

## Structural study of aqueous and amorphous precursors to crystallization

Beamtime: 22/11/2017-24/11/2017, 6 shifts (ES-608)

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### Objective and expected outcome:

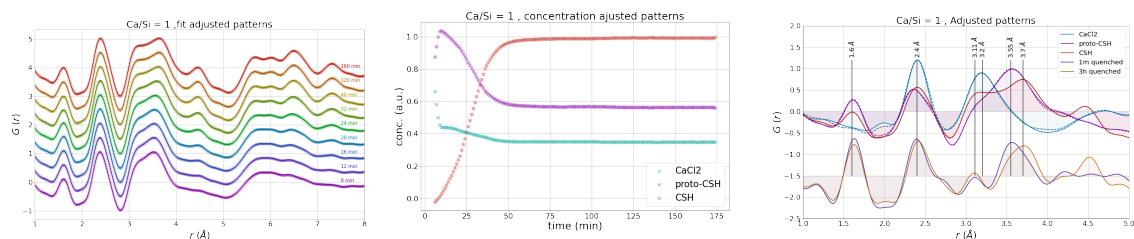
Aqueous precursor species and amorphous precipitates are important structural intermediates during the formation of ordered materials, such as biominerals, building materials or even protein crystals. To goal of this beamtime was to conduct in situ scattering experiments of crystallization from solution of different mineral systems to shed light onto the nature of the precursor phase of several common mineral phases and how the transition occurs to the final phase.

### Main results obtained from the beamtime:

We probed the initial stages of the precipitation pathway of  $\text{CaSO}_4$ ,  $\text{CaCO}_3$ ,  $\text{Ca}(\text{OH})_2$  and CSH, solid phases forming from solutions using a titration-based assay in which both relevant ions are added simultaneously generating slowly a solution supersaturated with respect to portlandite. This setup has the advantage that the experiment starts from a clear solution (no initial scattering signal) and the  $\text{Ca}^{2+}$  concentration, conductivity and turbidity was monitored for the entire duration of the experiment. The solution in the reaction vessel was continuously circulated by a peristaltic pump through a kapton capillary aligned with the X-ray beam to monitor the formation of the emerging particles. High-energy X-ray scattering ( $E \sim 55 \text{ keV}$ ) and a large angle 2D detector (CdTe Pilatus), covering a large Q-range ( $1\text{-}30 \text{ \AA}^{-1}$ ), were used. The collected time-resolved scattering patterns were used (after proper background subtraction) for pair distribution function analysis and allowed us to probe the structural changes of the pre-and post nucleation particles. For all mineral systems useful data were obtained, except for  $\text{CaCO}_3$ , where the obtained scattering intensity was too low for further meaningful analysis. Detailed analysis of time-resolved HEXS patterns using pair distribution function analysis has provided a wealth of data on the precursor phase of the  $\text{CaSO}_4$  mineral system in the presence of additives. This will be topic of forthcoming publication. Below a short overview of the main (preliminary) results obtained for the other two mineral systems are presented:

### Calcium-Silicate-Hydrate

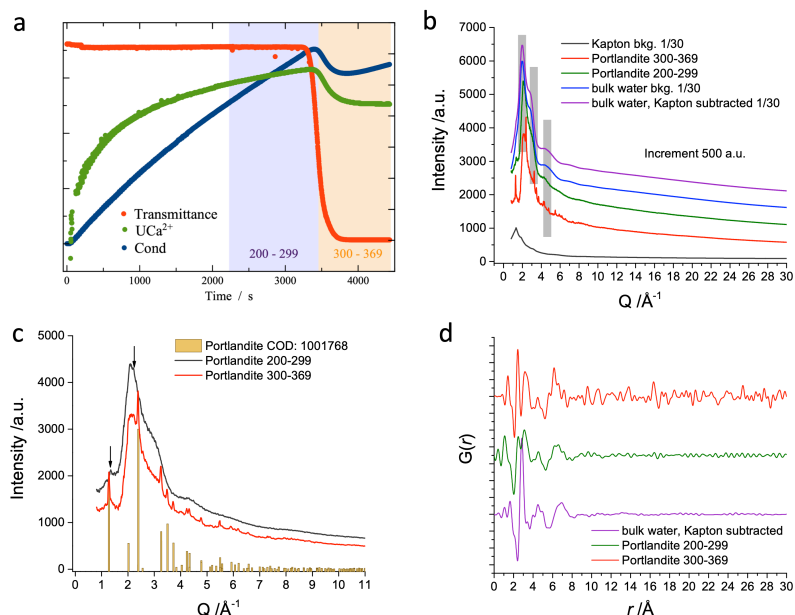
We tested two different initial Ca/Si ratios (i.e. 1 and 3), both leading to meaningful data. For example in the case of  $\text{Ca/Si} = 1$  we could monitor the evolution from dissolved ions to the formation of the precursor phase (proto-CSH) and transformation to the final CSH, as shown in the figures below. The obtained results were also compared to PDF analysis of scattering data from solid samples (i.e. ex-situ) quenched at different reaction times.



Please note that the concentration profiles are taken over patterns with a moving average of 15 frames and the first 4 frames still involve addition of  $\text{Na}_2\text{SiO}_3$  and  $\text{NaOH}$ , i.e. 1 min waiting time, 2 min titration/addition and some delay due to circulation. Thus,  $\text{CaCl}_2$  rapidly decreased in the first few frames due to dilution, while proto-CSH increased. After 4 frames  $\text{CaCl}_2$  leveled off but continued to decrease, proto-CSH decreases and CSH increases.

## Portlandite

Also the precipitation of  $\text{Ca}(\text{OH})_2$  was studied for the first using in situ scattering. The figure below summarize the obtained insight. These data, together with more detailed potentiometric titration data, in situ SAXS, ex situ TEM and TGA characterization will be presented into a upcoming publication on the multistep precipitation pathway of this mineral phase.



In situ monitoring of portlandite formation using potentiometric titration and high-energy x-ray scattering (a)  $\text{Ca}^{2+}$ -potential, conductivity and transmittance signals recorded simultaneously during the slow (0.1ml/min) co-titration of 1M NaOH and 0.5 M  $\text{CaCl}_2$  into 50 ml of deionized water. (b) Background subtracted averaged diffraction patterns of the precursor (purple shaded area) and final (orange shaded area) phase collected during the co-titration experiment shown in (a). For comparison the diffraction patterns of bulk water, Kapton capillary, and bulk water corrected for the capillary are also shown. The intensities of these three background patterns are scaled down by a factor of 30, so that the intensities are comparable with the water-subtracted precursor and final phase patterns. An offset of 500 a.u. was introduced to improve the clarity. (c) Background corrected average diffraction patterns of precursor and final phase compared to the reference diffraction pattern of portlandite. (d) Converted diffractograms shown in (b) into real-space pair distribution functions. For comparison also the converted diffraction pattern of bulk water is included.

### Comments, and outlook about the use of beam time:

The obtained experimental data are extremely valuable and have paved the way to achieve a more complete mechanistic understanding of  $\text{Ca}(\text{OH})_2$ , CSH and  $\text{CaSO}_4$  precipitation. Data analysis will be continued and subsequent publications will be submitted to present our findings. The next step is now to employ the experience gained from this combined high energy scattering and potentiometric setup measuring strategy to tackle additive controlled crystallization of industrial relevant materials such as  $\text{Ca}(\text{OH})_2$  and CSH.

**Noteworthy is also the truly excellent operation of the beamline and the great assistance received from the local contact.**