

**Experiment title:**

Effect of leaching on the crystallographic sites of trace metals in cement : case of Cr

Experiment**number:**
ME 317**Beamline:**

ID21

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15

Local contact(s):

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The main topic of this study is assessing Cr behaviour during cement alteration in water. Indeed the high affinity of cement phases (Ca-Si, Ca-Al, Ca-Al-Fe hydrates) for heavy metals (HM), has encouraged industries to use hazardous waste as fuel for the cement kilns to trap HM. HM total concentration in cement never exceeds a few hundred ppm. To predict long term metal behaviour during leaching and associated environmental and human health risks, it is crucial to determine the evolution of HM crystallographic site. The case of Cr is of particular interest since this element can reach concentrations up to 100 ppm and occurs in 2 oxidation states: Cr(III) and Cr(VI). The latter is known to be more toxic and mobile than Cr(III). According to literature, Cr³⁺ is less released during alteration experiments, compare to Cr^{VI} (Serclerat, 2000).

μ -XANES couple to μ -XRF aimed determining i) whether Cr(VI) is present in the altered zone, ii) to analyse Cr(III)/Cr(VI) evolution from the core to the altered area and iii) to determine nature of majors elements associated to both Cr(VI) and Cr(III) (Ca, Al, Si...). The main difficulty of this study was the very low concentration of Cr in the cement used (60 ppm). We thus compared natural and 2000 ppm doped samples after dynamic leaching, at pH=5, 40°C and during 42 days. After 42 days a degraded layer of approximately 0.5 mm depth was observed.

The evolution of Cr in the material was assessed by scanning microprobe across the sample, from the altered layer toward the core (between 1.5 and 2.5 mm length). Transverse scans were performed at two energies: 5.998 and 6.022ev characteristic of the presence of Cr(VI)(pre-edge) and total Cr respectively (fig.1). Ratio of the two spectra lines depicts Cr(VI) distribution. Ca, Ti and V K fluorescent lines were simultaneously acquired with a energy dispersive spectrometer associated to a multichannel analyser. The beam spot was focused down to 2x4 μm^2 using a 1.04 mm diameter Fresnel Zone Plate lens. The lines were performed in the vertical direction to exploit the better resolution. Intensity was checked with the Ca K fluorescent line intensity.

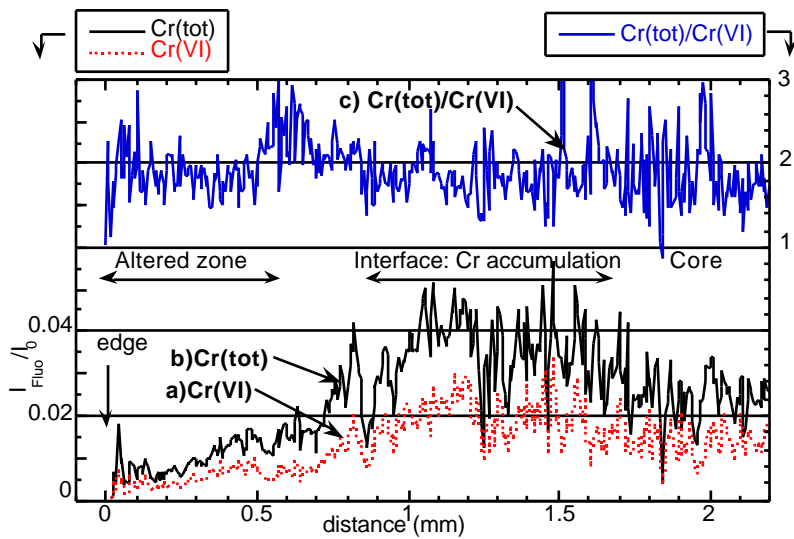


Figure 1 : line scans recorded at a) 5.998 (Cr(VI)) and b) 6.02 keV (Cr(Tot)) from the altered border to the core of the doped cement sample and c) Cr(tot)/Cr(VI) ratio

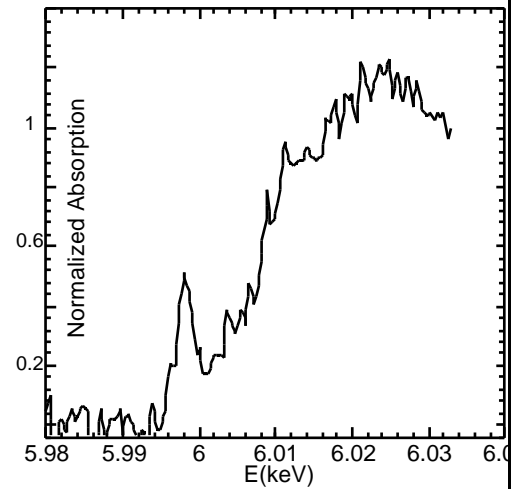


Figure 2 : Cr k-edge XANES in the altered zone of the natural cement (60 ppm)

Region of interests, Cr(VI) rich, were selected to perform XANES spectra. In the same regions fluorescence spectra were recorded to determine the nature of the major elements associated with Cr (Ca, S, Al, Si) and consequently to characterise Cr(VI) location among the different mineralogical phases. Because of the huge difference in concentration of Ca (%) and Cr (ppm) the detection of fluorescent lines was performed in a twofold procedure. The Ca fluorescence requires attenuators to avoid Ge solid state detector saturation during the detection of Cr fluorescence then light elements fluorescence was recorded in vacuum and no filters. Finally a similar strategy was adopted to characterise the natural cement with longer integration time (12 sec per point).

This study demonstrated the possibility of in situ determination of Cr speciation at extremely low concentrations (case of the undoped sample fig.2). To our knowledge, such an in-situ characterisation had never been reported for cement sample. Line scans of Cr(VI) for the doped sample indicate that the altered layer is characterised by a lower amount of Cr(VI), whereas an accumulation appears at the interface between the border and the core (fig.1). This interface, rich in Cr, could correspond to the ettringite (Ca-Al-SO₄ mineral) area as reported by previous works. However, the latter studies who also observed that Cr accumulation area using Excimer laser-ablation coupled to ICP, failed to give information concerning the oxidation state of Cr in that layer. Moreover the spot size used was larger than on ID21 (30x30µm² vs. 2*4µm²). Further interpretations of the data compared to SEM-EDX observations are still ongoing.

Another disconcerting result is the evolution of Cr(tot)/Cr(VI) ratio along the line spectra which is constant from the altered layer to the core (both for the doped and undoped samples). This means that same amounts of Cr(VI) and Cr(tot) are released during leaching. Even for the undoped sample, Cr(VI) was detected in the altered layer (fig.2). This result is inconsistent with literature which usually states that Cr(VI) is mainly leached out in the process. Although this result must be confirmed it clearly indicate that Cr(VI) may be less mobile than predicted by models.