Actinide geochemistry: From the molecular level to the real system

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Geochemical processes leading to either mobilization or retention of radionuclides in an aquifer are significantly influenced by their interaction with rock, sediment and colloid surfaces. Therefore, performance assessment of nuclear waste disposal requires the elucidation and quantification of those processes. State-of-the-art analytical techniques as e.g. laser - and X-ray spectroscopy are increasingly applied to study solid-liquid interface reactions and to obtain molecular level speciation insight.

We have studied the sorption of trivalent lanthanides and actinides (M(III)) onto aluminium oxides, hydroxides and purified clay minerals by the time-resolved laser fluorescence spectroscopy and X-Ray-Fluorescence spectroscopy [1, 2]. Chemical nature and structure of surface bound actinides are proposed based on spectroscopic information. Similarities of spectroscopic data obtained for M(III) sorbed onto γ-alumina, gibbsite and clay minerals suggest the formation of very comparable inner-sphere surface complexes like $\equiv$S-O-An(III)$(OH)_x^{(2-x)}(H_2O)_{5-x}$ at pH > 5. Those speciation data are found consistent with those predicted by surface complexation modelling. The applicability of data obtained for pure mineral phases to actinide sorption onto heterogeneously composed natural clay rock is investigated by experiments and by geochemical modelling.

The assessment of clay colloid borne actinide migration observed in the frame of in-situ experiments at the Grimsel underground laboratory [3] also calls for detailed information on actinide speciation. Combined spectroscopy and wet chemistry experiments provide a fairly consistent picture of the actinide speciation under given groundwater conditions and impart insight into the dynamics of actinide-colloid interaction. Notably for tetravalent actinides we observe significant impact of ageing on the rate of actinide desorption from clay colloids. Studies are ongoing to elucidate underlying mechanisms.

Above mentioned studies demonstrate the appropriateness of combining spectroscopy and wet chemistry as an appropriate strategy to validate geochemical model assumptions and to reduce uncertainties.

References

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Microbial reduction of arsenate with sulfide as electron donor at neutral pH

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Arsenic is a common trace element found in most natural waters, as well as a documented human carcinogen. In the environment, arsenic occurs in the valence states As(V) and As(III). The bioavailability of arsenic is in general controlled by the presence of iron, by sorption of arsenate (As(V)) to iron minerals, and sulfide, resulting in the precipitation of arsenite (As(III)) as arsenic sulfides.

It is well known that arsenate may be microbiologically reduced under anaerobic conditions, and recently microbial reduction of arsenate coupled to the use of sulfide as electron donor was described [1, 2]. This process occurred in soda lakes, with pH 10 and high salt concentration, conditions under which sulfide is less toxic due to the virtual absence of H_2S. Chemical reduction of arsenate with sulfide has been shown to take place at acidic to neutral pH.

We investigated the possibility of biological reduction of arsenate with sulfide as electron donor at neutral pH. Batch incubations were set-up using anaerobic sediment amended with arsenate and sulfide. Arsenate was removed from solution in 5-9 days. In control experiments with autoclaved sediment, part of the arsenate in solution was removed, which may indicate relatively slow sorption of arsenate on soil particles or chemical reduction of arsenate.

Incubations in which arsenate conversion occurred were transferred to fresh culture medium several times and yielded stable enrichment cultures. In these enrichment cultures two dominant bacterial species were present. Application of molecular biological techniques showed that the two species were related to the genus *Sulfurospirillum* and to sulfate reducing bacteria belonging to the delta-proteobacteria. We aim to isolate these two organisms in pure culture and study their physiology and ability to reduce arsenate with sulfide in more detail.

References

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