SUPPORTING INFORMATION FOR

Micro-scale investigations of Ni uptake by cement using a combination of scanning electron microscopy and synchrotron-based techniques

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Details of μ-XAS data reduction

All data were processed following the same procedure. The energy was converted to photoelectron wave vector units ($Å^{-1}$) by assigning the origin E_0 to the first inflection point of the absorption edge. Radial Structure Functions (RSF) were obtained by Fourier transforming the k^3-weighted $\chi(k)$ functions between 3.2 and 10.9 $Å^1$ with a Bessel window function with a smoothing parameter of 4. Multishell fits were performed in real space across the range of the first two shells (R+ΔR range=0.8-3.5 Å). The first coordination shell was fitted with Ni-O backscattering pairs. The second coordination shell was fitted solely using Ni-Ni pairs, because the discrimination of Ni-Ni and Ni-Al backscattering pairs in Ni-Al LDH is problematic (1). To be able to compare the coordination numbers (CN) of the Ni-Ni backscattering pairs (CN_{Ni-Ni}) of all samples and references, the Debye-Waller factor was set to 0.005 $Å^2$ (2). Theoretical scattering paths for the fit were calculated using FEFF 8.20 (3) and the structure of β-$Ni(OH)_2$ as a reference. The amplitude reduction factor (S_0^2) was determined to be 0.85 from the experimental β-$Ni(OH)_2$ XAS spectrum (1,2).

Table S1. Semi-quantitative EDS analyses of Ni-rich regions and cement phases in the Ni-doped HCP-samples. All data are given in wt% (spots are indicated in Fig. 1b, Fig. 2b and Figure S1).

Ni_cem_5000	**Ni**	**Al**	**Ca**	**Si**	**Fe**	**S**	**Sr**	**Mg**	**K**	**Na**	**Cr**	**Cl**	**O**	**Total**
a	0.00	0.37	34.92	11.37	0.68	1.20	0.00	0.18	0.06	0.07	0.00	0.01	51.14	100.00
b	0.13	0.03	53.86	1.10	0.03	0.19	0.00	0.06	0.02	0.09	0.04	0.00	44.45	100.00
c	28.33	3.33	10.21	1.85	0.12	1.17	0.58	0.00	0.03	0.00	0.05	0.04	54.31	100.02
d	27.42	3.44	10.54	2.09	0.17	1.01	0.42	0.17	0.01	0.10	0.06	0.01	54.58	100.02
e	22.50	3.54	15.71	4.80	0.41	0.90	1.28	0.38	0.02	0.08	0.00	0.05	50.33	100.00
f	9.22	1.12	34.42	6.66	0.53	0.56	0.00	0.37	0.07	0.13	0.00	0.00	46.92	100.00
g	2.46	0.88	33.54	9.37	0.78	1.23	0.00	0.34	0.04	0.00	0.10	0.13	51.14	100.01
h	5.51	1.48	28.57	9.95	0.43	1.11	0.00	0.72	0.04	0.00	0.00	0.02	52.17	100.00
i	0.24	0.91	24.03	8.94	0.47	0.78	0.00	0.24	0.05	0.00	0.02	0.00	64.33	100.01
j	0.00	0.37	21.25	8.91	0.27	0.63	0.00	0.47	0.00	0.12	0.04	0.03	67.91	100.00
k	0.01	0.23	29.64	9.06	0.06	0.11	0.00	0.27	0.04	0.17	0.00	0.02	60.40	100.01
l	10.85	1.92	25.63	8.43	0.48	0.79	1.96	0.43	0.01	0.08	0.00	0.03	49.41	100.02
m	7.51	1.44	26.10	8.21	0.48	0.58	1.88	0.63	0.00	0.28	0.05	0.00	52.85	100.01
n	4.23	1.54	33.89	6.96	1.16	0.77	1.70	0.51	0.00	0.00	0.01	0.05	49.16	99.98
o	5.97	1.43	38.21	8.08	1.07	0.78	2.02	0.38	0.06	0.00	0.08	0.08	41.84	100.00
p	13.16	2.46	24.38	8.49	0.32	0.70	2.02	0.42	0.07	0.00	0.02	0.02	47.96	100.02
q	12.27	2.29	25.81	8.27	0.47	0.96	2.01	0.30	0.02	0.00	0.07	0.07	47.45	99.99
Ni_cem_500														
r	0.24	0.49	36.18	10.67	0.74	0.95	2.62	0.79	0.00	0.05	0.00	0.02	47.25	100.00
s	2.51	0.65	34.25	9.67	0.42	1.28	2.48	0.52	0.17	0.05	0.06	0.13	47.80	99.99
t	4.00	0.77	33.52	9.70	0.37	0.92	2.29	0.50	0.17	0.10	0.07	0.04	47.56	100.01
u	4.45	0.89	31.35	9.22	0.49	1.06	2.18	0.70	0.15	0.00	0.00	0.00	49.52	100.01
v	2.52	0.65	32.16	9.29	0.34	0.93	2.19	0.55	0.15	0.55	0.00	0.07	50.60	100.00
Ni_cem_50														
w	0.21	0.13	55.51	2.06	0.14	0.59	0.20	0.03	0.05	0.14	0.05	0.03	40.85	99.99
x	0.17	0.86	37.46	10.72	1.08	1.15	0.00	0.58	0.06	0.12	0.01	0.00	47.81	100.02
y	3.08	1.26	34.17	10.12	1.18	1.49	0.00	0.65	0.08	0.00	0.07	0.06	47.84	100.00
z	1.12	1.02	38.33	10.41	1.24	1.54	0.00	0.32	0.09	0.09	0.00	0.09	45.74	99.99
errors: ~1 wt%														

Table S2. Structural information obtained from further selected μ-EXAFS Ni K-edge data analysis.

	Ni-O			Ni-Ni			Ni-Si				
Samples	**CN**	**R (Å)**	**σ^2 (Å)**	**CN**	**R (Å)**	**σ^2 (Å)**	**CN**	**R (Å)**	**σ^2 (Å)**	**ΔE_0**	**%Res**
References											
Ni-Phyllosilicate [a]	5.1	2.04	0.006	3.5	3.07	0.008[c]	3.7	3.26[Si]	0.008[c]	0.3	3.0
β-$Ni(OH)_2$	5.6	2.06	0.005	5.6	3.13	0.005[d]				-0.6	3.0
α–$Ni(OH)_2$	5.2	2.03	0.005	4.9	3.09	0.005[d]				3.0	4.4
Ni-Al LDH (LDH)	6.0	2.05	0.006	2.5	3.06	0.005[d]				1.1	4.5
Neo-formed Ni-Al LDH [b] (N-LDH)	5.7	2.04	0.004	3.9	3.07	0.005[d]				0.3	3.8
Cement samples											
Ni_cem_5000 (bulk-EXAFS) [e]	***7.3***	***2.05***	***0.007***	***3.0***	***3.11***	***0.005*** [d]				***1.3***	***7.9***
ROI S1	5.9	2.06	0.006	3.5	3.09	0.005[d]				1.5	4.8
ROI S2	4.6	2.06	0.002	3.0	3.11	0.005[d]				2.1	7.3
ROI S3	6.6	2.04	0.007	3.1	3.08	0.005[d]				-0.7	3.1
ROI S4	5.3	2.03	0.003	2.6	3.08	0.005[d]				-2.8	11.2

[a] Dähn et al. 2002, [b] Scheidegger et al., 1997, [c] correlated parameters and [d] fix parameters during fitting procedures, [e] Vespa et al. (2006)

R, CN, σ^2, ΔE_0 stand for interatomic distances, coordination numbers, Debye-Waller factors and inner potential corrections.

Estimated error: $R_{(Ni-O)}$ ±0.02 Å, $CN_{(Ni-O)}$ ±20%, $R_{(Ni-Ni)}$ ±0.02 Å, $CN_{(Ni-Ni)}$ ±20%

%Res: deviation between experimental data and fit given by the relative residual in percent.

N= number of data points, Y_{exp} and Y_{theo}: experimental and theoretical data points, respectively.

$$\%Res = \frac{\sum_{i=1}^{N} \left| y_{exp}(i) - y_{theo}(i) \right|}{\sum_{i=1}^{N} y_{exp}(i)} * 100$$

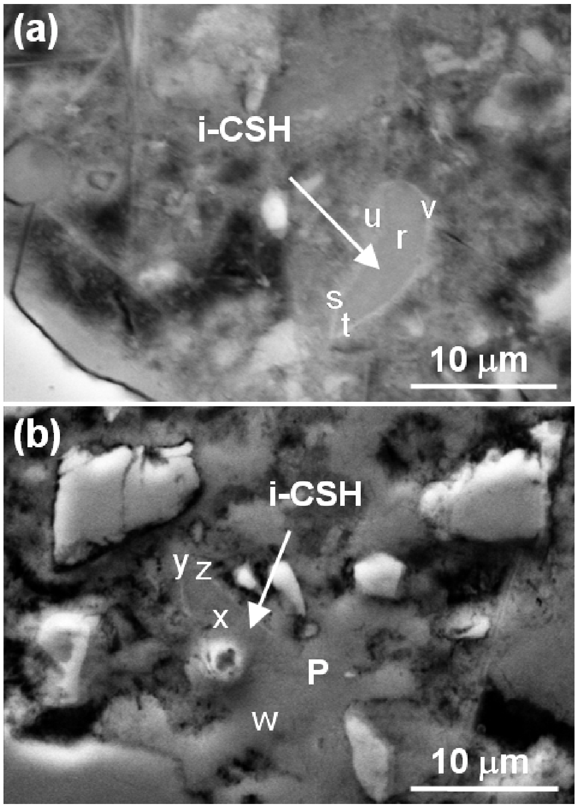

Figure S1. BSE images of the $Ni(NO_3)_2$-doped HCP sample with a water/cement ratio of 0.4 hydrated for 30 days and total metal concentrations of (a) 500 mg/kg and (b) 50 mg/kg. The lower case letters s to z indicate the regions of the SEM/EDS spot analyses shown in Table S1.

Literature Cited

References

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