



Experiment title:
Time-resolved SAXS/WAXS study of the formation and transformation of colloidal calcium carbonate under the influence of polymer additives

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Report:

This experiment was a continuation of the experiments about time-resolved SAXS-studies of the formation of calcium carbonate where we found out that the precursors of the crystalline modifications of calcium carbonate are colloidal amorphous particles (SC 786, results published in [1]), and a second study (SC1147, results published in [2]) where TRSAXS/WAXS studies were conducted in combination with the stopped flow device to investigate the formation and growth of calcium carbonate without and in the presence of polypeptide where we confirmed our previous findings concerning the amorphous character of the initially formed colloidal particles.

In this experiment, we studied the influence of polymeric additives on the nucleation and the growth of the primary particles and the resulting minerals at higher times. We compared three different polymers: A double-hydrophilic block-copolymer additive produced by the Group of H. Coelfen (MPI Potsdam), poly (aspartic acid) and Sokolan, a polymer with side chains based on poly(ethylene oxid). The last two polymers has been supported to us from BASF, Germany.

The polymer of the group of H. Coelfen shows an interesting effect: the primary particles remain unchanged, e.g. at starting frame ($t=0.005$ sec) the scattering intensity of the pure calcium carbonate and the one with added polymer are identical (see fig.1). At higher times the overall scattering intensity goes down, but the increase at small scattering vectors is steepening with time (fig.1).

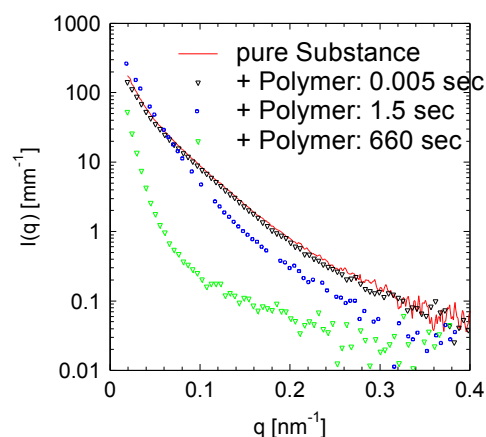


fig. 1: comparison of calcium carbonate as a function of time with and without added polymer

This shows the starting sedimentation and the aggregation of the primary particles with time. It has to be remarked that the sedimentation is much slower and the aggregation is reduced compared to the pure calcium carbonate. Wide angle X-ray diffraction (see fig.2) shows that a crystalline material is build up after several seconds similar to pure calcium carbonate. But with polymer, this sediment is extremely loose which can be seen by the point that the powder scattering is already seen at 0.4 mm down from the middle of the capillary. With only calcium carbonate, the powder scattering from the sediment could only be seen when going down to 0.65 mm from the middle (e.g. 0.05 mm about the bottom) of the capillary.

The double-hydrophilic block-copolymer therefore shows two effects: no change of the primary particles, neither in time nor in size or polydispersity, but a strong effect at higher times: aggregation number is reduced and the sedimentation is slowed down. It results in a very loose aggregate consisting of small crystalline particles connected by the polymeric additive. Results about this polymer are published in [3].

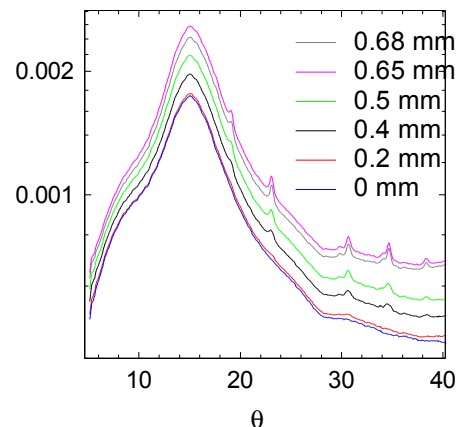


fig. 2: WAXD signal as a function of height (numbers means down from the middle) in the capillary

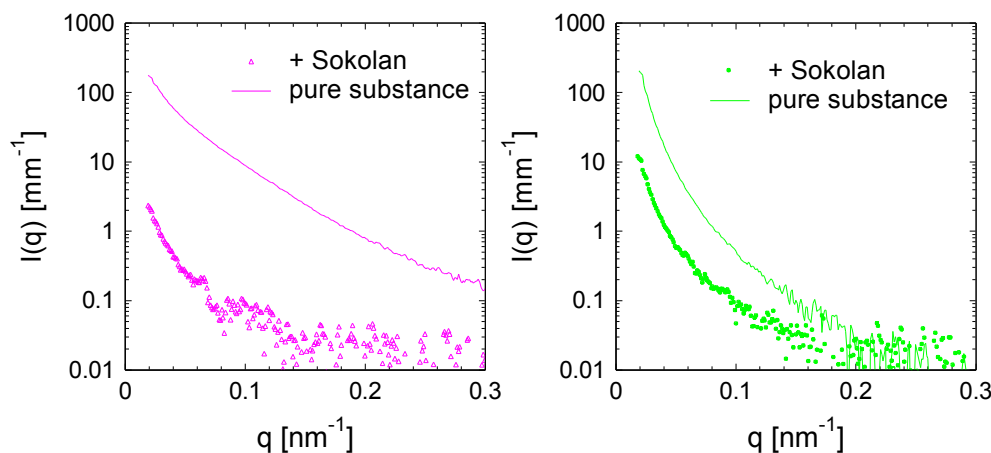


fig.3: scattering of calcium carbonate with (points) and without added polymer Sokolan (lines). Left side: starting curves (0.01 sec); right side: long time (10 min).

Fig. 3 demonstrate that the second polymer behaves completely different: The nucleation and the growth of the primary particle are retarded remarkably. Over all time scales under examination (< 10min) here the scattering intensity stays always lower than that of the pure substance. The last polymer, poly(aspartic acid), behaves similar to Sokolan, only the sedimentation is slowed down even more. With both polymers as additives we could see no sign of any crystalline material, the scattering was amorphous over all times and positions inside the capillary. This behaviour could be explained by smaller calcium carbonate particles with polymer enclosed in the particles preventing any crystallisation. Here it would be important to elongate the time scale to see if crystallisation is really prevented or only delayed.

The results demonstrate that these polymers could be divided into two groups: the first one does not affect the primary particles formed, but influences their growth and aggregation, the other polymers slow down the particle formation and influence the crystallinity of the resulting mineral.

Publications:

1. J. Bolze, B. Peng, N. Dingenouts, P. Panine, T. Narayanan, M. Ballauff, *Formation and growth of amorphous colloidal CaCO₃ precursor particles as detected by time-resolved SAXS*, Langmuir 2002, **18**, 8364.
2. D. Pontoni, J. Bolze, N. Dingenouts, T. Narayanan, M. Ballauff; *Crystallization of calcium carbonate observed in-situby combined small- and wide-angle X-ray scattering*, J. Phys. Chem. B. 2003, **107**, 5133.
3. J. Bolze, D. Pontoni, M. Ballauff, T. Narayanan, H. Cölfen, *Time-Resolved SAXS-Study on the Effect of a Double Hydrophilic Block-Copolymer on the Formation of CaCO₃...*, J. Colloid Interf. Sci. 2004, **277**, 84.