

# **Distribution and Solubility of Radionuclides and Neutron Absorbers in Waste Forms for Disposition of Plutonium Ash and Scraps, Excess Plutonium, and Miscellaneous Spent Nuclear Fuels<sup>(a)</sup>**

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(a) This title has been shortened from that of the proposal for brevity and clarity.

## Research Objective

Successful immobilization of actinides (Am, Cm, Th, Pu, Np, etc.) in crystalline and amorphous host matrixes with appropriate neutron absorbers (B, Hf, Gd, etc.) requires sound scientific knowledge of the local chemical environments of both the actinides (An) and the neutron absorbers and their interaction with the host matrixes. This understanding leads to a more systematic and efficient approach to predicting solubilities than the strictly empirical approach now used. The goals of this ongoing research are to determine solubility limits of representative actinides (Pu and U) and neutron absorbers (Hf and Gd) in crystalline and amorphous matrixes and to determine solution mechanisms of these species in the two types of systems. Actinides and neutron absorbers in amorphous systems have been studied at PNNL in collaboration with LBNL and University of Michigan and in crystalline systems at ANSTO. We believe that we are in a position to understand the chemical systematics of silicate melts so that the solubility of actinides, neutron absorbers, and, we would suggest, other metal species in glass no longer must be determined empirically but can be calculated from a set of equilibrium constants in a fashion similar to aqueous systems.

## Research Progress

For the first time, to the best of our knowledge, we have demonstrated in amorphous systems that at least 14.7 mol% Pu(III) plus 4.2 mol% Gd(III) is soluble in an alkali boro-aluminosilicate glass under reducing conditions. Under oxidizing conditions, considerably less Pu(IV) is soluble. X-ray absorption fine structure (XAFS) analyses of these glasses, performed at LBL, confirm that Pu(III) is a dominant species in the reduced glass and Pu(IV) in the oxidized glass.

The solution behavior of lanthanides [Ln(III)]: Ln = Gd, La, and Nd) in a variety of Na<sub>2</sub>O-Al<sub>2</sub>O<sub>3</sub>-B<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> glasses was studied with a host of complementary analytical techniques. Results from experiments with the lanthanides Gd, Nd, and La suggest that their behavior in the glass melt is similar. The solution behavior of Ln in these glasses was determined by the ratio of excess Na<sub>2</sub>O or excess Al<sub>2</sub>O<sub>3</sub>-to-B<sub>2</sub>O<sub>3</sub> in the melt.

In peralkaline melts (Na<sub>2</sub>O>Al<sub>2</sub>O<sub>3</sub>), when the ratio of excess Na<sub>2</sub>O (i.e., moles of Na<sub>2</sub>O less the moles of Al<sub>2</sub>O<sub>3</sub>) to B<sub>2</sub>O<sub>3</sub> is greater than 0.5, the compound Na<sub>x</sub>Ln<sub>9.33-0.33x</sub>Si<sub>6</sub>O<sub>26</sub> (0<x<1) precipitates from the melt at the Ln<sub>2</sub>O<sub>3</sub> solubility limit. The Ln<sub>2</sub>O<sub>3</sub> solubility in these glasses is determined by the concentration of each glass former. From the ultraviolet-visible (UV-Vis) and fluorescence spectroscopy results, lanthanides appear to dissolve uniformly at low concentrations in these glasses. When the B/Ln ratio is ≥3, intermediate range-ordered Ln-borate structural groups appear to form in clusters about 5 nm in diameter. The electron energy loss fine structure (ELFS) results suggest that the structure of these Ln-borate groups resembles lanthanide metaborate crystals. When B/Ln is less than 3, Ln appeared to partition among boron-rich and silicon-rich domains, forming different types of intermediate-ordered structural groups. The configuration of these groups has yet to be determined.

When the ratio of excess  $\text{Na}_2\text{O}$  to  $\text{B}_2\text{O}_3$  is less than 0.5 in these glasses, liquid-liquid phase separation occurs above the  $\text{Ln}_2\text{O}_3$  solubility limit with one phase rich in Ln and B. The  $\text{Ln}_2\text{O}_3$  solubility appears to be determined by the excess  $\text{Na}_2\text{O}$ . In these glasses, the borate and silicate portions are not well mixed. Phonon side band spectroscopy results suggest that Ln is incorporated into the borate portion of the melt in a double chain structure similar to that in lanthanide metaborate. The Ln behavior in peraluminous melts (moles of  $\text{Al}_2\text{O}_3 > \text{Na}_2\text{O}$ ) is similar to the behavior in peralkaline melts. When the excess  $\text{Al}_2\text{O}_3/\text{B}_2\text{O}_3 < 0.4$ , phase separation occurs at the solubility limit of  $\text{Ln}_2\text{O}_3$  with one phase rich in Ln and B. When the excess  $\text{Al}_2\text{O}_3/\text{B}_2\text{O}_3$  is greater than 0.4,  $\text{Na}_x\text{Ln}_{9.33-0.33x}\text{Si}_6\text{O}_{26}$  precipitates above the  $\text{Ln}_2\text{O}_3$  solubility limit.

Based on the assumption that the Pu(III) and Ln(III) solution behaviors are similar in these glasses, we anticipate that Pu(III) dissolves in glass in much the same way as Ln(III). Above Ln solubility in some glasses,  $\text{Na}_x\text{Ln}_{9.33-0.33x}\text{Si}_6\text{O}_{26}$  crystallizes from the melt. If this crystal accommodates significant quantities of Pu(III), the resulting glass ceramic could also be an acceptable waste form.

In contrast to the Gd results, at all concentrations up to the solubility limit, XAFS results indicate that Hf(IV) dissolves in these glass melts as  $(\text{HfO}_6)$ , octahedrally coordinated species in peralkaline glasses and less-than-octahedral in peraluminous glasses without clustering (Hf-O-Hf bonds). In our glasses,  $\text{HfO}_2$  solubility is observed to reach a minimum for glasses in which the molar concentrations of Na and Al are equal. Limited increases in  $\text{Al}_2\text{O}_3$  result in glasses (peraluminous) with slightly increased Hf solubility. Further increases in  $\text{Al}_2\text{O}_3$  result in glasses that can no longer be melted at  $1550^\circ\text{C}$ . When the  $\text{Na}_2\text{O}$ -to- $\text{Al}_2\text{O}_3$  ratio is greater than 1 (peralkaline glasses), there is an increase in the  $\text{HfO}_2$  solubility with an apparent increase in the  $\text{Na}_2\text{O}$  content. Results from XAFS suggest that the local structure around Hf is silicate-like for peralkaline glasses and siloxane-like for peraluminous glasses (i.e., the local structure is different for the two glass types). A comparison between the coordination environments of Pu(IV) and Hf(IV) is under way. The anticipated results from this study may suggest that An(IV) dissolves in these glass melts as monomeric species.

Compositional effects on  $\text{HfO}_2$  solubility are being studied extensively in these glasses. We have been able to model the  $\text{HfO}_2$  solubility in these glasses with a rule-of-mixtures approach using the measured  $\text{HfO}_2$  solubility in rudimentary compositions such as amorphous analogs of sodium disilicate, sodium diborate, albite, and reedmergnerite. From such a modeling approach, we find that the highest  $\text{HfO}_2$  solubility occurs in glasses containing the highest concentration of “ $\text{NaBO}_2$ ” stoichiometric units, perhaps indicating that the chemistry of Na and B in the silicate melt is the determining factor for  $\text{HfO}_2$ , and perhaps An(IV), solubility.

For the candidate ceramic host matrixes, substitution of Pu, U, Hf, and Gd in the host structures is now quantified and broadly understood in terms of the standard rule that the closer the sizes (~15% difference) of the guest and host ions, the higher is the solubility of the guest ions. In the current study, solid solubility limits, in formula units (f.u.) of U, Pu, Hf, and Gd, have been measured for single actinides and neutron absorbers. The matrixes were zircon ( $\text{ZrSiO}_4$ ), monazite ( $\text{CePO}_4$ ), titanite ( $\text{CaTiSiO}_5$ ), perovskite ( $\text{CaTiO}_3$ ), and apatite

(Ca<sub>10</sub>(PO<sub>4</sub>)<sub>6</sub>O). In almost all cases, these limits were not known before this study. Uranium (IV) is highly soluble in apatite achieving 0.5 f.u., while 8 f.u. of Gd is soluble. However, very limited solubility was found for Hf (< 0.1 f.u.). Titanite was observed to accommodate 0.02 f.u. of U(IV) and 0.02 f.u. of Pu(IV), both of which substitute for Ca. At solubility, UO<sub>2</sub> or PuO<sub>2</sub> form. Under reducing conditions, a higher solubility of Pu (0.05 f.u.) as Pu(III) was determined. The use of an argon atmosphere rather than air during sintering of these materials presumably causes Pu(III) to form instead of Pu(IV). Relatively large accommodations of neutron absorbers were observed in titanite, 0.3 f.u. of Gd in the Ca site and 0.5 f.u. of Hf in the Ti site. Plutonium has high solubility in monazite as Pu(IV) at up to 1 f.u. (at firing temperatures of < 800°C) and Pu(III) at 1 f.u., although there is almost no solubility for Hf (<0.01 f.u.). Perovskite accommodates high concentrations of the neutron absorbers Gd or Hf at 1 f.u. and Pu(III) at 1 f.u., but limited amounts of Pu(IV) (0.13 f.u.) and U(IV) (~0.1 f.u.). Previous studies showed that actinides and neutron absorber solubilities are high in zirconolite, 0.7 f.u. for U(IV) and Pu(IV) and 1.4 and 1 f.u. for Gd and Hf, respectively. In pyrochlore, the solubilities were known from previous studies to be 1, 2, 1, 2 and 0.3 f.u. for U(IV), Pu(III), Pu(IV), Gd, and Hf, respectively.

Using the new insight into the Pu, Gd, and Hf behavior in crystalline materials and glass melts, we have identified optimum formulations to incorporate the maximum amount of Pu. Studies are under way to validate these predictions. For crystalline materials, site substitution and charge compensation mechanisms of the actinides and neutron absorbers will be studied further. Interactive effects of actinide and neutron absorbers on their solubilities in both glasses and ceramics will be studied. In particular for glasses, we feel this approach can be extended to other metal species with the ultimate goal to develop a comprehensive model for silicate melts and glasses in which chemical systematics are well defined.