

ESRF

<b>Experiment title:</b> Crystal chemistry of trace metals in hydraulic binders (cement): Case of Lead	<b>Experiment number:</b> CH-466
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**Report:**

Cement materials manufactured in kilns fueled with hazardous waste contain trace metals and specially lead whose concentration is around 500 ppm. In order to assess the environmental risks linked to the use of these materials, it is essential to study this physico-chemical stability in the hydrated cement. One way to predict the long term behaviour is to know which type of links occurs between heavy metals and major elements (calcium, silicium, aluminium, iron). Thus, the scientific aim of this study was the investigation of the local environment of lead in hydrated cement phases using XAFS at Pb LIII-edge. Experiments have been carried out with the Si (111) monochromator crystals and by using the fluorescence detection mode due to the very low concentration of Pb in cements. 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 such a Pb concentration as seen in figure 1. These good spectra quality was also due to the fact that the sample's matrix is composed by light elements (Al, Si, Ca).

Preliminary experiments as sorption isotherms had allowed to determine that only two phases constituting a cement : the tricalcium silicate ( $3\text{CaO}\cdot\text{SiO}_2=\text{C}_3\text{S}$ ) and the calcium ferroaluminate ( $4\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{Fe}_2\text{O}_3=\text{C}_4\text{AF}$ ) were able to retained lead. Both phases were hydrated with lime water in presence of lead (a third sample was prepared by a prehydration of tricalcium silicate ( $\text{C}_3\text{S}+\text{H}_2\text{O}\Rightarrow\text{CSH}$ ) and then the introduction

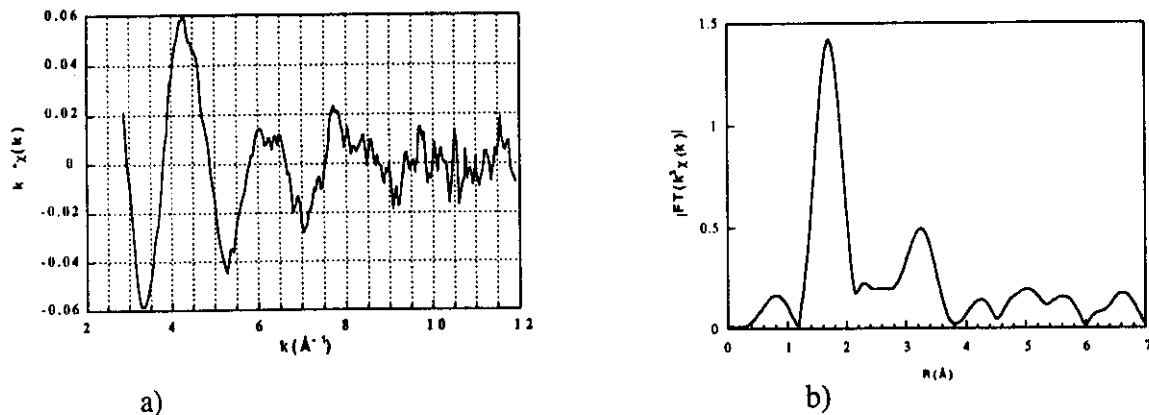


Figure 1 : a) EXAFS spectrum b) Fourier transform of CSH (hydrated  $C_3S$ ) + Pb .

of lead because of its hydration blocking effect). Cement samples doped with Lead non hydrated and hydrated were also studied.

The high quality of the EXAFS spectra and RDFs allowed us to modelized the first two atomic shells around lead in the various hydrated cement phases. The first results indicate that in the case of hydrated  $C_3S$ -Pb only one Pb-O contribution is detected suggesting that Pb is adsorbed to the surface of  $C_3S$ , thus inhibiting the hydration of this cement phase. The RDF obtained with CSH displays an additional peak at approximately 3.2 Å (distance uncorrected from phase shift) (fig.1-b). The modelling indicates the presence of  $1.0 \pm 0.2$  Si atom at a distance of 3.75 Å. This site has also been detected by  $^{29}Si$  NMR spectroscopy which shows that essentially  $Q_1$  sites are involved. With the  $C_4AF$  hydrated phase, besides the "oxygen peak" at 1.7 Å, there is a second major peak around 2.9 Å. This peak may correspond to a Pb-Fe contribution, especially since sorption data showed a enhanced affinity of the  $C_4AF$  phase for Pb compared to the other cement phases. Further modellings for natural cement have to be done. More over the importance of multiple scattering will be analysed using the Feff-7 code.

**Resume :** EXAFS experiments using the high brilliance of the ESRF synchrotron source provided for the first time pertinent informations concerning the crystallographic site of Pb (whose concentration was 500 ppm) in natural desordered cements. At the light of our first results it appears that Pb is strongly binded to two phases of cement : the tricalcium silicate ( $3CaO.SiO_2=C_3S$ ) and the calcium ferroaluminate ( $4CaO.Al_2O_3.Fe_2O_3=C_4AF$ ) through Pb-O-Si and Pb-O-Fe linkages respectively. Both structures correspond to Pb incorporated into phases. Then the solubility of Pb-cement phase is close to the solubility of this phase without lead. This structural determination of lead atomic environment explains its strong affinity to  $C_3S$  and  $C_4AF$  and can be predictive for its low capacity to be lixiviated into the environment.

The key point is that we did not have to artificially increase the Pb concentration in cement to obtain high signal/noise ration and thus no Pb-oxide precipitation had hidden the mechanism of Pb retention by cements.