

In-situ SyXRD Analysis of Cement Hydration on the ms-Scale

M. C. Schlegel^{1,2}, A. Sarfraz¹, U. Müller¹, U. Panne^{1,3}, F. Emmerling¹

¹BAM Federal Institute of Materials Research and Testing, Berlin, Germany

²Helmholtz Zentrum Berlin (HZB), Berlin, Germany

³Humboldt-Universität zu Berlin, Berlin Germany

Introduction

The backbone of our infrastructure and modern architecture are cementitious materials. Despite their substantial role for society and their common involvement in the built environment, basic aspects of the hydration processes of cement are still not completely understood. During the first seconds of a building's life, highly dynamic reaction processes prevail. These reactions have a direct influence on the properties of the final building. Moreover, these reactions are actively influenced by organic additives. The additives affect the initial formation of hydrate phases, which is often interpreted based on the changes in fluid behaviour and zeta potential.^[1-3] Up to now, their influence has not been characterized by analysing the changes in the crystallization processes directly.

Experimental Setup

Ordinary portland cement (OPC) pellets were prepared with a moulding press and cut into pieces of 0.1 g each. For contact-free analysis the pellets were placed in an acoustic levitator system to avoid any influence of the container wall material on the crystallization process.^[4-6] Three different PCE modifications (GLENIUM® SKY 591, 592 and 593) with low (PCE 1), medium (PCE 2) and high polymer backbone charge density (PCE 3) were dissolved in distilled water with an amount of 2 wt% of the amount of cement. During the experiment, the solution was injected by a piezo-electric microdrop dispenser until a w/c-value of 0.50 was reached.

High resolution X-ray diffraction (SyXRD) data were collected at the beamline ID11 at the European Synchrotron Research Facility with a wavelength of $\lambda = 0.3444 \text{ \AA}$. Data acquisition time of a single diffraction pattern was 500 ms, which provides high resolution time resolved analysis.

Results

The hydration process for pure OPC and OPC mixed with PCE was analysed *in situ* and the initial ettringite reflections were observed for all four specimens. During cement hydration the full-width-at-half-maximum (FWHM) of ettringite reflection does not change significantly, so that peak height can be used as an indicator of amount of initially formed ettringite. This offers to display the collected ettringite reflections in a side view (Figure 1).

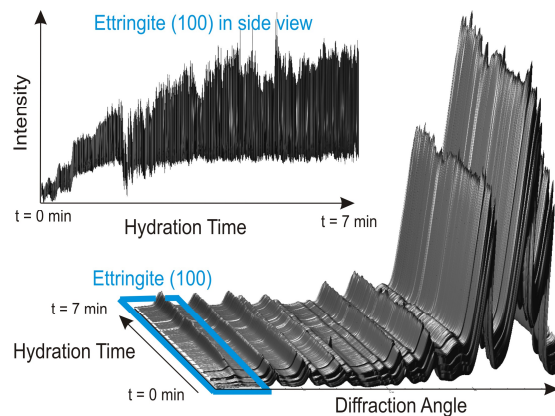


Fig. 1: Series of diffraction pattern collected during the hydration of OPC. In the upper left, the ettringite (100) reflection is enlarged and displayed in a side view.^[7]

Observing the ettringite (100)-reflection gives an overview of how ettringite formation changes due to the adsorption of different modifications of PCE. During the first minutes the intensity increase of the PCE containing OPCs differs compared to the hydration of pure binder material. All measurement series show an increase in the background contribution during water injection. This leads to an increase of the reflection intensities in the diffraction angle range where the ettringite (100)-reflection is observed. Finally, the increase of the background is more pronounced for the PCE containing specimens.

The ettringite (100)-reflection of the pure OPC shows exponential association increase over the whole time span of hydration. The increase of the PCE containing OPC shows exponential association increase as well, but only during the first seconds of hydration. Afterwards, the increase changes to a linear rise of the reflection intensity (Figure 2). The higher the backbone charge density of the PCE, the later the onset of linearity was observed.^[7]

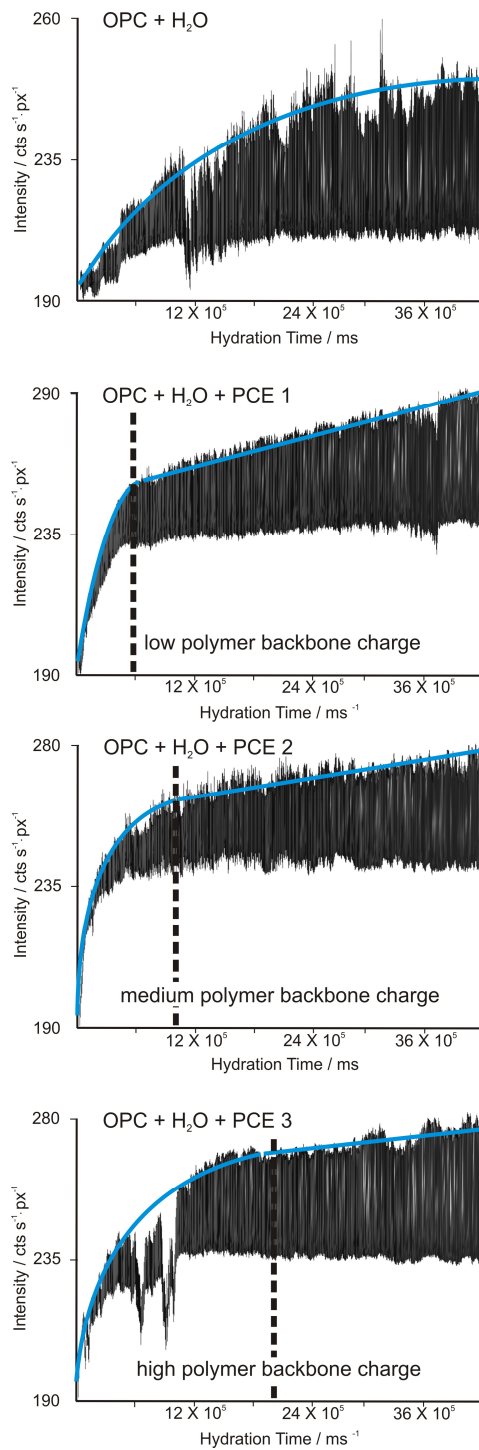


Fig. 2: Ettringite (100)-reflections in a side view collected during the hydration of pure OPC and OPC with different PCE modifications. The exponential association increase change to a linear rise of the reflection intensity (dashed line).^[7]

Discussion

Analysing the initial formation of ettringite offers additional information about the early hydration processes which are influenced by different PCE modifications. The change of the hydration behaviour is driven by the residual charge densities of the PCE. During hydration of pure OPC, C₃A reacts with SO₄²⁻ to ettringite, which leads to a high initial formation rate. The ettringite formation in PCE containing OPC is additionally influenced by the backbone charge density of the respective polymer. PCE adsorbs at the C₃A surface and only a small amount of ettringite crystallizes. During adsorption PCE is replaced by SO₄²⁻ of the pore solution. An equilibrium results between PCE adsorption and its replacement by SO₄²⁻ anions, which explains the linear increase of the ettringite amount. Consequently, a higher polymer backbone charge leads to retarded onset of the equilibration state and the formation of ettringite is decelerated. At the beginning of hydration the increasing background results from increasing amount of free water during injection, solution of crystalline phases and the formation of X-ray amorphous phases. The retarded formation of hydration products due to PCE also effects the background contribution. The less the amounts of hydration products the higher the amount of free water in the specimen.

Bibliographical references

- /1/ J. Plank, D. Zhimin, H. Keller, F. Von Hossle, W. Seidl: "Fundamental mechanisms for polycarboxylate intercalation into C(3)A hydrate phases and the role of sulfate present in cement" *Cem. Con. Res.* (2010) 40, 45-57
- /2/ C. Giraudeau, J.B.D. de Lacaillerie, Z. Souguir, A. Nonat, R.J. Flatt: "Surface and Intercalation Chemistry of Polycarboxylate Copolymers in Cementitious Systems" *J. Am. Ceram. Soc.* (2009) 92, 2471-2488
- /3/ A.P. Kirchheim, D.C. Dal Molin, P. Fischer, A.H. Emwas, J.L. Provis, P.J.M. Monteiro: "Real-Time High-Resolution X-ray Imaging and Nuclear Magnetic Resonance Study of the Hydration of Pure and Na-Doped C(3)A in the Presence of Sulfates" *Inorg. Chem.* (2011) 50, 1203-1212
- /4/ S.E. Wolf, J. Leiterer, M. Kappl, F. Emmerling, W. Tremel: "Early homogenous amorphous precursor stages of calcium carbonate and subsequent crystal growth in levitated droplets" *J. Am. Chem. Soc.* (2008) 130, 12342-12347
- /5/ A. Sarfraz, M.C. Schlegel, J. Wright, F. Emmerling: "Advanced gas hydrate studies at ambient conditions using suspended droplets" *Chem. Commun.* (2011) 47, 9369-9371
- /6/ J. Leiterer, W. Leitenberger, F. Emmerling, A.F. Thunemann, U. Panne: "Acoustically levitated droplets - A contactless sampling method for fluorescence studies" *J. Appl. Crystallogr.* (2006) 39, 771-773
- /7/ M.C. Schlegel, A. Sarfraz, U. Muller, U. Panne, F. Emmerling: "First Seconds in a Building's Life - In Situ Synchrotron X-Ray Diffraction Study of Cement Hydration on the Millisecond Timescale" *Angew. Chem. Int. Edit.* (2012) 51, 4993-4996