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In situ cement hydration in levitated droplets

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Micro Abstract
Building materials consist of cement, water and chemical admixtures, which adjust cement paste properties. Admixtures can act beyond their aimed functions causing undesirable side effects on the hydration course and the properties of the resulting building material. The mechanisms of these effects are still under investigation. We investigate cement hydration in levitated droplets using an ultrasonic levitator. The hydrate phase formation is followed in situ by synchrotron X-ray diffraction. The data allows detailed conclusions about the mechanisms of the admixture action in the ongoing hydration reactions.

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Introduction

The main component of cementitious system is a hydraulic binder cement. The hydration of cement involves several chemical reactions yielding hardened cementitious building material. Besides cement and water, cementitious systems contain minor components (admixtures). Addition of admixtures aims at specific modification of properties of the fresh cement paste or hardened cementitious building material. The hydration process starts at the first contact of water with dry cement powder and undergoes several stages. These stages differ with respect to the formation of the specific hydrate phases. Along with the progress of the cement hydration, the physical state of the cementitious system changes from flowable to solid. Assemblage of the cement hydrates formed during the hardening - cementitious matrix - determines properties of the resulting solid cementitious material.

Numerous admixtures are used in cementitious systems. Superplasticizers effectively improve the flowability of the fresh cement paste at the low water-to-cement ratio (w/c). The working period of superplasticizers is the early hydration stage, which continues for several hours. This stage is characterized by the intensive dissolution of the cement components. It is followed by the formation of the early hydrate phases, and the initial flowability loss (stiffening) occurs. However, superplasticizers seem to undesirably influence the early hydration reactions leading to delayed stiffening of the cementitious system. This retardation effect influences the course of the cement hydration and further the properties of the resulting hardened cementitious matrix. The occurrence of the retardation demonstrates the involvement of the admixture into the early hydration reactions. The mechanisms of the admixture action during the hydration process are still intensively investigated [1–6, 8]. A detailed understanding of the admixture activity in cementitious system during the early hydration stage is the key to its control and adjustment.

Since the presence of admixtures changes the hydration reactions, the identification of their products can give first insights into the admixture action. The time-resolved changes of the amounts of the reactants and of the resulting hydrates allow conclusions about the kinetics of the hydration process influenced by the admixture. A deep understanding and the control of the admixture impact on the hydration process is possible [7].

1 In situ measurements of the early hydration process

Here, we follow the early hydration process in situ by the synchrotron X-ray diffraction (SyXRD). In situ measurements are carried out using a setup based on an ultrasonic levitator. The ultrasonic levitator allows a containerless positioning of the sample specimen during the measurements. Containerless handling of the sample is especially advantageous for the samples consisting of crystalline and amorphous phases. The background contribution of the sample holder can be avoided. Both crystalline and amorphous components of sample can be evaluated directly. The uncertainty of the background correction is excluded.

An ultrasonic levitator consists of the transducer and the concave reflector, which are positioned coaxially (Figure 1, right). The emitted acoustic wave is multiply reflected from the concave reflector surface. The emitted and the reflected waves overlay and the standing wave results from the constructive interference between them. The standing wave has areas of the lower pressure - the nodes, in which small samples, typically liquid droplets or solids, can be hovered.
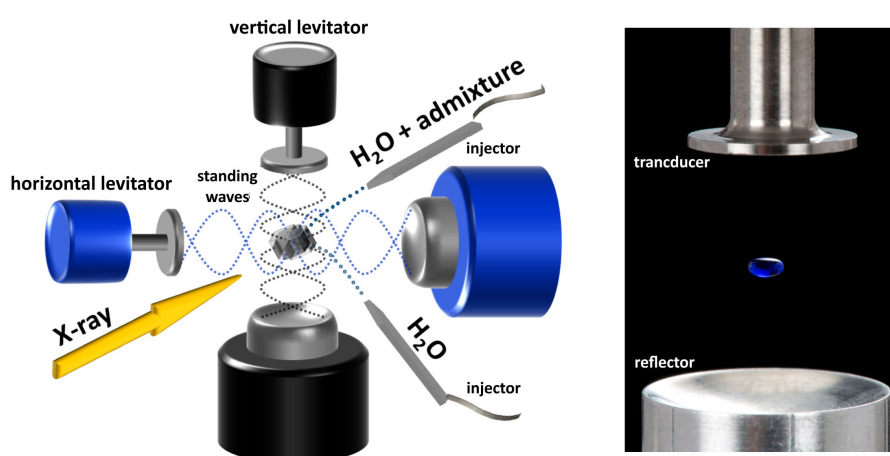

Figure 1. Experimental setup including two ultrasonic levitators for in situ measurements of the cement hydration course. Left: The schematic of the setup. Vertically positioned ultrasonic levitator holds the sample specimen in abeyance, while the acoustic wave of the horizontally positioned levitator inhibits its lateral instability. An injection system allows addition of up to two aqueous phases for an in situ start of the hydration process. Right: Levitated liquid droplet.

The measurement setup consists of two crossed ultrasonic levitators (Figure 1, left). This design enables stable levitation of the irregularly formed solid samples. An injection system consisting of two piezo-spraying devices (injectors) completes the setup. The hydration process is initiated during the data acquisition by adding of water or aqueous admixture solution. Different liquids can be added via injectors independently; the addition is remotely controlled. Initiation of the hydration in the levitator setup enables to avoid the time loss for the filling in sample holder.

The composition of the hydrating cementitious system is recorded in real time by the diffraction analysis. Fast measurements in transmission geometry are possible using intensive synchrotron radiation as the X-ray source. The temporal course of the composition changes in cementitious system is followed directly. The formed reaction products and the depletion of the reactants can be identified. From the acquired data, the amounts of the components of the cementitious system can be calculated and plotted along the time axis.

2 Results and Discussion

We analyze the influences of two individual superplasticizers (SP 11, SP 13) on the course of the Portland cement hydration. Ettringite is the crystalline hydrate phase formed preferentially during the early hydration stage. The development of the ettringite amount for cementitious systems with different SPs is compared to those without any superplasticizer. The development

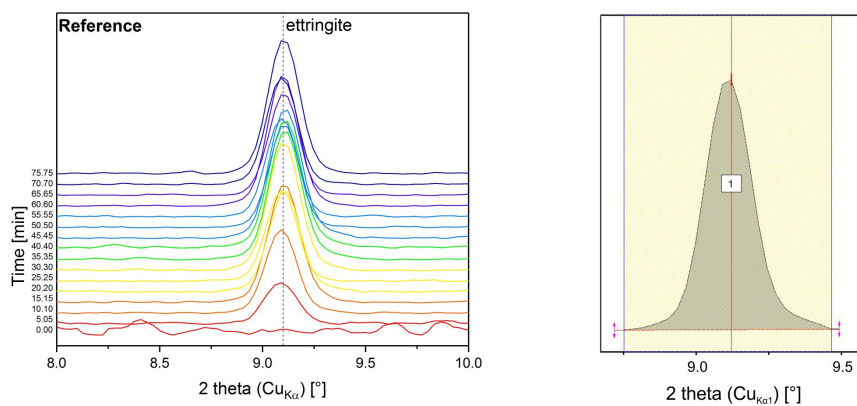of the ettringite reflection in the reference cementitious system is shown on Figure 2.

Figure 2. Left: Time-resolved course of the ettringite formation in the reference cementitious system demonstrated on its (100) reflection at 9.09 ° 2 theta ($Cu_{K\alpha 1}$) (corresponded to the lattice plane distance d=9.72 $\mathring{A}$). Right: An example of the peak area calculation.

The presence of superplasticizers suppresses the formation of the ettringite as shown on Figure 3. Its reflection intensity was lowered by the addition of SP 11. SP 13 inhibited ettringite formation in the analysed hydration period, since ettringite reflection is absent.
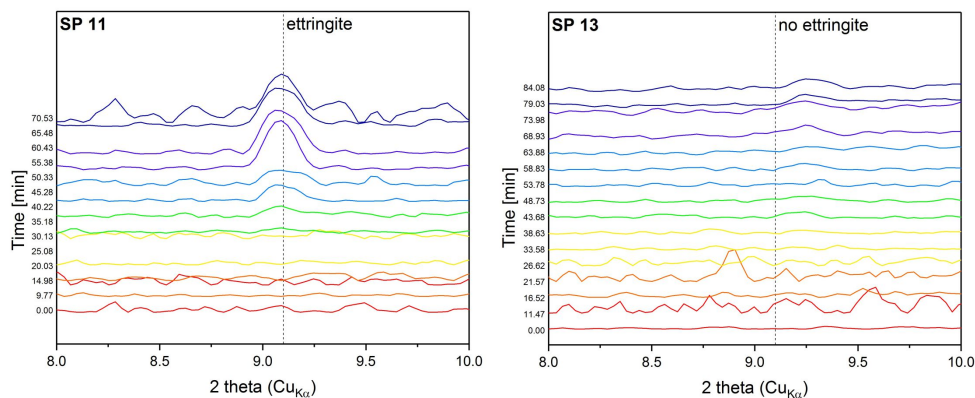

Figure 3. Time-resolved course of the ettringite formation in the cementitious system with admixture demonstrated on its (100) reflection at 9.09 ° 2 theta ($Cu_{K\alpha 1}$) (corresponded to the lattice plane distance d=9.72 $\mathring{A}$). Left: cementitious system with SP 11. Right: cementitious system with SP 13.

The information about the amount of the phase of interest formed in the cementitious system can be achieved from the evaluation of the area of its main peak (Figure 2, right). The diffractograms were normalized before the calculation of the peak area. The area of the ettringite's main reflection was calculated and plotted against the time for all analyzed cementitious systems (Figure 4). In the reference system, ettringite forms immediately after the water addition. It proceeds steep increase within 30 minutes and achieves a saturation plateau thereafter. The curves for cementitious systems with superplasticizers show strong reduction of the ettringite amount. SP 11 inhibits the formation of ettringite within 35 minutes after the hydration has started. Then, the amount of ettringite increases slightly and achieves saturation level after 55 minutes of hydration. In the cementitious system with SP 13, the formation of ettringite was inhibited in the analyzed hydration period.

Conclusions

In this study, the cement hydration process was analyzed in situ by the SyXRD. Using ultrasonic levitator setup allows to initiate the hydration during the data acquisition. Thus, the early
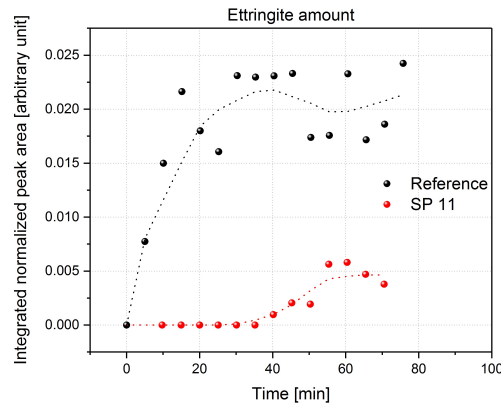
Figure 4. Development of the ettringite amount influenced by the presence of SP 11 (red) compared to the reference (black). Lines are shown for the trend visualization.

hydration period can be analyzed completely, without time losses at its very beginning. The measurement setup enables yielding detailed information about the processes of the hydrate phase's formation and depletion of unhydrated components. Correlation of the phase amounts to the hydration time allows insights into the hydration kinetics. This analysis is advantageous for the observation of the admixture activity in the hydrating cementitious system. This could be shown by analyzing of the influences of superplasticizers on the ettringite formation in the cementitious system based on Portland cement. The presence of admixture delayed the ettringite reaction and lowered its amount formed during the early hydration period. This causes the retardation of the hardening process.

References

[1] J. Cheung, A. Jeknavorian, L. Roberts, and D. Silva. Impact of admixtures on the hydration kinetics of Portland cement. *Cement and Concrete Research*, 41(12):1289–1309, 2011.

[2] F. Dalas, S. Pourchet, D. Rinaldi, A. Nonat, S. Sabio, and M. Mosquet. Modification of the rate of formation and surface area of ettringite by polycarboxylate ether superplasticizers during early C3A-CaSO4 hydration. *Cement and Concrete Research*, 69(0):105–113, 2015.

[3] F.-r. Kong, L.-s. Pan, C.-m. Wang, D.-l. Zhang, and N. Xu. Effects of polycarboxylate superplasticizers with different molecular structure on the hydration behavior of cement paste. *Construction and Building Materials*, 105:545–553, 2016.

[4] L. G. Li and A. K. H. Kwan. Effects of superplasticizer type on packing density, water film thickness and flowability of cementitious paste. *Construction and Building Materials*, 86:113–119, 2015.

[5] J. Plank, E. Sakai, C. Miao, C. Yu, and J. Hong. Chemical admixtures - Chemistry, applications and their impact on concrete microstructure and durability. *Cement and Concrete Research*, 78, Part A:81–99, 2015. Keynote papers from 14th International Congress on the Chemistry of Cement.

[6] C. Shi, G. Zhang, T. He, and Y. Li. Effects of superplasticizers on the stability and morphology of ettringite. *Construction and Building Materials*, 112:261–266, 2016.

[7] J. Stroh, M. C. Schlegel, W. Schmidt, Y. N. Thi, B. Meng, and F. Emmerling. Time-resolved in situ investigation of Portland cement hydration influenced by chemical admixtures. *Construction and Building Materials*, 106:18–26, 2016.

[8] Y. Zhang and X. Kong. Correlations of the dispersing capability of NSF and PCE types of superplasticizer and their impacts on cement hydration with the adsorption in fresh cement pastes. *Cement and Concrete Research*, 69:1–9, 2015.