Karlsruhe Institute of Technology

Institute for Nuclear Waste Disposal (INE)

Comparative U, Np and Pu M edge high energy resolution X-ray absorption spectroscopy (HR-XANES) investigations of model and genuine active waste glass

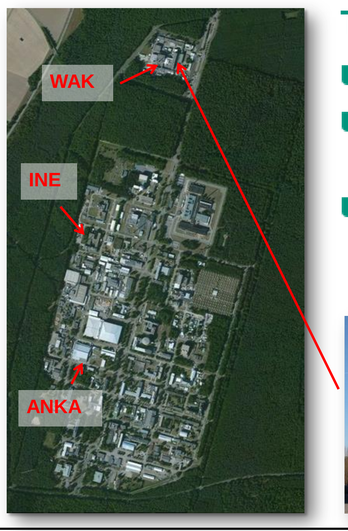
S. Bahl*[1], V. Koldeisz[1,2], E. Bohnert[1], E. González-Robles[1], D. Schild[1], B. Kienzler[1], K. O. Kvashnina[3], J. Rothe[1], K. Dardenne[1], J. Boshoven[4], L. Martel[4], I. Pidchenko[1], T. Prüßmann[1], G. Roth[1], H. Geckeis[1], T. Vitova[1]

[1]Karlsruhe Institute of Technology, Institute for Nuclear Waste Disposal, P.O. Box 3640, 76021 Karlsruhe, Germany, *e-mail: sebastian.bahl@kit.edu
[2]Department of Inorganic and Analytical Chemistry, Budapest University of Technology and Economics, H-1111 Budapest, Hungary
[3]European Synchrotron Radiation Facility, CS 40220, 38043 Grenoble Cedex 9, France
[4]European Commission, Joint Research Centre, Institute for Transuranium Elements, Karlsruhe, Germany

Motivation

High level waste (HLW) from nuclear fuel reprocessing is immobilized in borosilicate glass matrices to generate a disposable waste form [1]. The understanding of the long term behavior of "Verglasungseinrichtung Karlsruhe" (VEK) glass, or any other type of glass, requires a full and detailed characterization of the materials as-synthesized and during exposure to the environment. Industrial glasses are complex, and here we take a simplified separate effect approach to elucidate key structural properties and compare them for model glass and VEK glass sampled from the vitrification process of HLW. In particular, here we present a comparative investigation of U, Np and Pu oxidation states determined by U/Np/Pu M edge high energy resolution X-ray absorption near edge structure technique (HR-XANES) recently established at the INE-Beamline, supplemented by XPS and EXAFS investigations.

Background of VEK glass



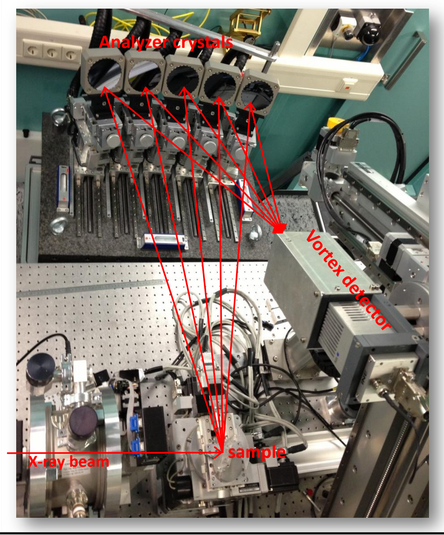
The Karlsruhe Reprocessing Plant (WAK):

- operated from 1971 to 1991 (reprocessing SNF)
- ~60 m^3 of highly active waste concentrates (HLW) stored on-site in liquid form
- Before decommissioning: HAWC vitrification

HLW vitrification plant (VEK):

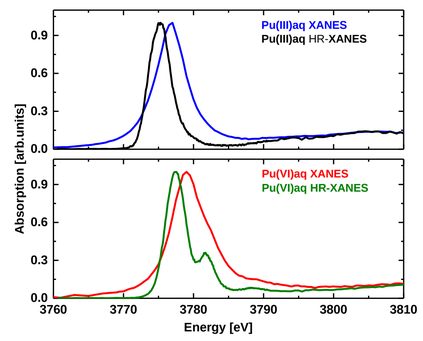
- Project start: 1996
- Cold test: April - July 2007
- Hot operation: Sep. 2009 – Nov. 2010
- 50 t of waste glass produced

The HR-XANES method

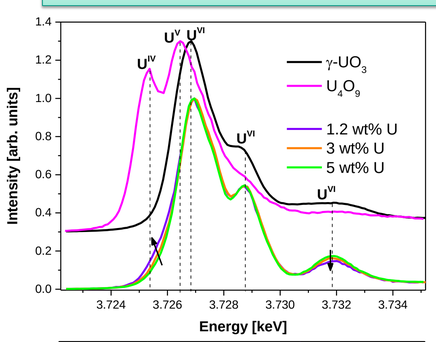


High energy resolution X-ray emission spectrometer

- Energy resolution: 0.5 – 2 eV
- New spectral features are revealed

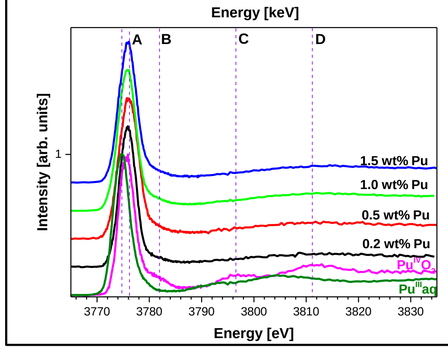


HR-XANES – U and Pu doped model glass



U doped model glass:

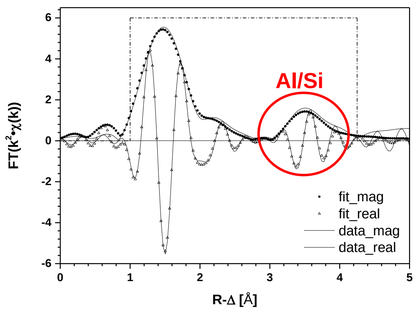
- U(VI) found
- Weak trend as a function of U loading
- Likely minor contribution of U(IV)
- Local structural distortion not found by EXAFS

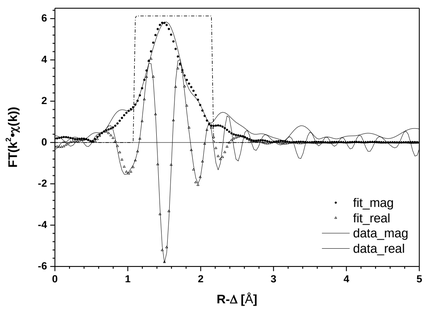


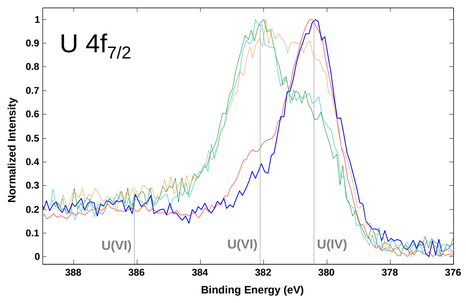
Pu doped model glass:

- Pu(IV) exclusively found
- No trend as a function of the Pu loading
- No formation of crystalline PuO_2 clusters

XPS and EXAFS – VEK and U doped model glass







VEK glass

- 2 O_{ax} @ 1.80 Å
- 5 O_{eq1} @ 2.27 Å
- 1.2 O_{eq2} @ 2.82 Å
- 2.6 **Al/Si** @ 3.97 Å

EXAFS:

- Significant differences in the second coordination shell

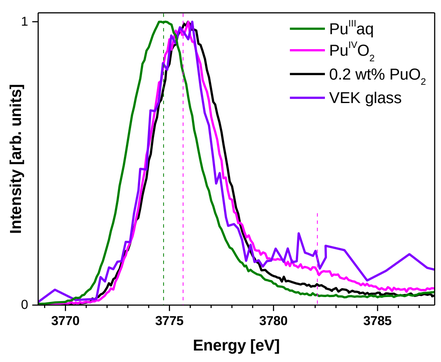
U model glass

- 2 O_{ax} @ 1.84 Å
- 5.4 O_{eq1} @ 2.29 Å
- 3 O_{eq2} @ 2.62 Å

XPS:

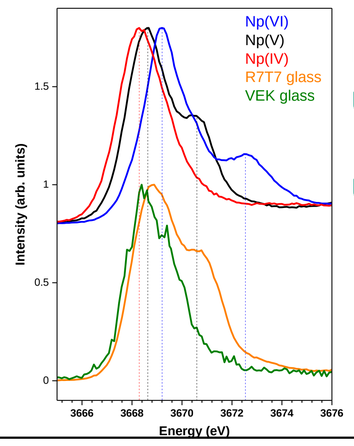
- U(IV) and U(VI) containing regions
- Strong U(VI)/U(IV) variations on the glass surface
- Similar U(VI) and U(IV) content for powder samples

HR-XANES - VEK glass



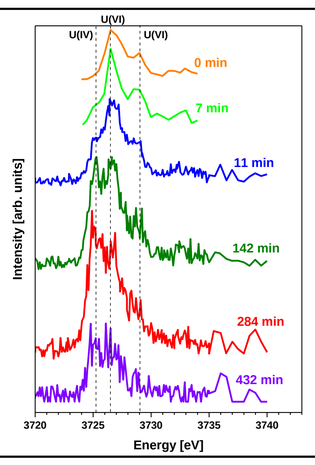
Pu M5 edge HR-XANES:

- Pu(IV) found
- Oxidation state similar for VEK and model glass
- Measurements with better statistics will verify presence of feature C (see Pu model glass)



Np M5 edge HR-XANES:

- R7T7 glass: Np(V) (neptunyl) dominates
- VEK glass: Np(IV) dominates



U M4 edge HR-XANES:

- Radiation damage after 10 min
- U(VI) reduction to U(IV)
  - Reversible?
- Takes place in VEK glass but not in U model glass
  - Redox partners?
  - Non found by EXAFS

Summary of results and raised questions

- Model and VEK glasses contain predominantly U(VI), Pu(IV) and Np(IV)/Np(V)?
- The oxidation state of U weekly depends on the U loading; no An-An interaction is found
- Can intrinsic radiation induce U reduction similar to the observed X-ray radiation damage?
- XPS and HR-XANES results indicate formation of U clusters with dominating U(IV) and U(VI) in the surface and in the bulk, respectively → verification of cluster formation by TEM
- U(IV) is not expected in the prepared in oxidizing conditions glass → possible redox partners of U are currently discussed

Reference

[1] R. J. Short, Möbus, G., Yang, G., Hand, R.J., Hyatt, N., Lee, W.E., *Materials Research Society Symposium Proceedings* **2004**.

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