



	<b>Experiment title:</b> Determination of Fe speciation in low pH cementitious materials	<b>Experiment number:</b> EV-265
<b>Beamline:</b> BM26A	<b>Date of experiment:</b> from: 19 October 2017 at 08:00 to: 23 October 2017 at 08:00	<b>Date of report:</b> January 2018
<b>Shifts:</b> 12	<b>Local contact(s):</b> BANERJEE Dipanjan	<i>Received at ESRF:</i>
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### Scientific background and aim

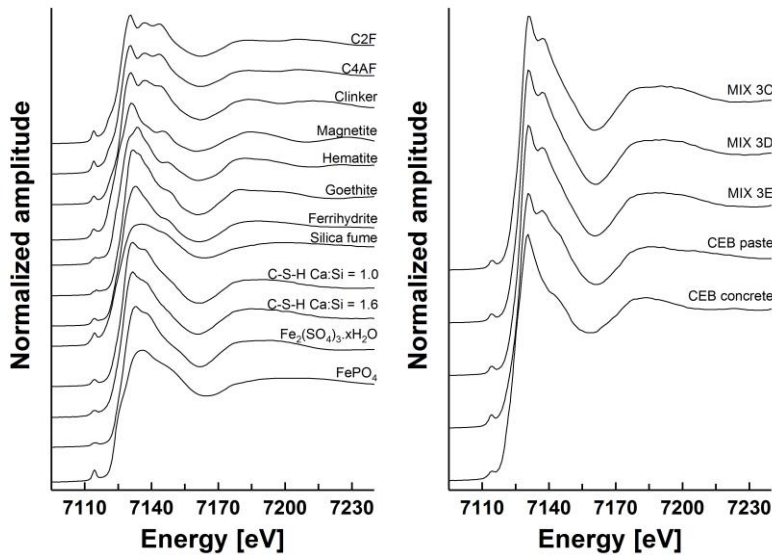
The safe disposal of nuclear waste relies on its confinement in deep facilities to isolate it from the biosphere. Concrete and clay minerals are typically used as confinement barriers in many concepts developed internationally. Depending on the design, cement could physically contact clay, or be sufficiently close so that porewater from both materials interact due to large concentration gradients across this interface, thereby affecting in time and space their physico-chemical properties. The porewater of “classical” cements is very alkaline (pH>13), and “low pH” cements have been developed to reduce the interaction between cement and clays. In the preparation of low pH cements the clinker content is partly substituted by silica fume or fly ashes [1] resulting in a less alkaline pore water (pH ~11) in the hydration process. These materials also have a Ca/Si ratio <1, C-S-H phases are the main solid present, and portlandite as hydrated solid phase is absent.

The initial microstructure and the chemical composition of low pH cements are among most important information needed to understand and model the degradation of these materials in contact with clays. In the frame of a PhD thesis, hydrated low pH cements have been prepared and characterized using various complementary analytical techniques. However, uncertainties remain concerning the iron speciation in the hydrated solid phases, which make difficult to perform a good prediction of Fe behavior in geochemical modeling. For example, Fe can substitute for Al in ettringite and could as well be present within C-S-H phases, thereby forming solid solutions. Identifying Fe-containing hydrate phases using standard techniques in the laboratory is complicated by overlapping signals from Fe- and Al-containing phases. The goal of this study was to apply X-ray absorption spectroscopy (XAS) at the Fe K-edge in order to identify and quantify Fe-phases present in the samples. XAS has already shown to be a complementary technique providing molecular-level information for classical cements [2], but not for low pH cementitious materials so far.

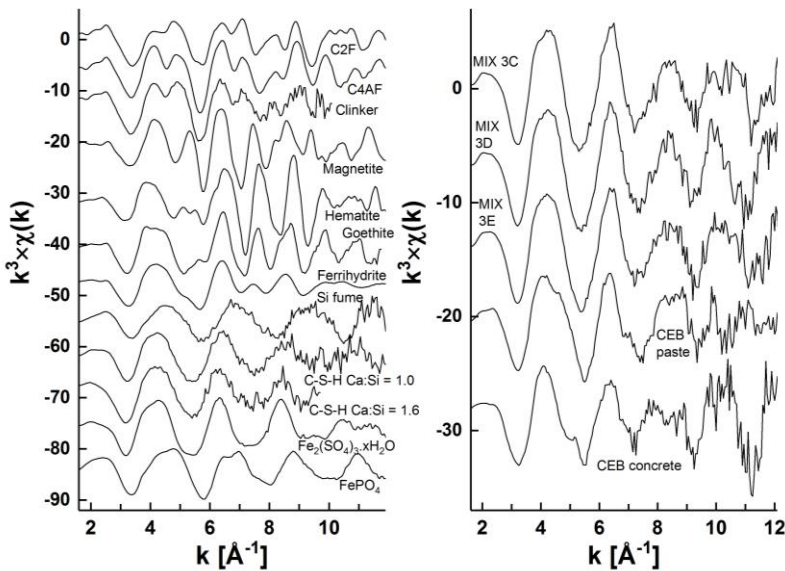
### Experiments and results

Fe K-edge XAS data were recorded for low pH hydrated cement pastes synthesized using either silica fume (MIX 3C, 3D, 3E) or a combination of silica fume and blast furnace slag to form a cement paste (CEB paste) and a concrete (CEB concrete). All samples were compared to several reference compounds. Samples and model compounds were prepared as pellet and spectra were recorded either in transmission or in fluorescence detection mode using a 9 element monolithic Ge fluorescence detector at the BM26A beamline [3].

XANES are shown in Figure 1 and EXAFS spectra in Figure 2. In all samples and reference compounds, the edge is located at the same energy position, except magnetite ( $\text{Fe}^{2+}\text{Fe}^{3+}_2\text{O}_4$ ), indicating that Fe is present only as  $\text{Fe}^{3+}$  in all samples (Figure 1). However, the intensity of the pre-edge and the structure of the main absorption edge (WL) differ from sample to sample indicating differences in local geometry and electronic state caused by the type, number and arrangement of neighboring atoms. The XANES of the ferrites C2F ( $\text{Ca}_2\text{Fe}_2\text{O}_5$ ) and C4AF ( $\text{Ca}_2(\text{Al},\text{Fe})_2\text{O}_5$ ) and of the clinker are similar, and the XANES of both C-S-H phases are also similar between them. Note also the similarities between the XANES of Fe(III) sulfate with that of



**Figure 2.** Experimental XANES of the reference compounds (left) and of the samples (right).



**Figure 1.** Experimental EXAFS spectra of the reference compounds (left) and of the samples (right).

the C-S-H phases. By comparison with the  $^{54}\text{Fe}^{3+}$  reference compound ( $\text{FePO}_4$ ), the intensity of the pre-edge suggests that ferrites and C-S-H phases contain fourfold coordinated Fe. The Fe speciation in the silica fume is close to that in  $\text{FePO}_4$ . XANES of all cement phases look similar to each another, indicating that Fe may be located in similar environment in these samples. Furthermore, the structure of their WL maximum is similar to that of the C-S-H phases, though the shoulder on the high energy side is of lower intensity in these reference compounds. This finding may suggest that Fe is not located in a single phase in the studied cement phases. The Fe speciation changed during the preparation of the concrete (CEB concrete) from the CEB paste cement. The intensity of the pre-edge significantly decreased and the WL has no shoulder. These results indicate the presence of  $^{6}\text{Fe}^{3+}$  in an environment different from that of the cements and reference compounds.

In agreement with XANES results, the EXAFS spectrum of both ferrites look similar, as well as that of both C-S-H phases and that of Fe(III) sulfate. The spectrum of the clinker looks most similar to that of the C4AF reference, while the oscillation maxima of the spectrum of the silica fume are matching best with that of  $\text{FePO}_4$ , meaning that  $^{54}\text{Fe}$  may be present in that sample. The spectrum of all four cement pastes look similar, though the oscillation maximum at  $k \sim 4.5 \text{ \AA}^{-1}$  in CEB paste has a feature that is absent in the others. The spectrum of the concrete differs from that of the cements in the oscillation maximum around  $5 \text{ \AA}^{-1}$  and

though noisier, the oscillation amplitudes are lower at  $k > 5 \text{ \AA}^{-1}$ . This hints at a change in binding environment, either in terms of types and number of neighboring atoms, or more likely in cancellation effects due to more than one binding environment. Fits to the experimental data will provide more detailed information allowing to identify more precisely in which environment Fe is located in the cements and in the concrete.

### Acknowledgements

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### References

- [1] Cau dit Coumes, C. *et al.* (2006) *Cem. Concr. Res.* **36**, 2152-2163. [2] Dilnessa, B.Z. *et al.* (2014) *Cem. Concr. Res.* **58**, 45-55. [3] Nikitenko, S. *et al.* (2008) *J. Synchrotron Rad.* **15**, 632-640.