ESRF	Experiment title: Determination of uptake mechanisms of Nd by calcium silicate hydrates.	Experiment number: EC 54
Beamline: BM 26	**Date of experiment**: from: 12.04.2006 to: 18.04.2006	**Date of report**: 14.12.2006
Shifts: 18	**Local contact(s)**: Sergey Nikitenko	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

R. Daehn*, P. Mandaliev*, M. Vespa*, E. Wieland*

Laboratory for Waste Management, Paul Scherrer Institute, CH-5232 Villigen, Switzerland

Report:

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. Thus, a mechanistic understanding of the processes controlling the binding of heavy metals, radionuclides and anionic species in cement systems is essential for predicting the environmental impact of cement-stabilized waste forms. Calcium silicate hydrates (C-S-H), $(CaO)_x(SiO_2)_y(H_2O)_z)$ are quantitatively the most important (~50 wt.%) and chemically the most stable minerals within hydrated cement paste [1]. Furthermore, C-S-H phases may control the long term release of radionuclides due to their low solubility within the cementitious near field.

Nd L_{III}-edge measurements were carried out on well crystalline C-S-H phases, e. g. tobermorite $(Ca_5Si_6O_{16}(OH)_2.7H_2O)$ and xonotlite $(Ca_6Si_6O_{17}(OH)_2)$, to gain molecular-level information on the Nd(III) uptake by C-S-H phases under different experimental conditions. Nd(III), a non-radioactive redox stable lanthanide, is considered to be an important rare earth element and can be used as a chemical analogue for trivalent radioactive contaminants, such as Am^{3+} and Cm^{3+}.

Fig. 1 shows the Fourier transforms (FT) of normalized, background subtracted, and k^3-weighted EXAFS spectra of Nd-doped tobermorite and xonotlite samples equilibrated for different time periods and Nd(III) loadings of 7 µmol/g. Fig. 1 reveals that all samples display a major peak at about R+ΔR ~2.0 Å, which corresponds to the contribution of the nearest O shells. Furthermore, the broad peaks at R+ΔR ~3.0 Å indicate backscattering contributions from more distant shells. The FT peak at about 2.0 Å was fitted by assuming the presence of a single oxygen shell. The coordination numbers (CN) for the samples equilibrated for 1 day were determined to be about 7 and 8 (for xonotlite and tobermorite, respectively). The distances of R_{Nd-O}=2.44-2.45 Å are shorter than R_{Nd-O}=2.51Å in $Nd(OH)_3$, indicating that the formation of $Nd(OH)_3$ in the Nd-doped systems can be excluded. The CN of the samples did not change significantly after long equilibration time (Table 1). Further neighboring shells could be fitted assuming Nd-Si and Nd-Ca

backscattering paths. The bond distances between the Nd-Si and Nd-Ca backscattering pairs of all the samples were found to increase with increasing reaction time (Fig. 1).

Increasing bond distances and the fact that CN remains unchanged during increasing reaction time suggest structural changes in the Nd(III) doped C-S-H phases and possible formation of solid solution. The formation of solid solutions can significantly reduce the solubility and therefore the mobility of the radionuclides in the geosphere
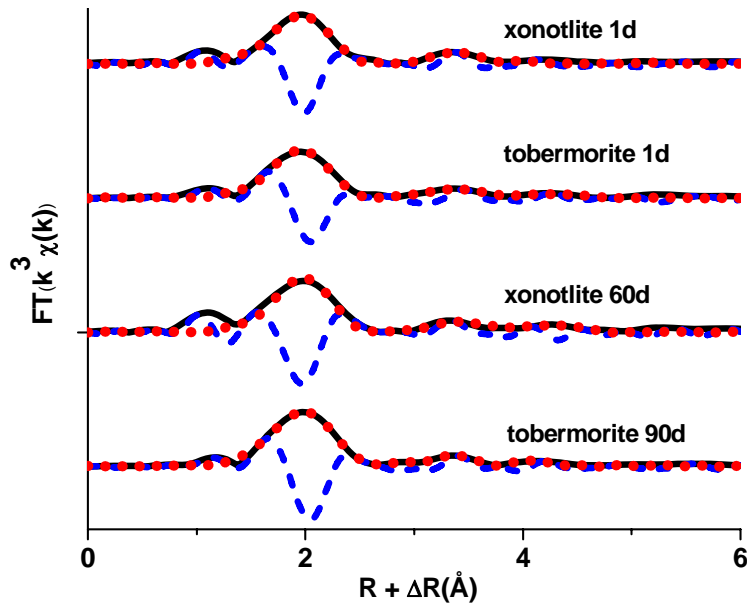

Fig. 1: FTs of k^3–weighted EXAFS spectra of experimental and fitted Nd-L$_{III}$-EXAFS for Nd treated cryst. C-S-H phases. (loading: 7 µmol/g; equilibration time: 1 day and 90 days for tobermorite and 1 – 60 day for xonotlite).

Table 1: Multi-shell fit analysis of Nd treated tobermorite and xonotlite (Nd(III) loading 7 µmol/g)
(Errors: CN±20 %; R±0.02 Å)

Sample	Nd-O			Nd-Si			Nd-Ca			ΔE_0
	CN	R(Å)	$\sigma^2(Å^2)$	CN	R(Å)	$\sigma^2(Å^2)$	CN	R(Å)	$\sigma^2(Å^2)$	$\Delta E0(eV)$
Tobermorite 1 day	8.1	2.44	0.01	1.7	3.75	0.01	2.0	3.78	0.006	6.0
Tobermorite 90 day	7.9	2.45	0.01	4.8	3.87	0.005	5.0	3.91	0.01	7.7
Xonotlite 1 day	6.9	2.45	0.01	1.2	3.66	0.005	1.7	3.73	0.01	6.4
Xonotlite 60 days	7.2	2.45	0.01	3.6	3.75	0.007	2.6	3.80	0.006	6.3

[1]   Lothenbach, B., Wieland, E. 2006. *Waste Management* **26**, 706.