

Americium retention by the smectite hectorite

Nicolas Finck, Kathy Dardenne

KIT-INE, P.O. Box 3640, D-76344 Karlsruhe, Germany.

Introduction

Clay minerals may play an important role in a high level nuclear waste disposal site. Smectites may be major components of backfill material used to enhance the retention properties of engineered barriers. Furthermore, they have also been detected in the alteration layer of nuclear waste glass corroded in laboratory experiments [1]. For example, the smectite hectorite ($\text{Na}_{0.33}[\text{Mg}_{2.67}\text{Li}_{0.33}\text{Si}_4\text{O}_{10}(\text{OH})_2]$) was identified as phase forming upon waste matrix dissolution and subsequent reprecipitation. Smectites are known to be highly reactive with respect to cations in aqueous systems. Several distinct molecular scale binding mechanisms may operate, but the most effective retention may occur by incorporation in the bulk structure, especially if a (meta)stable solid solution forms. Investigations showed the possibility to incorporate Lu(III) in a clay-like octahedral site in hectorite by coprecipitation [2]. Furthermore, luminescence studies on hectorite synthesized in the presence of Cm(III) [3] or Eu(III) [4] were consistent with an incorporation in the bulk structure. However, structural data such as coordination numbers and bond lengths are still missing for the actinides. In the present study, Am(III) was coprecipitated with and adsorbed on hectorite to decipher the actual retention mechanism(s).

Results and discussion

Hectorite was synthesized in the presence of Am(III) (sample AmCopHec) from an Am-containing brucite precursor phase. Briefly, brucite was freshly precipitated in the presence of Am(III) (Am:Mg molar ratio of 1:1175) and washed. The resulting sol was aged in a tightly closed vessel in the presence of LiF and silica sol for several days at 90°C. Separately, an Am-containing brucite phase (sample AmCopBru) was prepared under identical conditions as described above, and the americium aqua ions were adsorbed on hectorite ($m/V = 2 \text{ g/L}$, $[\text{Am(III)}]_{\text{tot}} = 105 \text{ } \mu\text{mol/L}$, $0.5 \text{ mol/L NaClO}_4$, $\text{pH} = 6.4(1)$, sample AmSorbHec) and used as reference samples.

X-ray diffraction data were collected for the solid phases prepared as oriented samples. The powder diffractogram collected for AmCopBru is similar to that of brucite and contains no additional peak. Consequently, brucite formed in the presence of Am(III). The diffractograms collected for AmCopHec and hectorite are also similar and no additional phase could be detected meaning that the smectite crystallized from the doped precursor. Furthermore, no X-ray amorphous Am-containing precipitate could be detected by SEM-EDX in AmCopBru and AmCopHec. Consequently, Am(III) is very likely homogeneously associated to the solid phases. Obviously, americium had no significant influence on the hectorite multi-step synthesis protocol.

Information on the Am crystallochemical environment was provided by probing the L_3 -edge by X-ray absorption spectroscopy (XAS). Upon coprecipitation with brucite, the number of ligated oxygen atoms was reduced from nine for the aqua ions to seven ($N_{\text{O}} = 7$) in AmCopBru. This decrease in coordination number is significative of a change in the chemical environment. The next nearest neighbors consist of two Mg backscatterers subshells located at 3.21 and 3.45 Å. These bond lengths point to face sharing and edge sharing, respectively, between the Am and the Mg polyhedra. Obviously brucite was able to accommodate this large cation, but the structure is highly distorted as evidenced by the split nearest cationic shell.

The XAS spectrum of AmCopHec differs from that of AmCopBru, indicating different environments. The Am(III) first coordination sphere contains $N_{\text{O}} = 6$ oxygen atoms in AmCopHec and the nearest cationic neighbors consists of Mg ($N_{\text{Mg}} = \sim 1$ atom) and Si ($N_{\text{Si}} = \sim 3$ atoms) shells detected at $d(\text{Am-Mg}) = 3.28 \text{ } \text{Å}$ and $d(\text{Am-Si}) = 3.52 \text{ } \text{Å}$. These data can be interpreted as Am(III) located in an octahedral clay-like environment. In contrast to the coprecipitation sample, Am(III) is bound to 7-8 oxygen atoms in AmAdsHec and the Si shell is located at significantly larger distance upon surface sorption ($d(\text{Am-Si}) = 3.81 \text{ } \text{Å}$). In addition, the Mg and Si coordination numbers are lower (< 1 atom

each shell) for AmAdsHec than for AmCopHec. The formation of Am(III) inner-sphere surface complexes at the hectorite platelet edges can best account for the AmAdsHec XAS data.

The results show that Am(III) did not influence the clay synthesis protocol and that the actinide is successively bound to various phases. Furthermore, Am(III) is located in different crystallochemical environments upon coprecipitation and upon adsorption. This investigation provides strong evidence to the possibility to entrap the large actinides in neo-formed secondary phases resulting in a very effective retention. The neo-formed alteration products represent themselves an effective barrier to the migration of radionuclide (RN) out of a deep nuclear waste disposal site. This information is of high importance for safety performance assessment calculations. However, the stability of such phases and the potential remobilization of RN need further investigations.

References

- [1] P. Jollivet, P. Frugier, G. Parisot, J.P. Mestre, E. Brackx, S. Gin, S. Schumacher, Effect of clayey groundwater on the dissolution rate of simulated nuclear waste glass SON68, *J. Nucl. Mater.* **420** (2012) 508-518.
- [2] N. Finck, M.L. Schlegel, D. Bosbach, Sites of Lu(III) sorbed to and coprecipitated with hectorite, *Environ. Sci. Technol.* **43**(2009) 8807-8812.
- [3] H. Brandt, D. Bosbach, P.J. Panak, T. Fanghänel, Structural incorporation of Cm(III) in trioctahedral smectite hectorite: A time-resolved laser fluorescence spectroscopy, *Geochim. Cosmochim. Acta* **71**(2006) 145-154.
- [4] N. Finck, T. Stumpf, C. Walther, D. Bosbach, TRLFS characterization of Eu(III)-doped synthetic organo-hectorite, *J. Contam. Hydrol.* **102** (2008) 253-262.