

DEVELOPMENT OF A SAMPLING METHOD FOR QUALIFICATION OF A CERAMIC HIGH-LEVEL WASTE FORM

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ABSTRACT

A ceramic waste form has been developed to immobilize the salt waste stream from electrometallurgical treatment of spent nuclear fuel. The ceramic waste form was originally prepared in a hot isostatic press (HIP). Small HIP capsules called witness tubes were used to obtain representative samples of material for process monitoring, waste form qualification, and archiving. Since installation of a full-scale HIP in existing facilities proved impractical, a new fabrication process was developed. This process fabricates waste forms inside a stainless steel container using a conventional furnace. Progress in developing a new method of obtaining representative samples is reported.

INTRODUCTION

Electrometallurgical treatment of spent nuclear fuel produces two waste streams: metal from cladding hulls and salt from electrorefining. A ceramic waste form has been developed to immobilize the salt waste. A hot isostatic press (HIP) was originally used to prepare the ceramic waste form. Small, easily fabricated HIP capsules called witness tubes were shown to be a practical way to obtain representative samples of ceramic waste form material for process monitoring, waste form qualification, and archiving.¹ However, the HIP was found to be impractical for production of full-scale waste forms. A "pressureless consolidation" process was developed to replace the HIP. This process uses a conventional furnace to fabricate waste forms inside a stainless steel container that becomes part of the waste form. A new method of obtaining representative samples for process monitoring, waste form qualification, and archiving must be developed and integrated into the full-scale production process.

The objective of this work is to develop and qualify a standardized method for obtaining samples for product consistency testing during production of the pressureless consolidated ceramic waste form. The effort is divided into two phases. During Phase I, candidate sampling methods will be developed using

small "laboratory" scale waste forms to investigate materials interaction issues and develop the methodology. The primary goal of Phase I is to specify the sampling method to be used on full-scale waste forms. A secondary goal is to identify a back-up methodology to reduce technical risk. All experiments during Phase I will be performed using non-radioactive materials.

During Phase II, the sampling methodology developed in Phase I will be tested with full-scale production equipment. This testing will be performed in conjunction with process development so that the candidate methodology will emerge from Phase II completely integrated with the production process. Phase II testing will involve extensive sampling in order to develop the data base necessary to establish the statistical relation between the properties of product consistency samples and the production waste form material.

Currently, we are engaged in Phase I of this effort. This paper reports progress to date, and outlines future plans.

TECHNICAL APPROACH

The Waste Acceptance System Requirements Document (WASRD)² requires that the Product Consistency Test (PCT)³, process knowledge, or a combination of the two be used to demonstrate that waste forms meet specifications during production. This approach has been adopted for the ceramic waste form produced during electrometallurgical treatment of metallic sodium bonded spent nuclear fuel as described in the Waste Form Compliance Plan.⁴ While waste form qualification during production will rely heavily on process knowledge, some sampling and testing will be conducted on a statistical basis. The samples required are not large (20 - 40 g) however, the size and weight of the production scale waste form (about 0.5 m in diameter and 1 m tall and weighing up to 450 Kg) makes sampling problematic. As the process is currently laid out, there is no room in the hot cell for equipment large enough to obtain samples of waste form material by conventional methods such as cutting or core drilling.

Sampling activities could take place at various times during the production process. Basically, the points during the process where sampling activities could occur can be defined based upon whether the waste form material is at processing temperature (hot) or has cooled to ambient temperature (cold). Furthermore, sampling can be defined as a two step process: probing the waste form to isolate a small amount of material, and physically retrieving the material. For example, the Defense Waste Processing Facility obtains samples of high-level waste glass by inserting a small cup into the molten glass pour stream (probing), then removing the cup after collecting enough molten glass for analysis (retrieving).⁵ This sampling activity would be described as hot probing and hot retrieving. On the other hand, the West Valley Demonstration Project obtained glass samples after the glass had cooled by reaching into the canister with remote manipulator

(probing) and removing a shard of glass (retrieving).⁶ This sampling activity would be described as cold probing and cold retrieving. Using these concepts, four types of potential sampling activities were defined for the ceramic waste form production process as shown in Table I.

Table I. Potential sampling activities defined in terms of the waste form temperature at each of the sampling steps, along with some waste form material properties that could be of interest

Probe	Retrieve	Material Properties of Interest
Hot	Hot	Viscosity, Rheology
Hot	Cold	Viscosity, Rheology, Chemical (interactions), Mechanical
Cold	Hot	Viscosity, Rheology
Cold	Cold	Chemical (interactions), Mechanical

EXPERIMENTAL

To test sampling methods, experimental waste forms were produced from a 3/1 (by weight) ratio of salt-occluded zeolite A to borosilicate glass frit. The salt was a eutectic mixture of LiCl and KCl, containing simulated (non-radioactive) fission product salts. This mixture of powders was placed into a 500 ml stainless steel beaker. A stainless steel weight slightly smaller in diameter than the inside of the beaker and 4.5 cm thick was placed on top of the powder charge to provide some pressure to assist in consolidation. The beaker was placed into a pot furnace, heated to 915° C, and held for six hours.

Three of the potential sampling activities described in Table I have been tested so far. A hot probe - hot retrieve sampling method was devised based on a method for obtaining soil samples.⁷ In this method, the hot probe step involves removing the steel weight and inserting a thin-walled stainless steel tube into the waste form material at the end of the heat cycle while still at maximum processing temperature. The steel tube had an outside diameter of 1.9 cm, an inside diameter of 1.7 cm, with a 60° taper on the outside of one end. The outside of the tube was coated with boron nitride mold release. The hot retrieve step is removing the stainless steel tube containing a hot sample of material.

Two variations of hot probe - cold retrieve methods were attempted. The first was simply a variation of the hot probe - hot retrieve method described above, where the stainless steel tube was not removed until after the waste form had cooled. In the second method, a cavity was drilled into the underside of the stainless steel weight. This was to allow material to flow into the cavity during the heat cycle (the hot probe step). The resulting protrusion of waste form material was to be mechanically removed after the waste form had cooled and the weight was removed (the cold retrieve step).

For the cold probe - cold retrieve method, a hole 1.6 cm in diameter was drilled completely through the stainless steel weight and coated with boron nitride mold release. After the stainless steel beaker was filled with starting material and the modified weight placed on top, the hole was filled about half way with additional starting material (the cold probe step). A steel rod the same length as the thickness of the weight and slightly smaller in diameter than the hole, coated with boron nitride mold release, was then inserted into the hole. The purpose of the rod was to apply the same pressure to the potential sample as was applied to the bulk of the waste form material. When the waste form had cooled after the heat cycle, the resulting protrusion was to be mechanically removed (the cold retrieve step).

RESULTS AND DISCUSSION

The hot probe - hot retrieve sampling method using a stainless steel tube failed to produce a sample. The tube only penetrated the waste form material about a centimeter, and only with great difficulty. The tube was easily removed, but no waste form material remained in the tube. This method was abandoned after several attempts.

The hot probe - cold retrieve method using the stainless steel tube also failed to produce a sample. After cooling, the tube was adhering to the bulk waste form, but it was easily broken free. However, no waste form material was retained in the tube. A curious ring structure remained in the annular depression in the waste form left by the tube. Scanning electron microscopy with energy dispersive X-ray spectroscopy revealed that this ring structure consisted essentially of a layer of oxidized stainless steel containing remnants of the boron nitride mold release (see Figure 1). Iron and chromium were also found to have diffused about ten to twenty microns into the waste form. These results indicate that the boron nitride mold release was ineffective in preventing the steel from adhering to the waste form. Separation occurred by mechanical failure within the oxide layer that had formed on the surface of the stainless steel.

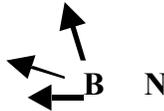


Figure 1. Back scattered electron image of the outer portion of the ring structure left behind when the stainless steel tube was removed from the waste form, showing the boron nitride and oxidized stainless steel layers.

The second hot probe - cold retrieve method using the modified weight failed to produce a useful sample. Only a small amount of material penetrated into the cavity during the heat cycle. This material broke free and remained in the cavity when the weight was removed, but was easily dislodged from the cavity. The waste form material that was retrieved was visibly more porous than the rest of the waste form, suggesting poor consolidation from lack of pressure in the immediate vicinity. The viscosity of the mixture of molten glass and salt occluded zeolite (or sodalite after the phase transition) at processing temperature is apparently too high to allow the amount of flow needed for this method.

The cold probe - cold retrieve method succeeded in producing a sample. When the modified weight was removed from the waste form, the protruding waste form material broke off from the bulk waste form, and was retained in the cavity. The sample was removed in one piece by tapping the steel rod to drive the sample out of the cavity.

In order to be useful for waste form qualification, the sample material must be representative of the bulk waste form material. Properties need not be identical, as long as differences are consistent and preferably small. Measurements of the heights of the weight and the steel rod were made before and after heat treatment to compare the consolidation of the bulk waste form and the sample. If a “consolidation factor” is defined as the ratio of the green height to the fired

height, then the bulk waste form achieved a consolidation factor of 1.83, compared to a consolidation factor of 1.77 for the sample. This suggests that the sample material did not achieve quite the fired density of the bulk waste form. Density measured by helium pycnometry (which does not measure open cell porosity) confirmed that the sample material was slightly less dense than the bulk waste form material. The bulk material had a density of 2.25 g/cm^3 , while the sample had a density of 2.17 g/cm^3 . Both the consolidation factor and the density of the sample material are only 3% less than the corresponding values measured for the bulk waste form material, which is very near the uncertainty in the measurement and therefore considered acceptable. These slight differences may be attributable to friction between the steel rod and the cavity walls that reduces the effective pressure applied to the sample material by the steel rod. If so, the small differences between the sample material and the bulk waste form material could presumably be eliminated by simply lengthening the steel rod.

X-ray powder diffraction was also performed to compare the phase composition of the sample to the phase composition of the bulk material. The results showed sodalite as the primary crystalline phase, with halite and nepheline as minor phases for both materials. This is the expected phase composition of the ceramic waste form. Most importantly, the phase compositions of the sample and bulk materials are virtually identical as shown in Figure 2.

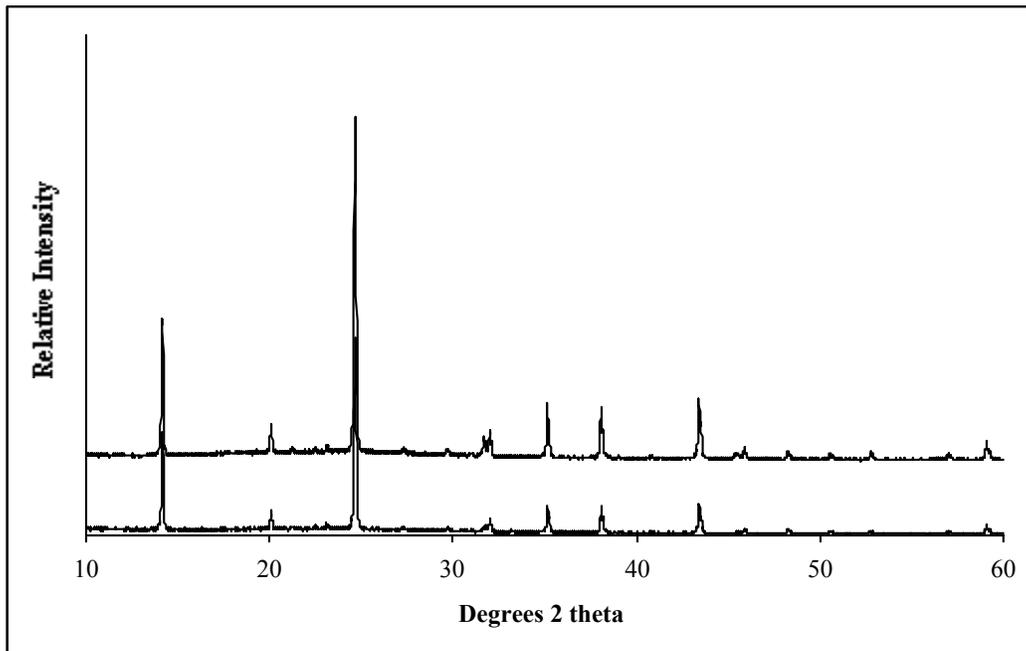


Figure 2. X-ray powder diffraction patterns of (top) bulk waste form material, and (bottom) sample material.

CONCLUSIONS

A sampling method has been demonstrated that can be used to obtain waste form qualification samples of ceramic waste form during production. The method is fairly simple, requires no large scale equipment, and should have little impact on the overall process. Samples obtained by this method are representative of the bulk material as determined by density and phase composition. Thus data obtained from such samples will be acceptable for waste form qualification and process verification.

FUTURE PLANS

Experiments with the cold probe – cold retrieve sampling method will continue in order to generate additional material for testing and characterization. The Product Consistency Test³ will be used to compare leach behavior of test material and bulk material. The use of different materials for the steel weight will also be investigated. Phase II activities will begin when full scale production equipment becomes available for testing.

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