

I-NERI-2007-004-K, Development and Characterization of New High- Level Waste Forms for Achieving Waste Minimization from Pyroprocessing

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September 2011



The INL is a U.S. Department of Energy National Laboratory
operated by Battelle Energy Alliance

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High-Level Waste Forms for Achieving Waste Minimization
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September 2011

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**Prepared for the
U.S. Department of Energy
Office of Nuclear Energy
Under DOE Idaho Operations Office
Contract DE-AC07-05ID14517**

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Summary

Work describe in this report represents the final year activities for the 3-year International Nuclear Energy Research Initiative (I-NERI) project: Development and Characterization of New High-Level Waste Forms for Achieving Waste Minimization from Pyroprocessing. Used electrorefiner salt that contained actinide chlorides and was highly loaded with surrogate fission products was processed into three candidate waste forms. The first waste form, a high-loaded ceramic waste form is a variant to the CWF produced during the treatment of Experimental Breeder Reactor-II used fuel at the Idaho National Laboratory (INL). The two other waste forms were developed by researchers at the Korean Atomic Energy Research Institute (KAERI). These materials are based on a silica-alumina-phosphate matrix and a zinc/titanium oxide matrix. The proposed waste forms, and the processes to fabricate them, were designed to immobilize spent electrorefiner chloride salts containing alkali, alkaline earth, lanthanide, and halide fission products that accumulate in the salt during the processing of used nuclear fuel.

This aspect of the I-NERI project was to demonstrate ‘hot cell’ fabrication and characterization of the proposed waste forms. The outline of the report includes the processing of the spent electrorefiner salt and the fabrication of each of the three waste forms. Also described is the characterization of the waste forms, and chemical durability testing of the material. While waste form fabrication and sample preparation for characterization must be accomplished in a radiological hot cell facility due to hazardous radioactivity levels, smaller quantities of each waste form were removed from the hot cell to perform various analyses. Characterization included density measurement, elemental analysis, x-ray diffraction, scanning electron microscopy and the Product Consistency Test, which is a leaching method to measure chemical durability. Favorable results from this demonstration project will provide additional options for fission product immobilization and waste management associated the electrochemical/pyrometallurgical processing of used nuclear fuel.

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ACRONYMS

AL	Analytical Laboratory
At%	atom percent
BSE	back scatter electron
CWF	ceramic waste form
EBR-II	Experimental Breeder Reactor-II
EDS	energy dispersive spectroscopy
EML	Electron Microscopy Laboratory
ER	electrorefiner
HFDA	Hot Fuels Dissolution Apparatus
HFEF	Hot Fuels Examination Facility
HL-CWF	high-loaded ceramic waste form
HLW	high-level waste
ICP-MS	inductively coupled plasma – mass spectrometry
ICP-AES	inductively coupled plasma – atomic emission spectroscopy
I-NERI	International Nuclear Energy Research Initiative
INL	Idaho National Laboratory
KAERI	Korean Atomic Energy Research Institute
LN	Lanthanide elements
MFC	Materials and Fuels Complex
NIST	National Institute of Science and Technology
ppm	parts-per-million
SAP	silica-alumina-phosphate
SEM	scanning electron microscopy
Wt%	weight percent
XRD	x-ray diffraction
ZIT	zinc-titania

I-NERI-2007-004-K, DEVELOPMENT AND CHARACTERIZATION OF NEW HIGH-LEVEL WASTE FORMS FOR ACHIEVING WASTE MINIMIZATION FROM PYROPROCESSING

1. INTRODUCTION

The purpose of this three-year, joint KAERI/INL I-NERI project is to develop novel high-level waste (HLW) forms and fabrication processes to dispose of active metal fission products that are removed from electrorefiner (ER) salts in the pyroprocessing-based fuel cycle. The current technology for disposing of active metal fission products from pyroprocessing of used fuel involves non-selectively discarding fission product loaded salt in a glass-bonded sodalite ceramic waste form. Selective removal of fission products from the molten salt would minimize the amount of HLW generated; and methods were developed to achieve selective separation of fission products during a previous I-NERI research project [1]. This I-NERI project expands from the previous project with the development of suitable waste forms to immobilize the separated fission products. Researchers at KAERI have developed two novel waste forms using surrogate waste materials for the immobilization of fission products in ER salts [2, 3]. Fabrication and characterization of these waste forms and a high-loaded ceramic waste form using actual ER salt was demonstrated in the hot-cell facilities at the INL as part of the 3rd year research activities. Characterized and tested was performed to determine, elemental, phase and microstructure composition, density and chemical durability of the three candidate waste form materials.

Results from the initial separation I-NERI project concluded with a number of options to separate and concentrate fission products from ER salt. Three of the most promising options for fission product separation and concentration were included as part of the waste form fabrication I-NERI demonstration performed at the INL, and supplied the starting material for waste form fabrication. These three options are illustrated in Figure 1. Option A is a modification of the EBR-II spent fuel treatment process, where, instead of adding ER salt to zeolite and processing a CWF with low loadings of fission products; the zeolite was contacted with ER salt containing high levels of fission products to produce a high-loaded CWF (HL-CWF). Development of options B and C was conducted at KAERI and first involve an oxygen sparging process in the molten ER salt to chemically react O₂ with the lanthanide (LN) chloride fission productions to produce lanthanide oxides and oxychlorides that precipitate out of the molten salt. Following oxygen sparging, one of two de-chlorination steps is conducted. The first de-chlorination process involves salt distillation to isolate the lanthanide precipitates. The salt and

other fission product chlorides are collected in the condenser of the distillation apparatus. The second de-chlorination method involves addition of a chemical reagent and reacting in an oxygen atmosphere at elevated temperature with the evolution of Cl_2 from the system. The isolated lanthanide precipitates are then immobilized in a zinc/titanium oxide (ZIT) matrix, while the salt with the remaining fission products is formed into a glass bonded silica-alumina-phosphate (SAP) waste form.

The outline of this report includes a description of the two part Li draw-down/ oxygen sparging experiment that processed the salt material used to fabricate the waste forms. The second part of the report describes waste form fabrication, and the last section of the report describes the characterization and testing of the waste forms along with the results from the characterization. This report completes the level 3 milestone (M31SW090810) requirement for the work package: Advanced Electrochemical Waste Forms (FTIN11SW0908).

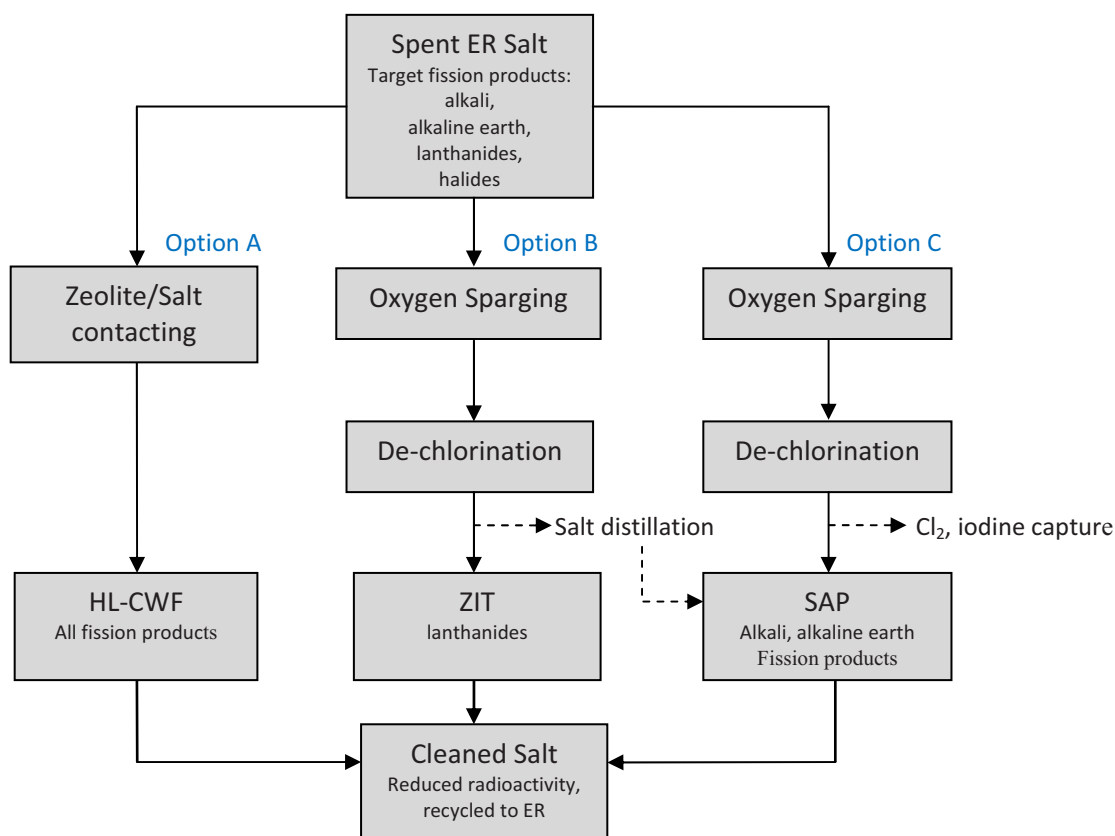


Figure 1. Separation options for the removal of fission products from electrorefiner salt.

2. LITHIUM DRAWDOWN - OXYGEN SPARGING EXPERIMENT

KAERI researchers have developed a chemical method to precipitate lanthanide fission products in ER salt by sparging oxygen gas through the molten salt. Molecular oxygen reacts with lanthanide chlorides to produce lanthanide oxides or oxychlorides that then will precipitate to the bottom of the molten salt bath. This allows for the physical separation of the precipitated lanthanide fission products from the salt and subsequent immobilization in a durable waste form. This salt/precipitate mixture is the starting material used to fabricate the three candidate waste forms for this I-NERI project. To produce this material, a small scale ER, referred to as the Hot Fuels Dissolution Apparatus (HFDA) was used. The HFDA is located in the main radiological cell (argon atmosphere) of the Hot Fuels Examination Facility (HFEF) at the Material and Fuels Complex (MFC) on the INL site. The HFDA consists of two main components, the base assembly, and the head assembly as shown in the cut-away diagram in figure 2. The base assembly contains the heaters and the molten salt crucible. The head assembly is remotely removable from the base, and contains the access ports, the heat shield baffles, and equipment to hold and rotate experimental apparatus in the molten salt.

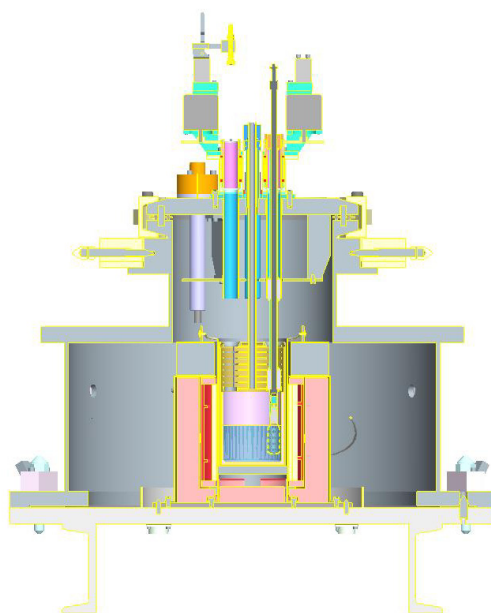


Figure 2. Hot Fuels Dissolution Apparatus (HFDA) located in the HFEF main cell. The HFDA is an experimental-scale electrorefiner that was used for the Li drawdown and oxygen sparging experiment to produce feed material for waste form development fabricated with electrorefiner salt.

The experimental plan to treat the ER salt used for waste form fabrication involved two parts. The first part of the experiment was a chemical reduction method to reduce actinide chlorides in the molten salt [4] followed by the precipitation of the reduced actinide metal into a collection pan placed in the bottom of the salt bath crucible of the HFDA. Lithium metal was

used as the reducing agent for actinide reduction. The salt used for the drawdown/oxygen sparging experiment contained moderately high loadings of actinide elements, but low loadings of fission product elements of approximately 2 weight percent (wt%) which is the currently fission product concentration of the in electrorefiners treating EBR-II fuel. For the waste form fabrication, it was desirable to have high fission product loadings in the salt. To accomplish this, representative, non-radioactive or surrogate fission product chlorides were added to the HFDA salt. The salt elemental composition following addition of the surrogate fission products is shown in table 1.

Table 1. Initial salt composition (in weight %) used for drawdown/oxygen sparging experiments in the HFDA. Surrogate fission product chlorides of Sr, La, Ce, Pr, Nd and CsI were added to obtain a representative fission product loading of approximately 15 wt%.

Initial Salt Composition	LiCl-KCl	SrCl ₂	CsI	LaCl ₃	CeCl ₃	PrCl ₃	NdCl ₃	UCl ₃	PuCl ₃
Wt%	80.6	1.1	4.2	1.4	2.7	1.2	4.4	1.5	2.3

The drawdown portion of the experiment involved addition of Li metal chunks to the molten salt in the HFDA and reacting for 24 hours. Following the actinide reduction, the HFDA head assembly was removed and the actinide collection pan lifted out of the molten salt crucible. A second collection pan was placed in the crucible and the HFDA head assembly replaced for oxygen sparging. The oxygen sparger was inserted into the molten salt bath with a flow of oxygen gas and the experiment initiated. After sparging, the LN precipitate was allowed to settle to the bottom of the collection pan followed by removal of the second collection pan from the molten salt crucible. The oxygen sparging experiment that produced the salt/precipitate material used for waste form production was performed on August of 2010. The sparger unit, shown in figure 3, is an open tube of 6.2 mm inside diameter and with 2 mm holes drilled near the tip to allow for bubble formation. The precipitate collection pan is 1.27 cm height and 8.5 cm in diameter as shown in figure 4 alongside the typical alumina crucibles used in the HFDA. The oxygen flow during sparging was 427 cm³/min and the total quantity of O₂ sparged into the molten salt during the 24 hour period was 680 L. The optimum molten salt bath temperature for lanthanide oxide/oxychloride formation is 800° C as determined at KAERI; however, the maximum operating temperature of the HFDA is 650 °C, and this is the temperature that oxygen sparging was conducted as opposed to the nominal 500° C operating temperature of the HFDA.

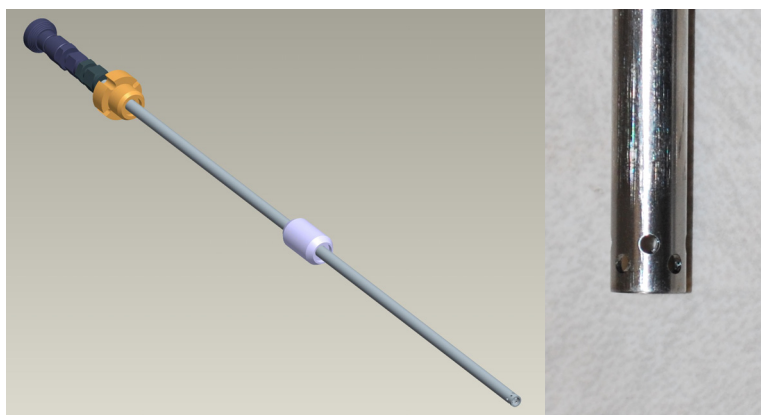


Figure 3. Oxygen sparger used during oxygen sparging experiment. The sparger is an open tube (6.2 mm ID) with 2 mm holes (right-hand image) drilled near the open tip of the sparger. This design resulted in larger O₂ bubbles that spiraled through the molten salt resulting in a stirring action. This design also prevented clogging of the sparger.



Figure 4. Typical HFDA alumina crucible (11.4 cm high x 10.2 cm OD) and stainless steel precipitate collection pan used during oxygen sparging experiment.

Following oxygen sparging and removal of the second collection pan, salt samples were taken for elemental analysis and the product salt/precipitate mixture broken out of the collection pan. The elemental analysis results obtained from pre- Li drawdown, post-drawdown, and post- oxygen sparging are shown in table 2. Data contained in table 2 indicates that Li drawdown of actinides elements was very effective as well as reducing lanthanides out of the salt mixture. Furthermore, results from post-oxygen sparging indicate minimal decrease in the lanthanide concentration in the salt. It is speculated that this is due to the non-optimal conditions of temperature and oxygen flow rate in the HFDA to adequately form the lanthanide oxides and oxychlorides. It is clear that to perform optimum oxygen sparging to form lanthanide oxides and oxychlorides, a new furnace and reaction vessel would have to be fabricated and installed into HFEF that would accommodate the required 800° C reaction

temperature and a new oxygen delivery system that would allow increased oxygen flow to the reaction vessel. The reaction vessel would also require a salt vapor condenser, or some other way to control the appreciable amount of salt vapor that is generated during oxygen sparging at 800° C. These requirements are beyond the scope of this demonstration project, and it was decided to continue with waste form production using whatever lanthanide precipitate material that had accumulated in the second collection pan.

Table 2. Elemental composition in salt samples before Li drawdown, after Li drawdown and after oxygen sparging (in wt% \pm 5%, or parts per million (ppm) as noted).

Salt Mixture	Li	K	Sr	Cs	La	Ce	Pr	Nd	U	Pu
Pre - Li drawdown	5.36	20.6	0.915	2.28	1.14	2.23	0.930	4.63	1.52	2.33
Post – Li drawdown	5.70	19.7	0.676	2.18	0.787	1.43	0.648	3.03	81 ppm	362 ppm
Post – oxygen sparging	6.42	22.6	0.776	2.47	0.840	0.580	0.646	2.97	172 ppm	614 ppm

Material collected from the second pan was then used for waste form fabrication as shown in figure 5. Close inspection of the salt/precipitate material that had been removed from the pan indicated a stratification of material and it was expected that a precipitated had collected on the bottom of the pan. This salt/precipitate mixture was then ground to a fine powder for subsequent waste form fabrication. The HFEF main cell maintains a high purity argon atmosphere with oxygen and moisture contamination levels typically below 100 ppm. Furthermore, salt material is stored in tight containers when not being process also to keep contaminates to the material at a minimum.

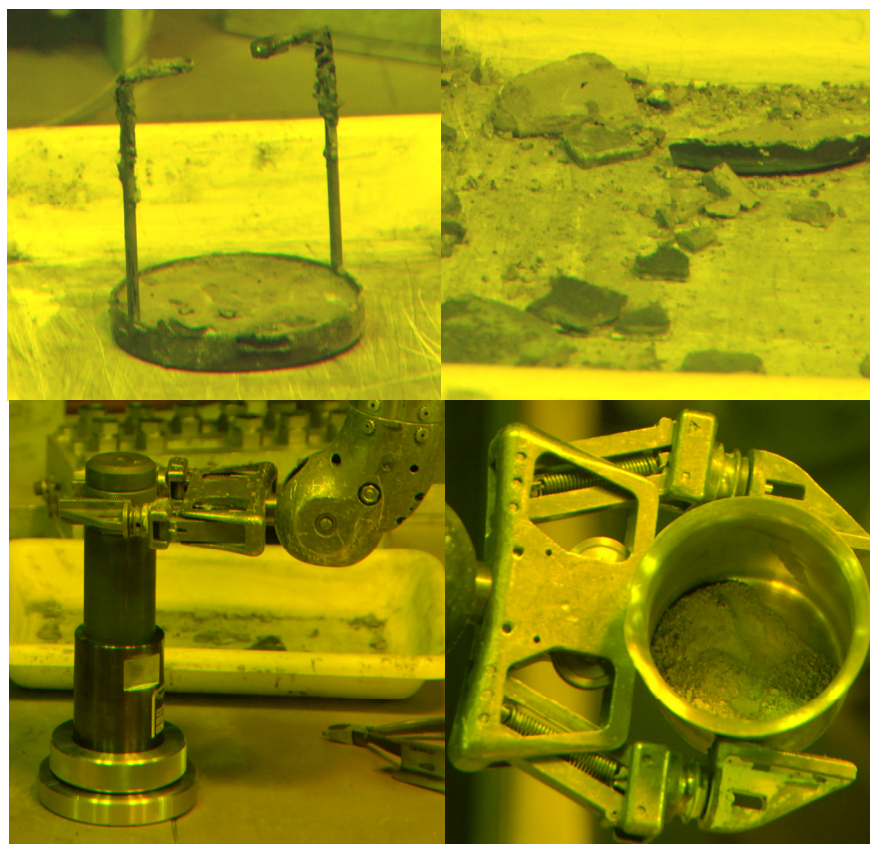


Figure 5. Images of salt/precipitate material collected from pan 2 and ground to powder for subsequent waste form fabrication. All operations conducted in the HFEF main argon cell.

3. WASTE FORM FABRICATION

The three candidate waste forms were fabricated in the HFEF main cell using processing methods either developed at KAERI, or the INL. Using the waste salt material described in section 2 above, small-scale waste forms of approximately 50 g in size were produced using the follow procedures. All waste forms were fabricated in 180 mL alumina crucibles (CoorsTek, Inc., Golden, CO) with internal dimensions of 5 cm in diameter and 9 cm height. The waste form body dimensions were ~5 cm in diameter and ~2 cm in height.

3.1 SAP Waste Form Fabrication

The SAP waste form is based on a formulation developed at KAERI involving immobilization of the metal fission products in a silica-alumina-phosphorus matrix [2]. Producing the waste form involves mixing waste salt with the SAP reagent material. This material was then placed in an alumina crucible that was then placed in an Inconel 617 alloy reaction assembly. Tubing was attached to the reaction assembly for the introduction of oxygen gas. Oxygen flowed through the reaction crucible and chlorine gas exited through another tube attached to the bottom of the vessel. The reaction assembly was placed into a four-zone, high-temperature 'DEOX'

furnace (Thermcraft, Inc. Winston-Salem, NC) with a maximum operating temperature of 1200° C. This furnace is located in the main cell of HFEF. The reaction apparatus and loaded furnace are shown in figure 6. The two step SAP fabrication first involves reacting the SAP/salt mixture at elevated temperature in the presence of oxygen. De-chlorination occurs during the reaction where fission product metal cations chemically bond to the SAP matrix phases and Cl_2 gas is evolved. Waste form solidification is then performed by mixing the reacted SAP product with an AlFe_3 /borosilicate glass binder and heated. The final SAP product was removed from the solidification crucible by breaking the crucible. The SAP product also broke into a number pieces, but cleanly separated from the crucible. No appreciable loss of material was recording during processing. The SAP waste form material is shown in figure 7. The exact SAP processing details are as follows:

- Mixed 6.1 g salt/precipitate with 18.1 g SAP reagent (1:3) in alumina crucible
- Crucible loaded into reaction assembly and assembly placed in zone 4 of DEOX furnace
- Oxygen flow to reaction chamber 1 scf/hr (0.008 L/s)
- Heated zone 4 of DEOX furnace to 750° C for 24 hours.
- After 24 hours, turned off oxygen flow and allowed furnace to cool, removed assembly
- Collected 21.6 g of reacted SAP product, mixed 12.8 g AlFe_3 glass frit to SAP product (65:35) mixed and loaded into new alumina crucible
- Placed crucible into steel holder and inserted into zone 4 of DEOX furnace
- Heat zone 4 of DEOX furnace to 1150° C, heat for 4 hours under Ar atmosphere
- After furnace cool down, recovered 34.4 g SAP waste form body from crucible.

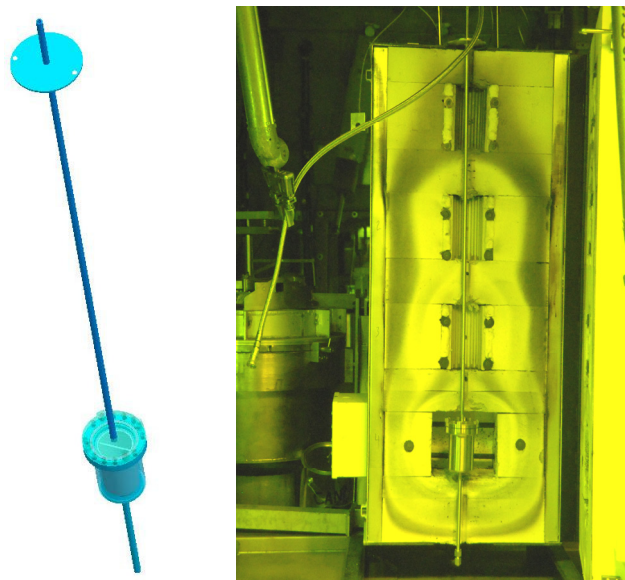


Figure 6. SAP reaction assembly (left-hand image) and assembly loaded into the 4-zone DEOX furnace in HFEF main cell. Oxygen is introduced through the top hose and passes through the reaction crucible in the vessel. Chlorine gas exits through the tube on the bottom of the vessel and out the furnace.

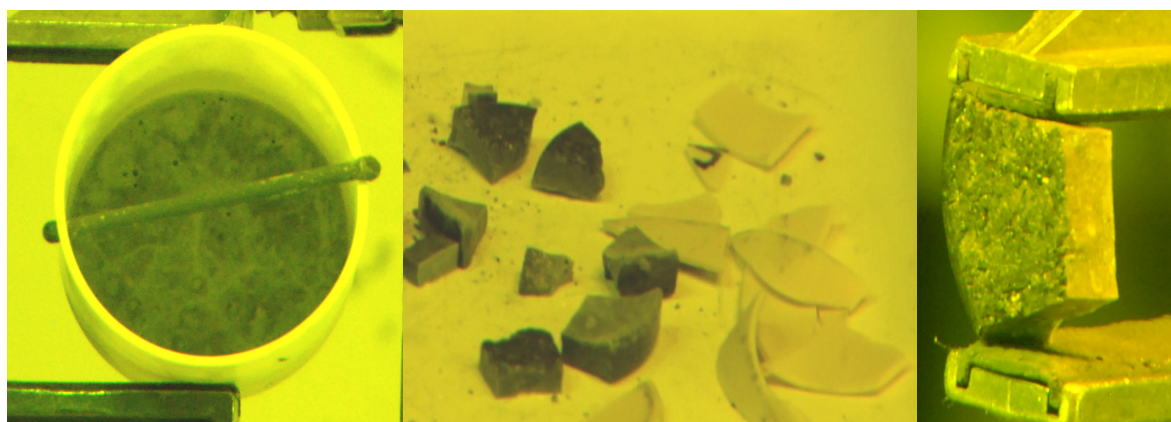


Figure 7. SAP waste form product after solidification with glass binder (left-hand image) and after breaking out of alumina crucible (middle image). Close up of SAP waste form piece used for density determination.

3.2 ZIT Waste Form Fabrication

Formation of the ZIT waste form product first involves a de-chlorination step very different from the SAP product. For ZIT production, the salt component of salt/precipitate mixture is vacuum distilled at elevated temperature. The salt vapor is collected in the condenser and the lanthanide precipitate remains in the product crucible. The LN precipitate is then mixed with the ZIT reagent and processed at high temperature to form the final waste form. The ZIT waste

form is a monazite-lanthanide host phase immobilized in a zinc titanate (Zn_2TiO_4) matrix [3] produced in a one step process (after salt distillation) at reasonable, elevated temperature. Both salt distillation and ZIT fabrication were performed using the DEOX furnace. The salt distillation apparatus is shown in figure 8, along with the temperature/time/pressure characteristics observed during distillation. The detail procedure is as follows:

- Placed 48.4 g salt/precipitate powder into product crucible of salt distillation apparatus – sealed salt distillation apparatus and placed in DEOX furnace with connected vacuum line
- Applied vacuum to salt distillation apparatus until a pressure of approximately 10 torr (13 Pa) was obtained.
- Heated condenser of distillation apparatus to $\sim 500^\circ\text{C}$ (zone 1 of furnace), then heated zone 4 of furnace (product crucible) to 1100°C , heat for 4 hours while under vacuum
- Allow furnace to cool and disassemble salt distillation apparatus
- Collected 28.3 g salt distillate from condenser and 12.7 g^{*} fission product precipitate from bottom chamber of salt distillation apparatus
- Collected fission product precipitate and mixed with 128 g^{*} ZIT reagent, transferred to waste form crucible (goal 1 part precipitate to 4 parts reagent)
- Placed crucible into steel holder and inserted into zone 4 of DEOX furnace
- Heated zone 4 of DEOX furnace to 1100°C , heat for 14 hours under Ar atmosphere

* Error occurred in weight determination of precipitate product. Error precipitate weight: 34.4 g, correct precipitate weight: 12.7. Excess ZIT reagent added due to precipitate weight error.

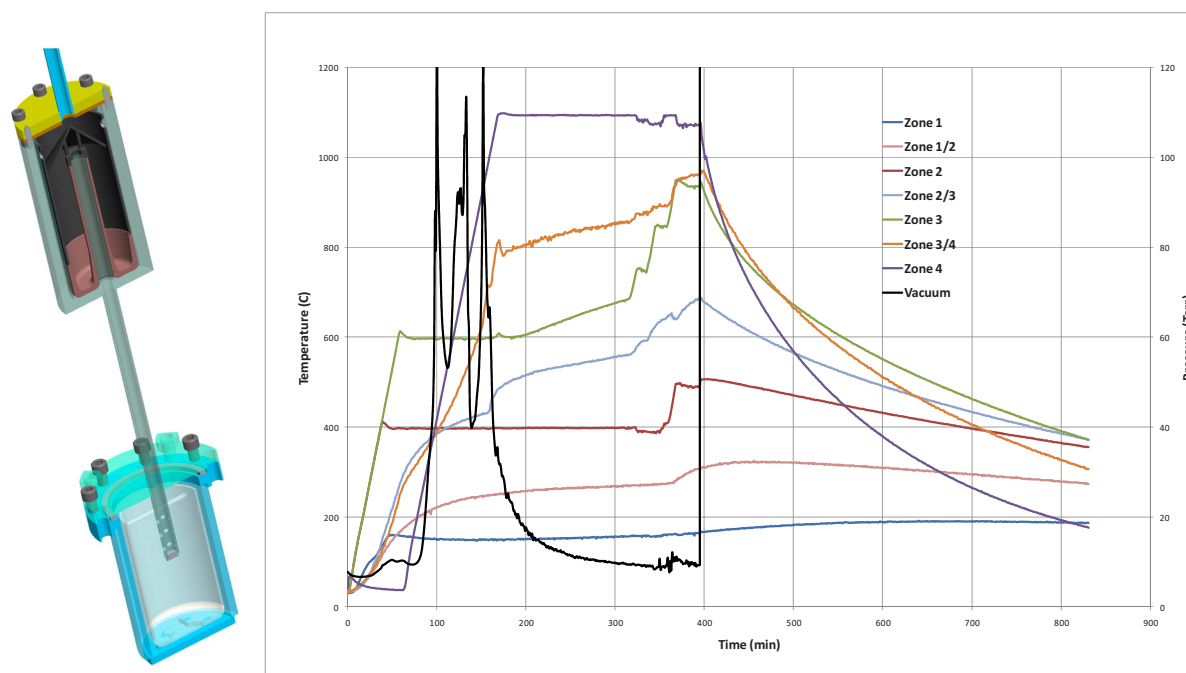


Figure 8. Schematic of salt distillation apparatus (left-hand image) used to isolate lanthanide precipitate in the bottom product chamber, while the salt component is collected in the upper condenser. Right-hand plot shows temperature and pressure characteristics during salt distillation. The maximum temperature in zone 4 (product crucible) was 1100° C, while the temperature of zone 1 (salt condenser) ranged from 400 to 600° C during the distillation period. The black plot shows the vacuum pressure during distillation with spikes in pressure corresponding to salt movement from zone 4 to the condenser in zone 1.

As indicated, a weighing error occurred in determining the isolated lanthanide precipitate product in which the actual weight was less than recorded during the experiment. As a result, excess ZIT reagent was added to the precipitate. This appears to have had little effect on the final product as evidenced by visual and chemical analysis of the waste form. Figure 9 shows both the salt product from the condenser and the remaining lanthanide precipitate product after salt distillation. Figure 10 shows the final ZIT waste form product after processing. The lighter, upper ZIT product is from excess reagent. The darker lower region contains the lanthanide product. Unlike the SAP or HL-CWF, the ZIT waste form was strongly adhered to the alumina processing crucible. Crucible material had to be ground away from the ZIT waste form before sample processing.

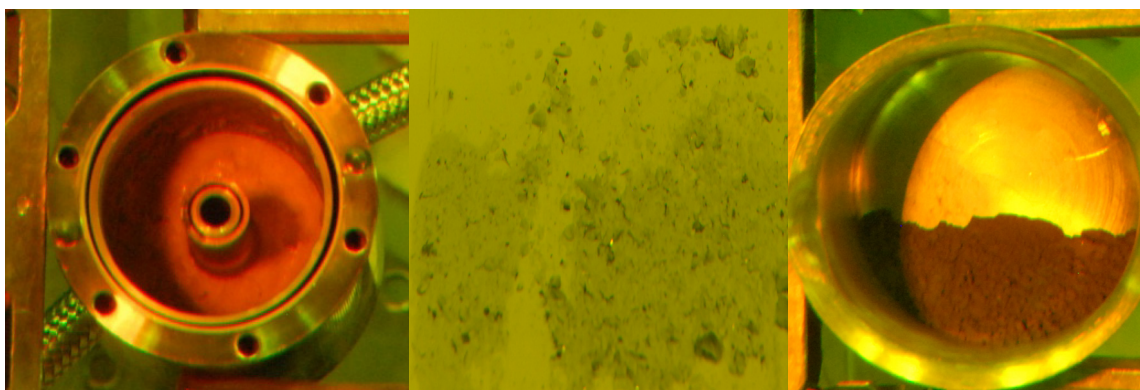


Figure 9. Left-hand image, view looking into opened salt condenser of salt distillation apparatus after distillation. Collected salt from condenser (middle-image) and collected lanthanide product (right-hand image) after salt distillation.

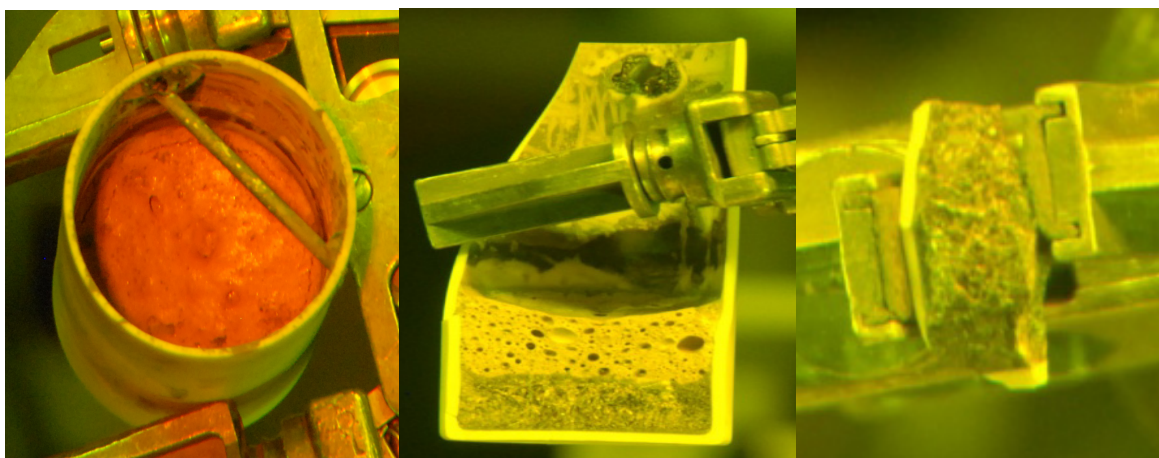


Figure 10. ZIT waste form product crucible after fabrication (left-hand image). Middle image shows cross-section of reaction crucible after attempt to break ZIT product out of crucible. The segmented product is due to excess ZIT reagent. Right-hand image shows lower segment of waste form containing lanthanide product with alumina crucible strongly adhering to ZIT product.

3.3 High-Loaded Ceramic Waste Form Fabrication

Fabrication of the HL-CWF was based on a modification of the typical CWF processing involved with EBR-II used fuel treatment [5]. Most significantly was salt occlusion into the zeolite material with these small-scale samples. With Full-scale CWF production, salt occlusion is performed in a heated V-mixer that allows simultaneous heating and mixing of the salt and zeolite. In this study, heating and mixing to the salt/zeolite material had to be separately. Similar to the SAP and ZIT waste forms, a portion of the original salt/precipitate mixture was mixed with dried, ground and sized ($\sim 125 \mu\text{m}$ particle diameter) zeolite 4A. Addition of the

lanthanide oxide/oxychloride precipitate directly to the zeolite was not deemed a detriment to the process performed for this demonstration as this is the final form of both actinides and lanthanides in the large-scale CWF [6]. After salt occlusion into zeolite, a borosilicate glass binder is mixed with the zeolite and heated to produce the waste form. During this process, zeolite 4A converts to sodalite. After processing, the HL-CWF body was cleanly removed from the alumina product crucible as shown in figure 11. The detailed process to produce the HL-CWF is as follows:

- Combined 10.0 g salt/precipitate powder with 33.5 g dried zeolite 4A (23 wt% salt loaded zeolite) in reaction crucible
- Placed crucible in zone 4 of DEOX furnace and heated to 500° C for 4 hours
- After furnace cool down, the salt occluded zeolite was removed from the crucible, re-mixed and re-heated at 500° C for 4 hours
- After furnace cool down, the salt occluded zeolite was then mixed with 43.2 g glass frit to salt-occluded zeolite in crucible (50:50 ratio)
- Placed crucible into steel holder and inserted into zone 4 of DEOX furnace
- Heated zone 4 of DEOX furnace to 925° C for 4 hours under Ar atmosphere
- After furnace cool down, recovered waste form body from crucible

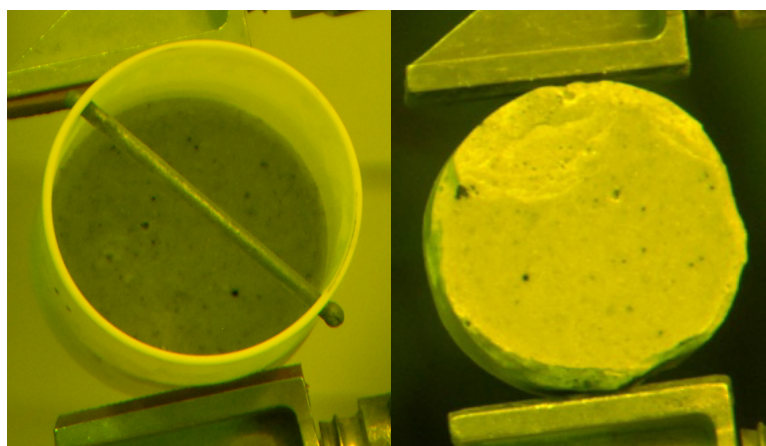


Figure 11. HL-CWF body after processing shown in the product crucible (left-hand image) and after removal from crucible (right-hand image).

4. WASTE FORM CHARACTERIZATION and TESTING

After fabrication of the three candidate waste forms, the next stage in the demonstration project was to initiate sample preparation for characterization and testing. This involved first breaking the waste form products into reasonable sizes for density determination and microscopy analysis. Initial sampling involved breaking with a blunt object, usually as a result of removing the waste form body from the crucible. Density samples ranged from 1 to 2 cm in length. Microscopy samples were roughly 1 mm in diameter. Each sample was packaged separately in the HFEF main cell awaiting analysis. Samples for XRD, elemental analysis, and

PCT were powdered, using an impact mortar then sizing the powder through sieves (Gilson Company, Inc. Lewis Center, OH).

4.1 Density Determination

Originally, density determination was to be performed by helium pycnometry in the HFEF air cell. Unfortunately, the hot-cell modified pycnometer (Quantachrome Instruments, Boynton Beach, FL) was inoperable due to electronic failure. It was then decided to transfer the samples to a radiological glovebox in the Analytical Laboratory (AL) at MFC. Samples were sized sufficiently small to allow handling in the glovebox while keeping radiological exposure to a minimum. Density was then performed by the immersion method in water using an analytical balance (model CP324S Sartorius, Elk Grove, IL). Figure 12 shows the balance and waste form samples. The density results for each waste form are listed in table 4 along with the laboratory reference density for each material.

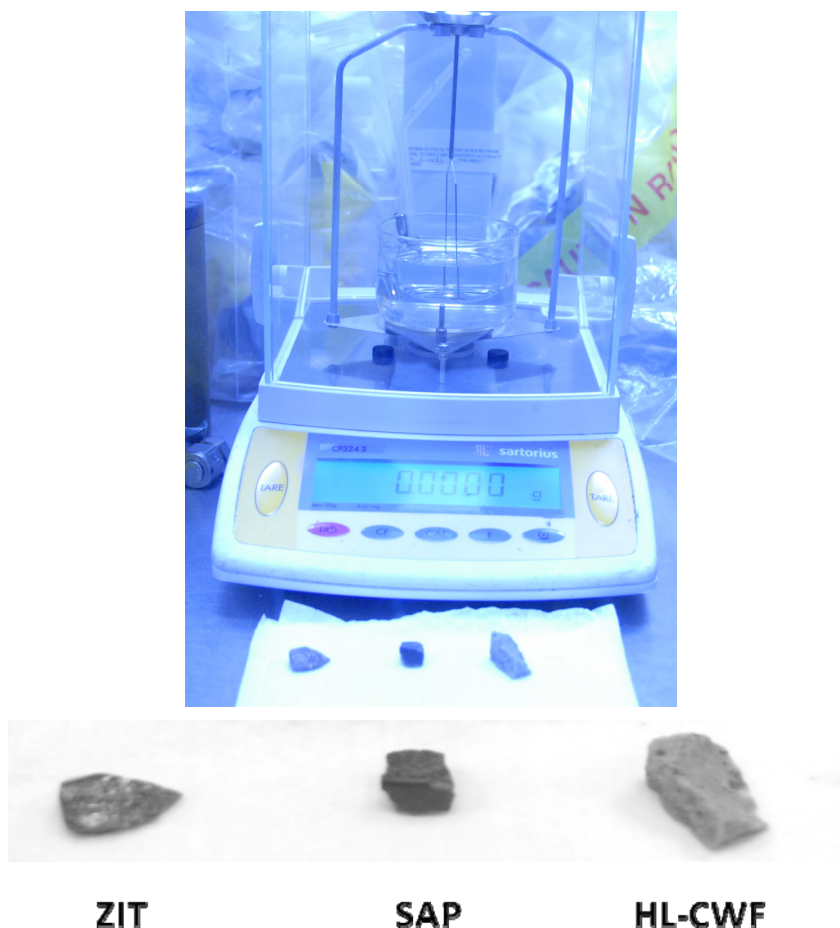


Figure 12. Density measurement apparatus and waste form samples used for density measurement.

Table 3. Measured density for each waste form and reference density determined from laboratory samples.

Sample	Measured Value g/cm ³	Reference Value g/cm ³
SAP	2.47 ± 0.12	2.32
ZIT	3.62 ± 0.17	4.3
HL-CWF	2.06 ± 0.21	2.34 ± 0.06

In general, the measured density values for the waste forms produced in HFEF agree well with the reference values within measurement uncertainties. The exception is the ZIT waste form that had a lower density than the reference value as determined from surrogate, laboratory produced waste forms. This may be due to the excess of ZIT reagent added to the LN precipitated during waste form fabrication.

4.2 X-ray Diffraction

Powdered samples used for XRD were obtained from the 'fines' or ground waste form powder that had passed through the 200 mesh (75 µm) sieve during the PCT sample preparation. This powder was collected for each waste form and transferred from the HFEF main cell to the AL. Once the material was in the AL, the powder was split – half for XRD and the other half for elemental analysis. The powder fraction for XRD, ~0.2 to 0.4 g, was applied to a zero-background XRD sample holder (Si wafer) as a thin film adhered to the holder with a thin layer of Vaseline petroleum jelly. The sample and holder was then covered with 0.4 mm Mylar film to prevent the possible spread of radioactive material. The holder was then transferred to the XRD instrument (Empyrean, PANalytical, Inc. Westborough, MA) for analysis. X-ray scattering from the Mylar film is observed on all XRD patterns by the broad peak at ~25.5 deg 2θ. After XRD pattern acquisition, the pattern was compared to the PDF-4 Powder Diffraction File Library [7] for phase identification. Matching PDF-4 library patterns are overlaid on the XRD pattern for each sample.

4.2.1 XRD of the SAP waste form

The XRD pattern obtained from the SAP waste form sample is shown in figure 13 with pattern matches to a lanthanide monazite type phase (LN-PO₄), a possible silicate phase, and the pattern also showed significant amorphous character from the broad background region above 30 deg 2θ.

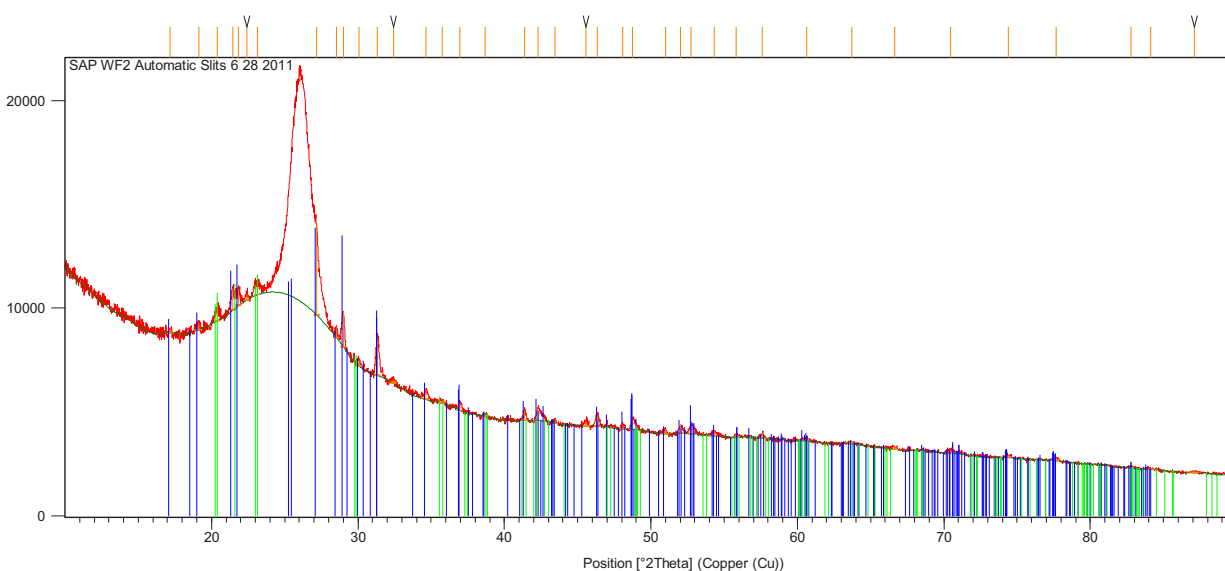


Figure 13. XRD pattern for SAP waste form with pattern matches to LN-PO₄ monazite phase (blue) and a possible silicate phase (green).

4.2.2 XRD of the ZIT Waste Form

The XRD pattern for the ZIT waste form is shown in figure 14 with pattern matches to TiO₂ (rutile) a possible silicate phase, zinc oxide and a possible lanthanide monazite phase.

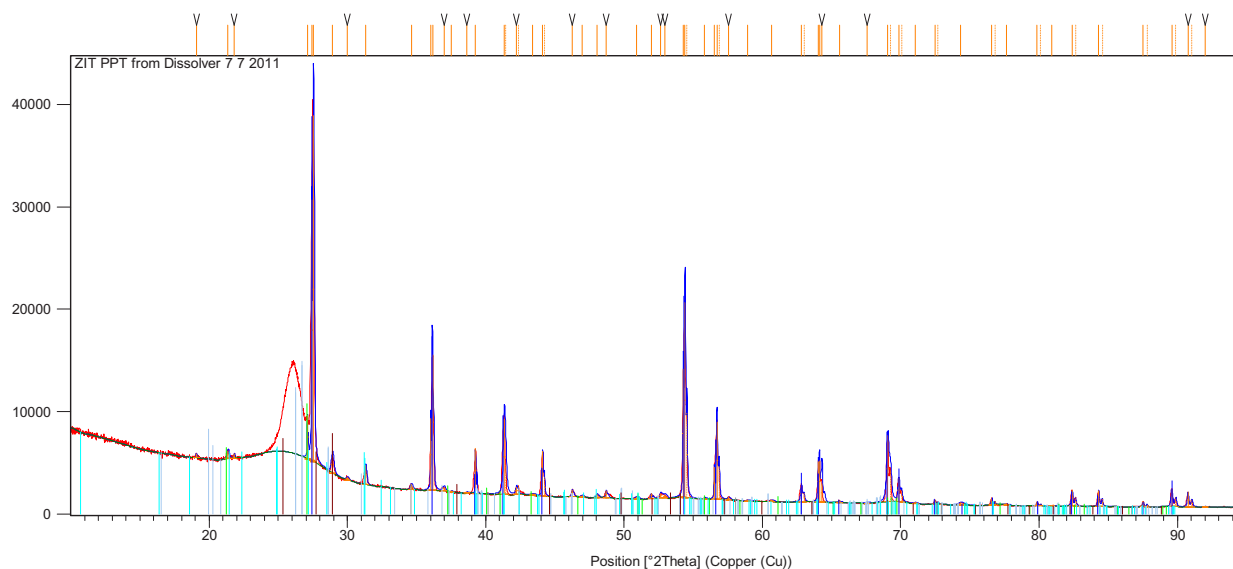


Figure 14. XRD pattern of ZIT waste form with pattern matches to rutile (TiO₂), shown in dark blue, a possible silicate phase (green), zinc oxide (gray), a monazite like phase of LN-PO₄ (light blue).

4.2.3 XRD of the HL-CWF

The XRD pattern for the HL-CWF is shown in figure 15 with the expected sodalite - $\text{Na}_8(\text{Al}_6\text{Si}_6\text{O}_{24})\text{Cl}_2$ phase (zeolite undergoes a phase transformation to sodalite during waste form processing at 925°C), a concentrated salt phase of sylvite (NaCl/KCl mixture) and a possible lanthanide oxide phase. The sodalite pattern in the CWF system is shifted to low 2θ values due to occlusion of Li that contracts the cage structure of the sodalite. Very little sodalite pattern shifting is observed in HL-CWF XRD pattern, and with the high salt phase pattern, it appears the salt occlusion into the zeolite cage prior to waste form production was not complete. This is probably due to the lack of hot (500°C) mixing during the salt/zeolite contacting step of the fabrication process. With the small sample size prepared for the I-NERI demonstration, the material was mixed at ambient temperature in the HFEF main cell, then heated to 500°C and the process repeated. This apparently was not adequate to occlude the salt into the zeolite structure.

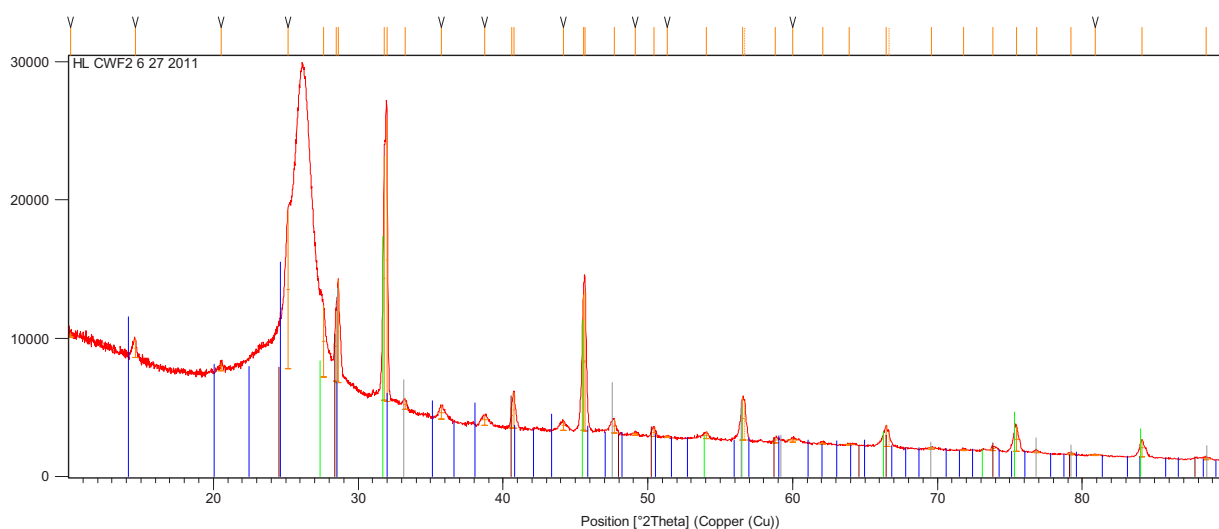


Figure 15. XRD pattern of HL-CWF material showing the sodalite phase (blue library pattern) and a very concentrated sylvite (NaCl/KCl) salt phase (green). Also present is a possible, minor lanthanide oxide (Ce_2O_3) phase (red).

4.3 Scanning Electron Microscopy

The small ($\sim 1\text{ mm}$) pieces selected from the center region of each waste form, collected in the HFEF main cell, were packaged and transferred to the Electron Microscopy Laboratory (EML) at MFC for sample preparation. All three waste form samples were mounted into a single 1" epoxy mount and polished to a 1200 diamond grit finish in the EML sample preparation glovebox. The sample mount was then decontaminated and removed from the glovebox and coated with a thin layer of gold to prevent surface charging from the electron beam during analysis, and to prevent the possible spread of radioactive contamination. The coated mount was then transferred to a LEO 1455UP SEM (Carl Zeiss, LLC North America) with

an Oxford Instruments, INCAx Systems x-ray energy dispersive spectrometer (EDS) detector (Oxfordshire, UK) used for elemental analysis.

4.3.1 Electron Microscopy of SAP Waste Form

A large area, backscattered electron (BSE) image of the SAP waste form is shown in figure 16. The image shows a rather complex structure comprised of at least four distinct regions. A white-contrast region with an elemental composition, as determined by EDS, of 40% Ce-15%Nd-14%P -1%K -30%O and most likely corresponding to the monazite phase identified by XRD. The structure also contains three discrete gray-contrast regions with an average elemental composition of ~2%Na-8%Al-21%Si-7%P-3%K-2%Ca-3%Fe-51%O. Cesium and Sr were identified by large-area EDS analysis, but were not detected in any one discrete region of the sample. This indicates that Cs and Sr are evenly distributed through the material. Figure 17 shows a higher magnification image of the SAP waste form (top image) and the corresponding elemental x-ray maps of the magnified region (bottom images) showing the elemental distribution in the waste form.

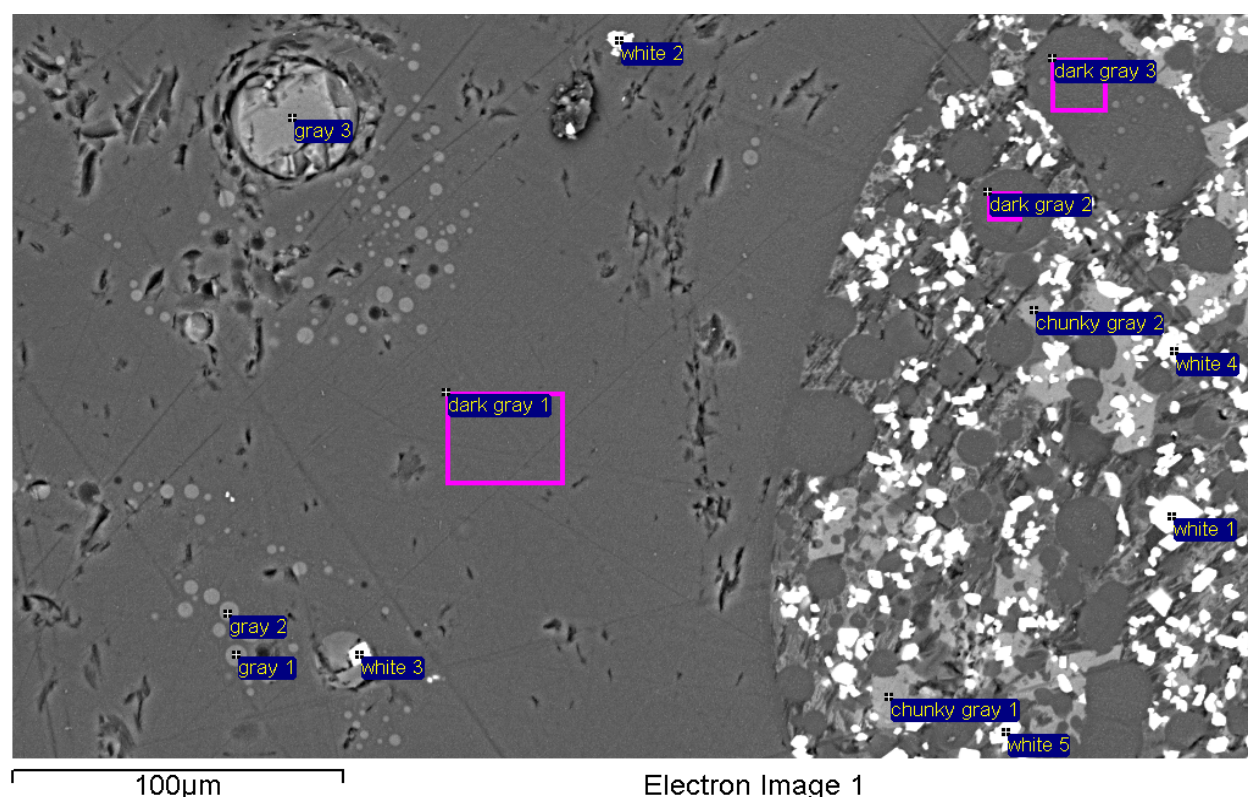


Figure 16. BSE image of SAP waste form showing four distinct regions (one white and three gray contrast areas). The white region corresponds to a monazite elemental composition and the gray areas correspond to a silicate rich area with varying composition.

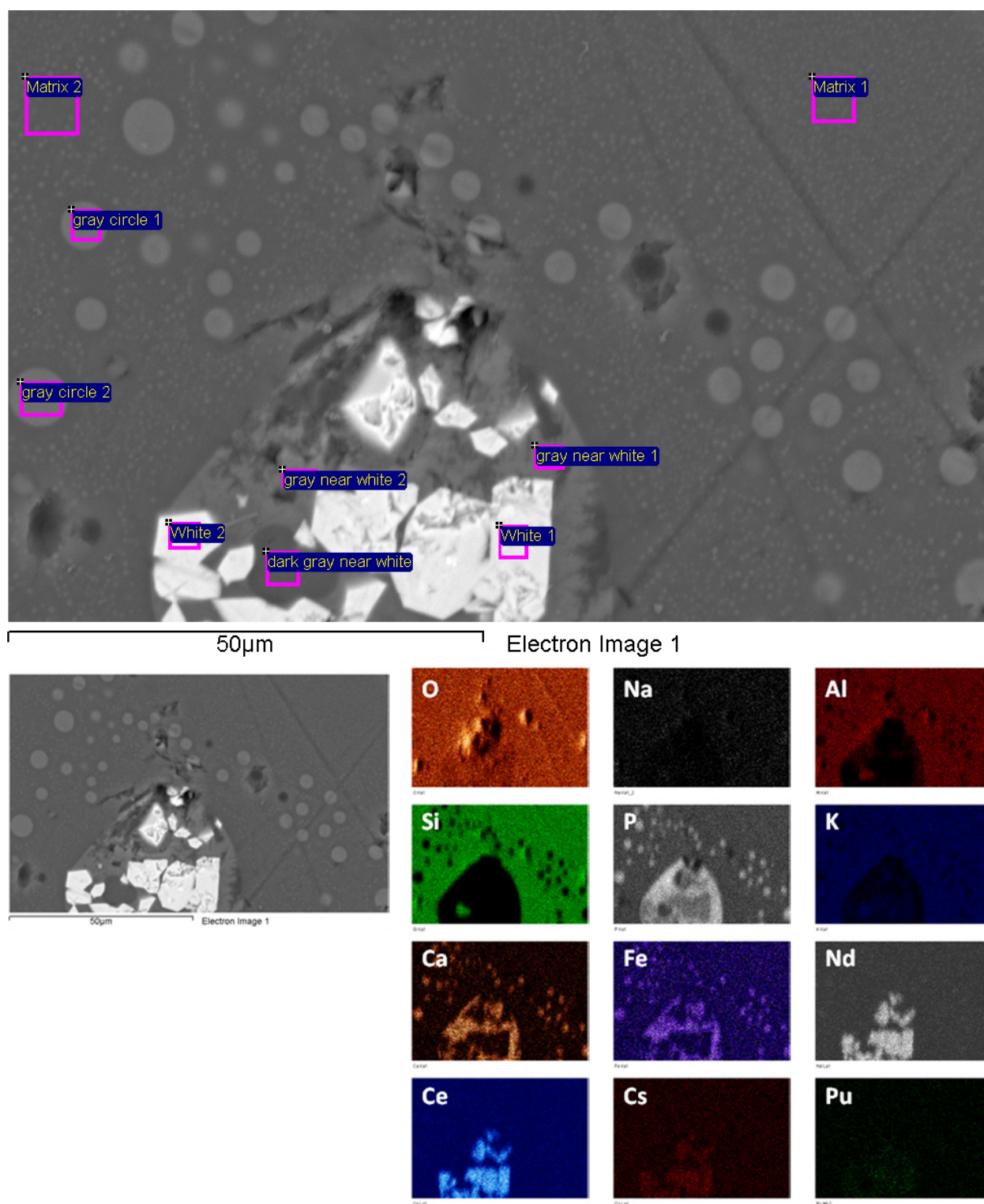


Figure 17. Higher magnification BSE image of SAP waste form. Top image shows greater detail of surface morphology including the crystalline-white monazite phase and the various gray

contrast regions. The lower images show elemental x-ray maps of the magnified top image with elemental distribution between various regions.

4.3.2 Electron Microscopy of ZIT Waste Form

The microstructure of the ZIT waste form is less complex with three distinct phases identified – a ZnO_2 matrix phase, needle-like rutile crystals embedded in the matrix and a white contrast monazite phase containing the majority of lanthanide and actinide elements. As expected, Cs and Sr were not detected due to salt distillation prior to waste form fabrication. Figures 18 and 19 show the BSE images of the ZIT waste form with the elemental composition (wt%) of the various phases indicated. Elemental x-ray maps of the material also shown in figure 19.

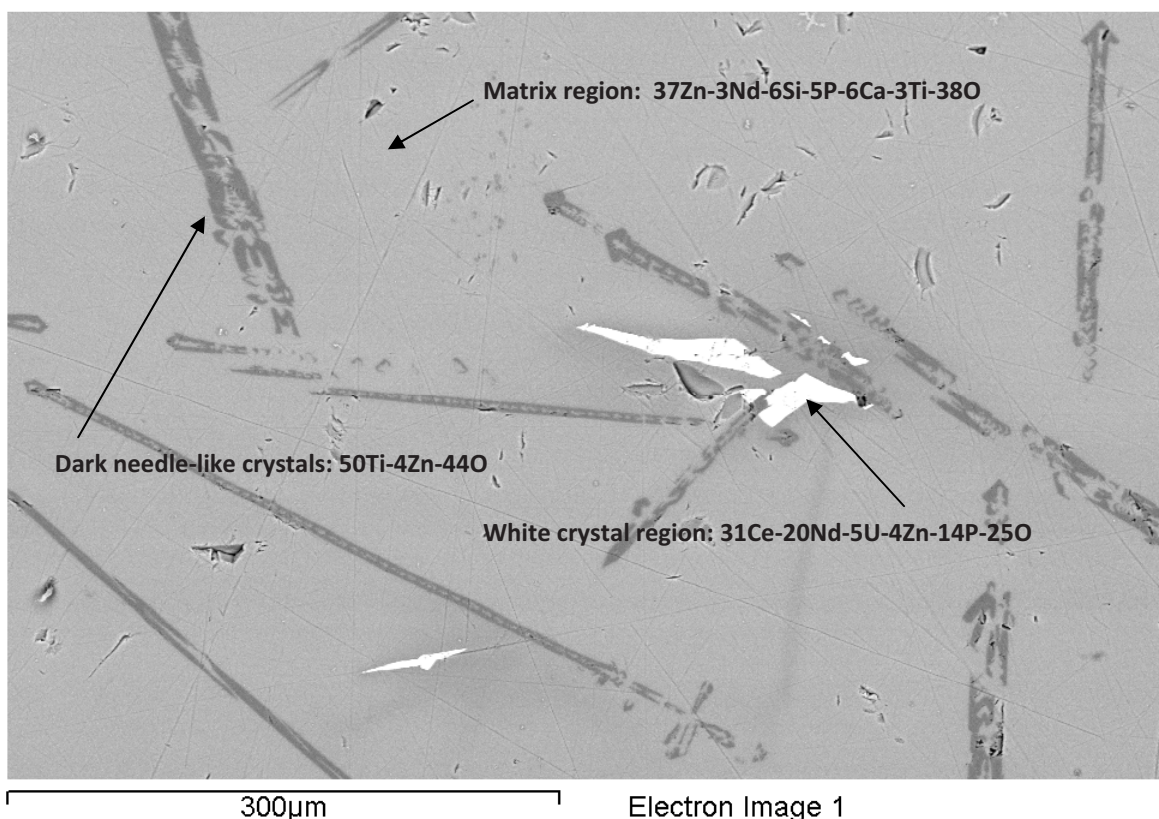


Figure 18. BSE image of ZIT waste form showing three distinct phases. The light gray contrast region is a high ZnO_2 matrix with lesser quantities of Si, P and T. Some lanthanide content is also found in the matrix region. The dark, needle-like crystal structure is the rutile (TiO_2) phase and the white phase resembles a monazite phase high in lanthanides and containing actinides.

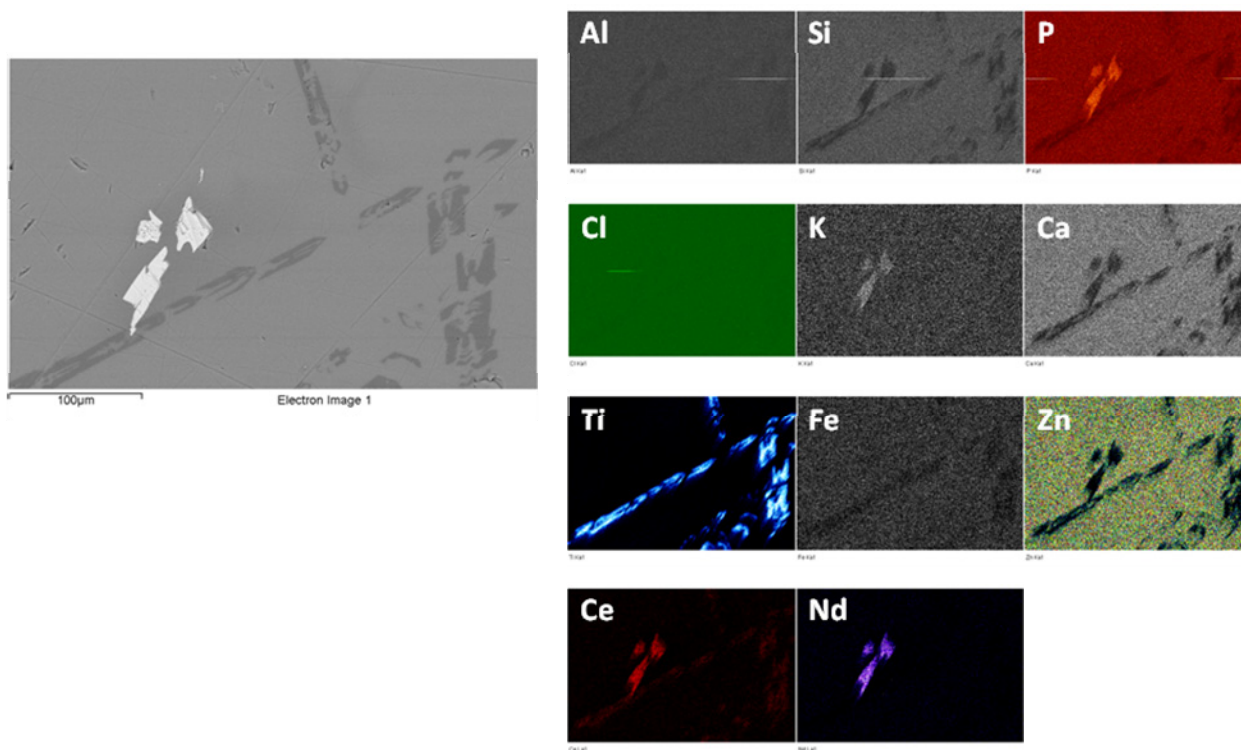


Figure 19. Higher magnification image of ZIT waste form and elemental x-ray maps of image region.

4.3.3 HL-CWF Microscopy

Microscopy of the HL-CWF confirmed the XRD analysis of the waste form that insufficient salt occlusion into the zeolite occurred. Large salt regions are observed in figure 20 that are comprised mainly of NaCl and KCl. Also observed in the HL-CWF are the glassy regions surrounding the sodalite regions. Also observed are lanthanide and actinide oxide and oxychloride regions indicating that the CWF provides a suitable host for these materials. As mentioned, insufficient salt occlusion into the zeolite occurred due to alternating mixing and heating steps during fabrication, as opposed to hot mixing as is performed during full-scale CWF production. It should be noted that halite (NaCl) is observed in both the XRD and SEM analysis of the full-scale CWF. This occurs because of the volume decrease of the zeolite cage structure in the conversion of zeolite to sodalite during processing. The smaller sodalite crystal lattice cannot incorporate as much salt per unit cell as zeolite. Thus excess salt forms discrete submicron phases in the glassy region of the waste form similar to the lanthanide and actinide oxides in the CWF.

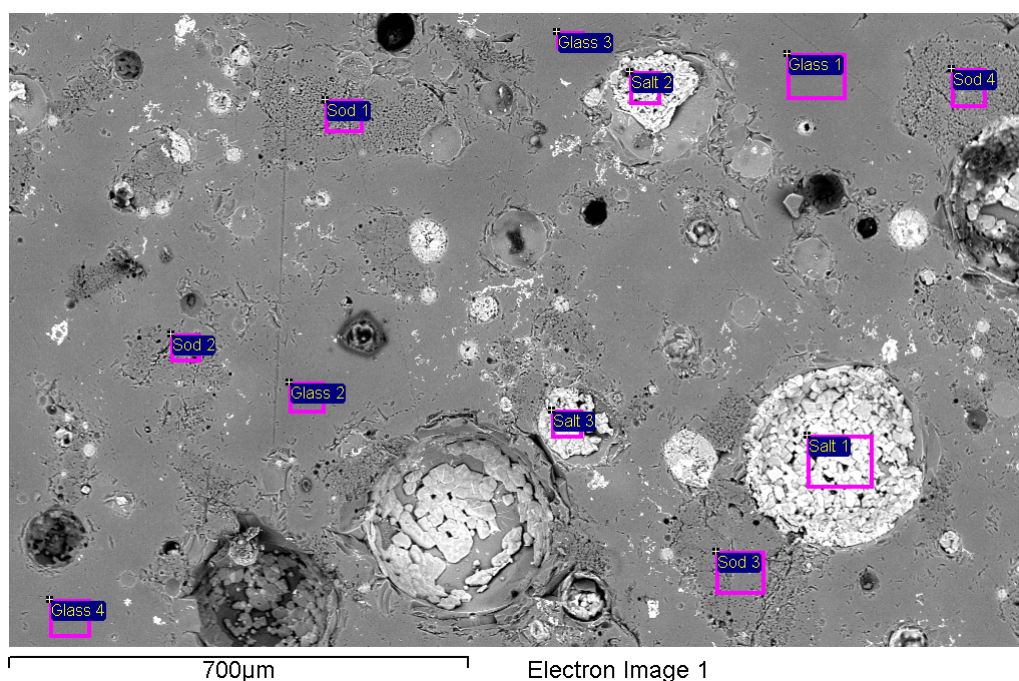


Figure 20. Large-area BSE image of the high-loaded ceramic waste form. The large white, circular areas are non-occluded salt (NaCl/KCl). Also observed are the glass regions (smooth gray areas) and sodalite regions (irregular gray areas). Small white-contrast phases corresponding to lanthanide or actinide oxides or oxychlorides are also observed.

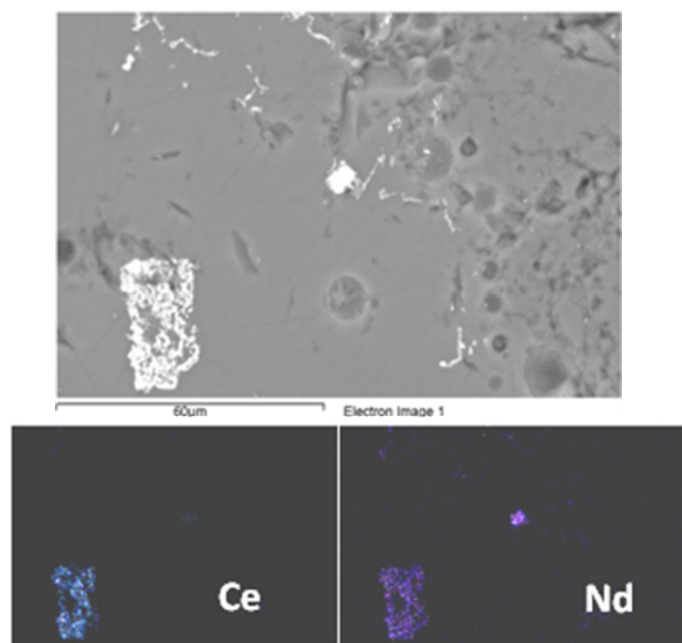


Figure 21. Higher magnification image of HL-CWF showing LN oxide or oxychloride regions. The CWF provides a suitable host material for these lanthanide or actinide species.

4.4 Product Consistency Test

4.4.1 Waste Form Elemental Composition

The accepted format for comparing element release measured from the PCT procedure is normalization of the measured elemental release to the original elemental composition of the material – thus a complete inventory of elemental composition is required. Typically, process knowledge of the feed material's elemental composition is used to determine total elemental composition. Occasionally, sample dissolution followed by elemental analysis is performed to determine any unknown element concentration in the waste form. An attempt to measure the chemical composition of each waste form was performed by dissolving a portion of the fine powder material that was also used for XRD analysis. The method involved dissolving approximately 0.5 g of the fine powder from each waste form in 20 mL aqua regia (3:1 conc. HCl and conc. HNO₃) with 2 mL conc. HF inside a Teflon beaker with gentle heating for several hours. Both the SAP and HL-CWF appeared to dissolve completely, whereas, only a small fraction the ZIT waste form dissolved. XRD of the undissolved ZIT material indicated that the rutile (TiO₂) phase did not dissolve. Other problems that often result from this strong acid dissolution are loss of volatile SiF₄, and B, and precipitation of lanthanide or actinide fluorides. The results for the attempted dissolution of the three waste forms are given in table 4, and as noted, incomplete dissolution and volatilization or precipitation of various elements occurred. Therefore the elemental analysis of the waste forms did not provide the complete elemental inventory.

Table 4. Elemental analysis of dissolved waste form samples. As noted in the text, both incomplete dissolution and element loss from volatilization (most notably Si) and precipitation occurred. Thus the analysis did not provide a complete elemental inventory of the waste forms.

SAP Elemental Composition weight % (ppm as indicated)													
Li	B	Na	Al	Si	K	Sr	Cs	La	Ce	Pr	Nd	U	Pu
0.9	0.514	1.34	5.07	0.11*	1.84	795 ppm	2120 ppm	528 ppm	0.363	780 ppm	0.308	1340 ppm	706 ppm
ZIT Elemental Composition weight % (ppm as indicated)													
910 ppm	2.52	ND	1.06	1.83	ND	3.88	705 ppm	198 ppm	0.14	1.06	0.198	0.796	2330 ppm
HL-CWF Elemental Composition weight % (ppm as indicated)													
0.56	1.43	7.22	5.61	1*	4.13	740 ppm	2044 ppm	0.11	0.98	0.17	0.71	2540 ppm	1540 ppm

As mentioned, it is often more convenient to compile elemental composition of the waste form from process knowledge of the feed materials than by dissolving and analyzing the very durable waste form. Unfortunately, at the time of this writing, a complete elemental composition of the ZIT and SAP reagent materials was not available. It was therefore not possible to express the elemental release from the PCT in normalized mass units for each element. The elemental release expressed in this report is elemental mass release per gram of sample material (not per mass of corresponding element in the sample as a function of surface area to leachate volume). The PCT method performed for this demonstration was the PCT-B [8], in which the waste form material was ground and collected from the sieved -100 +200 size fraction. This material was then washed to remove fine powder and dried. The powder was then loaded into Teflon vessels with a 10:1 volume of ASTM type I water to powder added to the vessel. Each waste form was tested in triplicate with ~ 1g sample size. Vessels were then sealed and placed in a 90°C oven for 7 days. After the test period, the vessels were cooled, weighed, and opened. The leachate was passed through a 0.4 µm filter and collected. The solution was then acidified and submitted for analysis. Analysis was performed either by inductively coupled plasma – optical emission spectroscopy (ICP-OES, Prodigy, Teledyne Leeman Labs, Hudson, NH), or ICP – mass spectrometry (ICP-MS, Perkin-Elmer Elan DRC II ICP/MS, Waltham, MA). In addition to the waste form samples an EA glass standard (Environmental Assessment Glass, SRNL, SC) and a blank solution were tested and analyzed. The results for the PCT of the three waste forms and the EA glass are shown in table 5.

Elemental release for waste form samples shown in table 5 is very low, but again, it must be stressed that the elemental compositions have not been normalized and it is not possible to compare release between samples, only within samples. It is anticipated that the complete elemental composition for the SAP and ZIT reagent materials will be available in the near future. Once these concentrations have been obtained it will be possible to compare normalized loss between samples in the conventional expression of g/m². Table 5 is separated into three elemental groups; salt components, matrix elements, and fission products/actinide elements. Elements concentrations listed in the table as ND were not detected and generally indicates that that particular element is not present in the material. On the other hand, Cs was detected in the EA glass standard, this comes from natural Cs-133 not fission product Cs. Also, Li and Na are present in the EA glass as matrix components, not from added salt. Release of salt components from the HL-CWF is greater than from the full-scale CWF. This is due to incomplete salt occlusion into zeolite during processing as describe earlier.

Table 5. Elemental release results from PCT of the ZIT, SAP and HL-CWF samples, and an EA glass standard. The results are expressed as total elemental release per gram of sample in concentration units of parts per million or parts per billion as shown. Measurement uncertainties are roughly $\pm 10\%$. The results cannot be compared between samples because the measured concentrations have not been normalized the elemental concentration in the sample. The results only give an indication of release from individual samples.

Element		Sample			
		EA Glass	ZIT	SAP	HL-CWF
Salt Components	Release: μg/g Sample				
Li		7400	142	1250	3083
Na		67415	312	335	14965
K		ND	519	293	7639
Cl		10	173	25	2970
Matrix Components	Release: μg/g Sample				
B		20381	7766	174	2076
Al		217	ND	1153	1880
Si		40553	305	2122	1916
P		ND	ND	2102	ND
Ca		ND	160	24	11
Ti		ND	ND	ND	ND
Fe		15	ND	9	8
Zn		ND	30	ND	ND
Fission Products/Actinides	Release: ng/g Sample				
Sr		ND	4486	108	9106
Cs		9*	2404	2634	65861
La		ND	7	17	39
Ce		ND	11	147	105
Pr		ND	ND	29	60
Nd		ND	84	2578	2157
U		ND	9	256	659
Pu		ND	ND	79	6

5. SUMMARY and CONCLUSIONS

Work describe in this report represents the final year activities for the 3-year International Nuclear Energy Research Initiative (I-NERI) project: Development and Characterization of New

High-Level Waste Forms for Achieving Waste Minimization from Pyroprocessing. Waste electrorefiner salt that contained actinide chlorides and was highly loaded in surrogate fission products was successfully processed into three candidate waste forms. The first waste form, a high-loaded ceramic waste form is a variant to the CWF produced during the treatment of Experimental Breeder Reactor-II used fuel at the Idaho National Laboratory (INL). The two other waste forms were developed by researchers at the Korean Atomic Energy Research Institute (KAERI). These materials are based on a silica-alumina-phosphate matrix and a zinc titania matrix. These proposed waste form materials, and the processes to fabricate them, were designed to immobilize spent electrorefiner chloride salts loaded with alkali, alkaline earth, lanthanide, and halide fission products that accumulate in the salt during the processing of used nuclear fuel.

This aspect of the I-NERI project demonstrated hot cell fabrication and characterization of the proposed waste forms. Fabricated waste forms were then prepared for characterization of the waste forms, and chemical durability testing. Waste form fabrication and sample preparation for characterization was performed in a radiological hot cell facility due to the hazardous radioactivity levels; however, smaller quantities of each waste form were removed from the hot cell to perform various analyses. Characterization included density measurement, elemental analysis, x-ray diffraction, scanning electron microscopy and the Product Consistency Test.

The small-scale fabrication methods were successfully implemented in producing three novel and durable waste forms in a hot-cell environment. In addition to fabrication and product characterization, the demonstration of the de-chlorination processes required for fabrication of the SAP and ZIT waste forms was accomplished. The favorable results from this demonstration project will provide increased options for fission product immobilization and waste management associated with the electrochemical/pyrometallurgical processing of used nuclear fuel.

6. REFERENCES

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