



	Experiment title: Determination of uptake mechanisms of metal ions onto cement phases using XAFS	Experiment number: 01-01-614
Beamline: BM1B	Date of experiment: from: 18-07-2003 to: 22-07-2003	Date of report: 31-10-2003
Shifts: 12	Local contact(s): Wouter VAN BEEK	<i>Received at ESRF:</i>
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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. 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. Ni is among the most important contaminants in the waste matrices, and therefore, Ni uptake by hardened cement paste (HCP) has been studied with the aim to gain a molecular-level understanding of the immobilisation process. For this, HCP doped with 5000 ppm Ni was prepared at a water/cement ratio of 0.4 using a sulfate-resisting Portland cement and hydrated for three and thirty days.

We have carried out Ni K-edge measurements for both reference and cement samples. Data analysis was performed using the WinXas 2.3 software package. Natural Ni-phyllsilicates, Ni(OH)₂ and a synthetic NiAl-layered double hydroxide (NiAl-LDH) are considered as being the most important reference materials to be used for the identification of the formed unknown Ni-phases in HCP. Distinct differences in the normalized, background-subtracted and k²-weighted spectra between the samples hydrated for 3 and 30 days were observed (Fig. 1a). A distinctive beat pattern at ~8Å⁻¹ was found for the 30 days sample. This characteristic feature can be used as an indication of the formation of NiAl-LDH phases (Scheinost & Sparks, 2000). The radial structure functions (RSFs) were calculated using a Bessel window in the k-range of 1.8 to 9.7 Å (Fig. 1b). Data analysis performed with FEFF 8.2 revealed similar interatomic distances and coordination numbers for both the 3 and 30 days hydrated cement samples (Table 1) suggesting that the same Ni phase dominates in both samples. The first RSF peak corresponds to a Ni-octahedral coordination with interatomic distances of 2.03-2.04 Å. For all samples, the second RSF peak was fitted with Ni alone, since the discrimination of Ni-Ni and Ni-Al/Si backscattering pairs in NiAl-LDH and Ni-phyllsilicates is problematic (Scheinost & Sparks, 2000). The fits reveal for the cements samples Ni-Ni distances (R_{Ni-Ni}= 3.09-3.10 Å) longer than in NiAl-LDH (3.06 Å). This finding suggests that not a pure NiAl-LDH phase has formed and that the longer R_{Ni-Ni} are caused by the presence of β-Ni(OH)₂ impurities (R_{Ni-Ni}= 3.12 Å). To test

whether this hypothesis would be consistent with the observed fit results, linear least-square fitting (LSF) of the experimental EXAFS spectra with linear combinations of reference spectra was performed. Best fit results were obtained using a combination of NiAl-LDH and β -Ni(OH)₂ (Fig. 2). The weight percentage of NiAl-LDH in the Ni-doped cement samples was found to increase with time (62% to about 86%) whereas β -Ni(OH)₂ decreases (32% to about 20%) accordingly. This finding clearly suggests that NiAl-LDH is the predominant phase in the cement samples. Furthermore it appears that NiAl-LDH is thermodynamically the most stable Ni phase in hydrated cement as previously suggested from Ni sorption experiments on HCP by Scheidegger et al. (2000). Data analysis is currently ongoing to refine the fitting approach presented above.

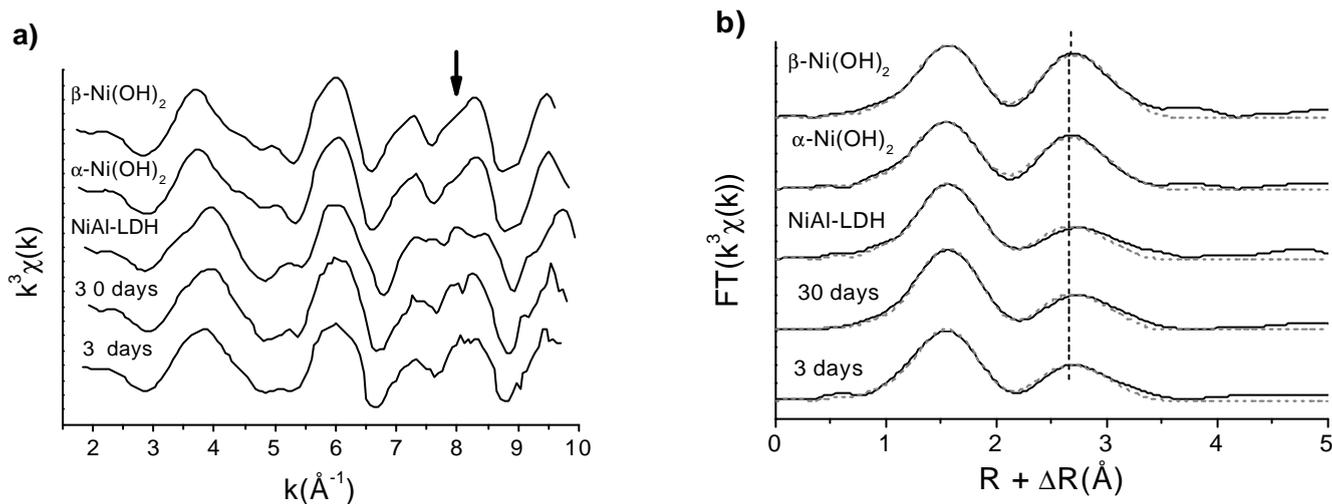


Fig. 1. a) k^3 -weighted, normalized, background-subtracted EXAFS spectra of Ni-doped cement with hydration times of 3 and 30 days, NiAl-LDH and α -Ni(OH)₂ and β -Ni(OH)₂. The arrow localizes the region at $\sim 8\text{\AA}^{-1}$ characteristic for NiAl-LDH; b) RSFs spectra of Ni-doped cement and reference compounds.

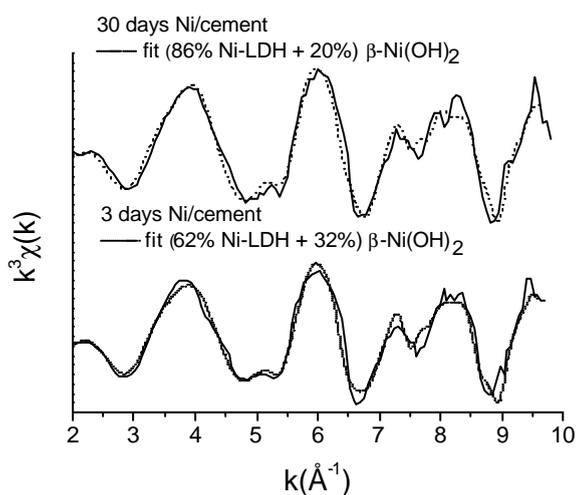


Fig. 2. LSF of experimental EXAFS spectra with linear combinations of reference spectra.

References

- Scheinost A.C. & Sparks D.L. (2000). *Journal of Colloid and Interface Science*, **223**, 167-178.
 Scheidegger A.M. et al. (2000). *Environ. Sci. Tech.* **34**, 4545-4548.

Table 1. Best fit parameters for experimental EXAFS Analysis.

Sample	$R_{\text{Ni-O}}$	CN	σ^2 (\AA^2)	$R_{\text{Ni-Ni}}$ (\AA)	C N	σ^2 (\AA^2)
β -Ni(OH) ₂	2.05	5.5	0.005	3.12	6.2	0.006
α -Ni(OH) ₂	2.03	5.2	0.005	3.09	6.1	0.008
NiAl-LDH	2.04	6.3	0.006	3.06	2.7	0.005
Ni/cement 30 days	2.04	6.3	0.005	3.09	3.0	0.005
Ni/cement 3 days	2.03	5.8	0.006	3.10	2.9	0.004

R , CN, σ^2 stand for interatomic distances, coordination numbers and Debye-Waller factors. Estimated error: $R_{\text{Ni-O}} \pm 0.02 \text{\AA}$, $\text{CN}_{\text{Ni-O}} \pm 20\%$, $R_{\text{Ni-Ni}} \pm 0.02 \text{\AA}$, $\text{CN}_{\text{Ni-Ni}} \pm 20\%$