

The Ceramic Waste Form Process at Idaho National Laboratory

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ABSTRACT

The treatment of spent nuclear fuel for disposition using an electrometallurgical technique results in two high-level waste forms: a ceramic waste form (CWF) and a metal waste form. Reactive metal fuel constituents, including all the transuranic metals and the majority of the fission products remain in the salt as chlorides and are processed into the CWF. The solidified salt is containerized and transferred to the CWF process where it is ground in an argon atmosphere. Zeolite 4A is ground and then dried in a mechanically-fluidized dryer. The salt and zeolite are mixed in a V-mixer and heated to 500°C to occlude the salt into the structure of the zeolite. The salt-loaded zeolite is cooled, mixed with borosilicate glass frit, and transferred to a crucible, which is placed in a furnace and heated to 925°C. During this process, known as pressureless consolidation, the zeolite is converted to the final sodalite form and the glass thoroughly encapsulates the sodalite, producing a dense, leach-resistant final waste form.

INTRODUCTION

Spent sodium-bonded metallic nuclear fuel from the Experimental Breeder Reactor II (EBR II) is treated in one of two electrorefiners (ER).(1, 2) The Mark-IV ER processes driver fuel and the Mark-V ER processes blanket fuel. Relatively pure uranium is separated from the rest of the fuel by electrotransport at 450°C to 500°C. The spent fuel is chopped and placed into a batch of LiCl-KCl eutectic salt that contains 2 mol% actinide chlorides. Current is passed between the fuel (anode) and a steel mandrel (cathode). As the fuel is oxidized, metal chlorides form in the salt and uranium chloride is reduced to metal at the cathode. Chemically noble fission products, fuel matrix materials, and cladding hulls are removed from the salt and processed into a metal waste form. Reactive metal fuel constituents, including all the transuranic (TRU) metals and the majority of the fission products remain in the salt as chlorides and are processed into a ceramic waste form (CWF). The TRU and fission products build up in the salt bath until one of the following conditions is met:

1. Sodium concentration – Sodium chloride has a higher melting point than the LiCl/KCl eutectic salt.
2. Plutonium quantity/concentration – The plutonium limits are associated with criticality assessments.
3. Decay heat content of fission products – The heat content of the fission products impacts the heat input to the electrorefiner.
4. Salt level – As fuel is processed, and as UCl_3 or $CdCl_2$ is added, the salt level will rise in the electrorefiner.

For the inventory of EBR II fuel, the limiting factor for both the Mark-IV and Mark-V is the plutonium inventory, which will be met when approximately 50% of the

drivers and 20% of the blankets have been processed, respectively. These limits are established specifically for the treatment of spent fuel from the EBR-II reactor, which has decayed for about 25 years. The limits could well be different for younger fuel.

Once this plutonium limit is reached, salt will be replaced at a rate to maintain the plutonium inventory below this limit. The removed salt is solidified and transferred to the CWF process.

CWF PROCESS

Salt Grinding

The composition of the electrorefiner salt that becomes the feed for the CWF process depends upon the type of fuel processed and the conditions under which salt is removed from the electrorefiner. Electrochemical processing of the spent fuel leads to the transuranics and alkali, alkaline earth, rare earth, and halide fission products being in the salt phase. Sodium in the fuel is also oxidized in the salt. The expected composition of the salt in the electrorefiners is shown in Table 1. The salt compositions are based on the plutonium inventory limitations given above.

Table 1 Salt composition resulting from processing EBR II driver and blanket fuel.

	Mark IV - EBR II Drivers		Mark V - EBR II Blankets	
	Wt % of chloride salt	Mole % of chloride salt	Wt % of chloride salt	Mole % of chloride salt
LiCl/KCl	70.91	66.53	71.98	87.47
NaCl	11.23	10.07	7.23	8.40
RbCl	0.21	0.09	0.00	0.00
SrCl ₂	0.60	0.20	0.01	0.00
YCl ₃	0.44	0.12	0.01	0.00
CsCl	1.53	0.47	0.05	0.02
BaCl ₂	0.78	0.20	0.03	0.01
LaCl ₃	0.76	0.16	0.02	0.01
CeCl ₃	1.43	0.30	0.04	0.01
PrCl ₃	0.71	0.15	0.02	0.01
NdCl ₃	2.43	0.51	0.07	0.02
PmCl ₃	0.03	0.01	0.00	0.00
SmCl ₃	0.46	0.09	0.01	0.01
EuCl ₃	0.03	0.01	0.00	0.00
NpCl ₃	0.08	0.01	0.01	0.00
UCl ₃	5.96	0.91	14.66	2.90
PuCl ₃	2.38	0.36	5.82	1.14

Salt, as received from the electrorefiners, is in truncated cones approximately 5 cm by 5 cm, which must be crushed and ground to a particle size range of 45µm to 250µm. Radioactive salt is crushed in a VD Chipmunk jaw crusher installed in a dry

argon atmosphere hot cell. It is then ground in a Prater mill/classifier and stored under argon.

To facilitate development work and reduce costs, two types of surrogate salts are used. The first type is a simple LiCl/KCl eutectic salt. This salt has been used in numerous small-scale tests of salt-zeolite occlusion and glass testing. A more representative surrogate salt contains non-radioactive isotopes, at the same concentrations as in the above salts, with the exception of UCl_3 and PuCl_3 . This surrogate salt yields good representative data without the need for containment or other provisions required for working with radioactive materials.

Surrogate salt is sized in an argon glovebox using a Sepor Inc. jaw crusher to crush large chunks of salt into fragments of about 0.5-cm diameter for feeding into a Mazzer mini electronic coffee grinder.

Zeolite 4A Grinding and Drying – Zeolites are crystalline aluminosilicate materials that have a high capacity for adsorption of various molecular species. Their structures are formed from the cross-linking of SiO_2 and AlO_2 tetrahedra. For the ceramic waste process, zeolite 4A is used for adsorbing waste salt. The composition of zeolite-4A is $\text{Na}_{12}(\text{SiO}_2)_{12}(\text{AlO}_2)_{12} \cdot x\text{H}_2\text{O}$, as shown in Figure 2.

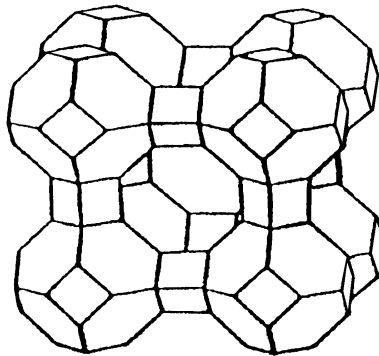


Figure 2. The Zeolite-4A α -Cage.

Zeolite 4A is received from UOP as beads with a particle size of about 1.5 mm. To improve salt occlusion and mixing, the zeolite is ground in a roller mill. Early development work used fine powders ($<10\mu\text{m}$) to improve salt occlusion. However, it was recognized that such fine powders can be difficult to handle, so a larger particle size was tested. Too large a particle size would cause problems mixing with the salt and glass. Therefore as a compromise, a particle size range of $45\mu\text{m}$ to $250\mu\text{m}$ was selected.

After being sized, the zeolite must be dried.(3) There are two motivating factors for zeolite drying. One is the effect of water on the salt/zeolite blending step in the v-mixer. The other is the effect of moisture on the waste form. The former effect is believed to be much more important, because, if the salt occlusion could tolerate moisture in the zeolite, that moisture would be subsequently driven off during the pressureless consolidation and would not impact the final waste form. The threshold for how much water in the zeolite is acceptable is not easily estimated. For this reason, the approach that was taken in developing the ceramic waste process was to dry the zeolite as much as

is reasonably achievable. A limit of 1.0 wt% has been selected and a range of 0.1 to 0.3 wt % has been typically achieved.

To dry the zeolite, Kemp Development Corporation (KDC) of Houston, Texas fabricated a vacuum mechanically fluidized dryer (MFD) to dry zeolite on a relatively large scale (30-50 kg/batch). The MFD system consists of a horizontal, cylindrical-shaped retort with cones on each end, which rotates inside a fixed furnace as shown in Figure 3. A photograph of the MFD is shown in Figure 4.

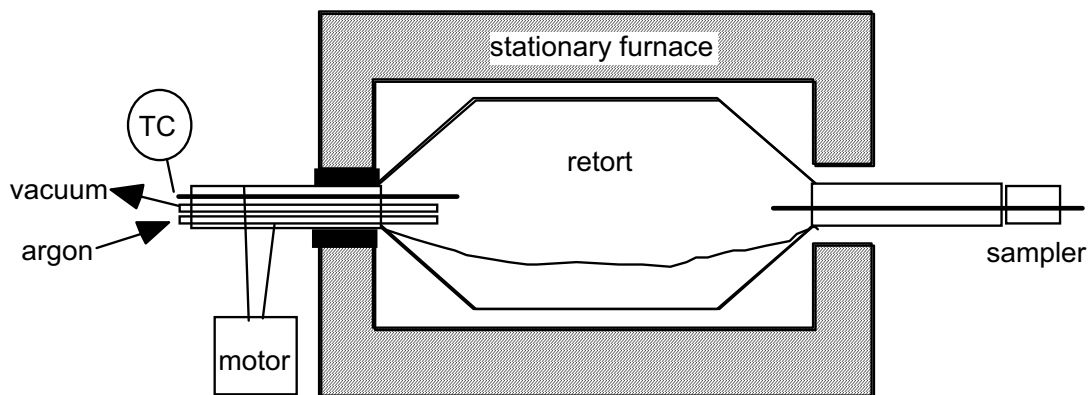


Figure 3. Schematic of mechanically fluidized dryer for zeolite

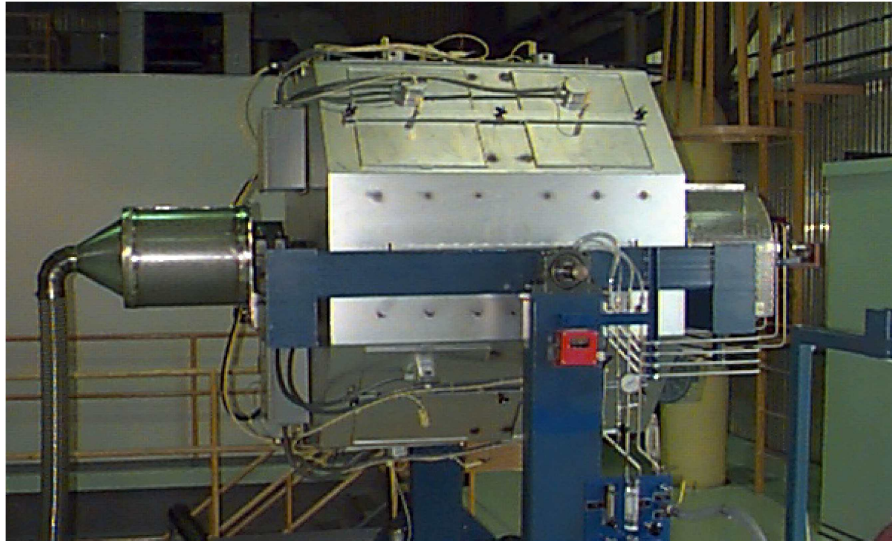


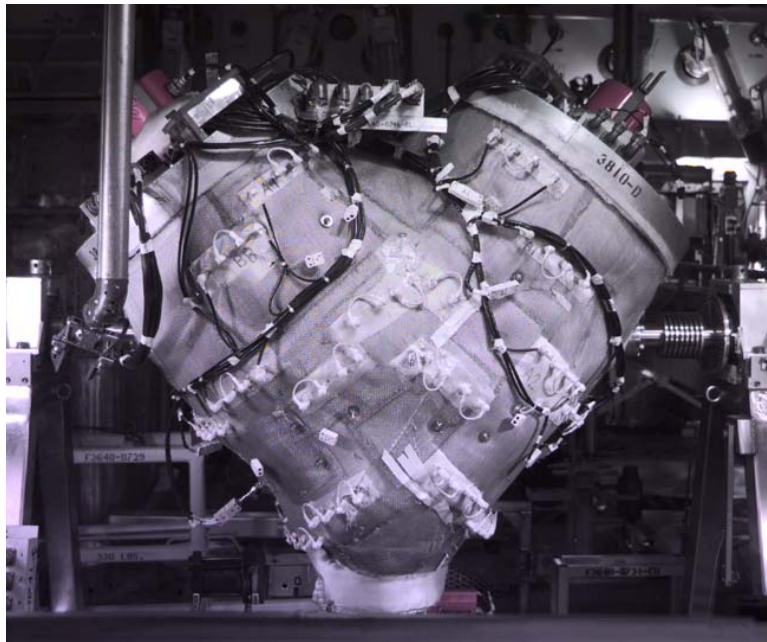
Figure 4. Photograph of the Mechanically Fluidized Dryer.

Zeolite is loaded into the MFD and the temperature is raised at 2°C/min to 550°C where it is held for about one hour. During this time the MFD is vented to atmosphere to allow the evolved moisture to escape. The vent is then closed and the pressure is reduced to less than 100 torr for five hours. The heaters are then turned off and the system is allowed to cool to ambient temperature and is filled with dry inert gas before being emptied.

Salt Occlusion

Because chloride by itself does not incorporate into a glass matrix, it must first be isolated by occlusion into a zeolite matrix.(4-6) The amount of zeolite required to contain a given amount of salt is determined by the number of Cl^- ions (with associated cations) that can be occluded into a unit cell of the zeolite. Tests have shown that a loading of 3.8 Cl^- ions/unit cell produces an acceptable final product, with free chloride generally less than 0.1%. The actual weight fraction of salt to zeolite depends upon the type of salt being processed, but ranges from about 0.10 to 0.13.

To occlude salt into the zeolite structure requires a temperature of about 500°C , which must be held for several hours while the salt and zeolite are continuously mixed. As the salt melts and evaporates it is absorbed into the zeolite forming a salt-loaded zeolite (SLZ). To accomplish this, a heated, offset V-mixer is used. Salt and zeolite are placed into the V-mixer, which has been purged with dry argon. The V-mixer is rotated at about 17 rpm. The heater controller is set at a heat-up rate of $5^\circ\text{C}/\text{min}$ with a final set point temperature of 525°C . A photograph of the V-mixer, which is located in a hot cell, is shown in Figure 5. It is assumed that there is no significant free liquid salt in the V-mixer. The V-mixer is maintained at this temperature for about 18 hours and is then allowed to cool to ambient while still rotating. When the V-mixer is cooled, three samples of salt-loaded zeolite (SLZ) are withdrawn to perform free chloride analysis. The SLZ is considered acceptable if the free chloride is less than 0.5%. Typically, the



free chloride concentration is less than 0.1%

Figure 5. Heated V-mixer used to produce salt-loaded zeolite

Pressureless Consolidation

When the free chloride has been shown to be acceptable, glass is added to the SLZ in the V-mixer and mixed at ambient temperature to produce a homogenous mixture (7). The fraction of glass in the mixture is about 25%. This mixture is then transferred to

a furnace for final processing. This process is known as pressureless consolidation (PC). In the PC process, the SLZ is converted to a sodalite mineral form ($\text{Na}_4\text{Al}_3(\text{SiO}_4)_3\text{Cl}$), which is encapsulated by the glass matrix.

A number of glasses of various compositions were tested during development of the CWF process. From that work, borosilicate glass was selected for the CWF process based on the following properties. Compositions of several borosilicate glasses that were tested are shown in Figure 6.

1. The glass needs to have a relatively low softening temperature ($<\sim 750^\circ\text{C}$).
2. The glass should have a relatively broad glass working range so the glass doesn't drain through the zeolite/sodalite.
3. The glass must wet the zeolite or sodalite-salt mixture.
4. The coefficient of thermal expansion of the glass should match the zeolite or sodalite-salt mixture.
5. The glass powder should be free flowing.
6. The glass should exhibit inherently efficient packing of $\sim 40\%$ to 45% theoretical density.
7. The glass should undergo uniform densification during heating cycle
8. The glass should produce a non-friable waste form surface

Table 2. Composition of several borosilicate glasses used in the ceramic waste form process.

Components	Pemco 57	Corning 7056	Schott 8250 K1	Schott 8250 Granular	Johnson Matthey RD 808
SiO_2	66.9%	70.1%	67.5%	68.8%	71.1%
B_2O_3	18.8%	21.8%	24.2%	23.4%	20.9%
Al_2O_3	7.2%	2.5%	2.5%	2.4%	2.8%
Na_2O	6.8%	2.3%	2.2%	2.0%	2.8%
K_2O		3.2%	3.1%	2.9%	2.0%
Li_2O	0.3%	0.0%	0.3%	0.3%	0.4%
MgO			0.3%	0.3%	0.0%

The heating profiles for various sizes of CWFs are similar, but the actual times are longer for larger sizes. For small test samples (1 kg) the furnace temperature is raised at $10^\circ\text{C}/\text{min}$ to 500°C where it is held for about two hours. This hold allows any residual moisture to evaporate. The temperature is then raised to 925°C for 15 hours. 140 kg specimens were made by holding the furnace at 925°C for 100 hours. The production-scale furnace will produce up to a 400 kg CWF, but it will be the same diameter as the 140 kg CWF. Because the furnace is radially heated, the heating times are expected to be

relatively independent of the length of the CWF. Therefore, the cycle times should be similar. The principal difference will be cool down time. The 140 kg CWF had no external cooling, whereas the production-scale furnace has the capability for forced argon cooling. The impact of forced cooling on process time will be investigated. The production-scale furnace has internal dimensions of 68 cm (26 3/4 in) in diameter by 312 cm (123 in) high. A photo of the production-scale furnace is shown in Figure 7. This furnace was made operational in 2006 and will be used for demonstration tests using surrogate material before it is installed in a hot cell where it will be used to process EBR-II salt.



Figure 7. Production-scale CWF furnace.

Thermal Modeling of the CWF Process

The PC process has been modeled to better understand the heating and cooling requirements for the full-scale furnace.(8) This modeling has accounted not only for the heat transfer to the CWF monolith from the furnace, but also the internal heat generated by:

1. radioactive decay of fission products within the salt,
2. conversion of zeolite to sodalite, and
3. material shrinkage.

The model, with the exception has been verified against experimental data using surrogate salt for 10 kg, 25 kg, 85 kg, and 140 kg waste forms. The temperature and density data from the 140 kg CWF experiment are plotted with the predictions for the model in Figures 8 and 9 respectively. The furnace temperature was raised to 500°C and held for about 60 hours. A second hold point was set at 560°C for about 50 hours. The

temperature was then slowly increased to 916°C over the next 60 hours and held there for an additional 80 hours. As is shown in Figure 8 the model accurately predicts the centerline temperature of the CWF. This is particularly important for the steep rise in temperature, because this was where the material properties changed significantly. For example, the thermal conductivity changed over an order of magnitude during this time. Additionally, the model was able to represent the exothermic reaction of what is believed to be the zeolite converting to sodalite.

The model also accurately tracked the rapid densification as the bulk temperature approached 567°C as shown at about 150 hours in Figure 9. The model continues to track the experiment during 915°C hold. The model also appeared to predict the thermal contraction of the material as it cooled at around 200 hours. The model predicted a final density before cooling of 1.85g/cm³, whereas the experiment yielded a final density of 1.87 ± 0.02g/cm³. After cooling, both the model and experimental data agree on a density of about 2.0 g/cc.

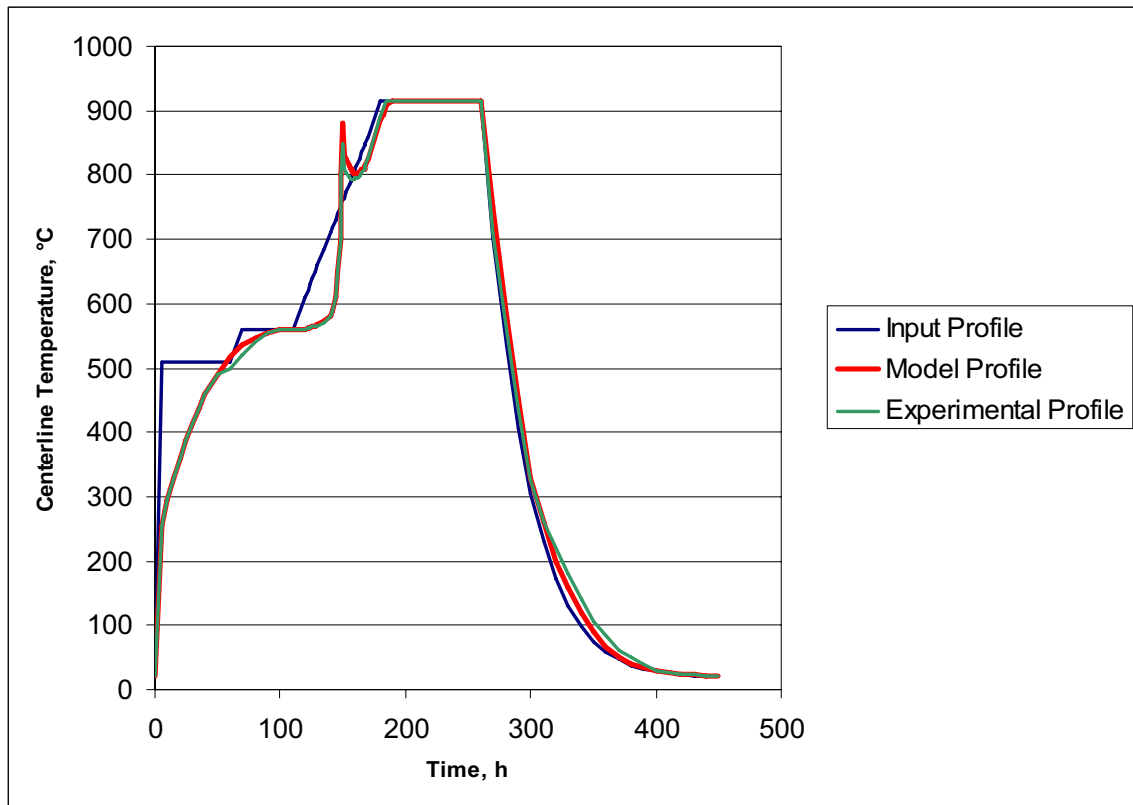


Figure 8. Comparison of centerline temperature model versus experimental temperature data for 140 kg CWF.

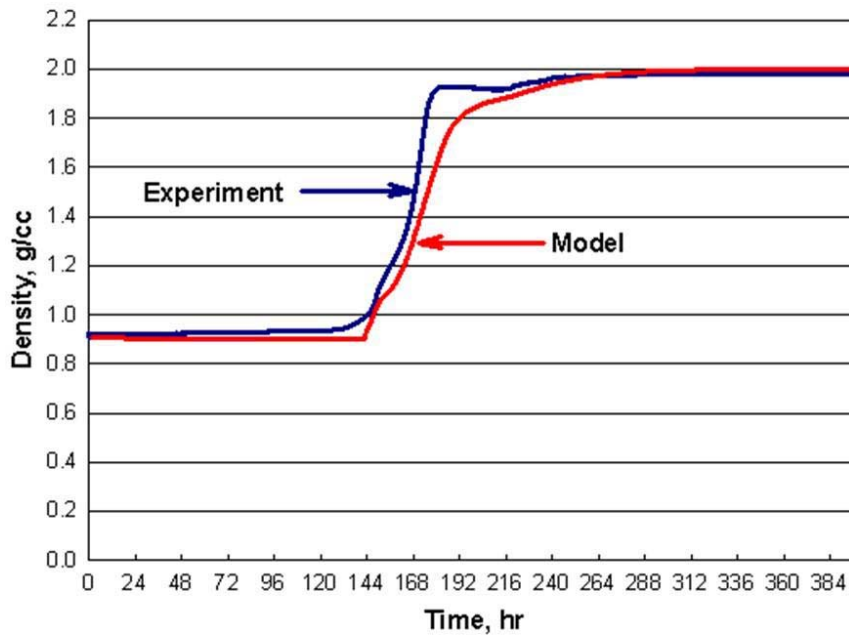


Figure 9. Comparison of experimental data with model results for 140 kg CWF.

CWF PRODUCT QUALITY

The quality of CWFs is established by visual observation, density, chemical durability, X-ray diffraction, and scanning electron microscopy.(9) Presented below are representative results of the most recent tests from a study of alternative glasses.

Visual Observation

CWFs are broken apart and examined visually for homogeneity and the presence of anomalies. Figure 10 is photograph of a typical CWF, which shows a uniform consistency with small inclusions and little porosity.



Figure 10. Photograph of CWF showing a fairly homogenous matrix with only minor inclusions, which may be unconverted zeolite.

Density

Density of the CWF is measured using helium pycnometry. The results typically range from 2.3 g/cm³ to 2.4 g/cm³.

X-ray Diffraction (XRD)

Samples from each CWF are ground into a fine powder (<75 µm) and analyzed as a thin film using XRD. The observed mineral phases are normally sodalite and halite (NaCl). The ratio of sodalite to halite ranges from about 0.6 to 1.5. The differences in ratio of sodalite to halite may be due to differences in the composition of the glasses, which may impact the dissolution of sodalite into the glass, and the ion exchange mechanism when converting zeolite to sodalite. It does not impact the product durability, but will be examined more fully in the future.

Chemical Durability

Chemical durability of the CWFs is determined using the standard product consistency test (PCT), according to ASTM c-1285 Test Method A. The test involves grinding (< 75 µm) and cleaning the sample material, then placing the material in demineralized water for 7 days at 90°C. The water leachate solution is then filtered to remove any solid material and analyzed for leached constituents of the waste form. The results from these tests are expressed as normalized mass loss of each elemental constituent. These values are shown in Table 2. Release rates of the all the matrix elements (Si, Al, B, and K) are at least an order of magnitude lower than a comparable environmental assessment (EA) glass. EA glass is used as the baseline for repository durability analyses. Example mass losses for several components in the EA glass are shown in Table 2. Cl is not measured for EA glass.

Table 2 PCT analysis results for CWF showing normalized mass loss

Element	Matrix Elements				Salt Elements		
	Si	Al	B	K	Li	Na	Cl
Normalized Mass Loss	0.047	0.045	0.138	0.226	0.59	0.39	2.04
EA Glass	4.2		17.7		10.0	14.8	

Scanning Electron Microscopy (SEM)

The micro-structural composition of the CWF is determined by SEM in both secondary electron (SE) and back scattered electron (BSE) modes. Figure 11 shows a representative pair of SE and BSE micrographs. The micrographs show two principal phases, glass and sodalite, with inclusions of halite and unconverted zeolite. It can be seen that the glass thoroughly encapsulates the sodalite phase with little or no porosity.

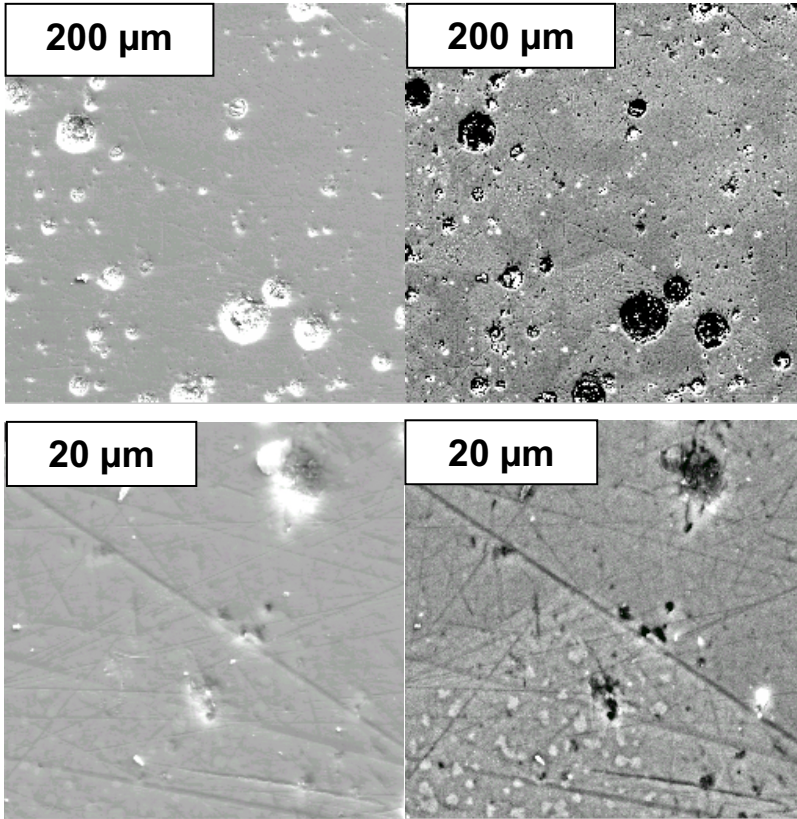


Figure 11. Micrograph of CWF. Lower magnification is shown on the top. SE images are shown on the left and BSE images are shown on the right.

Elemental compositions of the two primary phases, sodalite and glass, were also determined by acquiring energy dispersive spectroscopy (EDS) spectra from ten points in the glass and sodalite phases. These spectra were then analyzed and the results from each group of ten points were averaged. Recent results are shown in Figure 12. As can be seen from the graph, most of the chlorine has remained bound in the sodalite phase. It is also evident that ion exchange has occurred between the glass phase and the zeolite/sodalite phase. This is seen most evidently by the presence of potassium in the glass phase.

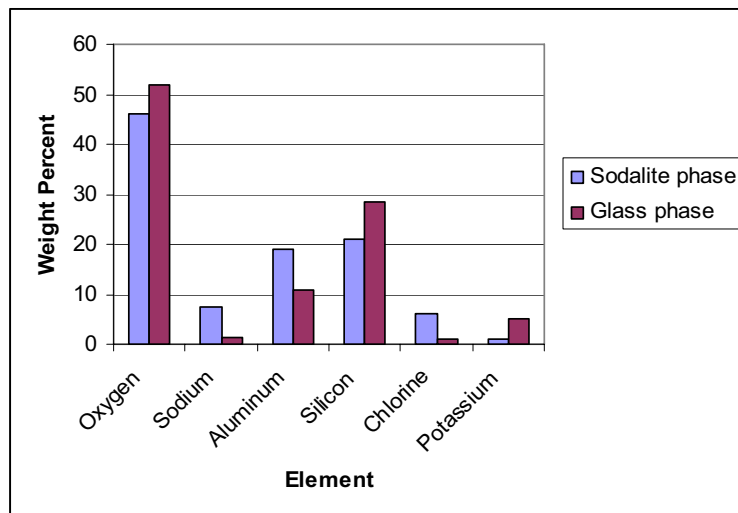


Figure 12. Elemental analysis of sodalite and glass phases in CWFs

SUMMARY

The process of occluding salt into a zeolite matrix and then converting that matrix to a sodalite form and encapsulating it in glass has been shown to be a robust method for isolating the salt byproduct from electrochemical treatment of spent EBR II fuel. The process has been demonstrated on surrogate materials up to near-production scale and on radioactive material on limited quantities. INL is working to complete and test a production-scale process and will then move on to treatment of remaining electrorefiner salt.

ACKNOWLEDGEMENT

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