environmental, earth and planetary science

Ni phases formed in cement and cement systems under highly alkaline conditions: an XAFS study

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X-ray absorption fine structure (XAFS) spectroscopy was applied to assess the solubility-limiting phase of Ni in cement and cement minerals. The study reveals the formation Ni and Al containing hydrotalcite-like layered double hydroxides (Ni-Al LDHs) when cement material (a complex mixture of CaO, SiO_2, Al_2O_3, Fe_2O_3 and SO_3) was treated with Ni in artificial cement pore water under highly alkaline conditions (pH = 13.3). This finding indicates that Ni-Al LDHs and not Ni-hydroxides determine the solubility of Ni in cement materials.

Keywords: cement, Ni, layered double hydroxides, XAFS

1. Introduction

Cementitious materials are commonly used worldwide in immobilization strategies for the disposal of hazardous and radioactive waste (Glasser, 1993; Gougar *et al.*, 1996). For the uptake of Ni by blended cement several uptake modes have been discussed (Atkins *et al.*, 1994): the formation of a 4:1 Ca:Ni phase (which is thought to replace $Ni(OH)_2$ as the solubility-limiting phase in cement systems), the presence of a poorly crystallized $Ni(OH)_2$ gel and the formation of a Ni and Al containing hydrotalcite-like layered double hydroxide (Ni-Al LDH). Recent XAFS studies have shown that the formation of Ni-Al LDHs can immobilize Ni and other heavy metal ions under neutral and slightly alkaline conditions in laboratory systems containing Al(hydr)oxides or clay minerals (Scheidegger *et al.*, 1997; Towle et al *et al.*, 1997, Scheidegger *et al.*, 1998; Scheinost *et al.*, 1999a; Thompson *et al.*; 1999; Scheinost *et al.*, 2000). In the present study we used XAFS to investigate the nature of the Ni phases formed with cement and cement constituents under the conditions relevant to cement systems (pH = 13.3).

2. Materials and Methods

2.1 Solids

The solids used in this study were quartz, calcium silicate hydrate (csh), portlandite ($Ca(OH)_2$), gibbsite ($Al(OH)_3$) and the size fraction ≤70 µm of a commercial Portland cement (trade name CPA 55 HTS, Lafarge, France). The composition of the cement material was 66.4 wt.% CaO, 23.8 wt.% SiO_2, 2.7 wt.% Al_2O_3, 2.8 wt.% Fe_2O_3 and 1.8 wt.% SO_3 as the main chemical compounds. Ni sorption experiments were carried out by adding aliquots of a 0.1 M Ni solution ($Ni(NO_3)_2 \cdot 6H_2O$) Ni to an artificial cement pore water (ACW; solid/liquid: $2.5 \ 10^{-2}$ kg L^{-1}). The samples were shaken end-over-end in a glove box under a N_2 atmosphere ($CO_2 < 5$ ppm, $O_2 < 5$ ppm) for 150 days and then centrifuged. The composition of ACW was equivalent to the chemical composition of a solution in equilibrium with freshly prepared pulverized hardened cement paste. Under these conditions, the pore water is a (Na,K)OH rich fluid saturated with respect to portlandite (pH = 13.3). Details on solid characterization and preparation of ACW are described elsewhere (Wieland *et al.*, 1998, Tits *et al.*, 2000).

XAFS spectra were collected at beamline X-11A (NSLS, Brookhaven National Laboratory, Upton, NY) using a Si(111) crystal monochromator. Fluorescence spectra were measured at room temperature using a solid-state detector (13-element detector, Canberra). The measurements were recorded in N_2 atmosphere to prevent CO_2 contamination. Further details on the experimental set-up and data collection are described elsewhere (Scheidegger *et al.*, 1997; Scheidegger *et al.*, 1998). XAFS data reduction was performed using WinXAS 97 1.3 software package following standard procedures (Ressler, 1998). Multishell fits were performed in real space across the range of the first two shells ($\Delta k = 3.2 - 12.0$ Å^{-1} (cement sample: 3.2 - 10.0 Å^{-1}); $\Delta R = 0.5$ to 4 Å). Theoretical scattering paths for the fit were calculated with FEFF 8.0 (Rehr *et al.*, 1991), using the structures of β-$Ni(OH)_2$ and hydrotalcite (Bellotto *et al.*, 1996). The amplitude reduction factor, S_0^2, was fixed at 0.85 (O'Day *et al.*, 1994). The R_{Ni-O} and R_{Ni-Ni} values are estimated to be accurate to ±0.02 Å, and ΔE_o values and the CN_{Ni-O} and CN_{Ni-Ni} values are estimated to be accurate to ±20% (Scheidegger *et al.*, 1998). Reference compounds used were β-$Ni(OH)_2$, α-$Ni(OH)_2$, Ni-phyllosilicate, and Ni-Al LDH phases (takovite ($Ni_6Al_2(OH)_{16}CO_3 \cdot H_2O$), a natural mineral and a synthetic Ni-Al LDH phase with an overall Ni:Al ratio of 1.3). Since for crystal chemical reasons the Ni:Al ratio in Ni-Al LDHs can not be lower than 2:1 (Bish and Brindley, 1977), it must be assumed that the synthetic phase contained impurities such as amorphous Al-(hydr)oxides. Synthesis and characterization of the reference compounds are described elsewhere (Scheinost *et al.*, 1999a).

2. Results and Discussions

Fig. 1 shows the normalized, background subtracted and k^3-weighted Ni-XAFS spectra. The figure reveals that the $k^3\chi(k)$ spectra of the Ni treated cement and gibbsite samples are similar to the spectra of takovite and the synthetic mixed Ni-Al LDH phase (syn. Ni-Al LDH), suggesting a similar structural environment. It has been demonstrated that a distinctive beat pattern between 8.0 and 8.5 Å^{-1} in the $k^3\chi(k)$ spectrum can be used as a fingerprint to unequivocally identify the presence of Ni-Al LDHs (Scheinost *et al.*, 2000). Indeed, Fig. 1 reveals the presence of this distinctive beat pattern at about 8 Å^{-1} in the Ni cement sample (see dashed lines in Fig. 1). Moreover, the beat pattern at about 8 Å^{-1} is similar to the beat pattern in the spectra of Ni-gibbsite, takovite and the synthetic Ni-Al LDH phase. While for Ni-Al LDHs the oscillation at about 8 Å^{-1} is truncated, other reference compounds and Ni treated cement constituents (α and β-$Ni(OH)_2$, Ni-phyllosilicate, Ni/csh, and Ni/quartz) show an elongated upward oscillation ending in a sharp tip at ≈8.5 Å^{-1}. Full multiple scattering simulations and experimental spectra of model compounds indicate that the beat pattern is due to the combination of focused multiple scattering of Ni and Al (Scheinost *et al.*, 2000). Thus, the presence of this feature in the $k^3\chi(k)$ spectrum clearly demonstrates that a Ni-Al LDH phase has been formed in Ni doped cement sample.
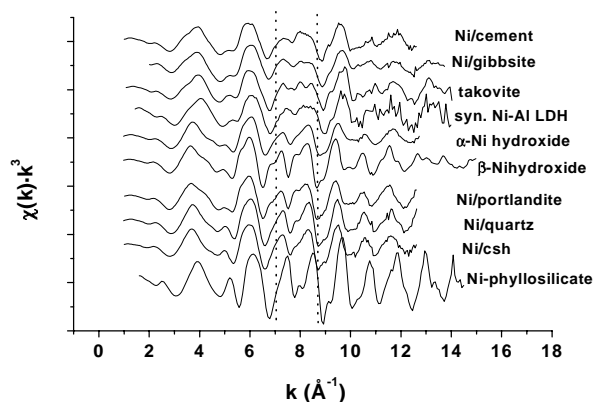
Figure 1

k^3-weighted, normalized, background-subtracted XAFS spectra of Ni treated cement, Ni treated gibbsite, takovite, a synthetic Ni-Al LDH, α-Ni(OH)$_2$, β-Ni(OH)$_2$, Ni treated portlandite, Ni treated quartz, Ni treated CSH and a synthetic Ni-phyllosilicate. The vertical dashed lines localize the region of the distinctive beat pattern at ~8 Å^{-1} characteristic for Ni-Al LDH phases.
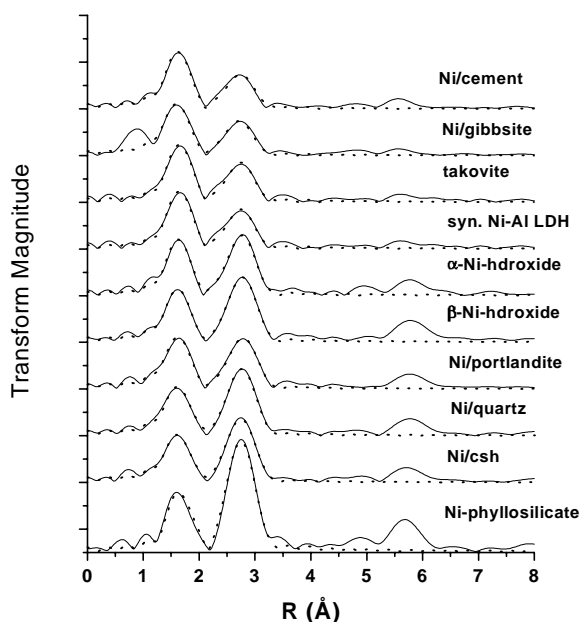

Figure 2

Fourier transforms (uncorrected for phase shift) of the $k^3\chi(k)$ spectra shown in Fig.1. The solid line represents the experimental data and the dashed line the fit.

The structural parameters derived from multishell XAFS analysis are summarized in Tab. 1. The table reveals that in the first coordination shell Ni is surrounded by ~6 oxygen atoms at 2.04-2.06 Å. This behavior indicates that Ni(II) is coordinated in an octahedral environment. For all samples fitting of the second radial structure function (RSF) peak was performed by using Ni alone since discrimination of Ni-Ni and Ni-Si/Al backscattering in Ni-Al LDH and Ni phyllosilicate phases is problematic (Manceau & Calas, 1985; Manceau & Calas, 1986; Towle *et al.*, 1997; Thompson *et al.*, 1999; Scheinost *et al.*, 2000). Tab. 1 shows that, as expected, the Ni-Ni coordination number (CN$_{(Ni-Ni)}$) in β-Ni(OH)$_2$ is close to 6. In Ni-phyllosilicates, however, the CN$_{Ni-Ni}$ is greater than 6 due to the

constructive interference of Si in the tetrahedral sheets at a distance between 3.2-3.3 Å resulting in an enhancement of the overall amplitude (Charlet & Manceau, 1994; Manceau *et al.,* 1999). In spite of the experimental error, it is possible (but not conclusive) that in the Ni/csh and Ni/quartz samples the CN$_{(Ni-Ni)}$'s (6.4 and 6.3) are also slightly enhanced due to at least partly the neoformation of a Ni-phyllosilicate phase in the reaction system. This explanation would agree with recent XAFS findings that the uptake of Co and Zn onto quartz and clay surfaces at neutral and slightly alkaline pH conditions can result in the neoformation of Co- and Zn-phyllosilicate phases (Manceau *et al.*, 1999; Schlegel *et al.*, 2001). In the synthesized Ni-Al LDH sample, however, the number of second shell neighbor atoms obtained is clearly reduced (CN$_{(Ni-Ni)}$ = 2.8). In Ni-Al LDHs Al is partially substituted by Ni resulting in a significant destructive interference between the Ni and the Al XAFS contribution and in an amplitude cancellation between the Ni and Al shells. The same characteristic is observed for CN$_{Ni-Ni}$ in takovite (CN$_{(Ni-Ni)}$ = 3.1) as well as for CN$_{Ni-Ni}$'s in the Ni treated cement and gibbsite samples (CN$_{(Ni-Ni)}$ = 2.7-3.2). For this reason, the CN$_{Ni-Ni}$'s determined by data analysis further support our finding that a Ni-Al LDH phase is formed in the cement sample. In Fig. 2 the Fourier transforms of the $k^3\chi(k)$ spectra are shown in comparison with the fit. The figure illustrates the findings discussed above. In Ni-Al LDH phases the amplitude of the second shell peak is clearly reduced (due to the destructive interference between the Ni and the Al XAFS contribution) compared to α and β-Ni(OH)$_2$.

Table 1
Structural Information Derived from XAFS Analysis

	Ni-O			Ni-Ni				
	CN	R [Å]	$\Delta\sigma^2$ [Å^2] 10^{-3}	CN	R$_{Ni-Ni}$ [Å]	$\Delta\sigma^2$ [Å^2] 10^{-3}	ΔE_0 [Å]	$\chi^2_{res\,\%}$
β-Ni hydroxide	5.9	2.06	5.3	5.8	3.13	5.3	0.2	6.9
α-Ni hydroxide	5.8	2.04	4.9	5.5	3.09	5.8	3.6	9.3
Ni phyllosilicate	5.8	2.06	3.8	6.7	3.08	2.8	3.9	10.9
syn. Ni-Al LDH	6.0	2.05	4.6	2.8	3.06	4.2	4.1	9.2
takovite	5.3	2.05	3.5	3.1	3.06	5.4	1.4	10.5
Ni/cement	5.9	2.05	4.4	2.7	3.09	4.7	0.8	4.7
Ni/csh	5.7	2.06	6.4	6.4	3.10	6.5	0.2	7.2
Ni/quartz	6.0	2.05	6.7	6.3	3.10	6.1	1.2	8.4
Ni/portlandite	6.0	2.06	5.9	5.1	3.13	6.0	0.4	10.0
Ni/gibbsite	6.0^f	2.04	5.9	3.2	3.06	6.1	0.1	18.4

CN, R, $\Delta\sigma^2$, ΔE_O stand for the coordination numbers, interatomic distances, Debye-Waller factors, and inner potential corrections
f: Fixed parameter during fitting.
$\chi^2_{res\%}$: Deviation between experimental data and fit given by the relative residual in percent. N represents the number of data points, and y_{exp} and y_{theo} the experimental and theoretical data points, respectively.

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

Ni-Ni distances in the sorption samples are 3.06 Å for the Ni treated gibbsite sample, 3.09 Å for the Ni treated cement sample, 3.10 Å for the Ni/quartz and Ni/csh samples, and 3.13 Å for Ni/portlandite. The last distance agrees well with Ni-Ni distances in β-Ni(OH)$_2$. The Ni-Ni distances in the Ni/quartz and Ni/csh samples appear to be slightly longer than the Ni-Ni distances in α-Ni(OH)$_2$ and Ni-Phyllosilicates (3.06-3.08 Å; Mellini, 1982; Scheinost *et al.*,

2000). Furthermore, an R_{Ni-Ni} of 3.09 Å for the cement sample seems to be on the longer side for Ni-Al LDHs (3.03-3.07 Å; Scheidegger *et al.*, 1998; Malherbe *et al.*, 1999; Thompson *et al.*; 1999).

We suspect that the longer Ni-Ni distances observed in the Ni/quartz, Ni/csh and Ni/cement sample are caused by the presence of a fraction of β-Ni(OH)$_2$. The formation of at least some β-Ni(OH)$_2$ in the samples would not be surprising. β-Ni(OH)$_2$ is the thermodynamically more stable than α-Ni(OH)$_2$ and the phase expected to be formed in solution under the highly alkaline reaction conditions. Indeed, Fig. 1 and data analysis suggest that in the Ni/portlandite sample β-Ni(OH)$_2$ and not α-Ni(OH)$_2$ is formed. To test whether a mineral mixture would be consistent with the observed cement spectrum, we fitted the XAFS spectrum of the Ni-treated cement with linear combinations of various reference compounds. Best fits were obtained with ~10% β-Ni(OH)$_2$ and ~90% Ni-Al LDHs (Ni/cement sample). Still, the results support our hypothesis that Ni is predominately fixed in Ni-Al LDHs.

Further evidence in support of the formation of Ni-Al LDHs in Ni treated cement and gibbsite samples is provided by diffuse reflectance spectroscopy (DRS). The band positions of Ni in Ni treated cement and in Ni treated gibbsite are fully in accord with the band positions of various Ni-Al LDH phases. Further details on DRS and the experimental results are presented elsewhere (Scheinost *et al.*, 1999b; Scheidegger *et al.*, 2000).

In conclusion, the XAFS study demonstrates that Ni-Al LDH phases can be formed when cement is treated with Ni under highly alkaline conditions (pH = 13.3). Furthermore, the study reveals that depending on the mineral surface present in the experimental system (csh, quartz, or portlandite) a different Ni phase can be formed. This work may lead to new approaches for modeling heavy metal binding in cement and cement systems and may allow better predictions of the performance of cement-based landfills and nuclear waste repositories.

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