

Synchrotron X-ray Absorption Spectroscopic Investigation of Uranyl-Chloride Aqueous Solutions at Hydrothermal Conditions

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Understanding chemical speciation and coordination of actinides in aqueous solutions at hydrothermal conditions is crucial to addressing a variety of environmental issues surrounding actinides such as their mobility at conditions of nuclear accidents (e.g. Fukushima disaster) and their behavior in high-level nuclear waste disposal in underground repositories. Of specific interest are actinide-bearing aqueous solutions containing ligands potentially found in these environments such as Cl⁻, SO₄²⁻, and CO₃²⁻ which can complex with actinide ions at high temperatures and pressures.

The coordination environment of UO₂²⁺ was probed with a combination of theoretical modeling and X-ray absorption spectroscopy (XAS), a powerful tool to characterize oxidation state and coordination environments. In this study, we performed *in-situ* U L-III edge XAS measurements on UO₂²⁺-Cl⁻ aqueous solutions ([UO₂²⁺]=50mM, [Cl⁻]=1M, 3M, 6M) at the Advanced Photon Source and the Stanford Synchrotron Radiation Lightsource. Room temperature to 500 °C was explored using a hydrothermal diamond anvil cell with a specially designed radiation enclosure [1]. Our theoretical modeling using density functional theory (DFT) predicts that at 25°C, UO₂²⁺ coordinates with 5 equatorial H₂O surrounding the U atom whereas at increased temperatures, the calculations predict Cl⁻ to coordinate, replacing the H₂O. Using the DFT optimized models, analysis of the extended X-ray absorption fine structure region (EXAFS) below 200°C revealed a change in chemical coordination of the UO₂²⁺ from 5-coordinated H₂O to 3-4-coordinated H₂O and 1-2-coordinated Cl⁻. At temperatures above 200°C, examination of the X-ray absorption near edge structure (XANES) region of our XAS spectra, we observed a possible X-ray induced reduction from U⁶⁺ to U⁴⁺.

[1] Dhakal *et al.* (2019) *Rev. Sci. Instrum.* 90, 083108.