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## The sorption processes of Np(V) and U(VI) onto metal oxide phases. The formation of sorption complexes and mechanistic aspects studied by in situ ATR FT-IR spectroscopy

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The migration behaviour of actinide ions in the geosphere is generally influenced by sorption processes in aqueous media. These processes occurring at solid/liquid interfaces can be monitored by in situ Attenuated Total Reflection Fourier-transform Infrared (ATR FT-IR) spectroscopy providing structural information on a molecular level.[1]

In this work, the sorption of neptunium(V) onto metal oxides was investigated for the first time by ATR FT-IR spectroscopy. From the Np(V) sorption studies on the metal oxides, stable surface species of  $\text{NpO}_2^+$  are derived. The type of the sorbed species can be elucidated by a spectral shift ( $\sim 30 \text{ cm}^{-1}$ ) to lower wavenumbers of the antisymmetric stretching vibration  $\nu_3(\text{NpO}_2^+)$  compared to the aqueous species suggesting an inner-sphere complexation. Outer-sphere complexation is found to play a minor role due to the pH independence of the sorption species throughout the pH range 4–7.6. The comparative spectroscopic experiments of Np(V) sorption onto  $\text{TiO}_2$ ,  $\text{SiO}_2$  and  $\text{ZnO}$  indicate structurally similar bidentate surface complexes.[2]

A detailed insight into the molecular mechanisms occurring during the formation of ternary actinide complexes at the solid/liquid interface is provided upon formation of uranyl carbonate complexes on ferrihydrite (Fh). The influence of the presence of atmospheric carbon dioxide during the sorption processes of the actinide ions was studied by sorption experiments which were carried out under inert gas conditions and in an ambient atmosphere. From the results, the formation of bidentate  $[\text{Fh}\cdots\text{UO}_2\cdots\text{O}_2\text{CO}]$  complexes can be derived under mildly acid conditions which is in agreement from recent EXAFS results obtained from batch samples.[3]

Furthermore, experiments with  $^{13}\text{C}$  labelled carbonate provide an unequivocal assignment of the spectral features reflecting the structural alterations of the carbonate ions upon sorption of uranyl cations onto Fh. From these assignments, the formation of the ternary uranyl complexes can be described at a molecular level.

### References

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- [2] Müller, K. et al. (2009) Environ. Sci. Technol., in press.
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