



	Experiment title: Identification of the Fe speciation in aged slag-containing cements	Experiment number: MA-4016
Beamline: BM 26A	Date of experiment: from: 7/5/2018 to: 10/5/2018	Date of report: 8/7/2019
Shifts: 12	Local contact(s): Dr. D. BANERJEE	<i>Received at ESRF:</i>
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Background and objective:

Ordinary Portland cement (OPC) is among the most important cementitious binders used worldwide. The production of OPC releases large quantities of CO₂ into the atmosphere. To improve sustainability of the manufacturing process, blended cements composed of small amounts of OPC and inorganic supplementary materials with high Fe(0) content, such as ground granulated blast-furnace slag (GGBFS), are likely to be increasingly used in the future. This study aimed at determining the Fe speciation in slag (Fe(0))-containing concrete sampled from various concrete structures. X-ray absorption spectroscopy (XAS) was employed to investigate “fresh” and aged slag-containing cement pastes. The latter materials had been aged up to 35 years, thus enabling long-term interaction of Fe(0) with cement paste to be studied. The materials were sampled from the cantilevers of two German bridges (Dausfeld, Auw an der Kyll) that had been aged for 5 years. The oldest slag-containing cement was sampled from the Vejle Fjord bridge in 2012, Denmark, which was built in 1975. The pillars of the latter bridge were constructed using a slag-containing CEM III/B cement (65 – 80 wt.% GGBFS, particle size from 2 to 50 µm) [1]. Synchrotron-based spectroscopy provides molecular-level information on the evolution of the Fe speciation in slag cements with time which is essential in connection with the development of thermodynamic models that allow the interaction of metallic iron with cement paste to be simulated as function of reaction time and the composition of cement.

Sample preparation and XAS measurements:

Material for bulk XAS measurements were prepared by crushing pieces of concrete sampled from the cantilevers and by dry sieving the crushed material to collect particles with size ≤ 60 µm. X-ray diffraction showed that the cement pastes consisted of cement phases that are typically observed after cement hydration. Laboratory X-ray fluorescence further allowed the elemental composition of the pastes to be determined. A series of relevant Fe(II) and Fe(III) reference compounds were also investigated by XAS along with the slag cements, such as Fe(II,III)-bearing cement phases. The references included the most important Fe(III)-bearing cement phases in unhydrated and hydrated cements, such as ferrite (C₂F, C₄AF) and Al/Fe siliceous hydrogarnet, as well as Fe(II)-loaded cement phases. Several slag-containing cements were studied including those from the aforementioned bridges and in addition freshly prepared slag-containing cement samples that had been aged for 1 month and 3 years using the same type of CEM III/B cement (1 - 2 wt.% Fe content) that had been used for the construction of the bridges. Furthermore, a few samples were prepared from a modern, alkali-activated slag cement that had been aged for up to 8 years. The Fe(II)-containing samples and slag cements were analysed at cryogenic temperature using the He cryostat available at BM 26A in order to avoid beam damage (Fe(II) oxidation to Fe(III)). EXAFS spectroscopy and XANES were carried out at the Fe K-edge (7112 eV).

Results:

Here, we focus on selected results from the XANES measurements. XANES spectra were collected for the references (Fig. 1, left) and several slag-containing cements (Vejle: Danish Vejle Fjord bridge aged for 35 years in marine environment; Auw: German bridge located in Auw an der Kyll aged for 5 years in continental environment; SSC: alkali-activated slag cement aged for 8 years in anoxic conditions in the laboratory) (Fig. 1, right). Linear combination (LC) fitting using the available reference spectra showed that several Fe species contribute to the XANES spectra of slag-containing cements (Tab. 1). Fe(0), the original chemical form of Fe in slag-containing cements, was determined in the Auw and SSC samples while Fe(0) was absent in the Vejle sample. This indicates that Fe(0) corrosion is slow in the Auw and SSC samples and that over the ageing period (i.e. 5 and 8 years, respectively), Fe(0) is only partly converted into Fe corrosion products which are mainly Fe₃O₄, FeOOH and FeS. Note that C₄AF is the Fe(III)-bearing clinker mineral which was not yet fully hydrated in the SSC sample. In the Vejle sample, however, Fe(0) was found to be completely corroded. FeO, Fe₂O₃, and FeCl₃ were identified as possible corrosion products based on LC fitting while Al/Fe siliceous hydrogarnet (Fe-Si-Hyd) results from the hydration of C₄AF. The above findings suggest that environmental conditions have an effect on the type of Fe corrosion products formed. Magnetite (Fe₃O₄) and FeS are preferentially formed in the lab samples aged in anoxic conditions while Fe(III) oxyhydroxides and FeS are formed in the bridge sample aged in continental environment. In the Vejle sample aged in marine environment, however, Fe(III)-bearing phases seem to preferentially form in addition to Cl-containing phases.

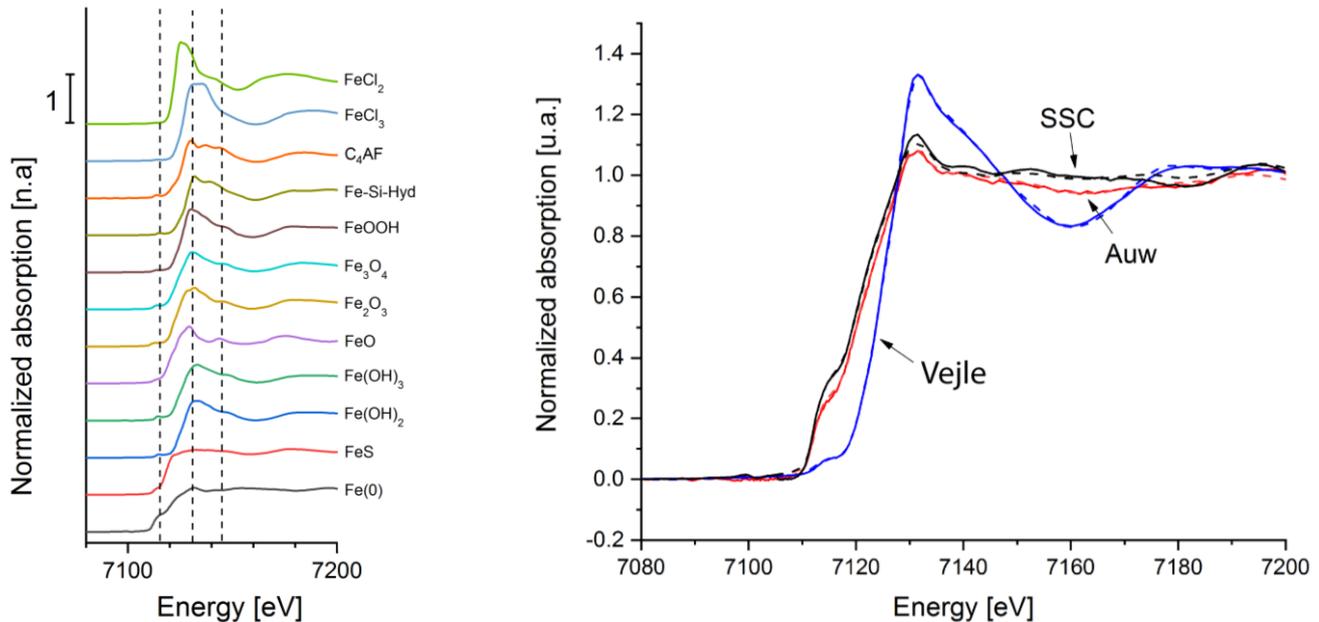


Fig. 1: Fe K-edge XANES spectra of references (left) and slag-containing cement samples (right) from a) the Danish Vejle Fjord bridge (blue), b) A German bridge (Auw an der Kyll) (red) and c) a modern, alkali-activated slag cement (SSC) (black).

Table 1: Fe species and their relative contribution to the XANES spectra of slag-containing cements

	Fe(0)	FeO	FeS	Fe ₂ O ₃	Fe ₃ O ₄	FeOOH	FeCl ₃	Fe-Si-Hyd	C ₄ AF	R-Factor
SSC	0.63(2)	-	0.10(2)	-	0.11(2)	-	-	-	0.16(3)	0.0005
Auw	0.82(1)	-	0.06(1)	-	-	0.12(2)	-	-	-	0.0014
Vejle	-	0.15(1)	-	0.27(3)	-	-	0.10(1)	0.48(1)	-	0.0002

Conclusions:

Slag-containing cements contain substantial amounts of Fe(0) which corrodes with time in cement pastes to form Fe(II,III)-bearing phases. The condition of exposition has an effect on the corrosion rate and the type of corrosion products formed. Complete corrosion of Fe(0) occurred in the sample exposed to marine environment over an ageing period of 35 years while in the samples aged in anoxic conditions and continental environment only partial corrosion was observed over a period of 8 years.

References:

[1] U. Hjorth Jakobsen, K. De Weerd, M. F. Geiker (2016). *Cem. Concr. Res.* 85, 12.