Karlsruhe Institute of Technology

Institute for Nuclear Waste Disposal (INE)

High energy resolution X-ray absorption near edge structure spectroscopy investigations of highly active genuine VEK glass

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Goals

Highly radioactive liquid waste (HLW) from nuclear fuel reprocessing is commonly 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 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 reprocessed HLW performed in VEK. In particular, here we present an comparative investigation of U and Pu oxidation states determined by U/Pu M edge high energy resolution X-ray absorption near edge structure technique (HR-XANES) recently established at the INE-Beamline.

Preparation model glasses

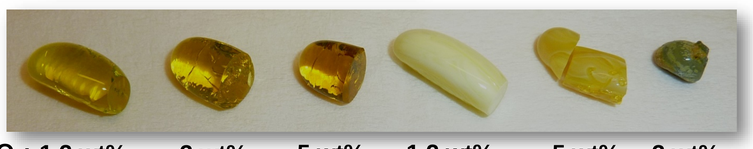
Borosilicate glass composition representing VEK glass

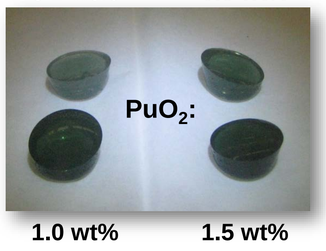
U bearing glasses:

- 1200 °C / 2 h, air
- Amorphous and MoO_3-crystalline glass

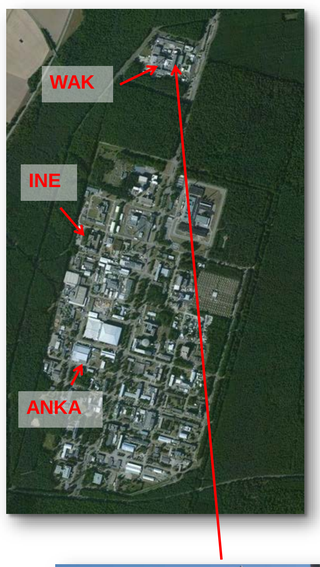
Pu bearing glasses:

- 1200 °C / 3h, 600 °C / 3h, air
- Amorphous glass





Background of VEK glass



The Karlsruhe Reprocessing Plant (WAK):

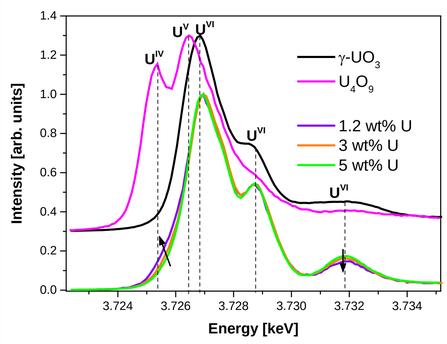
- operated from 1971 to 1991 (reprocessing SNF)
- ~60 m^3 of highly active waste concentrates (HAWC) stored on-site in liquid form
- Before decommissioning: HAWC vitrification

HAWC vitrification plant (VEK):

- Project start: 1996
- Cold test: April - July 2007
- Hot operation: Sep. 2009 – Nov. 2010

	Design data	Operating data
HLLW (m^3)	60	55
Waste glass (t)	50	48.8 (140 canisters)
Waste oxides (wt. %)	16	16.3
Operating time (months)	18	9

HR-XANES – model glasses

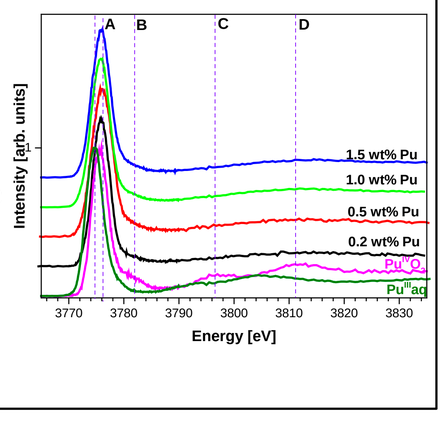


U model glass:

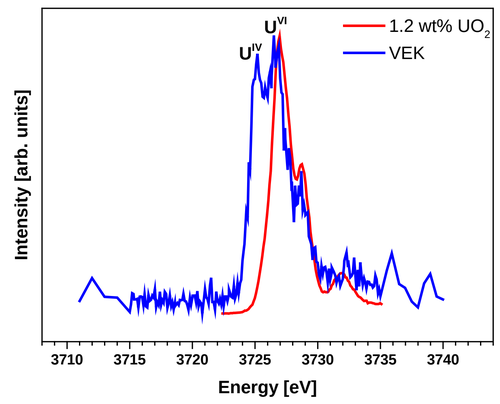
- U(VI) found
- Weak trend as function of U loading
- Likely small contribution of U^{IV}/U^{V}
- Local structural distortion? → EXAFS

Pu model glass:

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

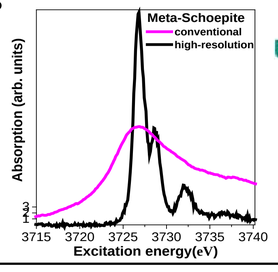


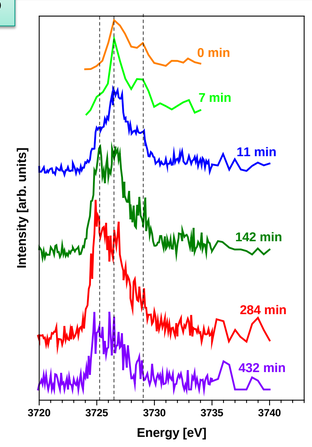
HR-XANES - VEK glass



U M4 edge XANES:

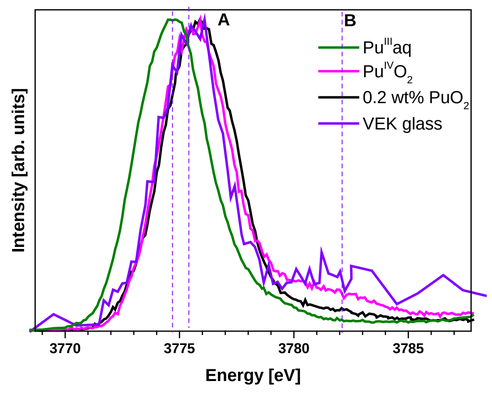
- Spectra show U(IV) (radiation damage!)
- U(VI) dominates





Radiation damage:

- Within first 142 min
- U(VI) reduction to U(IV)
  - Reversible?
- Takes place in VEK glass exclusively, not in U model glass
  - Redox partners?



Pu M5 edge 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)

Conclusion

- Model glasses and VEK glass form comparable An species: U(VI) and Pu(IV)
- Trend in HR-XANES spectra as function of the U loading → local structural distortion?
- No Pu-Pu interaction
- HR-XANES M edge spectroscopy is suitable method to determine An oxidation states in glass matrices

Reference

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

Acknowledgement

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