieve at least three bed turnovers
- concentrating the feed by at least a factor of 2
- collecting data to support mass balance analyses

- determining loss of volatiles (e.g. Cs)
- determining throughputs and glass production rates.

Run plans and sampling and analysis plans are under development to guide the testing.

7.3 Future Ceramic Waste Form Testing

The goal for the next ceramic CCIM campaign will be to run the CAF-5% TM-MP composition. This formulation is close to the baseline composition and is expected to produce the targeted phase assemblage while minimizing the formation of minor deleterious phases. However, to effectively process this composition, very high crucible temperatures will be required (likely in excess of 1600° C) and pour spout temperatures will need to be maintained at greater than 1550° C to ensure melting of crystalline material (a phenomena not typically required for tradition amorphous HLW forms). It is envisioned that the melter modifications made in FY15 will support CCIM operations to satisfy these high and demanding temperature requirements.

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