



Experiment title:
Nanostructural characterization of additive controlled crystallization

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MA-5000

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Report:

To investigate the nanostructural evolution of additive controlled crystallization of calcium carbonate (CaCO_3) and portlandite ($\text{Ca}(\text{OH})_2$), we utilized a titration set-up (Figure 1). This set-up included co-titration of two stock solutions, which allowed for a gradual build-up of the supersaturation with respect to the selected mineral and finally, nucleation. By constantly

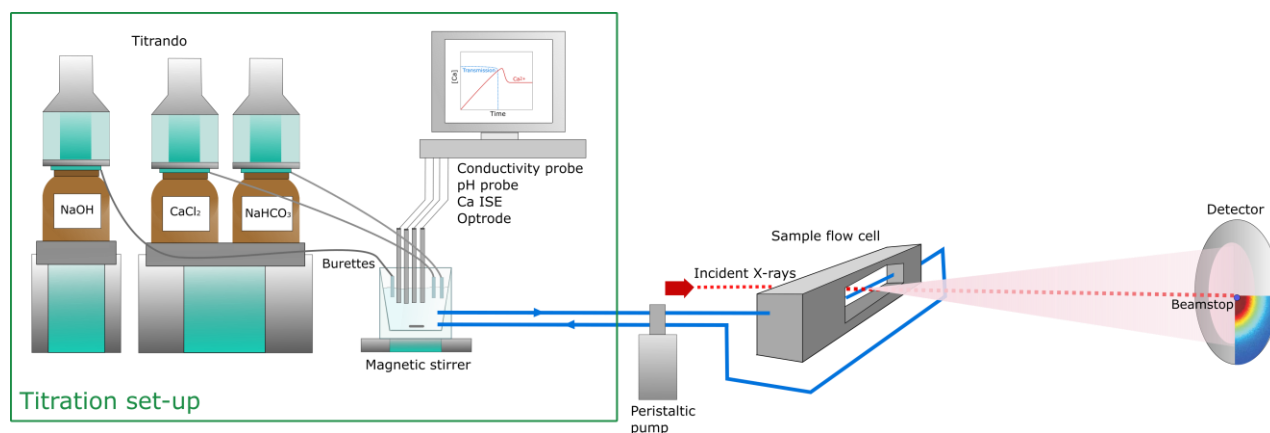


Figure 1. The experimental set-up included co-titration of two stock solutions (CaCl_2 and NaHCO_3 in the case of CaCO_3) into 50 mL deionized water containing an additive. In this example for CaCO_3 , NaOH was added to ensure a constant pH. The macroscale properties of the solution were measured by several probes. The solution was constantly circulated through a capillary, allowing for in situ X-ray measurements.

circulating the solution through a Kapton capillary aligned with the X-ray beam, we could track the process *in situ*. In addition to measuring nanoscale properties by the X-rays, we utilized several probes to measure the macroscale properties of the solution, such as transmittance (measured by an optrode).

Our PDF analysis of the portlandite ($\text{Ca}(\text{OH})_2$) system implies that different types of additives act distinctly on the portlandite nucleation process. In particular, the transmittance of the solution decreased in one step for the pure experiment and the experiment with the first type of additive, sodium gluconate (used among others in the cement industry). But, for a second type of additive, trisodium trimetaphosphate

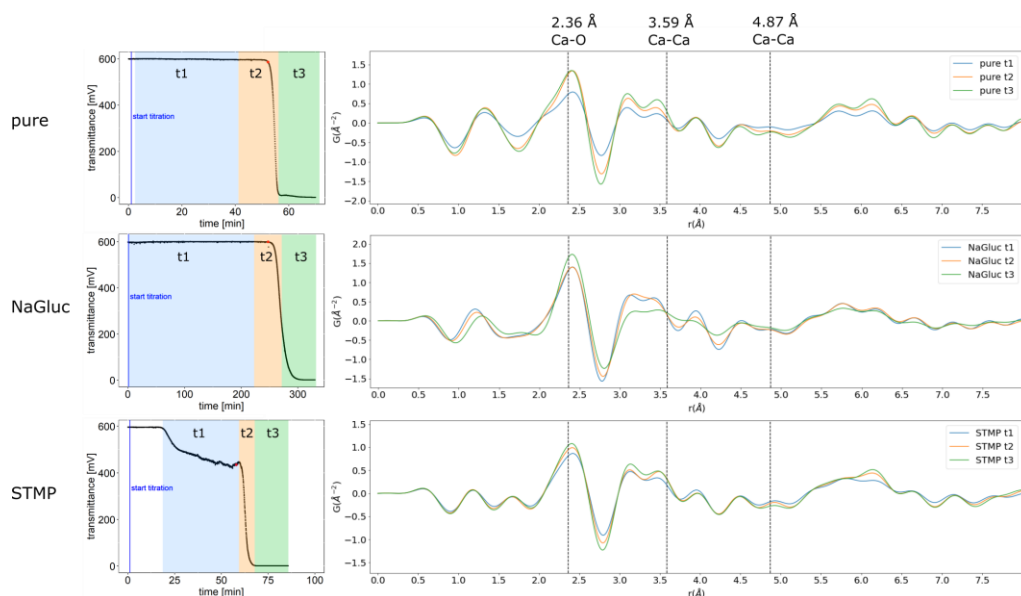


Figure 2. Comparison of PDF patterns and transmittance profiles resulting from *in situ* titration experiments in which portlandite nucleated from solution, either pure or in the presence of an additive: 50 ppm sodium gluconate (NaGluc) or 10000 ppm trisodium trimetaphosphate (STMP).

(STMP, used to control the setting time of cements), a characteristic two-step decrease was observed (Figure 2). Importantly, the PDF patterns imply different structures of the particles forming during the early stage of the crystallization process; for example, portlandite forming in additive-free solutions shows two inter-atomic correlations around 3.2 Å, whereas the experiments with additives show one broad peak, which shifts to higher interatomic distances with time in the case of sodium gluconate (Figure 2). Additionally, the amount of Ca-O interatomic distances (at 2.36 Å in pure portlandite) detected in the sample develops differently. This difference in behavior suggest different interactions of the additives with the mineral component.

PDF calculations of the CaCO_3 nucleation experiments showed that the signal is too weak to distinguish it from both statistical and detector noise. Hence, we reached the limit of the PDF method to elucidate structural characteristics during the formation of CaCO_3 . We currently developed a new method to study the nucleation of CaCO_3 in aqueous environments by simultaneously measuring a water reference sample, which is used to track noise changes with time. This method showed promising results in test measurements and therefore, we pursue to elucidate the nanostructural evolution of additive controlled crystallization of CaCO_3 .