

Competition behaviour of metal uptake in cementitious systems: An XRD and EXAFS investigation of Nd- and Zn-loaded 11 Å tobermorite



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ABSTRACT

Cement-based materials play an important role in multi-barrier concepts developed worldwide for the safe disposal of hazardous and radioactive wastes. Cement is used to condition and stabilize the waste materials and to construct the engineered barrier systems (container, backfill and liner materials) of repositories for radioactive waste. In this study, bulk-X-ray absorption spectroscopy (XAS) was used to investigate the uptake mechanism of Nd on the crystalline C–S–H phase 11 Å tobermorite in the presence of Zn (co-absorbing metal), and vice versa, as potential competitor under strongly alkaline conditions (pH = 12.5–13.3). The Zn and Nd concentration in all samples was 50,000 ppm, whereas the reaction times varied from 1 to 6 months.

Extended X-ray absorption fine structure (EXAFS) data of the Nd L_{III}-edge indicate that the local structural environment of Nd consists of ~7–8 O atoms at 2.42 Å, ~7–8 Si at ~3.67 Å and ~5–6 Ca at ~3.8 Å, and that this environment remains unchanged in the presence and absence of Zn. In contrary, Zn K-edge EXAFS data exhibit distinct differences in the presence and absence of Nd as co-absorbing element. Data analysis indicates that Zn is tetrahedrally coordinated (~4 O at ~1.96 Å) and the obtained structural data in the simultaneous presence of Nd and Zn are consistent with the formation of mixed Zn surface complexes and Zn bound in the interlayer remaining in these positions also with prolonged reaction times (up to 6 months). However, without the co-absorbing element Nd, strong structural changes in the uptake mechanisms of Zn are observable, e.g., after 3 month reaction time Zn–Zn backscattering pairs can be observed. These findings suggest that Nd has an influence on the incorporation of Zn in the tobermorite structure. In addition, the results of this study indicate that competitive uptake of metal cations with similar sorption behaviour by C–S–H phases can take place, deserving further attention in future assessments of the safe disposal of radioactive wastes in cement-based repositories.

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1. Introduction

Assuring safe disposal and long-term storage of hazardous and radioactive wastes represents a primary environmental task of industrial societies. The long-term disposal of hazardous waste is associated with landfilling of cement-stabilized waste (Schmidt et al., 1995), whereas deep geological disposal is foreseen for some categories of radioactive waste conditioned in cementitious materials (Chapman and McCombie, 2003). For example, more than

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90 wt.% of the near-field material of the planned Swiss deep geological repository for low- and intermediate-level waste consists of hardened cement paste (HCP) and cementitious backfill materials. HCP is used to condition radioactive waste (solidification and stabilization). The release of radionuclides from the cement matrix into the geosphere is retarded due to their strong interaction with cement phases. While in the past most studies on the retardation of radionuclides in (nuclear) waste repositories with cement materials were based on wet chemistry experiments, it has been realized that predictions on the long-term behaviour of radionuclides require a detailed molecular-level understanding of the retardation mechanisms. Hence, the use of extended X-ray absorption fine structure (EXAFS) spectroscopy has become an important research tool to investigate chemical processes in cementitious systems (Bonhoure et al., 2006, 2003, 2002; Dähn et al., 2011; Gaona

et al., 2013, 2011; Macé et al., 2013; Mandaliev et al., 2011, 2010b, 2009; Scheidegger et al., 2000; Vespa et al., 2007, 2006a, 2006b; Wieland et al., 2013, 2010a, 2010b; Ziegler et al., 2001).

In HCP, calcium silicate hydrates (C–S–H), $(\text{CaO})_x(\text{SiO}_2)_y(\text{H}_2\text{O})_z$ are quantitatively the most abundant and important phases (C–S–H > 50 wt.%; other minerals are Ca-hydroxide ~20 wt.% and calcium aluminates ~20 wt.%). They are chemically the most stable phases in a cementitious environment (pH > 12.5) and exhibit a wide diversity of structural sites exposed for cation binding. 11 Å tobermorite is a crystalline C–S–H phase for which the structure is well known (Fig. 1, $\text{Ca}_{4.5}\text{Si}_6\text{O}_{16}(\text{OH})\cdot 5\text{H}_2\text{O}$) (Merlino et al., 2001). The layered structure is built up of sheets of Ca polyhedra linked through non-bridging oxygens to chains of silicate tetrahedra on both sides. The interlayer space in between the sheets may contain water and calcium cations. The crystalline structure of 11 Å tobermorite is also closely related to the structure of amorphous C–S–H phases, which form in hydrated cement upon reaction with water (Lothenbach and Wieland, 2006; Richardson, 2004). In general, three different modes of heavy metal interaction with 11 Å tobermorite can be envisaged: (I) surface complexation (position 1), (II) uptake in the interlayer (position 2), and (III) incorporation in the Ca or Si sheets (position 3), respectively (Fig. 1). Spectroscopic investigations have provided evidence that all three positions are available for uptake processes. For example, investigations on the uptake of Sn(IV) onto C–S–H have shown that Sn sorbs on edges of the Si chain by corner sharing between Sn octahedra and Si tetrahedral (position 1, Fig. 1) (Bonhoure et al., 2003). EXAFS investigations of Nd(III) and Zn(II) uptake by C–S–H at low concentrations revealed that these metal ions tend to be incorporated in the interlayer of the C–S–H structure (position 2, Fig. 1) (Mandaliev et al., 2010b; Ziegler et al., 2001). Further studies on Nd(III) as well as Eu(III) uptake on crystalline C–S–H have shown that for long reaction times these metal can also substitute for Ca in the Ca sheets (position 3, Fig. 1, Mandaliev et al., 2011; Mandaliev et al., 2010b), while the $\text{Zn}(\text{O}, \text{OH})_4$ tetrahedra can also substitute for the silicate bridging, tetrahedra and/or at terminal silicate chain sites in C–S–H phases (Tommaseo and Kersten, 2002). These studies clearly demonstrate that the uptake mechanism of a heavy metal is highly specific with respect to the chemical properties of the element. The studies of Bradbury and Baeyens (Bradbury and Baeyens, 2005) on clay minerals further showed that metal ions with similar chemical behaviour compete with one another and that this process is very selective. To the best of our knowledge, competitive uptake of metal cations by C–S–H phases has not yet been investigated to date, and no attempt has been made so far to perform spectroscopic investigations on metal–metal competition in these systems.

The aim of this study is to gain molecular-level information on the uptake of Nd(III), a chemical homologue for trivalent

lanthanides and actinides, e.g., Cm(III) or Am(III), onto C–S–H in the presence of Zn(II) under different reaction times. In particular, the influence of the co-absorbing Zn(II) ion on the binding mechanism of Nd(III) is examined. The binding mechanism of Nd(III) and Zn(II), solely, to C–S–H is known (Mandaliev et al., 2010a, 2010b; Tommaseo and Kersten, 2002; Ziegler et al., 2001). One of the key questions is whether these metal ions, which are subject to the same uptake mechanism to C–S–H (position 2: incorporation in the interlayer; or position 3: incorporation in the Ca and Si sheets, Fig. 1) are in competition with each other and whether or not the uptake mechanism will change in the presence of a co-absorbing metal.

2. Materials and methods

2.1. Sample preparation

All experiments were carried out in a glovebox under controlled N_2 atmosphere (CO_2 , O_2 < 2 ppm, $T = 20 \pm 3$ °C). 11 Å tobermorite from Mandaliev and co-workers (Mandaliev et al., 2010b) was used as the crystalline C–S–H form.

The 11 Å tobermorite samples were loaded with both Nd and Zn (Table 1). The Nd (0.1 M) and Zn (0.2 M) stock solutions were prepared by dissolving the metal salt ($\text{Zn}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$, $\text{Nd}(\text{NO}_3)_3\cdot 6\text{H}_2\text{O}$, Merck “pro analysis”) in deionized water and adding an aliquote HNO_3 (10^{-3} M) for acidification.

The samples were prepared by adding 2.6 ml 0.1 M and 2.87 ml 0.2 M of the Nd and Zn stock solution, respectively, to 30 ml of tobermorite suspension. This resulted in Nd and Zn solution concentrations of $\sim 8 \times 10^{-3}$ and $\sim 1.7 \times 10^{-2}$ mol/l, respectively. Note that these concentrations are below the available Ca and Si concentration sites (~ 0.2 mol/l) of the tobermorite, thus, precipitation of solid phases is not expected (Stahl and Jacobs, 1997; Ziegler and Johnson, 2001). The Nd and Zn loadings of 11 Å tobermorite were always of $\sim 50,000$ ppm, whereas the reaction time was variable. The Nd loaded samples were reacted for 6 months by shaking the samples end-over-end. Zn was added either together with Nd or after pre-equilibrating Nd-loaded 11 Å tobermorite for 3 or 5 months. Therefore, Zn reacted with Nd-loaded 11 Å tobermorite for 1, 3 or 6 months, respectively. After equilibration, solid and liquid phases were separated by centrifugation (60 min at 95,000g). For bulk-XAS measurements the solid phase was filled into Plexiglas holders and sealed with Kapton tape. Additional reference samples with only one absorbing element present were prepared. The Nd-Ref-Tob-6 sample was reacted for 6 months, whereas the Zn-reference samples were reacted for 1, 3 and 6 months (Zn-Ref-Tob-1, -3 and -6, Table 1).

2.2. Bulk-XAS data collection and reduction

All bulk-XAS spectra at the Zn K- and the Nd L_{III} -edges were collected at the Dutch Belgium Beamline (BM26, DUBBLE) at the European Synchrotron Radiation Facility (ESRF) in Grenoble, France (Nikitenko et al., 2008). The measurements were conducted at room temperature in fluorescence mode using a 9 channel monolithic Ge-solid state detector. The beamline is equipped with a Si(111) crystal monochromator. The monochromator angle was calibrated for the Zn K- and Nd L_{III} -edges by assigning the energy of 9656 eV and 6539 eV to the first inflection point of the K-edge absorption spectrum of Zn and Mn metal foils, respectively.

All EXAFS spectra were extracted from raw data with the Athena interface of the IFFEFIT software (Newville, 2001; Ravel and Newville, 2005). The Fourier transforms (FT) were obtained from the k^3 -weighted $\chi(k)$ functions with a Bessel window function with a smoothing parameter of 4. Multishell fits were performed in real space across the range of the first two shells. Amplitude and phase shifts functions were calculated using the FEFF 8.20 code

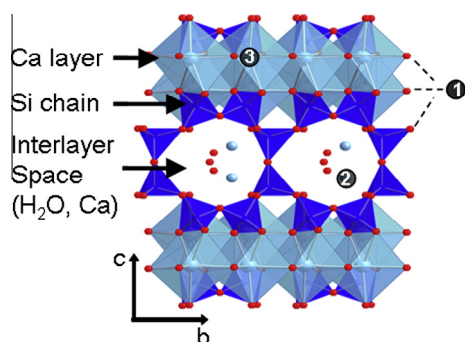


Fig. 1. The crystal structure of 11 Å tobermorite with possible positions of Ca in the Ca layers and interlayer Ca (●) as well as positions of structural oxygen and water molecules in the interlayer (●). Potential sites for metal sorption and structural incorporation (●) are labeled 1, 2 and 3.

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