

ROBL-CRG

Experiment title: Elucidation of structural environment of Th(IV) in clay minerals using EXAFS	Experiment number: ME-50	
Beamline: BM 20	Date of experiment: from: 7.4.2000 to: 10.4.2000	Date of report: 18.8.2000 <i>Received at ROBL:</i> 20.3.2001
Shifts: 12	Local contact(s): C. Hennig	

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Report:

Aims of the experiment and scientific background

The aim of this experiment is to develop and test models, and to acquire selected data in support of the performance assessments of Swiss nuclear waste repositories. The flow of ground water through a repository can potentially result in the release of radionuclides from waste matrices. The released radionuclides can then be transported through engineered barrier systems and the surrounding geosphere. The release of radionuclides can be considerably retarded due to interactions with solid phases. Thus, a detailed molecular level understanding of sorption mechanisms of radionuclides in clay systems is of great importance for safety assessment.

On clay minerals several uptake mechanisms of divalent metal ions such as Ni(II), Co(II), and Zn(II) have been proposed: Sorption on edge sites, sorption on interlayer sites, and the formation of lamellar nucleation phases such as neoformed layer silicates and mixed layered double hydroxides [1-4].

The aim of this study is to use EXAFS to determine sorption mechanisms of Th on montmorillonite. Montmorillonite is an important smectitic mineral responsible for the retention of metals in the geosphere. Furthermore, the clay is used as a backfill material in the Swiss concept for a high level radioactive waste repository and thus, metal sorption on montmorillonite has been investigated in our laboratory in great details [5].

Experiments + Results

Samples were prepared in a glove box by reacting Th and montmorillonite at pH 3.0 and at high ionic strength 0.1 M NaClO₄ to block cation exchange processes. The initial Th concentrations for the samples were 2.7·10⁻⁶ - 4·10⁻⁴ M Th. After a reaction time of 7 days the samples were centrifuged and the wet pastes were transferred into a sealed Plexiglas sample holder. Th-L_{III}-edge fluorescence were recorded for samples containing 1-157 μmol/g Th sorbed onto the montmorillonite. k³-weighted EXAFS spectra for Th sorbed on montmorillonite are shown in Fig. 1. With increasing Th loading the intensity of k³χ(k) increases and the wave frequency between ~6 and ~10 Å⁻¹ shifts to higher values. The corresponding experimental Radial Structure Functions (RSF's) are shown in Fig.2 . The figure reveals that the amplitude of the first peak (Th-O contribution) is decreasing with decreasing Th loading and that the peak is split into two oxygen shells. The second RSF peak (Th-Si contribution) increases with decreasing loading and its position is shifted to higher distances. To date, the data analysis is finalised using theoretical approaches.

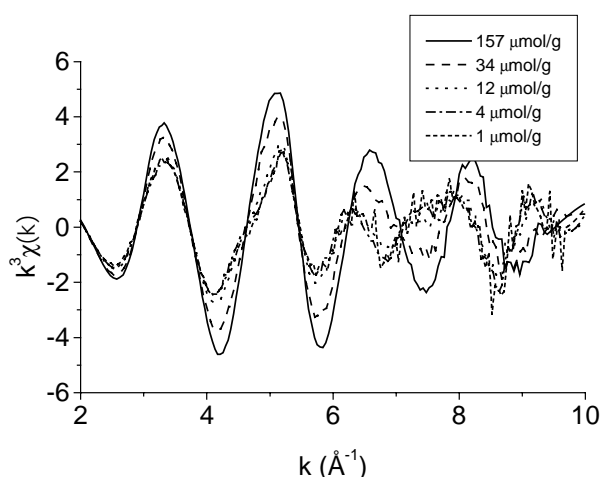


Figure 1: k³-weighted Th L_{III}-edge EXAFS spectra for different Th-concentrations sorbed onto montmorillonite

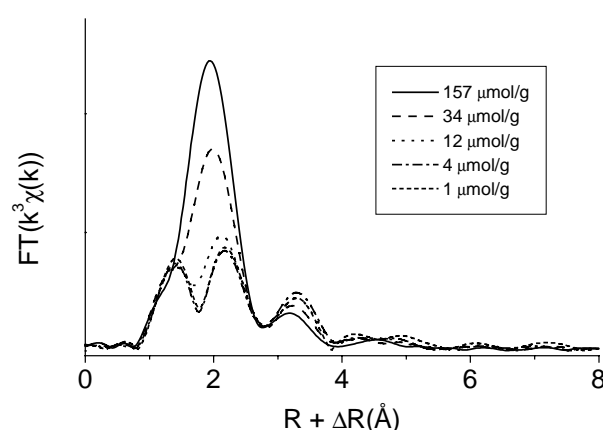


Figure 2: Concentration dependence of the Th L_{III}-edge RSFs of Th sorbed onto montmorillonite

References

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