

**Experiment title:**

Cement hydrates: the effect of leaching on the crystallographic sites of trace metals : case of Cr.

**Experiment**

**number:**  
**30-02-17**

**Beamline:**

BM30B  
FAME

**Date of experiment:**

from: September 7<sup>th</sup> to 10<sup>th</sup>, 2002

**Date of report:**

23-09-02

**Shifts:**

9

**Local contact(s):**

Olivier Proux

*Received at ESRF:*

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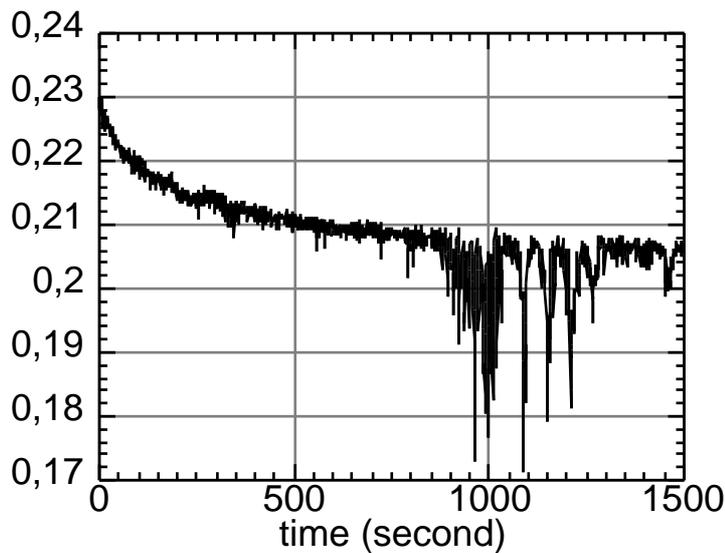
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**Report:**

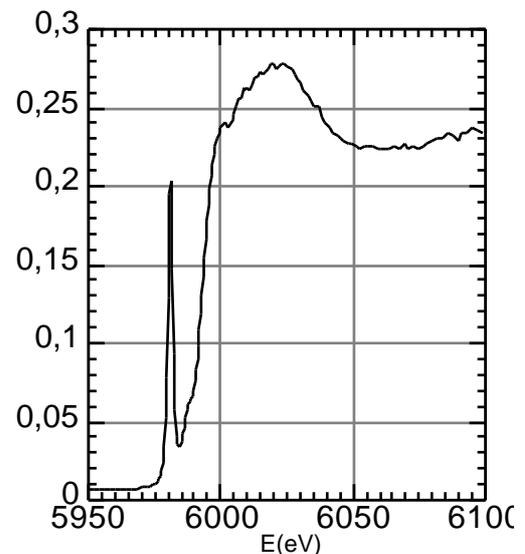
Cement high affinity for heavy metals (HM) has encouraged the industry to use hazardous waste as fuel for the cement kilns. This co-firing technique is really interesting in an environmental point of view, since the quantity of hazardous waste is reduced and heavy metals are trapped in cement. The concentrations of HM in cement never exceed few hundred ppm. To assess the environmental risks linked to the use of these materials, it is essential to study the effect of water on the physico-chemical stability of these metals in the hydrated materials. Standard leaching tests performed on cements manufactured with hazardous waste have revealed low levels of released metals; however, the total metal release was dependent on the cement and the secondary hydrate phase composition. Thus, to predict the long term metal leaching behavior and the associated environmental and human health risks, it is crucial to determine the evolution of the crystallographic sites of the heavy metals in the cement during the leaching. Our recent micro-Xanes experiments (ID21 ME317) indicated that Cr(VI) is present in the leached zone even after 40 days of leaching. The aim of XAS experiments was to implement micro-XANES results by determining the Cr crystallographic sites in the different zone of altered cements and to compare Portland cements with Slag-cements.

XAS experiments were conducted on the new French CRG beamline FAME (BM30B). Cr K-edge XANES and EXAFS experiments have been carried out with the Si (111) monochromator crystals and by using the fluorescence detection mode. By combining the high brilliance from the ESRF synchrotron source with a multi-channel fluorescence detector, we were able to obtain spectra with a very high signal/noise ratio for low Cr concentrations. The number of Cr X-ray fluorescence counts on FAME is 3 times higher than that obtained on the previous BM32 beamline, for similar Cr content. With this sensitivity improvement we were able to scan cement samples with 30 ppm in Cr. Unfortunately the 200x200  $\mu\text{m}$  spot with such high brilliance modified the redox state of Cr. Figure 1 presents the decrease of the pre-edge peak intensity with time. This pre-edge peak

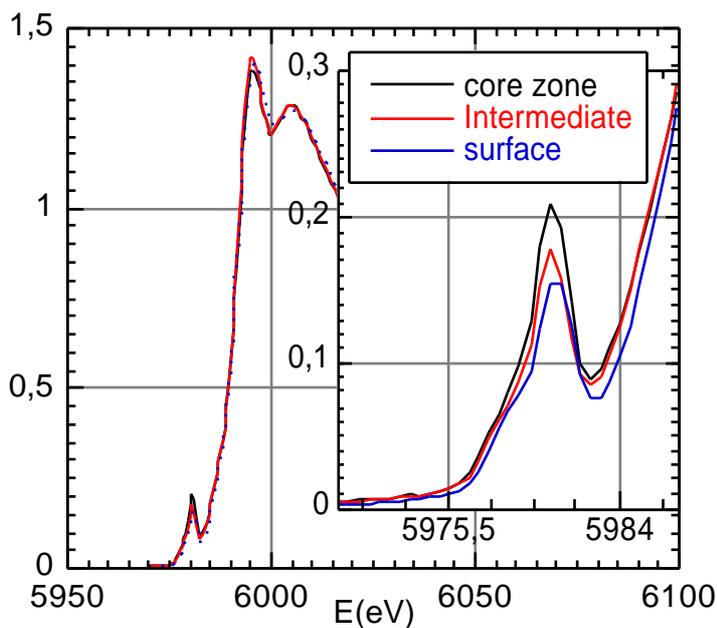
corresponds to the presence of Cr(VI) in cement samples. As it can be observed the curve reaches a constant value after 1000 to 1500 sec. The spectrum recorded after 1600 seconds (figure 2) indicates that the decrease of the pre-edge from 0.23 to 0.207 corresponds to a decrease of the Cr(VI)/Cr(tot) ratio from 92% to 82%. This Cr(VI) reduction during the first



**Figure 1 : intensity of the pre-edge peak as a function of time**



**Figure 2 : XANES recorded after 1600 sec.**



**Figure 3: Cr K-edge XANES of the three different altered layers of the Slag cement.**

20 to 25 minutes is a strong limitation in the determination of the actual Cr(VI)/Cr(tot) ratio.

XANES spectra of the altered and core zone of the Cr(VI) doped Portland cement suggest that the Cr(VI)/Cr(tot) ratio does not evolve strongly. This result confirm previous micro-XANES experiments. But in the case the Cr(VI) doped Slag cement the Cr(VI)/Cr(tot) ratio decreases from the core to the surface of the leached cement as indicated by the decrease of the height of the pre-edge (figure 3). This result is really interesting since Cr(III) is known to be less toxic and mobile than Cr(VI). The reduction of

Cr(VI) is certainly due to the presence of Fe(II) in the slag.

The modelling of the EXAFS part (under progress) will help the understanding of the Cr reduction in the case of Slag cements and the determination of the evolution of the crystallographic site of Cr.