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DISCLAIMER

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CHARACTERIZATION AND DURABILITY TESTING OF A GLASS-BONDED CERAMIC WASTE FORM

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ABSTRACT

Argonne National Laboratory is developing a glass bonded ceramic waste form for encapsulating the fission products and transuranics from the conditioning of metallic reactor fuel. This waste form is currently being scaled to the multi-kilogram size for encapsulation of actual high level waste. This paper will present characterization and durability testing of the ceramic waste form. An emphasis on results from application of glass durability tests such as the Product Consistency Test and characterization methods such as X-ray diffraction and scanning electron microscopy. The information presented is based on a suite of tests utilized for assessing product quality during scale-up and parametric testing.

INTRODUCTION

Argonne National Laboratory has developed an electrometallurgical process for conditioning nuclear spent fuel prior to emplacement into a geologic repository [1]. A demonstration of this technology is taking place using spent fuel from the Experimental Breeder Reactor II (EBR-II). This technology involves the use of a molten salt electrorefiner that separates the active fission products, i.e., Cs, Sr, Ba, Rb, the rare earth elements, and the transuranics, i.e., Pu, Np, Am, Cm, from the uranium and noble metal fission products when processing spent metallic alloy fuel. The active fission products and the transuranics remain in the salt which is a eutectic mixture of KCl and LiCl.

The salt from the electrorefiner is removed and prepared for encapsulation after the conditioning of the fuel. Contacting the electrorefiner salt at elevated temperatures with zeolite 4A enables the capture and encapsulation of the salt with the fission products into the alumino silicate framework of the zeolite [2]. The resulting zeolite is then mixed with a small amount of glass binder (25 wt%) and subjected to high pressure and temperature in a specially designed steel can [3]. This processing takes place in a Hot Isostatic Press (HIP). The typical processing conditions involve temperatures in the 973-1173 K (700-900 °C) range and pressures of 103-172 MPa (15-25 kpsi). The zeolite undergoes a phase transformation to sodalite. This process has been extensively researched and developed by the team at Argonne in Illinois[2]. The scale-up of this process has been underway for two years at Argonne in Idaho [4]. The physical and material aspects of this scale-up have been addressed in the literature [4] and will not be discussed further here. However, there is another issue that begs attention, that of devising the appropriate criteria for judging the process itself. This issue has been raised with other High Level Waste producers [5]. Argonne's process differs from that of the HLW glass producers in that the traditional HLW producer obtains their waste feedstream from the PUREX process while Argonne bypasses the reprocessing step entirely. This difference leads to a different selection of criteria to demonstrate the level of control of the process. Traditional HLW glass producers have been reliant upon the sole application of the Product Consistency Test for demonstration of their product quality; this approach is not appropriate for a multiphase ceramic waste form such as Argonne's.

This paper will address a battery of tests that could be applied to the products of the process for the ceramic waste form produced at Argonne to assess the control of the process. This battery of tests is termed Measures of Product Quality (MPQ). The purpose of MPQ are: 1) demonstrate product consistency during production for waste form qualification and 2) provide a timely but meaningful measure of the quality of the ceramic product produced during the demonstration and inventory reduction phases of the spent fuel treatment program. The information gathered may also serve some role in performance assessment area, but this is not the primary goal.

The tests or methods recommended below are not meant to be inclusive in describing all properties associated with the waste form. The MPQ are intended to provide information that is relevant and important to the processing, production and qualification of the ceramic waste form. It is with this goal in mind that the focus for the MPQ are on following properties: 1) proper consolidation of HIP cans, 2) providing corroborating evidence that the material in the HIP can experienced the appropriate processing conditions, i.e., temperature and pressure, and 3) that the final product behaves in a predictable fashion, i.e., the product is of a known and acceptable "quality". This information must be obtained in a timely fashion or it will not serve its purpose of supporting the production of the ceramic waste forms in the demonstration and inventory reduction phases of the spent fuel treatment project.

Currently, "cold" operations use a "demonstration" scale can that contains approximately 2 kg of material. The "inventory reduction" scale ceramic waste form will contain approximately 300 kg of material, and be undertaken in the near future. Thus the methods described below have some caveats in their application based on the size of the waste form produced.

EXPERIMENTAL

I. Sample Production

Hot Isostatic Press (HIP)

The HIP uses high temperatures and pressures to produce void-free ceramic waste forms for the disposal of salt from the electrorefiner. The HIP, model MIH-9, was bought commercially from ABB Autoclave (Columbus, OH). The HIP has a working cavity of 15 cm (6 inch) diameter with a 30 cm (12 inch) height. The HIP has a maximum operating temperatures of 1450 °C and a maximum operating pressure of 206 MPa (30,000 psi). The HIP is controlled using a computer controlled operator control station and uses the computer software FIX-32. The various functions of the HIP are controlled from the computer console.

The ceramic waste material discussed in this paper was prepared at Argonne. This batch used zeolite 4A powder that had 1.25% free chloride. This is considerably above the "in-house" specification for free chloride, 0.05 wt. %, however, this can was part of a greater study that will be described elsewhere. The free chloride is determined by performing a water wash on the zeolite after it is contacted with the salt at elevated temperature, 500 °C. The small quantity of water, typically 60 ml for 1 g of salt occluded zeolite is shaken with the material and then filtered. The chloride concentration is then measured using a ion selective electrode. The salt contacted zeolite (75 wt. %) was mixed with P-4N-57-P glass frit (25 wt. %) (Bayer Co., Baltimore, MD).

The initial dimensions of the HIP can was 11.43 cm in diameter by 21.1 cm in height. The cycle used for processing, started with the pressure at 2.4 MPa (350 psi). The temperature was ramped to 973 K(700 °C). Temperature and pressure were held for one hour. Pressure was ramped to 170 MPa (24500 psi) and temperature was ramped to 1123 K(850 °C). Temperature and pressure were again held for one hour. After this second hold, temperature was ramped down to 873K(600 °C). At this point, pressure started to vent and temperature continued to decrease. The final height of the HIP can was 8.7 cm while the diameter was unchanged resulting in a volume reduction of 59%.

II. Characterization and Testing

A) <u>X-ray Diffractometer (XRD)</u>

The X-ray diffractometer used is a Scintag X1 Powder X-Ray diffractometer (Scintag Inc., CA) with a theta-theta goniometer, Cu K-alpha X-Ray tube with normal focus and top loading powder sample holder.

B) <u>Scanning Electron Microscopy (SEM) with Energy Dispersive Spectroscopy (EDS)</u>

The SEM work was performed with a Zeiss DSM 960A digital scanning electron microscope. The energy dispersive detector was provided by Oxford Instruments.

C) <u>Durability Testing</u>

The samples were subjected to a crushed leaching test. This was conducted in manner consistent with ASTM C1285-94, the Product Consistency Test (PCT) [6]. The test was conducted for 7 days at 363 K (90 °C) using a surface area to volume of leachant ratio of 2000 m^{-1}. The test material was the -100 to +200 mesh size fraction. ASTM type I water was used as a leachant.

D) Density Measurements

The densities were determined using a helium pycnometer. The pycnometer (Quantochrome Co., Boynton Beach, FL) uses helium gas to obtain an accurate volume determination of an object and combines that with a known mass to determine the density.

RESULTS

The following list and supporting justifications describes our proposal for tests and methods to be used as measures of product quality. Some of these are very qualitative in nature and others are more subjective in the information they provide. In summary, there are three criteria that form the basis of the MPQ a basis to evaluate: 1) consolidation of the ceramic waste form material, 2) the extent to which the material has been processed appropriately and 3) the "quality" of the final product.

<u>Measures of Product Quality</u>

1) Density should be determined on the ceramic waste form.

This can be performed using one of two variations of a single method, helium gas pycnometry, for the demonstration sized cans. It can be performed on the entire can in a non-destructive fashion. It can also be performed on smaller samples of the ceramic material, if it is destructively analyzed. The value obtained for the entire canned product will not be a "true" density. However, it is a value that can be measured routinely for both "cold" and "hot" products and can be used as a measure for the degree of consolidation, i.e., it is a relative measure. The density of a small sample of the ceramic waste form can be obtained for all HIP products that are destructively analyzed for both "cold" and "hot" products. These measurements can be accomplished using one of two chambers for the helium gas pycnometer that are remotely operated within a hot cell. A typical density obtained for sample of the ceramic waste form is 2.40 g/cm^3.

2) The phases present in the final product should be determined and quantified, as much as possible.

This will be performed using several methods, XRD, SEM, and TEM. The application of these techniques is dependent upon a destructive sampling of the respective HIP can. For fully "hot" cans the application of XRD methodology may be problematic. Sample preparation for SEM and TEM samples will be more time consuming but faces no overwhelming hurdles for "hot" products. These techniques will yield information on the type of phases present and the microstructure of the ceramic waste form product.

Our current demonstration scale product is featured in Figures 1 and 2. The XRD pattern in Fig. 1 shows a major sodalite phase with very minor halite (NaCl) and nepheline phases present also. The largest reflection extends beyond the bounds of the plot, as noted.

Figure 2 features a backscattered electron SEM micrograph of material from the same HIP can as that displayed in Fig. 1. Three phases are commonly observed in the ceramic waste form: sodalite, glass and a rare earth oxide or oxychloride or some combination of the two. These are identified in Fig. 2. The exact stiochiometry of the typical rare earth phase observed varies in oxygen content, chloride content and the mixture of rare earth cations present. The remainder of the surrogate fission products present in the salt are dispersed within the sodalite phase. The rare earths tend to react the small amount of residual moisture present in the zeolite 4A precursor and form rare earth oxychlorides during the salt contacting step and then are converted to oxides, at least partially, when processed in the HIP.

3) The "quality" of the product should be assessed via a durability test.

A short term test of 7 days duration using a crushed sample in a water leachant at 90 C using a surface area to volume of leachant ratio of 2000 m-1 should be effective as a measure of the behavior of the waste form. There are of course a variety of tests that could be conducted of differing durations, leachants, temperatures and surface/area to volume of leachant ratios, however, this test should be of reasonable length and applicability in a hot cell setting. The standard Product Consistency Test (PCT), ASTM C1285-94 [6], is very appropriate in application here. The purpose of conducting a durability test of this nature is to evaluate the consistency of the product in a manner that is somewhat more quantitative than SEM, XRD or density. A static leach test performed on a crushed sample provides such a means. The normalized leach rates obtained from this test will be used in a comparison to baseline basis. SEM work has shown that no sorting of phases occurs during the preparation of the -100 to +200 mesh size fraction. The phases involved are very much smaller than the typical particles used for the PCT. Typical release rates for salt constituents and matrix elements will be presented during the paper presentation. In brief, they are equivalent or better than those normalized release rates stated as criteria for HLW glass.

In summary, the table below contains the recommendations for the measures of product quality to be applied to ceramic waste form samples.

Table I. Tests and techniques to be applied to ceramic waste samples as a measures of product quality.

Test or Technique	Information to obtained
1) Density	the degree of consolidation
2) XRD	the phases formed and direct feed-back to proper processing conditions
3) SEM	microstructure and phases composition data
4) TEM	microstructure and phase composition data
5) 7 day crushed sample Durability Test	a relative performance measure

This recommendation is based on our experience of characterizing over 60 demonstration scale HIP products. We feel that it provides a balance between timely turn around of process knowledge and a comprehensive understanding of each and every ceramic waste form produced. In one case the information is obtained quickly, but may be incomplete whereas in the second case the knowledge level is relatively complete but the turn around time renders the knowledge to be worthless to the process engineer.

A special note is appropriate here. In the inventory reduction phase of the spent fuel treatment process we are recommending the use of statistical sampling to provide material for testing as prescribed above. The development of a predictive model for properties such as density and durability would aid tremendously in the application of a statistical sampling regimen. The phase composition of the ceramic waste form should be adequately predicted via strict control and characterization of the feed streams and the process parameters.

A further recommendation that could be of tremendous use during the inventory reduction phase of the project is the application of "witness" tubes. These would be small tubes of material identical to that used to fill the HIP cans and that would be HIPed simultaneously with the larger cans. Initially, these would be analyzed along with the larger cans; this would occur during the cold start-up of the larger HIP. During this time the correlation between can and tube would be established so that by analyzing the smaller "witness" tubes the material in the larger cans would be fit within a known and acceptable compositional envelope. Such a program is currently under development at Argonne now.

CONCLUSIONS

This paper recommends a battery of tests and methods for application to the high level waste form under development at Argonne National Laboratory. Several examples of typical results obtained on "cold" ceramic waste forms applying these criteria are included. This series of tests can be applied to both "cold" and "hot" waste forms that will be generated in the course of qualifying the waste form production process. A recommendation for the application of small "witness" samples has also been made for use when the larger and more unwieldy inventory reduction phase of the production ensues. These witness samples will enable the systematic analysis of the production of the inventory reduction sized ceramic waste forms in an efficient manner and with minimal waste.

This recommendation should not be viewed as a complete solution to the issue of proof of process control, this is best obtained by strict input process stream control and characterization. However, these measures of product quality should be thought of as a complementary tool for proving control of the process.

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REFERENCES

[1] Prog. Nucl. Energy, **31** (1997).

[2] Lewis, M. A., Hash, M., Glandoff, D., "Effect of Different Glass and Zeolite A Compositions on the Leach Resistance of Ceramic Waste Forms", *Scientific Basis for Waste Management XX*, W. Gray and I. Triay, ed., MRS, Pittsburgh, vol. **465**, 433-440, (1997).

[3] Goff, K. M., Simpson, M. F., Johnson, S. G., Bateman, K. J., Battisti, T. J., Frank, S. M., paper contributed to the ANS topical conference on Spent Fuel, Charleston, SC (1998).

[4] Goff, K. M., Benedict, R. W., Bateman, K., Lewis, M. A., Periera, C., Musick, C. A., "Spent Fuel Treatment and Mineral Waste Form Development at Argonne National Laboratory-West", *Spectrum '96*, ANS, La Grange, IL, 2436-2443, (1996).

[5] Bibler, N. E. and Bates, J. K., "Product Consistency Leach Tests of Savannah River Site Radioactive Waste Glasses", *Scientific Basis for Waste Management XIII*, V. Oversby and P. W. Brown, ed., MRS, Pittsburgh, vol. **173**, 327-338, (1990).

[6] ASTM C1285-94, ASTM, Philadelphia (1995).

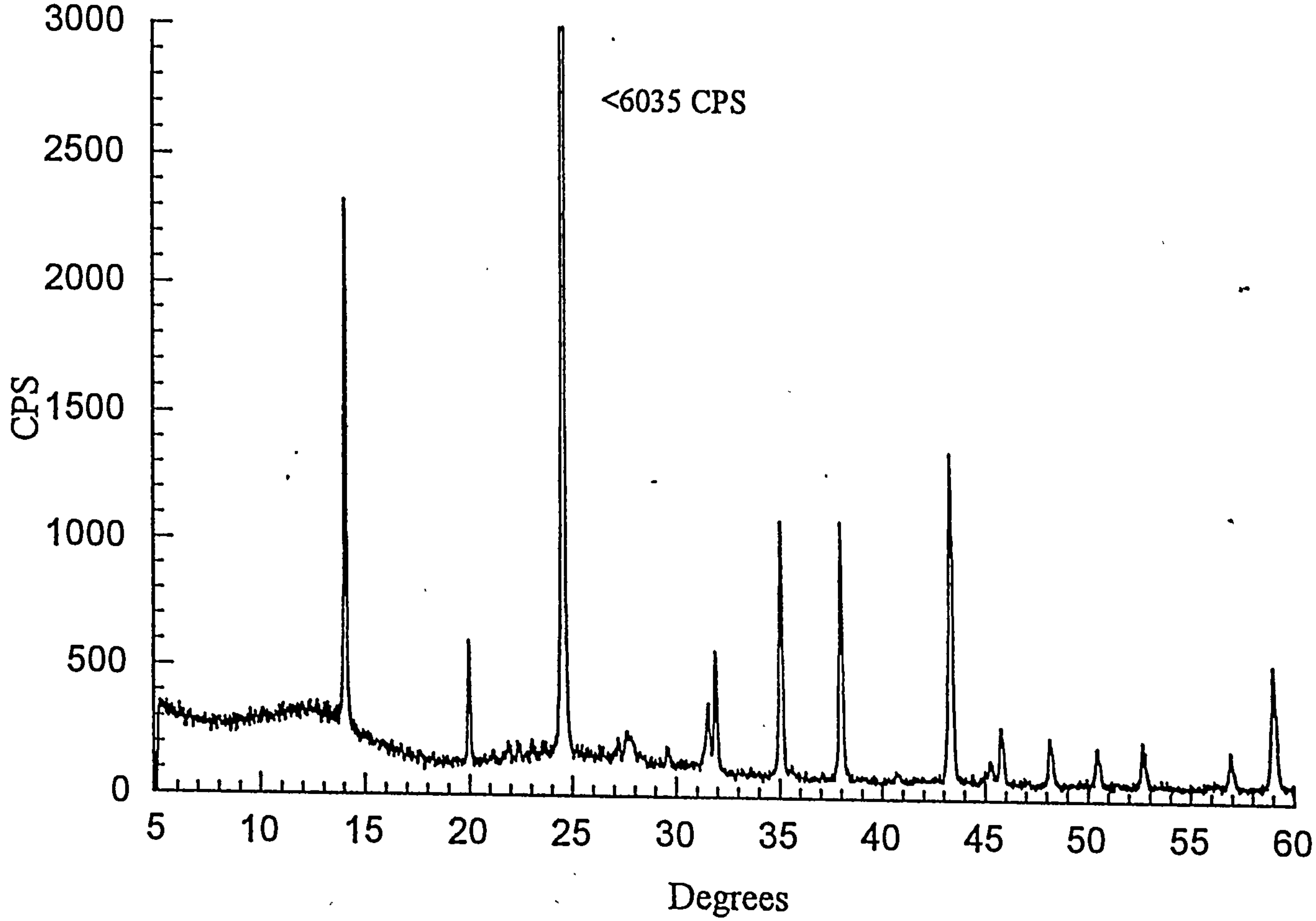

Figure 1. XRD pattern for a typical ceramic waste form product. The major phase is sodalite ($Na_6Al_6Si_6O_{24}\cdot 2NaCl$). Two minor phases are also observed: nepheline ($NaAlSiO_4$) and halite ($NaCl$).

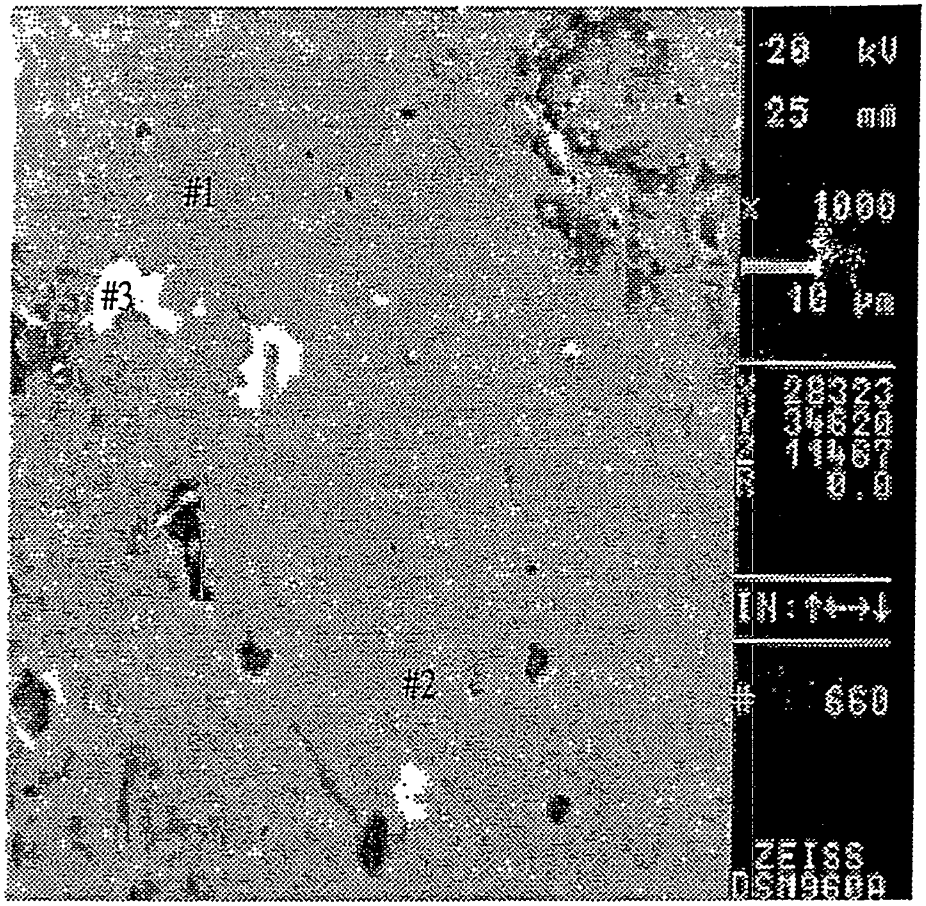

Figure 2. Back scattered SEM micrograph of a the same product featured in the Fig. 1. The major phases, #1 (Sodalite), #2 (Glass) and #3 (Rare earth oxide or oxychloride), are identified.