ESRF	**Experiment title:** EXAFS study of Np(IV/V/VI) binding mechanisms to cementitious materials	**Experiment number**: EC-617
Beamline: **BM-20**	**Date of experiment:** **from: 30/04/2010 to: 05/05/2010**	**Date of report**: 25/08/2010 *Received at ESRF:*
Shifts: **15**	**Local contact(s)**: Dr. Andreas Scheinost	

Names and affiliations of applicants (* indicates experimentalists):
X. Gaona*, R. Daehn*, J. Tits*, D. Kunz* and E. Wieland
Laboratory for Waste Management, Paul Scherrer Institut, Villigen PSI, Switzerland

Report:

Cementitious materials will be used for the construction of the engineered barrier in repositories for long-lived intermediate level wastes (ILW), which may contain significant amounts of ^{237}Np ($t_{1/2} = 2.14\cdot10^6$ y). Predicting the long-term behaviour of Np in a cement-based repository requires a sufficiently detailed understanding of its interaction with the main phases of cement. Several Np redox states are expected under these conditions, although the corresponding stability fields and the binding mechanisms to cement are still poorly understood. The objectives of the project were: a) to assess the molecular environment of Np(IV/V) sorbed onto calcium silicate hydrates (C-S-H) and cement; b) to evaluate the stability field of Np(VI) within the pH range 10-14, and to assess its molecular environment when sorbed onto C-S-H phases and cement.

Results:

Sorption of Np(IV) onto C-S-H phases and cement

EXAFS measurements were performed on wet-pastes of C-S-H phases and cement doped with about 10000 ppm of Np(IV) tracer and equilibrated for 2 months in a N_2-filled glovebox. Four types of C-S-H phases with different Ca:Si ratio were prepared (0.7, 1.0, 1.6 and 1.0 in alkali-rich artificial cement pore water of pH = 13.3), representing different degradation steps of cement. Very reducing conditions were generated by $5\cdot10^{-3}$M $Na_2S_2O_4$. An additional sample of C-S-H with Ca:Si = 1.0 was prepared in absence of $Na_2S_2O_4$, in order to check the stability of unbuffered Np(IV) in C-S-H systems. As a lesson learnt from the previous campaign (see experiment EC-425), the samples were kept in liquid N_2 for the transport and storage during the measurements. The cryostat available at ROBL was used for all measurements (liquid-He temperature).

The transport and storage of Np(IV) samples in liquid N_2 was found to avoid oxidation to Np(V). Once left at room temperature and presence of air, the oxidation of Np(IV) took place within few hours. No differences in the EXAFS spectra were observed for Np(IV) samples prepared in presence and absence of $Na_2S_2O_4$, despite the unavoidable O_2-traces present in the glovebox. This observation indicates a strong stabilization of Np(IV) by C-S-H phases, in agreement with the very high distribution coefficients (R_d) determined in wet chemistry experiments (10^5-10^6 L·kg^{-1}).

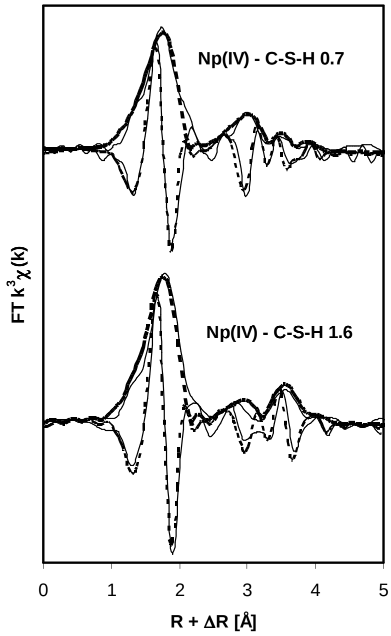

Fig. 1. *Experimental and theoretical Fourier transforms (modulus and imaginary parts) of Np(IV) sorbed on C-S-H 0.7 and 1.6.*

The principal component analysis (PCA) carried out using spectra of Np(IV)-doped C-S-H phases in $\chi(k)$, $k\chi(k)$, $k^2\chi(k)$, $k^3\chi(k)$ and energy spaces clearly indicates that only 2 components are needed to explain the spectra of all samples. The comparison of these compounds in ITFA mode with the original spectra strongly correlates them with Np(IV)-doped C-S-H 0.7 and 1.6. Linear combinations of these two “species” were found to satisfactorily explain EXAFS spectra of Np(IV) sorbed in C-S-H phases with Ca:Si ratio = 1.0, therefore allowing a mechanistic interpretation of Np(IV) uptake by C-S-H phases within the whole degradation sequence of cement. The Fourier-transformed k^3-weighted Np L_{III}-edge EXAFS (experimental and fits) for these samples are shown in Fig. 1. The resulting structural parameters are listed in Table 1. This information suggests an incorporation mechanism where Np(IV) (very likely) is bound in the interlayer of the C-S-H structure.

Sorption of Np(V) and Np(VI) onto C-S-H phases and cement

EXAFS measurements of Np(V) and Np(VI) were performed on weted-pastes, which were prepared in the same way as Np(IV) doped samples. No redox buffer was added to Np(V)-doped C-S-H and cement samples, whereas $5 \cdot 10^{-3}$M NaOCl was used for the preparation of the Np(VI) doped samples.

Sample	Shell	N	R [Å]	σ^2 [Å^{-2}]	ΔE^0 [eV]	R-factor
Np(IV) – C-S-H 0.7	O	6.8 ± 0.8	2.27 ± 0.01	0.010 ± 0.002	**5.8**	**0.068**
	Si	5.0 ± 1.5	3.57 ± 0.03	0.009 ± 0.004		
	Ca_1	2.2 ± 0.9	4.05 ± 0.05	0.006*		
	Ca_2	2.1 ± 1.0	4.22 ± 0.05	0.006*		
Np(IV) – C-S-H 1.6	O	7.7 ± 1.2	2.27 ± 0.01	0.009 ± 0.003	**5.5**	**0.090**
	Si	3.6 ± 0.7	3.59 ± 0.03	0.009*		
	Ca_1	4.3 ± 1.1	4.12 ± 0.03	0.006*		
	Ca_2	3.3 ± 1.2	4.28 ± 0.05	0.006*		

* parameters fixed in the fit

Table 1. *Structural information derived from the EXAFS analysis of Np(IV)-doped C-S-H samples with Ca:Si = 0.7 and 1.6.*

Sample	Shell	N	R [Å]	σ^2 [Å^{-2}]	ΔE^0 [eV]	R-factor
Np(V) – C-S-H 0.7	O_{ax}	2*	1.88 ± 0.01	0.002 ± 0.001	**13.0**	**0.02**
	O_{eq}	5.7 ± 1.0	2.39 ± 0.01	0.014 ± 0.004		
	Si	2.5 ± 1.9	3.21 ± 0.04	0.014 ± 0.011		
Np(V) – C-S-H 1.6	O_{ax}	2*	1.89 ± 0.01	0.002 ± 0.001	**12.2**	**0.01**
	O_{eq}	5.5 ± 0.6	2.39 ± 0.01	0.010 ± 0.002		
	Si_1	2.9 ± 0.9	3.24 ± 0.02	0.014*		
	Si_2	1.7 ± 1.5	3.86 ± 0.08	0.014*		
Np(VI) – C-S-H 0.7	O_{ax}	2*	1.79 ± 0.01	0.002 ± 0.001	**11.0**	**0.01**
	O_{eq}	4.2 ± 0.4	2.25 ± 0.01	0.005 ± 0.001		
	Si_1	0.5 ± 0.4	3.08 ± 0.04	0.004**		
	Si_2	1.8 ± 0.7	3.56 ± 0.02	0.004***		
	Si_3	1.3 ± 0.8	3.81 ± 0.04	0.004***		
Np(VI) – C-S-H 1.6	O_{ax}	2*	1.85 ± 0.01	0.004 ± 0.001	**10.2**	**0.06**
	O_{eq}	3.5 ± 0.8	2.24 ± 0.02	0.007 ± 0.003		
	$\mathit{Si_1}$	*0.4 ± 0.6*	*3.22 ± 0.11*	*0.004***		
	$\mathit{Si_2}$	*0.9 ± 1.2*	*3.65 ± 0.11*	*0.004****		
	$\mathit{Si_3}$	*1.5 ± 1.3*	*3.83 ± 0.08*	*0.004****		

* parameters fixed in the fit

** parameter left originally free. After the first iteration, it was fixed to reduce the uncertainty in N_{Si}

*** parameters defined originally = σ^2_{Si1}. After the first iteration, they were fixed to reduce the uncertainty in N_{Si}

Table 2. *Structural information derived from the EXAFS analysis of Np(V)- and Np(VI)-doped C-S-H samples with Ca:Si = 0.7 and 1.6.*

In contrast to Np(IV), the EXAFS spectra of Np(V) and Np(VI) provided only qualitative indications of an incorporation mechanism, mainly based on the identification of neighboring Si-atoms. Structural parameters determined for C-S-H samples of Ca:Si = 0.7 and 1.6 doped with either Np(V) or Np(VI) are given in Table 2. The Np(V/VI)-Si distances determined from the analysis of the EXAFS data significantly agree with those expected for Si-atoms mono- and di-coordinated to Np, and further they are in line with observations made on U(VI) in C-S-H environments (Macé et al., 2010; Harfouche et al., 2006). In contrast to Np(IV/V), the coordination environment of Np(VI) taken up by C-S-H phases seems to depend not only on the Ca:Si ratio but also on pH. Fig. 2 compares the Radial Structure Functions for samples of Np(VI)-doped C-S-H 0.7 (pH=10.1), 1.0 (pH=12.1), 1.6 (pH=12.5), 1.0 ACW (pH=13.3) and cement (pH=13.3). Axial and equatorial Np-O distances (r_{Np-Oax} and r_{Np-Oeq}) enlarge at lower pH. A similar behavior is to be expected for the transition of $NpO_2(OH)_3^-$ (with one additional coordinated H_2O) and $NpO_2(OH)_4^{2-}$. Analogously to U(VI), this transition (in the aqueous phase) may occur at pH 12-12.5 (Guillaumont et al., 2003).

The study shows that C-S-H phases play an important role in Np(IV/V/VI) immobilization in cementitious materials. Incorporation in the C-S-H structure is regarded as the predominant uptake mechanism.

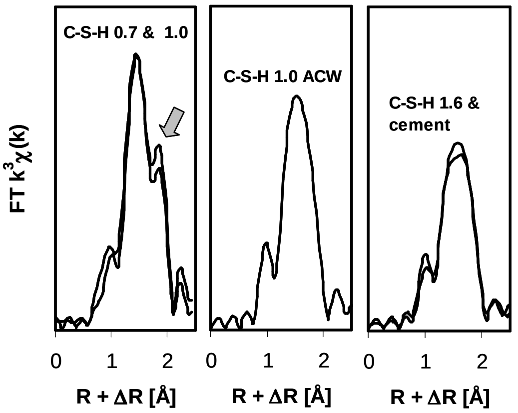

Fig. 2. *Comparison of experimental Radial Structure Functions obtained for Np(VI)-doped C-S-H 0.7, 1.0, 1.0 ACW, 1.6 and cement.*

References

Guillaumont, R., Fanghänel, J., Neck, V., Fuger, J., Palmer, D.A., Grenthe, I., Rand, M.H. (2003) Chemical Thermodynamics 5. Update on the Chemical Thermodynamics of Uranium, Neptunium, Plutonium, Americium and Technetium. NEA OECD, Elsevier

Harfouche, M., Wieland, E., Daehn, R., Fujita, T., Tits, J., Kunz, D., Tsukamoto, M. (2006). EXAFS study of U(VI) uptake by calcium silicate hydrates. Journal of Colloid and Interface Science, 303, 195-204

Macé N., Dähn R., Tits J., Scheinost A., Wieland E. (2010b). EXAFS study of U(VI) sorption on cementitious materials (in preparation)