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| <br>ROBL-CRG   | <b>Experiment title:</b><br>Spectroelectrochemical cell for in situ XAS measurements of uranium solution species | <b>Experiment number:</b><br>20-01-618   |
|   | <b>Beamline:</b><br>BM 20  | <b>Date of experiment:</b><br>from: 31. 01. 07      to: 03. 02. 07<br>16. 05. 07           17. 05. 07<br>02. 11. 07           03. 11. 07 |
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Actual, the speciation and complex formation of U(IV) in sulfuric media is not well understood. The current NEA thermodynamic database reports only two sulfate species,  $\text{USO}_4^{2+}$  and  $\text{U}(\text{SO}_4)_2(\text{aq})$ . This was the motivation to use a spectro-electrochemical cell to perform *in situ* EXAFS measurements under anoxic conditions while and maintaining uranium in reduced oxidation state. Figure 1, left side, shows the FT of EXAFS spectra of 50 mM U(IV) in sulfate media with increasing  $[\text{SO}_4]^{2-}$  at pH 1.

The pure U(IV) hydrate is coordinated by nine water molecules with a U-O distance of 2.40 Å. The Fourier transformed spectrum of U(IV) sulfate comprises two additional peaks at 3.08 Å and 3.67 Å, indicative of bidentate and monodentate sulfate groups, respectively. Figure 1, right side, shows the coordination number  $N_{S_{bid}}$  and  $N_{S_{mon}}$  as a function of the sulfate concentration. The coordination number  $N_{S_{bid}}$  increases, whereas  $N_{S_{mon}}$  decreases with increasing  $[\text{SO}_4^{2-}]$ . Hence, with increasing sulfate concentration the bidentate coordination becomes more dominant. In consequence, U(IV) in acidic solutions with high sulfate concentration can be coordinated by 4 and 5  $\text{SO}_4^{2-}$  molecules. EXAFS can provide the coordination number and the type of sulfate coordination, but not the spatial arrangement of the ligands.

Therefore, in further experiments, where the pH value has been restricted to 1.5, single crystals have been grown from this solution with the aim to preserve the solution species in the crystal structure [1]. The obtained compound  $\text{Na}_{1.5}(\text{NH}_4)_{4.5}[\text{U}(\text{SO}_4)_5 \cdot \text{H}_2\text{O}] \cdot \text{H}_2\text{O}$  crystallizes in the triclinic space group  $P\bar{1}$  with

two  $[\text{U}(\text{SO}_4)_5 \cdot \text{H}_2\text{O}]^{6-}$  units in the unit cell. In this structure U(IV) is coordinated by 2 monodentate and 3 bidentate sulfate ions and one water molecule. This coordination may represent the coordination geometry of the solution species. The high coordination numbers of 4 and 5 sulfate groups which have been observed can count for a high solubility and stability of U(IV) sulfate in aqueous solution which may enforce the migration of uranium in an low pH environment.

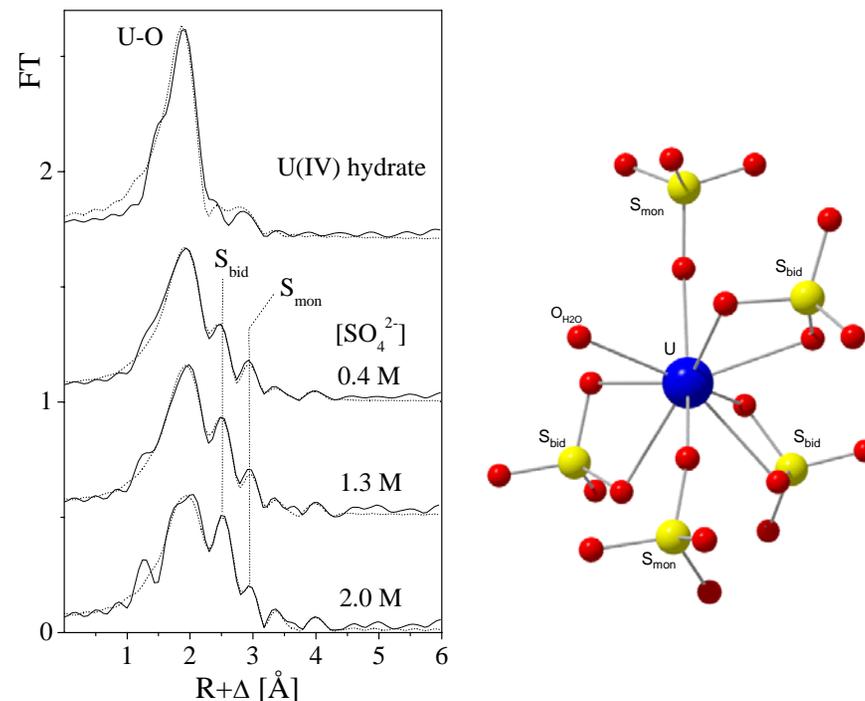


Fig. 1: Left side: Fourier transform of U  $L_3$ -edge  $k^2$ -weighted EXAFS data of U(IV) hydrate and sulfato species. Right side: Coordination of the  $[\text{U}(\text{SO}_4)_5 \cdot \text{H}_2\text{O}]^{6-}$  unit.

[1] Hennig, C., Kraus, W., Emmerling, F., Ikeda, A., Scheinost, A.C. Coordination of a uranium(IV) monomer in aqueous solution and in solid state *Inorg. Chem.* **47** (2008) 1634-1638.