Speciation of heavy metals in cement-stabilized waste forms: A micro-spectroscopic study

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Abstract

Cement-based materials play an important role in multi-barrier concepts developed worldwide for the safe disposal of industrial and radioactive waste in underground repositories. In this study, synchrotron based-techniques (micro X-ray spectroscopy (XAS) and micro X-ray fluorescence (XRF)) were used to investigate Co and Ni uptake by Hardened Cement Paste (HCP) with the aim of improving our understanding of the immobilization process of heavy metals in cement at the molecular level. For Ni and Co, XRF mapping revealed a highly heterogeneous element distribution as far as the concentration is concerned. The XAS studies further showed that Ni(II) forms predominantly layered double hydroxide (LDH) phases. In contrast to Ni, Co was found to be present in the oxidation states II and III. Co(II) is predominately incorporated into newly formed Co(II) hydroxide-like phases ($Co(OH)_2$), Co-LDH or Co-phyllosilicates, whereas Co(III) tends to be incorporated into a Co(III)O(OH)-like phase or a Co-phyllomanganate.
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1. Introduction

Assuring safe disposal and long-term storage of hazardous and radioactive wastes represents a primary environmental task of industrial societies. The long-term disposal of the hazardous wastes is associated with land-filling of cement-stabilized waste, whereas some radioactive wastes are also disposed of in cementitious underground repositories. For example, more than 90 wt.% of the near-field material of the planned deep underground repository for intermediate-level waste in Switzerland consists of HCP and cementitious backfill materials. Therefore, HCP plays an important role in the immobilization of heavy metals. From a chemical stand-point, HCP is a very heterogeneous material with discrete particles typically in the size range of about 2–200 μm. Overall, the material consists of mainly calcium (aluminium) silicate hydrates, calcium hydroxide and calcium aluminates.

Co and Ni isotopes are important contaminants in waste materials resulting from a variety of industrial processes, and they are activation products in metallic structures of nuclear power plants. Previous experiments of Ni uptake by blended cement (Atkins et al., 1994) and Ni sorption onto a powdered material prepared from a sulfate-resisting cement (Scheidegger et al., 2000, 2001) indicate that within an alkaline environment like the one in a compacted cement matrix (pH > 12.5) poorly crystalline $Ni(OH)_2$ and Ni–Al LDH phases are formed. Co speciation has been extensively

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studied in clay systems (e.g. Manceau et al., 1999; Schlegel et al., 1999; Thompson et al., 1999), but it is poorly known in cement systems.

In the present study we have combined micro-XAS with micro-XRF to gain micro-scale information on the chemical speciation and structural coordination environment of Co and Ni in cement. The micro-spectroscopic study was complemented with bulk-XAS experiments to assess whether the locally observed Ni and Co phases are representative of the entire cement system.

2. Method

2.1. Sample preparation

The cement samples were prepared from a commercial sulfate-resisting Portland cement (CEM I 52.5 N HTS, Lafarge, France) used to condition waste materials and foreseen to be used for the construction of engineered barrier systems (container, backfill and linear materials) in the Swiss disposal program. Metal doped HCP was prepared by mixing nitrate salt solutions of the Ni and Co metals to the unhydrated cement at a water-to-cement ratio (w/c) of 0.4. The final concentration of the metal in the cement matrix was 5000 ppm. After hydration times of 3, 30 and 150 days the hardened metal-doped cement paste was cut into several slices of ~1 cm thickness. Some of the slices were crushed to prepare a powder material for bulk-XAS measurements. Other slices were used to prepare polished thin sections for synchrotron based micro-XAS and micro-XRF investigations.

2.2. Characterization of the Ni- and Co-phases

The characterization was carried out by using bulk-XAS and micro-XAS. Micro-XRF/XAS measurements were performed on beamline 10.3.2 of the Advanced Light Source (ALS), Lawrence Berkley National Laboratory, Berkley, USA. The beam size was 5×5 μm^2 for both fluorescence mapping and the collected micro-XAS spectra. Co and Ni K-edges bulk-XAS spectra of the powdered materials were collected at the Swiss Norwegian Beam Line (SNBL) at the European Synchrotron Radiation Facility (ESRF) in Grenoble, France.

Data reduction of both micro- and bulk-XAS data was performed using the WinXAS 3.1 software package following standard procedures. Theoretical scattering paths for the fit were calculated using

FEFF 8.2. The amplitude reduction factor (S_0^2) was fixed to 0.85 for both Ni and Co (O'Day et al., 1994).

3. Results

The study on the Ni speciation in the cement matrix reveals that Ni is highly heterogeneously distributed and forms Ni-rich "hot spots" (spot size up to ~50 μm^2). XAS spectra of the "hot spots" and the bulk-XAS data show a distinctive beat pattern at ~8 $Å^{-1}$. This characteristic feature indicates the formation of Ni–Al LDH phases (Scheinost and Sparks, 2000). For both bulk- and micro-XAS data, data analysis reveals Ni–Ni distances (R_{Ni-Ni}=3.09–3.11 Å) longer than in pure Ni–Al LDH phases (3.06 Å). The longer R_{Ni-Ni} are caused by the presence of β-Ni(OH)$_2$ impurities (R_{Ni-Ni}=3.12 Å) (Scheidegger et al., 2000). Linear least-square fitting (LSF) of the experimental XAS (bulk and micro) spectra with linear combinations of reference spectra (Ni–Al LDH, Ni(OH)$_2$ and Ni-Phyllosilicate) suggests that the sample is composed mainly of Ni–Al LDH (~60%) and some Ni(OH)$_2$ (~40%).

For the Co-doped cement system, the micro-XRF maps show that Co is also heterogeneously distributed in the cement matrix (Fig. 1a,b). On the one hand there are Co-rich spots up to ~50 μm^2 in size (as observed for Ni). On the other hand Co-rich ring-like structures with diameters up to ~200 μm were observed. Fig. 1c shows the normalized, background-subtracted and k^3-weighted spectra of bulk-XAS and micro-XAS data of a Co-rich spot and a Co ring-like structure (3 days hydration time) together with reference compounds. The spectrum of spot 2 was collected on the ring-like structure and shows a clear shift of the first oscillation compared to spot 1 and the bulk data. From the comparison of the data with reference compounds it clearly appears that spot 1 and the bulk data exhibit similarities with respect to Co(II) speciation, whereas spot 2 shows more similarities to Co(III) compounds. For spot 1 and the bulk data, data analysis reveal longer Co–O (2.06 Å) and Co–Co (3.16 and 3.13 Å) distances than for spot 2 (R_{Co-O}=1.90 Å; R_{Co-Co}=2.80 Å). The longer distances are comparable to Co–O and Co–Co distances in Co(II) compounds such as Co(II) hydroxide-like phases (Co(OH)$_2$) (R_{Co-O}=2.09 Å; R_{Co-Co}=3.17 Å), Co–Al LDH (R_{Co-O}=2.08 Å; R_{Co-Co}=3.09 Å) or Co-phyllosilicates (e.g. Co-kerolite; R_{Co-O}=2.09 Å, R_{Co-Co}=3.13 Å (Manceau et al., 1999). The shorter distances, observed at spot 2, suggest that Co is present
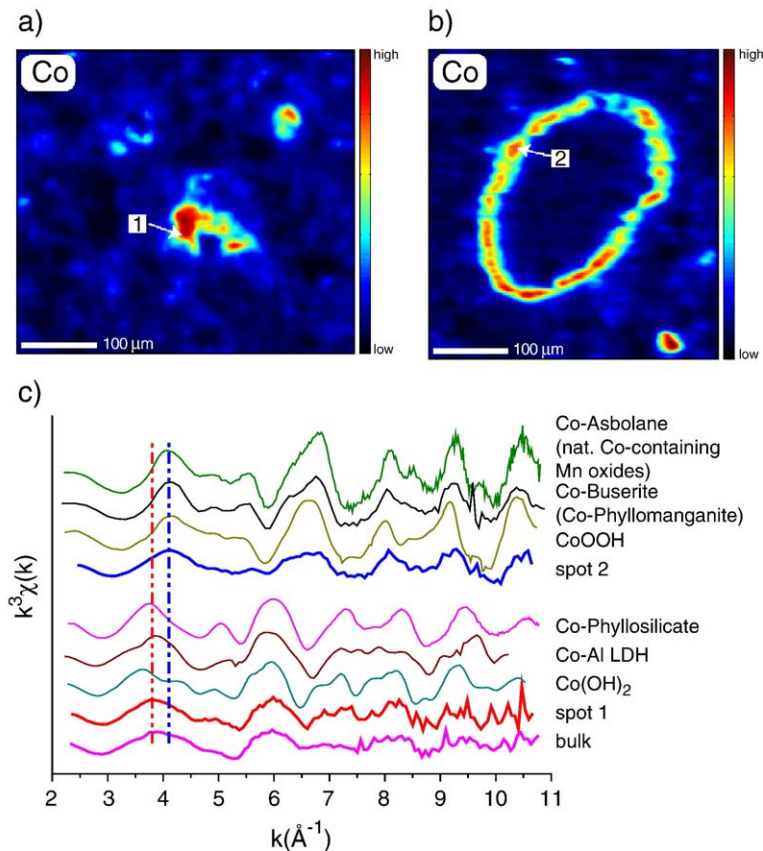
Fig. 1. Element distribution map of Co after 3 days of hydration for (a) Co-rich spot 1 and (b) Co-rich spot 2; (c) k^3-weighted, normalized, background-subtracted XAS spectra of Co enriched cement after 3 days of hydration, reference material and micro-XAS of Co-rich spots.

as Co(III) incorporated into a Co(III)O(OH)-like phase (R_{Co-O}=1.90 Å, R_{Co-Co}=2.85 Å) or a Co-phyllomanganate (Co-asbolane or Co-buserite; R_{Co-O}=1.89 Å, R_{Co-Co}=2.80 Å (Manceau et al., 1987, 1997).

4. Conclusions

The micro-spectroscopy study shows a heterogeneous distribution of Ni in the metal-doped compact cement matrix. Ni(II) predominantly forms Ni–Al LDH phases and to a minor extent Ni(OH)$_2$. These results are consistent with XAS studies of Ni sorption on powdered material of HCP material (Scheidegger et al., 2000, 2001).

For Co(II), the spectroscopic investigations reveal that Co(II) was oxidized to Co(III) during the hydration process of HCP and accumulated at some Co-rich spots (ring-like structure). The oxidation process is possible due to the low redox potential of Co at pH>12.5. The micro-XAS data further suggest that Co(III) tends to be incorporated into a Co(III)O(OH)-like phase or a Co-phyllomanganate. At other spots of interest, however,

Co(II) was not oxidized. Similarly to Ni(II), Co(II) is predominately incorporated into newly formed Co(II) hydroxide-like phases (Co(OH)$_2$), Co-Al LDH or Co-phyllosilicates. The oxidation of Co is a locally occurring process. Future works will focus on the identification of the potential oxidizing agent, such as traces of O$_2$, Mn(IV) or Fe(III).

The findings from the micro-spectroscopic study indicate that Co and Ni react differently during the hydration of cement and that both became immobilized in specific cement minerals. These immobilization processes are expected to reduce the mobility of Co and Ni in the cement matrix. Furthermore, it proves that the immobilization potential of cement is element-specific.

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