



	Experiment title: Determination of the Fe speciation in synthetic iron cements	Experiment number: 01-01-884
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Background and objective:

Unhydrated cement mainly consist of the clinker phases produced at 1450 °C, i.e. alite (Ca_3SiO_5), belite (Ca_2SiO_4), aluminat ($\text{Ca}_3\text{Al}_2\text{O}_6$) and alumino-ferrite ($\text{Ca}_4(\text{Fe}_{1-x}\text{Al}_x)_4\text{O}_{10}$), and minor amounts of added gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) and limestone (CaCO_3). In contact with water the hydration process starts as clinker phases are unstable and dissolve slowly while secondary precipitates such as calcium silicate hydrates (C-S-H), ettringite or other hydrate phases form. This process can be modelled thermodynamically, which allows cement hydration to be predicted as a function of time and varying cement compositions [e.g. 1]. The predictive capability of the modelling approach rests strongly on a detailed knowledge of the speciation of the matrix-forming elements such as Fe. Here, we summarize the preliminary XAFS measurements on aged OPC samples and synthetic iron containing materials with the supplementary materials fly ash and slag carried out at SNBL.

Sample preparation and XAS measurements:

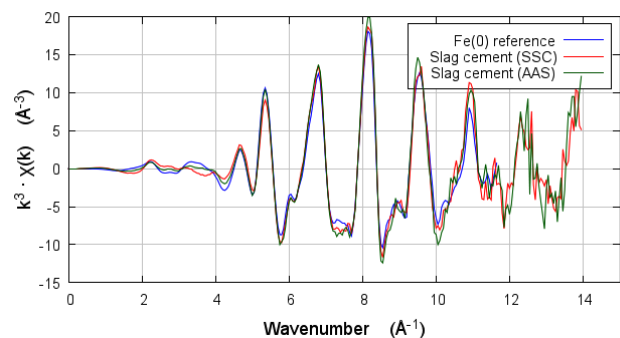
A series of relevant Fe(II) and Fe(III) references compounds were analysed. The compounds were either commercial products (e.g. Fe(0) powders, or Fe(III)-bearing cement phases that had been synthesized in the framework of earlier studies e.g. ferrite (C_2F , C_4AF) and Fe-siliceous hydrogarnet synthesized in various conditions (room temperature and equilibrated for 1 and 3 years, hydrothermally synthesized and aged for 1 year and 5 days) [2]. The cementitious materials comprised strongly hydrated and Fe(II,III) doped calcium silicate hydrates (C-S-H phases) as reference materials and cementitious materials consisting of mixtures of OPC and fly ash aged for 30 days as well as alkali activated slag-containing cement (AAS) and super-sulphated slag-containing cement (SSC) aged for 30 day. The materials were crushed, packed in Plexiglas sample holders and sealed with Kapton tape. Fe K-edge (7.112 keV) XAFS measurements were conducted at room temperature in transmission (references) or fluorescence mode (cement samples).

Results:

In the strongly hydrated and the aged OPC samples we were able to confirm on the basis of the XAFS measurements at SNBL that Fe-siliceous hydrogarnet is the only Fe(III)-bearing cement phase [2]. This indicates that in strongly reacted and aged OPCs, that is in cement systems where the hydration process is complete, Fe-siliceous hydrogarnet is the thermodynamically most stable phase. Comparison of the structural data obtained from data fitting and a Wavelet analysis of the experimental data further revealed that the Fe-bearing siliceous hydrogarnet formed during cement hydration is in fact a Fe-Al solid solution where Al is partially replaced by Fe in the hydrogarnet structure [3].

For slag containing cements, we confirmed the presence of Fe(0), which was previously identified by XRD (Fig. 1). No additional Fe species could be identified with certainty above the detection limit of XAFS on the basis of a linear combination fitting using the available reference spectra and in particular we were not able to determine Fe(II) in these systems. The most complex Fe speciation was observed in the cements consisting of mixtures of OPC and fly ash. There, the Fe(III) sources are ferrite (C_4AF from OPC) and magnetite, hematite and a Fe(III)-bearing glassy, amorphous phase in the untreated material. In the hydrated sample the XAFS data suggest that ferrite and the Fe-bearing glassy phase dissolved during hydration and further, that Fe(III) was bound in a secondary phase. Preliminary data analysis suggests that Fe(III) hydroxide could be the main secondary Fe-bearing product generated during hydration.

Fig. 1: Comparison of the Fe K-edge EXAFS spectra of the slag cements (SSC, AAS) with the reference spectra (Fe(0) powder).



Conclusion:

Al/Fe-bearing siliceous hydrogarnet was confirmed to be the thermodynamically most stable Fe-bearing phase in aged OPC as reported elsewhere [2]. The structure of the hydrogarnet was identified [3]. This phase, however, was not observed in synthetic iron cements, in particular blended cement systems containing fly ash and slag. In these systems the Fe speciation is dominated by Fe(0) in the slag cements and Fe(III)-hydroxide in the OPC/fly ash mix.

References:

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- [3] Vespa, M., Wieland, E., Dähn, R., Lothenbach, B., 2015. Identification of the thermodynamically stable Fe-containing phase in aged cement pastes. *J. Am. Ceram. Soc.* 98, 2286.