Contract No:

This document was prepared in conjunction with work accomplished under Contract No. DE-AC09-08SR22470 with the U.S. Department of Energy (DOE) Office of Environmental Management (EM).

Disclaimer:

This work was prepared under an agreement with and funded by the U.S. Government. Neither the U. S. Government or its employees, nor any of its contractors, subcontractors or their employees, makes any express or implied:

1) warranty or assumes any legal liability for the accuracy, completeness, or for the use or results of such use of any information, product, or process disclosed; or
2) representation that such use or results of such use would not infringe privately owned rights; or
3) endorsement or recommendation of any specifically identified commercial product, process, or service.

Any views and opinions of authors expressed in this work do not necessarily state or reflect those of the United States Government, or its contractors, or subcontractors.

Progress and Technology Assessment of Melt-cast Ceramic Waste Forms

Nuclear Technology Research & Development

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

J.W. Amoroso

June, 2020
SRNL-STI-2020-00201

DISCLAIMER

This work was prepared under an agreement with and funded by the U.S. Government. Neither the U.S. Government or its employees, nor any of its contractors, subcontractors or their employees, makes any express or implied:

1. warranty or assumes any legal liability for the accuracy, completeness, or for the use or results of such use of any information, product, or process disclosed; or
2. representation that such use or results of such use would not infringe privately owned rights; or
3. endorsement or recommendation of any specifically identified commercial product, process, or service.

Any views and opinions of authors expressed in this work do not necessarily state or reflect those of the United States Government, or its contractors, or subcontractors.

Printed in the United States of America

Prepared for
U.S. Department of Energy

Keywords: *Ceramic Waste Form, Leach Testing*

Retention: *Permanent*

Progress and Technology Assessment of Melt-cast Ceramic Waste Forms

Jake W. Amoroso

June 2020

Prepared for the U.S. Department of Energy under contract number DE-AC09-08SR22470.

Government License Notice

This work was prepared under an agreement with and funded by the U.S. Government. Neither the U. S. Government or its employees, nor any of its contractors, subcontractors or their employees, makes any express or implied: 1. warranty or assumes any legal liability for the accuracy, completeness, or for the use or results of such use of any information, product, or process disclosed; or 2. representation that such use or results of such use would not infringe privately owned rights; or 3. endorsement or recommendation of any specifically identified commercial product, process, or service. Any views and opinions of authors expressed in this work do not necessarily state or reflect those of the United States Government, or its contractors, or subcontractors.

This document has been created by Savannah River Nuclear Solutions, LLC, Operator of Savannah River National Laboratory under Contract No. DE-AC09-08SR22470. The U.S. Government retains for itself, and others acting on its behalf, a paid-up nonexclusive, irrevocable worldwide license in said article to reproduce, prepare derivative works, distribute copies to the public, and perform publicly and display publicly, by or on behalf of the Government.

This work was supported by the U.S. Department of Energy, Office of Nuclear Energy, under Contract DE-AC02-06CH11357.

CONTENTS

EXECUTIVE SUMMARY

The Savannah River National Laboratory (SRNL) conducted research from FY2011 – FY2020 to develop ceramic waste forms to treat High-Level Waste (HLW) resulting from reprocessing of commercial Used Nuclear Fuel (UNF) as part of the Department of Energy (DOE) office of Nuclear Energy (NE) Fuel Cycle Technologies (FCT) research program. The objective of the research was to develop a reference ceramic waste form and process technology needed to immobilize the combined HLW raffinate stream, including undissolved solids and soluble technetium, and potentially the TRU waste stream resulting from reprocessing processes. This report compiles the relevant literature produced under, and pertinent to, the program objectives and provides a perspective on the technology development as well as prospects for future.

1 Summary

Between 2011 and 2020 the Savannah River National Laboratory (SRNL) conducted research into melt-cast ceramic waste forms designed to crystallize upon cooling from a melt. The objectives of the research were to develop a (1) reference ceramic waste form and (2) processing technology to immobilize a high-level waste (HLW) stream in a ceramic matrix. The envisioned HLW stream would originate from an aqueous reprocessing scheme proposed for used nuclear fuel (UNF) in the United States.

In the proposed scheme, the HLW would be split into fractions with common chemistry that could be treated as individual waste streams or combined and treated as a single waste stream. The primary waste streams for consideration included an undissolved solids stream, a Cs/Sr separated stream, HLW raffinate resulting from the transuranic extraction (TRUEX) process, and lanthanide series elements resulting from the Trivalent Actinide - Lanthanide Separation by Phosphorous reagent Extraction from Aqueous Komplexes (TALSPEAK) process.

In 2008, a trade study concluded that it was beneficial, from a cost analysis, to treat a single combined HLW stream using existing technologies (i.e. vitrification) compared to the cost required to realize multiple waste treatment strategies for a partitioned waste stream.[1] Borosilicate glass was identified as the preferred waste form for the envisioned waste since borosilicate glass has been demonstrated to accommodate a wide range of fission products and vitrification technology is mature.[2-6] However, several characteristics of borosilicate glass provide an opportunity to explore alternative waste forms. For example, some fission products in the HLW stream have limited solubility in borosilicate glass,[7-8] which is also known to be susceptible to hydrothermal leaching, a condition to be expected in geologic disposal.[9-12] Furthermore, the HLW stream would contain significant amounts of Cs and Mo, which, under oxidizing conditions, readily form water soluble phases detrimental to the performance of the waste form.[13] The campaign identified glass-ceramics and ceramics as two promising research and development directions to potentially reduce life-cycle costs via increased waste loading and durability. The glass-ceramic and ceramic research was led by Pacific Northwest National Laboratory (PNNL) and SRNL, respectively.

Ceramic waste forms are well known, and large amounts of literature exists detailing their use in nuclear waste applications. Researchers in Australia have pioneered ceramic waste form development since the 1970's, including the SYNROC phases and the hot isostatic pressing (HIP) method to produce them. Those methods are well-developed and continue to be advanced through work at the Australian Nuclear Science and Technology Organization (ANSTO) as well as by others.[14-1819] From the outset, the SRNL ceramics waste form program intended to explore ceramic waste form development distinctly different from that of the existing HIP technology.

Although HIP processing is a viable technology for fabricating complex (i.e. multiphase) ceramic waste forms, the HIP process is mechanically complex and has a significant potential for airborne radionuclide contamination compared to a liquid fed melting process. The approach at SRNL has been to design waste form compositions based on a simulated waste stream that, when combined with appropriate additives, can be melted and will fully crystallize into a desirable ceramic phase assemblage upon cooling. The ceramic waste forms are designed to be multiphase, which allows for a broad range of waste elements (e.g. from a combined HLW waste stream) to be incorporated into the different crystalline phases. The development of the melter technology to enable processing of these ceramics was a significant component of the research, especially in the later years of the project, to demonstrate technology readiness of ceramic waste form fabrication.

The SRNL team first explored single phase ceramic composition development in order to establish a set of target phases for which to immobilize the various waste constituents. Four phases, pyrochlore, perovskite, zirconolite, and hollandite type phases were selected in the early years of the project from which to develop multiphase compositions. Of those phases, only the hollandite phase required significant composition development. Hollandite is the host for Cs, which is difficult to immobilize and readily reacts in oxidizing environments to form non-durable phases. After demonstrating the potential to reduce parasitic phase formation through controlled melt process chemistry, SRNL endeavored to demonstrate the feasibility of the melt-cast process for ceramic waste forms. Demonstrations at the laboratory, bench, and pilot scale were performed.

This program was supported by university and international efforts through the use of the Nuclear Energy University Program (NEUP), a Coordinated Research Project (CRP), as well as in-kind technical support between ANSTO and SRNL including sharing of samples, results, and other information. These are summarized below:

- DOE-Nuclear Energy University Program (NEUP) partnership CFA-12-3809: “Alternative High-Performance Ceramic Waste Forms,” (Alfred University lead)
- DOE-Nuclear Energy University Program (NEUP) partnership CFA-14-6357: “A New Paradigm for Understanding Multiphase Ceramic Waste Form Performance,” (Clemson University lead)
- Coordinated Research Project (T2.10.27) International Atomic Energy Agency (IAEA) (2014-2015)
- Cooperative Research and Development Agreement (CRADA) with Australian Nuclear Science and Technology Organization (ANSTO), “Joint Waste Forms Development” (2012-2020)

In addition, the campaign supported interlaboratory efforts which included complementary irradiation and characterization performed at Los Alamos National Laboratory as well as a Cold Crucible Induction Melter (CCIM) demonstration at the Idaho National Laboratory (INL).

A list of the most pertinent documents related to the activities and results from this work, and perspectives on the technology assessment and future research directions, based on the author’s familiarity with the work are presented subsequently.

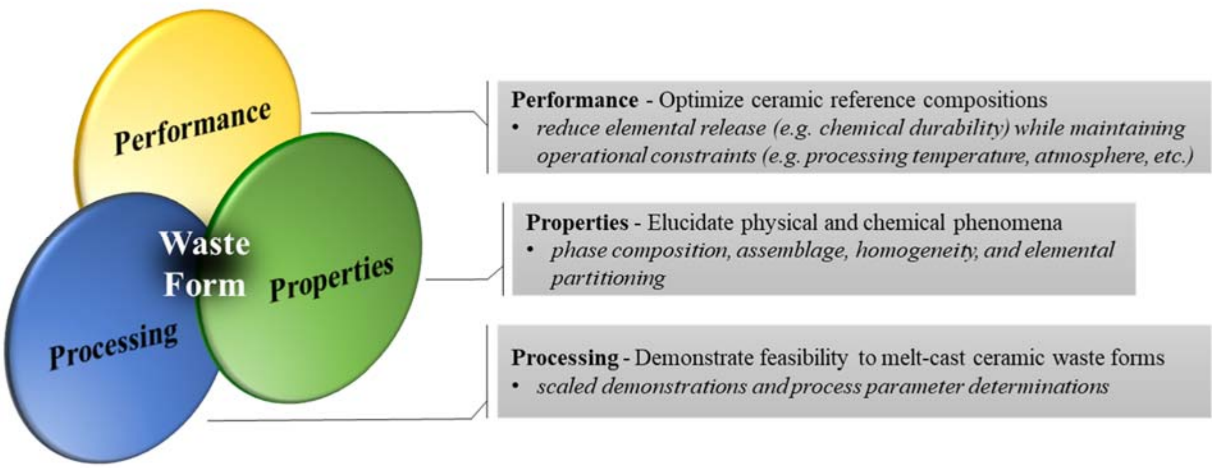
2 Progress and Technology Assessment

A report issued in 2015[20] identified four primary research challenges needed to develop advanced ceramic waste forms for an integrated reprocessing/HLW scheme:

- Optimize the melting and crystallization process to obtain desired product quality while minimizing volatility,
- Perform detailed characterization to determine elemental partitioning in phases, grain boundaries, etc. to facilitate a product control strategy and product qualification,

- Develop a fundamental understanding of durability for individual end member phases, minority phases and grain boundary phases as related to durability of multiphase product,
- Develop a waste compliance plan that describes how the multiphase ceramic waste form will be qualified for disposal.

The results from this work have advanced significant technical progress towards the first three research needs, which can be used to develop waste acceptance criteria and qualification standards for disposal. A phased approach to understand processing, properties, and performance relationships in ceramic waste forms through integrated and iterative research in those areas was performed. The following schematic shows the general research directions and aims that were investigated:



Processing: One of the long-term goals of the project was to demonstrate the melt-process on a sufficient scale to evaluate the feasibility of the ceramic and requisite process technology for waste form production. During the course of the project, melt-processed ceramics were prepared at quantities ranging from crucible and laboratory scale (gram quantities) to bench and pilot scale quantities (kilogram quantities). SRNL has demonstrated ceramic melts suitable for immobilization of HLW can be poured and cast with relative ease. While the ceramic does not have the working range characteristic of glasses, the viscosity of the melt easily flows and will likely fill a moderately sized container or canister.

SRNL has demonstrated a practical method to fabricate a crystalline ceramic waste form with a desired phase assemblage based on thermodynamic principles. Specifically, through the development of a melt-process, thermodynamically favorable phase evolution as a function of temperature can be controlled to sequentially crystallize different phases during processing. The significance of this approach is that it can be used to energetically suppress parasitic and deleterious phase formation.

During a conventional sintering process, all phases develop simultaneously at a sub-liquidus temperature, which leads to competition among the phases. Phases that require less energy to form will have an increased propensity to form, provided they are not kinetically limited. These phases that are intrinsically easier to form often lead to off-stoichiometry and chemically substituted phases that are less energetically stable than a pure phase, leading ultimately to non-ideal measured durability. The development of low-durability phases is undesirable, and in chemically complex systems such as HLW, which contain elements across the periodic table groups (e.g. alkali, transition metal, etc.), parasitic phase evolution is problematic. The melt-processing approach has been demonstrated through experiment and provides a theoretical basis for physicochemical stability of ceramic waste forms. The combination of the ability to tailor the phase assemblage in combination with a fundamental understanding of its formation is a significant step towards developing predictive durability models.

Properties: The microstructure of ceramics are dependent on their intrinsic transport properties as well as processing method. Melt-cast and sintered ceramics produced in this research exhibited distinctly different microstructure. Not surprisingly, melt-cast materials exhibited exaggerated grain growth and directional solidification, whereas sintered samples exhibited fine grained microstructures. Melt-cast samples were dense with homogeneous phase distribution and element partitioning. Sintered samples exhibited less homogeneous phase development with concentrated areas of element partitioning and required special processing (e.g. HIP, SPS) to obtain dense samples.

In order to control and understand element partitioning and phase assemblage in melt-cast ceramics, extensive characterization and testing was performed on synthesized samples. Samples were prepared in gram and kilogram quantities. In addition to the melt-process, several processing methods including HIP, spark plasma sintering (SPS) and solution combustion synthesis (SCS) were used to prepare samples for comparison purposes. The general approach was to measure gross microstructure, phase assemblage, and chemical composition via x-ray diffraction (XRD) and inductively coupled plasma (ICP) spectroscopy and correlate those results to specific element partitioning via Energy Dispersive Spectroscopy (EDS). Complementary to these general methods, advanced characterization of the phases and grain boundaries was carried out. This work was performed in collaboration with other academic and laboratory institutions and included, for example, transmission electron microscopy (TEM), selected area electron diffraction (SAED), x-ray spectroscopy (XPS), x-ray absorption near edge structure (XANES), and contrast x-ray nanotomography (XNT). Measurements were used to obtain spatial distribution of phases, probe minor phase content below detection in gross measurement techniques, as well as elucidate chemical and structural parameters including charge state, site occupancy, etc. These methods were used to inform interpretation of durability and stability measurements.

Performance: Stability of the ceramic waste forms was investigated through accelerated chemical durability experiments and irradiation induced damage studies. Aqueous leach testing (e.g. ASTM 1285, 1220, and 1663) was used to investigate element release. Ion beam irradiation, combined with localized characterization, was used to impart damage that would be expected during the life of the ceramic waste form to the materials.

Chemical durability of the ceramic waste forms was focused on Cs leaching, which is of the greatest concern and most difficult to control. Melt-cast multiphase ceramics with excellent element retention were produced through control of the phase assemblage and element partitioning. Comparison of melt-cast and HIP methods demonstrated how performance is coupled to processing and that either process can be used to produce a satisfactory, or inferior, waste form depending on the target composition. Extensive analysis of leaching results also indicated excellent reproducibility, indicating physiochemical homogeneity throughout melt-cast multiphase ceramic waste forms. While Cs retention was affected by irradiation in some samples, stability and damage measurements confirmed the robust nature of ceramics and resistance to radiation damage, regardless of synthesis method.

Throughout the course of this research, several significant milestones and technological accomplishments were achieved to advance ceramic waste form technology readiness including:

- Development of reference ceramic compositions with reduced elemental release (e.g. chemical durability) while maintaining operational constraints (e.g. processing temperature, atmosphere, etc.) compared to baseline,
- Development of a melt-technology required to process durable ceramic waste forms with desirable phase composition, assemblage, homogeneity, and elemental,
- Advancement of the scientific understanding of physical and chemical phenomena affecting ceramic waste form phase stability, and
- Demonstration of the feasibility to melt-cast ceramic waste forms at the pilot scale.

Details and results of the research and development related to the ceramic waste form task have been documented in reports, memorandum, journal publication, and technical presentations throughout the project. The sub-sections below provide citations for the reader which include pertinent DOE Reports and Journal Articles produced as part of the campaign. Some of the listed citations are duplications of references in this report, but they are retained in the listing for completeness.

2.1 List of citations – Background Information to the Campaign

Vienna, J. D.; Collins, E. D.; Crum, J. V.; Ebert, W. L.; Frank, S. M.; Garn, T. G.; Gombert, D.; Jones, R.; Jubin, R. T.; Maio, V. C.; Marra, J. C.; Matyas, J.; Nenoff, T. M.; Riley, B. J.; Sevigny, G. J.; Soelberg, N. R.; Strachan, D. M.; Thallapally, P. K.; Westsik, J. H. *Closed Fuel Cycle Waste Treatment Strategy*; INL/EXT-15-34504 (FCRD-MRWFD-2015-000674); Idaho National Laboratory: Idaho Falls, ID, 2015.

Billings, A. L.; Brinkman, K. S.; Fox, K. M.; Marra, J. C.; Tang, M.; Sickafus, K. E. *Preliminary Study of Ceramics for Immobilization of Advanced Fuel Cycle Reprocessing Wastes*; SRNL-STI-2010-00560, (FCRD-WAST-2010-000158); Savannah River National Laboratory: Aiken, SC, 2010.

Crum, J. V.; Billings, A. L.; Lang, J. B.; Marra, J. C.; Rodriguez, C. P.; Ryan, J. V.; Vienna, J. D. *Baseline Glass Development for Combined Fission Products Waste Streams*; AFCI-WAST-WAST-MI-DV-2009-000075; Pacific Northwest National Laboratory: Richland, WA., 2009.

Gombert, D.; Piet, S.; Trickel, T.; Carter, J.; Vienna, J.; Ebert, B.; Matthern, G. *Combined Waste Form Cost Trade Study*; INL/EXT-08-14993 (GNEP-SYSA-PMO-MI-DV-2009-000003); Idaho National Laboratory: Idaho Falls, ID, 2008.

2.2 List of citations – Select DOE Reports Produced During the Campaign

Amoroso, J. W. *Summary of Melt-cast Ceramic Research*; SRNL-STI-2018-00531/ NTRD-MRWFD-2018-000178; Savannah River National Laboratory: Aiken SC, 2018.

Brinkman, K.; Bordia, R.; Reifsnider, K.; Chiu, W.; Amoroso, J. *Final Project Report CFA-14-6357: A New Paradigm for Understanding Multiphase Ceramic Waste Form Performance*; 2017.

Amoroso, J. W.; Dandeneau, C. S.; Brinkman, K. S.; Tang, M. *Material Recovery & Waste Form Development – Ceramic Waste Form Fabrication Comparison*; SRNL-STI-2016-00197s; Savannah River National Laboratory: Aiken SC, 2017.

Sundaram, S. K.; Clark, B. M.; tumurugoti, P.; Misture, S. T.; Amoroso, J. W.; Marra, J. C.; Tang, M. *Final Project Report 12-3809: Alternative High-Performance Ceramic Waste Forms*; M2NU-12-NY-AY # 0202-0410; 2016.

Dandeneau, C. S.; Amoroso, J. W. *Multi-phase Ceramic Waste Forms: Comparison of Melt and Hot Isostatic Pressing Methods*; SRNL-STI-2016-00690; Savannah River National Laboratory: Aiken SC, 2016.
Amoroso, J. W. *FY16 Annual Accomplishments – Waste Form Development and Performance*; SRNL-STI-2016-00613; Savannah River National Laboratory: Aiken SC, 2016.

Maio, V. C.; Benefiel, B.; Scott, C.; Crum, J.; Rodriguez, C.; Amoroso, J. W.; Marra, J. C. *Cold Crucible Induction Melter (CCIM) Testing on Glass Ceramic and Ceramic Waste Forms*; SRNL-STI-2015-00186 (FCRD-MRWFD-2015-000758); Savannah River National Laboratory: Aiken SC, 2015.

Amoroso, J. W.; Marra, J. C. *Melt Processed Crystalline Ceramic Waste Forms for Advanced Nuclear Fuel Cycles - Final CRP Report for Research Agreement No. 17208*; SRNL-STI-2015-00437; Savannah River National Laboratory: Aiken SC, 2015.

Amoroso, J. W.; Marra, J. C. *Characterization of Ceramic Material Produced from a Cold Crucible Induction Melter Test*; SRNL-STI-2015-00188 (FCRD-MRWFD-2015-000133); Savannah River National Laboratory: Aiken SC, 2015.

Amoroso, J. W.; Edwards, T. B.; Johnson, F. C.; Peeler, D. K. *Development of Compositional Relationships for a Glassy Slag Material for Municipal Waste Residues Resulting from a Gasification Process*; SRNL-STI-2015-00514; Savannah River National Laboratory: Aiken, SC, 2015.

Amoroso, J. W. *Material Recovery & Waste Form Development – Ceramics Formulation optimization activities in FY15 – Preliminary Results (M4FT-15SR0307025)*; SRNL-L3100-2015-00185; Savannah River National Laboratory: Aiken SC, 2015.

Maio, V. C. *Production of a Low Temperature SYNROC All Ceramic Surrogate High Level Waste Form in INL's Cold Crucible Induction Melter Pilot –Validation of Test Completion*; INL/MIS-14-34012 (FCRD-SWF-2015-00256); Idaho National Laboratory: Idaho Falls, ID, 2014.

Amoroso, J. W.; Marra, J. C. *Ceramic Waste Form Data Package: Fuel Cycle Research and Development*; SRNL-STI-2014-00247 (FCRD-SWF-2014-000581); Savannah River National Laboratory: Aiken SC, 2014.

Amoroso, J. W.; Marra, J. C. *SRNL CRP Progress Report: Development of Melt Processed Ceramics for Nuclear Waste Immobilization*; SRNL-STI-2014-00467; Savannah River National Laboratory: Aiken SC, 2014.

Brinkman, K.; Amoroso, J.; Marra, J.; Tang, M. *Crystalline Ceramic Waste Forms: Comparison of Reference Process for Ceramic Waste Form Fabrication*; SRNL-STI-2013-00442 (FCRD-SWF-2013-000229); Savannah River National Laboratory: Aiken SC, 2013.

Brinkman, K. S.; Fox, K. M.; Amoroso, J. W.; Marra, J. C.; Tang, M. *Crystalline Ceramic Waste Forms: Report Detailing Data Collection in Support of Potential FY13 Pilot Scale Melter Test*; FCRD-SWF-2012-000329 (SRNL-STI-2012-00587); Savannah River and Los Alamos National Laboratory's: Aiken, SC, 2012.

Brinkman, K.; Fox, K.; Marra, J.; Tang, M. *Development of Crystalline Ceramics for Immobilization of Advanced Fuel Cycle Reprocessing Wastes*; SRNL-STI-2012-00281 (FCRD-SWF-2012-000116); Savannah River National Laboratory: Aiken, SC, 2012.

Brinkman, K.; Fox, K.; Tang, M. *Development of Crystalline Ceramics for Immobilization of Advanced Fuel Cycle Reprocessing Wastes*; SRNL-STI-2011-00516 (FCRD-SWF-2011-000310, 2011); Savannah River National Laboratory: Aiken, SC, 2011.

2.3 List of citations – Select Journal Publications Produced During the Campaign

Grote, R.; Zhao, M.; Shuller Nickles, L.; Amoroso, J.; Gong, W.; Lilova, K.; Navrotsky, A.; Tang, M.; Brinkman, K., Compositional Control of Tunnel Features in Hollandite Based Ceramics: Structure and Stability of $(Ba,Cs)_{1.33}(Zn,Ti)_8O_{16}$. *Journal of Materials Science* **2019,** (54), 1112-1125.

Grote, R.; Hong, T.; Shuller Nickles, L.; Amoroso, J.; Tang, M.; Brinkman, K. S., Radiation tolerant ceramics for nuclear waste immobilization: Structure and stability of cesium containing hollandite of the form $(Ba,Cs)_{1.33}(Zn,Ti)_8O_{16}$ and $(Ba,Cs)_{1.33}(Ga,Ti)_8O_{16}$. *J. Nucl. Mater.* **2019,** *518*, 166-176.

Damian, P. J. C.; Cocco, A. P.; Wrubel, J. A.; Hong, T.; Bordia, R. K.; Lin, Y.; Pianetta, P.; Amoroso, J.; Brinkman, K. S.; Chiu, W. K. S., Simultaneous 3-D Elemental Mapping of Hollandite and Pyrochlore Phases in Ceramic Waste Form Materials. *J. Am. Ceram. Soc.* **2019,** *00*, 1-12.

Dandeneau, C. S.; Hong, T.; Brinkman, K. S.; Vance, E. R.; Amoroso, J. W., Comparison of Structure, Morphology, and Leach Characteristics of Multi-phase Ceramics Produced via Melt Processing and Hot Isostatic Pressing. *J. Nucl. Mater.* **2018,** *502*, 113-122.

Tumurugoti, P.; Clark, B. M.; Edwards, D. J.; Amoroso, J.; Sundaram, S. K., Cesium Incorporation in Hollandite-rich Multiphasic Ceramic Waste Forms. *Journal of Solid State Chemistry* **2017,** *246*, 107-112.

Rabbi, F.; Brinkman, K.; Amoroso, J.; Reifsnider, K., Finite Element analysis of ion transport in Solid State Nuclear Waste Form Materials. *J. Nucl. Mater.* **2017,** *493*, 303-309.

Cocco, A. P.; DeGostin, M. B.; Wrubel, J. A.; Damian, P. J.; Hong, T.; Xu, Y.; Lin, Y.; Pianetta, P.; Amoroso, J.; Brinkman, K. S.; Chiu, W. K. S., Three-Dimensional Mapping of Crystalline Ceramic Waste Form Materials. *J. Am. Ceram. Soc.* **2017,** *100*, 3722-3735.

Amoroso, J. W.; Marra, J.; Dandeneau, C. S.; Brinkman, K.; Xu, Y.; Tang, M.; Maio, V.; Webb, S.; Chiu, W. K. S., Cold Crucible Induction Melter Test for Crystalline Ceramic Waste Form Fabrication: A Feasibility Assessment. *J. Nucl. Mater.* **2017,** *486*, 283-297.

Xu, Y.; Wen, Y.; Grote, R.; Amoroso, J.; Shuller Nickles, L.; Brinkman, K. S., A-site compositional effects in Ga-doped hollandite materials of the form BaxCsyGa2x+yTi8−2x−yO16: implications for Cs immobilization in crystalline ceramic waste forms. *Scientific Reports* **2016,** *6*, 27412.

Tumurugoti, P.; Sundaram, S. K.; Misture, S. T.; Marra, J. C.; Amoroso, J. W., Crystallization behavior during melt-processing of ceramic waste forms. *J. Nucl. Mater.* **2016,** *473*, 178-188.

Tang, M.; Tumurugoti, P.; Clark, B. M.; Sundaram, S. K.; Amoroso, J.; Marra, J.; Sun, C.; Lu, P.; Wang, Y.; Jiang, Y.-B., Heavy ion irradiations on synthetic hollandite-type materials: $Ba_{1.0}Cs_{0.3}A_{2.3}Ti_{5.7}O_{16}$ (A = Cr, Fe, Al). *Journal of Solid State Chemistry* **2016,** *239*, 58-63.

Tumurugoti, P.; Sundaram, S. K.; Brinkman, K. S.; Amoroso, J. W.; Fox, K. M., Melt-Processed Multiphase Ceramic Waste Forms. In *Advances in Materials Science for Environmental and Energy Technologies III*, Ohji, T.; Matyas, J.; Manjooran, N. J.; Pickrell, G.; Jitianu, A., Eds. John Wiley & Sons, Inc: 2014; pp 205-212.

Tang, M.; Kossoy, A.; Jarvinen, G.; Crum, J.; Turo, L.; Riley, B.; Brinkman, K.; Fox, K.; Amoroso, J.; Marra, J., Radiation stability test on multiphase glass ceramic and crystalline ceramic waste forms. *Nuclear Instruments and Methods in Physical Research Section B* **2014,** *326*, 293-297.

Clark, B. M.; Tumurugoti, P.; Sundaram, S. K.; Amoroso, J. W.; Marra, J. C.; Brinkman, K. S., Microstructures of Melt-Processed and Spark Plasma Sintered Ceramic Waste Forms. *Materials for Energy Systems E* **2014,** *1* (4), 341-348.

Clark, B. M.; Tumurugoti, P.; Sundaram, S. K.; Amoroso, J. W.; Marra, J. C.; Brinkman, K. S., Microstructure-Property Relations in Melt-Processed and Spark Plasma Sintered Ceramic Waste Forms. *Microscopy and Microanalysis* **2014,** *20* (S3), 1932-33.

Clark, B. M.; Sundaram, S. K.; Brinkman, K. S.; Fox, K. M.; Amoroso, J. W., Spark Plasma Sintering of Neodymium Titanate Pyrochlore for Advanced Ceramic Waste Forms. In *Advances in Materials Science for Environmental and*

Energy Technologies III, Ohji, T.; Matyas, J.; Manjooran, N. J.; Pickrell, G.; Jitianu, A., Eds. John Wiley & Sons, Inc: 2014; pp 127-135.

Brinkman, K.; Fox, K.; Marra, J.; Reppert, J.; Crum, J.; Tang, M., Single phase melt processed powellite (Ba,Ca)MoO4 for the immobilization of Mo-rich nuclear waste. *J. Alloys Compd.* **2013,** *551*, 136-142.

Amoroso, J.; Marra, J. C.; Tang, M.; Lin, Y.; Chen, F.; Su, D.; Brinkman, K. S., Melt processed multiphase ceramic waste forms for nuclear waste immobilization. *J. Nucl. Mater.* **2014,** *454* (1-3), 12-21.

Amoroso, J.; Marra, J.; Conradson, S. D.; Tang, M.; Brinkman, K., Melt Processed Single Phase Hollandite Waste Forms for Nuclear Waste Immobilization: Ba1.0Cs0.3A2.3Ti5.7O16; A = Cr, Fe, Al. *J. Alloys Compd.* **2014,** *584*, 590-99.

2.4 List of citations – Further Reading Regarding Ceramic Waste Form Development

Donald, I. W., Immobilization of Radioactive Materials as a Ceramic Wasteform. In *Waste Immobilization in Glass and Ceramic Based Hosts: Radioactive, Toxic and Hazardous Wastes*, John Wiley & Sons: Great Britain, 2010; pp 185-203.

Stefanovsky, S. V.; Ptashkin, A. G.; Knyazev, O. A.; Dmitriev, S. A.; Yudintsev, S. V.; Nikonov, B. S., Inductive cold crucible melting of actinide-bearing murataite-based ceramics. *J. Alloys Compd.* **2007,** *444*, 438-442.

Aubin-Chevaldonnet, V.; Caurant, D.; Dannoux, A.; Gourier, D.; Charpentier, T.; Mazerolles, L.; Advocat, T., Preparation and Characterization of $(Ba,Cs)(M,Ti)_8O_{16}$ ($M = Al^{3+}$, Fe^{3+}, Ga^{3+}, Cr^{3+}, Sc^{3+}, Mg^{2+}) Hollandite Ceramics Developed for Radioactive Cesium Immmobilization. *J. Nucl. Mater.* **2007,** *366* (1-2), 137-160.

Carter, M. L.; Vance, E. R.; Li, H., Hollandite-rich Ceramic Melts for Immobilization of Cs. *Mat. Res. Soc. Symp. Proc.* **2003,** *807*, 249-254.

Jostsons, A. *Synroc - progress and future prospects*; Australia, 2001; p 198.

Sobolev, I. A.; Stefanovskii, S. V.; Omelianenko, B. I.; Ioudintsev, S. V.; Vance, E. R.; Jostons, A., Comparative Study of Synroc-C Ceramics Produced by Hot-pressing and Inductive Melting. *Mat. Res. Soc. Symp. Proc.* **1997,** *465*, 371-378.

Ewing, R. C.; Lutze, W., High-Level Nuclear Waste Immobilization with Ceramics. *Ceramics International* **1990,** *17*, 287-293.

Kesson, S. E., The Immobilization of Cesium in SYNROC Hollandite. *Radioactive Waste Manag. Environ. Restor.* **1983,** *4* (1), 53-72.

Ringwood, A. E.; Kesson, S. E.; Ware, N. G.; Hibberson, W.; Major, A., Immobilization of High-level Nuclear-Reactor Wastes in SYNROC. *Nature* **1979,** *278* (5701), 219-223.

Carter, M. L., et al., Fabrication, characterization, and leach testing of hollandite, (Ba,Cs)(Al,Ti)(2)Ti6O16. Journal of Materials Research, 2002. 17(10): p. 2578-2589.

3 Prospects and Concluding Remarks

The ceramic waste form research performed by SRNL and under the auspices of DOE’s Office of Nuclear Energy (NE) Fuel Cycle Technologies (FCT) program has achieved significant progress towards demonstrating the feasibility of processing and application of ceramic waste form materials. Through process demonstrations and expanded scientific understanding of ceramic waste form systems, we have attempted to advance the technology readiness for ceramic waste forms. Nevertheless, there remains engineering and technical challenges, but this research has also uncovered new opportunities to pursue for ceramic waste forms.

While batch processing and semi-continuous operations have been demonstrated, a robust melter capable of withstand the extreme operational requirements demanded of melt-cast ceramics is needed to better support technology evaluation and maturation for life cycle projection and analysis. A new melter design, based on operation data collected during this research has been proposed but has yet to be deployed. Specifically, the design changes the way in which the melter pours to minimize temperature gradients between the melt in the vessel and at the pour exit.

A standard reference material(s) and commensurate method for evaluating ceramic waste forms that have broad compositional ranges and exhibit varying microstructural features is an outstanding prerequisite for ceramic waste form qualification. The importance of standards, from which to compare ceramic waste forms, has been known for some time. Without such baselines, research and development relies heavily on iterative improvement, at the expense of theoretical understanding. While this research has made a significant contribution toward the latter through a systematic theoretical approach towards property, processing, and performance relationships, a defined target would enable research to progress more efficiently. Ultimately, a scientific consensus for ceramic waste forms is needed to attract more attention to their value and realize their applications.

Through the course of this work, significant contributions to the scientific community have been made, advancing the understanding of chemical and physical phenomena in ceramic systems. The integrated research approach, which brought together experts and capabilities from across the DOE complex, academia, and international collaborations, has produced results that have spawned new research directions and opportunities, including programs for the DOE Office of Science. In addition, this research, as well as others, has demonstrated the practical scientific merit and potential application needed to warrant further exploration and research of uncharted composition spaces and unknown physicochemical relationships in ceramics for nuclear applications.

4 References

1. Gombert, D.; Piet, S.; Trickel, T.; Carter, J.; Vienna, J.; Ebert, B.; Matthern, G. *Combined Waste Form Cost Trade Study*; INL/EXT-08-14993 (GNEP-SYSA-PMO-MI-DV-2009-000003); Idaho National Laboratory: Idaho Falls, ID, 2008.

2. Bowan II, B. W.; Meigs, R.; Smith, E. C., Advancements in Joule Heated Melter Technology for Processing U.S. Department of Energy High Level Waste. In *Proceedings of Global 2003: Atoms for Prosperity: Updating Eisenhowers Global Vision for Nuclear Energy*, American Nuclear Society: New Orleans, LA, 2003; pp 1090-96.

3. Chapman, C. C.; Buelt, J. L., *Vitrification of High-Level Waste in a Joule-Heated Ceramic Melter*. 1979; Vol. 75, p 56-60.

4. Robert, S.; Gassot Guilbert, F.; Carpentier, B.; Naline, S.; Gouyaud, F.; Girold, C., A Milestone in Vitrification: The Replacement of a "Hot Metallic Crucible" With a "Cold Crucible Melter" in a Hot Cell at the La Hague Plant, France. **2010,** (54532), 399-406.

5. Sobloev, I. A.; Dmitriev, S. A.; Lifanov, F. A.; Stefenovsky, S. V.; Kobelev, A. P. In *SIA 'radon' experience in radioactive, waste vitrification*, Proceedings of International Symposium on Radiation Safety Management, Korea, Republic of, Korea Electric Power Research Institute: Korea, Republic of, 1997; p 573.

6. Tobie, W.; Weisenburger, S. *Advanced Joule-heated nuclear waste glass melters*; United States, 1990; pp 771-778.

7. Caurant, D.; Majerus, O.; Fadel, E.; Lenoir, M., Effect of Molybdenum on the Structure and on the Crystallization of SiO_2-Na_2O-CaO-B_2O_3 Glasses. *Journal of the American Ceramics Society* **2007,** *90* (3), 774-83.

8. Crum, J. V.; Billings, A. L.; Lang, J. B.; Marra, J. C.; Rodriguez, C. P.; Ryan, J. V.; Vienna, J. D. *Baseline Glass Development for Combined Fission Products Waste Streams*; AFCI-WAST-WAST-MI-DV-2009-000075; Pacific Northwest National Laboratory: Richland, WA., 2009.

9. Donald, I. W., Immobilization of Radioactive Materials as a Ceramic Wasteform. In *Waste Immobilization in Glass and Ceramic Based Hosts: Radioactive, Toxic and Hazardous Wastes*, John Wiley & Sons: Great Britain, 2010; pp 185-203.

10. Ewing, R. C.; Lutze, W., High-Level Nuclear Waste Immobilization with Ceramics. *Ceramics International* **1990,** *17*, 287-293.

11. Jostsons, A. *Synroc - progress and future prospects*; Australia, 2001; p 198.

12. Lutze, W.; Ewing, R. C., Sumamry and Evaluation of Nuclear Waste Forms. In *Radioactive Waste Forms for the Future*, Lutze, W.; Ewing, R. C., Eds. North Holland: Amsterdam, 1988; pp 699-740.

13. Kesson, S. E., The Immobilization of Cesium in SYNROC Hollandite. *Radioactive Waste Manag. Environ. Restor.* **1983,** *4* (1), 53-72.

14. Donald, I. W., *Waste Immobilization in Glass and Ceramic Based Hosts: Radioactive, Toxic and Hazardous Wastes*. Wiley: West Sussex, 2010.

15. Ringwood, A. E., Disposal of high-level nuclear wastes: a geological perspective. *Mineralogical Magazine* **1985,** *49*, 159-176.

16. Ringwood, A. E.; Kesson, S. E.; Ware, N. G.; Hibberson, W.; Major, A., Immobilisation of high level nuclear reactor wastes in SYNROC. *Nature* **1979,** *278* (5701), 219-223.

17. Sobolev, I. A.; Lifanov, F. A.; Stefanovsky, S. V.; Dmitriev, S. A. In *Development of Synroc melting process*, Waste Management, Tucson, AZ, Tucson, AZ, 1995; pp 1-9.

18. Sobolev, I. A.; Stefanovsky, S. V.; Omelianenko, B. I.; Ioudintsev, S. V., Comparative Study of Synroc-C Ceramics Produced by Hot-Pressing and Inductive Melting. *Materials Research Society Symposium Proceedings* **1996,** *465*, 371-378.

19. Ringwood, A. E.; Kesson, S. E.; Ware, N. G.; Hibberson, W.; Major, A., Immobilization of High-level Nuclear-Reactor Wastes in SYNROC. *Nature* **1979,** *278* (5701), 219-223.

20. Vienna, J. D.; Collins, E. D.; Crum, J. V.; Ebert, W. L.; Frank, S. M.; Garn, T. G.; Gombert, D.; Jones, R.; Jubin, R. T.; Maio, V. C.; Marra, J. C.; Matyas, J.; Nenoff, T. M.; Riley, B. J.; Sevigny, G. J.; Soelberg, N. R.; Strachan, D. M.; Thallapally, P. K.; Westsik, J. H. *Closed Fuel Cycle Waste Treatment Strategy*; INL/EXT-15-34504 (FCRD-MRWFD-2015-000674); Idaho National Laboratory: Idaho Falls, ID, 2015.