Received by OSTI

AUG 1 9 1986 CONF-860608--4

# PHOTOELECTRON, NUCLEAR GAMMA-RAY AND INFRARED ABSORPTION SPECTROSCOPIC STUDIES OF NEPTUNIUM IN SODIUM SILICATE GLASS*

B. W. Veal, W. T. Carnall**, B. D. Dunlap,
A. W. Mitchell, and D. J. Lam
Materials Science and Technology Division
Argonne National Laboratory
Argonne, IL 60439

**Chemistry Division
Argonne National Laboratory
Argonne, IL 60439

MASTER

CONF-860608--4

DE86 014489

April 1986

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.

## 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.

Submitted for publication in the Proceedings of the World Congress on High Tech Ceramics (6th CIMTEC), June 23-27, 1986, Milan, Italy.

*Work supported by the U.S. Department of Energy, BES-Materials Sciences, under Contract W-31-109-Eng-38.

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

Title -> PHOTOELECTRON, NUCLEAR GAMMA-RAY AND INFRARED ABSORPTION SPECTROSCOPIC STUDIES OF NEPTUNIUM IN SODIUM SILICATE GLASS*

B. W. VEAL,[1] W. T. CARNALL,[2] B. D. DUNLAP,[1] A. W. MITCHELL,[1] and D. J. LAM[1]

[1]Materials Science and Technology Division, Argonne National Laboratory, Argonne, IL 60439 U.S.A.

[2]Chemistry Division, Argonne National Laboratory, Argonne, IL 60439 U.S.A.

SUMMARY

The valence state of neptunium ions in sodium silicate glasses prepared under reducing and oxidizing conditions has been investigated by the X-ray photoelectron, Mössbauer and optical absorption spectroscopic techniques. The results indicate that the Np ions are tetravalent in glasses prepared under reducing conditions and pentavalent in glasses prepared under oxidizing conditions.

INTRODUCTION

Alkali silicate glasses containing dissolved actinide elements U, Np, Pu and Am have been studied by a variety of experimental techniques to determine valence state(s) of the dissolved actinide ions (refs. 1-5). Apparently, properties of the glasses are strongly influenced by valence state, which is the case of U ions, depends on the sample preparation technique (refs. 1,4). Dissolution of $UO_2$ or $UO_3$ into sodium silicate glass melted in an atmosphere of oxygen or air produces a glass in which uranium appears only in the hexavalent state. In order to obtain dissolved tetravalent uranium ions, it is necessary to melt the glass in very reducing conditions. In contrast, the valence state of Pu ions in alkali silicate glass appears to be independent of melting atmosphere (refs. 3,4). These ions are tetravalent. [While both 3+ and 4+ Pu ions have been observed in X-ray photoelectron spectroscopy (XPS) (ref. 5), it appears that the lower valence state is formed in the near-surface region during measurement (ref. 4).] For Np ions, however, the existing valence states and conditions under which they appear in silicate glasses are less clearly resolved. Both Mössbauer (ref. 3) and XPS (refs. 4,5) data have been interpreted to show that the Np ions are tetravalent in silicate and borosilicate glasses. However, results obtained from EXAFS and

*Work supported by the U.S. Department of Energy, BES-Materials Sciences, under Contract W-31-109-Eng-38.

solubility studies suggested that the valence state of Np ions is normally 5+ and may be dependent on the melting conditions (ref. 6). In order to resolve this discrepancy, we have studied the valence state of Np ions in sodium silicate glasses prepared in oxidizing and reducing conditions using XPS, Mössbauer, and optical absorption spectroscopic techniques.

Title →

EXPERIMENTAL

The neptunium glasses were prepared by adding $NpO_2$ to a master batch of sodium silicate glass prepared by mixing appropriate amounts of $Na_2Co_3$ and $SiO_2$ in an argon atmosphere glove box and then melting the mix in air or flowing oxygen in a platinum crucible at 1250 C. The master batch was then powdered, mixed with the appropriate amount of $NpO_2$, remelted and held for several hours at 1250 C in flowing oxygen or a reducing $CO/CO_2$ atmosphere. The samples were cooled from 1250 C to room temperature in an argon atmosphere inside a glove box. To insure homogeniety, each Np-glass sample was then crushed, thoroughly mixed and remelted. This procedure was repeated four times. After the final melting, the samples were visually examined for gross color nonuniformity. If found, the samples were again crushed and melted. X-ray powder diffraction patterns were then taken to check for the presence of crystalline phases. Solubility limits were determined by the concentration dependent appearance of crystalline residues in the samples.

Compositions of the glass samples used in this study are listed in Table 1. For samples 3 through 9, varying amounts of $NpO_2$ were added to the sodium disilicate master batch. These samples were melted in oxygen. Samples 1 and 2 had the same premelt compositions, but sample 2 was melted under flowing oxygen and sample 1 in a $CO/CO_2$ atmosphere consisting of seven parts CO to one part $CO_2$. Samples for XPS, Mössbauer, and optical absorption measurements were cut from the same ingot with a diamond wafering saw using methanol as a coolant.

XPS data were taken on the glasses using a Physical Electronics Model 548 spectrometer modified for placement in a glove box. The modification allows the system to be used for studying radioactive samples. Spectra were taken using Al $K_\alpha$ radiation (1486.6 eV). The overall energy resolution of the spectrometer was ~1.2 eV when an analyzer pass energy of 25 eV was used. The spectrometer controls were interfaced to a Nicolet 1180 minicomputer providing automatic data acquisition and analysis capability. Bar samples were fractured in the ultra-high vacuum ($8 \times 10^{-10}$ torr) chamber of the spectrometer to expose clean surfaces for measurement.

For optical absorption measurements, discs 1-2 mm in thickness and 15 mm diameter were mounted in special holders which aligned the samples in a

TABLE 1

Compositions of Glass Samples.

Title →

| Sample number | Composition (mole fraction) | Melting atmosphere |
|---|---|---|
| 1 | $\{[(Na_2O)_{0.25}(SiO_2)_{0.75}]_{0.964}(TiO_2)_{0.036}\}_{0.98}(NpO_2)_{0.02}$ | $CO/CO_2 = 7$ |
| 2 | $\{[(Na_2O)_{0.25}(SiO_2)_{0.75}]_{0.964}(TiO_2)_{0.036}\}_{0.98}(NpO_2)_{0.02}$ | $O_2$ |
| 3 | $[(Na_2O)_{0.33}(SiO_2)_{0.67}]_{0.98}(NpO_2)_{0.02}$ | $O_2$ |
| 4 | $[(Na_2O)_{0.33}(SiO_2)_{0.67}]_{0.97}(NpO_2)_{0.03}$ | $O_2$ |
| 5 | $[(Na_2O)_{0.33}(SiO_2)_{0.67}]_{0.96}(NpO_2)_{0.04}$ | $O_2$ |
| 6 | $[(Na_2O)_{0.33}(SiO_2)_{0.67}]_{0.95}(NpO_2)_{0.05}$ | $O_2$ |
| 7 | $[(Na_2O)_{0.33}(SiO_2)_{0.67}]_{0.94}(NpO_2)_{0.06}$ | $O_2$ |
| 8 | $[(Na_2O)_{0.33}(SiO_2)_{0.67}]_{0.93}(NpO_2)_{0.07}$ | $O_2$ |
| 9 | $[(Na_2O)_{0.33}(SiO_2)_{0.67}]_{0.92}(NpO_2)_{0.08}$ | $O_2$ |

3/4 meter prism-grating recording spectrophotometer with scanning range 200-3000 nm. Some of the samples were placed in a low temperature dewar and spectra were acquired at liquid nitrogen (77 K) or liquid helium (4.2 K) temperatures. The low temperature spectra showed some band narrowing, but did not provide additional information to assist in the identification of Np ion valence states. Consequently, only the 298 K spectra are considered here. Details of the Mössbauer measurement techniques for actinide samples were discussed previously (ref. 7).

## RESULTS AND DISCUSSION

The solubility of $NpO_2$ in sodium silicate glasses depends strongly on the melting conditions. Melting under reducing conditions ($CO/CO_2 = 7$), the solubility of $NpO_2$ in sodium disilicate, at 1250 C, is less than three mole %. The solubility increases to 9 mole % under oxidizing conditions at the same melting temperature. This large difference in $NpO_2$ solubility is very similar to that reported for $UO_2$. The solubility of $UO_2$ in sodium disilicate is 5 mole % when prepared, at 1250 C, under the reducing conditions and ~30 mole % if prepared in the oxidizing atmosphere. The valence state of the uranium ions is +4 and +6 in the reduced and oxidized U-glasses, respectively (refs. 1,4).

Similarly, the glasses show high neptunium solubility when the preparation conditions favor a high Np oxidation state. These results suggest that, like the uranium glasses, Np ions occur in the glasses in different valence states (or mixtures of valence states) depending on the preparation conditions.

In addition to the solubility studies, spectroscopic measurements were taken to monitor the properties of selected samples listed in Table 1. In this paper, we present results only for samples 1 and 2 which show the contrast between oxidizing and reducing preparation conditions. In the spectroscopic measurements, differences observed between (oxidized) samples 2, 3, and 8 could be attributed to variations in signal intensity.

Title →

Mössbauer spectra, obtained at 4.2 K with the 60 keV resonance of $^{237}Np$, superscript using a $^{241}Am$ metal source, are shown in Fig. 1. The spectrum (a), obtained from the sample prepared under oxidizing conditions, shows electric quadrupole hyperfine splitting, while the spectrum (b), obtained from the sample prepared under reducing conditions, shows magnetic hyperfine splitting. This difference is a consequence of the different preparation conditions. For the reduced sample, slow paramagnetic relaxation effects lead to magnetic splittings. For the oxidized sample, stronger spin-spin interactions between Np ions may increase the spin relaxation rates to average out the magnetic hyperfine field and leave only a quadrupole splitting. Both samples show line broadenings due to the distribution of Np ion environments expected in a glass. While these complexities have prevented a detailed analysis, approximate isomer shifts are shown by the arrows in Fig. 1. These correspond to -9 mm/sec for Fig. 1(a) and +7 mm/sec for Fig. 1(b). Comparison with isomer shifts for known chemical compounds (ref. 7) shows that the ions are $Np^{4+}$ and $Np^{5+}$ for the reduced (b) and oxidized (a) cases, respectively.

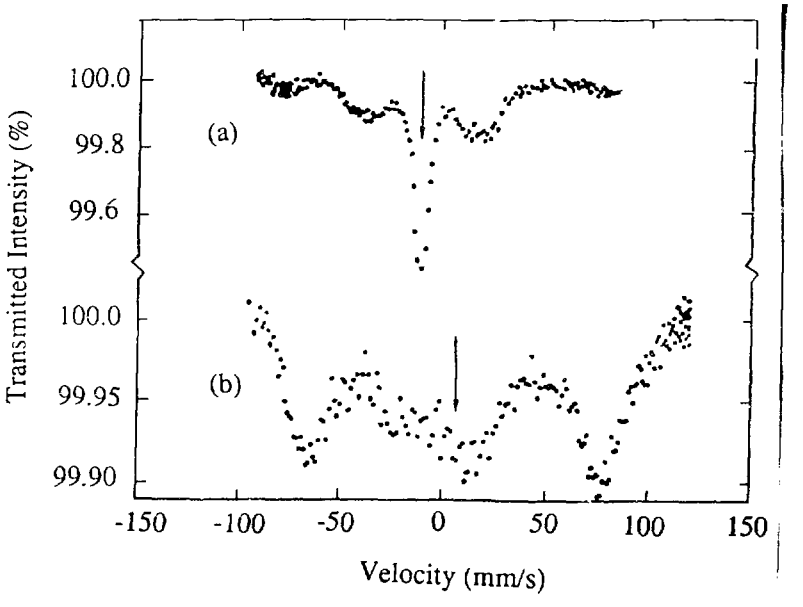


Fig. 1. $^{237}Np$ Mössbauer spectra for (a) oxidized glass and (b) reduced glass.

Karraker (ref. 3) obtained a $^{237}Np$ Mössbauer spectrum for a Np-doped air melted borosilicate glass which shows a single relatively broad resonance with an isomer shift which he assigned to a valence state of +4. This conclusion appears to conflict with the results for the simpler alkali silicates reported in this study where $Np^{5+}$ ions are identified in the air melted glasses. However, the apparent disagreement may be attributable to sample differences. Karraker's samples were complex, multicomponent borosilicates containing substantial quantities of boron and calcium in addition to alkalies. More systematic studies are needed to clarify this issue.

Figure 2(a) shows XPS spectra for Np 4f core levels of the oxidized glass (sample 2 of Table 1), and Fig. 2(b) shows results for the reduced glass (sample 1 of Table 1). The two spectra are identical except for small differences in line widths and satellite intensities. After careful comparison with Np 4f spectra from a series of Np oxide and oxyfluoride compounds (ref. 8), we assigned a valence state of +4 for the Np ions in both glasses. Figure 3 shows spectra for $NpO_2$ and $Np_2O_5$, typical 4+ and 5+ neptunium-oxygen compounds. The spectra are very different, particularly with respect to the nature of their satellites; binding energies of the 4f main lines are relatively unshifted. Recent work (refs. 8,9) has demonstrated that valence state information can be obtained from an analysis of XPS satellites, with the higher valence states generally being associated with higher binding energy satellites (as in Fig. 3). Comparison of Fig. 2 and Fig. 3 strongly indicates that XPS has monitored tetravalent Np ions in both samples. The slight broadening in Fig. 2(a) might indicate a small admixture of another valence state (presumably $Np^{5+}$).

The XPS results are in serious conflict with the Mössbauer results and would appear to be inconsistent with the solubility studies. As Fig. 3 demonstrates, XPS measurements are sensitive to the valence states of the dissolved actinide ions but the technique is very surface sensitive and in-situ reduction (during measurement) of high valence species is often observed (refs. 4,10). For example, while 3+ and 4+ Pu ions have been observed, by XPS, in alkali silicate glasses (refs. 4,5), it appears that the lower valence state develops in the near-surface region during the measurement process. This is a particularly worrisome issue in dilute actinide glasses where long data accumulation times are needed to acquire adequate signal-to-noise ratios. In (ref. 4), the reduction process of Pu ions was verified by temporarily monitoring XPS spectra, observing the growth of the 3+ valence state. However, for the glasses of Table 1, no in-situ reduction could be verified. Unlike the Pu ions, observation of the small binding energy shifts

Title →

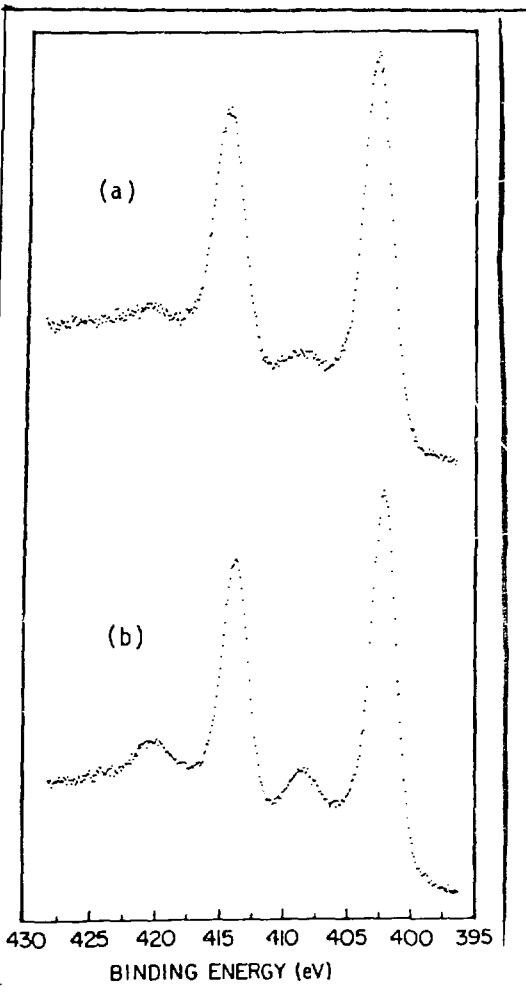


Fig. 2. XPS from Np4f levels for (a) oxidized glass and (b) reduced glass.

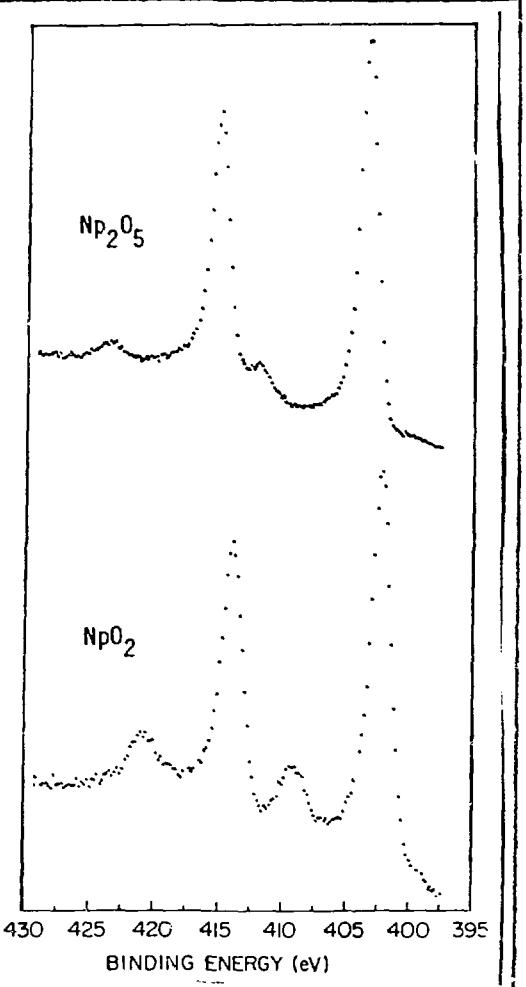


Fig. 3. XPS from Np 4f levels in $Np_2O_5$ ($Np^{5+}$) and $NpO_2$ ($Np^{4+}$).

of the main Np 4f XPS line corresponding to the different valence states (ref. 8) also requires long measurement times. (Note that Pu reduction could not have been readily monitored from a study of the satellites.) Thus, it seems likely that the spectra of Fig. 2 represent Np $4^+$ ions which appear in the near-surface region of the glasses but in a valence state that most probably developed during the course of measurement and is not characteristic of the bulk.

Figure 4 shows optical absorption spectra of the oxidized (a) and the reduced (b) glasses (samples 2 and 1 of Table 1, respectively). Consistent with the Mössbauer and solubility studies, these spectra show a strong dependence on the preparation conditions. After detailed comparison of the spectra of Fig. 4 with spectra obtained from samples of $Np^{4+}$ and $Np^{5+}$ compounds as well as with Np ions in aqueous solution, we conclude that the Np

ions are primarily pentavalent in the oxidized glass (a) and tetravalent in the reduced glass (b). Specifically, the $Np^{5+}$ ions in oxygen-containing environments exhibit the $NpO_2^+$ structure, which characteristically shows a very intense absorption band at ~1000 nm, a much less prominent band at 1100 nm, and a band centered at ~1600 nm (ref 11). These features correlate well with the spectra of Fig. 4a.

In the spectrum of Fig. 4b (reduced glass), the two broad absorption bands without a strong central absorption peak that occur between 1400-2000 nm strongly resemble the spectrum of the tetravalent Np compound $Np(OH)_2SO_4$ (ref. 12). Also, below 1300 nm, there is good correlation between the spectrum of the reduced glass and the spectrum of the $Np^{4+}$ ions in aqueous solution (ref. 11). The difference between $Np^{4+}$ and $Np^{5+}$ spectra is more pronounced for wavelengths greater than 1000 nm than for wavelengths less than 1000 nm as shown in Fig. 4.

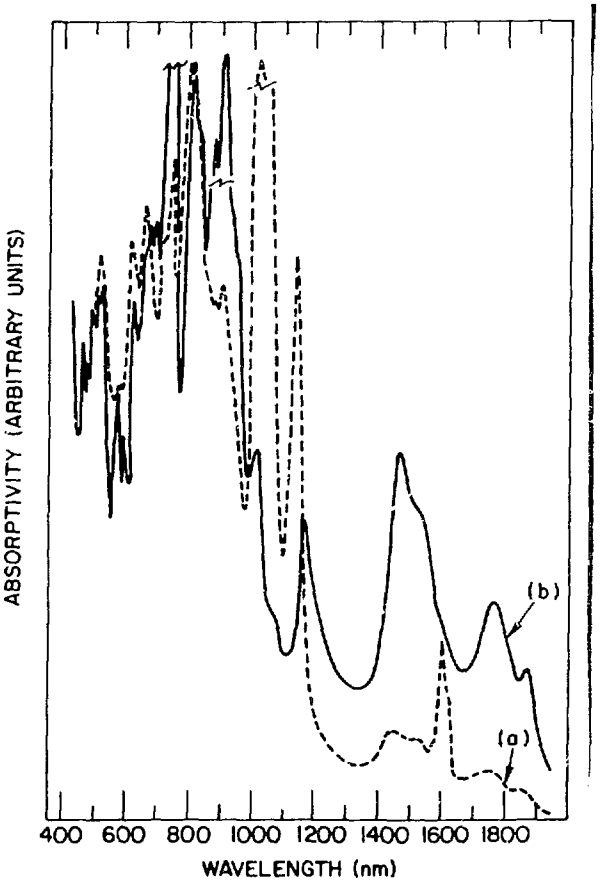


Fig. 4. Optical absorption spectra for (a) oxidized glass and (b) reduced glass.

The absorption spectra support the conclusion derived from Mössbauer and solubility studies that the different (oxidized and reduced) glasses contain Np ions in different valence states. Detailed comparison with standards also supports the valence state assignment from the Mössbauer studies. Apparently, XPS measurements on highly oxidized Np ions in dilute solution in alkali silicates are unreliable since reduction processes occur in the surface region of the sample on a time scale sufficiently short so that the high valence state cannot be monitored.

Title →

Results of solubility, Mössbauer, XPS, and optical absorption studies show that Np ions dissolved into alkali silicate glasses prepared under a reducing atmosphere are tetravalent. The dissolved Np ions are pentavalent when the glasses are melted in air or oxygen.

REFERENCES


1 D. J. Lam, B. W. Veal, H. Chen and G. S. Knapp, Bonding of metal oxides in sodium silicate glass, in G. J. McCarthy (Ed.), Scientific Basis for Nuclear Waste Management, Vol. 1, Plenum, NY, 1979, pp. 97-107.

2 A. T. Aldred, Magnetic susceptibility of sodium disilicate glasses containing $PuO_2$, J. non-cryst. solids 40 (1980) 347-352.

3. D. G. Karaker, Actinide valences in borosilicate glass, J. Am. Ceram. Soc. 65 (1982) 53-55.

4. D. J. Lam, B. W. Veal and A. P. Paulikas, X-ray photoemission spectroscopy study of uranium, neptunium and plutonium oxides in silicate-based glasses, in W. T. Carnall and G. R. Choppin (Ed.), ACS Symposium Series No. 216, Am. Chem. Soc, 1983, pp. 145-154.

5. D. P. Karim, D. J. Lam, H. Diamond, A. M. Friedman, D. G. Coles, F. Bazan and G. L. McVay, XPS valence state determination of Np and Pu in multi-component borosilicate glass and application to leached 76-68 waste glass surfaces, in: S. Topp (Ed.), Scientific Basis for Nuclear Waste Management, Elsevier, Amsterdam, 1982, Vol 6, pp. 67-73.

6. G. S. Knapp, B. W. Veal, A. P. Paulikas, A. W. Mitchell, D. J. Lam and T. E. Klippert, EXAFS studies of sodium silicate glasses containing dissolved actinides, in K. O. Hodgson, B. Hedman and J. E. Penner-Hahn (Ed.), EXAFS and Near Edge Structure III, Springer-Verlag, Berlin, 1984, pp 305-307.

7. B. D. Dunlap and G. M. Kalvius, Hyperfine studies in actinide series using Mössbauer resonance and angular correlation techniques, in A. J. Freeman and G. H. Lander (Ed.), Handbook on the Physics and Chemistry of the Actinides, North Holland, Amsterdam, 1985, Vol. 2, pp. 329-434.

8. B. W. Veal, W. T. Carnall, R. H. Banks, A. P. Paulikas and D. J. Lam unpublished.

9. B. W. Veal and A. P. Paulikas, Final state screening and chemical shifts in photoelectron spectroscopy, Phys. Rev. B 31 (1985) 5399-5416.

10. B. W. Veal and D. J. Lam, Photoemission spectra, in K. Buschbeck and C. Keller (Ed.), Gmelin Handbook of Inorganic Chemistry: Uranium, Springer-Verlag, Berlin, 1982, Suppl. to Vol. A5, pp. 176-210.

11. W. C. Waggoner, Measurement of absorption spectra of neptunium ions in heavy water solution from .35 to 1.85 microns, J. Phys. Chem. 62 (1958) 382-383.

12. D. W. Wester, J. Mulak, R. Banks and W. T. Carnall, The synthesis and characterization of neptunium hydroxysulfate, $Np(OH)_2SO_4$, J. Solid State Chem. 45 (1982) 235-240.