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American Ceramic Society
101st Annual Meeting
Symposium: Waste Management Science and Technology in the Ceramic and Nuclear
Industries

Indianapolis, Indiana
April 25 - April 30, 1999

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PLUTONIUM AND SURROGATE FISSION PRODUCTS IN A COMPOSITE CERAMIC WASTE FORM

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ABSTRACT

Argonne National Laboratory is developing a ceramic waste form to immobilize salt containing fission products and transuranic elements. Preliminary results have been presented for ceramic waste forms containing surrogate fission products such as cesium and the lanthanides.¹ In this work, results from scanning electron microscopy/energy dispersive spectroscopy and x-ray diffraction are presented in greater detail for ceramic waste forms containing surrogate fission products. Additionally, results for waste forms containing plutonium and surrogate fission products are presented. Most of the surrogate fission products appear to be silicates or aluminosilicates whereas the plutonium is usually found in an oxide form. There is also evidence for the presence of plutonium within the sodalite phase although the chemical speciation of the plutonium is not known.

INTRODUCTION

Argonne National Laboratory is developing an electrometallurgical process for the treatment of metallic spent nuclear fuel to condition the material for disposal in a geologic repository. In this process, sectioned spent fuel elements are lowered in a steel basket into a molten salt electrolyte and anodically dissolved from the cladding. Pure uranium is deposited on steel cathodes while the transuranic elements and fission products remain in the salt or with the cladding hulls. The transuranic elements and active fission products are left in the salt to be incorporated into a ceramic waste form. A metal waste form incorporates the fission products that are "noble" to the process and remain with the cladding hulls.

PRODUCTION OF THE CERAMIC WASTE FORM

The ceramic waste forms described in this study, which are being used to demonstrate electrometallurgical technology, incorporate a eutectic salt that contains surrogate fission products or surrogate fission products and plutonium. For the waste form containing solely surrogate fission products, the surrogate fission product salt constitutes 0.7 wt% of the waste form and were introduced as these chemical forms: KBr, RbCl, SrCl₂, YCl₃, KI, CsCl, BaCl₂, LaCl₃, CeCl₃, PrCl₃, NdCl₃, SmCl₃, and EuCl₃.² For the plutonium-bearing waste form with the same surrogate fission product salt loading, PuCl₃ is 4.5 wt% of the waste form. The relative isotopic amounts of plutonium are 82% ²³⁸Pu and 18% ²³⁹Pu. The ²³⁸Pu was used in order to conduct an alpha damage study currently underway. The exact content of the fission products and transuranic elements in the ceramic waste when the facility is in production will vary; however, the plutonium concentration will be 0.2-1.0 wt%.

To produce the ceramic waste form, dried zeolite 4A is blended with salt to obtain an average salt loading of 10.3 wt%. The salt-loaded zeolite is then mixed with glass so that the weight ratio of salt-loaded zeolite to glass is 75:25. This mixture was hot isostatically pressed at 1123K and 170 MPa for the ceramic waste form containing surrogate fission products.³ For the ceramic waste form containing surrogate fission products and plutonium, the mixture was hot uniaxially pressed at 1023K and 35 MPa. Under these aggressive processing conditions, the zeolite 4A transforms *in situ* to sodalite.

EXPERIMENTAL

X-ray diffraction was done on a Scintag X1 diffractometer, which has a theta-theta goniometer configuration and utilizes Cu-K_α x-rays. Pattern search routines were performed using DMSNT software from Scintag, Inc. (Cupertino, CA). To determine differences in lattice parameters in sodalite, LaB₆ (NIST SRM 660) was added as an internal standard for peak positioning and GSAS⁴ was used to refine the lattice parameter.

Scanning electron microscopy was done with a Zeiss DSM 960A scanning electron microscope (Thornwood, NY). Energy dispersive x-ray spectroscopy and wavelength dispersive spectroscopy (WDS) were done by interfacing the detectors and instrumentation of the microscope to an Oxford ISIS series 300 x-ray analysis system, software version 3.2 (Oxford, UK).

PRIMARY CRYSTALLINE PHASES IN THE CERAMIC WASTE FORM

X-ray diffraction patterns of ceramic waste forms containing either surrogate fission products or plutonium are shown in Figures 1 and 2, respectively. Phases observed in both these patterns are sodalite (major) and halite (minor). In the

pattern for the plutonium-bearing waste form, additional peaks result from the added LaB_6 standard and from the plutonium oxide present in the waste form.

Lattice parameters determined for the sodalite phase in these waste forms are similar. The edge of the cubic sodalite unit cell is about 8.856 \AA for the plutonium-bearing waste form and 8.837 \AA for the waste form containing only surrogate fission products. For comparison, the edge of the cubic unit cell is 9.253 \AA for $\text{K}_8(\text{Al}_6\text{Si}_6\text{O}_{24})\text{Cl}_2$, 8.881 \AA for $\text{Na}_8(\text{Al}_6\text{Si}_6\text{O}_{24})\text{Cl}_2$, and 8.447 \AA for $\text{Li}_8(\text{Al}_6\text{Si}_6\text{O}_{24})\text{Cl}_2$ at 20°C .⁵ The predominate cation in the sodalite phase for these waste forms is sodium so it is not surprising that the lattice parameters obtained were closest to that of $\text{Na}_8(\text{Al}_6\text{Si}_6\text{O}_{24})\text{Cl}_2$. More details on the sodalite structure may be found in the literature.^{6,7}

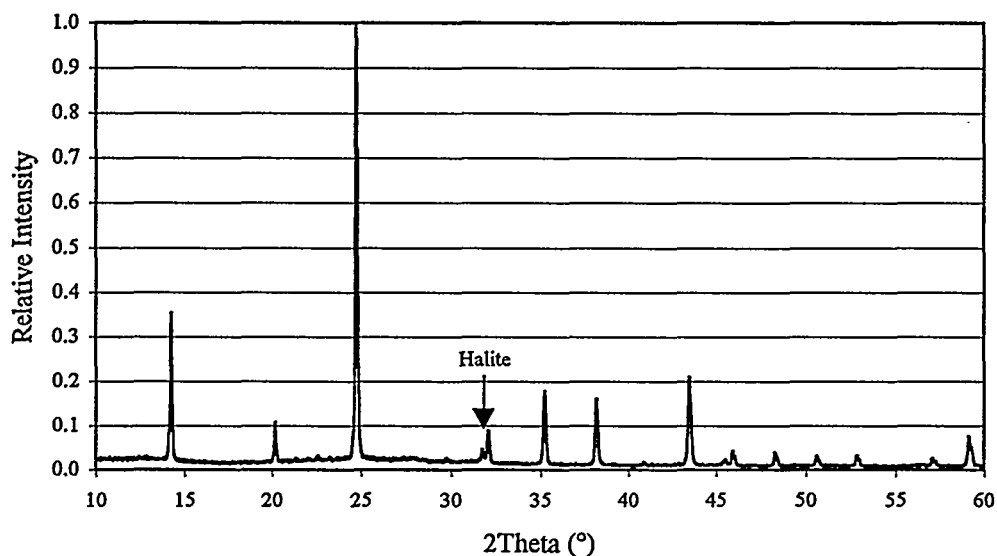


Figure 1. XRD pattern of the ceramic waste form containing surrogate fission products. All peaks attributed to sodalite unless otherwise indicated.

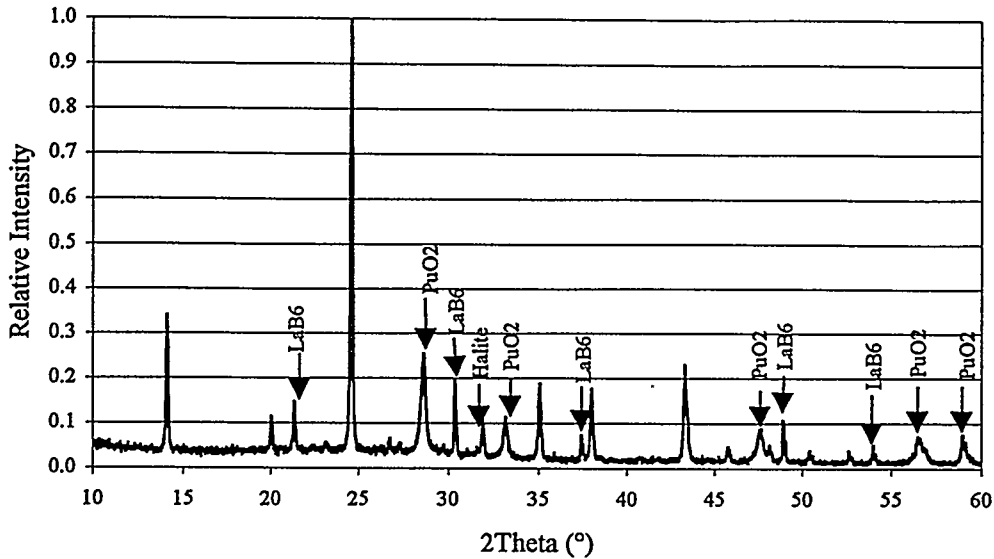


Figure 2. XRD pattern of a ceramic waste form containing plutonium and surrogate fission products. All peaks attributed to sodalite unless otherwise indicated.

MICROSTRUCTURE OF THE CERAMIC WASTE FORM

The ceramic waste form containing only surrogate fission products consists of aluminosilicate-rich grains surrounded by a silica-rich intergranular phase as shown in Figure 3. The aluminosilicate-rich grains, presumably sodalite, are usually a few microns to 10 μm in size. The silica-rich or "glassy" phases typically range from submicron to a few microns in size. Porosity concentrates along the intergranular glassy phase and consists of pores sub-micron to a few microns in size. Halite inclusions, which are often circular and range from submicron to several microns in size, are distributed throughout but tend to concentrate in the silica-rich phase. Most of the surrogate fission products are believed to be uniformly distributed in the samples. Rare earth inclusions, including Ce and Sm, are usually aluminosilicates or silicates as for the waste form containing only surrogates. These observations agree with those from transmission electron microscopy/electron diffraction (TEM/ED) results.⁸

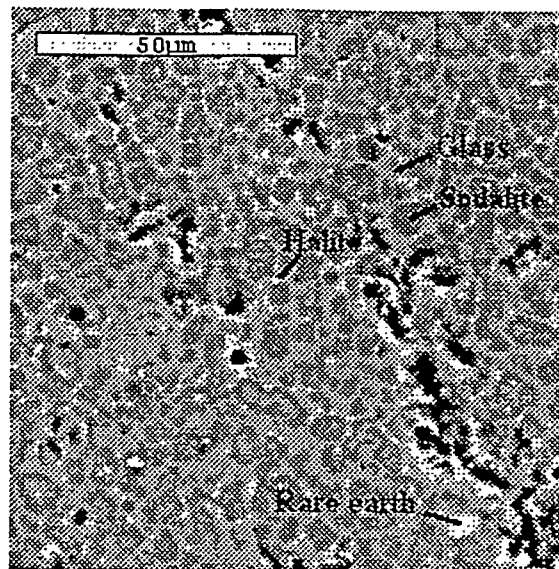


Figure 3. Backscatter electron image of a ceramic waste form containing surrogate fission products.

The microstructure of the plutonium-bearing waste form is similar to that for ceramic waste forms containing only surrogate fission products. A backscatter electron image of this waste form is given in Figure 4. Though rare earth phases usually are aluminosilicates or silicates as for the other waste form, cerium was also found as an oxide. Plutonium is frequently found as small plutonium oxide inclusions along the intergranular glassy phase. Occasionally, there are inclusions containing plutonium with a similar composition to sodalite. These inclusions may be sodalite or other aluminosilicate structures incorporating plutonium. An aluminosilicate phase containing plutonium has been made observed during TEM/ED analyses but no sodalite with plutonium has been found.⁸ The aluminosilicate phase, which is not sodalite, is not observed in x-ray diffraction patterns. Using WDS, low concentrations of plutonium were detected throughout the sodalite and glassy phases. This plutonium may possibly be small inclusions of plutonium oxide embedded in the phases or actually incorporated into the sodalite or glassy phases.

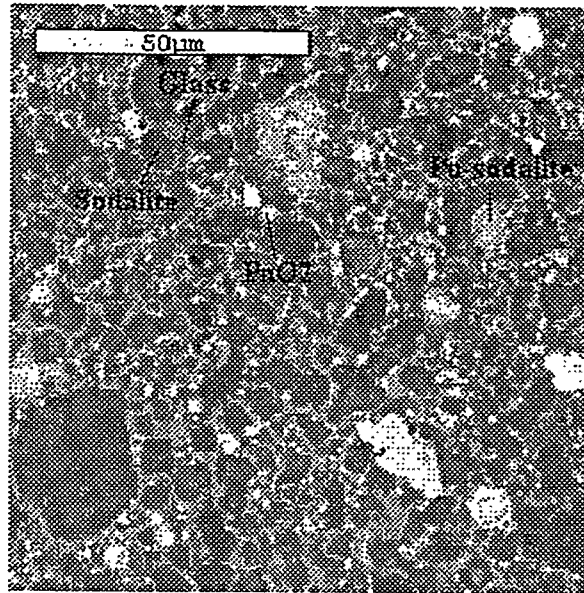


Figure 4. Backscatter electron image of ceramic waste form containing plutonium and surrogate fission products.

SUMMARY AND CONCLUSIONS

The ceramic waste form primarily consists of small sodalite grains surrounded by an intergranular glassy phase. Halite, a minor phase, is usually found as small, circular inclusions that tend to concentrate within the intergranular glassy phase. Most of the surrogate fission products are believed to be uniformly distributed throughout the waste form. Rare earth inclusions, which were large enough for semi-quantitative elemental analyses, were often in the form of aluminosilicates or silicates. One rare earth inclusion containing cerium was observed as an oxide. Plutonium frequently formed oxides that tended to concentrate along the intergranular phase. Some of the plutonium was incorporated in sodalite or other aluminosilicate phase, but no conclusions can be drawn from EDS/WDS analyses on the crystalline structure of this phase. However, TEM/ED results do confirm the presence of an aluminosilicate phase, which incorporates the plutonium but is not sodalite.⁸ The remainder of the plutonium is found in low concentrations throughout the sodalite and glassy phases. The chemical form of this plutonium is unknown but is believed to be an oxide.

The ceramic waste form containing plutonium is not dramatically different from the ceramic waste form containing only surrogate fission products. The only significant difference was additional plutonium phases (oxide and aluminosilicate). There may be slight modifications in the sodalite structure, as evidenced by a slight difference in lattice parameters. These structural changes

might be explained by a change in salt loading or the presence of plutonium oxide in the sodalite unit cell, though no conclusion has been reached.

Although cerium and samarium are typical surrogates for plutonium^{9,10}, this is not applicable in the case of the ceramic waste form. Though these elements were found as aluminosilicates and oxides, the predominate forms of cerium and samarium were not the same as plutonium. Cerium and samarium were most frequently found as aluminosilicates or silicates whereas plutonium was usually in the form of an oxide.

ACKNOWLEDGEMENTS

Argonne National Laboratory is operated for the US Department of Energy by the University of Chicago. This work was supported by the Department of Energy, Nuclear Energy Research and Development Program, under contract no. W-31-109-ENG-38. Special thanks to M. Simpson and K. Bateman for producing the waste forms and processing information.

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