

CERAMIC WASTE FORM PRODUCTION AND DEVELOPMENT AT ANL-WEST

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ABSTRACT

Argonne National Laboratory has developed a method to stabilize spent electrolyte salt discarded from electrorefiners (ER) used to treat spent nuclear fuel. The salt is stabilized in a ceramic using a pressureless consolidation technique¹. The starting material is zeolite 4A which is used as the host for the fission product and actinide rich salt. Glass frit is added to the salt loaded zeolite before processing to act as a binder. The zeolite 4A is converted to sodalite during processing via pressureless consolidation. This process differs from one used in the past that employed a hot isostatic press. Ceramic is created at 925°C and atmospheric pressure instead of the high pressures used in hot isostatic pressing. Process flow sheets, off-gas test results, processing equipment, and leach test results are presented.

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INTRODUCTION

High-Level form development has been an integral part of spent nuclear fuel processing at ANL since the eighties. Development of this process coincided with the development of the electrometallurgical treatment for spent sodium bond fuel. During the EMT process, where uranium is selectively extracted from the spent fuel, fission products, actinides and sodium accumulate in the lithium chloride/potassium chloride electrolyte salt. Electrorefiner salt must be removed and replaced periodically to control its melting point and limit plutonium buildup. Salt that is removed from the ER is then processed into a ceramic waste form.

Salt removed from the ER is ground and contacted with zeolite 4A particulate in a heated v-mixer at 500°C. During heat up of the mixer, the salt is melted and absorbed into the zeolite where it is occluded in the zeolite's crystalline structure. Once the salt is fully absorbed, the mixer is shut off and allowed to cool before adding the glass. After addition of the glass, the salt loaded zeolite and glass are cold mixed for two hours. The glass acts as a binder in the ceramic waste form.

In the past, processing of the ceramic waste form has been accomplished at high temperatures (up to 850°C) and high pressures (up to 25,000 psi) using a hot isostatic press (HIP). However, research into the use of Pressureless Consolidation (PC) has been conducted in the last two years as an alternative to HIPing. The trend from HIP to PC processed wastefoms stems from the engineering difficulty of placing a full sized HIP, capable of producing

400+kg wasteforms, in an existing hot cell at ANL-West.

Process Overview

Salt Processing

The overall process flowsheet for the ceramic waste form is shown in Fig. 1. ER salt is removed from the electrorefiner via a dipping assembly. The dipping assembly is manufactured with 5.08 cm nominal diameter by 5.08 cm tall conical traps. The salt is loaded into the assembly and removed from the ER and allowed to freeze at ambient temperature. Once frozen, the salt cones are removed from the assembly, placed into a transfer can, and transferred from the Fuel Conditioning Facility (FCF) to the Hot Fuel Examination Facility (HFEF) for further processing.

Upon delivery at HFEF, the salt is taken out of the transfer can and batches of ten cones are loaded into magazines. These magazines are mated with the inlet of a jaw crusher where they are crushed to a <10 cm size. The salt granules are collected at the bottom end of the jaw crusher and transferred to a mill/classifier for further processing.

A Prater CLM-18 Mill/Classifier is used to decrease the particle size of the salt to 45-250 microns. The mill/classifier is paired to the vacuum side of a Rotron DR-6 Regenerative Blower to supply gas flow. The mill is an impact mill and offers two stages of particle size reduction. Initially, salt is fed into the back side of the mill rotor where its size is initially decreased. At the perimeter of the mill rotor is a set of 3.125mm screens. Once the particle size of the salt is smaller than the screen size, salt particulate is passed from the mill section through the screens and into the classifier section of the mill/classifier. Once in the classifier section of the unit, particulate that is small enough to get entrained in the gas vortex, caused by both the mill rotor and classifier rotor, leaves the classification section through stainless pipe and flows into a cyclone separator for collection. Particulate not small enough to leave the classifier is then thrown back into the mill rotor and the size is decreased until it will pass through the equipment.

As mentioned earlier, a cyclone separator is used for particulate collection. The cyclone in use is a G.E. Environmental High efficiency Cyclone, designed to collect particulate 3 microns and larger with 99.999% efficiency. Less than 1% of the salt ground in the mill classifier is smaller than 45 microns therefore particulate blow-by through the cyclone is insignificant. In the event that particulate is passed through the cyclone, polishing filters are located at the top of the cyclone along with HEPA filters at the exit side of the blower.

Zeolite Processing

Bulk zeolite 4A pellets, purchased from UOP, are processed similar to the ER salt. A Prater CLM-18 mill/classifier is used to take the zeolite pellets from a nominal diameter of 2mm down to the desired 45-250 micron size range. Zeolite is processed in a semi-dry air containment box.

Zeolite is first passed through the mill/classifier and the resulting particulate is collected again via a high efficiency cyclone. Because of the nature of the zeolite, fines are produced that pass through the cyclone. Therefore, at the backend of the cyclone a baghouse is used to collect any fines that pass.

Material collected with the cyclone is transferred to a Rotex 12A-SSSS sieve shaker table where the zeolite particulate is separated into three streams; oversize (>250 microns), product (45-250 microns), and fines (<45 microns). The oversized particulate is stored to be reprocessed in the mill/classifier, the fines are discarded, and the product is placed in a container for further treatment.

Once a batch of zeolite has been ground to the correct particle size

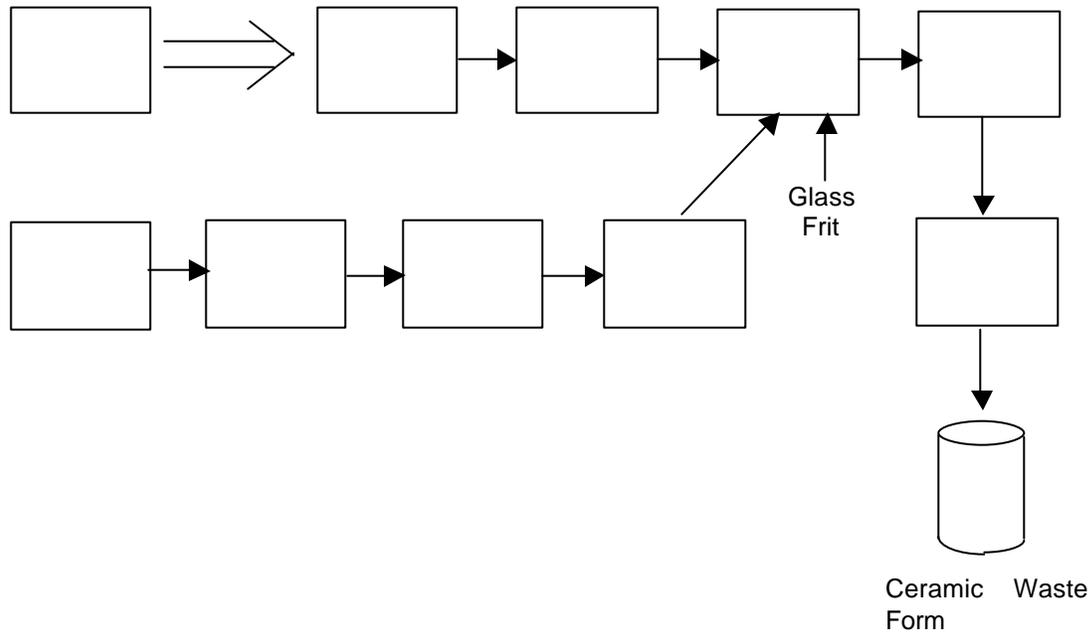


Figure 1. Process flow diagram for ceramic waste process at ANL-W

distribution, it is dried under 100 Torr. vacuum at 550°C for 6 hours in a Mechanically Fluidized Drier (MFD). Once the drying cycle has completed, a sample of zeolite is analyzed to ensure its water content is below 1.0 wt%. The zeolite container is then filled with a nitrogen head and stored for future use in the ceramic waste form. Figures 2-4 show the zeolite processing equipment.

Figure 2. Prater CLM-18 Mill/Classifier, Cyclone Separator, and Baghouse used for grinding zeolite.



Figure 3. Rotex model 12A-SSSS Sieve Shaker Table used in processing ground zeolite.



Ceramic Waste Processing

Once the salt and zeolite have been ground to the proper size and the zeolite dried, the

materials are loaded into a heated v-mixer. Due to the fact that the zeolite is eventually converted to sodalite during the consolidation process, salt is loaded at a 3.8 Cl⁻ per unit cell instead of the 12 Cl⁻ per unit cell for zeolite.



Figure 4. Mechanically Fluidized Dryer.

After the zeolite and salt have been placed into the v-mixer, the v-mixer is heated to 500°C for 15 hours during which the salt is absorbed into the zeolite. As the salt is absorbed into the zeolite, fission products and actinides are occluded into the crystalline zeolite pore structure by adsorption.

After cool down of the v-mixer, a sample of the salt loaded zeolite is taken and analyzed for free salt, salt that is still on the surface of the zeolite. A high free salt value may result in a product with a higher leach rate. The free salt must be less than 0.5 wt% of the salt loaded zeolite. Upon determining that the free salt content is lower than the set reference, glass frit, particle size range 45-250 microns, is added at 25 wt% and cold mixed for an hour. The salt loaded zeolite/glass frit mixture is unloaded from the v-mixer into a storage can in preparation for the PC furnace.

The salt loaded zeolite/glass frit is placed into a PC can assembly. The can assembly is made up of the PC can, a can extension, and a setter plug. The can and setter are made from stainless steel while the can extension is made of graphite. See Fig. 5. The can assembly is filled with the salt loaded zeolite/glass in order to produce a fully loaded can once the PC processing is complete.

A full can assembly is placed in the PC furnace and the furnace is brought up to 915°C where the zeolite 4A is converted to sodalite. The time at temperature is dependent on the size of the waste form. Once the PC process is done, the can extension is parted from the PC can, the setter plug is removed, and a lid is welded on the PC can.

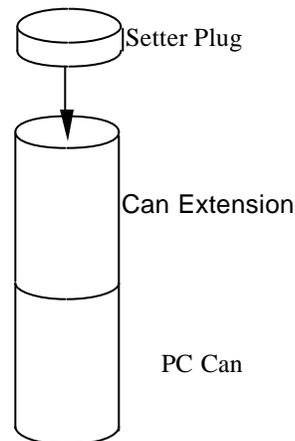


Figure 5. Pressureless Consolidation Can Assembly.

PRESSURELESS CONSOLIDATION. COMPARISONS WITH HIP'ED PRODUCTS AND RESULTS

Pressureless consolidation differs from hot Isostatic pressing in that the process operates under ambient pressures and a different style can is used. Although HIPing produces a denser product, 99.9% theoretical density, the can used for HIPing is constructed in a bellows fashion to allow for axial compaction. During processing, the can is compressed axially and the bellows flatten. The bellows contain no ceramic and therefore add unused volume to the waste form. In the PC process, a straight walled can is used which allows for maximum volume utilization by the waste form.

As stated earlier, HIPing is done at high pressures. Because of this, HIP's are very large in size with respect to the size of a waste form that can be produced in them. This was the determining factor with the change from a HIP to

PC at ANL. Another caveat with the HIP is that the loaded HIP can must be baked out in a furnace and vacuum sealed prior to processing in the HIP. This process requires the same type furnace that is used for the PC process. Thus by eliminating the HIP, a process step is eliminated.

Physical Property comparison of PC vs HIPed Ceramics

There was some concern as to whether a PC waste form would be as robust as a HIPed waste form due to the processing differences. Therefore, a battery of tests was conducted on PC waste forms in order to compare the results with HIPed waste form results. These tests included density measurements and product consistency tests (PCT).

Density measurements for PC and HIPed ceramics were determined using the buoyancy method as well as helium picnometry respectively. Results from the density tests revealed the PC waste form to have a density of roughly 2 g/cc whereas the HIPed waste form was 2.3 g/cc. Small pores formed from gas pockets were found to be present in the PC waste form which accounts for a portion of the decrease in product density. Although there is a 13% increase in ceramic volume when PC is used relative to HIP, the fact that the entire waste processing can is utilized with PC waste forms allows for a higher packing density in the final waste disposal can.

Product consistency tests (PCT) were also conducted on PC waste forms and compared with results obtained from HIPed waste forms [1-2]. Normalized elemental mass loss (NL) was determined for Si, B, Li, and Al. Results from these tests are shown in Table 1.

Results from the tests show that the PC waste form is consistent with HIPed waste forms as measured with the PCT method.

CESIUM OFF-GAS TESTING

Cesium off-gas testing was conducted in order to determine whether Cs would be volatilized from the salt loaded zeolite/glass mix during PC processing. Six radioactive samples were tested during this experiment in HFEF.

Approximately 1.5 kg of material was used in each test.

Element	NL, g/m2			
	PC		HIP	
	Average	Std Dev	Average	Std Dev
Li	0.66	0.14	0.45	0.17
Si	0.05	0.01	0.09	0.015
Al	0.06	0.02	0.097	0.012
B	0.25	0.37	0.38	0.24

Table 1. Normalized Release Rates for PC and HIPed waste forms produced at ANL.

The material was loaded into cans 10.16 cm in dia. X 26.35 cm in height. A shroud with 2.54 cm tubing extending from the top was placed on the can. See Fig. 6. The tubing was loaded with 75 grams of dried zeolite 4A pellets. A steel plug was placed on top of the material and used to aid in consolidation of the material. The can assemblies were capable of being evacuated to 100 mtorr.



Figure 6 . Cesium Off-Gas Testing Aparatus.

The can assemblies were placed in the furnace used to bake out ceramic waste form samples for processing in the HIP, and connected to a vacuum pump via the extending tube. Each can

assembly was processed at 900°C for ten hours. After four hours of processing, the vacuum pump was activated.

Ceramic waste forms produced by PC are not processed under vacuum. Vacuum was applied in this circumstance in order to trap any cesium that was off-gassed within the zeolite located in the tube.

The cesium release and amount in the waste was determined by gamma scanning. Results of the experiment showed that an average of 0.3% of the total Cs in the can was released to the tube. Under normal operating conditions during the PC process, i.e. under ambient pressure, it is doubtful much cesium will be released during the processing.

MODELING OF PRESSURELESS CONSOLIDATION PROCESS

Processing time and product density, with respect to ceramic waste processing, is dependant on the size of the waste form being produced. In order to predict the processing time needed for production size waste forms, a finite difference model was developed at ANL-W. The model used material property data found in the literature and these data were refined as the model was put into use.

Material properties were initially refined by processing a 0.4 kg PC waste form. The waste can was fit with thermocouples and temperature/density data were recorded throughout the processing. Using the data from the run, the model was fit to the thermal and density data to refine the model. Once the 0.4 kg waste form was completed, the same test was performed on a 10 kg PC waste form and the properties refined further.

Using the refined data for the 0.4 kg and 10 kg waste forms, experiments were conducted on 25 kg and 85 kg waste forms. Results from the tests revealed the model was within 1% of determining the final density of the product and predicted the time to process accurately. Fig. 7 and 8 show results of the tests for the 25 kg run.

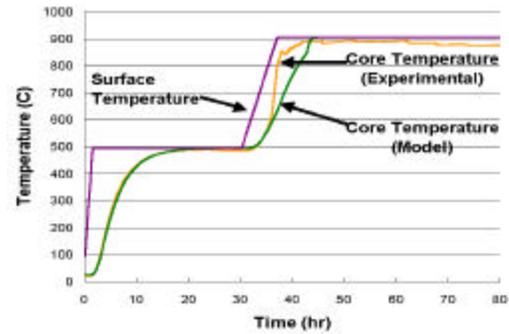


Figure 7. Finite Difference Model results for 25 kg PC waste form. Temperature vs. Time.

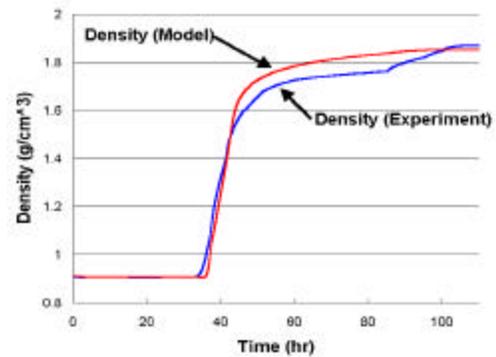


Figure 8. Finite Difference Model results for 25 kg PC waste form. Density vs. Time.

CONCLUSIONS

Production of the ceramic waste form using the PC method has shown promising results compared to the HIP method. Although material densities are lower for the PC waste form, waste package densities are higher. Model development for the process has proven useful in predicting time of processing and final material density. Cesium off-gas tests showed minimal release of cesium during processing under extreme conditions.

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