Identification of Uranium Oxychloride Phases in Uranium Chlorides with Wavelet-transformed EXAFS

Seokjoo Yoon, Seungmo Yeon, Jong-Il Yun*
Department of Nuclear and Quantum Engineering, KAIST, Korea
**Corresponding Author: jiyun@kaist.ac.kr*

***Keywords : Uranium chloridem, Uranium oxychloride, Wavelet-transformed EXAFS**

1. Introduction

Molten salt reactors (MSRs) utilize molten salt as a reactor fuel. Chloride molten salt reactors, which employ uranium(III) chloride (UCl_3) as fuel, are widely being investigated for their advantages in fast neutron spectrum operation and high actinide solubility [1]. However, due to the hygroscopic nature of the chloride salts, the UCl_3 can be easily oxidized to oxychlorides such as UOCl, $UOCl_2$, etc. These impurities can interact with the salt or degrade the material, resulting in negative impacts on the operation of chloride molten salt reactors.

Extended X-ray absorption fine structure (EXAFS) spectroscopy can be employed to identify the elements—such as oxygen or chlorine—bonded to uranium in oxychlorides and chlorides. The analysis of EXAFS enables the determination of both the types of neighboring atoms and their respective bond distance. Therefore, applying EXAFS to uranium chlorides can verify whether the oxygen impurities are bound to uranium or not.

For EXAFS analysis, the Fourier-transform based method (FT-EXAFS) has been widely adopted. However, a primary limitation of FT-EXAFS is its insufficient resolution to distinguish between different bonds with similar lengths. For uranium chlorides and oxychlorides, the U-Cl distance of UCl_3 is about 2.9 to 3.0 Å [2], while the U-Cl distance from UOCl is also about 3.0 Å [3]. Consequently, an alternative approach is required to resolve these overlapping U-Cl scattering paths in uranium chloride salts.

One of the techniques that can distinguish the different bonds with similar distances in EXAFS is applying wavelet-transformed EXAFS (WT-EXAFS). Unlike the one-dimensional (1D) transformation of k-space to R-space in FT-EXAFS, WT-EXAFS performs a two-dimensional (2D) transformation, providing a simultaneous visualization of the signal in both k-space and R-space [4]. This dual-space representation enables the resolution of overlapping peaks by exploiting the k-dependence of the scattering atoms, even when their R-space positions are nearly identical.

This study investigated the application of WT-EXAFS to distinguish different U-Cl scattering paths in uranium chloride samples. After synthesizing the uranium chloride samples, WT-EXAFS was applied to identify if any oxychloride phases were present as impurities in the sample.

2. Methods

2.1. Preparation of U(III) compound

The synthesis of U(III) compound was performed in two steps: reduction of uranyl nitrate hexahydrate (UNH) to U(IV) with hexachloropropene (HCP), and reduction of U(IV) to U(III) with $ZrCl_4$ and Zr.

UNH (Fluka, puriss. p.a.) was dried at 180℃ for 24 hours to remove moisture, and the dried compound was mixed with HCP and heated up to 180℃ for 12 hours. Then it was cooled down to room temperature and washed with dichloromethane (CH_2Cl_2, DCM) to remove residue. The EXAFS analysis of this compound, shown in Fig. 1., indicated the presence of uranium oxychloride phases ($UOCl_2$) in this compound [5].

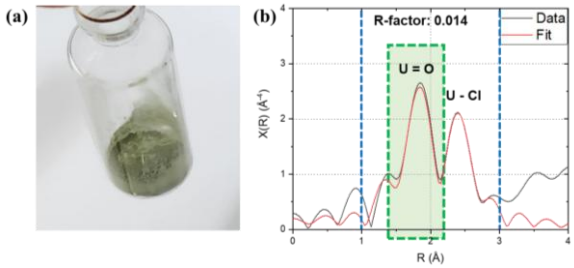

Fig. 1. (a) Synthesized U(IV) compound and (b) EXAFS analysis of the U(IV) compound

The U(IV) was then further reduced to U(III) using Zr^{4+} and Zr metal. To reduce U(IV) to U(III) and also remove O from U(IV), $ZrCl_4$ and Zr metal were both used. As $ZrCl_4$ sublimes at temperatures below 400℃, $ZrCl_4$ was first mixed with NaCl and heated up to 400℃ gradually in glovebox, forming Na_2ZrCl_6 which is less volatile than pure $ZrCl_4$. Then the Zr metal was inserted in the mixture of synthesized Na_2ZrCl_6 and U(IV) compound at 600℃, with different Zr(IV) to U(IV) ratios (1:2 and 1:0.5). The synthesized compound was found to be NaU_2Cl_6 from XRD (Fig. 2.), a U(III) compound for NaCl-containing salt.

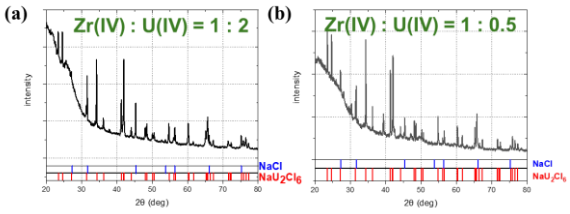

Fig. 2. XRD results of NaU_2Cl_6 synthesized with Zr(IV) to U(IV) ratio of (a) 1:2 and (b) 1:0.5

2.2. EXAFS spectrum measurements and analysis

To measure the EXAFS of synthesized NaU_2Cl_6, the sample was ground with a mortar and pestle, and then mixed with BN powder with a NaU_2Cl_6 to BN ratio of 1 to 4. This was then pelletized using a hydraulic press, and the pellet was sealed with Kapton tape to minimize the intrusion of H_2O and O_2.

The sealed pellets were then measured with a laboratory-based X-ray absorption spectroscopy system (hiXAS, HP spectroscopy). The blank measurement (I_0) was performed for 4 hours, and sample measurement (I) was performed for 16 hours. The energy value was calibrated with Y_2O_3 (E_0 = 17,050 eV). The FT-EXAFS was performed with the Demeter software package [6]. For the WT-EXAFS analysis, the HAMA software package was utilized [4].

4. Results and Discussion

First, the analysis of the EXAFS of the NaU_2Cl_6 compound was performed with conventional Fourier-transformed (FT-EXAFS) method, as shown in Fig. 3. Although the XRD patterns of the two experimental samples were identical, their EXAFS spectra revealed significant differences. The compound synthesized with lower Zr(IV) content could not be fitted to the U-Cl bond of NaU_2Cl_6, yielding an R-factor of 0.038 – much higher than the accepted threshold of 0.02 for reliable EXAFS analysis. This discrepancy suggests the presence of additional peaks overlapping within the same region. Meanwhile, the sample synthesized with a higher Zr(IV) ratio achieved an R-factor of 0.008, indicating that this peak corresponds to U-Cl bonds from NaU_2Cl_6.

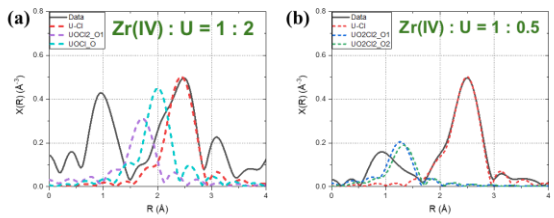

Fig. 3. FT-EXAFS of NaU_2Cl_6 synthesized with Zr(IV) to U(IV) ratio of (a) 1:2 and (b) 1:0.5

To further analyze the EXAFS results of the synthesized compounds, Fig. 4. presents the WT-EXAFS of the synthesized compounds. For the sample with lower Zr(IV) amount (Zr(IV):U(IV) = 1:2), two distinct contours are observed in the region of U-Cl bond (R in 2 - 3 Å), indicating the presence of at least two different types of U-Cl bond are present in this sample. In contrast, sample synthesized with higher Zr(IV) ratio showed only a single contour, corresponding to the U-Cl bond from NaU_2Cl_6. By comparing the experimental spectrum with the simulated WT-EXAFS of U-Cl bond from different uranium chloride and oxychlorides, the additional contour in the sample with lower Zr(IV) content is expected to be the U-Cl bond from UOCl, as shown in Fig. 5.

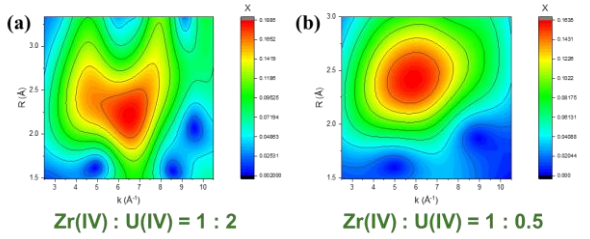

Fig. 4. WT-EXAFS of NaU_2Cl_6 synthesized with Zr(IV) to U(IV) ratio of (a) 1:2 and (b) 1:0.5

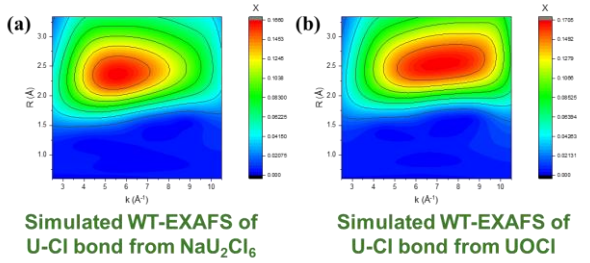

Fig. 5. Simulated WT-EXAFS of U-Cl bond from (a) NaU_2Cl_6 and (b) UOCl

5. Conclusion

This study demonstrated the efficacy of WT-EXAFS for characterizing NaU_2Cl_6 synthesized with different Zr(IV) to U(IV) ratios. Compared to higher Zr(IV) ratio where only U-Cl bond from NaU_2Cl_6 was observed, the analysis for the lower Zr(IV) ratio revealed the presence of oxychloride impurities, evidenced by the two distinct contours in the U-Cl peak region. These findings confirm that WT-EXAFS can successfully resolve overlapping U-Cl bond distances from distinct compounds. Furthermore, this approach provides a robust method for identifying oxychloride contamination in uranium chloride salts."

Acknowledgement

This research was supported by the Nuclear Safety Research Program through the Korea Foundation Of Nuclear Safety (KoFONS) using the financial resource granted by the Nuclear Safety and Security Commission (NSSC) of the Republic of Korea (RS-2025–02220594).

REFERENCES

[1] D. E. Holcomb, G. F. Flanagan, B. W. Patton, G. C. Gehin, R. L. Howard, T. J. Harrison, Fast Spectrum Molten Salt Reactor Options, ORNL/TM-2011/105 (2011).

[2] J. C. Taylor, P. W. Wilson, The structure of uranium(iii) trichloride by neutron diffraction profile analysis. Acta Crystallogr. B. 30(12) (1974) 2803-2805

[3] J. C. Levet, H. Noel, Synthesis, crystallographic and magnetic properties of the trivalent uranium oxyhalides UOCl, UOBr, and UOI, J. Inorg. Nucl. Chem. 43(8) (1981) 1841-1843
[4] H. Funke, A.C. Scheinost, M. Chukalina, Wavelet analysis of extended x-ray absorption fine structure data, Phys. Rev. B Condens. Matter Mater. Phys. 71(9) (2005) 094110
[5] S. Yeon, S. Yoon, J. W. Park, J. Jung, J.-I. Yun, Synthesis and characterization of uranium chlorides for molten salt reactors using hexachloropropene, (2025) 2025 KRS Autumn meeting, Nov 13 -14
[6] B. Ravel, M. Newville, ATHENA, ARTEMIS, HEPHAESTUS: data analysis for X-ray absorption spectroscopy using IFEFFIT, J. Synchrotron Radiat., 12(4) (2005) 537-541