Spectroscopic identification of ternary carbonate complexes upon U(VI)-sorption onto ferrihydrite

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The sorption processes of uranium(VI) onto ferrihydrite (Fh) were investigated by *in situ* Attenuated Total Reflection Fourier-transform Infrared (ATR FT-IR) spectroscopy. This technique provides structural information of the molecular complexes occurring during the sorption processes of actinide ions on mineral phases in aqueous solution [1].

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.

The spectra demonstrate that the uranyl ion recovers in a similar molecular environment irrespective to the prevailing atmospheric conditions. However, the carbonate ions sorbed to the mineral phase in ambient atmosphere undergo significant structural changes upon the sorption of the actinide ions. While carbonate binds monodentately to the pristine Fh-surface, it forms bidendate surface complexes upon the sorption of U(VI). Moreover, the formation of ternary inner-sphere complexes can be derived from spectra recorded during the sorption processes of atmospheric carbonate onto a Fh-film which was preloaded with U(VI) under inert gas conditions. With respect to the absorption frequency of the uranyl ion sorbed onto Fh under different conditions, we suggest the formation of $[Fh\cdots UO_2\cdots O_2CO]$ complexes. Surface complexes with carbonate serving as a bridging ligand between Fh and UO_2^{2+} ions were found in our experiments. These findings are in good agreement with recent EXAFS results [2].

Furthermore, we investigated the sorption processes at acidic (5.5) and at ambient (7.8) pH values. No significant differences were observed in the spectra. However, the sorption processes obviously occur with reduced velocity at higher pH values which might be due to the dominating aqueous U(VI) species at different pH values [3].

[1] Lefèvre (2004) *Adv. Colloid Interface Sci.* **107**, 109-123.
[2] Rossberg *et al.* (2009) *Environ. Sci. Technol.*, in press.
[3] Müller *et al.* (2008) *Inorg. Chem.* **47**, 10127-10134.

Anaerobic hydrocarbon degradation in oil sands tailings

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Background

Extraction of bitumen from oil sands in northern Alberta, Canada produces enormous volumes of tailings waste as slurries of water, sand, silt and clay particles, unrecovered bitumen and a small proportion of hydrocarbon solvent used during extraction. The tailings are deposited into catchments, allowing the solids to settle and generate “mature fine tailings” (MFT). We previously reported that certain components of the naphtha solvent used by Syncrude Canada Ltd., including C_6-C_{10} *n*-alkanes and some BTEX components (particularly toluene and xylenes) are biodegraded to methane by established microbial communities in Syncrude MFT [1, 2]. In contrast, the diluent used by Albian Sands Energy Inc. contains primarily short-chain aliphatics (C_5 and C_6). We investigated whether this aliphatic solvent supported methane production by the much younger Albian Sands MFT.

Results

Anaerobic microcosms were prepared using five different samples of Albian Sands MFT, methanogenic medium lacking a carbon source, a headspace of 30% CO_2/balance N_2 gas and aliphatic diluent at 0.1–0.5 vol% (maximum concentrations in tailings). None of the MFT samples produced methane greater than live baseline control microcosms with no additional diluent. Similarly, incubation of Albian MFT with a defined mixture of paraffins or isoparaffins known to be present in the Albian diluent did not yield additional methane, nor did incubation of Albian Sands MFT with Syncrude naphtha. However, incubation of Syncrude MFT with the Albian diluent did produce methane after a lag time of ~140 d. These results indicate that components of the Albian Sands diluent can support methanogenesis but suggest that the Albian Sands MFT has not yet developed a competent microbial community for anaerobic hydrocarbon degradation. Instead, the Albian Sands MFT microbial community appears to be using citrate, added as a water conditioning agent to Albian Sands tailings, as the carbon source for methanogenesis.

[1] Siddique *et al.* (2006) *Environ. Sci. & Technol.* **40,** 5459-5464. [2] Siddique *et al.* (2007) *Environ. Sci. & Technol.* **41**, 2350-2356.