![ESRF logo]	**Experiment title:** The Uptake of Iodine onto Cementitious Materials	**Experiment number**: EC-655
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Report:

^{129}I is expected to be released from radioactive waste in underground repositories as dissolved anionic species as iodide (I^-) and is predicted to be dose-determining in performance assessments due to its long half-life and its weak retention by common minerals from the repository near-field (clays, carbonates and sulphates). However, such predictions usually disregard the uptake of anionic species by minor minerals from the cementitious barriers. AFm phases are potential candidates for iodine retention during cement alteration. AFm-type cement minerals are composed of edge-sharing octahedral sheets occupied by Ca^{II} and Al^{III} hydroxides, stacked with H_2O and charge compensating anions ($[Ca_2Al(OH)_6][X^{n-}]_{1/n} (H_2O)_m$ where X^{n-} = CO_3^{2-}, SO_4^{2-} or Cl^-). Replacement of X^{n-} by I^- in AFm phases could potentially reduce the mobility of ^{129}I. The iodine uptake mechanism was investigated using Extended X-ray Absorption Fine Structure (EXAFS) spectroscopy at the iodine K-edge to obtain a molecular-level understanding of the coordination environment of iodine.

Pure AFm-I_2 samples were synthesized in a glove box under a N_2 atmosphere (O_2, CO_2 < 2 ppm) at various temperatures (4°C, 23 ± 2°C and 60°C) and aged for 14 days up to 84 days. C_3A was reacted with CaI_2 at a liquid-to-solid ratio of 10 using degassed Milli-Q® water. In addition, pure AFm-I_2 samples aged for 28 days were exchanged with various amounts of potassium salts (as $KX_{2/n}$) during 48 hours, where X^{n-} = SO_4^{2-}, CO_3^{2-} and Cl^- in order to obtain various AFm-(I_2,X_n) compositions. AFm-(I_2,X_n) phases were also synthesized by coprecipitation reaction of C_3A with various ratios of CaI_2 and $CaX_{2/n}$. The solids were extracted by centrifugation or by filtration through 0.2 µm nylon filters. The solids were quickly washed with Milli-Q® water and then further thoroughly rinsed with degassed absolute ethanol in order to remove all impurities of un-reacted salts. The solids were dried over a saturated solution of $CaCl_2$ and stored in the glove box before solid characterization by X-ray Diffraction (XRD) and EXAFS spectroscopy.

EXAFS spectra for each sample were recorded in transmission at the I-K edge. A large improvement in data quality of the EXAFS spectra was noticed when measurements were acquired at 15 K instead of 90 K. All samples were therefore measured at 15 K. Figure 1 shows the EXAFS spectra at the I K-edge of pure AFm-I_2 and mixtures of AFm-I_2 with 50% Cl_2, CO_3 and SO_4.

The spectra were similar up to R+ΔR ~ 8 Å for all AFm-I_2 phases synthesized under the various temperature and ageing time conditions (the k^3-weighted spectrum and its FT of the 100% I_2 sample synthesized at 23°C during 28 days are given as an example in Fig. 1). Large amplitudes at k > 12 Å^{-1} (Fig. 1a 100% I_2) suggest the presence of heavy (high Z) backscattering atoms, such as neighboring iodine atoms.

The spectra of coprecipitated and exchanged AFm-(I_2,Cl_2) samples were found to be very similar to those of the pure AFm-I_2 samples. This suggests that the coordination environment of iodine in AFm-(I_2,Cl_2) is similar to pure AFm-I_2 (the k^3-weighted spectrum and its FT of a 50% I_2 + 50% Cl_2 sample are given as an

example in Fig. 1). AFm-(I$_2$,CO$_3$) prepared by exchange reaction showed spectra similar to those of pure AFm-I$_2$. This suggests that the coordination environment of iodine in AFm-(I$_2$,CO$_3$) is also similar to pure AFm-I$_2$ (the k^3-weighted spectrum and its FT of the 50% I$_2$ + 50% CO$_3$ exchange sample are given as an example in Fig. 1). Note that XRD results showed the formation of distinct crystalline phases (AFm-I$_2$ and AFm-Cl$_2$) in both coprecipitation and exchange experiments of AFm-(I$_2$,Cl$_2$). Similarly, two distinct crystalline phases (AFm-I$_2$ and AFm-CO$_3$) were detected by XRD for AFm-(I$_2$,CO$_3$) prepared by exchange reaction. AFm-I$_2$ and either AFm-Cl$_2$ or AFm-CO$_3$ phases can form therefore simultaneously without changing the iodine configuration in the interlayer, as shown in the EXAFS measurements.

In contrast, AFm-(I$_2$,CO$_3$) prepared by coprecipitation revealed a more limited short-range ordering of iodine in the interlayer with a single shell at R+ΔR ~ 3 Å (the k^3-weighted spectrum and its FT of a 50% I$_2$ + 50% CO$_3$ coprecipitation sample is given as an example in Fig. 1). The backscattering amplitude was small at high k (Fig. 1a 50% I$_2$ + 50% CO$_3$ coprecipitated), indicating either the absence of heavy backscattering atoms or strong disorder, respectively. XRD revealed the formation of alternate interlayer galleries filled with I$^-$ and (CO$_3^{2-}$,OH$^-$). The stacking of I$^-$ and (CO$_3^{2-}$,OH$^-$) interlayers seems to strongly affect the short-range ordering of iodine as shown in the EXAFS measurements.

The EXAFS spectra were similar for all coprecipitated and exchanged AFm-(I$_2$,SO$_4$) samples. The AFm-(I$_2$,SO$_4$) FT spectra showed a splitting of the first coordination shell with an additional peak at R+ΔR ~ 3.4 Å (the k^3-weighted spectrum and its FT of a 50% I$_2$ + 50% SO$_4$ sample are given as an example in Fig. 1). No enhanced amplitude was observed at high k (Fig. 1b 50% I$_2$ + 50% SO$_4$) compared to the pure AFm-I$_2$. This suggests the absence of heavy backscattering atoms like iodine or the presence of a strong disorder, respectively. Furthermore, the intensity of the shell at R+ΔR ~ 3.4 Å was found to increase with increasing SO$_4^{2-}$ content (Fig. 1.b. 50% I$_2$ + 50% SO$_4$). The coordination environment of iodine seems thus to be significantly influenced by the presence of SO$_4^{2-}$. The two species may not only occupy the same interlayers, but they may also occupy neighbouring positions. This implies that a complete mixing of I$^-$ and SO$_4^{2-}$ even at short range distances could be favoured. Multi-shell fitting of the EXAFS spectra is on-going in order to confirm the above findings. XRD results confirmed that AFm-I$_2$ – AFm-SO$_4$ form a continuous solid solution series. The formation of the continuous solid solution between AFm-I$_2$ and AFm-SO$_4$, including a complete mixing of I$^-$ and SO$_4^{2-}$ even at short range distances, underpins its potential to act as a sink for ^{129}I.
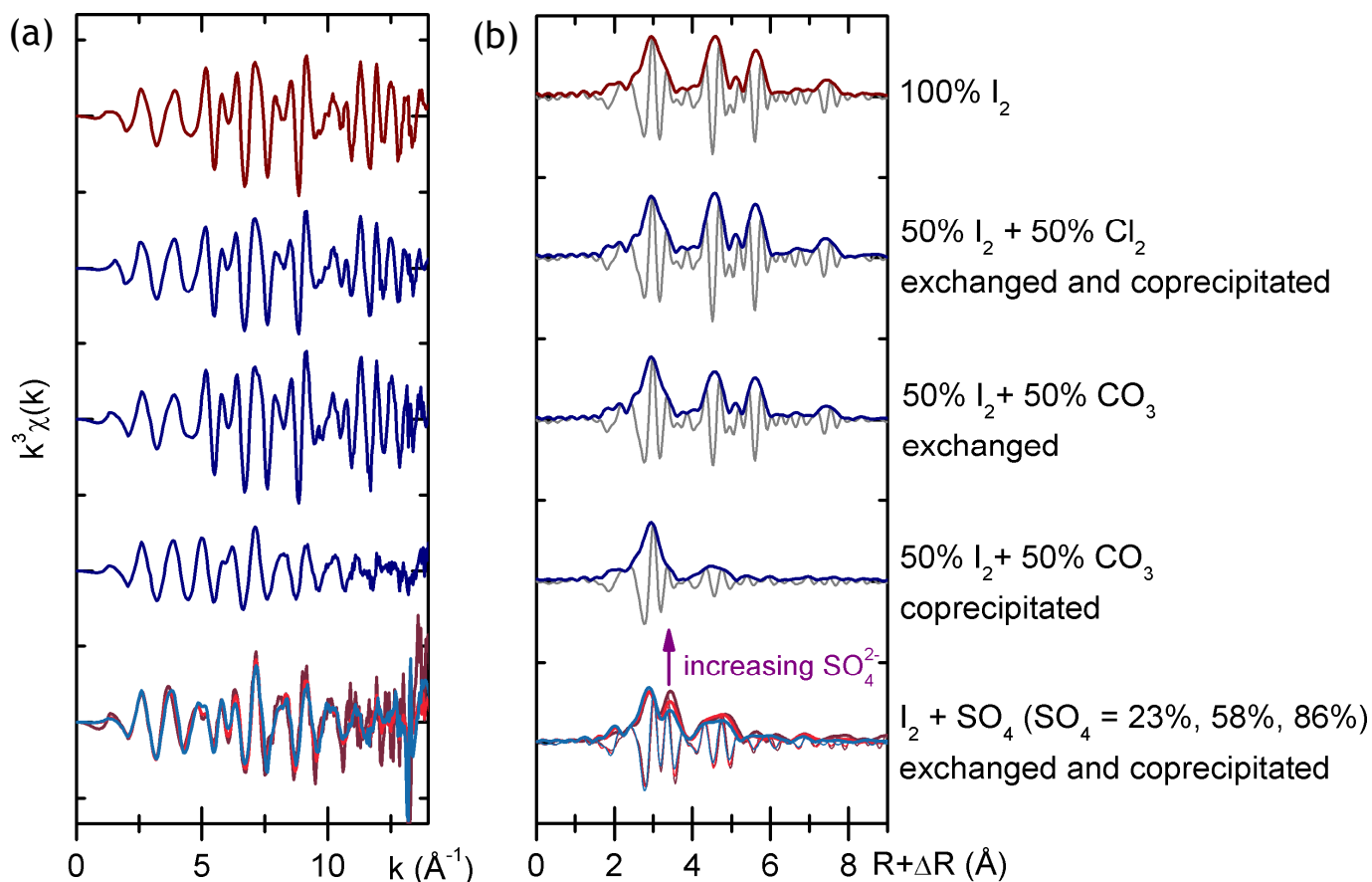

Fig. 1. Iodine K-edge spectra recorded at 15 K for various iodine-bearing AFm samples: (a) k^3-weighted spectra; (b) Fourier Transform (modulus and imaginary part).