



Experiment title:
Comparative investigation of the uranium complexation onto γ -Al₂O₃ by means of FT-IR and EXAFS spectroscopy

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CH-3205

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Report:

For a better understanding of the sorption mechanisms of uranium(VI) on solid alumina oxide (γ -Al₂O₃) phases, structural information on a molecular level of the surface complexes is needed. In our recent comprehensive studies on γ -Al₂O₃, the formation of different surface complexes as a function of different surface loadings was found between the actinyl ions and the solid phase using *in situ* infrared (IR) spectroscopy. From the spectral data with increasing U(VI) concentration at the alumina-water interface, monomeric and oligomeric surface complexes and the formation of a surface precipitate was deduced. Furthermore, the data evidence the contribution of atmospheric carbonate during surface complexation reactions. Because of overlapping bands in the IR spectra obtained, possibly generated by the aqueous species and the surface precipitate, further information of the molecular structures is required. In particular, a confirmation of the vibrational spectroscopic findings of surface precipitation and polymerization at different U(VI) loading rates of the solid phase was a main goal of the EXAFS experiments.

A series of batch samples of sorbed U(VI) onto γ -Al₂O₃ was prepared in presence of atmospheric carbonate, showing different degree of U(VI) loading. These samples were expected to reflect the different stages of the sorption processes in analogy to the IR spectra recorded *in situ*.

RESULTS. EXAFS spectra of a sufficiently high quality for factor analysis (FA) [1] were obtained from all samples. Considering the γ -Al₂O₃ sorption samples with increasing U(VI) loading of the solid phase (samples 3-11, Fig 1), three different single components could be extracted from FA. For the characterization of these components, several reference spectra from the data pool were tested. A sufficient reproduction of the data was obtained by assigning the three components to a mononuclear edge sharing (ES) surface complex, to the aqueous UO₂(CO₃)₃⁴⁻ complex and to meta-schoepite (Fig. 1), respectively.

Furthermore, the set of reference spectra allows the quantification of the species for each sorption sample by iterative target testing (Fig. 1, right) [1]. It is found that the ES complex is the dominant species in all

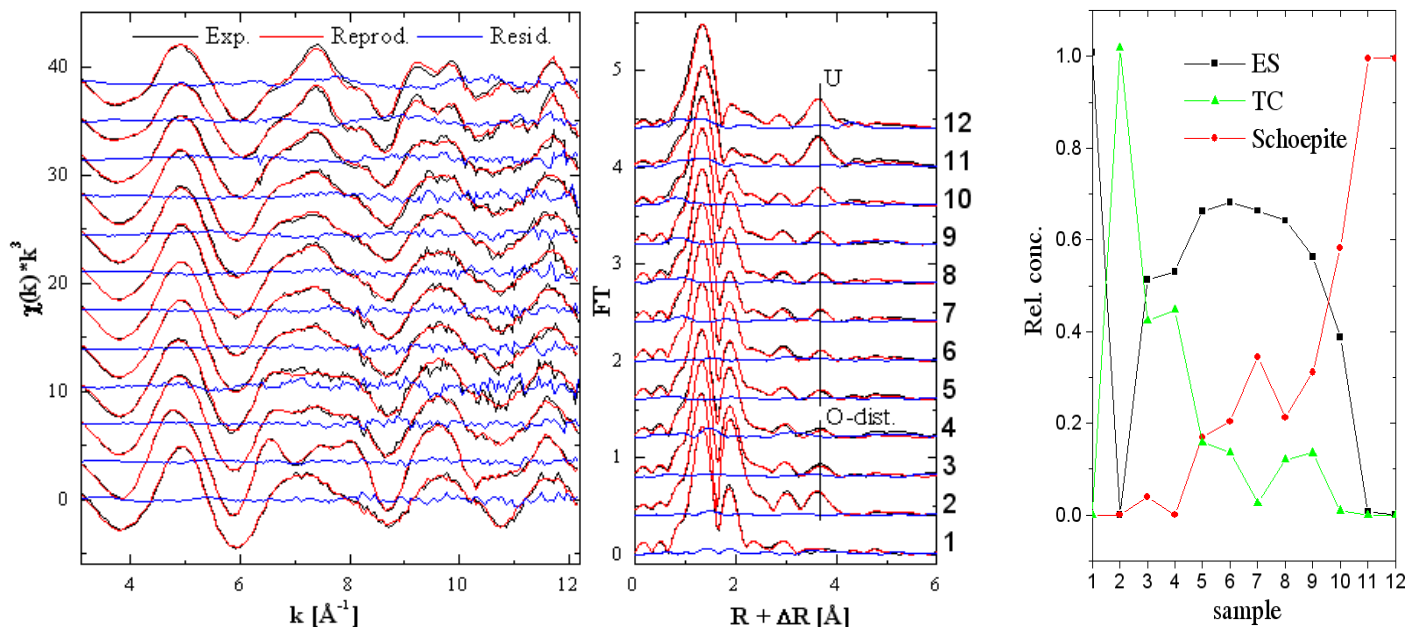


Fig. 1: EXAFS spectra (left panel) and the corresponding Fourier transforms (FT) (middle panel) of the batch samples of U(VI) on γ -Al₂O₃ and reference spectra with their FA reproduction and residuals. References: sample 1: mononuclear edge sharing complex (ES), sample 2: aqueous UO₂(CO₃)₃⁴⁻ (TC), sample 12: meta-schoepite. Samples 3-11 represent the investigated γ -Al₂O₃ sorption samples with increasing U(VI) loading of the solid phase. The vertical line in the FT shows special features/interactions: “U” - uranium, “O-dist.” distal oxygen atom of a bidentately coordinated carboxylic group. The relative concentrations of the three components in the samples obtained by FA are shown in the right panel.

γ -Al₂O₃ samples, except for the sample with the highest U(VI) loading (sample 11, Fig. 1, right) where the formation of meta-schoepite as a surface precipitate becomes predominant. In addition, in samples 3 and 4, that is at very low U(VI) loading, a sorbed ternary carbonato complex (TC) contributes strongly in addition to the ES complex.

The results of the EXAFS experiments generally confirm our conclusions drawn from recent IR spectroscopic investigations from which the formation of an inner-sphere complex was derived during the first minutes after induced sorption. Now, this complex is identified as an ES complex by EXAFS. Contributions from carbonate anions to the surface speciation were also suggested from IR spectroscopy [2] and are now confirmed for very low surface coverage of U(VI). However, the presence of a TC complex implies a strongly red shifted uranyl band in the IR spectra which was actually not observed. The EXAFS results make it mandatory to reevaluate our IR data recorded at a very early point of time after induced sorption. Alternatively, the formation of the TC complex is characteristic for batch samples used for EXAFS. The main goal of this proposal, the unequivocal identification of the surface precipitate (schoepite) observed *in situ* at prolonged U(VI) sorption by IR spectroscopy, was attained by the EXAFS spectra of the sample with the highest U(VI) accumulation at the alumina-water interface (sample 11, Fig. 1, right). In addition, homologies of the EXAFS shell fit structural parameter of the ES and TC complex were found for the U(VI)- γ -Al₂O₃ and the U(VI)-ferrihydrite sorption systems [3].

REFERENCES.

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