



	Experiment title: Investigation into the Fe speciation in alternative binder materials using XAFS	Experiment number: MA-2011
Beamline: BM 26	Date of experiment: from: 24/1/2014 to: 28/1/2014	Date of report: 8/8/2014
Shifts: 12	Local contact(s): Dr. D. BANERJEE	<i>Received at ESRF:</i>
Names and affiliations of applicants (* indicates experimentalists): Erich Wieland* ¹ , Marika Vespa* ² , Rainer Dähn* ¹ , Barbara Lothenbach ³ ¹ Laboratory for Waste Management, Paul Scherrer Institut, 5232 Villigen PSI, Switzerland. ² Institute for Nuclear Waste Disposal, KIT, 76344 Eggenstein-Leopoldshafen, Germany. ³ Laboratory for Concrete and Construction Chemistry, Empa, 8600 Dübendorf, Switzerland.		

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 in water and dissolve slowly while secondary precipitates such as calcium silicate hydrates (C-S-H), ettringite and other hydrate phases form. This process can be modelled thermodynamically to predict the composition of hydrated cement as a function of time and varying cement compositions [e.g. 1]. The predictive capability of the modelling approach rests strongly on the detailed knowledge of the speciation of the matrix-forming elements such as Fe. In this context, an extensive study is currently being undertaken to identify the Fe-bearing phases in hydrating OPC and alternative binders, i.e. cements containing supplementary materials such as fly ash and slags [2, this work]. Here, we report on XAFS investigations on aged OPC samples and cement samples containing OPC and the supplementary materials fly ash and slag.

Sample preparation and XAS measurements:

A series of relevant Fe(0, II, III) reference 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 [2,3], e.g. ferrite (C_2F , C_4AF) [3] and Fe-siliceous hydrogarnets synthesized at room temperature and equilibrated for 1 and 3 years (Fe-Hg-20-1y, Fe-Hg-20-3y) and under hydrothermal conditions and ageing times of 1 year and 5 days (Fe-Hg-80-1y, Fe-Hg-110-5d [3]), and hydrothermally synthesized Al/Fe solid solutions of siliceous hydrogarnet aged for 5 days (Fe-Al-Hg-110-5d [4]). The cement samples comprised strongly hydrated and aged OPC samples, i.e. a sulphate-resisting cement aged at a high water/cement (w/c) ratio (w/c = 1.3) for 30 days (HTS S1) [1] and OPC samples (w/c = 0.45) prepared in 1958-59 (OPC LTS 15) [2], 2) cementitious materials consisting of mixtures of OPC and fly ash aged for 30 days, and 3) alkali activated slag-containing cement (AAS) and super sulphated slag-containing cement (SSC) aged for 30 days. 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 identify Al/Fe-siliceous hydrogarnet as the only Fe-bearing cement phase (Fig. 1). Comparison of the structural data obtained from data fitting and a Wavelet analysis of the experimental data indicates that in strongly reacted and aged OPCs, that is in cement systems where the hydration process is complete, Al/Fe-bearing siliceous hydrogarnet is the thermo-

dynamically most stable phase [5]. In the latter cement phase, Al(III) is partially replaced by Fe(III) in the hydrogarnet structure.

For slag-containing cements, we observed Fe(0) as the dominant Fe species (Fig. 2). Presence of Fe(0) was previously suggested from X-ray diffraction. 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 sources are ferrite (C_4AF from OPC), 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 formed during hydration.

Fig. 1: Fe K-edge experimental spectra of the cement paste samples OPC LTS 15 and HTS S1 along with the hydrogarnet reference samples for a) k^3 -weighted, normalized, back-ground-subtracted EXAFS spectra; b) Radial Structure Functions (modulus and imaginary parts) obtained from the Fourier transform of the EXAFS spectra; c) experimental (solid line) and theoretical (dashed line) k^3 -weighted EXAFS function of the Fourier-backtransform spectra (range: $R + \Delta R = 1-4.4 \text{ \AA}$). Structural parameters are reported elsewhere [5].

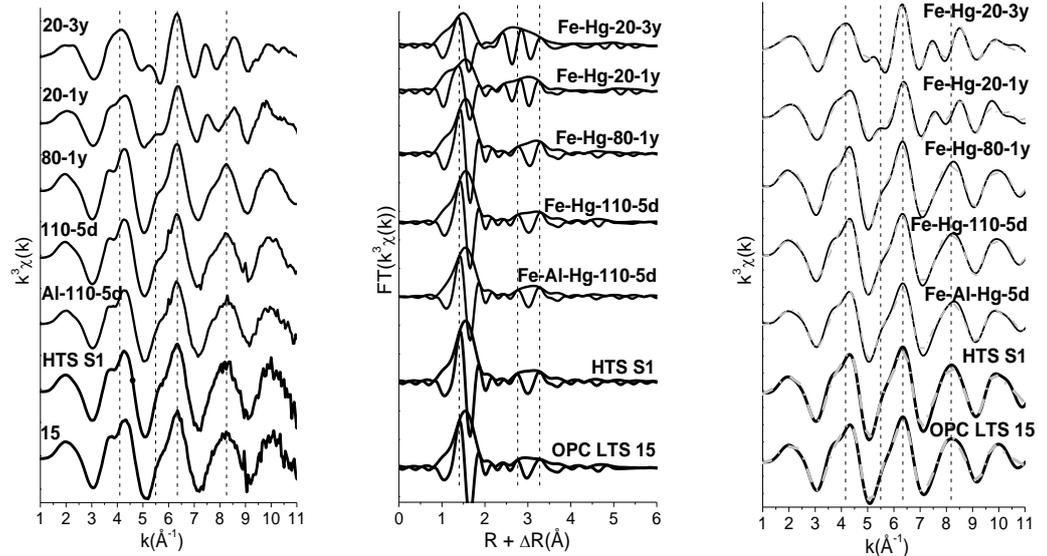
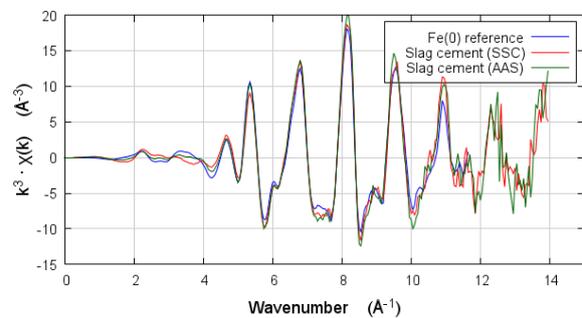


Fig. 2: Comparison of the Fe K-edge EXAFS spectra of the slag cements (SSC, AAS) with the reference spectra (Fe(0) powder).



Conclusion:

Al/Fe-bearing siliceous hydrogarnet was identified as the thermodynamically stable Fe-bearing phase in fully hydrated and aged OPC. This phase, however, was not observed in 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:

- [1] Lothenbach, B., Wieland, E., 2006. A thermodynamic approach to the hydration of sulphate-resisting Portland cement. *Waste Manage.* 26, 706-719.
- [2] Dilnesa, B.Z., Wieland, E., Lothenbach, B., Dähn, R., Scrivener, K.L., 2014a. Fe-containing phases in hydrated cements. *Cem. Concr. Res.* 58, 45-55.
- [3] Dilnesa, B.Z., Lothenbach, B., Renaudin, G., Wichser, A., Kulik, D., 2014b. Synthesis and characterization of hydrogarnet $Ca_3(Al_xFe_{1-x})_2(SiO_4)_y(OH)_{4(3-y)}$. *Cem. Concr. Res.* 59, 96-111.
- [4] Dilnesa, B.Z., 2012. Fe-containing hydrates and their fate during cement hydration: Thermodynamic data and experimental study, Thesis No. 5262, Swiss Federal Institute of Technology, Lausanne.
- [5] Vespa, M., Wieland, E., Dähn, R., Lothenbach, B., 2014. Identification of the thermodynamically stable Fe-containing phase in aged cement pastes. *Chem. Mater.* (submitted).