

CONF-961202--93

submitted: Proceedings Fall MRS Meeting  
Symposium II  
2-6 December 1996  
Boston MA

RECEIVED

MAR 25 1997

OSTI

**ACTINIDE SPECIATION IN GLASS LEACH-LAYERS: AN EXAFS  
STUDY**

BRUCE M. BIWER#, L. SODERHOLM#, R.B. GREGOR† and F.W.  
LYTLE§

#Argonne National Laboratory, Argonne IL 60439, †The Boeing Company,  
Seattle, WA 98124 and §The EXAFS Company, Pioche, NV 89043

The submitted manuscript has been authored  
by a contractor of the U. S. Government  
under contract No. W-31-109-ENG-38.  
Accordingly, the U. S. Government retains a  
nonexclusive, royalty-free license to publish  
or reproduce the published form of this  
contribution, or allow others to do so, for  
U. S. Government purposes.

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

MASTER

**DISCLAIMER**

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

Portions of this document may be illegible  
in electronic image products. Images are  
produced from the best available original  
document.

**DISCLAIMER**

# ACTINIDE SPECIATION IN GLASS LEACH-LAYERS: AN EXAFS STUDY

BRUCE M. BIWER#, L. SODERHOLM#, R.B. GREGOR† and F.W. LYTLE§

#Argonne National Laboratory, Argonne IL 60439, †The Boeing Company, Seattle, WA 98124  
and §The EXAFS Company, Pioche, NV 89043

## ABSTRACT

Uranium L<sub>3</sub> X-ray absorption data were obtained from two borosilicate glasses, which are considered as models for radioactive wastefoms, both before and after leaching. Surface sensitivity to uranium speciation was attained by a novel application of simultaneous fluorescence and electron-yield detection. Changes in speciation are clearly discernable, from U(VI) in the bulk to (UO<sub>2</sub>)<sup>2+</sup>-uranyl in the leach layer. The leach-layer uranium concentration variations with leaching times are also determined from the data.

## INTRODUCTION

There has been relatively little work done to determine the valence and coordination environment of metal ions in the surface layers of glasses after leaching. This speciation is of particular concern when the leach layers occur on glasses under consideration for radioactive-waste disposal. An excellent technique for determining metal-ion speciation in non-crystalline media is XAS (X-ray absorption spectroscopy) [1] although it is normally not a surface-sensitive technique, and therefore has not been used extensively to study the speciation of metal ions in glass leach layers. Surface sensitivity has been achieved in XAS for some uranium-bearing corroded borosilicate glasses by employing glancing-incident detection [2]. This technique relies on the fact that a monochromatic X-ray beam incident on a flat surface has a well-defined critical angle of incidence below which the X-rays are totally reflected. By measuring an absorption spectrum with incident-beam angles below and above this critical angle, it was possible to discern changes that had occurred within about 30 Å of the surface (for the U L<sub>3</sub> edge energy). Although surface modifications were observed, because the total reflection geometry requires very flat, polished surfaces, leaching times were very restricted, i.e. limited to 90 minutes or less. This is insufficient time to allow the diffusion-controlled chemical changes, such as solid-phase formation, that are expected to occur in the surface layer [3,4].

In this manuscript we present a novel combination of fluorescence and electron-yield XAFS detection designed to probe the thick surface layer of leached wastefoms. For the L edges, electron yield relies on the detection of LMM Auger electrons, emitted by the absorbing ion, which for uranium have a range of only about 3000 Å in borosilicate glass. This means that electron yield detection has a sampling depth (defined as 1/e, the mean free path) such that it provides only information from the leached layer of the samples under study here [5,6], whereas the more standard fluorescence detection is expected to have a sampling depth of approximately 1000 times

that. Because the leached layer is such a small percentage of the total sample probed (less than 10%), the fluorescence signal is representative of only the bulk sample. Therefore, by simultaneously measuring both the fluorescence signal and the electron-yield, we demonstrate herein that the valence and coordination environments of the U present in our samples can be determined in both the bulk, and in the leached layer to a depth of approximately 3000 Å.

We examined the uranium L X-ray absorption spectra as a function of leach time of two sodium borosilicate glasses that have been considered as model waste storage media, SRL-131 and ATM-1c. The SRL-131 type glass has been chosen because previous results from leach tests are available [4,7] and have been used in the development of models to predict glass performance [8,9]. The objective here was to define the oxidation state and environment of uranium in the unreacted glasses, and to look for changes at the surface of the glass as they were leached. Although the compositions of these glasses are not expected to be used in final production, these studies may provide information useful to the understanding of uranium speciation in complex glasses.

## EXPERIMENTAL SECTION

### Sample Preparation

SRL-131 and ATM-1c are two high Fe complex classes with respective U percentages (as  $\text{UO}_2$ ) of 1.3 and 4.0 %, that have been considered as prototypes for radioactive wasteforms [4,7]. The uranium-doped SRL-131 glass samples used here were synthesized by mixing base SRL-131 frit, as supplied by Savannah River Laboratory in finely powdered form, with  $\text{U}_3\text{O}_8$  in the appropriate stoichiometry, heating in air in a Pt crucible at 1150°C for 4 hours which completely melted the sample, followed by quenching into water. The sample was reground and melted at 1150°C for 15 min, and then poured into a Pt loaf mold, where it was annealed for 2 hours at 500°C, and then allowed to cool to room temperature. Chemical analyses were confirmed using a combination of acid dissolution/ICP techniques. The ATM-1C glass was used as supplied by Pacific Northwest Laboratory [10].

The sample discs were prepared as previously described [4,7]. Hydrothermal leaching experiments were conducted at 90°C in Teflon<sup>®</sup> vessels in static leach tests using a modified MCC-1 testing procedure [11]. SRL 131 glass was leached at surface area-to-volume (SA/V) ratios of 10  $\text{m}^{-1}$  and 100  $\text{m}^{-1}$ . ATM-1c glass samples were leached at SA/V ratios of 4  $\text{m}^{-1}$  and 10  $\text{m}^{-1}$ . Deionized water was used as the reaction leachant in all experiments. Leaching times varied from 7 to 92 days. After each experiment was terminated, the monoliths were rinsed with distilled water, allowed to air dry, and stored in a dry, dust-free container. Preliminary examinations of the altered glass surfaces were performed by both optical and scanning electron microscopy (SEM). In addition to the glass surface, cross-sections of some samples were prepared for SEM analyses of the layer thickness and structure. The leached layer was shown to consist of an about 0.1  $\mu\text{m}$  surface layer of smectite clay overlaying a thin Fe-rich layer covering a 2-10  $\mu\text{m}$  thick dealcalized

gel-like phase containing clay precursors. Details of the analyses for similar SRL-131 glass experiments are published elsewhere where the electron microscopy of the sectioned surface is analyzed [4,7]. From these data we conclude that the sampling depth of our electron channel was always within the surface leach layer, except for the reference-glass samples before leaching.

### XAS data collection and analysis

The U L<sub>3</sub> and L<sub>1</sub> spectra were recorded at the Stanford Synchrotron Radiation Laboratory (SSRL) on beam line 4-3. The double crystal monochromator was equipped with Si(220) crystals and was detuned 20% to reject harmonics. The entrance slit to the monochromator, set at 1 mm, defined an energy band width of ~5 eV, which was considerably less than the 8 or 11 eV uncertainty broadening expected for U L<sub>3</sub> or U L<sub>1</sub>, respectively [12].

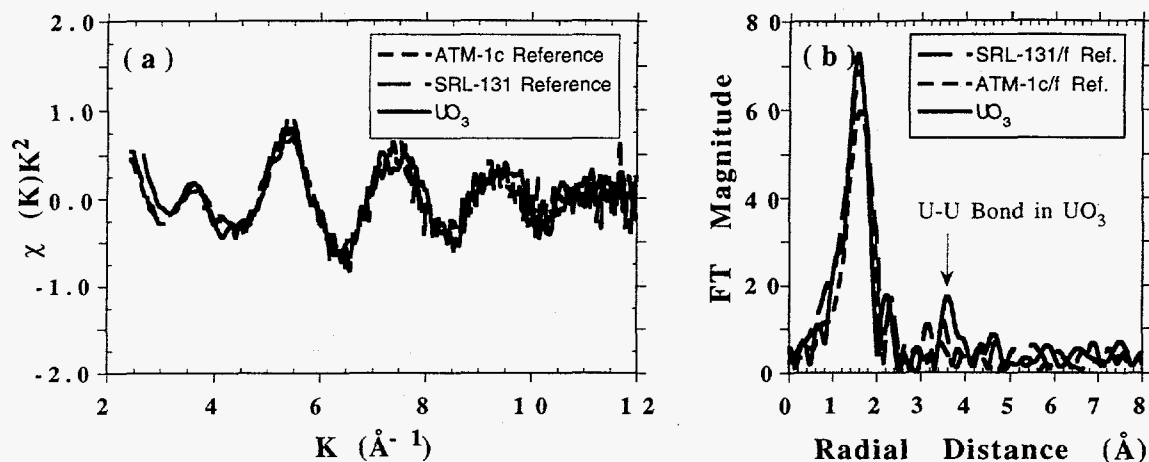
The beam line was equipped with a linear chain of ion chambers to measure the incident beam, I<sub>0</sub>, the transmitted beam, I<sub>t</sub>, and a reference UO<sub>2</sub> sample, I<sub>r</sub>. In addition a combination x-ray fluorescence ion chamber, I<sub>f</sub>, and electron yield detector, I<sub>e</sub>, was located between I<sub>0</sub> and I<sub>t</sub>. Note that the e and f channels were measured simultaneously with a detector comprised of an electron collecting chamber separate from and transparent to the fluorescent x-rays [13]. At least two spectra (averaged) were collected for each sample. The L<sub>1</sub> data are not included here for brevity, but their results are consistent with those described for the L<sub>3</sub> analyses.

The data were reduced to normalized x-ray absorption near edge spectra (XANES) and extended x-ray absorption fine structure (EXAFS) files using standard techniques [1]. The data were fit over K from 2-12 Å<sup>-1</sup> from a back transform over R from 0.5-2.5 Å. Fitting two separate bond distances required 7 parameters. Inclusion of a 3rd bond distance would be the absolute limit (ten variables) for this range of data. The reference compounds were either separated into two-shell entities by Fourier filtering (UO<sub>2</sub>) or by averaging the different coordination distances into two groups.

## RESULTS AND DISCUSSION

### Glass-EXAFS

The U L<sub>3</sub> EXAFS, obtained from the SRL-131 and ATM-1c bulk glasses by monitoring the fluorescence yield, are compared with a standard UO<sub>3</sub> spectrum in Figure 1a. These three spectra appear indistinguishable, as confirmed by the fitted parameters listed in Table I. The FT of the EXAFS spectra are shown in Figure 1b. The broad, single shell observed for both the glasses under study is compared with known U coordinations in Table I. The coordination environment of approximately 2 oxygen at 1.85 Å and approximately 4 oxygen at a slightly longer distance of 2.28 Å is similar to the U coordination found in other borosilicate glasses [2,14,15]. The glass data are inconsistent with the distinctive 2 short (1.76 Å) and 6 longer (2.46 Å) bonds expected for the uranyl coordination, as demonstrated for NaUO<sub>2</sub>(CH<sub>3</sub>COO)<sub>3</sub> in Figure 2b. Instead the data are consistent with the pseudo octahedral coordination found for U in UO<sub>3</sub> [16,17]. The coordination



**Figure 1.** (a) A comparison of the  $K^3$ -weighted EXAFS (before phase correction) obtained from glasses with those from  $UO_3$ . The Fourier Transform (FT) of these spectra, shown in (b) do not have the two peaks characteristic of uranyl. The peak at  $\sim 3.7 \text{\AA}$  in  $UO_3$  is due to U-U scattering environment for U is also somewhat similar to the metamict betafite [18], although the U-O average bond distance is slightly shorter in our case.

environment for U is also somewhat similar to the metamict betafite [18], although the U-O average bond distance is slightly shorter in our case.

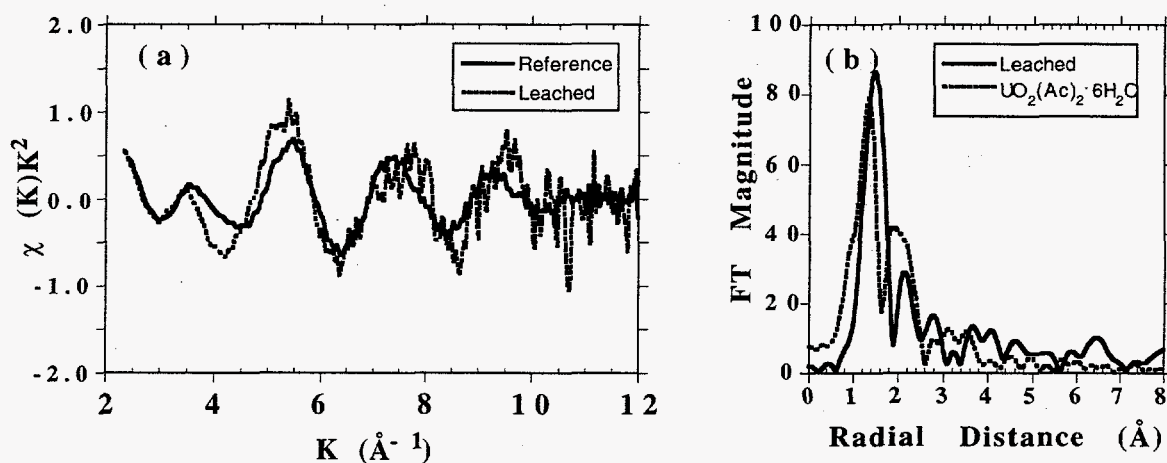
Not shown is the comparison of the bulk (fluorescence) and surface (e-yield) EXAFS from the samples before leaching, which again are indistinguishable, indicating that the uranium speciation in the bulk is similar to that at the surface for the starting glass. The finding of a similar surface and bulk uranium speciation in the unreacted glass does not contradict the presence of a thin, 50  $\text{\AA}$  surface hydration layer such as has been previously proposed for samples in contact with air [19]. The EXAFS of the bulk glass remains unchanged for all leached samples, but the near-surface EXAFS show marked changes with leaching, as demonstrated in Figure 2. Whereas the fit to leached layer spectra looks good, a two-shell model does not adequately represent the data. It appears that approximately 30% of the uranium has converted to a uranyl-type coordination, hence the average environment is very complex, and requires more parameters than are warranted statistically. The finding of some uranyl-type coordination at the surface after leaching is supported by the XANES results.

### Glass-XANES

The XANES data, collected in the fluorescence mode, were the same for all the samples measured, as shown in Figure 3a. In addition, the XANES data obtained from the bulk were indistinguishable for the electron-yield data obtained from the near surface for samples before leaching. These spectra show no evidence for the presence of the uranyl moiety, which can be identified by the high energy shoulder on the  $L_3$ -edge spectra [15,20]. Instead the spectra show a edge shift of approximately 2.7 eV to lower energy than expected from the uranyl ion. A shift in the edge to lower energy of this magnitude is often considered evidence for a reduced-metal

**Table I** The parameters obtained by fitting the EXAFS data from the glasses and the standards. N1/R1 are the coordination number and the corresponding distance of the 1st coordination shell,  $\sigma^2$  are the Debye Waller factors, and the Standard Deviation (S.D.), calculated from the  $K^3$  weighted data, were determined from  $S.D. = [S(A_{fit} - A_{data})^2/n]^{1/2}$ . The EXAFS data from the leached SRL-131 glasses are too noisy to fit.

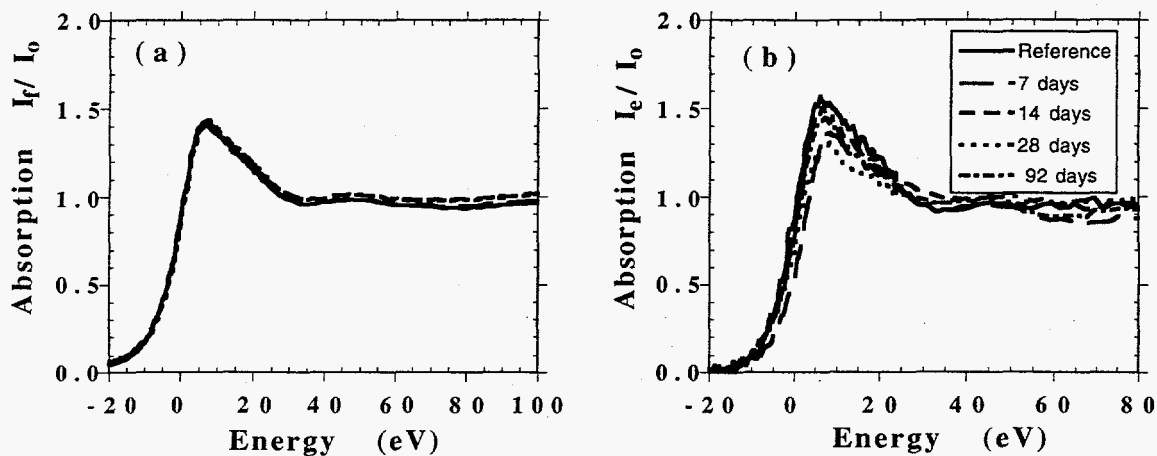
Sample	N1/R1 (Å)	N2/R2 (Å)	$\sigma^2/\sigma^2_2$ (Å <sup>2</sup> )	S. D. (K <sup>3</sup> )
SRL-131 -ref	2.1 O/1.86	4.5 O/2.29	0/.0019	0.3
-leached	NA	NA	NA	NA
ATM-1c -ref	1.7 O/1.85	3.9 O/2.28	0/.0019	0.36
-leached	3.2 O/1.84	2.7 O/2.28	0/.0019	0.49
<b>Standards</b>				
-UO <sub>2</sub>	8 O/2.38	12 U/3.864	.0062/.0052	0.5/0.12
-UO <sub>3</sub>	2 O/1.865	4 O/2.262	0/.0019	0.78
-NaUO <sub>2</sub> Ac <sub>3</sub>	2 O/1.788	6 O/2.450	.0040/.0084	0.28



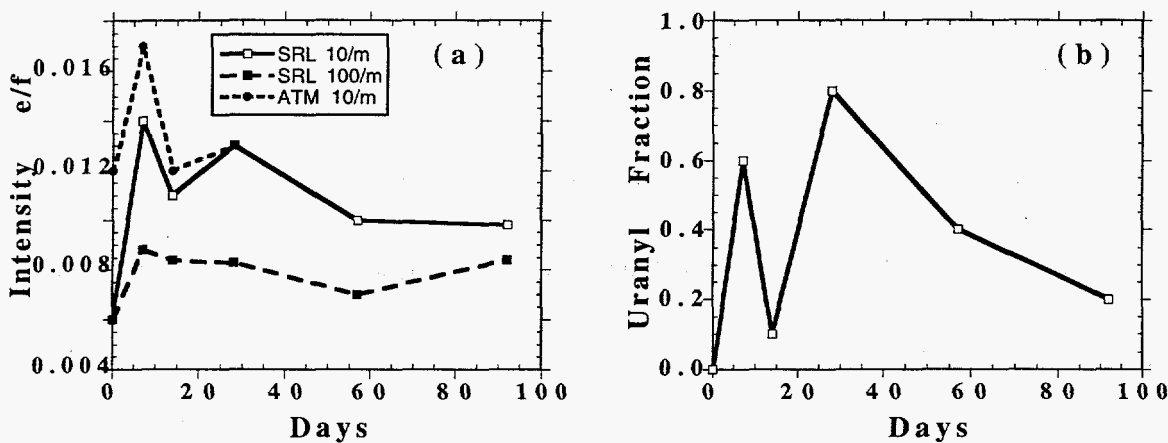
**Figure 2.** A comparison of the surface (e-yield) data obtained before and after leaching. The FT shows the presence of some uranyl.

species, which in this case would be expected to be U(IV). However the presence of a reduced uranium species in our samples is very unlikely based on the synthesis conditions of the glass, the presence of only Fe(III) [21] as evidenced by Mossbauer spectroscopy [22] and the EXAFS data from the same samples (see the comparison of EXAFS functions in Figure 1). A similar edge shift to lower energy has been previously reported in other studies of borosilicate glasses [2,14].

In contrast to the XANES from the bulk, the e-yield data in Figure 3b show marked changes near the surface with leaching times. This result is consistent with previous work, in which glancing angle X-ray absorption spectroscopy was used to show changes in U speciation at the surface of a glass after as little as 15 minutes exposure to leaching conditions [2]. The



**Figure 3.** (a) Fluorescence XANES from all the samples appear similar. These data lack the high energy shoulder indicative of the uranyl ion. In addition, the edge energy is lower than expected for uranyl. (b) changes in XANES with leaching times are attributable to increased uranyl ion.



**Figure 4.** (a) The normalized edge jump intensities, plotted as a function of time, obtained from the electron-yield data for three different samples. These data demonstrate changes are occurring in the leach-layer uranium concentration. (b) The fraction of total uranium in the leach layer that has converted to a uranyl-like speciation.

evolution of the spectra with leaching times involve changes in both uranium speciation and concentration. The changes in speciation can be modeled with an increase in the percentage of the total uranium present at the surface with uranyl-type coordination. The percentage of uranyl ion can be estimated by taking the initial unreacted XANES pattern, and adding to it a spectrum from the uranyl ion. This method models all of the XANES data well. In the SRL-131 surface layer probed by e-yield, up to 80% of the uranium is in the form of uranyl after 92 days of leaching, whereas approximately 30% of the U in the leach layer of the ATM-1c glass is present as the uranyl ion after 28 days of leaching.

In addition to the changes in the uranium coordination environment, the XANES data show evidence for changing total uranium concentration in the leach layer as a function of leach time.



The amplitude of the edge jump is proportional to the amount of the absorbing element contributing to the detector signal, therefore it is possible to evaluate changes in concentration within the experimental sampling depth. This is particularly interesting for the leached layer, for which changes in metal ion concentrations have been previously reported [2,23]. Using the fluorescence signal from each of the samples as a normalizing factor, the edge jump of the electron-yield signal provides an estimate of the uranium concentration within the leach layer. The magnitude of the e/f channel, plotted vs. leach time for all of the leaching sequences, is shown in Figure 4a. For both glasses there was an initial sharp rise for the 7 day samples followed by a gradual decrease for the longer times; however, in all leached glasses there was significant U enrichment in the near surface. The degree of surface enrichment depended on the SA/V ratio (the largest enrichment occurred for the largest volume of leachant) and the duration of the leach test. The initial U surface enrichment in the 4% UO<sub>2</sub> ATM-1c glass was 40%. The initial U surface enrichment in the 1.3% UO<sub>2</sub> SRL-131 glass series was 130% for the 10 m<sup>-1</sup> and 50% in the 100 m<sup>-1</sup> series. After 92 days the surface U enrichments of in the now thicker leach-layers for the same samples were 66% and 30%, respectively.

Our use of a novel combination of fluorescent x-ray and electron-yield technique has provided unique insight into the speciation of uranium in glass leach layers prior to dissolution. The x-ray channel probed the bulk and the electron channel probed the surface to a 1/e depth of 3000 Å. This effort extends metal-ion speciation to glasses that have undergone significant surface modification, conditions for which glancing-angle detection is not possible. We found that the speciation of U in two high Fe sodium-borosilicate glasses undergo a significant modification during leaching in water at 90° C, with leach periods from 7-92 days. We demonstrate that the U converts to a uranyl-like coordination at the surface. Within the hydration layer, the U was first concentrated and then converted to a uranyl moiety that was subsequently leached from the glass over a period of days. We argue that this conversion is necessary before the uranium dissolves into water as the uranyl, UO<sub>2</sub><sup>2+</sup> ion. The fraction of uranyl at the surface did not increase in a totally uniform manner with time, as shown in Figure 4b. Instead, there was appreciable scatter in the uranyl fraction. Some of the longer leach period surfaces had a greater fraction of uranyl than others as if the dissolution of uranyl was more rapid in some of the samples than others. This result is consistent with models that suggest that some of the leach layer spalls from the glass as colloids, although there is no direct evidence from the EXAFS of either U clustering or crystalline phase [24]. These results support the interesting possibility that U dissolution could be retarded if it could be kept from converting to a uranyl-type coordination.

## ACKNOWLEDGMENTS

We thank Dr. Mark Antonio for the Mossbauer data, and for help discussions. This work was supported by the US-DOE, BES-Chemical Sciences, under contract W-31-109-ENG-38. The efforts of RBG were supported by the U.S. DOE, BES, under Grant No DE-FG06-84ER45121.

For user support and synchrotron beamtime, we thank SSRL, which is funded by the Department of Energy.

## REFERENCES

1. F.W. Lytle, in *Applications of Synchrotron Radiation*, H. Winick, *et al.*, Editors. 1989, Gordon and Breach, p. 135.
2. G.N. Greaves, N.T. Barrett, G.M. Antonini, F.R. Thornley, B.T.M. Willis, and A. Steel, *J. Am. Chem. Soc.*, **111**, 4313 (1989).
3. T.A. Abrajano, J.K. Bates, A.B. Woodland, J.P. Bradley, and W.L. Bourcier, *Clays & Clay Minerals*, **38**, 537 (1990).
4. J.J. Mazer, J.K. Bates, B.M. Biwer, and C.R. Bradley, *Mat. Res. Soc. Symp. Proc.*, **257**, 73 (1992).
5. W.T. Elam, J.P. Kirkland, R.A. Neiser, and P.D. Wolf, *Phys. Rev. B*, **38**, 26 (1988).
6. T. Girardeau, M. Mimault, M. Jaouen, P. Chartier, and G. Tourillon, *Phys. Rev. B*, **46**, 7144 (1992).
7. B.M. Biwer, J.K. Bates, T.A. Abrajano, and J.P. Bradley, *Mat. Res. Soc. Symp. Proc.*, **176**, 255 (1990).
8. W.L. Bourcier, *Mat. Res. Soc. Symp. Proc.*, **112**, 3 (1991).
9. B. Grambow and D.M. Strachan, *Mat. Res. Soc. Symp. Proc.*, **112**, 713 (1991).
10. J.W. Wald, 1985, Pacific Northwest Laboratory.
11. *MCC-IP Static Leach Test Method, Nuclear Waste Materials Handbook* 1981, Materials Characterization Center.
12. O. Keski-Rahkonen and M.O. Krause, *At. Data Nucl. Data Tables*, **14**, 139 (1974).
13. The EXAFS Co. Pioche NV 89043.
14. P.G. Eller, G.D. Jarvinen, J.D. Purson, R.A. Penneman, R.R. Ryan, F.W. Lytle, and R.B. Gregor, *Radiochim. Acta*, **39**, 17 (1985).
15. J. Petiau, G. Calas, D. Petitmaire, A. Bianconi, M. Benfatto, and A. Marcelli, *Phys. Rev. B*, **34**, 7350 (1986).
16. W.H. Zachariasen, *Acta Crystallogr.*, **1**, 265 (1948).
17. S. Siegel, H.R. Hoekstra, and E. Sherry, *Acta Crystallogr.*, **20**, 292 (1966).
18. R.B. Gregor, F.W. Lytle, B.C. Chakoumakos, G.R. Lumpkin, and R.C. Ewing, *Mat. Res. Soc. Symp. Proc.*, **50**, 387 (1985).
19. L. Hench, D. E. Clark, and E.L. Yen-Bower, *Nucl. Chem. Waste Manag.*, **1**, 59 (1980).
20. E.A. Hudson, J.J. Rehr, and J.J. Bucher, *Phys. Rev. B*, **22**, 13815 (1995-I).
21. H.D. Schreiber, L.M. Minnix, G.B. Balazs, and B.E. Carpenter, *Phys. Chem. Glasses*, **25**, 1 (1984).
22. M.R. Antonio and L. Soderholm (unpublished).
23. H.D. Schreiber, G.B. Balazs, and T.N. Solberg, *Phys. Chem. Glasses*, **26**, 35 (1985).
24. X. Feng, E.C. Buck, C. Mertz, J.K. Bates, J.C. Cunnane, and D.J. Chaiko, *Radiochim. Acta*, **66/67**, 197 (1994).