

In-situ XRD experiments under hydrothermal conditions

Relevant for: Hydrothermal reactions, autoclave aerated concrete, mineralogy, tobermorite formation

A newly developed autoclave chamber has been applied for use in in-situ X-ray diffraction studies in Bragg-Brentano geometry. Quartz dissolution and tobermorite formation are monitored under hydrothermal conditions on a conventional laboratory diffractometer.



1 Introduction

Until now in-situ X-ray diffraction measurements of hydrothermal reactions have only been possible in transmission geometry. Such transmission cells have been used at synchrotron beamlines to study the formation of tobermorite or other calcium silicate hydrates most frequently at saturated vapor temperatures of 463 K. The transmission cells have been made by modification of standard laboratory autoclaves.

As synchrotron beamtime is limited and such experiments can take up to 14 hours, an autoclave chamber was developed by Anton Paar GmbH to make in-situ monitoring of hydrothermal reactions in reflection geometry with conventional laboratory X-ray diffractometers possible.

2 Experimental

The test sample was prepared analogously to industrial autoclave aerated concrete (AAC) production with a water-to-solid ratio of 0.73 and 48.3% quartz (99.1% SiO₂; D50 23 μm), 38.1% ordinary Portland cement, 8.7% lime (93% CaO), 5.0% calcium fluoride (> 99%; sintered at 973 K for 3 h) and 0.1% aluminum powder. Calcium fluoride is only added as internal standard and usually not found in AAC. The slurry was transferred into the sample tray and covered with a thread-seal

tape, a polyethylene (PE) foil and a planar weight to obtain an even surface. The PE foil also prevented moisture loss from the sample. Analogously to AAC production, the added aluminum powder induces the release of hydrogen gas and the subsequent foaming gives a thickness of 3 – 5 mm. The viscosity increases rapidly and the sample is expected to set within 1 h. For further cement hydration, it was kept at 343 K for 7 h and afterwards at room temperature for 2 days prior to in-situ measurement.

The autoclave chamber of Anton Paar (Figure 1) consists of a stainless steel body, a thermal insulation and a Beryllium X-ray window protected by a Kapton foil. Saturated steam is supplied via an external boiler and enters via the stainless steel body, ensuring that a homogeneous temperature is maintained which is measured by a Pt100 temperature sensor located below the specimen. An analogue gauge with an accuracy of ±0.025 MPa was chosen to measure the pressure at the condensate outlet.

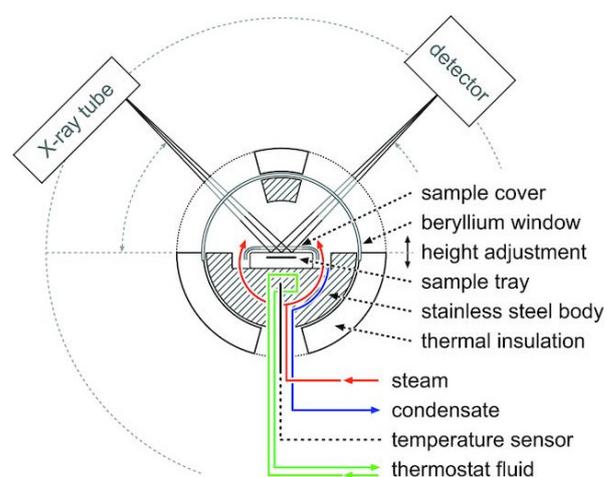


Figure 1: Schematic of the autoclave chamber.

Condensate can drain out of the system or reflux to the steam supply boiler. An external circulation thermostat is connected through separate tubing within the stainless steel body.

Measurements were performed on a standard laboratory diffractometer using a sealed-tube X-ray source (Cu 40 kV, 40 mA). The autoclave chamber was pre-heated (< 363 K) using the circulation thermostat after placing the sample in the chamber. After flushing the chamber with saturated water vapor, the vent was sealed (0 min) to allow pressure to build up. By steadily increasing the boiler and thermostat temperature, hydrothermal conditions at 466 K and 1.35 MPa were obtained (230 min). After a reaction period of 5.7 h, the steam supply boiler was switched off (570 min) and the system cooled down slowly.

In-situ monitoring was performed between 14.2° and $50.8^\circ 2\theta$. Control measurements under ambient conditions of the original and homogenized samples were performed afterwards.

3 Results and discussion

The comparison of the measured diffractograms (Figure 2) shows a decrease of the quartz 101 reflection intensity and an increase of the tobermorite 110 reflection intensity, while the fluorite 111 reflection serves as an internal standard.

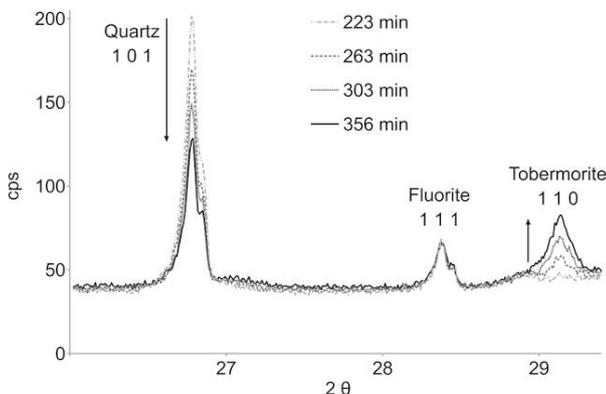


Figure 2: Diffractograms taken between 26° and $29.3^\circ 2\theta$, close to and after reaching constant hydrothermal conditions at 466 K and 1.35 MPa (> 230 min).

Below 443 K, the normalized intensities (Figure 3) show a proportional decrease of quartz and fluorite. The steam density inside the autoclave chamber changes from 0.59 kg m^{-3} at 373 K to 6.86 kg m^{-3} at 466 K and leads to an increase in X-ray absorption (1). Above 443 K, the quartz peak decreases much faster than the fluorite peak, this marks the beginning of hydrothermal dissolution. The tobermorite peak starts to increase > 443 K. Both the decrease of the quartz peak and the increase of the tobermorite peak can be approximated with a first-order reaction behavior (solid lines in Figure 3) after applying temperature corrections with $k = 7.8 \times 10^5 \text{ s}^{-1}$

for the quartz dissolution and $k = 6.1 \times 10^{-5} \text{ s}^{-1}$ for the tobermorite formation.

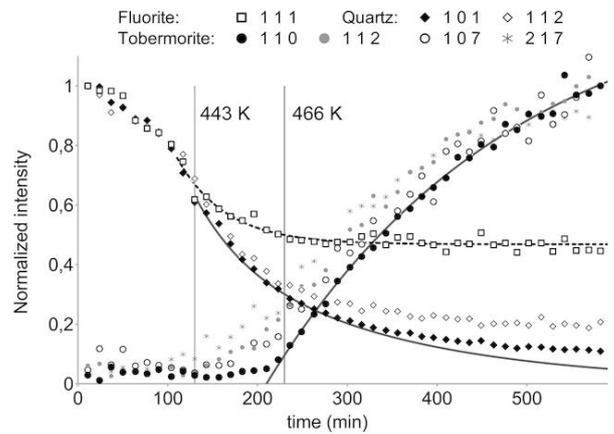


Figure 3: Normalized reflection intensities from 373 K to constant conditions at 466 K at 1.35 MPa. The approximation (solid line) is a combination of temperature correction (dashed line) and a first-order behavior.

As known from earlier studies, tobermorite formation occurs via poorly crystalline calcium silicate hydrates and is initially limited by the dissolution of quartz (2).

For interpretation of the reaction rates, surface sensitivity must be considered. Tobermorite seems to grow preferentially on the sample surface, which could be the reason for the slight decrease of the fluorite reflection intensity at 466 K (230 min) (see Figure 3 and Figure 4). After homogenization, the fluorite peak returns to its initial intensity, while the tobermorite peak shows a lower intensity. Homogenization also leads to an increase in the intensity of the quartz peak, which could be related to the initial gravitational settling of larger, less reactive quartz grains.

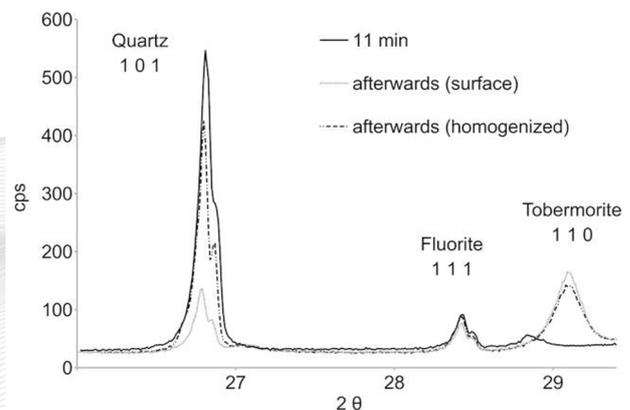


Figure 4: θ -corrected X-ray diffractograms before and after hydrothermal reaction.

4 Summary and conclusion

Despite certain limitations compared to a transmission setup, the reflection setup of the autoclave chamber used here is suitable for monitoring hydrothermal reactions in-situ. It can provide routine information for time-resolved phase quantification as well as additional spatial information on the nature of the hydrothermal reactions at interfaces due to the surface sensitivity of the reflection geometry. This could also be of interest for in-situ monitoring of other systems, provided a stable and even surface can be obtained which is necessary for measurements in Bragg-Brentano geometry.

5 References

1. Harvey, A. (1998). NIST Interagency/Internal Report No. 5078, pp. 5–7. National Institute of Standards and Technology, Gaithersburg, MD, USA.
2. Matsui, K., Kikuma, J., Tsunashima, M., Ishikawa, T., Matsuno, S., Ogawa, A. & Sato, M. (2011). *Cem. Concr. Res.* 41, 510–519.

6 Acknowledgement

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Contact Anton Paar GmbH

Tel: +43 316 257-0

support-xrd@anton-paar.com | www.anton-paar.com