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# Spectroscopic Evidence for the Formation of Layered Ni–Al Double Hydroxides in Cement

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X-ray absorption fine structure (XAFS) spectroscopy and diffuse reflectance spectroscopy (DRS) were applied to assess the solubility-limiting phase of Ni in cement systems. The study provides first direct spectroscopic evidence for the formation of Ni- and Al-containing hydrotalcite-like layered double hydroxides (Ni–Al LDHs) when cement material (a complex mixture of mainly CaO, SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, MgO, and SO<sub>3</sub>) was treated with Ni in artificial cement pore water under highly alkaline conditions (pH = 13.3). The study shows that Ni–Al LDHs were formed in cement suspensions oversaturated with respect to  $\beta$ -Ni(OH)<sub>2</sub> and aged at room temperature for 150 days. This finding indicates that Ni–Al LDHs and not Ni-hydroxides may determine the solubility of Ni in cement materials.

## Introduction

Cementitious materials are commonly used worldwide in immobilization strategies for the disposal of hazardous and radioactive waste. The waste loading potential of cement materials and their performance in leaching tests has been demonstrated by a large number of studies (e.g., ref 1). It has been proposed that the immobilization potential originates from the selective binding properties of cement for waste cations and anions (2, 3). Atkins et al. (4) conducted studies to describe the mechanisms of immobilization of Ni by cement. Ni uptake by blended cement has been attributed to the formation of a 4:1 Ca:Ni phase, which is thought to replace Ni(OH)<sub>2</sub> as the solubility-limiting phase in cement systems. However, X-ray diffraction of Ni-doped cement pastes showed only the presence of a poorly crystallized Ni(OH)<sub>2</sub> gel. The formation of Ni–Al LDHs as a possible uptake mode in cement systems was also postulated in the same work (4). The authors were successful in synthesizing Ni salts of the hydrotalcite group under highly alkaline conditions indicating that Ni–Al-oxyhydroxides are potential host phases for Ni in cement. Recent studies have shown that the formation of secondary mixed Ni–Al-oxyhydroxides (Ni–Al LDHs) can immobilize Ni and other heavy metal ions under neutral and slightly alkaline conditions in natural systems containing Al(hydro)oxides or clay minerals (5–10). LDHs are a family of natural and synthetic materials of the general type  $[M^{2+}_{1-x}M^{3+}_x(OH)_2]^{x+} \cdot (x/n)A^{n-} \cdot mH_2O$ , where, for

example, M<sup>2+</sup> is Mg(II), Ni(II), Co(II), Zn(II), Mn(II), and Fe(II), and M<sup>3+</sup> is Al(III), Fe(III), and Cr(III). The LDH structure is built up of stacked sheets of edge-sharing metal octahedra separated by anions between the interlayer spaces (11, 12). Bocclair and Braterman (13) recently found that LDHs stability increases in the order Mg < Mn < Co ~ Ni < Zn for Me(II) and Al < Fe for Me(III). The flexible structure of LDHs make them potentially important reservoir minerals under ambient conditions as well as at high pH, e.g., in the technical barriers employed for waste ion immobilization.

In the present study we used X-ray absorption fine structure (XAFS) spectroscopy and diffuse reflectance spectroscopy (DRS) to investigate the nature of the Ni precipitates formed under the conditions relevant to cement systems. Ni precipitates were synthesized in the presence of gibbsite (simulating an Al source in cement) and pulverized hardened cement paste (HCP) immersed in artificial cement pore water (ACW). Structural data of the precipitates obtained by XAFS and DRS were then compared to a set of natural and synthesized Ni reference phases.

## Materials and Methods

**Solids.** The cement material was prepared from a commercial Portland cement (trade name CPA 55 HTS, Lafarge, France). This cement is composed of 66.4 wt % CaO, 23.8 wt % SiO<sub>2</sub>, 2.7 wt % Al<sub>2</sub>O<sub>3</sub>, 2.8 wt % Fe<sub>2</sub>O<sub>3</sub>, and 1.8 wt % SO<sub>3</sub> as the main chemical components. A cement paste was prepared and cured at room temperature (100% relative humidity) for about 6 months under CO<sub>2</sub> free conditions. Powdered material was then prepared by crushing cylindrical samples of hydrated hardened cement paste (HCP) in a mortar under CO<sub>2</sub> free conditions and sieving the material to collect the size fraction  $\leq 70 \mu\text{m}$ , which was used in the experiments.

The gibbsite used in this study was hydrated alumina obtained from ALCOA (USA) (Aluminum Company of America). Chemical analysis revealed only minor impurities of Fe (less than 0.006% as Fe<sub>2</sub>O<sub>3</sub>), Si (less than 0.07% as SiO<sub>2</sub>), and Na (less than 0.42% as Na<sub>2</sub>O). The solid was used without pretreatment.

**Sample Preparation.** Ni precipitation studies were carried out in acid-washed 40 mL polyallomere centrifuge tubes (Beckman Instruments, Inc.). The solids (1 g powdered HCP or gibbsite), 36 mL ACW and 4 mL aliquots of a 0.1 M Ni solution (Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O) were added simultaneously to the centrifuge tubes (solid/liquid ratio:  $2.5 \cdot 10^{-2} \text{ kg L}^{-1}$ ). The samples were shaken end-over-end for 150 days. Samples for XAFS and DRS measurements were prepared from the residual wet pastes obtained after centrifugation of the suspensions (60 min at  $95,000 \times g$  (max.)). Sample preparation and equilibration steps were carried out in a glovebox under a N<sub>2</sub> atmosphere (CO<sub>2</sub> < 5 ppm, O<sub>2</sub> < 5 ppm).

The composition of ACW was equivalent to the chemical composition of a solution in equilibrium with freshly prepared HCP. Under these conditions, the pore water is a (Na,K)OH rich fluid saturated with respect to portlandite (pH = 13.3). The preparation of ACW is described elsewhere (14).

**Characterization of Solid Ni Phases.** Solid Ni phases were characterized using X-ray absorption fine structure (XAFS) spectroscopy and diffuse reflectance spectroscopy (DRS).

XAFS spectra were collected at beamline X-11 A at the National Synchrotron Light Source, Brookhaven National Laboratory, Upton, NY using a Si(111) crystal monochromator. Fluorescence spectra were measured at room temperature using an Ar-filled Stern-Heald detector with Soller slits and a Co-3 filter. For the Ni treated cement sample, a solid-state detector (13 element detector, Canberra) was used.

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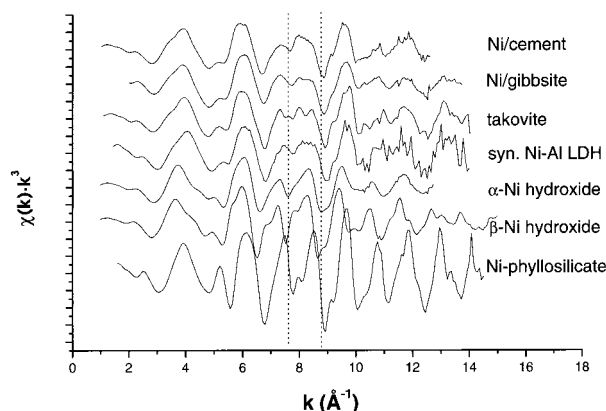


FIGURE 1.  $k^3$ -weighted, normalized, background-subtracted XAFS spectra of Ni treated cement, Ni treated gibbsite, takovite, a synthetic Ni-Al LDH,  $\alpha$ -Ni(OH) $_2$ ,  $\beta$ -Ni(OH) $_2$ , and a synthetic Ni-phyllsilicate. The vertical dashed lines localize the region of the distinctive beat pattern at  $\sim 8 \text{ \AA}^{-1}$  characteristic for Ni-Al LDH phases.

To prevent CO $_2$  contamination, the samples were placed in a Plexiglas chamber equipped with Kapton windows, which was continuously purged with N $_2$  during the measurements. Further details on the experimental setup and data collection are described elsewhere (5, 6).

XAFS data reduction was performed using WinXAS 97.1.1 following standard procedures (15). The resulting  $\chi(k)$  functions were weighed by  $k^3$  to account for the damping of oscillations with increasing  $k$  and Fourier transformed to achieve radial structure functions (RSF). A Bessel window with a smoothing parameter of 3 was used to suppress artifacts due to the finite Fourier filtering range between 3.2 and 12.0  $\text{\AA}^{-1}$  (cement samples: 3.2 and 10.0  $\text{\AA}^{-1}$ ). Multishell fits were performed in real space across the range of the first two shells (0.5 to 4  $\text{\AA}$ ). Theoretical scattering paths for the fit were calculated with FEFF 8.02 (16), using the structures of  $\beta$ -Ni(OH) $_2$  and hydrotalcite (11). To reduce the number of adjustable parameters, the amplitude reduction factor,  $S_0^2$ , was fixed at 0.85 (17). The  $R_{\text{Ni-O}}$  and  $R_{\text{Ni-Ni}}$  values are estimated to be accurate to  $\pm 0.02 \text{ \AA}$ , and  $\Delta E_0$  values and the  $\text{CN}_{\text{Ni-O}}$  and  $\text{CN}_{\text{Ni-Ni}}$  are estimated to be accurate to  $\pm 20\%$ . The accuracy estimates are based on the results of theoretical fits to spectra of the reference compounds of known structure (6).

DRS experiments were conducted with a Perkin-Elmer double-beam Lambda 9 spectrophotometer equipped with a 5-cm Spectralon-coated integrating sphere over the wavelength range 500–1000 nm. Blanks, i.e., samples prepared in the same way as the sorption samples but without Ni, were used for spectral background removal. The position of the  $\nu_2$  band was determined by peak fitting. Further details of the DRS principles and the experimental procedure are described in refs 7 and 18.

As reference compounds for the XAFS and DRS studies a synthetic  $\beta$ -Ni(OH) $_2$  (Johnson Matthew Co.) and a natural Ni-Al LDH phase (takovite;  $\text{Ni}_6\text{Al}_2(\text{OH})_{16}\text{CO}_3 \cdot \text{H}_2\text{O}$ ) (Kambalda W. A., Australia) were used. Further reference phases containing Ni, Al, and/or Si were a Ni-phyllsilicate, a  $\alpha$ -Ni(OH) $_2$  and a synthetic Ni-Al LDH phase (syn. Ni-Al LDH) with a Ni:Al ratio of 1.3 in the structure. Synthesis and characterization of the reference compounds are described elsewhere (7).

## Results and Discussions

Figure 1 shows the normalized, background subtracted and  $k^3$ -weighted Ni-XAFS spectrum of cement paste treated with Ni in ACW (pH = 13.3) for 150 days. For comparison, the figure also shows the spectrum of a gibbsite sample treated

with Ni under identical reaction conditions and the spectra of Ni reference compounds. The figure reveals that the  $\chi(k^3)$  spectra of the Ni treated cement and gibbsite samples are very similar, both in amplitude as well as with respect to the phase. Among the various reference compounds, the spectra of takovite and the synthetic mixed Ni-Al LDH phase (synth. Ni-Al LDH) show clearly the most similarities with the spectra of Ni treated sorption samples. This finding suggests that Ni in the cement and gibbsite samples is present in a similar structural environment as in Ni-Al LDHs.

Scheinost and Sparks (8) have demonstrated that a distinctive beat pattern between 8.0 and 8.5  $\text{\AA}^{-1}$  in the  $\chi(k^3)$  spectrum can be used as a fingerprint to unequivocally identify the presence of Ni-Al LDHs. Indeed, Figure 1 reveals the presence of this distinctive beat pattern at about 8  $\text{\AA}^{-1}$  in the Ni cement sample (see dashed lines in Figure 1). Moreover, the beat pattern at about 8  $\text{\AA}^{-1}$  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  $\text{\AA}^{-1}$  is truncated, the other reference compounds ( $\alpha$  and  $\beta$ -Ni(OH) $_2$  and Ni-phyllsilicate) show an elongated upward oscillation ending in a sharp tip at ca. 8.5  $\text{\AA}^{-1}$ . Full multiple scattering simulations and experimental spectra of model compounds indicate that the beat pattern is due to focused multiple scattering at Ni/Al ratios between 1 and 4 (8). Thus, the presence of this feature in the  $\chi(k^3)$  spectrum clearly demonstrates that a Ni-Al LDH phase has been formed in Ni doped cement samples.

The structural parameters derived from multishell XAFS analysis are summarized in Table 1. The data reveal that the first coordination shell of Ni comprises  $\sim 6$  oxygen atoms at 2.04–2.06  $\text{\AA}$ . This behavior indicates that Ni(II) is coordinated in an octahedral environment. For all samples, fitting of the second RSF peak was performed by using Ni alone (9, 10). Table 1 shows that, as expected, the Ni-Ni coordination number ( $\text{CN}_{\text{Ni-Ni}}$ ) in  $\beta$ -Ni(OH) $_2$  is close to 6. In  $\alpha$ -Ni(OH) $_2$   $\text{CN}_{\text{Ni-Ni}}$  is slightly lower (5.5) and supports the existence of Ni vacancies in the brucite-like Ni(OH) $_2$  layer. In the Ni-phyllsilicate sample, the  $\text{CN}_{\text{Ni-Ni}}$  is greater than 6 due to the constructive interference of Si in the tetrahedral sheets at a distance between 3.2 and 3.3  $\text{\AA}$  resulting in an enhancement of the overall amplitude (19, 20). In the synthesized Ni-Al LDH sample, however, the number of second shell neighbor atoms obtained is strongly reduced ( $\text{CN}_{\text{Ni-Ni}} = 2.8$ ). 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 characteristics are observed for  $\text{CN}_{\text{Ni-Ni}}$  in takovite ( $\text{CN}_{\text{Ni-Ni}} = 3.1$ ) as well as for  $\text{CN}_{\text{Ni-Ni}}$ 's in the Ni treated cement and gibbsite samples ( $\text{CN}_{\text{Ni-Ni}} = 2.7$ –3.2). Thus the  $\text{CN}_{\text{Ni-Ni}}$  determined by data analysis further support our finding that a Ni-Al LDH phase is formed in the cement sample.

Data analysis suggests a Ni-Ni distance of 3.06  $\text{\AA}$  for the Ni treated gibbsite sample and 3.09  $\text{\AA}$  for the Ni treated cement sample. For comparison, Ni-Ni distances in the reference compounds vary between 3.06 and 3.13  $\text{\AA}$ . In  $\beta$ -Ni(OH) $_2$ , the Ni-Ni distance ( $R_{\text{Ni-Ni}}$ ) is 3.13  $\text{\AA}$  which corresponds well to the  $R_{\text{Ni-Ni}}$  derived from neutron diffraction (21), XRD (22), and previous XAFS studies (6, 17). The  $R_{\text{Ni-Ni}}$  of 3.09  $\text{\AA}$  of  $\alpha$ -Ni(OH) $_2$  is consistent with the range of 3.07 to 3.09  $\text{\AA}$  found by Pandya et al. (23). For Ni-Al LDHs (synthetic Ni-Al LDH and takovite) and Ni-phyllsilicate the Ni-Ni distances observed also agree with those reported in the literature (3.03–3.07  $\text{\AA}$  for Ni-Al LDHs (6, 9, 24) and 3.06–3.07  $\text{\AA}$  for Ni-phyllsilicate (8, 20, 25)). It must be mentioned that, despite experimental error ( $\pm 0.002 \text{ \AA}$ ), an  $R_{\text{Ni-Ni}}$  of 3.09  $\text{\AA}$  for the cement sample seems to be on the long side for Ni-Al LDH's. To explain the longer Ni-Ni

TABLE 1. Structural Information Derived from XAFS Analysis

	CN <sub>Ni-O</sub> <sup>a</sup>	R <sub>Ni-O</sub> [Å] <sup>a</sup>	σ <sup>2</sup> <sub>Ni-O</sub> [Å <sup>2</sup> ] <sup>a</sup>	CN <sub>Ni-Ni</sub> <sup>a</sup>	R <sub>Ni-Ni</sub> [Å] <sup>a</sup>	σ <sup>2</sup> <sub>Ni-Ni</sub> [Å <sup>2</sup> ] <sup>a</sup>	ΔE <sub>0</sub> [eV] <sup>a</sup>	χ <sup>2</sup> <sub>res</sub> % <sup>d</sup>
β-Ni hydroxide	5.9	2.06	0.0053	5.8	3.13	0.0053	0.2	6.9
α-Ni hydroxide	5.8	2.04	0.0049	5.5	3.09	0.0058	3.6	9.3
Ni phyllosilicate	5.8	2.06	0.0038	6.7	3.08	0.0028	3.9	10.9
syn. Ni-Al LDH	6.0	2.05	0.0046	2.8	3.06	0.0042	4.1	9.2
takovite	5.3	2.05	0.0035	3.1	3.06	0.0054	1.4	10.5
Ni/cement	5.9	2.05	0.0044	2.7	3.09	0.0047	0.8	4.7
Ni/gibbsite	6.0 <sup>c</sup>	2.04	0.0059	3.2	3.06	0.0061	0.1	18.4

<sup>a</sup> CN, R, Δσ<sup>2</sup>, ΔE<sub>0</sub> stand for the coordination numbers, interatomic distances, Debye-Waller factors, and inner potential corrections. <sup>b</sup> Estimated accuracies: R<sub>(Ni-O)</sub> ±0.02 Å, CN<sub>(Ni-O)</sub> ±20%, R<sub>(Ni-Ni)</sub> ±0.02 Å, CN<sub>(Ni-Ni)</sub> ±20%, ΔE<sub>0</sub> ±20%. <sup>c</sup> Fixed parameter during fitting. <sup>d</sup> χ<sup>2</sup><sub>res</sub> %: Deviation between experimental data and fit given by the relative residual in percent. N represents the number of data points, and y<sub>exp</sub> and y<sub>theo</sub> the experimental and theoretical data points, respectively.

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

distances one may speculate about the formation of a Ni-Fe(III) LDH phase in the cement sample. In honessite (Ni<sub>6</sub>Fe<sub>2</sub>(OH)<sub>16</sub>SO<sub>4</sub>·4H<sub>2</sub>O), a natural Ni-Fe(III) LDH phase, Ni-Ni distances (3.08 Å; ref 12 and references therein) agree well with those in the cement sample (3.09 Å). However, we question the possibility that the formation of a Ni-Fe(III) LDH phase (in which Fe is partially substituted by Ni) could be an important sink for Ni in our cement sample. Ni and Fe have a very similar backscattering behavior (Fe and Ni are difficult to differentiate by XAFS) which results in a constructive XAFS interference between Ni and neighboring Fe atoms. As a consequence the CN<sub>(Ni-Ni)</sub> should be close to the CN<sub>(Ni-Ni)</sub> observed in Ni-hydroxides (5.5–6). The cement spectrum, however, reveals a reduced CN<sub>(Ni-Ni)</sub> (2.7) and the presence of the distinctive beat pattern at about 8 Å<sup>-1</sup>. Both findings clearly suggest the presence of a Ni-Al LDH phase and not a Ni-Fe LDH phase.

We suspect that the longer Ni-Ni distances observed in the cement sample are caused by the presence of minor quantities of β-Ni(OH)<sub>2</sub>. The formation of at least some β-Ni(OH)<sub>2</sub> in the samples would not be surprising. β-Ni(OH)<sub>2</sub> is thermodynamically more stable than α-Ni(OH)<sub>2</sub> and is expected to be formed in homogeneous solutions under highly alkaline reaction conditions. To test whether a mineral mixture would be consistent with the observed spectrum, we fitted the XAFS spectrum of the Ni-treated cement with linear combinations of Ni-Al LDHs and β-Ni(OH)<sub>2</sub>. The best fit was obtained with 9% β-Ni(OH)<sub>2</sub> and 91% Ni-Al LDHs. The XAFS data were also fitted by assuming two different Ni-Ni distances. For this purpose, CN<sub>(Ni-Ni)</sub> and R<sub>(Ni-Ni)</sub> were fixed to 0.6 and 3.13 Å corresponding to ~10% β-Ni(OH)<sub>2</sub>. The fitting procedure resulted in a decrease of R<sub>Ni-Ni</sub> in the Ni-Al LDH fraction of the cement sample from 3.09 to 3.07 Å. Thus, the R<sub>(Ni-Ni)</sub> of 3.09 Å is caused by the presence of a small portion of β-Ni(OH)<sub>2</sub>. Still, the result supports 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 DRS. The crystal field splitting of Ni<sup>2+</sup> in an octahedral oxygen cage is very sensitive to small changes in Ni-O bond distances (2θ). Therefore, DRS can also be used to distinguish among Ni-Al LDH, Ni phyllosilicates, and α-Ni(OH)<sub>2</sub> (8). The ν<sub>2</sub> band positions of Ni in Ni treated cement (15 430 cm<sup>-1</sup>) and in Ni treated gibbsite (15 270 cm<sup>-1</sup>) are fully in accord with the ν<sub>2</sub> band positions of various Ni-Al LDHs given by Scheinost et al. (8) (15 220 cm<sup>-1</sup>–15 430 cm<sup>-1</sup>). For comparison, in Ni-phyllosilicates the ν<sub>2</sub> band is ~15 150 cm<sup>-1</sup>, and in Ni-hydroxides the position of the ν<sub>2</sub> band is even further decreased to 14 750 cm<sup>-1</sup>–14 920 cm<sup>-1</sup>. Thus, the DRS

measurements fully support the XAFS findings and suggest the formation of a precipitate with Ni in a brucite-like hydroxide layer partly substituted by Al.

In conclusion, the study demonstrates that the formation of Ni-Al LDHs is a relevant binding mechanism for Ni(II) in cement. LDHs may act as important reservoir minerals for Ni(II) and, presumably, other bi- and trivalent cations under ambient conditions as well as in the technical barriers employed for waste immobilization. Thus, this work may lead to new modeling approaches of the heavy metal binding by cement which may allow in the future more detailed predictions of the performance of cement-based landfills for hazardous waste and the cementitious near field of repositories for radioactive waste.

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