



	Experiment title: EXAFS study of Neptunium binding mechanism to cementitious materials	Experiment number: EC-425
Beamline: BM-20	Date of experiment: from: 26/06/2009 to: 30/06/2009	Date of report: 19/08/2009
Shifts: 12	Local contact(s): Dr. André Rossberg	Received at ESRF:
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 ($t_{1/2} = 2.14 \cdot 10^6$ y). Predicting the long-term behaviour of Np in a cement-based repository requires an adequate 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 study the aqueous speciation of Np(V/VI) under hyper-alkaline conditions; b) to assess the molecular environment of Np(IV/V/VI) sorbed onto calcium silicate hydrates (C-S-H) and cement. Determination of the stability field of the aqueous species is essential prior to sorption studies, while C-S-H phases are the main constituent of cement.

Results:

Aqueous speciation of Np(V/VI) under hyper-alkaline conditions

EXAFS measurements were performed on two aqueous samples (S1 and S2) containing $2.8 \cdot 10^{-3}$ M Np(V) tracer. The hyper-alkaline matrix was provided by tetramethylammonium hydroxide (TMAOH, pH 13.5) to avoid the undesired precipitation of Na/K neptunates. The carbonate impurities of TMAOH led to a final carbonate concentration (at pH = 13.5) of ca. $2 \cdot 10^{-3}$ M. An oxidizing agent (NaOCl $5 \cdot 10^{-3}$ M) was added to sample S2.

Fig. 1 shows the Fourier-transformed k^3 -weighted Np L_{III} -edge EXAFS at pH 13.5 in the absence (S1) and presence (S2) of NaOCl. EXAFS fitting of both samples shows significant structural differences caused by the presence of NaOCl. A larger Np-O_{ax} distance and splitting of the equatorial oxygen shell characterize sample S1 (Table 1). A backscattering contribution from neighboring carbon was introduced ($R_{\text{Np-C}} = 3.06 \pm 0.04$ Å), although its presence cannot be unambiguously ascertained. Nevertheless, this assumption is in line with the study of Neck et al. [1], which showed the formation of the Np(V) ternary compound $\text{NpO}_2(\text{OH})(\text{CO}_3)_2^{4-}$ under similar experimental conditions using UV-vis spectroscopy. A rather short Np-O_{ax} distance ($R_{\text{Np-Oax}} = 1.80 \pm 0.01$ Å) was observed for sample S2. The shorter distance in the sample compared to the axial oxygen distance of Np(V) in sample S1 is attributed to the formation of Np(VI) in the presence of the strong oxidizing agent NaOCl. The distance of the four equatorial oxygen atoms in this sample was determined to be $R_{\text{Np-Oeq}} = 2.27 \pm 0.01$ Å. This distance is much shorter than those reported in the

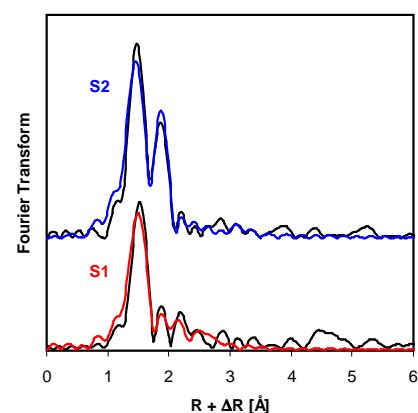


Fig. 1. Fourier-transformed Np L_{III} -edge EXAFS for samples S1 and S2. Black lines: experimental; blue/red lines: fit

Sample	Np-O _{ax}	Np-O _{eq}	Np-C
S1	N = 2 (s) $r = 1.86 \pm 0.01$ Å $\sigma^2 = 0.0021 \pm 0.0008$	N _{eq1} = 2.3 ± 2.2 $r_{\text{eq1}} = 2.26 \pm 0.05$ Å $\sigma^2 = 0.009 \pm 0.011$	N _c = 2.1 (s) $r_{\text{Np-C}} = 3.06 \pm 0.04$ Å $\sigma^2 = 0.003$ (s)
		N _{eq2} = 4 (s) $r_{\text{eq2}} = 2.45 \pm 0.04$ Å $\sigma^2 = 0.01 \pm 0.05$	
S2	N = 2 (s) $r = 1.80 \pm 0.01$ Å $\sigma^2 = 0.0010 \pm 0.0004$	N = 4.2 (s) $r = 2.27 \pm 0.01$ Å $\sigma^2 = 0.005 \pm 0.001$	

Table 1. Structural information derived from the EXAFS analysis of samples S1 and S2.

literature for Np(VI)-O_{eq} distances where O belonged either to water (R = 2.34 – 2.41 Å) or to sulphate (R = 2.51 Å). This evidence, together with the analogy with U(VI), suggest the presence of OH groups in the equatorial shell, and therefore the formation of the NpO₂(OH)₄²⁻ species. Np(VII/VI) EXAFS studies conducted by Williams et al. [2] in NaOH 1M, as well as theoretical calculations performed by Bolvin et al. [3] for the species NpO₂(OH)₄²⁻ reported Np-O distances in good agreement with those obtained in this study.

No thermodynamic data have been selected in the NEA thermodynamic series [4] for Np(VI) species forming under hyper-alkaline conditions. The predominance diagram shown in Fig. 2 was calculated with NEA TDB for Np, complemented with log*β° for NpO₂(OH)₃⁻ and NpO₂(OH)₄²⁻ species in analogy with U(VI). The experimental pH and E_H conditions determined for the samples S1 and S2 are indicated in Fig.2. The proposed stability fields agree very well with the predicted transition from Np(V) to Np(VI) as observed in this study. This work provides spectroscopic evidences for the formation of Np(VI) hydroxo species under controlled [CO₃²⁻], E_H and pH conditions, which is essential for further improvements of the thermodynamic properties of Np(VI).

Assessment of Np(IV/V/VI) sorption species on C-S-H phases and cement

C-S-H and cement suspensions were equilibrated with $8 \cdot 10^{-5} \text{M} < [\text{Np}] < 1 \cdot 10^{-4} \text{M}$ in a glovebox ([CO₂], [O₂] < 2 ppm). Samples were conditioned to obtain three different redox states of Np (starting redox states): a) Np(IV) tracer in Na₂S₂O₄ (reducing agent); b) Np(V) tracer; c) Np(V) tracer in NaOCl (oxidizing agent, expected to promote the formation of Np(VI)). The E_H of all suspensions was monitored during equilibration. The Np(V) samples prepared in the absence of NaOCl showed a significant decrease of E_H (0.3/0.1V → -0.1/-0.3V), suggesting the predominance of Np(IV) (Fig. 2). The Np-doped C-S-H/cement wet pastes were sealed with a double layer of Kapton foils and encapsulated in two additional plastic containments. The samples remained under air-atmosphere for 7 days prior to the measurements at the beamline due to legal regulations in conjunction with the transport of radioactive samples.

Axial and equatorial oxygen atoms had to be considered in the fitting of all samples (Fig. 3 and Table 2). Acceptable fits for the Np(IV) and Np(V) samples were only obtained by including both O_{ax}- and O_{eq}-shells, and either setting N_{Oax} or σ²_{Oax}. Setting σ²_{Oax} provided slightly lower R-factors, resulting in N_{Oax} of 1.2 - 1.4. The latter finding could indicate the presence of Np(IV/V) mixtures in these samples rather than presence of pure Np(IV) or Np(V) species, respectively, in line with the study of Denecke et al. [5]. Thus, one may assume that Np(IV) was present in both samples, i.e., the ones starting with Np(IV) and Np(V), and that Np(IV) oxidized to Np(V) during sample transport. This finding suggests that Np(IV) was also present in those sorption samples starting with Np(V), and further that particular precautions (liquid N₂, air tight transport) should be taken in subsequent campaigns. Under oxidizing conditions in presence of NaOCl short Np-O_{ax} and Np-O_{eq} distances were observed, thus indicating the formation of sorbed Np(VI) species.

References

[1] Neck et al. (1997). Radiochim. Acta, 77, 167-175; [2] Williams et al. (2001). J. Am. Chem. Soc., 123, 4346-4347; [3] Bolvin et al. (2001). J. Phys. Chem. A, 105, 11441-11445; [4] Guillaumont et al. (2003). NEA Thermodynamic Series. Elsevier; [5] Denecke et al. (2005). Talanta, 65, 1008-1014.

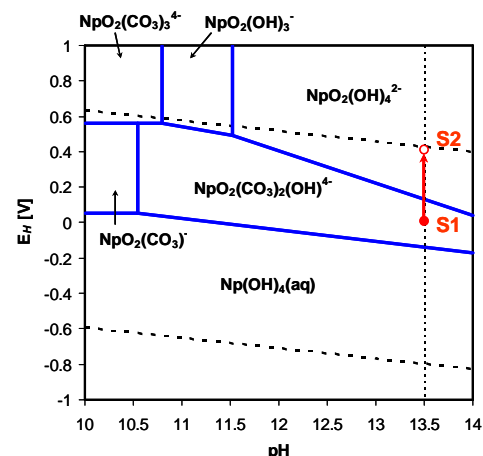


Fig. 2. Np predominance diagram calculated for 10 < pH < 14 and -1V < E_H < +1V.

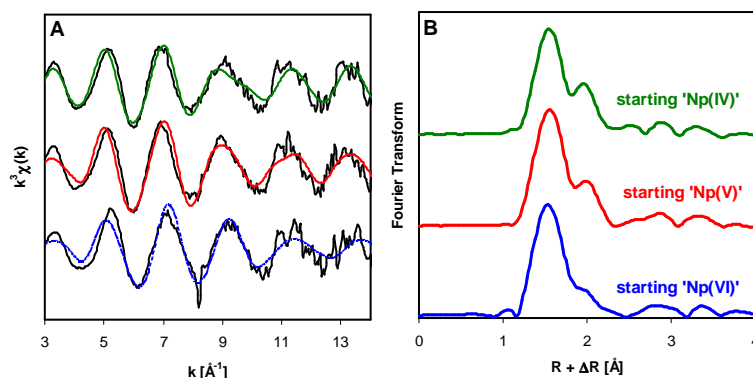


Fig. 3. EXAFS spectra (A) and Fourier-transformed EXAFS for Np(IV), Np(V) and Np(VI) sorbed on C-S-H (Ca/Si = 1.0).

Sample	Np-O _{ax}	Np-O _{eq}	R-factor
start Np(IV)	N = 1.2 ± 0.2 r = 1.87 ± 0.01 Å σ ² = 0.001 (s)	N _{eq} = 5.1 ± 0.7 r _{eq} = 2.34 ± 0.02 Å σ ² = 0.010 ± 0.003	0.059
start Np(V)	N = 2(s) r = 1.87 ± 0.01 Å σ ² = 0.003 ± 0.001	N _{eq} = 6.1 ± 0.8 r _{eq} = 2.30 ± 0.01 Å σ ² = 0.011 ± 0.003	0.078
start Np(VI)	N = 2 (s) r = 1.82 ± 0.01 Å σ ² = 0.004 ± 0.001	N = 5.5 ± 0.8 r = 2.21 ± 0.01 Å σ ² = 0.009 ± 0.002	0.094

(s): parameters fixed in the fitting process

Table 2. Structural information derived from the EXAFS analysis of Np-doped C-S-H samples.