Iodine species uptake by cement and CSH studied by I *K*-edge X-ray absorption spectroscopy

By Isabelle Bonhoure*, André M. Scheidegger, Erich Wieland and Rainer Dähn

Paul Scherrer Institute, Waste Management Laboratory, CH-5232 Villigen PSI, Switzerland

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Summary. The uptake of iodine species (I^-/IO_3^-) by HCP (hardened cement paste) and a CSH (calcium silicate hydrate) phase under highly alkaline conditions has been investigated using X-ray absorption spectroscopy (XAS). The study was performed at the I *K*-edge (33.169 keV) instead of the I *L*₃-edge (4.557 keV) to avoid interference with Ca (*K*-edge = 4.038 keV), a major element in HCP and CSH phases. The XANES (X-rays absorption near-edge structure) spectra revealed no changes in the formal oxidation state of iodide ($\text{I}(-\text{I})^-$) and iodate ($\text{I}(\text{V})\text{O}_3^-$) upon uptake by HCP and CSH. The EXAFS (extended X-ray absorption fine structure) oscillations from I⁻-treated HCP and CSH samples were found to be extremely weak, limiting interpretation of the EXAFS data. The IO_3^- EXAFS spectra showed that the IO_3^- entity consisting of three oxygen atoms with a characteristic I–O distance ($\sim 1.78 \text{ \AA}$) is maintained upon uptake by HCP and CSH. XANES further indicated that CSH is not the uptake-controlling phase in HCP.

1. Introduction

Cement-based materials play an important role in multi-barrier concepts developed worldwide for the safe disposal of low- and intermediate level (L/ILW and LL-ILW) radioactive wastes in underground repositories. Cement is used to condition the waste materials, as well as for the construction of the repositories. The near-field of a cementitious repository acts as chemical barrier for radionuclides, retarding migration of waste ions into the far-field. The retardation of iodine species by HCP and concrete is of major interest in nuclear waste management due to the long half-life of ^{129}I ($t_{1/2} = 1.6 \times 10^7 \text{ y}$), the main iodine isotope in the waste matrix, and its poor sorption properties on most geological materials [1–3]. Iodine is expected to exist predominantly as iodide (I^-) in cement systems except under oxic conditions, where iodate (IO_3^-) may be the dominant species. Several studies have indicated the potential of individual cement minerals to immobilize I^- and IO_3^- [3–6], e.g., calcium silicate hydrates (CSH), sulfoaluminates such as AFm (monosulfate: $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{CaSO}_4\cdot 12\text{H}_2\text{O}$) and AFt (ettringite: $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 3\text{CaSO}_4\cdot 32\text{H}_2\text{O}$), and, most recently, tetracalcium aluminate hydrate ($4\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot \text{XH}_2\text{O}$ ($X = 13$

to 19)). AFm was reported to exhibit the highest potential for I^- sorption [3, 5]. Substitution of SO_4^{2-} by I^- is considered to be the predominant uptake process [3, 4]. For example, Brown *et al.* [5] were able to easily synthesize the monoiodide $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{CaI}_2\cdot 12\text{H}_2\text{O}$, where CaSO_4 is replaced by CaI_2 , suggesting the formation of a solid solution. Moreover, the greater affinity of CSH phases for IO_3^- over I^- was observed and interpreted as being due to direct bonding between CSH and IO_3^- or to the precipitation of a Ca/IO_3^- containing solid phases [2, 4]. Whereas the potential of individual cement phases to immobilize iodine has been demonstrated [5–7], any direct evidence as to the identity of the uptake-controlling phase in the cement matrix on a molecular level is still lacking. We therefore focused our work on probing the chemical environment of I^- and IO_3^- species in cement systems in an attempt to elucidate a molecular-scale mechanism for the I^-/IO_3^- interaction with HCP and CSH, which is one of the main constituents of HCP. Previous studies on the interaction of Zn and Ni with HCP carried out in our laboratory demonstrated that XAS is a powerful tool for studying uptake mechanisms in cementitious systems [8–10].

The number of studies using XAS to determine the local coordination environment of iodine species in natural minerals and other solid phases is very limited. Fuhrmann *et al.* [11] studied the redox reactions occurring during the sorption of I^- and IO_3^- onto various minerals using XANES. Furthermore, surface-EXAFS spectroscopy was applied to probe the environment of irreversibly sorbed iodine on Pt{111} and Pt{100} surfaces [12]. Both studies were performed at the I *L*₃-edge (4.557 keV). To avoid an interference with the Ca *K*-edge (4.038 keV) (CaO content: $\sim 50 \text{ wt. \%}$ in CSH and $\sim 54 \text{ wt. \%}$ in HCP), the present study was performed at the I *K*-edge (33.169 keV). Only few studies have been performed at the *K* edge, such as investigations on the coordination environment of liquid I_2 [13, 14] and of iodine in hexafluoro-molybdates [15], $\text{C}_{60/70}(\text{I}_2)_x$ molecules [16] and iodine-doped polyvinyl alcohols [17].

2. Materials and methods

2.1 Wet chemistry experiments and XAS sample preparation

Wet chemistry studies and XAS samples preparation were carried out in a glove box (N_2 atmosphere; CO_2 , $\text{O}_2 < 5 \text{ ppm}$;

* Author for correspondence (E-mail: isabelle.bonhoure@psi.ch).

$T = 25 \pm 3^\circ\text{C}$) using chemicals of reagent (or higher) grade quality. HCP prepared from commercial sulphate-resisting cement (Type CPA 55 HTS, Lafarge, France) was manufactured as reported by Sarott *et al.* [18] and used as crushed material (for details on the preparation and characterisation see [19]). A CSH gel with a $\text{CaO} : \text{SiO}_2$ (C : S) ratio of 0.95 ± 0.05 , determined using SEM/EDS, was synthesised using a standard procedure [20, 21]. X-ray diffraction (XRD) data indicated the presence of a semi-crystalline CSH-I phase. Differential thermal analysis and thermogravimetry (DTA/TG) showed that $\text{Ca}(\text{OH})_2$ and CaCO_3 were the only impurities present at trace levels.

Uptake kinetics of I^- and a sorption isotherm for I^- were determined on HCP material in an artificial cement pore water (ACW, pH 13.3) at a solid to liquid (S/L) ratio of $2.5 \times 10^{-2} \text{ kg L}^{-1}$. The composition of ACW is equivalent to the chemical composition of a solution in equilibrium with a freshly prepared HCP [19, 22]. The cement suspensions were pre-equilibrated for 28 days prior to adding the tracer solution. Uptake was determined using ^{125}I (β -emitter, $t_{1/2} = 59.4 \text{ d}$). For the kinetic experiments, an ^{125}I containing solution ($[\text{I}]_{\text{tot}} = 10^{-8} \text{ M}$) was added to the cement suspensions, which were then shaken end-over-end for, at a maximum, 180 days. For the isotherm experiments, ^{125}I containing stock solutions were added to the suspensions to give total iodide concentrations ranging from 10^{-9} M to $5 \times 10^{-4} \text{ M}$. These samples were shaken end-over-end for 7 days. After equilibration (isotherm) or appropriate time periods (kinetics), the suspensions were centrifuged (60 min at 95 000 g). For radionuclide assay, 2 ml aliquots of the supernatant solution were mixed with 2 ml of a scintillation cocktail and activities determined together with standards using a Canberra Packard Tri-carb 2250 CA liquid scintillation analyser (energy window: 6–70 keV).

XAS samples were prepared by mixing 1 g of solid material (HCP or CSH) with 40 mL ACW, pre-equilibrating the suspensions (HCP: 28 days/CSH: 14 days), adding stable I^- or IO_3^- solutions ($[\text{I}]_{\text{tot}} = 10^{-3} \text{ M}$ and 10^{-2} M) and equilibrating again the suspensions for 28 days. The residual wet paste obtained after centrifugation was used for the XAS measurements. For CSH, equilibrium conditions were checked by analysing Ca and Si concentrations in solution [21]. The reference compounds ($\text{CaI}_2 \cdot 4\text{H}_2\text{O}$, KI, $\text{Ca}(\text{IO}_3)_2$ and KIO_3) were prepared by diluting commercially available chemicals (Merck) with boronitride (BN). The reference solutions were prepared by dissolving $\text{CaI}_2 \cdot 4\text{H}_2\text{O}$ and $\text{Ca}(\text{IO}_3)_2$ in Milli-Q water to obtain $[\text{I}]_{\text{tot}}$ equal to 0.02 and 0.03 M, respectively.

2.2 X-ray absorption spectroscopy

XAS measurements were carried out at the Swiss Norwegian Beam Line (SNBL) at the European Synchrotron Radiation Facility (ESRF), Grenoble, France, using a channel cut crystal monochromator (Si 111), in transmission mode (ionization chambers; 75% N_2 and 25% Kr) and fluorescence mode (Lytle detector; 100% Kr; Sn filter). An ethanol solution saturated with I_2 was used for energy calibration [13].

Treatment of the IO_3^- EXAFS data was carried out using the set of programs “EXAFS pour le Mac” [23]. A linear function was used for pre-edge extrapolation, atomic ab-

sorption was modeled by a sixth order polynomial function and normalization was done using the Heitler–Heisenberger method. The origin energy E_0 was assigned to the inflexion point of the absorption edge. The pseudo radial distribution functions (PRDF) were obtained by Fourier transformation (FT) of the EXAFS oscillations in k^3 space (k -range: $4.2\text{--}15.2 \text{ \AA}^{-1}$) using a Kaiser window ($\tau = 3$). Data analyses were conducted using phases and amplitudes calculated with FEFF7 [24] and fitting was performed with the Round Midnight code on the $k\chi(k)$ function using Fourier filtered spectra (R range = $1.16\text{--}1.71 \text{ \AA}$) assuming only one I–O distance. Floating parameters were: the Debye–Waller factor, $\sigma_{\text{I–O}}$, the backscatterer distance, $R_{\text{I–O}}$, and the relative energy threshold, ΔE_0 . $N_{\text{I–O}}$ was set to three. The reduction factor, S_0^2 , and the mean free path, $\Gamma (= k/\lambda(k))$, were calculated by FEFF7 and included in the fit. Accuracy of $R_{\text{I–O}}$ was estimated to be $\pm 0.01 \text{ \AA}$.

3. Results

3.1 Wet chemistry

I^- uptake by HCP is shown in Fig. 1. Significant uptake was observed under the given experimental conditions, *i.e.*, S/L ratio = $2.5 \times 10^{-2} \text{ kg L}^{-1}$, with R_d values ranging from $\sim 0.1 \text{ m}^3 \text{ kg}^{-1}$ to $\sim 0.2 \text{ m}^3 \text{ kg}^{-1}$ (kinetic study) and from $\sim 0.02 \text{ m}^3 \text{ kg}^{-1}$ to $\sim 0.15 \text{ m}^3 \text{ kg}^{-1}$ (isotherm). Note that R_d values deduced from the sorption isotherm were found to be about a factor of two lower (equilibration time = 7 days) than the R_d values determined after 180 days equilibration. The sorption isotherm had a slope of 0.87 indicating decreasing R_d values with increasing I^- concentration. The wet chemistry results corroborate earlier findings that HCP and cement minerals tend to be more reactive towards I^- and IO_3^- than most geological materials [2–4].

3.2 XANES

The XANES spectra of I^- and IO_3^- treated HCP and CSH and the reference compounds (Fig. 2) showed a broad edge caused by the substantial core-hole lifetime at the I K -edge

Fig. 1. Sorption isotherm for I^- on HCP. Inset: Uptake kinetics of I^- . (For experimental details, see text).

Fig. 2. (a) I *K*-edge XANES spectra of IO_3^- reference compounds ($\text{Ca}(\text{IO}_3)_2$ solution, $\text{Ca}(\text{IO}_3)_2$ solid and KIO_3 solid) and of IO_3^- immobilized in solid matrices (HCP/IO_3^- and CSH/IO_3^-). (b) I *K*-edge XANES spectra of I^- reference compounds (CaI_2 solution, $\text{CaI}_2 \cdot 4\text{H}_2\text{O}$ solid and KI solid) and of I^- immobilized on solid matrices (HCP/I^- and CSH/I^-).

(full width at half maximum of 10.6 eV [25]). XANES spectra were found to be highly characteristic for each of the different oxidation states of iodine. The spectra revealed no change of oxidation states upon uptake by HCP and CSH. The XANES spectra of IO_3^- (Fig. 2a) showed a white line (edge maximum) followed by strong oscillations caused by the three oxygens of the rigid IO_3^- anion. In contrast to the IO_3^- samples, neither a white line nor any strong absorption features was observed in the XANES spectra of I^- (Fig. 2b).

The featureless spectra appeared “gas like” and suggested the absence of backscattering atoms at short distances.

While the XANES spectra of all I^- samples were found to be similar, significant differences in the CSH/IO_3^- and HCP/IO_3^- spectra were evident (Fig. 2a). The XANES of HCP/IO_3^- and the spectrum of the $\text{Ca}(\text{IO}_3)_2$ solution were similar, whereas the XANES of CSH/IO_3^- resembled the spectra of solid $\text{Ca}(\text{IO}_3)_2$ and KIO_3 . This finding suggested that the coordination environment of IO_3^- in HCP and CSH was different.

3.3 EXAFS: Structural environment of I^-

The intensity of the I^- EXAFS oscillations (not shown) was found to be very weak, giving rise to an unusually low signal/noise ratio and high *k* noise. As a consequence, only a small *k*-range ($\Delta k = 4.3\text{--}8.2 \text{ \AA}^{-1}$) could be used for Fourier transformation resulting in poor *R* resolution. The structural parameters obtained from data analysis indicated long distances between I^- and the first neighbors ($> 3 \text{ \AA}$) corresponding to the distances reported in the literature [26, 27]. However, a more detailed interpretation of the chemical environment of I^- in these systems caused difficulties due to the poor quality of the data. Note that, given the long I-first neighbors distances, the I^- oscillations amplitude is expected to be intrinsically weak. We suspect that, in addition, it has been damped due to the poor energy resolution of the Si(111) monochromator crystal at high energy ($> 33.2 \text{ keV}$).

3.4 EXAFS: Structural environment of IO_3^-

Fig. 3a shows the *k*-weighted EXAFS spectra of IO_3^- treated HCP and CSH and the reference compounds. All the spectra revealed a single oscillation with comparable frequency and amplitude, indicating similarities in iodine coordination environment. The PRDF for all IO_3^- treated samples (cf. Fig. 3b) exhibit a peak at about $1.35 \text{ \AA}$ (not corrected for phase shift) and no other PRDF peaks at longer distances. Since no change in formal oxidation state was observed (see section XANES), it was assumed that the IO_3^- entity remained intact upon uptake by HCP and CSH. Consequently, the single peak was assigned to the closest O neighbors and the number of O neighbors was set to three. It is noted that the goodness of fits (Table 1) supported this approach. I–O distances deduced from data analysis were found to be identical for all the samples ($1.78\text{--}1.80 \text{ \AA}$) within the experimental error ($\pm 0.01 \text{ \AA}$ for $R_{\text{I-O}}$). We thus infer that the IO_3^- anion does not undergo any major modification upon uptake by HCP or CSH.

4. Discussion

4.1 I^-/IO_3^- formal oxidation states in HCP and CSH

The question as to whether changes in the formal oxidation state of iodine species may occur in cement systems under highly alkaline conditions and, thereby, affect their sorption properties, was an aspect which prompted the current study. Earlier studies indicated that tracer solutions of I^- may not

Table 1. Structural parameters of IO_3^- samples obtained from EXAFS data analysis. N is the number of oxygen neighbors, R is the I–O distance (Å), σ is the Debye–Waller factor (Å), ΔE_0 the energy shift (eV). The residual factor ($\text{rf} = \frac{\sum_{i=1}^n [k\chi_{\text{exp}} - k\chi_{\text{theo}}]^2}{\sum_{i=1}^n [k\chi_{\text{exp}}]^2}$) represents the quality of the fit.

KIO_3 (solid)	$\text{Ca}(\text{IO}_3)_2$ (solid)	$\text{Ca}(\text{IO}_3)_2$ (solution)	HCP/ IO_3^-	CSH/ IO_3^-
$N_{\text{I-O}} = 3$ $R_{\text{I-O}} = 1.80$ $\sigma = 0.062$ $\Delta E = 9.9$ $\text{rf} = 1.0\%$	$N_{\text{I-O}} = 3$ $R_{\text{I-O}} = 1.79$ $\sigma = 0.050$ $\Delta E = 8.7$ $\text{rf} = 5.1\%$	$N_{\text{I-O}} = 3$ $R_{\text{I-O}} = 1.78$ $\sigma = 0.021$ $\Delta E = 9.9$ $\text{rf} = 1.0\%$	$N_{\text{I-O}} = 3$ $R_{\text{I-O}} = 1.78$ $\sigma = 0.039$ $\Delta E = 8.9$ $\text{rf} = 2.4\%$	$N_{\text{I-O}} = 3$ $R_{\text{I-O}} = 1.80$ $\sigma = 0.042$ $\Delta E = 10.4$ $\text{rf} = 2.1\%$

Fig. 3. (a) I K-edge raw EXAFS spectra for IO_3^- reference compounds ($\text{Ca}(\text{IO}_3)_2$ solid, KIO_3 solid and $\text{Ca}(\text{IO}_3)_2$ solution) and for IO_3^- immobilized on solid matrices (HCP/ IO_3^- and CSH/ IO_3^-). (b) Modulus and imaginary part of the PRDF of the corresponding EXAFS spectra.

be stable and oxidize to IO_3^- , which could lead to an incorrect assessment of the sorption behavior of I^- [e.g., 11]. No changes in the formal oxidation state of I^- following uptake

by HCP and CSH was observed in the present work. Both redox states, *i.e.*, $\text{I}(-\text{I})$ and $\text{I}(\text{V})$, were found to be stable in the cement systems under the given experimental conditions and for time periods up to 28 days. Therefore, we conclude that any effects on sorption due to a change in redox state of iodine species can be excluded in these systems.

4.2 IO_3^- speciation in HCP and CSH

The EXAFS study demonstrated that the IO_3^- structural entity remained when IO_3^- interacted with HCP and CSH. The I–O distances (1.78–1.80 Å) determined in the present study were consistent with I–O distances observed for IO_3^- compounds [28, 29]. Since the FT spectra showed no further PRDF peaks at larger distances (Fig. 3b), the structural information obtained by EXAFS data analysis was limited to the first coordination shell and no significant differences were observed among the samples. The XANES spectra (Fig. 2a) however showed differences between the IO_3^- treated HCP and CSH samples, suggesting that the iodine second shell of neighbors was different in the two matrices: IO_3^- appeared to be present in HCP as free solvated anion as IO_3^- in a water solution, whereas IO_3^- in CSH seemed to be immobilized in a solid as in the $\text{Ca}(\text{IO}_3)_2$ and KIO_3 solid references. This finding is consistent with the hypothesis reported in the literature, suggesting a direct bonding between CSH and IO_3^- [2, 4]. However, the IO_3^- bonding mode observed in treated CSH is not the major bonding mode in treated HCP. This finding provides direct evidence that CSH, although being one of the main constituents of HCP, is not the phase controlling IO_3^- uptake in HCP.

5. Conclusion

It was demonstrated that I K-edge XAS is capable of yielding information on I^- and IO_3^- speciation in complex matrices such as HCP and CSH, where interference at the I L_3 -edge caused by Ca occurs. Redox reactions do not influence sorption processes in the cementitious systems studied here as no change of oxidation states was observed upon uptake of the iodine species by HCP and CSH. The study further showed that CSH, one of the main constituents of HCP, does not account for IO_3^- uptake by the cement matrix. This finding revealed that, even in complex multi-phases solid systems, XAS can be used to determine the specific sorption properties of individual phases.

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