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X-Ray Photoemission Spectroscopy (XPS) Study of Uranium,  
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Using XPS as the principal investigative tool, we are in the process of examining the bonding properties of selected metal oxides added to silicate glass. In this paper, we present results of XPS studies of uranium, neptunium, and plutonium in binary and multi-component silicate-based glasses. Models are proposed to account for the very diverse bonding properties of 6+ and 4+ actinide ions in the glasses.

Silicate glasses are being considered as possible media for long term storage of radioactive wastes. Actinide elements are among those active species which must be isolated from the biosphere for many centuries. Thus it is important to understand bonding properties of actinides in the glasses in order to formulate the most effective storage medium and to discover potential failure modes.

As part of a more extensive study of metal oxides dissolved in simple glasses (1-5), we report results for U, Np, and Pu oxides dissolved in sodium silicate glass. For this work, we rely primarily on XPS data. Valence states of the incorporated ions can be quite reliably determined through a careful examination of binding energy shifts, 5f electron intensities, and the satellite structure associated with core level excitation (1). For suitably concentrated samples, the actinyl structure can be recognized in the splitting of the An (actinide) 6p<sub>3/2</sub> level (2). (Data for hexavalent Np oxides are similar to results reported for U<sup>6+</sup> compounds (6)). These (actinyl) results can also be tested with EXAFS spectra where the An-O separation can be directly measured (7). The spectral analyses, solubility data, and observed property changes associated with addition of actinide elements to glasses have enabled us to suggest bonding models of An 4+ and 6+ ions in silicate glasses.

## Experimental

The samples were prepared by melting appropriate amounts of constituent oxides with powdered sodium trisilicate glass. To minimize the compositional variation of the samples, a large batch of sodium-trisilicate glass was prepared. This glass was then used to prepare the Np and Pu glasses as well as the multicomponent glass samples. The glasses were melted in an atmosphere of flowing oxygen or in a reducing atmosphere of controlled CO/CO<sub>2</sub> ratio, at 1250°C in platinum crucibles for several hours. The samples were crushed, thoroughly mixed and remelted several times to insure homogeneity. X-ray powder diffraction patterns were taken for several randomly selected samples to check for the presence of crystalline phases. After the final melting, the samples were visually examined for gross nonuniformity of color distribution. If found, the sample was crushed and remelted. Most of the samples studied were furnace cooled from 1250°C to room temperature. To check the effect of cooling rate on the XPS spectra, several samples were air quenched and reannealed at 400°C. No apparent differences were found between the furnace cooled and reannealed specimens. Two bar shaped samples measuring approximately 3x3x15 mm were cut from the ingots with a diamond wafering saw using methanol as coolant. The bars were scored and were subsequently fractured in the ultra-high ( $6 \times 10^{-10}$  Torr) vacuum chamber of the spectrometer to expose clean surfaces of the bulk glass composition for examination with XPS.

The spectrometer was a Physical Electronics Model 548 modified for emplacement in a glovebox so that actinide samples could be examined. Spectra were taken using AlK <sub>$\alpha$</sub>  radiation (1486.6 eV). The overall energy resolution of the spectrometer was ~1.2 eV using an analyzer pass energy of 25 eV. The spectrometer control was interfaced to a Nicolet 1180 minicomputer providing automatic data acquisition and analysis capability.

## Experimental Results

We have previously reported that dissolution of UO<sub>2</sub> or UO<sub>3</sub> in sodium silicate glasses in an atmosphere of oxygen or air produces a glass in which uranium appears only in the hexavalent state (2). In order to obtain dissolved tetravalent uranium ions, it is necessary to melt the glass in very reducing conditions. In contrast, the melting of NpO<sub>2</sub> and PuO<sub>2</sub> into silicate glass in flowing oxygen will not oxidize the Np or Pu to a higher valence state. The solubility of NpO<sub>2</sub> and PuO<sub>2</sub> in sodium trisilicate glass at 1250°C is three and two mole percent, respectively. When attempts were made to dissolve higher concentrations of Np or Pu oxide, nonglassy residues were obtained. For UO<sub>2</sub> dissolved into the same glass

at 1250°C, the solubility is five (for U<sup>4+</sup>) and twenty (for U<sup>6+</sup>) mole percent when melted in atmospheres of CO/CO<sub>2</sub> = 7 and in air, respectively. The large difference in solubility between hexavalent and tetravalent uranium in these glasses will be discussed below.

The valence states of Pu and Np ions in complex borosilicate glasses (designated 76101 and 7668, glasses prepared by Battelle Pacific Northwest Laboratories for waste form simulation) were previously investigated with XPS (1). Nominal compositions of these glasses are given in ref. 1. Both trivalent and tetravalent states of Pu were readily observed in the glasses but Np was present essentially in a single valence state (+4), in both glasses. Similar results are seen in Fig. 1, which shows an XPS spectrum that includes actinide 4f core levels for the 76101 glass into which one mole percent each of UO<sub>3</sub>, NpO<sub>2</sub>, and PuO<sub>2</sub> has been added. Two valence states for Pu (+4 and +3) and U (+6 and +4) are discernable while Np appears only in the 4+ state.

The Ti 2p doublet appears on the extreme left side of Fig. 1. TiO<sub>2</sub> was added to the glass because it is present in nuclear waste and also because it is useful as an internal reference for binding energy determinations (1). The sodium trisilicate glasses with various additive oxides, listed in Table I, were studied by XPS.

Although multiple valence states were frequently observed with XPS, caution should be exercised in associating these valence states with the unperturbed bulk glass. Particularly for Pu<sup>4+</sup>, a significant amount of reduction (to Pu<sup>3+</sup>) occurred during the XPS data accumulation time. This is particularly troublesome for dilute samples where long data acquisition times are needed to obtain an adequate signal-to-noise ratio. The effect is illustrated in Fig. 2 which shows progressive changes of Pu 4f spectra for glass I (see Table I) as a function of data acquisition time. Spectrum (a) is a 10 minute scan acquired immediately after fracture. Each successive spectrum, run for an additional ten minutes, was acquired immediately after the previous spectrum. The spectra were then smoothed, using a 5 point Savitsky-Golay routine supplied by Nicolet. After extended X-ray exposure (several hours), the relative concentrations of 4+ and 3+ ions became approximately equal. Since the photoelectron escape depth is ~20-30 Å, it appears that Pu ions in the top ~15 Å layer were reduced. A low energy electron beam was used during measurement to maintain charge neutralization at the sample surface. To test for possible reduction resulting from the neutralization beam, the sample was exposed overnight to the beam. No reduction from this source was detectable. (This source also produces more sample heating than the X-ray beam so we rule out thermal decomposition.) Thus reduction of tetravalent Pu and hexa-

valent U was caused by the X-ray flux under UHV conditions. Probably, oxygen desorption was stimulated by photons or secondary electrons. It is not known whether those oxygen atoms in the vicinity of actinide ions are preferentially removed or if O atoms come from the surface randomly. (We note, however, that similar reduction behavior often occurs from simple uranate salts where the  $U^{6+}$  ions always have a relatively close association with all oxygen atoms.)

The ease of reduction of the Pu  $4+$  ions apparently can be affected by inclusion in the glass of additional additives. Whereas the addition of  $TiO_2$  apparently does not affect in-situ reduction, the addition of CaO, ZnO, or  $B_2O_3$  appreciably accelerated reduction of the Pu  $4+$  ions. This effect is demonstrated with 4f core level spectra of glasses F, G, H, and I shown in Fig. 3. Each sample was subjected to the same X-ray exposure, i.e., the same number of scans at the same flux. (Note that the concentrations of additive oxides differ. No attempt has been made to scale this effect with additive concentration). This curious reduction effect is not easily understood but emphasizes the complex nature of the glasses including the possible cooperative involvement of the multiple components. Similarly complex phenomena might influence leaching behavior in the complex, multicomponent glasses of interest for radioactive waste storage.

### Discussion

A consideration of the structure of silicate glasses provides a useful starting point for examining bonding properties of elements incorporated into the glasses. It is commonly believed that added metal ions are randomly situated in large interstitial spaces or holes of the amorphous  $SiO_2$  network. Variation of the bond angles between  $SiO_4$  tetrahedra give rise to the holes of irregular shape and size. This model of glass structure, developed by Zachariasen (8) and Warren (9), would imply that solubilities of incorporated elements should be determined, in large part, by the ionic size of the added element. With this view, it is surprising that the difference in the solubility of hexavalent (ionic radius,  $r_c = 0.8 \text{ \AA}$ ) and tetravalent ( $r_c = 0.97 \text{ \AA}$ ) uranium is so large, i.e., 20 versus 5 mole percent. In contrast to experimental observation, it would also be expected that the solubility of tetravalent Np ions ( $r_c = 0.95 \text{ \AA}$ ) and Pu ions ( $r_c = 0.93 \text{ \AA}$ ) should be larger or at least equal to that of the tetravalent U in the same glass. Previous studies of hexavalent U in silicate glasses have indicated that U appears in the uranyl structure (2, 7, 10). If both the  $U^{+4}$  ions and the  $UO_2^{++}$  ions are situated in the interstitial holes of the glass network, then the solubility of  $UO_2^{++}$  should be smaller, instead of much larger than the

U<sup>4+</sup> ion.

For our purposes, we use a crystal chemistry approach and consider crystal structures of silicates with chemical compositions approximating the glasses of interest. Structural features of these crystal forms should be preserved in varying degrees in the glasses. For example, the SiO<sub>4</sub> tetrahedron is a structural element common to all of the silicate glasses. Of comparable importance, but more difficult to demonstrate, is the possibility that extended range chains or sheets, readily observable in the crystalline forms, may also appear in the glasses and play an important role in determining the physical properties of a particular glass.

Consider the  $\alpha$ -Na<sub>2</sub>O.2SiO<sub>2</sub> crystalline form (11). This silicate consists of identifiable sheets that are assembled from SiO<sub>4</sub> tetrahedra. Three "bridging" oxygen bonds join the tetrahedra with bond strengths comparable to those found in pure SiO<sub>2</sub>. A single "nonbridging" oxygen (joining an alkali atom) on each tetrahedron provides a termination layer of alkali atoms on the sheet surface. Thus, the sheets, which contain strong internal bonds, are weakly joined through ionically bonded, monovalent alkali atoms. However, if metal atoms of higher valence were added to the compound and adjacent sheets were bonded (cross linked) through these polyvalent additives, one might expect to find profound changes in the physical properties of the glass.

An example of this contrast in bonding conditions for crystals silicates is provided by the compound Li<sub>2</sub>O.2SiO<sub>2</sub> (12) which displays very weak intersheet bonding and the mineral petalite (13), which has the composition Li<sub>2</sub>O.Al<sub>2</sub>O<sub>3</sub>.8SiO<sub>2</sub>. To convert the disilicate to petalite requires the replacement of three Li atoms with one Al, a process that is accomplished entirely within the intersheet region without significantly perturbing the sheet structure of the parent disilicate. The Al thus cross links the silica sheets with a strong bond and profoundly alters the physical properties.

It is our view that similar phenomena occur in glassy silicates. Probably, chains or sheets of silica with strong internal bonds form in the melt at an early stage of cooling. Additive elements that form strong cross links between these sheets will then be expected to significantly affect the glass rigidity. Such hardening (analogous to the cross linking of chains in polymers) is commonly observed in glasses. One manifestation of the cross linking is increased viscosity, often apparent when polyvalent metals are added to simple silicate glasses (14).

Utilizing this description of silicate glass formation, we suggest models to explain the incorporation of 4+ and 6+ actinide ions in sodium disilicate glass. During cooldown, SiO<sub>4</sub> tetrahedra link together to form a sheet-like structure

with, on average, one nonbridging oxygen per tetrahedron. The sodium ions, being completely ionized (5) and relatively large, are situated in the interstitial spaces between the sheets, weakly bonding those sheets together. Presumably, the tetravalent actinide ions are also located in the "intersheet" regions but they bond with greater strength than alkalis to oxygens of the tetrahedra, thus crosslinking the distorted silica layers. This glassy structure will be frozen in as the sample is cooled. This "strong cross linking" model is consistent with the (qualitative) observation that, with addition of actinide 4+ ions, the glass viscosity increases.

It would appear that a rather different picture is needed to explain the bonding of U 6+ in silicate glasses. Strong evidence is now available to support the assertion that U 6+ appears in a uranyl configuration (2,7,10). In the glasses, the  $UO_2^{++}$  ion has a linear structure with U-O separation of about 1.8 Å (7). Alkali uranates containing hexavalent uranium in the uranyl structure form easily and in considerable variety. They often display sheet structures (sometimes distorted) with sheets separated by alkali or alkaline earth atoms. These same features, sheets separated by alkalis, are characteristic of crystalline alkali disilicates. It thus appears likely that, during cooldown of U 6+ glasses, uranyl structures form and bond into the interstice regions between silica sheets. This dissolution mode permits a large U 6+ solubility. Since alkalis play the role of delineating silica or uranate sheets, structural rigidity should be weak. The relatively low viscosity of U 6+ silicate glasses (again a qualitative observation) supports this picture. Uranates are not stable at 1250°C where the samples were melted so we do not expect macroscopic phase separated regions of U 6+ uranate. (Furthermore, X-ray diffraction data do not show the presence of crystalline second phase regions.) Rather, it appears that a thin uranate layer is formed between silica sheets and held in place by layers of alkali atoms.

The different bonding characteristics of  $U^{+4}$  and  $U^{+6}$  in alkali silicate glasses may have important implications to the leaching properties of high level waste glasses. In the  $UO_3$  glasses, the uranyl structures probably occur in association with alkalis (similar to alkali uranates), an association that dramatically increases bonding of the sodium ions in the glass. This conclusion is supported by qualitative leaching studies of sodium disilicate glass containing  $UO_3$  (15). It was observed that the glass maintained its structural integrity and no significant change in the leachant pH was detected after (static) leaching in distilled water for 180 days at room temperature.

In contrast, disilicate glasses containing U 4+ showed much less leach resistance. The 4+ glass was only slightly more

leach resistant than pure sodium disilicate glass which is water soluble. For 4+ glasses, the ph of the leach solution rose to 10.7 under the same leaching conditions used for the U 6+ glass. The U 4+ ions, which are soluble in low concentration, apparently cross link silica sheets to produce significant physical property changes. However, this cross linking process would not appear to significantly affect the bonding of alkali ions in the glass, so that the ability of a simple silicate glass to withstand leach attack is not appreciably increased by adding U 4+ ions.

More quantitative leaching data is needed for well characterized sodium silicate glasses containing  $U^{+4}$  and  $U^{+6}$  ions. It is clear, however, that the general practice of using air-melted uranium glass ( $U^{6+}$ ) to simulate leaching behavior of transuranic actinides in waste glasses should be discarded. Since transuranics in silicates do not, in general, appear in the 6+ valence state, this is not a reliable simulation. Also U 6+ ions appear to have bonding properties (associated with a strong tendency to form the uranyl structure) in glasses that are not typical of transuranic ions.

SYMPOSIUM SERIES

Table I. Composition of Various Samples Studied

<u>Glass Samples</u>	<u>Composition (mole fraction</u>
A	0.25 Na <sub>2</sub> O•0.75 SiO <sub>2</sub>
B	(0.25 Na <sub>2</sub> O•0.75 SiO <sub>2</sub> ) <sub>0.964</sub> (TiO <sub>2</sub> ) <sub>0.036</sub>
C	(0.25 Na <sub>2</sub> O•0.75 SiO <sub>2</sub> ) <sub>0.985</sub> (PuO <sub>2</sub> ) <sub>0.015</sub>
D	(0.25Na <sub>2</sub> O•0.75SiO <sub>2</sub> ) <sub>0.914</sub> (TiO <sub>2</sub> ) <sub>0.036</sub> (UO <sub>3</sub> ) <sub>0.050</sub>
E	(0.25Na <sub>2</sub> O•0.75SiO <sub>2</sub> ) <sub>0.944</sub> (TiO <sub>2</sub> ) <sub>0.036</sub> (NpO <sub>2</sub> ) <sub>0.020</sub>
F	(0.25Na <sub>2</sub> O•0.75SiO <sub>2</sub> ) <sub>0.949</sub> (TiO <sub>2</sub> ) <sub>0.036</sub> (PuO <sub>2</sub> ) <sub>0.015</sub>
G	(0.25Na <sub>2</sub> O•0.75SiO <sub>2</sub> ) <sub>0.909</sub> (TiO <sub>2</sub> ) <sub>0.036</sub> (PuO <sub>2</sub> ) <sub>0.015</sub> (CaO) <sub>0.040</sub>
H	(0.25Na <sub>2</sub> O•0.75SiO <sub>2</sub> ) <sub>0.889</sub> (TiO <sub>2</sub> ) <sub>0.036</sub> (PuO <sub>2</sub> ) <sub>0.015</sub> (ZnO) <sub>0.060</sub>
I	(0.25Na <sub>2</sub> O•0.75SiO <sub>2</sub> ) <sub>0.809</sub> (TiO <sub>2</sub> ) <sub>0.036</sub> (PuO <sub>2</sub> ) <sub>0.015</sub> (B <sub>2</sub> O <sub>3</sub> ) <sub>0.140</sub>

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Figure Captions

Fig. 1. XPS 4f core level spectra for glass 76101 containing dissolved  $UO_3$ ,  $NpO_2$  and  $PuO_2$ . Multiple valence states appear for U and Pu. Intensities of the low valence states are enhanced by in-situ reduction during the XPS measurement.

Fig. 2. 4f core level spectra for glass I (Table I) demonstrating the strong tendency of the  $Pu^{4+}$  ions to reduce in the XPS spectrometer. Spectra (a) through (e) are short (10 min) sequential runs showing accumulative reduction of  $Pu^{4+}$  to  $Pu^{3+}$ .

Fig. 3. 4f core level spectra for a series of glasses containing Ca, Zn, or B oxide additives (glass sample F, G, H, and I of Table I). The rate of reduction of  $Pu^{4+}$  to  $Pu^{3+}$  during XPS measurement is apparently influenced by the choice of additive (see text).





