

Spectroscopic study of influence of silica on the stability of actinide(IV) colloids at near-neutral pH

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The migration of tetravalent actinides in natural waters occurs predominantly as sorption complexes at the surface of colloidal particles like clay, but also by the formation of actinide oxyhydroxide colloids ($M(OH)_{4-2n}mH_2O$ where $M = Th$ or U [1]). Colloid-facilitated migration of plutonium has also been documented in subsurface groundwater conditions [2]. In a recent study it was observed that the stability of U(IV) and Th(IV) oxyhydroxide colloids is dramatically enhanced by the presence of silica [3]. In this study we investigate the influence of silica on the formation and stability of U and Th colloids at near-neutral pH conditions, which might have important environmental implications due to the ubiquitous nature of silica in aquifers and surface waters.

U and Th colloids with varying U/Si and Th/Si ratios were synthesized and characterized using a range of spectroscopic and microscopic techniques. TEM and XRD measurements indicated that the structure of thorium/silica colloids is highly amorphous, which is clearly different from the ordered actinide(IV) oxyhydroxide colloids which are stable at $pH < 3$ but agglomerate and precipitate at near neutral pH within minutes. Comparison of O 1s X-ray photoelectron spectra (XPS) of actinide(IV)-silica and actinide(IV)-oxyhydroxide colloids revealed that two types of oxygen bonds (oxo and hydroxo) occur in presence of silica, which may explain the high degree of structural disorder. Moreover, the presence of O-Si bonds at near-neutral pH values suggest that silica is able to stabilize such colloids through modification of the structure by replacing the An-O(H)-An bonds of the oxyhydroxide structure with An-O(H)-Si bonds and consequently influencing the surface charge. These observations are consistent with X-ray absorption spectroscopy (XAS) data which demonstrate higher An-Si interaction and lower An-An interaction with increasing silica content in these colloids.

[1] Rothe *et al.* (2002) *Inorg. Chem.* **41**, 249-258. [2] Kersting *et al.* (1999) *Nature* **397**, 56-59. [3] Dreissig *et al.* (2011) *GCA* **75**, 352-367.

Sorption and redox behavior of neptunium on Opalinus clay and Callovo-Oxfordian argillite

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Clay stone is considered as a potential host rock for a high level deep nuclear waste repository. The Opalinus clay (OPA) and the Callovo-Oxfordian argillites (COx) are being investigated as candidate host rock formation at the underground research laboratory in Mont-Terri (Switzerland) and at Bure (France), respectively. The migration behavior of Np is strongly influenced by the oxidizing and reducing conditions of the geological environment. The understanding of Np sorption and diffusion mechanisms in argillaceous rocks is necessary for the safety assessments of a nuclear waste repository.

The objective of the present work is to use Kd values determined by batch experiments for transport modeling, and to gain understanding in underlying coupled redox and sorption phenomena. The batch sorption experiments of Np(V) on OPA (pH 7.6) and COx (pH 7.2) are performed at four different solid to liquid ratios, S/L (10, 20, 50, 200), in artificial pore water under argon atmosphere (<1 ppm O₂) with 1% CO₂ conditions, at Np concentrations between 3.0×10^{-4} and 1.0×10^{-8} M and with contact times up to 1 year. Np redox speciation in clay suspension is followed at low Np concentration by TTA extraction and capillary electrophoresis coupled to ICP-MS and at high Np concentration by UV-Vis, XAFS, and XPS spectroscopy.

Np(V) sorption increases with increasing sorbent amounts (S/L ratio) and with increasing contact time. More than 80 % of Np sorbed on the clay rocks within 4 months. The preliminary Kd values are calculated to 1.03 mL/g for OPA and 0.85 mL/g for COx (S/L ratio: 20) after 4 months contact time. In concentration series at 10^{-4} M, Np was identified on the clay in the form of Np(V) by XAFS and XPS spectroscopy after 1 week contact time, whereas in solution Np(V) is detected by TTA extraction and UV-Vis spectroscopy. At $<10^7$ M, Np(V) is found in solution by TTA extraction after 1 week contact time, while after 4 months Np(IV)/Np(V) mixtures are analyzed. The obtained results will be presented.