

The use of (micro)-X-ray absorption spectroscopy in cement research

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Abstract

Long-term predictions on the mobility and the fate of radionuclides and contaminants in cementitious waste repositories require a molecular-level understanding of the geochemical immobilization processes involved. In this study, the use of X-ray absorption spectroscopy (XAS) for chemical speciation of trace elements in cementitious materials will be outlined presenting two examples relevant for nuclear waste management. The first example addresses the use of XAS on powdered cementitious materials to determine the local coordination environment of Sn(IV) bound to calcium silicate hydrates (C–S–H). Sn K-edge XAS data of Sn(IV) doped C–S–H can be rationalized by corner sharing binding of Sn octahedra to Si tetrahedra of the C–S–H structure. XAS was further applied to determine the binding mechanism of Sn(IV) in the complex cement matrix. The second example illustrates the potential of emerging synchrotron-based X-ray micro-probe techniques for elucidating the spatial distribution and the speciation of contaminants in highly heterogeneous cementitious materials at the micro-scale. Micro X-ray fluorescence (XRF) and micro-XAS investigations were carried out on Co(II) doped hardened cement paste. These preliminary investigations reveal a highly heterogeneous spatial Co distribution. The presence of a Co(II)-hydroxide-like phase $\text{Co}(\text{OH})_2$ and/or Co–Al layered double hydroxide (Co–Al LDH) or Co-phyllsilicate was observed. Surprisingly, some of the initial Co(II) was partially oxidized and incorporated into a $\text{Co}(\text{III})\text{O}(\text{OH})$ -like phase or a Co-phyllomanganate.

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1. Introduction

The long-term immobilization and safe disposal of radioactive and industrial wastes in landfills and deep geological waste repositories is worldwide one of the challenging tasks to endorse the sustainable development of modern civilization (Spence, 1993; Agency, 1999). Although new technologies focusing on waste minimization and recycling will undoubtedly reduce waste arising in the future, an increase in the amounts of intractable waste will be unavoidable. Thus, for any disposal facility, release of hazardous substances must be limited to the lowest level technically (and economically) achievable. Furthermore, strategies are needed to ensure the safe disposal of these waste forms to minimize their environmental impacts (Levi et al., 1990; Agency, 1999).

The present study is focusing on the molecular-level investigation of geochemical processes related to the long-term fate of radioactive and industrial waste in cement-based materials. Mixing ‘fugitive’ hazardous waste products into a cementitious binder system improves the stabilization and the solidification of waste materials (Atkins et al., 1994). Consequently, the migration of radionuclides and other heavy metals from cement-based landfills and waste repositories into the environment can be significantly retarded and possible impacts on the environmental quality can be minimized. For this reason, as well as for engineering purposes, cement-based materials play an important role in multi-barrier concepts for the safe disposal of radioactive wastes in underground repositories. For example, approx. 90 wt% of the near-field material of the planned Swiss disposal cavern for intermediate level waste consists of cement and cementitious backfill materials. From a mineralogical standpoint cement consists mainly of calcium (aluminium) silicate hydrates (C(A)SH phases, ~50 wt%), portlandite

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(~20 wt%) and calcium aluminates (~18 wt%, namely AFm ($\text{Al}_2\text{O}_3\text{--Fe}_2\text{O}_3\text{-mono}$)-type and AFt ($\text{Al}_2\text{O}_3\text{--Fe}_2\text{O}_3\text{-tri}$)-type phases; compositions of calcium aluminates are discussed in detail in Taylor (1997)). Furthermore, it contains ~9 wt% minor phases (e.g., hydrotalcite, hydrogarnet, ferrite, and phosphate minerals) that can expose highly reactive surface sites for sorption and act as storage minerals for waste ions.

Due to interactions with cementitious solid phases the release of radionuclides into the surrounding geosphere (far-field) is retarded and the maximum safety over long time periods is provided by isolating the waste until its activity has decayed to safe levels. Thus, an in-depth understanding of the immobilization processes occurring in cementitious materials (ion exchange, adsorption, precipitation, solid solution formation, etc.; Agency (1999) and references therein) is needed. The best approach to gain process understanding in cementitious systems is to combine macroscopic experiments (e.g., batch-type sorption, leaching, degradation and column studies) with molecular-level investigations.

2. Analytical tools

A wide variety of bulk characterization techniques are routinely employed in the field of cement research. These techniques can reveal average compositional, chemical, structural or morphological information of cementitious materials. For example, thermogravimetry-differential scanning calorimetry (TG-DSC) allows the identification of specific cement minerals based on characteristic dehydration temperatures (Taylor, 1997). X-ray diffraction (XRD) is a widely used technique in cement industry for quality control (Struble, 1991). The Rietveld method (Izumi, 1993) provides an efficient method for quantitative phase analysis of multi-phase mixtures and is used for quantitative clinker phase analysis (e.g., Mansoutre and Lequex, 1996; Plötze, 2000; Scrivener et al., 2004). The method is based on the calculation of X-ray diffraction patterns that are iteratively adjusted to measured diffractograms by convenient variation of phase specific parameters and phase content.

Other analytical techniques used in cement research to gain (micro)structural information include magnetic (e.g., ^1H , ^{27}Al , ^{29}Si , and ^{43}Ca NMR; Brunet et al., 2004) and vibrational (FTIR and Raman) spectroscopies, and image techniques such as atomic force microscopy (AFM), transmission electron microscopy (TEM), and backscattered scanning electron (BSE) microscopy (Colombet et al., 1998). BSE imaging is based on the spatial variation of the electron density and allows the optical identification of typical constituents of cement phases based on grey level contrast and the morphology (Famy et al., 2002). When BSE imaging is combined with energy dispersive X-ray microanalysis (EDX), spatially-resolved quantitative information of the chemical composition can be obtained (Famy et al., 2002).

Surface-sensitive techniques such as X-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES) and secondary ion mass spectrometry (SIMS) have been utilized for elucidating the chemical environment of waste ions in solidified waste components (e.g., Cocker and Mollah, 1993). In particular XPS is widely used to investigate binding mechanisms of metal ions in cementitious materials. XPS allows relatively straight-forward analysis of the near-surface of materials. The technique utilizes soft X-rays which impinge on a surface, ejecting photoelectrons from valence and core levels of the surface and near-surface atoms. Thus XPS, by measuring the binding energy of electrons, allows elemental identification and provides chemical information about the oxidation state of the surface and near-surface atoms. Nevertheless, structural information gained from surface analysis techniques such as XPS is limited. For example, structural parameters of sorbing species such as bond lengths and the type of atoms adjacent to the sorbing species cannot be deduced.

3. Synchrotron-based X-ray absorption spectroscopy (XAS) in cement research

Over the past decade synchrotron light sources have had a major impact exploring chemical processes in natural and engineered material systems and will, in all likelihood, continue to grow in importance in these areas in foreseeable future. This trend has resulted in a fast improvement of spectroscopic techniques for applications in environmental science-related fields such as geochemistry and waste management. Much of our understanding of immobilization processes of trace elements in complex natural and engineered materials has been obtained by XAS. XAS corresponds to a powerful collection of techniques able to provide molecular-level characterization of materials (Teo, 1986; Königsberger and Prins, 1988; Brown, 1990; Stöhr, 1992; Saisho and Gohshi, 1996). Most frequently used XAS techniques are X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) spectroscopies. While XRD experiments probe the long-range order of crystalline samples, XAS is a local probe. The method is well suited for the distinction of oxidation states and the determination of the coordination sphere (i.e., type of neighboring atoms, bond length and coordination numbers) of the X-ray absorber atom of interest. Dilute samples can be examined (concentration of X-ray absorber down to a few tens of ppm) and the experiments can be performed on amorphous solids, surface adsorbed complexes, or species in solution.

In the past years Ca and Al K-edge XAS has been increasingly utilized to examine the structure of hydrating calcium aluminates and poorly-crystallized C–S–H phases (e.g., Richard et al., 1995, 1998; Kirkpatrick et al., 1997; Lequex et al., 1999). Investigations of the local coordination environment of Ca are particularly relevant to the development of model structures for C–S–H. In addition, XAS has become an increasingly important analytical tool

to elucidate immobilization processes in cementitious systems. For example, XAS has been used to determine the chemical speciation of trace elements such as Tc, U and Cr in hydrated cement (Allen et al., 1997; Rinehart et al., 1997; Zhao et al., 2000; Rose et al., 2003). Several XAS studies have focused on metal binding mechanisms onto C–S–H, the quantitatively most important cement mineral in hydrated cement (Rose et al., 2000, 2001; Pomiès et al., 2001; Ziegler et al., 2001; Tommaseo and Kersten, 2002; Schlegel et al., 2004). The molecular-level information obtained by XAS indicates that Zn(II) and Pb(II) are incorporated within the C–S–H matrix and directly linked at the end of the silicate chains through Pb–O–Si and Zn–O–Si bonds and do not substitute in the interlayer positions (Rose et al., 2000, 2001; Tommaseo and Kersten, 2002). The Eu(III)/C–S–H uptake system behaves differently and the XAS data indicate that sorbed or coprecipitated Eu is located at Ca structural sites in a C–S–H-like environment (Schlegel et al., 2004).

At the Laboratory for Waste Management at PSI we have conducted XAS studies to gain information about the interactions of safety-relevant radionuclides (e.g., Ni, Sr, Se, U, and I) with hardened cement paste (HCP) and cement phases. For example, a XAS study provided the first spectroscopic evidence for the formation of a Ni–Al LDH phase when HCP was doped with Ni under highly alkaline conditions ($\text{pH} = 13.3$; Scheidegger et al., 2000). We also used XAS to gain information about the iodine redox-state and chemical environment after the reaction of I^- and IO_3^- with HCP and cement phases (Bonhoure et al., 2002). The XAS study showed the absence of any redox reaction in the uptake system and revealed that the IO_3^- entity is maintained when IO_3^- is immobilized by HCP. Similarly, a XAS study on the immobilization of selenite (SeO_3^{2-}) and selenate (SeO_4^{2-}) by cement and major cement constituents revealed an “outer-sphere”-type binding of Se(IV) and Se(VI) to HCP as well as to the major cement constituents (C–S–H, portlandite, AFm, and Aft) (Bonhoure et al., 2005).

To illustrate the potential of XAS experiments for chemical speciation studies on powdered cementitious materials, we will briefly outline a XAS study on the immobilization mechanism of Sn(IV) onto C–S–H and HCP (Bonhoure et al., 2003). In this study Sn(IV) was considered to be a representative of the strongly hydrolyzing metal cations present in the waste matrix. In a cementitious environment (i.e., $\text{pH} = 12\text{--}14$, $-400 \text{ mV} < E_h < +200 \text{ mV}$; Glasser, 1993), Sn is stable in its tetravalent form, and Sn(IV)(OH)_5^- and Sn(IV)(OH)_6^{2-} are the dominating hydrolytic species (Brookins, 1988). Based on XAS data, evidence is presented demonstrating the formation of a Sn(IV) inner-sphere surface complex on C–S–H with a CaO:SiO₂ weight ratio of 0.7. The Fourier Transform (FT) of Sn(IV) doped C–S–H reveals the presence of two distinct coordination shells at $R + \Delta R \sim 1.6 \text{ \AA}$ and $R + \Delta R \sim 2.8 \text{ \AA}$ (Fig. 1a; uncorrected for phase shift). XAS data analysis indicates that Sn is surrounded by ~ 6

O next-near neighboring atoms at 2.05 \AA . The further distant coordination shell consists of 1–2 Sn–Si backscatterer pairs at 3.33 \AA and 1–2 Sn–Ca backscatterer pairs at 3.69 \AA . Based on these structural parameters, a possible structural model was developed, implying corner sharing between the Sn octahedra and Si tetrahedra located at the end of Si chains of C–S–H (Fig. 1b; C–S–H structure based on 1.1 nm tobermorite; Bonhoure et al., 2003).

In a subsequent study we also conducted XAS investigations on Sn(IV) doped HCP in order to examine Sn(IV) binding mechanisms in the complex cement matrix. The structural parameters deduced from XAS were found to differ from those determined on the Sn/C–S–H system. At high Sn(IV) concentrations the XAS data is coincident with the spectrum of calcium stannate, indicating that Sn(IV) immobilization in HCP occurred by precipitation of CaSn(OH)_6 . At lower Sn(IV) concentrations, however, the bond length to neighboring atoms of the second coordination shell was found to be significantly longer than in the Sn/C–S–H system, suggesting that C–S–H is not the uptake-controlling phase for Sn(IV) in the cement matrix. Therefore, an alternative structural model for Sn(IV) binding in HCP was proposed based on an Aft-type phase acting as the uptake-controlling phase (Bonhoure et al., 2003).

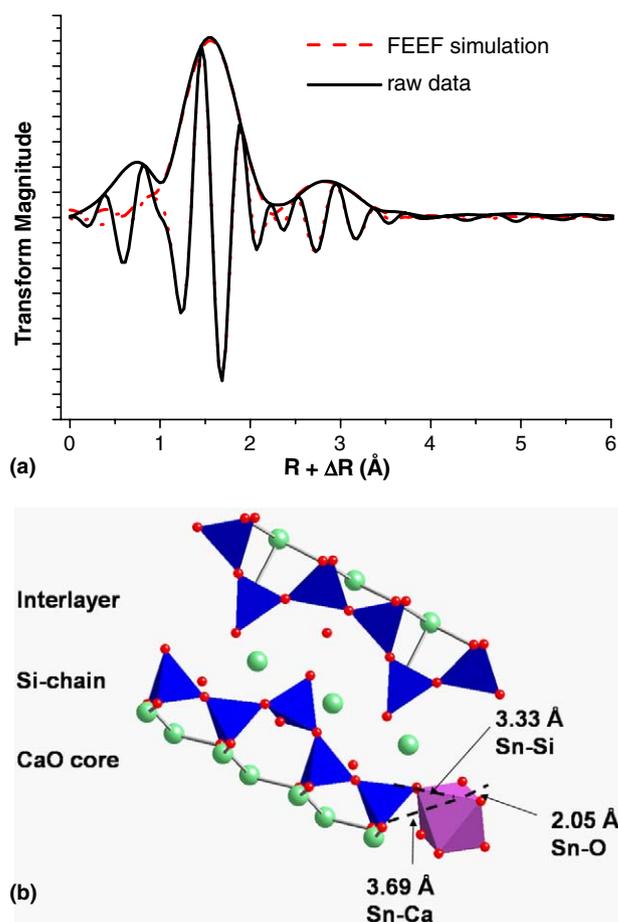


Fig. 1. Sn(IV) uptake on C–S–H-0.7: (a) Fourier transforms (modulus and imaginary parts) of Sn K-edge raw data (—) and data simulated by FEEF (---); (b) a proposed structural model for Sn binding onto C–S–H-0.7; modified after (Bonhoure et al., 2003).

4. X-ray micro probes

Although XAS is the method of choice for defining reactions in complex natural and engineered materials, the application of XAS becomes problematic when mechanisms operative on the micro-scale have larger consequences. XAS does normally not yield spatially-resolved structural data since the dimension of the X-ray beam is much bigger (at most beamlines $>100 \times 100 \mu\text{m}^2$) than the particle size of minerals under investigation (normally $<20 \times 20 \mu\text{m}^2$). Thus, the speciation of a contaminant is determined indirectly from the averaged XAS signal issued from all individual species ('bulk' XAS measurements). Fitting a combination of XAS spectra from reference compounds with the measured bulk XAS spectrum allows in principle the identification and the determination of the concentration of each compound in the sample. The method is particularly of interest when the minimum number of relevant (principle) species and the most likely candidate phases in a given set of samples is determined by principle component analysis and target transformation (e.g., Wassermann et al., 1999; Ressler et al., 2000). Nevertheless, the method can fail because the procedure depends on the availability of reference standards of the phases present in the real sample. Bulk XAS in the context of cement research studies will remain challenging due to the fact that both XAS investigations of the waste ion of interest with the complex matrix as well as of individual cement minerals are needed. Unfortunately, cement minerals often have a variable composition and are not well described (e.g., solid solutions). This may be the reason why XAS studies on hydrated cement are still sparse in spite of obvious advantages of the technique.

In view of the importance of small-scale mechanisms and molecular-level processes in complex heterogeneous systems, there has been a considerable effort to develop high resolution analytical synchrotron-based X-ray probes with which the wealth of structural information provided by XAS can be obtained on a micro-scale (Rivers et al., 1988; Vanlangevelde et al., 1990; Devoti et al., 1991; Suzuki and Uchida, 1992; Janssens et al., 1993; Chevallier et al., 1996; Hayakawa et al., 1998; Newville et al., 1999; Bohic et al., 2001; Somogyi et al., 2001; Janousch et al., 2004; Marcus et al., 2004; Scheidegger et al., 2005). For reviews on micro-probe beamlines and applications of micro-spectroscopy, the reader is referred to Bertsch and Hunter (2001), Manceau et al. (2002) and Sutton et al. (2002). Key advantages of synchrotron-based analytical facilities are the high photon flux, wavelength tunability, and the polarization of the synchrotron radiation. For example at the Swiss Light Source (SLS) a new hard X-ray micro-probe facility is currently being commissioned. The optics of the micro-XAS beamline is optimized for micro-focusing, with a spatial resolution in the $1 \times 1 \mu\text{m}^2$ range. The beam characteristics fulfill all the requirements for optimized micro-XAS measurements, such as spatial stability, high photon flux and flux density, high energy tunability

(~ 4 to ~ 20 keV), high energy resolution ($\Delta E/E < 10^{-4}$), and minimized contamination by high energy radiation (harmonics). As a unique feature, micro-spectroscopic experiments can also be conducted with active samples (Scheidegger et al., 2005).

Thus far most micro-XRF/XAS studies conducted with complex and inherently heterogeneous materials have been performed in the hard X-ray regime (above ~ 4 keV). Micro-spectroscopy studies in the soft X-ray region are more challenging since a different instrumental set-up is required and the experiments must be performed under vacuum. The new LUCIA beamline at SLS is a unique beamline dedicated to microXAS/XRF studies within the energy regime from 1 to 7 keV (Janousch et al., 2004). With this energy range, the chemical speciation of elements such as S (K-edge: 2.4 keV), P (K-edge: 2.1 keV), Mg (K-edge: 1.3 keV), Ca (K-edge: 4.0 keV), Si (K-edge: 1.8 keV) Al (K-edge: 1.6 keV) and Na (K-edge: 1.1 keV) can be probed. Since the above elements are essential for determining the reactivity of cement, it can be anticipated that the use of micro-XRF/XAS in the soft X-ray region will add a new dimension to chemical speciation and understanding chemical reactivities in cementitious materials.

In many scientific disciplines spatially-resolved molecular-level information is the key to understand the fundamental physiochemistry of processes. In most cases, the information sought can be obtained by the synergistic use of micro-X-ray fluorescence (micro-XRF), micro-XAS, and micro-XRD. Micro-XRF is essential in a first stage to map the partitioning of trace contaminants among co-existing mineral phases in the investigated sample. Micro-XAS opens up the possibility to identify individually the different mechanisms of metal uptake on a molecular-level. Finally, micro-XRD allows X-ray diffraction determination to be performed on small particles and is thus suited for micron size phase identifications required to determine which mineral species the trace element is bound/associated to. However, one must keep in mind that the quality of XRD is degraded as crystallite size decreases. Therefore the success of micro-XRD experiments declines as grain size decreases to sub micron dimensions. Electron diffraction often usefully complements XRD for very small crystals.

In the following we will present a case study of an ongoing work addressing the influence of the inherent spatial heterogeneity of solidified cementitious waste on the speciation of Co. Cement minerals are typically present as discrete particles in the size range of a few nanometers to a few hundred micrometers. It is this very feature that may control the overall chemical reactivity of cement and makes cementitious systems so difficult to understand.

5. Micro-spectroscopic investigations on Co immobilization in cement

Micro-XRF and micro-XAS were used to investigate Co uptake by HCP. The samples were prepared from a com-

mercial calcite-containing sulfate-resisting Portland cement (CEM I 52.5 N HTS) by mixing Co(II) nitrate salt solutions to unhydrated cement at a water-to-cement ratio (w/c) of 0.4 (final Co concentration in the cement matrix: 5000 ppm hydration time of 3 days) (see also Lothenbach and Wieland, 2005). The micro-spectroscopic investigations on polished thin sections were conducted at beamline 10.3.2 (Advanced Light Source, Berkeley, USA) using a beam size of $5 \times 5 \mu\text{m}^2$ (Marcus et al., 2004).

The micro-XRF maps show that Co is heterogeneously distributed in the cement matrix (Fig. 2a and b). Typically Co-rich spots up to $\sim 50 \mu\text{m}^2$ in size (e.g., spot 1) as well as characteristic Co-rich ring-like structures with diameters up to $\sim 200 \mu\text{m}$ (e.g., spot 2) were observed. Fig. 2c shows the normalized, background-subtracted and k^3 -weighted micro-XAS spectra of spot 1 and 2 together with Co reference compounds. The spectrum of spot 2 was collected on the ring-like structure and shows a change in frequency and a clear shift of the first oscillation compared to spot 1. By comparing the micro-XAS data with Co reference spectra it becomes evident that the spectrum of spot 1 exhibits similarities with the spectra of Co(II) references, whereas the spectrum of spot 2 shows similarities with the spectra of Co(III) compounds. Data analysis finally revealed that Co–O and Co–Co bond distances for spot 1 ($R_{\text{Co–O}} = 2.06 \text{ \AA}$; $R_{\text{Co–Co}} = 3.13$) are in the same range as Co–O and Co–Co distances in Co(II) compounds such as Co(II)-hydroxide-like phases (Co(OH)_2 : $R_{\text{Co–O}} = 2.09 \text{ \AA}$,

$R_{\text{Co–Co}} = 3.17 \text{ \AA}$; Co–Al LDH: $R_{\text{Co–O}} = 2.08 \text{ \AA}$, $R_{\text{Co–Co}} = 3.09 \text{ \AA}$) or Co-phyllsilicates (e.g., Co-kerolite: $\text{Co}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$, $R_{\text{Co–O}} = 2.09 \text{ \AA}$, $R_{\text{Co–Co}} = 3.13 \text{ \AA}$; Manceau et al., 1999). Shorter Co–O and Co–Co distances are observed for spot 2 ($R_{\text{Co–O}} = 1.90 \text{ \AA}$, $R_{\text{Co–Co}} = 2.80 \text{ \AA}$), suggesting that Co is present as Co(III) that is incorporated into a Co(III)O(OH)-like phase ($R_{\text{Co–O}} = 1.90 \text{ \AA}$, $R_{\text{Co–Co}} = 2.85 \text{ \AA}$) or a Co-phyllomanganate (Co-asbolane ($\text{Co, Ni}_{1-y}(\text{MnO}_2)_{2-x}(\text{OH})_{2-y-2x} \cdot n\text{H}_2\text{O}$ and Co-buserite (Mn^{2+} , Co^{2+})_{0.07} (Mn^{3+} , Co^{3+})_{0.05} [$\text{Mn}_{0.74}^{4+}(\text{Mn}^{3+}, \text{Co}^{3+})_{0.16}\text{Mn}_{0.10}$]O_{1.73} (OH)_{0.27}; $R_{\text{Co–O}} = 1.89 \text{ \AA}$, $R_{\text{Co–Co}} = 2.80 \text{ \AA}$; Manceau et al., 1987, 1997).

The micro-spectroscopic findings demonstrate the presence of a Co(II) hydroxide-like phase at some spots in the Co-doped cement sample. At other spots of interest, however, Co was found to be oxidized to Co(III) and incorporated into a Co(III)O(OH)-like phase or a Co-phyllomanganate. The micro-XRF experiments suggest that the Co(III) phase seems to form ring-like structures. The oxidation of Co(II) to Co(III) is attributed to the presence of oxidizing agents such as traces of O₂, Mn(IV) or Fe(III) species. A surprising result of the micro-spectroscopic study is that oxidation of Co(II) is a locally occurring process. This finding demonstrates that the inherent heterogeneity of cement may well control the overall chemical reactivity of Co in cement. Future works will focus on the identification of the oxidizing agent responsible for Co(II)/Co(III) redox processes occurring

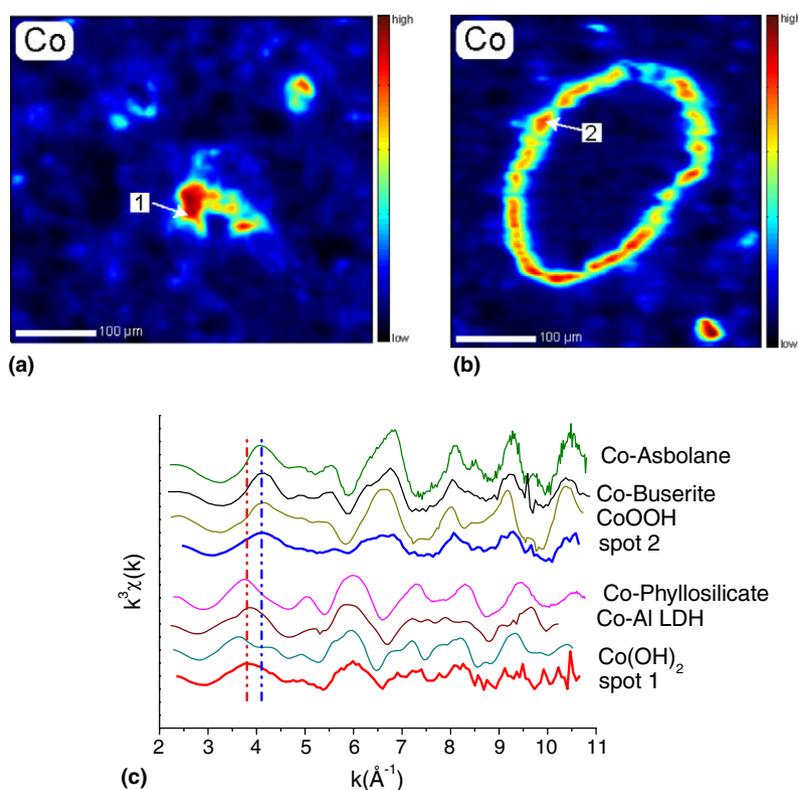


Fig. 2. Elemental Co distribution map of a Co-doped cement sample hydrated for 3 days: (a) Co-rich spot 1; (b) Co-rich spot 2; (c) k^3 -weighted, normalized, background-subtracted Co K-edge XAS spectra collected at spot 1 and 2 in comparison with the spectra of Co reference compounds (Co-phyllsilicate: Manceau et al. (1999); Co-asbolane: Manceau et al. (1987); Co-buserite: Manceau et al. (1997), other references: this study).

in hydrating cement. Further, a multi-technique approach is presently developed, which will allow complementary investigations using micro-XRF/XAS and BSE imaging of the same sample area. With the novel approach, information on the local chemical speciation gained by microXAS can be put in context with the cement constituents identified by BSE, based on grey values and morphologies.

6. Outlook

Synchrotron-based micro-XRF, micro-XRD, and micro-XAS offer a great potential for investigating complex and highly heterogeneous samples such as cement in a non-destructive fashion. While micro-XRF can yield spatially-resolved information on the trace element distribution, micro-XRD allows micron size phase identifications. Finally, micro-XAS gives spatially-resolved molecular-level information on the spatial variability of chemical speciation. Given the characteristic length-scale of the phenomena of interest (e.g., size range of discrete cementitious particles, spatial extent of corrosion layers), achieving micrometer resolution is important. While alternative micro-probe techniques could also provide elemental distributions, the spatially resolved determination of chemical speciation is restricted to micro-XAS techniques. Molecular-level speciation, however, is often the key to decipher physical-chemical processes in cementitious materials.

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