Uptake of Eu(III) by 11 Å tobermorite and xonotlite: A TRLFS and EXAFS study

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Abstract

The uptake of Eu(III) by crystalline calcium silicate hydrate (C–S–H) phases 11 Å tobermorite and xonotlite has been investigated by the combined use of time-resolved laser fluorescence spectroscopy (TRLFS) and extended X-ray absorption fine structure (EXAFS) spectroscopy. Eu(III) doped tobermorite and xonotlite samples with varying metal loading (0.4, 7 and 35 μmol Eu/g solid phase) and reaction time (1–570 days) were investigated. The structural environment of Eu(III) taken up by tobermorite and xonotlite was found to depend on both parameters.

At high Eu(III) loading (7 μmol Eu/g solid phase), TRLFS data indicated presence of three Eu(III) species with different fluorescence lifetimes after 1 day reaction time. The emission lifetimes deduced for the different species correspond to ∼4.7, ∼1 and 0 water molecules in the first coordination sphere, thus suggesting the presence of one surface species forming an inner-sphere surface complex and two species incorporated in the crystal structure. After longer contact times (90 days, 570 days), the surface species was not observed. At the lower Eu(III) loading (0.4 μmol Eu/g solid phase) and reaction times between 1 and 310 days only two Eu(III) species with ∼1–2 and 0 water molecules were detected, corresponding to Eu(III) being incorporated in the crystal structure. The results from EXAFS showed that the distances between Eu(III) and neighboring Ca and Si atoms in Eu(III) doped tobermorite increase after prolonged reaction time. Furthermore, the number of neighboring Ca and Si atoms was found to increase with time. This study demonstrates that binding into the structure of 11 Å tobermorite and xonotlite is the dominant mode of Eu(III) immobilization after long reaction time. This finding is essential for an overall assessment of the safe disposal of actinides in deep geological repositories for radioactive waste, as incorporation into the crystal structure suggests long-term immobilization in the repository environment.
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1. INTRODUCTION

Calcium silicate hydrate (C–S–H) phases occur in nature as hydrothermal alteration products found in contact zones of Ca-bearing rocks with basic igneous rocks (e.g. Henmi and Kusachi, 1992). They also form as secondary solid phases at elevated temperature in the hyper-alkaline environments surrounding cement-based nuclear and toxic waste sites (e.g. Atkinson et al., 1995). C–S–H may also precipitate as secondary minerals in the chemically disturbed zone of a repository for radioactive waste due to the interaction of

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hyper-alkaline fluids emanating from the cementitious near field with sedimentary host rock (e.g. De Windt et al., 2004). 11 Å tobermorite, $Ca_{4.5}Si_6O_{16}(OH)\cdot 5H_2O$, and xonotlite, $Ca_6Si_6O_{17}(OH)_2$, are two crystalline members among the large number of C–S–H for which the structure has been solved (Prodan et al., 1983; Merlino et al., 1999, 2001; Hejny and Armbruster, 2001). The structure and chemistry of the minerals of the tobermorite group are closely related to the structure of amorphous C–S–H phases, which form upon reaction of water with the clinker minerals of cement (Taylor, 1986; Richardson, 2004). C–S–H phases are considered to be particularly important in governing immobilization processes in cementitious materials, because they are the main constituent of fresh and degraded cement (~50 weight (wt)%) (Atkins and Glasser, 1992). Therefore, due to their stability during the evolution of the cementitious near field, C–S–H phases may control the long-term release of radionuclides (Berner, 1992).

The structure of 11 Å tobermorite and xonotlite are built up of sheets of six and seven coordinated Ca polyhedra, which are ribbed on both sides by wollastonite-type silicate chains (Hejny and Armbruster, 2001; Merlino et al., 2001). The silica chains are built up by Si_2O_7 groups ("paired" silica tetrahedra) connected to the central Ca sheet and, via "bridging" Si tetrahedra, to the adjacent layer. In 11 Å tobermorite the cavity between two adjacent building layers stacked along the *c*-axis, the so-called "interlayer space", may contain water (~2.5 water molecules/formula unit) and calcium cations. There is no interlayer space in the xonotlite structure. The structure of xonotlite may contain OH^- groups (~1 OH molecules/formula unit). Four xonotlite polytypes can be distinguished according to the different arrangements of building layers along *c* (Gard, 1966). The nomenclature of polytypes and the mechanism of defects formation in the crystal structure of xonotlite have been discussed in detail elsewhere (Hejny and Armbruster, 2001; Churakov and Mandaliev, 2008).

Several authors have investigated the interaction of lanthanides and trivalent actinides with C–S–H phases in the past decade (e.g. Pointeau et al., 2001; Tits et al., 2003; Schlegel et al., 2004). Pointeau et al. (2001) investigated the uptake of Eu(III) by amorphous C–S–H phases with varying calcium-to-silica (C/S) ratios (0.34–1.65) and 14 Å tobermorite in the pH range 10.0–12.4 using time-resolved laser fluorescence spectroscopy (TRLFS). Two Eu(III) species with different fluorescence lifetimes (390 and 990 μs) were observed, suggesting that Eu(III) was sorbed onto or incorporated in amorphous C–S–H phases and tobermorite. The Eu(III) species with the long lifetime was attributed to Ca replacement by Eu(III) in the C–S–H structure. The second Eu(III) with shorter lifetime was attributed to Eu(III) being sorbed on the surface of C–S–H. Tits et al. (2003) investigated the interaction of Eu(III) and Cm(III) with a C–S–H phase with C/S ratio of about ~1.0 at pH 13.3 in batch-type sorption experiments and using TRLFS. The results of the TRLFS study allowed three different Cm(III) species to be distinguished. A non-fluorescing species identified as a surface-precipitate, and two fluorescing species with 1–2 and 0 H_2O molecules in their first coordination sphere were observed, suggesting that these species

were incorporated into the interlayer and the Ca-octaheder sheets of the C–S–H structure. The increasing fluorescence intensity as a function of time was attributed to an increase in the incorporated Cm(III) fraction and a decrease of the Cm(III) fraction forming a surface precipitate. Schlegel et al. (2004) investigated the uptake of Eu(III) by amorphous C–S–H phases as function of the added Eu(III), the C/S ratio of the C–S–H phases and reaction time using extended X-ray absorption fine structure (EXAFS) spectroscopy. The results of this EXAFS study suggested incorporation of Eu(III) into the structure of C–S–H phases at the Ca structural sites.

The aim of this study was to investigate Eu(III) uptake by 11 Å tobermorite and xonotlite at the molecular scale. In contrast to the studies discussed above, which focused on lanthanide interaction with amorphous C–S–H phases, two well-ordered crystalline C–S–H phases were used in the present study. This should allow a more detailed description of the local structural environment of the incorporated Eu(III) species. The combined use of TRLFS and EXAFS spectroscopy allows surface sorption and incorporation into the lattice of C–S–H to be distinguished from each other. Eu(III) was chosen as a non-radioactive analogue for trivalent actinides because of its unique spectroscopic properties allowing speciation in the μ-mol range (Stumpf et al., 2007). The position of the main Eu(III) bands ($^5D_0 \rightarrow {}^7F_J$ transitions; $J = 0, 1, 2, 3, 4$) are almost independent of the chemical environment of the metal ion. Only the intensity of the $^5D_0 \rightarrow {}^7F_2$ transition changes significantly when Eu(III) forms complexes (Jorgensen and Judd, 1964). From the splitting of the fluorescence emission bands, in particular at low temperature, information on the ligand field and, hence, on the geometry of the coordination site of the Eu(III) ion can be deduced (Bünzli and Choppin, 1989). The ground state $^7F_0$ is non-degenerate. Hence, the number of peaks observed in the $^5D_0 \rightarrow {}^7F_0$ band corresponds to the number of Eu(III) species. TRLFS also allows the hydration state of the Eu(III)/C–S–H species to be studied using the linear correlation between the decay rate and the number of the H_2O molecules or OH groups, respectively, in the first coordination sphere of Eu(III) (Horrocks and Sudnick, 1979; Pointeau et al., 2001; Tits et al., 2003). Complementary information on atomic distances and coordination numbers of the Eu(III)/C–S–H species can be derived from EXAFS spectroscopy. Thus, the combined use of the two spectroscopic methods provides complementary structural information essential for the development of a mechanistic picture of Eu(III) immobilization by 11 Å tobermorite and xonotlite.

2. MATERIALS AND METHODS

2.1. Sample preparation

Throughout this study Fluka (Sigma–Aldrich, Buchs, Switzerland) or Merck (Dietikon, Switzerland) "pro analysis" chemicals and high-purity de-ionised water generated by a Milli-Q Gradient A10 system (Millipore, Bedford, USA) were used. All experiments were carried out in a glovebox under a N_2 atmosphere and at ambient temperature