

**FINAL REPORT**  
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**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**

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## **Executive Summary**

The initial goal of this project was to investigate the solubility of radionuclides in glass and other potential waste forms for the purpose of increasing the waste loading in glass and ceramic waste forms. About one year into the project, the project decided to focus on two potential waste forms – glass at PNNL and titanate ceramics at the Australian Nuclear Science and Technology Organisation (ANSTO). The work performed at ANSTO has been reported separately.

At PNNL, work centered on a series of glasses with the basic elements that comprise nuclear waste glasses—silicon dioxide, boron oxide, sodium oxide, and aluminum oxide. Initially, gadolinium oxide and hafnium oxide were used as stand-in elements for plutonium oxide. It was generally understood that these elements would behave similar to the two most likely forms of plutonium oxide—the three and four oxidation states. The results with these elements would be confirmed with plutonium oxide, albeit with a fewer number of glass compositions. This reduced the cost while yielding a large amount of results.

As a result of these studies, a new understanding of the glass state was developed to the rudimentary stage. It was determined that for gadolinium, the amount of free boron and free sodium in the glass melt determined the solubility of gadolinium oxide in the glass. Depending on glass composition, gadolinium oxide “dissolved” in the glass melt by association with boron-rich areas of the glass. Various spectroscopic methods were used to show how the gadolinium was distributed in the glass upon solidification.

Hafnium offered a less tractable challenge. Because of its nature, very few spectroscopic techniques could be used to determine its behavior in the glasses. However, the available techniques yielded results that suggested that the behavior of hafnium is different than gadolinium—much different. In the case of

hafnium, the hafnium oxide appears to be associated with the silica lattice rather than the boron-rich areas.

This suggests that the two chemical forms of plutonium behave much different in glasses. For example, at low sodium, essentially no hafnium oxide could be incorporated into the glasses. At low sodium, additions of gadolinium oxide resulted in high melting glasses with precipitates. Adding additional gadolinium oxide to the mix eventually yielded clear glasses. Therefore, it is anticipated that the +3 oxidation state of plutonium is more soluble than the +4 oxidation state. Preliminary data suggest this to be the case.

Actual work with plutonium was to start in the third year of the project. We began the process of obtaining the plutonium in the forth quarter of the second year. It took one year to obtain the necessary plutonium. This left little time to perform any experiments. We prepared about ten glasses. We used our models based on our results with gadolinium and hafnium to calculate the expected solubility limits for the plutonium oxide. We were in the process of characterizing one of these samples when the analyst inadvertently touched the glass specimen with the microscope lens. The amount of plutonium released was small, weighing approximately 1 microgram. The resulting effort to remove the contamination from the laboratory consumed the remaining funds, and the characterization was never completed. Fortunately, the personnel in the laboratory at the time did not receive any plutonium internally or externally.

In the course of analyzing the data from the gadolinium oxide and hafnium oxide-containing glasses, a model for the solubility of these oxides in glasses was developed. At the time the project ended, the model was being generalized so that it would be applicable to other metal oxides. This was the subject of a proposal for additional EMSP funds to continue the development, but this was an unsuccessful attempt. Had this proposal been funded, we feel certain that the model would allow us to put glass development on

a sound scientific basis so that the composition of glasses could be calculated for specific wastes rather than use the existing empirical approach.

Sufficient results were obtained during this study to indicate it is possible to reduce the amount of effort needed to develop glasses for the immobilization of DOE waste materials. This effort is mainly empirical; having a more scientifically based approach would enable glass developers to determine the optimum glass composition for a given set of desired properties. This would significantly reduce the amount of funds needed to develop glasses for special waste streams or optimized glass compositions for the immobilization of existing waste streams.

## Research Objectives

The objective of this multi-institutional research effort was to understand how radionuclides, neutron absorbers, and other waste species are incorporated into single-phase amorphous matrices and ceramics. This was to provide DOE with a methodology to develop glasses and ceramics with optimum concentrations of radionuclides, neutron absorbers, and other waste components and with optimum glass properties. This effort would replace the largely empirical approach currently used in the DOE system for the development of glasses and ceramics for waste management.

## Methods and Results

We successfully determined the solubility behavior of hafnium, gadolinium, and other lanthanides in sodium boro-aluminosilicate glasses. Sufficient information was gathered with glasses containing hafnium and/or gadolinium that a semi-empirical model was developed.

Throughout our Environmental Management Science Program (EMSP) project, actinides and neutron absorbers in amorphous systems were studied at Pacific Northwest National Laboratory (PNNL) in collaboration with Lawrence Berkeley National Laboratory (LBNL) and the University of Michigan and in crystalline systems at the Australian Nuclear Science and Technology Organisation (ANSTO). The contributions from the ANSTO team have been reported separately (Vance et al. 2001).

Under one segment of our current EMSP program, we have demonstrated for the first time, to the best of our knowledge, that at least 14.7 mol% plutonium, as predominantly Pu(III), plus 4.2 mol% Gd(III) is soluble in an alkali boro-aluminosilicate base glass under reducing melt conditions. Under oxidizing melt conditions, considerably less plutonium, as predominantly Pu(IV), was soluble in the base glass. Results from X-ray absorption fine structure (XAFS) analyses of these plutonium-containing base glasses confirmed that Pu(III) is a dominant species in the glass produced under reducing conditions, and Pu(IV) in the glass produced under oxidizing. These results are consistent with initial assumptions by many authors that the Pu(III) is typically more soluble in oxide glasses than Pu(IV). The effect of plutonium redox on its solubility (Feng et al. 1999) is shown to be comparable to that found for cerium in similar borosilicate glasses (Li et al. 1997), although, as will be addressed below, there is a significant difference in redox potential between plutonium and cerium.

While waiting for delivery of plutonium<sup>(a)</sup>, we extensively studied the incorporation of neutron absorbers in glass. Previous work (Li et al. 1997; Darab et al. 1998) in which cerium was used as a potential surrogate for plutonium also indicated that Ce(III) was typically more soluble than Ce(IV) in similar glass compositions. Although these solubility results reinforce the belief that cerium was a reasonable surrogate for plutonium, melt-redox comparisons (Darab et al. 1997) provided a different picture. Both cerium and plutonium occurred in the +3 or +4

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(a) It took over a year and a half to obtain Pu from the Hanford Site. Work on an extensive matrix of glasses containing Pu was never completed.

oxidation state in typical glass melts and glasses. However, the  $M^{4+/3+}$  melt reduction potential for plutonium was sufficiently different from that of cerium to render the latter inappropriate as a surrogate for the former under oxidizing melt conditions. As an example, for similar glasses, differing only in whether the same molar concentrations of cerium or plutonium was added and melted under identical conditions, >95% of the Ce was found as Ce(III), whereas >80% of the Pu was found as Pu(IV) (Darab et al. 1997).

In terms of non-actinide studies then, for oxidizing melts, a non-radioactive metal with a stable +4 oxidation state best simulates the redox chemistry of plutonium, which limits one to essentially Zr and Hf. Since  $HfO_2$  is used in some cases or is anticipated to be included in glass formulations containing fissile components in the future (Myers et al. 1998), Hf(IV) compounds made a good first-principles surrogate for Pu(IV) in our glass studies. From the discussions given above, however, it is apparent that surrogates for An(III) species were also required. Since Gd is generally required to be in glass waste forms with high concentrations of Pu and Gd to simulate the behavior of An(III) species reasonably well, Gd(III) compounds provided an obvious first-principles choice for An(III) surrogates.

This provided the rationale for another segment of our current EMSP program: the detailed study of the incorporation of Ln(III) and Hf(IV) species in a systematic series of  $Na_2O-Al_2O_3-B_2O_3-SiO_2$  melts and glasses. We decided to determine practical solubility limits<sup>(a)</sup> of  $Ln_2O_3$  (Li et al. 1999) and  $HfO_2$  (Davis et al. 1999) and later to compare them with the solubility limits of plutonium under reducing and oxidizing conditions, respectively (Feng et al. 1999). In such a way, no complication of mixed redox effect on solubility of both species would occur.

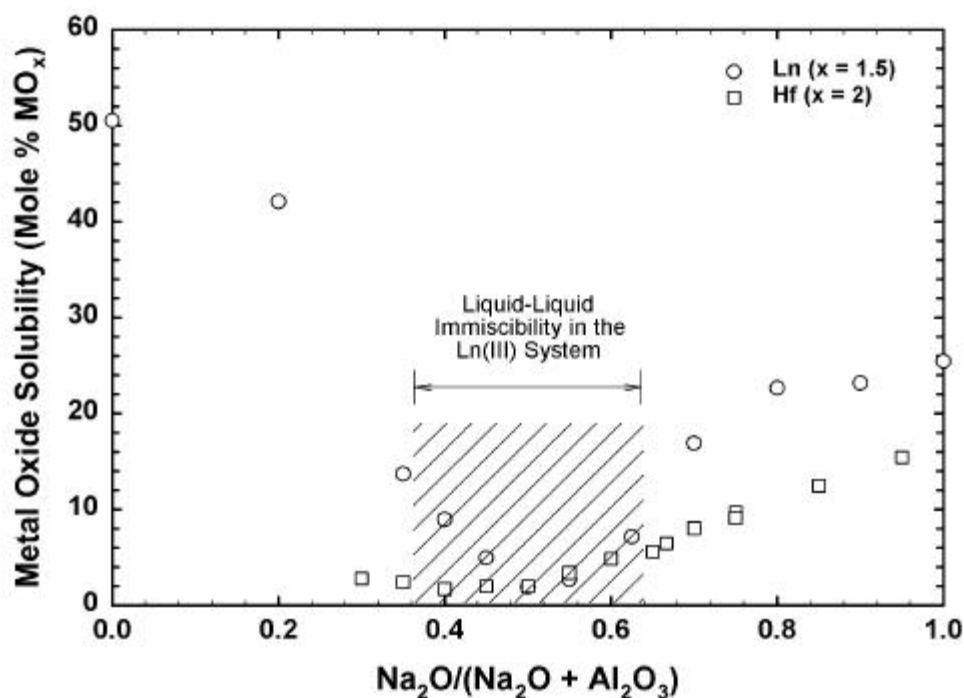
We found it useful to evaluate the properties (e.g., the solubility limit of  $Gd_2O_3$  and  $HfO_2$ ) of a glass in relation its compositional peralkalinity. The concept of peralkalinity dates back to the classic geologic work of Shand (Shand 1943). Shand devised a rock-classification system based on the chemical parameters that most affect the characteristic mineralogy of different rock types. Shand's subdivision of rock types had four categories that were delineated by the relative concentrations of  $Al_2O_3$ ,  $K_2O$ ,  $Na_2O$ , and  $CaO$ . We refer to two of these classifications to describe the compositions that we studied and, since neither  $CaO$  nor  $K_2O$  were part of our compositional matrices, they were not included in our limiting equations. Thus, throughout our work, we refer to peralkaline glasses in which  $(Al_2O_3)/(Na_2O) < 1$  and peraluminous glasses in which  $(Al_2O_3)/(Na_2O) > 1$ .

In  $Ln_2O_3$ -containing peralkaline melts with a ratio of excess  $Na_2O$   $[(Na_2O)_{xs}]$ , i.e.  $(Na_2O)_{xs} = (Na_2O) - (Al_2O_3)$ , to  $B_2O_3$   $[(Na_2O)_{xs}/B_2O_3]$  greater than 0.5, the  $Ln_2O_3$  solubility limit in these glasses is determined by the concentrations of  $SiO_2$ ,  $B_2O_3$ , and  $Al_2O_3$  (Figure 1). Increasing  $B_2O_3$  and  $SiO_2$  increases the  $Ln_2O_3$  solubility limit, while increasing  $Al_2O_3$  decreases it (Figure 1). Results from UV-Vis and laser fluorescence spectroscopic studies indicate that when the  $(BO_{1.5})/(LnO_{1.5}) \gg 3$  (low  $Ln_2O_3$  concentrations), Ln(III) cations appear to be uniformly dissolved in the glass matrix. We are currently studying the coordination environment of Ln(III) in these glasses with extended x-ray absorption fine structure (EXAFS) and energy loss fine structure (ELFS). At higher concentrations of  $Ln_2O_3$ , such that  $(BO_{1.5})/(LnO_{1.5}) \approx 3$ ,

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(a) We define the practical solubility limit as the first appearance of a crystalline phase or a liquid-liquid phase separation as determined with the optical microscope under the highest magnification.

intermediate-range ordering occurs with the formation of lanthanum- and boron-rich heterogeneities of about 5 nm in diameter. These have been identified with transmission electron microscopy (TEM) and ELFS. These regions could represent lanthanum clustering<sup>(a)</sup> and/or the formation of species containing a heteropolymeric B-O-Ln-O-B-O-Ln-O- bonding arrangement. When the  $(\text{BO}_{1.5})/(\text{LnO}_{1.5}) < 3$ , the extra Ln(III) cations are believed to become associated with silicate sites, causing the formation of another type of heterogeneity. The nature of these different types of heterogeneities is still under investigation. Although nanometer-sized heterogeneities were found in these glasses, the addition of  $\text{Ln}_2\text{O}_3$  yielded only clear glasses until the solubility limit was reached, at which point the precipitation of crystalline  $\text{Na}_x\text{Ln}_{9.33-0.33x}\text{Si}_6\text{O}_{26}$  ( $0 < x < 1$ ) was observed.



**Figure 1.** Solubility of  $\text{LnO}_{1.5}$  and  $\text{HfO}_2$  in the Glasses Used in this Study

Still considering  $\text{Ln}_2\text{O}_3$ -containing peralkaline glasses, a clear glass turned opalescent with increasing  $\text{Ln}_2\text{O}_3$  when  $(\text{Na}_2\text{O})_{\text{xs}}/(\text{B}_2\text{O}_3) < 0.5$ . This liquid-liquid phase separation defined the *practical* solubility limit, which was actually the limit of miscibility in this region. The secondary phase was determined with TEM and ELFS to be rich in Ln and B. The amount of  $\text{Ln}_2\text{O}_3$  that was needed to reach the practical solubility limit for these glasses depended on  $(\text{Na}_2\text{O})_{\text{xs}}$ . Increasing  $(\text{Na}_2\text{O})_{\text{xs}}$  increased the  $\text{Ln}_2\text{O}_3$  practical solubility limit. When more  $\text{Ln}_2\text{O}_3$

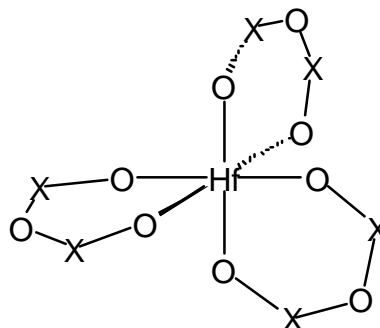
(a) A Ln cluster is defined as a moiety in which a homopolymeric O-Ln-O-Ln-O bonding arrangement occurs.



was added in excess of the *practical* solubility limit, results indicated that it was incorporated into silicate sites and when the  $\text{Ln}_2\text{O}_3$  concentration reached the *actual* solubility limit,  $\text{Na}_x\text{Ln}_{9.33-0.33x}\text{Si}_6\text{O}_{26}$  crystallized from the melt.

In  $\text{HfO}_2$ -containing peralkaline melts, the  $\text{HfO}_2$  solubility limit is observed to be at a minimum for glasses in which  $(\text{Al}_2\text{O}_3)/(\text{Na}_2\text{O}) = 1$ , which is the equivalent to  $(\text{Na}_2\text{O})/[(\text{Na}_2\text{O})+(\text{Al}_2\text{O}_3)] = 0.5$ , and increases with increasing  $(\text{Na}_2\text{O})/[(\text{Na}_2\text{O})+(\text{Al}_2\text{O}_3)]$ , i.e., increasing alkalinity (peralkaline glasses) (Figure 1). For all concentrations of  $\text{HfO}_2$  up to the solubility limit, EXAFS results indicate that the predominant hafnium species has a  $[\text{Hf}(\text{O})_6]$ , octahedrally coordinated, first nearest neighbor environment. Fitting of the XAFS data to include next nearest neighbor (i.e., Si, Al, B, O) interactions indicate that six-membered  $\text{Hf}-\text{O}-(\text{Si,Al,B})-\text{O}-(\text{Si,Al,B})-\text{O}-\text{Hf}$  rings may be present. By analogy with chemical terminology, the  $\text{Hf}(\text{IV})$  in peralkaline glasses can be considered to be complexed by three bidentate  $^-\text{O}-\text{X}-\text{O}-\text{O}^-$  ligands where  $\text{X} = \text{Si, Al, or B}$  (Figure 2).

This structure is very much different from that of  $\text{HfSiO}_4$ , which contains four-membered  $\text{Hf}-\text{O}-\text{Si}-\text{O}-\text{Hf}$  rings, i.e.  $\text{Hf}(\text{IV})$ , complexed by bidentate  $^-\text{O}-\text{M}-\text{O}^-$  ligands. No indication of  $\text{Hf}-\text{O}-\text{Hf}$  interactions were found, indicating that perhaps the  $\text{Hf}(\text{IV})$  cations are uniformly dissolved in the glass matrix without the apparent formation of clusters. Recent small-angle X-ray scattering (SAXS) results on these glasses identified the presence of heterogeneities about 0.7 nm in diameter, perhaps indicating the presence of heteropolymeric species similar to those found in  $\text{Ln}_2\text{O}_3$ -containing glasses or some other species that is not well mixed with the remaining glass matrix. Above the solubility limit, hafnia ( $\text{HfO}_2$ ) crystallizes from the melt.



**Figure 2.** Structure of  $\text{Hf}(\text{IV})$  in Peralkaline Sodium Boro-Aluminosilicate Glasses

In contrast to the liquid-liquid phase separation that occurs in certain  $\text{Ln}_2\text{O}_3$ -containing peralkaline glasses, macroscopically homogenous  $\text{HfO}_2$ -containing peralkaline glasses are formed over the entire range of  $[(\text{Na}_2\text{O})-(\text{Al}_2\text{O}_3)]/\text{B}_2\text{O}_3$  studied, at all concentrations of  $\text{HfO}_2$  up to the solubility limit.

Compositional effects on  $\text{HfO}_2$  solubility have been extensively studied. We have been able to model the  $\text{HfO}_2$  solubility limit in peralkaline glasses using an interesting approach. Starting with a given base-glass composition expressed in terms of mole percentages of  $\text{Na}_2\text{O}$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{B}_2\text{O}_3$ , and  $\text{SiO}_2$ , we re-expressed the composition based on mole percentages of structurally stable rudimentary compounds such as sodium disilicate ( $\text{Na}_2\text{Si}_2\text{O}_5$ ), sodium diborate ( $\text{Na}_2\text{B}_4\text{O}_7$ ), albite ( $\text{NaAlSi}_3\text{O}_8$ ), and reedmergnerite ( $\text{NaBSi}_3\text{O}_8$ ). We do not mean to imply with this approach that assemblages of these compounds exist in glass, but rather that certain chemical moieties, which can best be accounted for using the compounds that they are usually associated with, can be found in the glass. Each of these moieties has a specific  $\text{Hf}(\text{IV})$  solvating power, which can be probed by determining the solubility limit of  $\text{HfO}_2$  in these rudimentary amorphous compounds.

Then, using a rule-of-mixtures approach and the measured  $\text{HfO}_2$  solubility limits in rudimentary amorphous compounds, we were able to accurately calculate the solubility limit of  $\text{HfO}_2$  in all of the peralkaline glasses. We found that reedmergnerite and sodium diborate exhibited the highest solubility for  $\text{HfO}_2$ , and in fact, for each mole of “ $\text{NaBO}_2$ ” stoichiometric unit contained within these compounds, approximately 0.6 mole of  $\text{HfO}_2$  was solubilized. Sodium silicates provided lower solubilities for  $\text{HfO}_2$  than reedmergnerite and the sodium borates. There was practically no solubility of  $\text{HfO}_2$  in aluminum-containing compounds. These results indicated that the chemistry of sodium and boron in the silicate melt may have been the determining factor for  $\text{Hf(IV)}$ , and perhaps  $\text{An(IV)}$ , solubility. Interestingly, the XAFS results obtained from hafnium-containing reedmergnerite, sodium disilicate, and sodium diborate indicate that the nearest neighbor environment around the  $\text{Hf(IV)}$  in all of these systems was very similar.

At the opposite extreme of composition are the peraluminous melts, i.e.  $(\text{Al}_2\text{O}_3) > (\text{Na}_2\text{O})$ , where the concentration of  $\text{Al}_2\text{O}_3$  is relatively high and  $\text{Na}_2\text{O}$  low (Figure 1). At relatively small values of  $(\text{Na}_2\text{O})/[(\text{Na}_2\text{O})+(\text{Al}_2\text{O}_3)]$ , i.e. less than 0.4, for  $\text{Ln}_2\text{O}_3$ -containing compositions, a minimum  $\text{Ln}_2\text{O}_3$  concentration is required to produce a pure vitreous product. This minimum  $\text{Ln}_2\text{O}_3$  concentration is related to  $(\text{AlO}_{1.5})-(\text{NaO}_{0.5})-(\text{BO}_{1.5})$ . Increasing  $(\text{AlO}_{1.5})-(\text{NaO}_{0.5})-(\text{BO}_{1.5})$  increases the minimum  $\text{Ln}_2\text{O}_3$  concentration required to form a glass. If there is insufficient  $\text{Ln}_2\text{O}_3$  present, mullite (ideally,  $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ ) crystallizes from the melt (not shown in Figure 1). Presumably this is because the  $\text{Ln(III)}$  cations are required to stabilize the aluminum in tetrahedral coordination, since there was insufficient  $\text{Na}_2\text{O}$ , which normally plays the role of stabilizer. In fact, results from many nuclear magnetic resonance (NMR) studies with lanthanide aluminosilicate and lanthanide aluminoborate systems (Brow et al. 1997; Shelby and Kohli 1990; Lin et al. 1996; Kohli et al. 1992) indicate that increasing lanthanides can increase tetrahedrally coordinated aluminum. The relationship between the minimum concentration of  $\text{Ln}_2\text{O}_3$  and  $(\text{AlO}_{1.5})-(\text{NaO}_{0.5})-(\text{BO}_{1.5})$  suggests that increasing the  $\text{B}_2\text{O}_3$  must also assist in the stabilization of tetrahedrally coordinated aluminum. As the  $\text{Na}_2\text{O}$  is decreased further, the solubility of  $\text{Ln}_2\text{O}_3$  increases as does the amount of  $\text{Ln}_2\text{O}_3$  needed to obtain a clear glass without mullite. The phase that precipitates above  $\text{Ln}_2\text{O}_3$  saturation is  $\text{Na}_x\text{Ln}_{9.33-0.33x}\text{Si}_6\text{O}_{26}$ , where  $x$  decreases to zero as the  $\text{Na}_2\text{O}$  in the bulk glass decreases to zero. For  $\text{HfO}_2$ -containing peraluminous glasses, a limited increase in  $\text{HfO}_2$  solubility is observed for decreasing values of  $(\text{Na}_2\text{O})/[(\text{Na}_2\text{O})+(\text{Al}_2\text{O}_3)]$  in the range of 0.3 to 0.4. Further decreases in the value of  $(\text{Na}_2\text{O})/[(\text{Na}_2\text{O})+(\text{Al}_2\text{O}_3)]$  result in glasses that can no longer be melted at  $1560^\circ\text{C}$ . Our XAFS results suggest that the local structure around  $\text{Hf(IV)}$  is more silicate-like for the peraluminous glasses (i.e.,  $^-\text{O-X-O}^-$  ligands) as opposed to the structure in peralkaline glasses (i.e.,  $^-\text{O-X-O-X-O}^-$  ligands).

In peraluminous boro-aluminosilicate glasses without  $\text{Na}_2\text{O}$ , the local chemical environment of Nd was systematically studied using optical and NMR spectroscopies, magnetization measurements, and TEM. Using the Judd-Ofelt (JO) optical oscillator parameters extracted from the optical data, the degree of ligand field symmetry (LFS) and bond covalency (BC) was evaluated. In a study of  $\text{Al}_2\text{O}_3$ - $\text{B}_2\text{O}_3$ - $\text{SiO}_2$  glasses containing 7 to 25 mol%  $\text{Nd}_2\text{O}_3$  (the solubility limit was greater than 25 mol%), the JO parameters were determined by fitting the experimental data for the  $4f^3$ - $4f^3$  transition using the JO theory for electric-dipole interaction. A plot of these JO parameters against the concentration of  $\text{Nd}_2\text{O}_3$  in the glass yielded a behavior with two transition concentrations. The first transition concentration is defined by

$(\text{NdO}_{1.5})/[(\text{BO}_{1.5})+(\text{AlO}_{1.5})] = 0.33$  and the second by  $(\text{NdO}_{1.5})/[(\text{BO}_{1.5})+(\text{AlO}_{1.5})+(\text{SiO}_2)] = 0.33$ . For  $\text{Nd}_2\text{O}_3$  concentrations below the first transition concentration, the two relevant JO parameters were nearly independent of  $\text{Nd}_2\text{O}_3$  concentration. Between the first and the second transitions, these JO parameters increased with increasing  $\text{Nd}_2\text{O}_3$  concentration and then decreased above the second transition. Reviewing the literature data of lanthanide cations in  $\text{Na}_2\text{O}-\text{B}_2\text{O}_3$ ,  $\text{Na}_2\text{O}-\text{SiO}_2$ ,  $\text{Na}_2\text{O}-\text{B}_2\text{O}_3-\text{SiO}_2$ , and  $\text{Al}_2\text{O}_3-\text{B}_2\text{O}_3$  systems, we propose that up to the first transition, Nd(III) preferentially dissolves in sites composed of two trigonally coordinated boron,  $\text{B}_{\text{III}}$ , and one tetrahedrally coordinated boron  $\text{B}_{\text{IV}}$  (where  $\text{Al}_{\text{IV}}$  can substitute for  $\text{B}_{\text{IV}}$ ). A further increase in  $\text{Nd}_2\text{O}_3$  concentration results in partitioning the excess Nd(III) to various silicate sites. Crystallization of Nd-silicate above its solubility limit, 25– to 30 mol%  $\text{Nd}_2\text{O}_3$ , indirectly supports the proposed  $\text{Nd}_2\text{O}_3$  dissolution mechanisms.

Interestingly, results of magnetization measurements on these same  $\text{Nd}_2\text{O}_3$ -containing boro-aluminosilicate glasses mimic the behavior of the JO parameters at low concentrations of  $\text{Nd}_2\text{O}_3$ . The Nd(III) occurs in magnetically isolated paramagnetic sites, whereas above the first transition concentration, the Nd(III) occurs super-paramagnetic sites, i.e. sites most likely containing Nd(III)-O-Nd(III) linkages or clusters. The current results suggest that boro-aluminosilicate glass can be postulated as a mixture of B-rich and Si-rich domains (or heterogeneities). Hence, dissolution of lanthanide elements in boro-aluminosilicate may be best described in terms of their partitioning each domain.

Using the new insight into the Pu(III), Pu(IV), Gd(III), and Hf(IV) behavior in glass melts, we have identified optimum glass formulations to incorporate the maximum amount of  $\text{PuO}_2$ . Studies are underway to validate these formulations. 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.

## Relevance

The work performed under this EMSP should lead to a more efficient methodology for developing glasses for waste immobilization. Because the basic chemistry of the glass-forming process is better understood, much of the empiricism in glass development would be removed. This yields much more efficient processes for the immobilization of DOE wastes. More efficient processes lead to reduced costs by reducing the time it takes to convert waste into glass. A recent study (Perez et. al 2001) has shown that the major cost savings come in the form of reduced operation time.

As a result of the research reported here, models are available to begin the process of understanding the chemistry that takes place when a metal oxide is dissolved into a glass melt. Additional research is needed to fully expand the model from a semi-empirical model to one that is more fundamentally based and can be used reliably to calculate glass properties, or, starting with the needed glass properties, calculate the optimum glass composition. This would reduce the time needed to make glasses with compositions appropriate for the disposal of wastes with varying composition. As a result of the research performed under this EMSP, we have a better

knowledge of how to develop glasses for specific uses. We have semi-empirical models for the solubilities of  $\text{Gd}_2\text{O}_3$  and  $\text{HfO}_2$  in a variety of glasses.

### **Productivity**

With respect to developing a model and an understanding of the chemistry of neutron absorbers in boro-aluminosilicate glasses, we were quite productive. The systematics of Gd and Hf in these glasses is better understood. The model that we developed needs to be verified against experimental results with other glass systems and with other metal oxides. We were not so productive with respect to our development of the actinide systematics. This was because we were unable to obtain Pu for this study in time to do an adequate number of experiments. The only set of experiments we were able to perform with Pu remain uncompleted because of a contamination event. Recovery from this event consumed the available time and budget.

The initial scope of work that was proposed by the original principal investigator was found to be too large for the time and budget allotted. The scope of the experiments was revised downward to include a limited number of waste forms and radionuclides. Only Pu-bearing glasses were to be investigated, rather than a host of radionuclides. Unfortunately, the late delivery of Pu and the contamination event prevented us from completing the revised scope of work.

### **Personnel Supported**

At PNNL, the following people were supported:

- Denis M. Strachan (replacement PI)
- John Darab (Senior Research Scientist)
- Hong Li (Scientist, currently at PPG)
- Linda Davis (Post Doc, currently at University of Northern Illinois)
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- Michael Schweiger (Technical Specialist)
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- DK Shuh (Professor)
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M. L. Carter (Scientist)  
G. R. Lumpkin (Senior Scientist)  
R. A. Day (Scientist)  
B. D. Begg (Scientist)

## Publications

Darab, J. G., H. Li, and J. D. Vienna. 1998. "X-ray absorption spectroscopic investigation of the environment of cerium in glasses based on complex cerium alkali borosilicate compositions." Journal of Non-Crystalline Solids **226**(1-2): 162-174.

Davis, L. L., L. Li, J. G. Darab, H. Li, and D. M. Strachan. 1999. "The Effects of Na<sub>2</sub>O, Al<sub>2</sub>O<sub>3</sub>, and B<sub>2</sub>O<sub>3</sub> on HfO<sub>2</sub> Solubility in Borosilicate Glass." *Scientific Basis for Nuclear Waste Management XII*, Pittsburgh, Pennsylvania, Materials Research Society.

Davis, L. L., P. G. Allen, J. J. Bucher, D. L. Caulder, I. M. Craig, J. G. Darab, N. M. Edelstein, H. Li, L. Li, P. Liu, W. Lukens, H. Nitsche, L. Rao, D. K. Shuh, and D. Strachan. 1999a. "Speciation of uranium and plutonium in wasteform glasses by x- ray absorption fine structure spectroscopy." Abstracts of Papers of the American Chemical Society **218**: 93-NUCL.

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Feng X., H. Li, L. L. Davis, L. Li, J. G. Darab, M. J. Schweiger, J. D. Vienna, B. C. Bunker, P. G. Allen, J. J. Bucher, I. M. Craig, N. M. Edelstein, D. K. Shuh, R. C. Ewing, L. M. Wang, and E. R. Vance. 1999. "Distribution and Solubility of Radionuclides in Waste Forms for Disposition of Pu and Spent Nuclear Fuels: Preliminary Results." *Ceramic Transactions*, Vol. 93, J.C. Marra and G. T. Chandler, editors, American Ceramic Society, Westerville, Ohio

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**ANSTO Publications (also reported in their report)**

- Vance, E. R., M. L. Carter, B. D. Begg, R. A. Day and S. H. F. Leung. 2000. "Solid Solubilities of Pu, U, Hf and Gd in Candidate Ceramic Phases for Actinide Waste Immobilisation," Mat. Res. Soc. Symp. Proc. Vol. 608, R. W. Smith and D. W. Shoesmith, eds., Materials Research Society, Warrendale, PA.
- Vance, E. R., J. N. Watson, M. L. Carter, R. A. Day, G. R. Lumpkin, K. P. Hart, Y. Zhang, P. J. McGlinn, M. W. A. Stewart and D. J. Cassidy. 2000. "Crystal chemistry, radiation effects and

aqueous leaching of brannerite,  $UTi_2O_6$ .” In *Environmental Issues and Waste Management Technologies V*, G. Chandler and X. Feng, eds., American Ceramic Society, 561.

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Vance, E. R., G. R. Lumpkin, M. L. Carter, C. J. Ball and B. D. Begg, The Incorporation of U in Zirconolite ( $CaZrTi_2O_7$ ), submitted to J. Amer. Ceram. Soc.

Vance, E. R., M. L. Carter, R. A. Day and B. D. Begg, Solubilities of different U valences in perovskite,  $CaTiO_3$ , in preparation

Vance, E. R., K. L. Smith, G. R. Lumpkin, B. D. Begg, C. J. Ball, and J. H. Hadley, Jr., Cation Vacancies in Titanate Phases, in preparation

Vance, E. R., M. L. Carter and R. A. Day, Solubility of Pu and U in Apatite, in preparation

### **Interactions**

Several presentations are documented in the publication list. The main conferences that were attended are the American Chemical Society, American Ceramic Society, and the Materials Research Society.

No consultant activities resulted from this work.

This work was carried out in collaboration between the participants in this EMSP. These were PNNL, ANSTO, University of Michigan, and Lawrence Berkeley National Laboratory.

### **Transitions**

As stated in the main conclusions of this report, the primary use of this study is as a lead-in to work that will put the development of glasses on a sound scientific basis, rather than the empirical basis of today.

### **Patents**

No patents were received for work under this project.

### **Future Work**

The only future work that is planned at the time of the writing of this report is the submission of a proposal for follow-on work and another proposal when an appropriate EMSP call from proposals is issued.

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