

Extended Development Work to Validate a HLW Calcine Waste Form Via INL's Cold Crucible Induction Melter

James A. King
Vince C. Maio

September 2011



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operated by Battelle Energy Alliance

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**Idaho National Laboratory
Idaho Falls, Idaho 83415**

<http://www.inl.gov>

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ABSTRACT

To accomplish high level waste (HLW) calcine treatment objectives, the Idaho Clean-up Project contractor at the Idaho National Laboratory (INL), CWI, has chosen to immobilize the calcine in a glass-ceramic via the use of a Hot-Isostatic-Press (HIP). The choice for HIPing has been formally documented in a 2010 Record of Decision (ROD). Even though the HIP process may prove suitable for the calcine as specified in the ROD and validated in a number of past value engineering sessions, DOE is evaluating back-up treatment methods for the calcine as a result of the technical, schedule, and cost risk associated with the HIPing process. Consequently DOE-HQ has requested DOE-ID to make INL's bench-scale cold-crucible induction melter (CCIM) available for investigating its viability as a process alternate to calcine treatment.

Providing a solid, stable, low volume and durable material that can be easily stored and/or disposed is the rationale for the immobilization of radioactive waste material (i.e. HLW calcine) in either a glass, ceramic, or glass-ceramic form. In addition, the waste form is the most controllable of the key components in immobilizing and isolating radioactive waste in a deep geological repository. In general ceramic and glass-ceramics waste forms offer an alternative to the traditional borosilicate glass HLW forms. Ceramics typically accommodate higher waste loadings than borosilicate glass, leading to smaller intermediate and long-term disposal facilities. Many ceramic phases are known to possess superior chemical durability as compared to borosilicate glass due to their similarity to natural analog minerals that geologically contain natural actinides. However, pure ceramics are generally multiphase systems containing many minor phases that make characterization and prediction of performance challenging within a repository environment. Therefore, many investigators have proposed using glass-ceramics as a compromise between the more inexpensive, easier to characterize glass waste forms and the more durable ceramic waste forms. Glass-ceramics have several advantages over traditional borosilicate glasses as a waste form. Borosilicate glasses can inadvertently denitrify, leading to a less durable product that could crack during cooling and unwanted crystals may be prone to dissolution. By designing glass-ceramics, the risks of deleterious effects from devitrification are removed. Glass-ceramics should provide a waste form with the advantages of both glass and ceramics—ease of manufacture (especially via the CCIM)—with improved mechanical properties, thermal stability, and chemical durability.

The INL's bench-scale CCIM is a unique technology that is extremely well suited for the generation of all these types of waste forms, especially glass-ceramics. The CCIM's attributes, if validated through testing, may provide a calcine waste form and a corresponding waste process that results in high waste form durability, loading, throughput, and robustness; all of which may be equivalent or superior to the HIPing process and the glass-ceramic calcine waste form it produces. As such, this report emphasizes the aspects relevant for the validation of the CCIM's use in the production of glass-ceramic waste forms for all classes of INL HLW calcine.

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ACRONYMS

BEA	Battelle Energy Alliance
BSG	Borosilicate Glass
CCIM	Cold Crucible Induction Melter
CSSF	Calcine Solid Storage Facility
DOE	Department of Energy
EM	US DOE Department of Environmental Management
FSU	Former Soviet Union
HIP	Hot Isostatic Press
HLW	High-Level- Waste
ICP	Idaho Clean-up Project
IEDF	INL Engineering Demonstration Facility
INL	Idaho National Laboratory
IWTU	Idaho Waste Treatment Unit
JHM	Joule Heated Melter
NWCF	New Waste Calcining Facility
PCT	Product Consistency Test
RCRA	Research Conservation and Recovery Act
ROD	Record of Decision
SRS	Savannah River Site
TCLP	Toxic Characteristic Leaching Procedure

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1. Background

The Department of Energy's (DOE's) Idaho National Laboratory (INL)—through its clean-up contractor attached to the Idaho Clean-up Project (ICP)—is required under a State of Idaho agreement to remove and treat, for eventual disposal, over 4,000 m³ of solid radioactive High-Level-Waste (HLW) calcine by 2035. The HLW calcine was generated as a result of reprocessing defense and unique nuclear reactor fuels for over 40 years. Since the reprocessing method was an aqueous technique, the calcine was generated by solidifying the liquid raffinate in a de-nitrating fluidized bed to a particulate with an average diameter of ~3 mm. Even though the calcine step reduced the HLW raffinate volume by over eight fold, the calcine, which is currently stored in six different vaulted bin sets, is not acceptable for direct disposal in any future HLW/spent fuel repository. As such, the calcine must be properly immobilized to contain its fission products, long-term alpha emitting radionuclides (unrecovered actinides and transuranics) and hazardous RCRA metals.

To accomplish the calcine treatment objectives, the Idaho Clean-up Project contractor, CWI, has chosen to immobilize the calcine in a glass-ceramic via the use of a Hot-Isostatic-Press (HIP); a treatment selection formally documented in a 2010 Record of Decision (ROD) [1, 2]. The HIP process is currently under both development and design and present plans call for adding HIPing via modifications to the Idaho Waste Treatment Unit (IWTU) [3], a facility recently constructed for treating liquid radioactive tank waste. Even though the HIP process may prove suitable for the calcine as specified in the ROD and validated in a number of past value engineering sessions, DOE is evaluating back-up treatment methods for the calcine as a result of the technical, schedule, and cost risk associated with the HIPing process. Consequently DOE-HQ has requested DOE-ID to make INL's bench-scale cold-crucible induction melter (CCIM) available for investigating its viability as a process alternate to calcine treatment. With that backdrop, this document provides a generalized report for CCIM testing of all classes of simulated non-radioactive calcine in INL's bench scale CCIM, with the major objective of generating glass-ceramic waste forms for the HLW calcine. A test plan involving one class of surrogate calcine for exploration of phosphate-based glass waste forms to be generated in the CCIM has been developed [4] and discussions concerning the CCIM vitrification of all calcine classes are not extensively covered in this report.

2. Introduction

The INL's bench-scale Cold Crucible Induction melter (CCIM) is located in Idaho Falls, Idaho at the DOE's Idaho Engineering Development Facility- IEDF (Pilot-Plant test bay number 1) and will be the location of the potential calcine/glass ceramic tests described in this plan. Details of the bench scale CCIM and its unique technology can be found in various references (examples: [5, 6]) and are not being provided here. For general information a simplified schematic of the major CCIM systems is shown in Figure 1 below and a photo of the 10.25-inch diameter CCIM crucible (showing induction coils) during the draining of melted glass/waste is shown in Figure 2. Both figures highlight the major design features that provide improvements over the conventional Joule Heated Melters (JHM) currently in wide use for HLW. These features include the induction coils, which eliminate in-bed electrodes subject to high corrosion and the vertical cooling tubes that make up the crucible wall, which in turn create a solid glass skull layer at the crucible wall that negates the need for corrosive refractory.

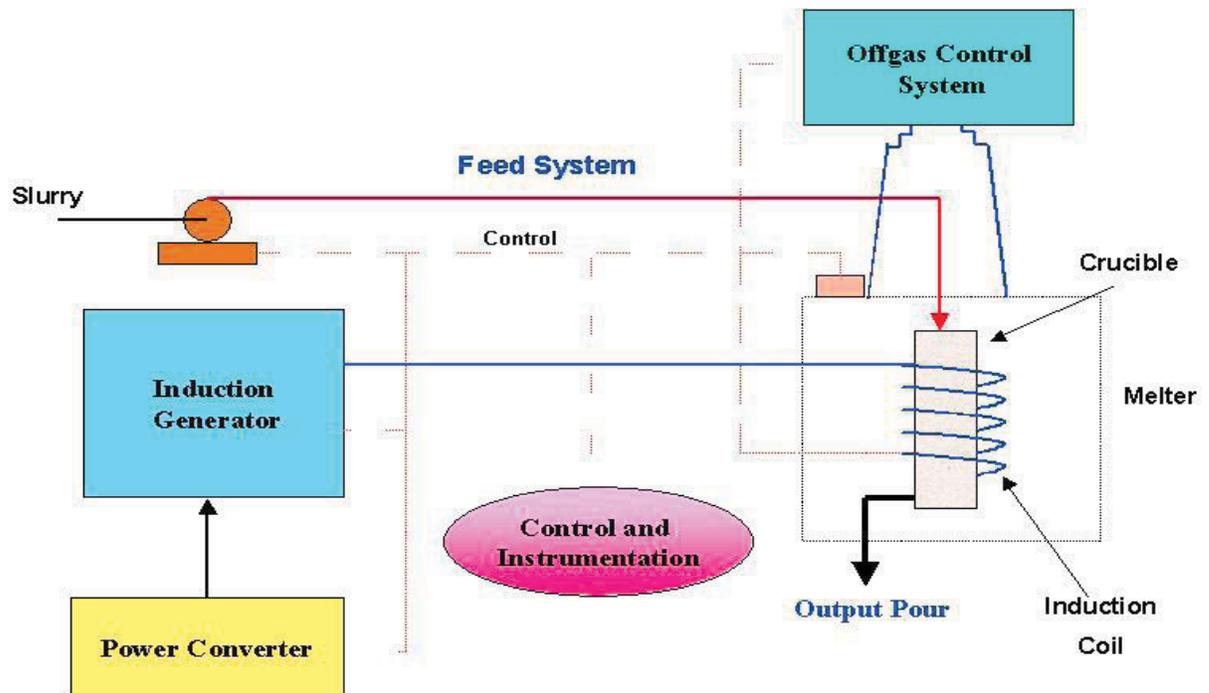


Figure 1 Simplified Schematic of the Major INL Bench scale CCIM System.



Figure 2 Photo of the INL CCIM during a Melt Drain.

Operated by the Battelle Energy Alliance (BEA) since 2003, the CCIM is the only cold-wall induction melter used for waste processing in the United States. The CCIM is a unique design as opposed to the traditional Joule-heated design. The latter design is being utilized at DOE's Savannah River Site (SRS) and will be deployed at DOE's Hanford site to vitrify defense liquid HLW into glass. However, past and present testing in CCIM pilot plants and international full-scale operations in France, South Korea, and the Former Soviet Union (FSU) indicate some clear advantages of the CCIM over the conventional JHMs, all of which may prove beneficial for the calcine waste. These benefits are a direct result of the CCIM's unique design features (i.e., no electrodes or melter refractory exposed to corrosion at high temperatures) that provide for higher temperature melter operations up to 2000° C as compared to

1000° C in the JHM. As a result, higher HLW loadings, greater waste throughputs and smaller footprints for the melter space are potentially achievable with the CCIM relative to the JHM. As such, if CCIM/calcine glass-ceramic tests prove acceptable in the performance objectives outlined below, the CCIM may be an acceptable cost, schedule, and technically risk adverse alternative to the baseline calcine treatment option (i.e., HIPing).

3. Radioactive Calcine Composition

Knowledge of the radioactive calcine composition is important for designing plans for validating a waste form via the CCIM. Information on the radioactive calcine was obtained from an Idaho National Engineering and Environmental Laboratory Report (INEEL/EXT-98-00455 Rev. 3) on the calcined waste stored at the Idaho Nuclear Technology and Engineering Center [7]. Tables are recreated from this report and their findings are summarized in this section.

From December 1963 until May 2000, aqueous nuclear fuel reprocessing waste (i.e., first cycle raffinate) was calcined to a solid form in fluidized beds. The waste was heated to 400-600° C where it underwent thermal decomposition to metal oxides, fluorides, nitrogen oxides, or water vapor. The solids from this process were transported to a Calcine Solid Storage Facility (CSSF) for temporary storage. Each CSSF is composed of several stainless storage bins within a concrete vault. Currently there are six CSSFs (i.e., Bin sets) with radioactive calcine storage; five at near capacity and one partially filled. A summary of capacity and holdings of the six CSSFs is given in Table 1.

Table 1 Capacity and Holdings of CSSFs.

CSSF Facility	Total volume ft ³	Useable volume ft ³	Filled volume ft ³ (m ³)	% Full
I	8,300	8,000	7,760 (220)	97
II	31,600	30,000	30,000 (851)	100
III	40,000	39,900	39,500 (1120)	99
IV	17,700	17,100	17,200 (487)	100
V	36,200	35,600	35,600 (1010)	100
VI	55,200	53,200	25,200 (713)	47

Few historical calcine samples with extensive analysis were performed. Obtaining additional representative calcine samples from the CSSFs would be difficult and costly and may not provide reliable composition data due to the heterogeneity of the calcine. Further complicating the question of the calcine composition is the fact that the calcine within the CSSF bins is not homogenous and cannot be mixed. Each bin is likely to contain multiple layers of chemically and radiologically distinct material. Additionally, within the six CSSFs there are a total of 43 bins each containing six to 12 sections, resulting in different calcine compositions. Therefore, sampling to determine a representative composition is cost prohibitive. Thus, the composition of the calcine stored in CSSFs is estimated from operating data of waste calcining facilities including volume and composition of liquid waste calcined, operation of the CSSFs, and other INTEC fuel and waste processing information. Calcine composition corresponds to the liquids treated in the calciner and the base material added to calciner.

Over the 30 years of operation, various calciner chemistries were used to treat varying liquid HLWs from reprocessing; therefore the radioactive calcine stored in CSSF vaults is comprised of many different compositions. Liquid wastes and corresponding calcines are typically named for the cladding of nuclear fuel from which they came and/or the principle waste component [7]. Calcining campaigns treated liquid wastes from the reprocessing of a variety of spent nuclear fuels from numerous reactors. Differences in

fuel cladding dictated the use of different chemicals for dissolution and reprocessing: such as nitric acid, hydrofluoric acid, mercury, chromium, and cadmium. Reprocessing these various fuels resulted in chemically different liquid wastes producing chemically different calcines. However, the entire existing radioactive HLW calcine stored in the 6 bin sets at the INL can be classified into four broad categories for CCIM test purposes; zirconium oxide based, aluminum oxide based, zirconium/sodium blend and a calcine consisting of an aluminum nitrate/sodium blend. For most cases, the classification corresponds to the cladding metal of the original reprocessed fuel.

Calcine compositions are calculated by the historical processing model (HPM). The “HPM uses the composition and volumes of the liquid wastes that were calcined, CSSF bin filling history and temperature data, ORIGEN2-based radioactivity calculations, calciner operating history, and other fuel and waste processing data to calculate the calcine composition” [7]. The typical chemical content of the four most common calcine classes is shown in Table 2.

Table 2 Chemical Contents of the Four Classes of INTEC (INL) calcines.

Chemical Species	Units	Type of Calcine			
		Aluminum*	Zirconium*	Zirconium (Fluorinel) / Sodium Blend*	Aluminum Nitrate /Sodium Blend*
Aluminum	wt%	47.0	11.0	5.0	37.0
Boron	wt%	0.3	1.0	1.0	0.1
Cadmium	wt%			5.5	0.2
Calcium	wt%		25.0	28.0	3.2
Chloride	wt%			0.1	0.4
Chromium	wt%	0.1	0.3	0.1	0.1
Fluoride	wt%		27.0	18.0	1.8
Iron	wt%	0.1	0.3	0.3	0.6
Mercury	wt%	2.1			
Nitrate	wt%	4.3	0.1	6.7	6.1
Oxygen	wt%	42.0	17.0	15.0	37.0
Potassium	wt%	0.3	0.1	0.8	1.9
Sodium	wt%	2.2		3.3	8.6
Sulfate	wt%	1.0		3.5	0.3
Tin	wt%		0.3	0.2	
Zirconium	wt%		18.0	12.0	1.4

*Column totals are not exactly 100% due to rounding values and the exclusion of trace components.

4. Calcine Surrogate Formulation

4.1 T-2 Non-Radioactive Calcine

The calcine simulant to be used in the CCIM glass test run referenced in this report [4] is only representative of the HLW aluminum nitrate/sodium blend calcine that is in INL bin set 6. This calcine test in the CCIM will be performed in a manner to make phosphate based glass as opposed to a glass ceramic (as discussed below) for the other major calcine classes

The simulant to be used for the phosphate glass test will be obtained from ~20,500 kgs of stored non-radioactive calcine that was formulated during the 1982 cold start-up of the (now shut down) INL New

Waste Calcining Facility (NWCF). This cold calcine which is ~64%-76% aluminum oxide and 1%-6.1% dolomite was removed from the NWCF prior to NWCF “hot” operations and then stored in one of two temporary buildings. As such it has been given the designation of *T-2 calcine*. In particular, the T-2 is a mixture of startup bed dolomite (containing calcium/magnesium oxides and carbonates) and 3 different feeds. The three feeds were similar in that they were primarily aluminum nitrate, with varying amounts of sodium nitrate and some boron oxide.

4.2 Modifications Required for T-2 Calcine to Prepare Calcine Surrogates Representative of all Classes

In terms of radioactive calcine volume, about 75% is zirconium based and the remaining 25% is about equal amounts of aluminum based and the aluminum nitrate/sodium blend. As such, the T-2 calcine is representative of only 12-13% of the total calcine inventory (i.e., the aluminum nitrate/sodium blend). Additionally, no RCRA metals were used in making the T-2 calcine.

To appropriately simulate the calcines stored in CSSFs it will be necessary to spike T-2 calcine with a composition similar to the radioactive calcine as well as ensure sufficient levels of zirconium and aluminum oxide. T-2 calcine must be spiked with RCRA metals and since the T-2 calcine is not radioactive, it is necessary to add an actinide surrogate to ensure that formulations will partition the radioactive components to the ceramic phase within the glass-ceramic. Neodymium has been used as a surrogate for plutonium and trivalent minor actinides previously in studies focused on glass-ceramics, at up to 6.27 wt% neodymium oxide [8-12]. The radioactive calcine has ≤ 400 ppm Uranium, ≤ 400 ppm Cesium, and 0.003 wt% ^{90}Sr , thus a neodymium oxide concentration of ~1.2 wt % would approximate the concentration of actinides in the radioactive calcine. Surrogate calcine compositions of cadmium at a concentration of 55, 000 ppm [5.5 wt %] will be achieved by spiking the T-2 calcine with amorphous cadmium oxide to reflect the composition of the actual HLW calcine and ensure the objectives of the CCIM test run are achieved.

5. Glass and Glass-Ceramic Waste Forms

The waste form is the key component for the immobilization and long-term isolation of radioactive waste. Providing a solid, stable, and durable waste form with high calcine waste loadings (with a reliable and efficient process) that can be temporarily stored and indefinitely disposed is the rationale for the immobilization of HLW calcine [13]. Immobilization is accomplished by either chemical dissolution within the atomic structure of the waste form matrix or encapsulation within the inert matrix. A viable waste form must have the ability to incorporate radioactive elements within its chemical structure and remain stable and chemically durable over geologic time frames [14]. The maximum waste loading for a given waste form will dictate the size of the intermediate and long-term storage/disposal facility [13].

Many DOE legacy wastes contain high concentrations of materials that are difficult to incorporate into glass waste forms. Examples of problematic materials include plutonium and other actinides, technetium, calcium, fluoride, sulfate, chloride, phosphate, and high concentrations of alumina, zirconium, cesium, strontium, mercury, cadmium, organics and PCBs [15]. As noted above the radioactive calcine stored in CSSFs contain high concentrations of zirconium which promotes crystal formation and fluoride which negatively impacts viscosity and corrosivity of the melt. The high alumina concentrations can lead to refractory-based corrosive melts that tend toward crystallization of nepheline [16]. Combined these could lead to glass waste forms with poor durability or glass waste forms with unacceptable waste loadings.

5.1 Glass Waste Forms produced in the CCIM

The immobilization of HLW by vitrification is a well established process that is in current deployment and has been extensively investigated over the last 60 years. Many different glass types have been proposed as potential candidates for immobilization of radioactive wastes, but the current standard is borosilicate glass or BSG. Many commercial vitrification plants are in operation around the world using borosilicate glass to immobilize HLW [13].

The main advantages of vitrification of the HLW calcine classes in the CCIM include the following: glass is a good solvent for most all the constituents in the calcine, glass can be processed at reasonable low temperatures, glass is tolerant to variations in waste composition, glass shows acceptable chemical durability, and glass is radiation resistant and can accommodate some changes during radioactive decay [13]. The choice of a glass composition waste form is a compromise amongst HLW solubility, low leachability in repository environments, and the temperature at which the glass is formed. Suitable glass forms make it possible to incorporate up to 25-30 wt. % HLW into a glass [13]. There have been several reports using CCIM technology to develop glass waste forms, for example [17-19].

5.2 Glass-Ceramics produced in the CCIM

5.2.1 Benefits of Glass-Ceramics

Ceramic and glass ceramic waste forms offer an attractive alternative to traditional borosilicate glass (or a phosphate-based glass) waste forms and, if proven to be formable in the CCIM, may result in a calcine waste form with equivalent loadings and durability to those created via HIPing. Pure ceramics (i.e., waste forms made up of single or multiple phases of only synthetic crystalline minerals) can usually accommodate higher waste loadings than borosilicate glass [13], leading to smaller intermediate and long-term storage/disposal facilities. Many ceramic phases are known to possess superior chemical durability as compared to borosilicate glass [13]. However, ceramics are generally multiphase systems containing many minor phase that make characterization and prediction of performance within a repository challenging. Additionally, the technologies employed in ceramic manufacture are typically more complex and expensive. Thus, many investigators have proposed using glass-ceramics as a compromise between the more inexpensive, easier to characterize glass waste forms and the more durable ceramic waste forms. Glass-ceramics have several advantages over traditional borosilicate glasses as a waste form. Borosilicate glasses can inadvertently devitrify, leading to a less durable product that could crack during cooling and crystals may be prone to dissolution. By designing a glass-ceramics, the risks of deleterious effects from devitrification are removed. Furthermore, glass-ceramics have higher mechanical strength and impact strengths [20] and possess greater chemical durability as noted above. Glass-ceramics should provide a waste form with the advantages of glass—ease of manufacture—with improved mechanical properties, thermal stability, and chemical durability [21].

Zirconolite ($\text{CaZrTi}_2\text{O}_7$) has long been recognized as a suitable ceramic crystalline host for actinides since Uranium and Plutonium are incorporated into the Ca and Zr sites as tetravalent ions [13, 22]. Zirconolite is a crystalline phase that is chemically durable and radiation resistant and has a high capacity to incorporate actinides and lanthanides within its crystal lattice [13]. Due to the high concentrations of ZrO_2 in the radioactive calcine (see table 2) the production of a glass-ceramic containing zirconolite is recommended. In addition to zirconolite, many other crystalline phases are suitable for the very long-term tie-up of actinides. Examples of the many others, that may or may not be suitable for the HLW calcine classes, include the crystalline ceramics of: pyrochlore, apatite, zircon, monazite, and baddeleyite.

5.2.2 Glass-Ceramic Waste Form Production

Glass-ceramics are partially crystalline solids prepared by the partial devitrification of precursor glass [20]. The preparation of useful glass-ceramics is accomplished with a better understanding of the nucleation and growth of crystals within glass. Once the waste form has been cast, crystallization is accomplished by an additional heat treatment schedule. This schedule can include controlled cooling to nucleation temperature for initial crystallization followed by heating or holding at temperature for crystal growth. For glass-ceramics designed for nuclear waste the volume fraction of residual glass is typically > 50%, which yields discreet crystalline structures within the vitreous matrix [20].

Several demonstrations of glasses with ceramic phases within them have been completed using CCIM technology [15, 23-25]. A CCIM has been used at full scale (crucible inside diameter = 418 mm with a melt height ~860 mm) in the former Soviet Union to make glass-ceramic waste forms from simulated Savannah River samples [24, 25]. Several of these tests had waste loadings up to 60% wt.

A study on the formation of glass-ceramics using a CCIM has been performed with calcines simulating those stored in CSSFs [23]. This study focused efforts on formulating a glass-ceramic that could accommodate a wide range of waste compositions while limiting potential for volatility of some radionuclides and pouring into standard US canisters. *Key to developing a suitable glass-ceramic waste form is the formulation of the base glass and cooling schedule. While information of the base glass is not included, Day et al. evaluated 400 different formulations/cooling scenarios and showed, using simulated INL calcine, that the formation of major crystalline phases (Zirconolite, rutile, zirconia, and fluorite) was not very sensitive to the cooling rate [23].*

Several papers from Loiseau, Caurant, and coworkers have explored different glass-ceramic formulations and their influence for the crystallization of Zirconolite and partitioning of Neodymium (i.e., the actinide surrogate) into the crystalline (i.e., the ceramic) phases [8-12, 26, 27]. In two papers [11, 12], Loiseau and coworkers started with an aluminosilicate glass ($\text{SiO}_2\text{-Al}_2\text{O}_3\text{-CaO}$) and varied the recipe by changing the weight (molar) percentage of CaO , TiO_2 and ZrO_2 added to the melts. This represents an excellent starting point for production of glass-ceramics using INL calcine, since as previously discussed (Table 2), it contains a high concentration of Al_2O_3 and ZrO_2 . After melting and pouring the glassy matrix, the glass was annealed at 750 °C, prior to promoting crystallization at 850 °C. Different heat schedules were used for each of the three glass compositions (all with crystallization temperature above transformation temperature) to explore how temperature altered crystallization. This work showed that different formulations have different responses to different heat schedules, but zirconolite was the only crystalline phase formed in the bulk of the glass with crystallization temperatures of 1050° and 1200° C. Furthermore, the wt% of CaO , TiO_2 and ZrO_2 increased the volume fraction of zirconolite crystals and the incorporation of Nd within zirconolite. When comparing nucleation temperatures, 1050° C was more consistent for incorporation of Nd within zirconolite than 1200° C. Caurant, Loiseau, and coworkers also evaluated the effects of increased Al_2O_3 content on the crystallization of zirconolite [9]. With their additive formulation it was shown that increased Al_2O_3 increased the nucleation of zirconolite crystals in the bulk and increased the incorporation of Neodymium into the zirconolite phase. Thus, the high concentration of Al_2O_3 in the radioactive calcine may help increase nucleation of zirconolite crystals and partitioning of actinides to this phase. Additionally, they show that at nucleation temperatures of 1050° and 1200°C zirconolite is the only crystalline phase in bulk within the $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-CaO}$ glass formulation [9].

6. Recommendations

It is recommended that several different CCIM tests be performed to evaluate the formation of glass-ceramics using at least 2 of the major classes of INL simulated calcines (i.e., zirconium and aluminum oxide based). These tests should be broken up into two separate tasks: (1) identification of an additive composition starting with $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-CaO}$ glass that will accomplish the goals listed in section 6.1 and (2) demonstration of CCIM processing to further explore the effects of heat schedules (annealing, nucleation temperature, crystallization temperature, and hold times), waste loading, and feed/pour rates. Specific efforts should be focused on minimizing volatility of the melt, including cesium. This will allow for techno-economic analysis to determine if CCIM production of glass-ceramics is a viable fall back technology for calcine treatment.

6.1 Waste Form Performance Requirements

A desired list of qualities for a glass-ceramic waste form is given below:

- Due to the variability of the radioactive calcine (Table 2), the ability to accommodate a wide range of waste compositions is necessary.
- To minimize costs associated with the waste form, it should be able to accommodate high waste loadings $\geq 50\%$ wt.
- The glass-ceramic waste form should have an additive formulation that:
 - Minimizes volatility of the melt, including cesium.
 - Allows for pouring into canisters and controlled canister cooling to ensure formation of the correct glass-ceramic phases.
 - Where possible (as determined by the composition of the waste) minimizes the number of phases within the glass-ceramic.
- Quality compatible with disposal into future geologic facilities with clear qualification requirements that eliminate past requirements that were not technically supported since they were based on the long time periods associated with the alpha decay of the remaining actinides in the calcine. Since the ceramic portion of the glass-ceramic is considered to be more durable than the surrounding glass, one quality indicator may be the same as what is used for glass, PCT leach testing.
- Maintains quality over a wide range of cooling scenarios, by avoiding the formation of crystal phases detrimental to the waste form such as nepheline $[\text{NaAlSiO}_4]$, anorthite $[(\text{Ca},\text{Na})(\text{Si},\text{Al})_4\text{O}_8]$, and nosean $[\text{Na}_8\text{Al}_6\text{Si}_6\text{O}_{24}\text{SO}_4]$.

6.2 Modifications to CCIM

Prior to operating the CCIM for simulated radioactive calcine, there are a number of critical modifications that must be completed if formation of a glass ceramic waste form is possible, they are as follows:

- Removal of the current CCIM liquid simulant feed system.
- Design, installation, and testing of a dry solid feed system suitable for dry feeding the calcine surrogate.
- Design and installation of dry auger feed system access and vents to ensure minimal and regulatory compliant worker exposure to the RCRA hazardous metal(s) in the dry particulate feed that constitutes the surrogate calcine.

- Resetting of the CCIM’s radio frequency generator frequency to ensure inductive coupling of the generated magnetic field to the unique electrical resistivity of the surrogate calcine and the glass-ceramic frits and additives
- Revision of the approved Laboratory Instruction in a manner to accommodate for the hazards associated with a particulate feed containing RCRA hazardous metals.
- CCIM melter drain and melt collection canister modifications and associated temperature control equipment as needed to ensure the post melt heating /cooling rates necessary to form the proper glass –ceramic phases

6.3 Unknowns

While operating the CCIM in the future for the purpose of validating a glass-ceramic waste form for the calcine, besides waste form quality, additional data should be collected to preliminary assess if the CCIM technology is even operationally feasible for the INL’s IWTU. This data will support, in part, the first unknown addressed in this section. Latter unknowns addressed include issues of CCIM melt pouring and post melt heat treatment

6.3.1 Throughput to be Competitive with HIP Processing

Approximately 12,200,000 lbs of radioactive calcine are stored in CSSF vaults at INTEC. This waste must be treated and readied for transport out of Idaho by December 31, 2035, as required by the Idaho Settlement Agreement [28]. A 2009 modification to the CWI contract states that the design and processing of radioactive calcine “shall be based on treatment (if required), packaging, and shipment/storage of all HLW within a 12-year period” [29]. To prepare the 12.2 million pounds within this time frame will require processing approximately 3,980 lbs of HLW calcine per day:

It is assumed that glass-ceramic produced within the CCIM to accommodate a loading of at least 50% calcine, thus in total (additives + calcine) the throughput from CCIM must be approximately 7,960 lbs per day:

Several groups have published throughputs of their CCIM on a mass per time per area basis, for example [18, 30-32]. Stefanovsky, et al., give a process throughput rate of 890 kg/m²/hr [processed 2.7 kg in 20 min (8.1 kg/hr) in a 108 mm ID CCIM = 884.2 kg/m²/hr] [32]. Given this throughput and the known pounds per day required CCIM to complete the processing goal, a crucible with an inside diameter of at least 18.4 inches is required:

In a 50 cm diameter CCIM (Sugilal et. al., reported a glass melting rate of 20-40 kg/hr depending upon power input [18]. This gave a much lower throughput than that of Stefanovsky, at approximately 102 to

204 kg/m²/hr. Using this worst case scenario the required diameter would increase to 1.37 m or 54 inches.

Kobelev and co-workers used the full scale, 41.8 cm inside diameter CCIM at the Radon facility in the former Soviet Union to examine the vitrification of SRS SBW at a high loading [31]. They were only able to achieve a specific glass production rate of ~1085 kg/m²/day. Extrapolating this production rate to the diameter required to process 12.2 million pounds of calcine within timeline would require a diameter of approximately 81 inches (206 cm).

In another test with a new simulated waste and glass modifier at the same facility using the same size crucible Kobelev and co-workers were able to achieve a specific glass production rate of 2453 kg/m²/day [30]. If this specific productivity number to satisfy the calcine treatment requirements would require a crucible to be approximately 1.37m (53.9 inches) inside diameter.

The tests conducted by Kobelev et al. [30, 31], highlight how different feed materials can greatly influence the throughput of the process and requires further investigation using the INL CCIM.

Given the variability seen in specific production rates it will be necessary to conduct tests to determine the nominal acceptable calcine throughput of the 10.25 inch diameter CCIM at INL. This number is required to properly size a full scale CCIM to achieve calcine processing goals and make economic comparisons with the HIP process as well as validate if sufficient CCIM foot print is available in the INL's IWTU. Depending upon throughput it may be possible to use a single CCIM system to meet production goals.

6.3.2 Heating Schedule/Cooling Rates

Heating schedules and cooling rates will have a significant effect on the waste form produced in the CCIM. Small scale tests with optimized glass additives yield "almost homogeneous glass" with traces of spinal type crystalline phase only observed at a waste loading of 60% [30]. They surmise that larger melt volumes in the CCIM may have caused increased crystallization, but it is also possible that differences in heating schedules for small-scale (50 mL) vs. large-scale pours differ, with the large-scale pour retaining heat longer, influencing crystallization. This point outs a significant challenge in scaling up, the importance of understanding how changes in parameters influence the waste form quality, and highlights a need to address questions related to cooling rates for the calcine /glass ceramic waste form post pour from the CCIM

As noted above, Day et al, evaluated 400 different formulation/cooling scenarios [23]. Their findings suggest that the formation of the major phases is not very sensitive to cooling rate once their

ideal formulation was identified. However, to identify this set of cooling conditions many were tested for dropping the temperature from 1300° C to ~ room temperature ranging from rapid quenching on a stainless steel plate to cooling at $\leq 24^{\circ}$ C. This approach should be repeated with the knowledge gained from the tests of Loiseau, Curren, and coworkers [8-12, 26, 27]. Their work suggests that a nucleation temperature of 1050° C held for ~ 2 hours will yield a consistently high crystal fraction with the vast preponderance being zirconolite. This should be used as a starting point for studies exploring nucleation and crystal growth for forming the glass-ceramic calcine waste forms via the CCIM.

6.3.3 Feed and Pouring Rates

In the CCIM a fed-batch approach is assumed to be the mode of operation. In this case the material fed into the CCIM will be allowed to mix with melted material. After a set amount of time a portion of the well mixed glass will be poured into waste canisters. After pouring the feed/pour cycle will continue.

Higher feed rates will lead to the formation of a “cold cap” whereas lower feed rates will not. The cold cap could be used to reduce losses of volatile materials. Comparisons of the retained volatile material under feed rates that lead to cold cap vs. no cap should be evaluated.

Smith et al, tested the ability to maintain a cold cap in a 500 mm ID CCIM operating at 1250° C at the NETEC facility in South Korea [33]. At a feed rate from 15 to 30 liters per hour approximately 60 % coverage was preserved. At 50 liters/hour the cold cap coverage was ~ 80%. Higher feed rates were not tested due to increased pressure drop in the off-gas system causing the end of the demonstration. During the same demonstration pouring of the glass through the drain-discharge valve became more difficult with time, possibly due to crystallization of the melt within the drain valve. This highlights two potential problems that must be evaluated during testing.

6.3.4 Canister size

Several options are available for canister size, although it will be important to appropriately size the canister for the pouring rate. Given the size of our pilot scale CCIM is not practical to use standard 2' DOE canisters for testing. A smaller scale canister could be insulated such that it will have similar cooling characteristics as the standard 2' can. This canister should also allow for cooling along the centerline, i.e. Canister Centerline Cooling (CCC). Furthermore, the canister should be sufficiently tall enough to allow for multiple pours from the CCIM. This multiple pour test is more representative of the full scale version, where it is unlikely that a single pour will fill the standard 2' diameter can.

6.4 Post Production Testing

A standard suite of tests should be performed to analyze the quality of the waste forms produced during testing and to compare between different formulations and waste loadings. Product consistency testing (PCT) is designed to give normalized release values for the major components in the glass. This test will help determine how increased calcine loading influences the quality of the waste form and the maximum waste loading. Use of Scanning Electron Microscope with Energy Dispersive Spectroscopy (SEM-EDS) will allow for visualization of the different phases within the waste form as well as chemical characterization of these phases and should be used. This technique will allow for a compositional microanalysis of the crystalline phases and the surrounding glass. X-ray diffraction (XRD) should be used to garner information about the crystallographic structure and chemical composition of the waste form.

During testing of the CCIM several off-gas parameters should be closely monitored. These include off-gas flow rate and composition (especially for Cr, Cd, and Hg) and particulate matter. A mass balance for Cr and Cd should be completed using the total scrubber water volume and composition and the

composition of the waste form. This information will be used to validate the retention of volatiles within the waste form as well as ensure that the waste form not only immobilizes the radioactive constituents of the calcine, but also meets RCRA requirements.

7. Conclusions

This report provides recommendations for the production of HLW calcine glass-ceramic waste forms using the CCIM located at INL. Glass-ceramics have several advantages over traditional borosilicate glasses as a waste form. By designing a glass-ceramic, the risks of deleterious effects from devitrification are removed; and glass-ceramics will provide a waste form with the advantages of both glass and ceramics: ease of manufacture with improved mechanical properties, higher waste loadings, thermal stability, and chemical durability.

This report does not recommend that any future research on pure glass formulations for the calcine waste forms should not be undertaken. Certainly the calcine compositions and the CCIM's increased temperature capability are well suited for making both borosilicate and phosphate based glass waste forms. However, our evaluations conclude that only the glass-ceramics can compete with the performance of the HIPing process and the glass-ceramic it produces.

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