

Talk 4.2

In situ ATR - FTIR study of uranyl sorption at illite - solution interface in the presence of phosphate ions

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Introduction: Gaining insights into mechanisms and species of uranyl sorption onto illite, at a realistic and low concentration of uranyl in the micromole range per liter, is highly needed for providing refined mechanistic process understanding of radionuclide retention in clay systems. Moreover, studying uranyl sorption processes due to the presence of aqueous ligands (such as phosphate) is mandatory for the transferability of experimental results on radionuclide retention to "the real system". Materials and methods: Na-homo-ionic form illite du Puy (NaldP) < 75µm was used as "received illite" material. Batch experiments were performed under atmospheric conditions at pH 3 - 8, solid-to-liquid ratios ($R_{s/l}$): 0.5g - 3g/L, $[UO_2^{2+}]$: 1-10µM and $[PO_4^{3-}]$: 20-100µM. We monitored by ATR-FTIR spectroscopy the dynamics of uranyl-phosphate species at the NaldP-solution interface during sorption process. We have focused the IR spectra on the frequency region characteristics of phosphate ions (900-1200cm⁻¹).

Phosphate sorption at NaldP-Solution interface: Sorption isotherms of phosphate at pH 4 showed an increasing amount of sorbed phosphate with increasing initial aqueous phosphate concentration, until reaching a plateau. The result of sorption edge showed that the amount of removed phosphate remained almost constant at acidic pH and decreased at near-neutral pH. Examining changes in IR spectra during phosphate sorption, suggested the existence of two types of sorption mechanisms. Resolving IR spectra of phosphate-NaldP interface showed an increase of IR bands at 1075 and 1157 cm⁻¹, with increasing initial phosphate concentrations, as well as appearance of bands at 1009 and 1040 cm⁻¹ at high phosphate concentrations. This suggested formation of an outer sphere surface complex of phosphate and an increasing contribution of an inner-sphere phosphate surface complex forming at high concentrations. It is hypothesized that the latter is probably a bidentate phosphate surface complex formed at aluminol / ferrinol sites present at edges of illite.

Uranyl sorption at NaldP-Solution interface: Sorption edge of uranyl indicated that: (1) the amount of removed uranyl increased with the increasing acidic pH and reached a plateau at higher pH; (2) the presence of phosphate ions increased the removal of uranyl at acidic pH, then reached a plateau and showed no significant differences comparing to that in the absence of phosphates ions at higher pH. Blank experiments (without NaldP) showed that uranyl containing colloidal phases were predominantly present in the solution at higher pH. This suggested that the removed uranyl mainly presented as uranyl-colloidal and uranyl-phosphate-colloidal phases at higher pH. Sorption isotherms of uranyl at pH 4 showed that: (1) the amount of removed uranyl increased with increasing initial concentration of uranyl until reaching a plateau, and (2) the presence of phosphate ions increased the uranyl adsorption. Resolving IR spectra of uranyl-phosphate (co)sorption at NaldP-solution interface showed an increase of IR band at 1050 cm⁻¹ with increasing initial concentration of uranyl while a decrease of IR bands at 1075 and 1160 cm⁻¹. This suggested an outer sphere surface complex of phosphate decreasing with an increasing contribution of an uranyl-phosphate inner-sphere surface complex or an uranyl-phosphate surface precipitation at higher concentrations of uranyl. An increase of IR bands at 992, 1081 and 1114 cm⁻¹ was also showed during "a long time" sorption process which suggested an autunite-like phase surface precipitation.