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Cement has been used worldwide for the stabilization of hazardous and nuclear wastes in order to prevent or lower the mobility of contaminants associated with the waste matrices. Calcium silicate hydrate (C-S-H: $(CaO)_x(SiO_2)_y(H_2O)_z$) phases are considered to be important in governing immobilization processes in cementitious materials, because they are quantitatively the most important (~50 wt.%) and chemically the most stable minerals within hydrated cement paste.

During the hardening of cement (semi-)crystalline and amorphous C-S-H phases form. Furthermore, different crystalline C-S-H phases with varying calcium-to-silica (C/S) ratios form as secondary solid phases at elevated temperature in the hyper-alkaline environment surrounding cement-based nuclear and toxic waste sites. Eu L_{III}-edge (6.977 keV) EXAFS measurements on Eu(III) doped tobermorite and xonotlite samples, which had been equilibrated for time periods up to 480 days, were carried out with the aim of gaining a molecular-level understanding of the lanthanide uptake by crystalline C-S-H phases over long contact times. The structural data were compared with those obtained from hydrothermally synthesized (T = 160 - 220° C) C-S-H phases with varying C/S ratios. Eu(III) is regarded as suitable chemical analogue for trivalent actinides (Am^{3+}, Cm^{3+}) based on comparable ionic radii and similarities in their complexation behaviour.

Figure 1 shows the k^3-weighted, normalized, background subtracted EXAFS spectra, the corresponding radial structure function (RSF) and the Fourier backtransform (R + ΔR = 1.5-4.0 Å) of selected Eu(III) doped C-S-H samples. The structural parameters, which were derived from multi-shell analysis (R + ΔR = 1.5-4.0 Å) of the EXAFS spectra (Δk =1.7 – 10.6 Å^{-1}), are summarized in Table 1.

The RSFs of all Eu(III) doped C-S-H samples show a peak at R + ΔR ~ 2.0 Å, which was fitted by assuming the presence of a single oxygen shell. The number of neighboring oxygen atoms, N_O, and the Eu-O distances, R_{Eu-O}, for the Eu(III) doped tobermorite and xonotlite samples were similar within the experimental uncertainties, e.g. N_O = 6.7-7.2 and R_{Eu-O} = 2.39-2.40 Å (Table 1). Interestingly, the latter coordination numbers are lower and the Eu-O distances are shorter than those determined for the Eu(III) doped, hydrothermally synthesized C-S-H sample (CSH-350-14).

Presence of further backscattering atoms is indicated by the broad peak in the Fourier transforms at R+ΔR ~2.8-3.8 Å in all samples. This peak was fitted by taking into account Eu-Si and Eu-Ca backscattering paths. In the CSH-350-14 sample Eu-Eu backscattering pairs were taken into account in addition to the Eu-Si and Eu-Ca backscattering paths. Significant differences in the structural parameters of the Eu(III) doped xonotlite/tobermorite and C-S-H-350-14 samples were observed. The Eu-Si bond distances are similar in Eu doped tobermorite and xonotlite (R_{Eu-Si} = 3.76 - 3.77 Å), while these distances are significantly shorter in the

C-S-H-350-14 sample (Table 1). The Eu-Ca distances in Eu doped tobermorite and xonotlite are different and further, they are significantly shorter than those determined in the C-S-H-350-14 sample (Table 1). The Eu-Eu distance in the latter sample was determined to be 4.13 Å. Note that neighboring Eu atoms were not detected in the other samples.

The findings from this study suggests different coordination environments of Eu(III) taken up by tobermorite and xonotlite after 480 days reaction time, and the Eu(III) doped, hydrothermally synthesized C-S-H sample. The EXAFS results provide a first set of structural data, which will be used for ab initio calculations of Eu(III) substitution in the structure of C-S-H phases. Furthermore, these data will be compared with those deduced from powder diffraction measurements on the Eu(III) doped, hydrothermally synthesized C-S-H phase using ab initio structural refinements. The combined use of these techniques on Eu doped C-S-H materials is novel and will allow a detailed structural model of lanthanide immobilization to be developed. Mechanistic models are essential for long-term predictions of immobilization processes with a view to assessing the safe disposal of actinides in the cementitious near field of a repository for radioactive waste.
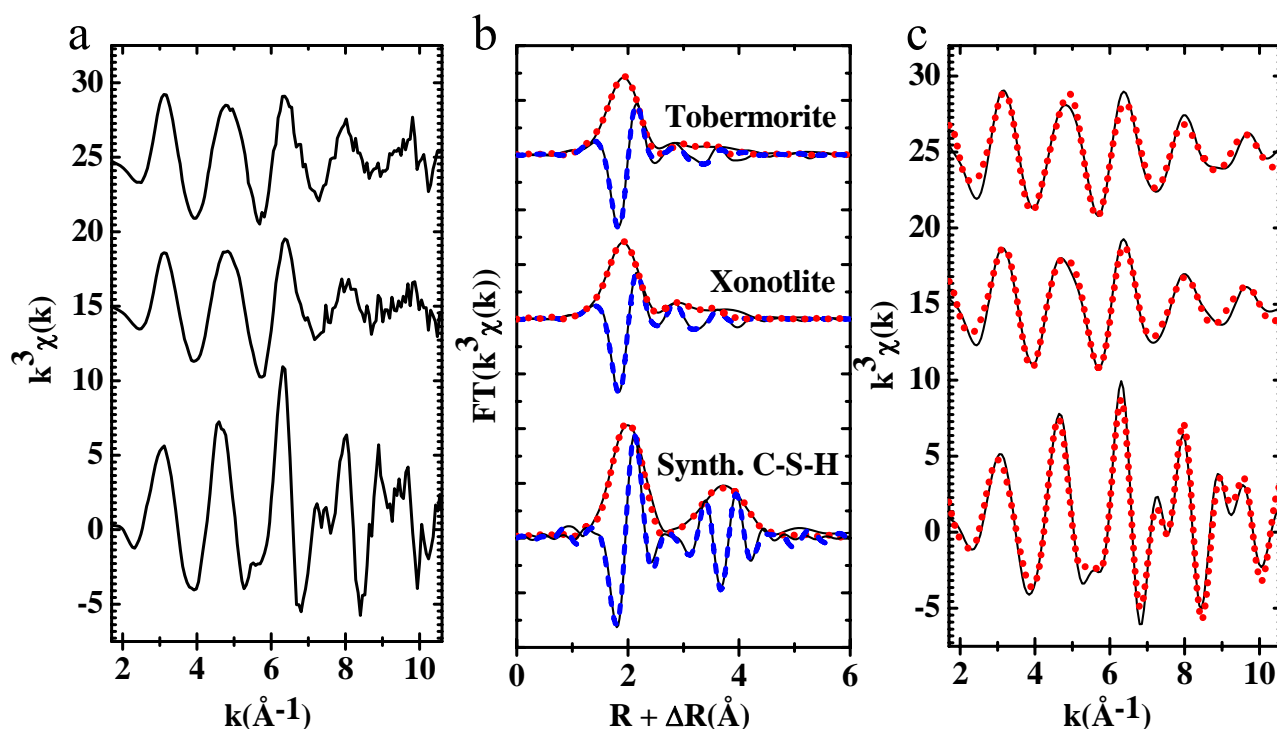

Fig. 1 EXAFS data of Eu doped tobermorite, xonotlite and a hydrothermally synthesized C-S-H phase (C/S = 0.8); a) k^3-weighted spectra, b) experimental (solid line) and fitted (dashed and broken lines for the imaginary and the real part, respectively) of the corresponding RSFs, c) k^3-weighted EXAFS data for the Fourier backtransform spectra obtained from Figure 1b (range: R + ΔR = 1.7-4.0 Å).

Table 1: Multi-shell fit analysis of Eu doped tobermorite (Tob) and xonotlite (Xon) equilibrated for 480 days (Eu(III) loading 35 µmol/g), and hydrothermally synthesized C-S-H with C/S = 0.8 (Eu(III) loading 350 µmol/g), (estimated uncertainties: CN±20 %; R±0.02 Å) [1].

Sample	Eu-O			Eu-Si [2]			Eu-Ca			Eu-Eu		
	CN	R(Å)	σ^2(Å^2)	CN	R(Å)	σ^2(Å^2)	CN	R(Å)	σ^2(Å^2)	CN	R(Å)	σ^2(Å^2)
Tob	6.7	2.40	0.009	5.1	3.76	0.007	4.2	3.82	0.010			
Xon	7.2	2.39	0.009	4.9	3.77	0.006	5.3	3.88	0.017			
				0.7	3.20	0.004						
C-S-H	8.3	2.47	0.005	3.4	3.84	0.005	3.6	4.01	0.003	3.3	4.13	0.003

[1] ΔE$_0$: 6.4 - 7.3 eV; Residual R$_f$: 7.3 - 8.6 %

[2] For xonotlite two Si shells were taken into account