QUANTITATIVE IN-SITU X-RAY DIFFRACTION ANALYSIS OF EARLY HYDRATION OF PORTLAND CEMENT AT DEFINED TEMPERATURES

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ABSTRACT
Investigation into the early hydration of Portland cement was performed by in-situ X-ray diffraction (XRD). Technical white cement was used for the XRD analysis on a D5000 diffractometer (Siemens). All diffraction patterns of the in-situ measurement which were recorded up to 22 hours of hydration at defined temperatures were analyzed by Rietveld refinement. The resulting phase composition was transformed with respect to free water and C-S-H leading to the total composition of the cement paste. The hydration reactions can be observed by dissolution of clinker phases as well as by the formation of the hydrate phases ettringite and portlandite. With increasing temperatures the reactions proceed faster. The formation of ettringite is directly influenced by the rate of dissolution of anhydrite and tricalcium aluminate (C₃A). The beginning of the main period of hydration is marked by the start of portlandite formation. The experiments point out that a quantitative phase analysis of the cement hydration is feasible with standard lab diffractometers.

INTRODUCTION
The hydration of ordinary Portland cement (OPC) is a complex process yielding to the hardening of cement paste while forming different hydrate phases. Ettringite (C₃A·3CS·H₃₂)¹ is formed from anhydrite (CS), C₃A, and water during the aluminate reaction [1]. The silicate reaction describes the formation of portlandite (CH) and an amorphous calcium silicate hydrate gel (C-S-H) from tricalcium silicate (C₃S) and water [1]. The composition of C-S-H, especially the Ca/Si-ratio is reported to vary in a large range between 0.5 and 3.0 [2], depending on hydration time and cement type. For the early hydration of OPC a Ca/Si-ratio of 1.7 is assumed with different water content [1,3]. OPC hydration is often analyzed by heat flow calorimetry but this method provides only information about the kinetics without regard to the proceeding reactions. Therefore the advantage of quantitative phase analysis which is widely used in the determination of the phase compositions of dry cements should be used for the investigation of the hydration process. In-situ analysis of cement hydration is usually done by synchrotron X-ray powder diffraction [4,5] but this method is very expensive and cannot work as standard analysis method. Therefore the aim of this investigation was the development of a quantitative in-situ XRD

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¹ cement nomenclature is used: C…CaO, S…SiO₂, A…Al₂O₃, H…H₂O, S;…SO₃
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analysis of early cement hydration with standard lab diffractometers. Former investigations of cement hydration have shown that the temperature has a strong influence on the reaction kinetics [6,7]. Hence temperature during analysis has to be controlled.

MATERIALS AND METHODS

Commercial white cement (WCem) with a mineralogical composition given in Tab. 1 was used for the experiments. Cement and water were weighted according to a water to cement (w/c) ratio of 0.5. All materials and tools needed for the sample preparation were thermally equilibrated at the measurement temperature. For the in-situ XRD analysis a custom made sample holder was used which controls the temperature during the measurement [8]. The temperature is set thermoelectrically by a Peltier element below the sample which is controlled by the software MAETRE (Mesicon). Cement and water were mixed by external stirring for 1 minute and then the paste was filled into the sample holder. The surface of the paste was smoothed and then covered by a 7.5 µm thick Kapton film. The diffraction patterns were recorded by a D5000 diffractometer (Siemens) equipped with a SolX detector (Bruker). CuKα radiation was used at a voltage of 40 kV and a current of 30 mA. The measurements were carried out in a 2θ range of 7°–41° with a step width of 0.024° and 0.6 s time per step. 88 patterns were recorded within 22 hours. The measurement of one diffraction pattern lasts approximately 15 minutes. Therefore the Rietveld result reflects an average of these 15 minutes.

Tab. 1: Phase composition of used white cement. Values are given in wt.-%.

<table>
<thead>
<tr>
<th></th>
<th>C₃S</th>
<th>C₂S</th>
<th>C₃A</th>
<th>anhydrite</th>
<th>bassanite</th>
<th>portlandite</th>
<th>calcite</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>63.8</td>
<td>20.5</td>
<td>4.0</td>
<td>2.9</td>
<td>1.6</td>
<td>3.0</td>
<td>4.2</td>
</tr>
</tbody>
</table>

The quantitative analysis with the Rietveld method was done with the software Topas 3.0 (Bruker). Three successive measurements of one sample were refined jointly leading to an average phase composition between these three measurements. This method is practicable due to the slow changes in phase composition during hydration and leads to more stable values of the phase development. Refined parameters are lattice parameters and crystallite size for the hydrate phases as well as preferred orientation for portlandite, ettringite, C₃S, and anhydrite. The lattice parameters, microstrain, and crystallite size for C₃S, C₃A, C₂S, calcite, and anhydrite were determined by Rietveld refinement of dry cement. These parameters were not refined during analysis of in-situ patterns because they underwent no changes during hydration. Additionally, a peak phase was used for the simulation of the diffuse diffraction maximum caused by the Kapton film (Fig. 1). The peak phase was not refined during Rietveld analysis of the in-situ
measurements. The same starting refinement model was used for all samples and ranges. Besides the XRD analysis, the cement hydration was investigated by isothermal heat flow calorimetry.

Fig. 1: Peak phase of the diffuse diffraction maximum caused by Kapton film. The pattern of the Kapton film (circles) was recorded by the preparation of the film on a silicon single crystal sample carrier measured under the same conditions like the cement paste.

RESULTS AND DISCUSSION
The diffraction patterns displayed in Fig. 2 reflect the changes in the phase composition of the cement paste with the help of a level plot.

Fig. 2: Level plot of in-situ XRD measurement of white cement at 23 °C hydrated with w/c = 0.5

The Rietveld analysis results in the phase composition of all crystalline phases in the cement paste. But because of free water and the forming of an amorphous C-S-H phase the total phase composition of the cement paste has to be calculated. The C-S-H content is calculated from the
formation of portlandite in accordance to Eq. 1 for OPC. Afterwards, the content of free water ($H_{\text{free}}$) is calculated with respect to the w/c-ratio and bonded water ($H_{\text{bond}}$) in the hydrate phases by summation of all dry phases, bonded water, and free water to a total sum of 150 wt.-% depending on the used w/c-ratio. The process map of the calculation procedure is given in Fig. 3. The following discussion is based on the transformed values.

Eq. 1: \[ C_3S + 3.9 H \rightarrow C_{1.7}SH_{2.6} + 1.3 CH \]

![Fig. 3](image1.png)

**Fig. 3:** Calculation procedure for the determination of the phase composition of the cement paste. $H_{\text{bond}}$...crystalline bonded water, $H_{\text{free}}$...free water in the paste

![Fig. 4](image2.png)

**Fig. 4:** Phase development of ettringite and $C_3A$ at 23 °C. Black lines are the smoothing result with a Fourier function.

![Fig. 5](image3.png)

**Fig. 5:** Measured heat flow for the hydration of white cement at 23 °C with w/c = 0.5. The initial period is additionally plotted on the right side.
The values for the phase evolution of the hydrate and the cement phases, respectively, show only low scatter (Fig. 4) with exception of minor phases like C₃A (cubic+orthorhombic) and anhydrite. Quantification of C₃A is difficult due to an overlapping of the main analytic reflections with α'-C₂S and determination of anhydrite content is complicated by a preferred orientation in (020) direction.

The cement hydration starts directly after adding water to cement. Within the first 30 minutes a part of C₃A and of the sulfate carrier (bassanite and anhydrite) is dissolved rapidly resulting in a strong increase in ettringite content. This very fast process leads to high heat flow during the initial period of hydration (Fig. 5). The content of ettringite increases within the first 0.5 h from 0 wt.-% up to 4 wt.-% depending on temperature.

Fig. 6: Phase content development for ettringite (A) and portlandite (B) at different temperatures. Curves are the average of two measurements.

The ettringite formation rate in the initial period decreases with increasing temperature due to the lower solubility of bassanite with increasing temperature. At 37 °C the formation of ettringite is slower than at 23 °C in the first 0.5 hours. But with ongoing hydration the formation of ettringite runs faster with increasing temperatures until the content reaches its maximum (Fig. 6-A). At 23 °C the ettringite content shows a stronger increase around 11 hours linked with second heat flow maximum in the main period of hydration. Anhydrite is dissolved in Phase I whereas the content of C₃A decreases very slowly (Fig. 7). After the anhydrite is nearly dissolved a stronger decrease in C₃A content is observed connected with an increase in ettringite content (Phase II). The determination of the point of complete dissolution of anhydrite is difficult due to the low phase content close to the quantification limit and the detection limit, respectively.
The silicate reaction is marked by the phase development of portlandite (Fig. 6-B). With increasing temperature the start of the portlandite formation occurs earlier. The C₃S content decreases after the start of the silicate reaction at the same time as portlandite increases.

Fig. 7: Interrelationship between the dissolution of anhydrite and C₃A, respectively, and the formation of ettringite. Curves are the average of two measurements.

CONCLUSION

The method of quantitative in-situ XRD analysis is a workable tool for a standard investigation of the early hydration of ordinary Portland cement. This method provides also the possibility for an investigation of the interaction between cement and organic additives.

REFERENCES