



	Experiment title: Comparative investigation of the uranium complexation onto γ-Al₂O₃ by means of FT-IR and EXAFS spectroscopy	Experiment number: 20-01 699
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Report:

For a better understanding of the sorption mechanisms of uranium(VI) on solid alumina oxide phases, structural information on a molecular level of the surface complexes is needed. In our recent comprehensive studies, a dependence between the formation of different surface complexes and the contact time was found between the actinyl ions and the solid phase using in situ infrared spectroscopy. From the spectra, an outer-sphere coordination followed by surface precipitation or polymerization was deduced.

However, because of overlapping vibrational bands in the IR spectra obtained, generated as well by aqueous species and 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 higher U(VI) loading rates of the solid phase was a main goal of the EXAFS experiments.

Therefore, a series of batch samples of sorbed U(VI) onto alumina was prepared 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.

RESULTS

Five out of six samples provided EXAFS spectra of a sufficiently high quality for factor analysis (FA). Figure 1 shows the EXAFS spectra obtained and the corresponding FT's. The amount of U(VI) sorbed onto

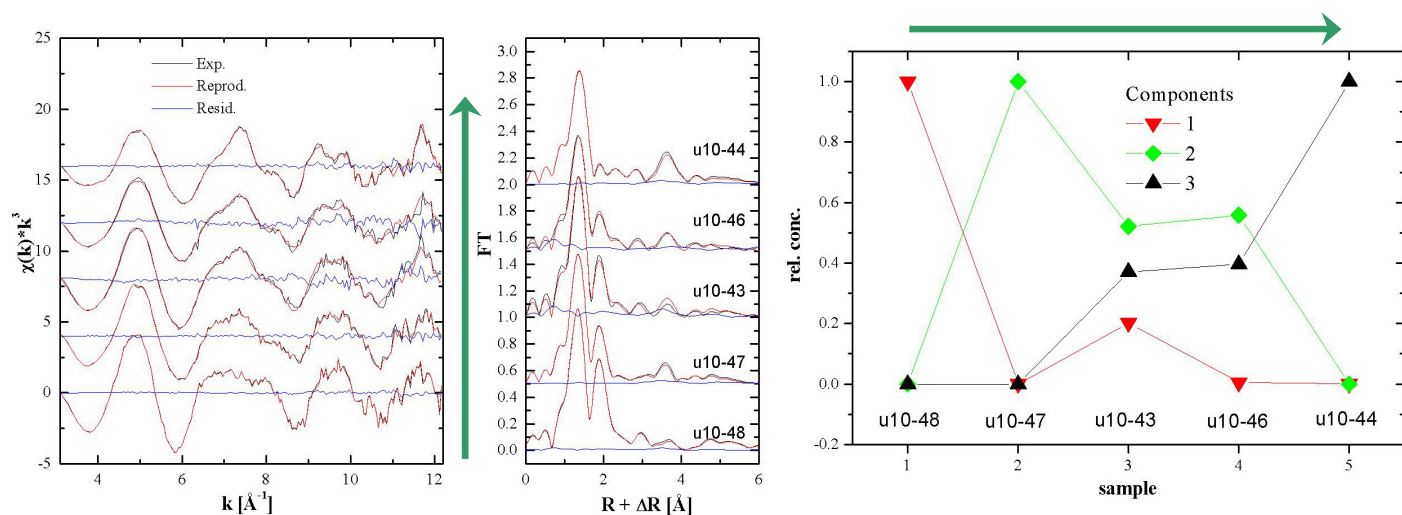


Fig. 1: EXAFS spectra (left panel) and the corresponding Fourier transforms (middle panel) of the batch samples of U(VI) on γ -Al₂O₃. The reproduced spectra after factor analysis (FA) and the residuals are also given. Composition of the three components obtained by FA in the samples (right panel). The arrows indicate the increasing U(VI) loading of the samples.

the solid phase was determined by ICP-MS and the spectra are listed with increasing U(VI) loading indicated by the arrow. In addition, the respective spectra reproduced by FA and the residuals are also given in the figure.

The main result of FA was the extraction of three components. The fractions of each component in the different samples change with the degree of U(VI) loading (Fig.1, right panel). Each component found by FA is tentatively assigned to different surface species upon comparison of the spectra with reference data.

Component 1 is obviously dominant at low U(VI) loading rates and most probably represents a sorption complex as it already suggested from IR spectra recorded during the first minutes after induced sorption. A detailed analysis and further experiments have to be carried for a comprehensive identification of this species.

Component 2 probably represents a sorption complex showing distinct U–U distances. This can be interpreted as a sorbed trimeric U(VI) species or another polymeric species formed under the prevailing conditions, that is an increased U(VI) loading.

Component 3 represents a surface precipitate, that is schoepite.

These findings confirm our previous results from IR spectroscopy of the proceeding sorption process. From these spectra, we assigned a characteristic spectral feature to the formation of a surface precipitate.

Future experiments will provide a more detailed insight into the early steps of U(VI) sorption on γ -Al₂O₃. In particular, additional structural information of the sorption complex (component 1) as well of the intermediate component 2 is still required. But also the impact of atmospheric carbonate on the sorption complexation has to be investigated. This will lead to a comprehensive description of the molecular processes occurring at the solid-liquid interface.