

# Supplementary information for: Evidence of an amorphous intermediate phase during non-classical calcium hydroxide crystallization from cementitious pore solutions

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## S1 OPC analysis

### S1.1 Determination of the quantitative phase content

PXRD measurements were performed on a *Bruker* D8 ADVANCE diffractometer with a  $\theta - \theta$  configuration, a Lynxeye XET detector, and Cu-K $_{\alpha}$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ). Scans were collected from  $7^{\circ}$  to  $71^{\circ} 2\theta$  with a step size of  $0.02^{\circ}$  and a measurement time of 0.25 s per step. Samples were prepared by back-loading, micromilling the cement powder in isopropanol for 10 min, followed by vacuum drying. The mineralogical composition of the cement was determined by Rietveld refinement of the PXRD data using TOPAS-Academic V7 (*Coelho Software*, Brisbane, Australia) [1]. The ICSD codes for the reference phases used in the refinement are listed in Table S1. Previous studies have shown that vacuum drying micromilled cement can partially dehydrate gypsum to bassanite, which may not fully represent the original state of the anhydrous cement [2]. Additionally, quantitative Rietveld refinement has an inherent uncertainty of at least  $\pm 1 \text{ wt\%}$ , limiting sensitivity to minor phases, such as residual gypsum.

**Table S1:** ICSD codes for the phases used in the Rietveld refinement.

| Mineral                       | ICSD-Code | Reference |
|-------------------------------|-----------|-----------|
| Alite                         | 64 759    | [3]       |
| Belite                        | 81 096    | [4]       |
| C <sub>3</sub> A cubic        | 1841      | [5]       |
| C <sub>3</sub> A orthorhombic | 1880      | [6]       |
| C <sub>4</sub> AF             | 9197      | [7]       |
| Anhydrite                     | 15 876    | [8]       |
| Calcite                       | 73 446    | [9]       |
| Periclase                     | 9863      | [10]      |
| Portlandite                   | 202 220   | [11]      |
| Syngenite                     | 157 072   | [12]      |
| Arcanite                      | 79 777    | [13]      |
| Bassanite                     | 79 529    | [14]      |
| Aphthitalite                  | 26 014    | [15]      |
| Dolomite                      | 66 333    | [16]      |
| Quartz                        | 174       | [17]      |
| Lime                          | 75 786    | [18]      |
| Gypsum                        | 409 581   | [19]      |

## S1.2 Determination of the chemical composition

1.00 g of the OPC was heated in a muffle furnace at 1000 °C for 1 h to determine the loss on ignition, which was calculated from the mass difference. Next, 0.20 g of the uncalcined OPC was transferred to a digestion cell. To this sample, a mixture of 65% nitric acid, 40% hydrofluoric acid, and 30% hydrogen peroxide was added. This solution was subjected to microwave digestion using the HF method. In this method, the solution was heated to 200 °C over 30 min, maintained at 200 °C for 20 min, and then cooled to 60 °C.

Following the first digestion, the solution was allowed to cool to room temperature, after which boric acid was added for the second digestion, known as the  $\text{H}_3\text{BO}_3$  method. In this step, the solution was heated to 170 °C within 30 min, held at that temperature for 20 min, and then cooled to 60 °C. After the second digestion, the solution was once again cooled to room temperature and transferred to a 250 mL volumetric flask. The flask was filled with water up to the calibration mark. Depending on the amount of 40% hydrofluoric acid used, the solution was then diluted 1:10 or 1:20 with water and acidified with 65% nitric acid.

ICP-OES analysis was performed on a *PerkinElmer* Avio to determine elemental concentrations. The data from the ICP-OES measurement, along with the results from the ignition loss determination, collectively approached nearly 100%. ICP-OES analysis of OPC is reliable and produces results comparable to those obtained from X-ray fluorescence (XRF) analysis for determining the chemical composition of cement [20].

## S2 TEM data

### S2.1 TEM sample preparation methods

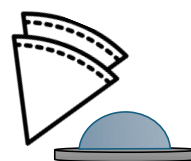
#### 1) Drop casting

Dropping one droplet of the pore solution (10  $\mu\text{L}$ ) onto the TEM grid lying on a filter paper immediately after separation (within a minute). TEM-Grid was air-dried overnight on a filter paper.



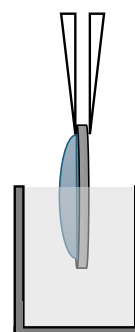
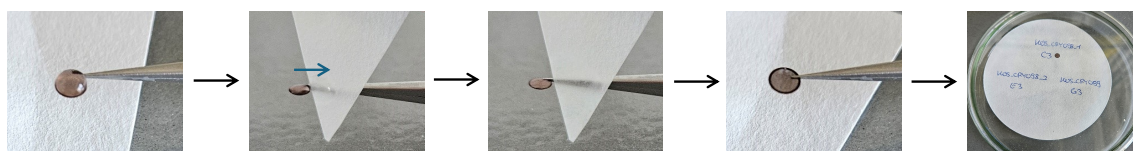
#### 2) Blotting

Careful application of one droplet of the pore solution (10  $\mu\text{L}$ ) on the TEM grid immediately after separation (within a minute), waiting for 60 seconds, then removal of the remaining solvent using filter paper. TEM-Grid was air-dried overnight on a filter paper.



#### 3) EtOH Quenching

EtOH was added to the pore solution in a ratio of 1 to 10 immediately after separation (within a minute). The TEM grid was then prepared using this solution in the same way as for blotting.

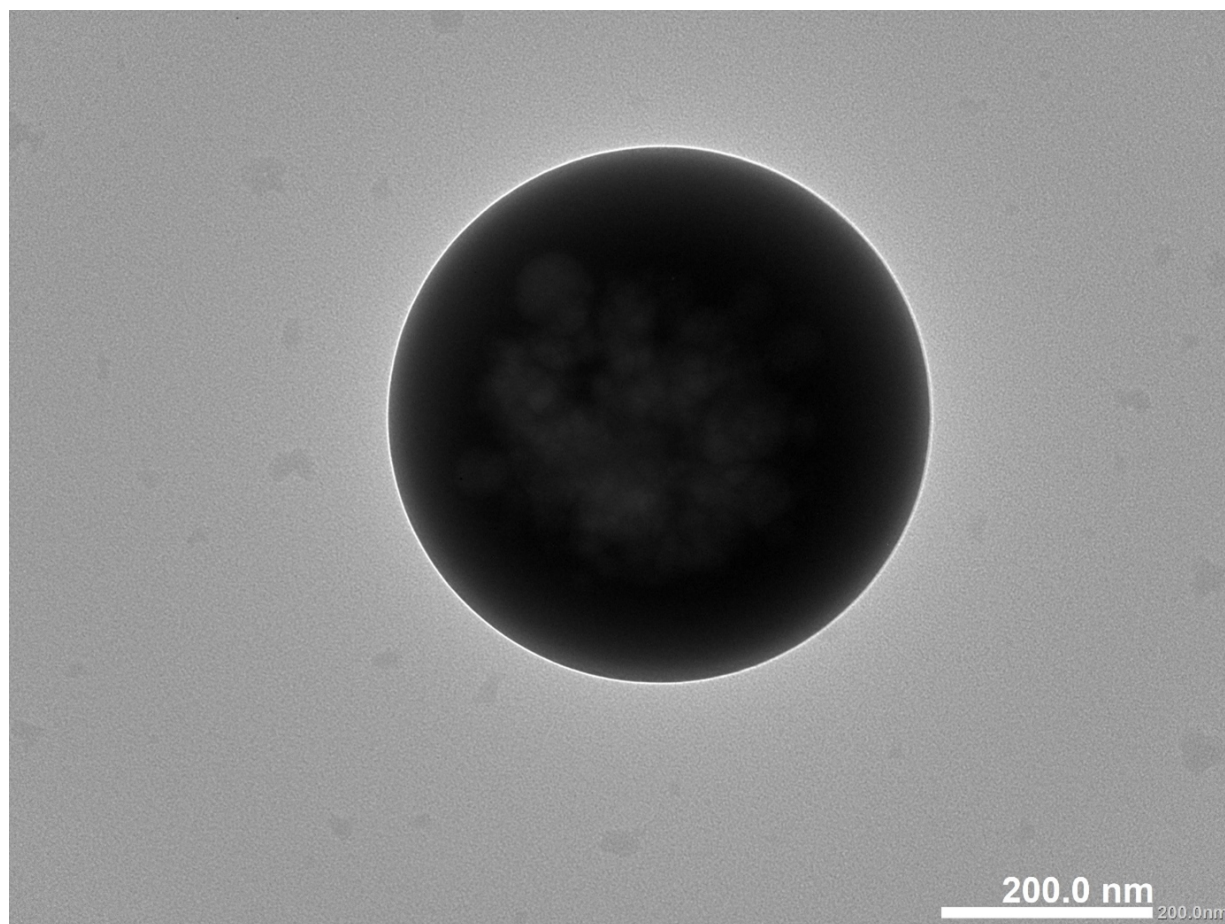


#### 4) Cryo-TEM preparation

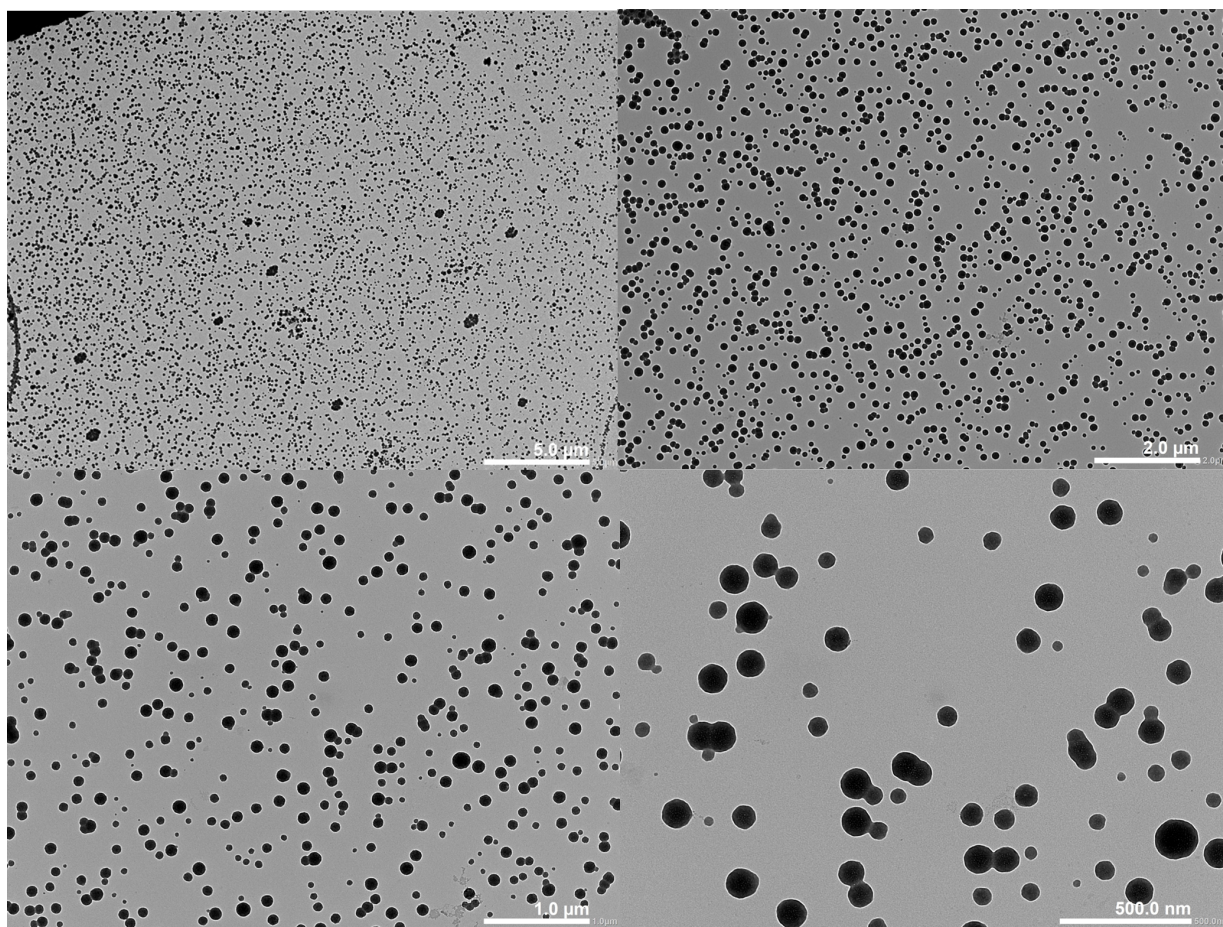
Glow-discharging the TEM grid to make the carbon film hydrophilic. Vitrification using an automated Vitrobot system under controlled conditions. Application of 5  $\mu\text{L}$  to the grid, then blotting away excess liquid to create a thin aqueous layer. Plunge freezing into liquid ethane/propane to create a thin, non-crystalline ice layer. Storage in liquid nitrogen until TEM examination.

**Figure S1: TEM sample preparation methods.** TEM samples were prepared by four different standard methods: 1) Drop-casting of one drop (10  $\mu\text{L}$ ) of the pore solution onto a TEM grid, 2) carefully placing one drop (10  $\mu\text{L}$ ) of the pore solution onto a TEM grid and then blotting away the excess liquid from the side using a filter paper, 3) chemical quenching of the pore solution with ethanol in a ratio of 1:10 before blotting 10  $\mu\text{L}$  of the suspension onto the TEM grid, 4) vitrification of the pore solution (5  $\mu\text{L}$ ) into a thin layer of amorphous ice to enable imaging in its native state.

## S2.2 ACH formed during drying of cementitious pore solution

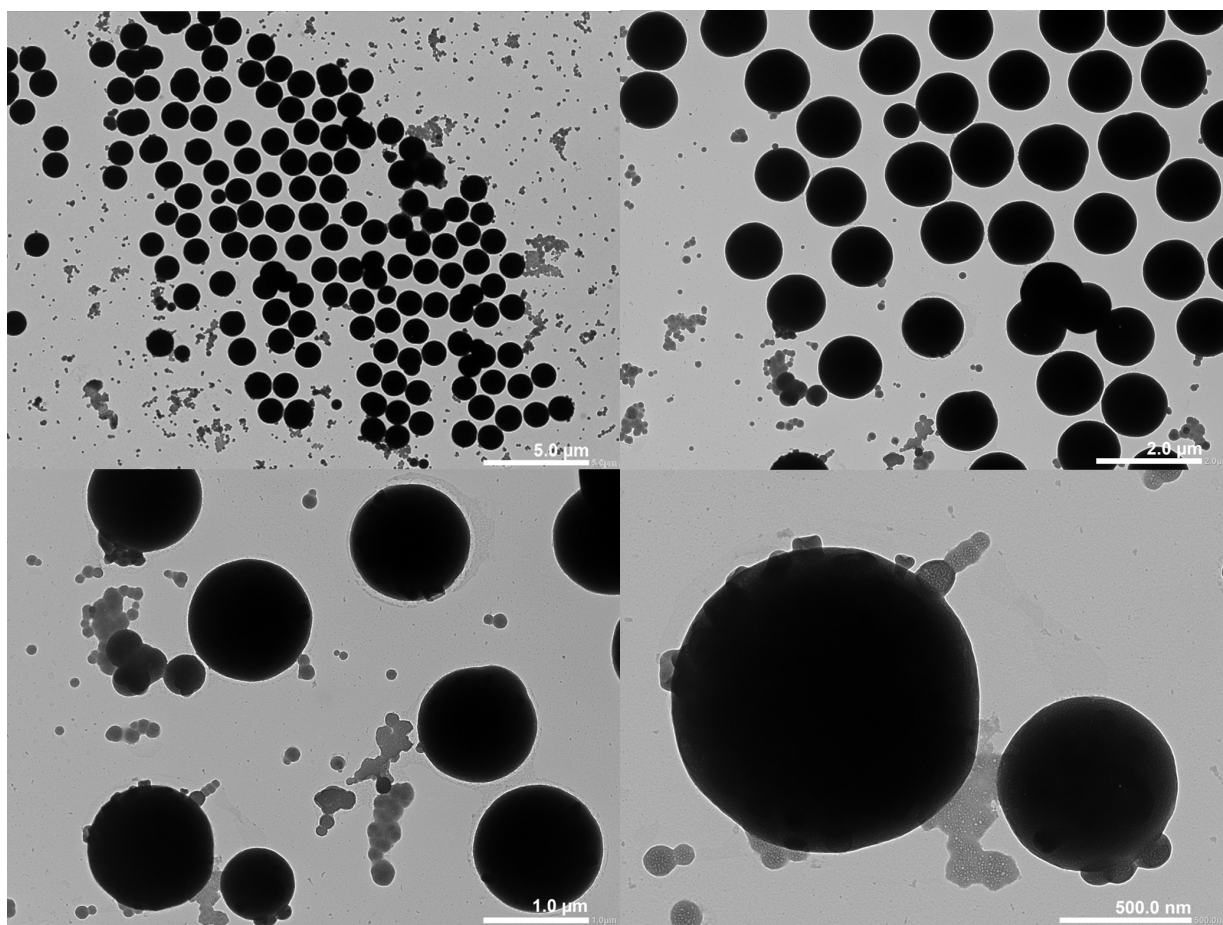


**Figure S2:** The electron micrograph was taken on a *JEOL JEM-1400plus* of dried cementitious pore solution, separated by dead-end filtration 15 min after the hydration started. Amorphous species, which occur in the form of perfect spheres, can be detected in electron microscope images when a cementitious pore solution is dried on a TEM grid. Additional imaged areas of the same sample are shown in Figure S3 and S4.



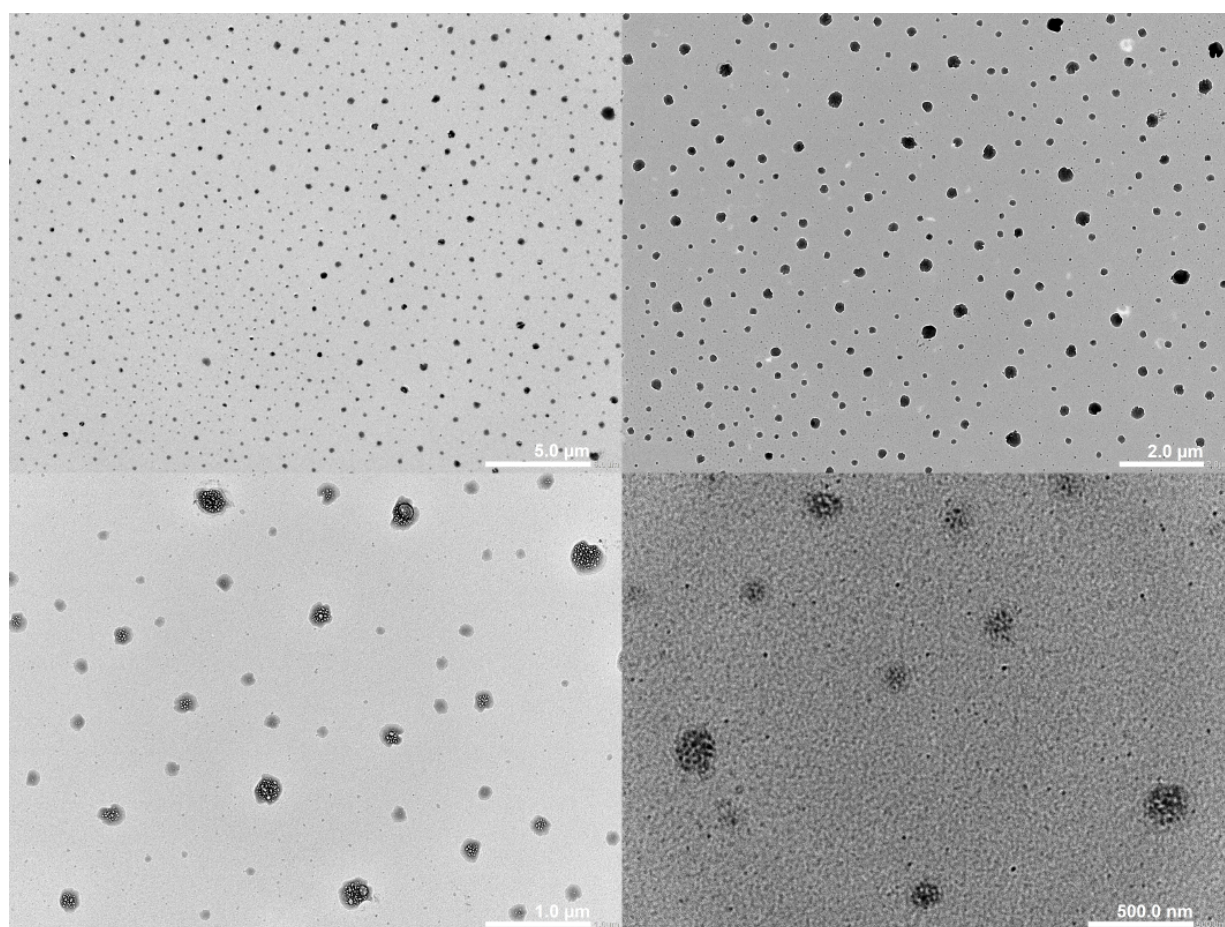
**Figure S3:** Electron micrographs taken on a *JEOL JEM-1400plus* of dried cementitious pore solution, separated by dead-end filtration 15 min after the hydration started. The spherical amorphous particles are evenly distributed on the carbon film and vary in size, ranging from 50 to 200 nm. Additional imaged areas of the same sample are shown in Figure S2 and S4.





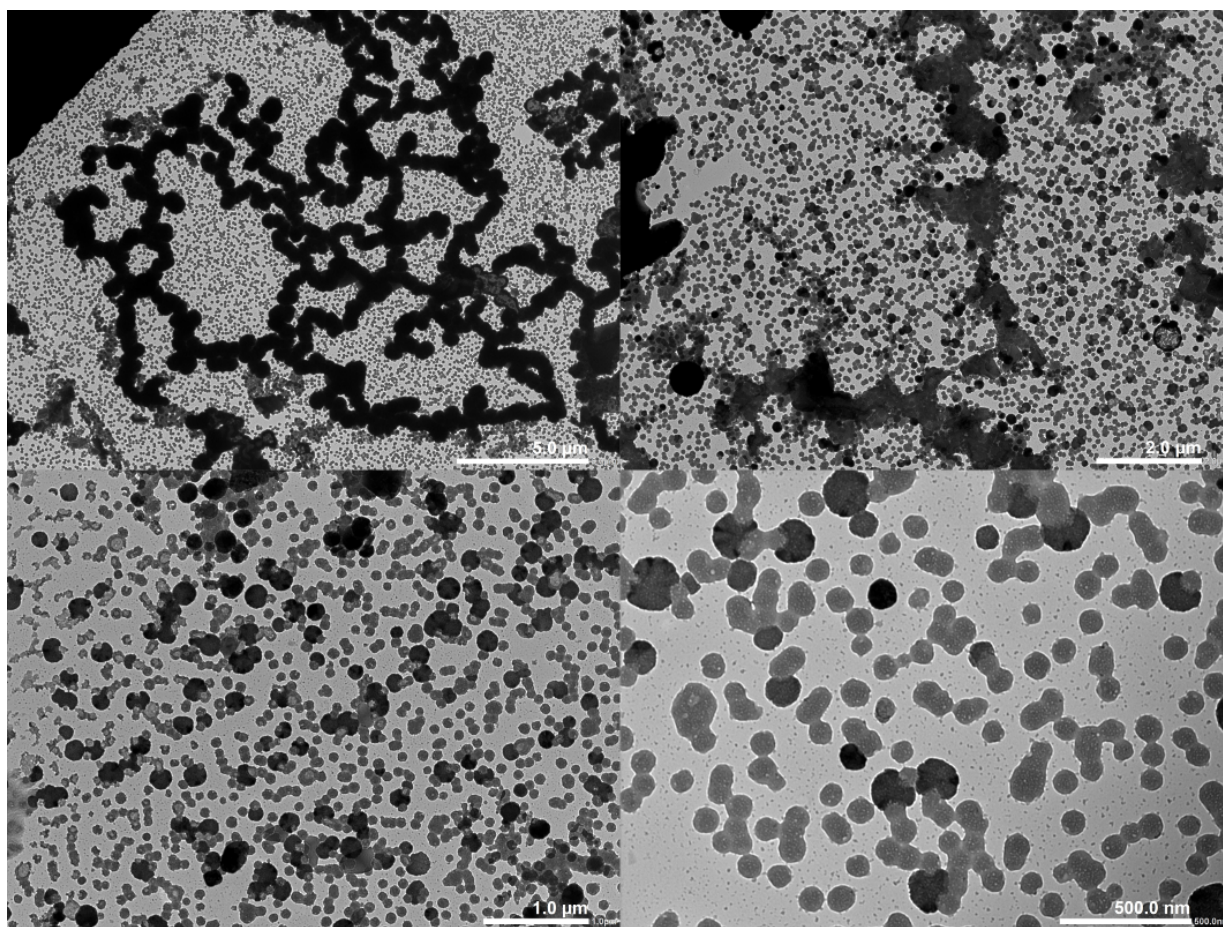
**Figure S4:** Electron micrographs taken on a *JEOL JEM-1400plus* of dried cementitious pore solution, separated by dead-end filtration 15 min after the hydration started. The spherical amorphous particles vary in size and can grow to a diameter of 1  $\mu\text{m}$ . Additional imaged areas of the same sample are shown in Figure S2 and S3.

### S2.3 Pore solution separation methods



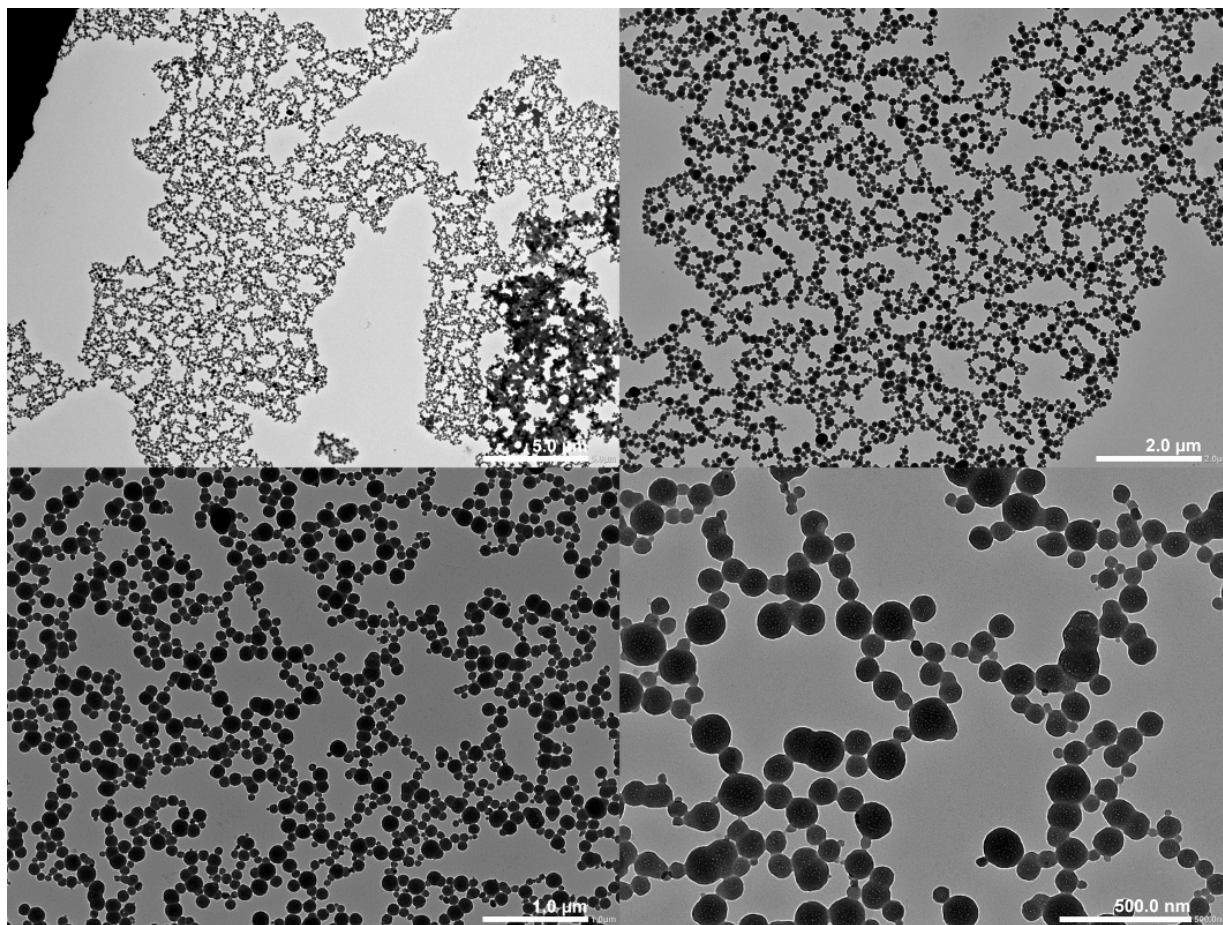
**Figure S5:** Electron micrographs taken on a *JEOL JEM-1400plus* of cementitious pore solution, separated by **dead-end filtration using a PES 0.22 μm membrane filter** 15 min after the hydration started. The TEM grid was prepared by the blotting method. The ACH particles are spherical, finely distributed, and vary in size. They appear to consist of associations of smaller primary particles.



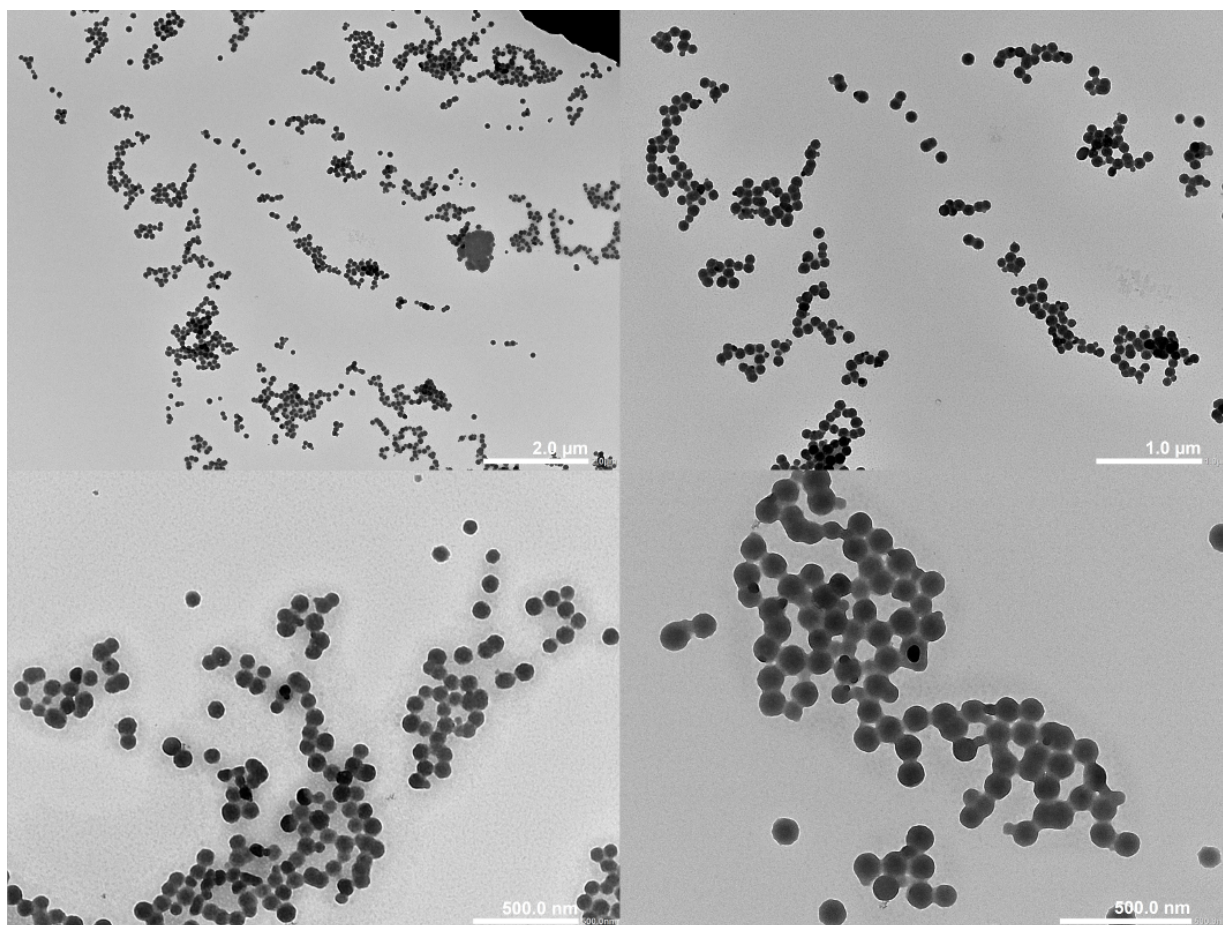


**Figure S6:** Electron micrographs taken on a *JEOL JEM-1400plus* of cementitious pore solution, separated by **dead-end filtration using a PES 0.45 μm membrane filter** 15 min after the hydration started. The TEM grid was prepared by the blotting method. Along with the numerous spherical ACH particles, huge agglomerates also cover the grid.





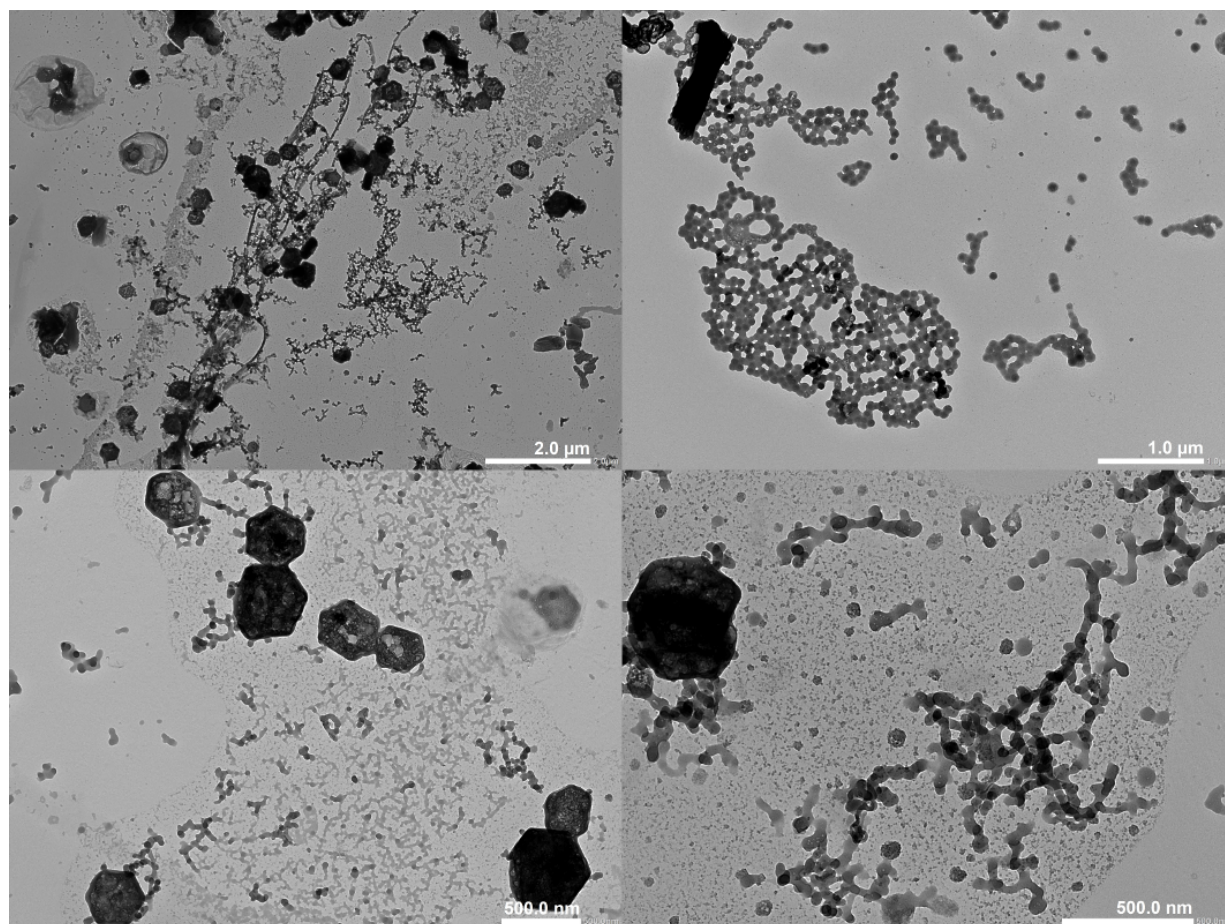
**Figure S7:** Electron micrographs taken on a *JEOL JEM-1400plus* of cementitious pore solution, separated by **continuous cross-flow filtration** 15 min after the hydration started. The TEM grid was prepared by the blotting method. Aggregates of differently sized spherical ACH particles arranged in layers were observed.



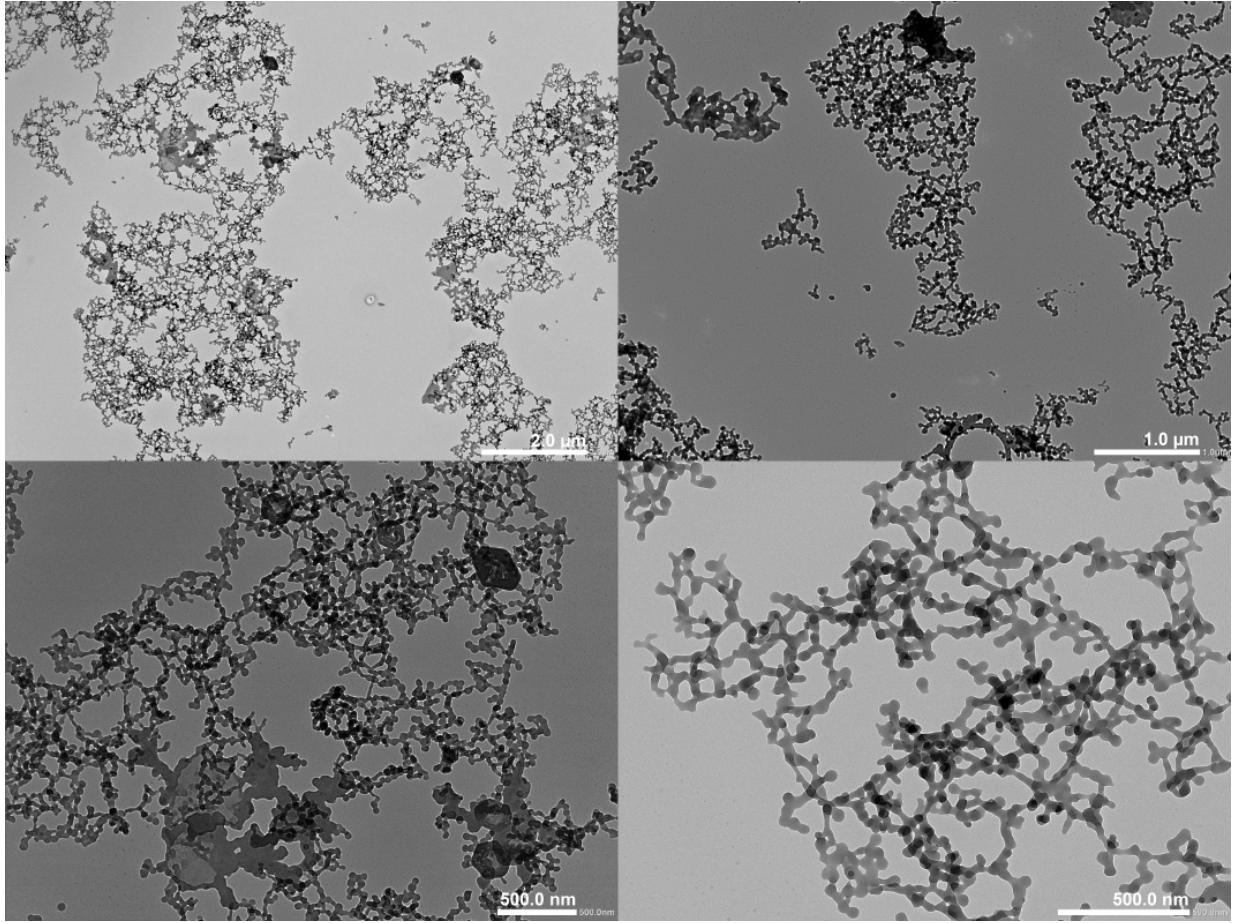
**Figure S8:** Electron micrographs taken on a *JEOL JEM-1400plus* of cementitious pore solution, separated by **centrifugation** 15 min after the hydration started. The TEM grid was prepared by the blotting method. Smaller aggregates of uniformly sized spherical ACH particles were found.



## S2.4 ACH obtained from other systems

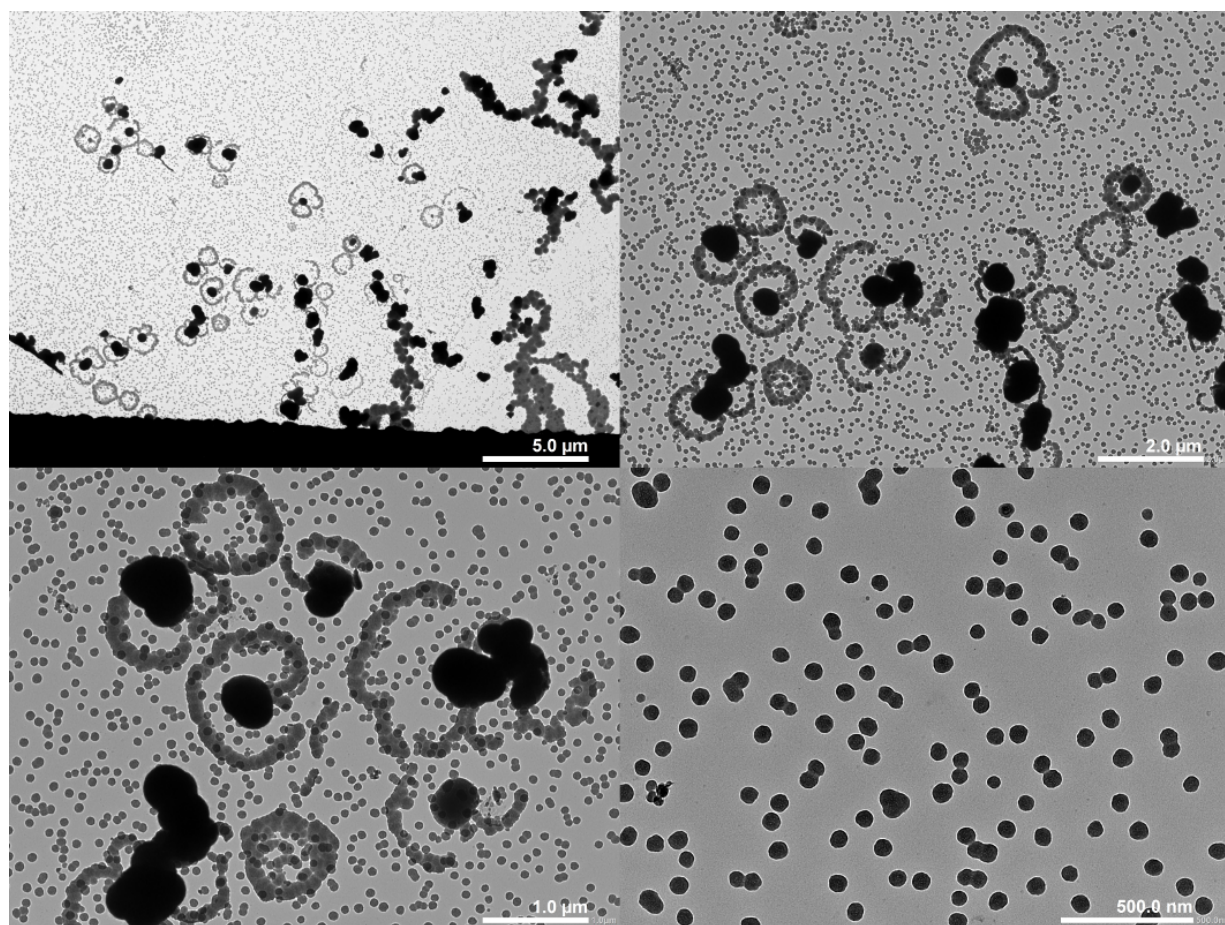


**Figure S9:** Electron micrographs taken on a *JEOL JEM-1400plus* of cementitious pore solution, separated by centrifugation 15 min after the hydration started. The TEM grid was prepared by the blotting method, and the cement was mixed with a **w/c ratio of 0.5**. Aggregates of the spherical ACH particles are found alongside hexagonal structures.

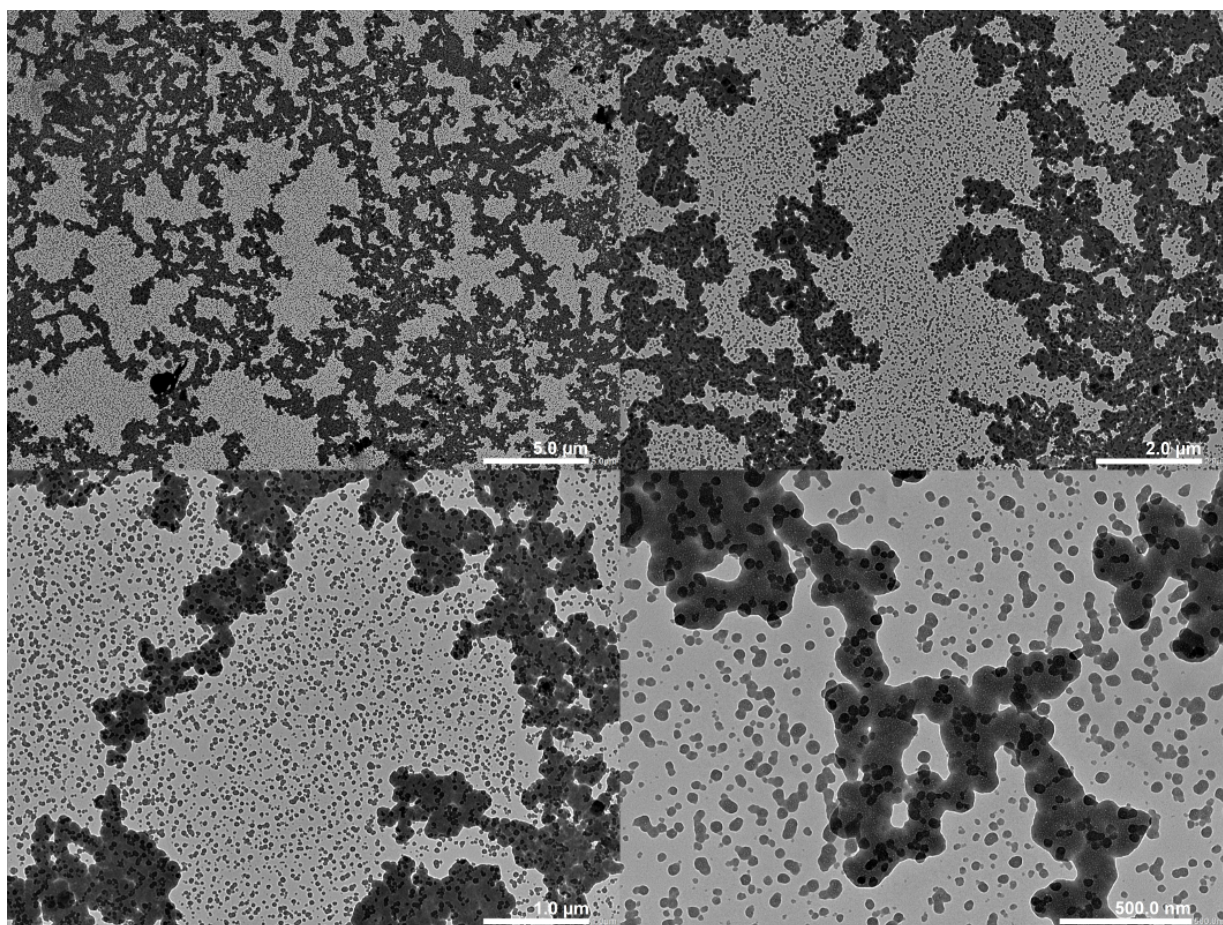


**Figure S10:** Electron micrographs taken on a *JEOL JEM-1400plus* of cementitious pore solution, separated by centrifugation 15 min after the hydration started. The TEM grid was prepared by the blotting method, and the cement was mixed with a **w/c ratio of 0.75**. Aggregates of the spherical ACH particles are found alongside hexagonal structures.



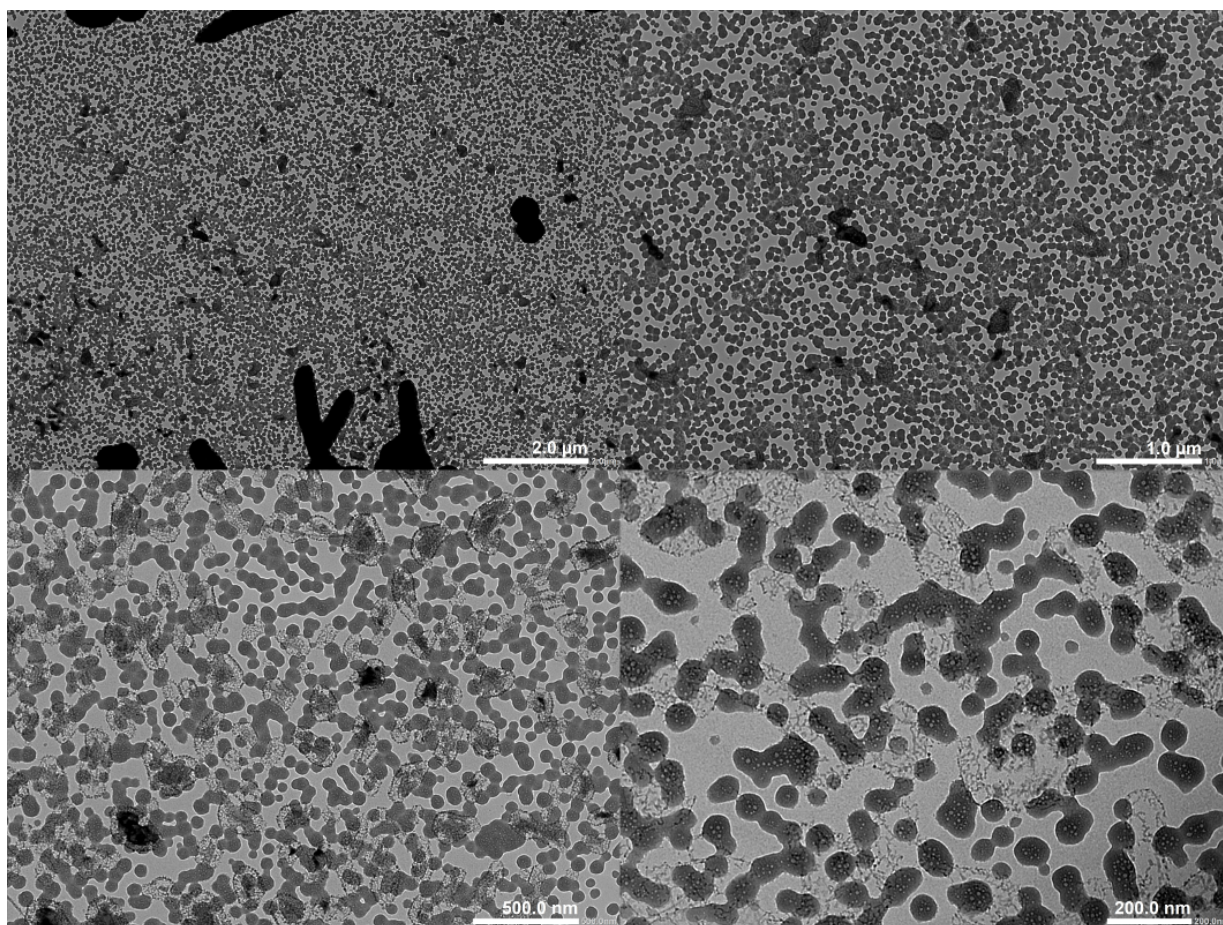


**Figure S11:** Electron micrographs taken on a *JEOL JEM-1400plus* of a **supersaturated CH solution prepared by dissolving 140 mg (2.5 mmol) CaO in 100 mL water**. The TEM grid was prepared by the blotting method. Alongside the evenly distributed spherical ACH particles, larger particles and open ring-shaped structures were also observed.

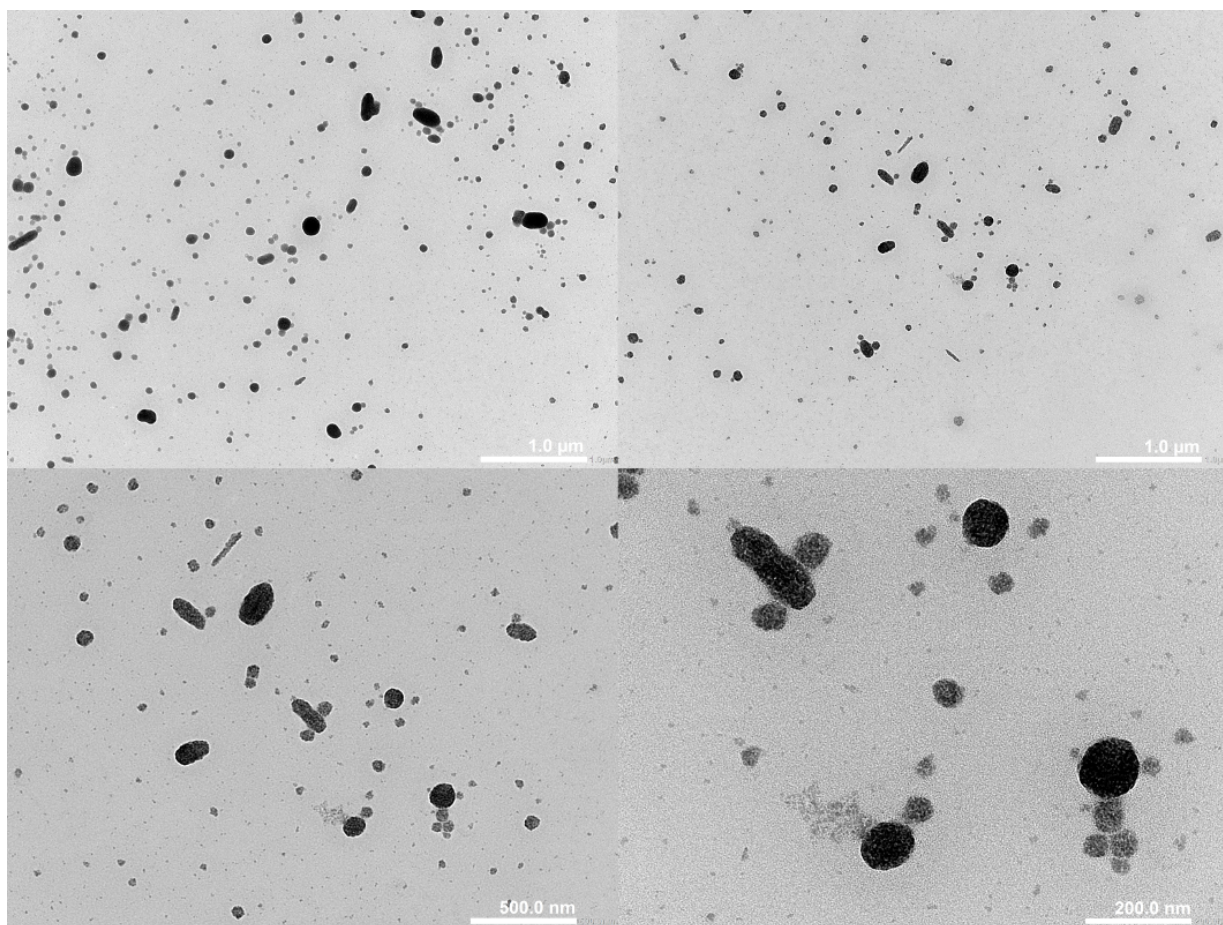


**Figure S12:** Electron micrographs taken on a *JEOL JEM-1400plus* of a **supersaturated CH solution prepared by dissolving 100 mg (2.5 mmol) calcium metal (Ca) in 100 mL water**. The TEM grid was prepared by the blotting method. Besides the spherical ACH particles, the grid was also covered by large agglomerates.



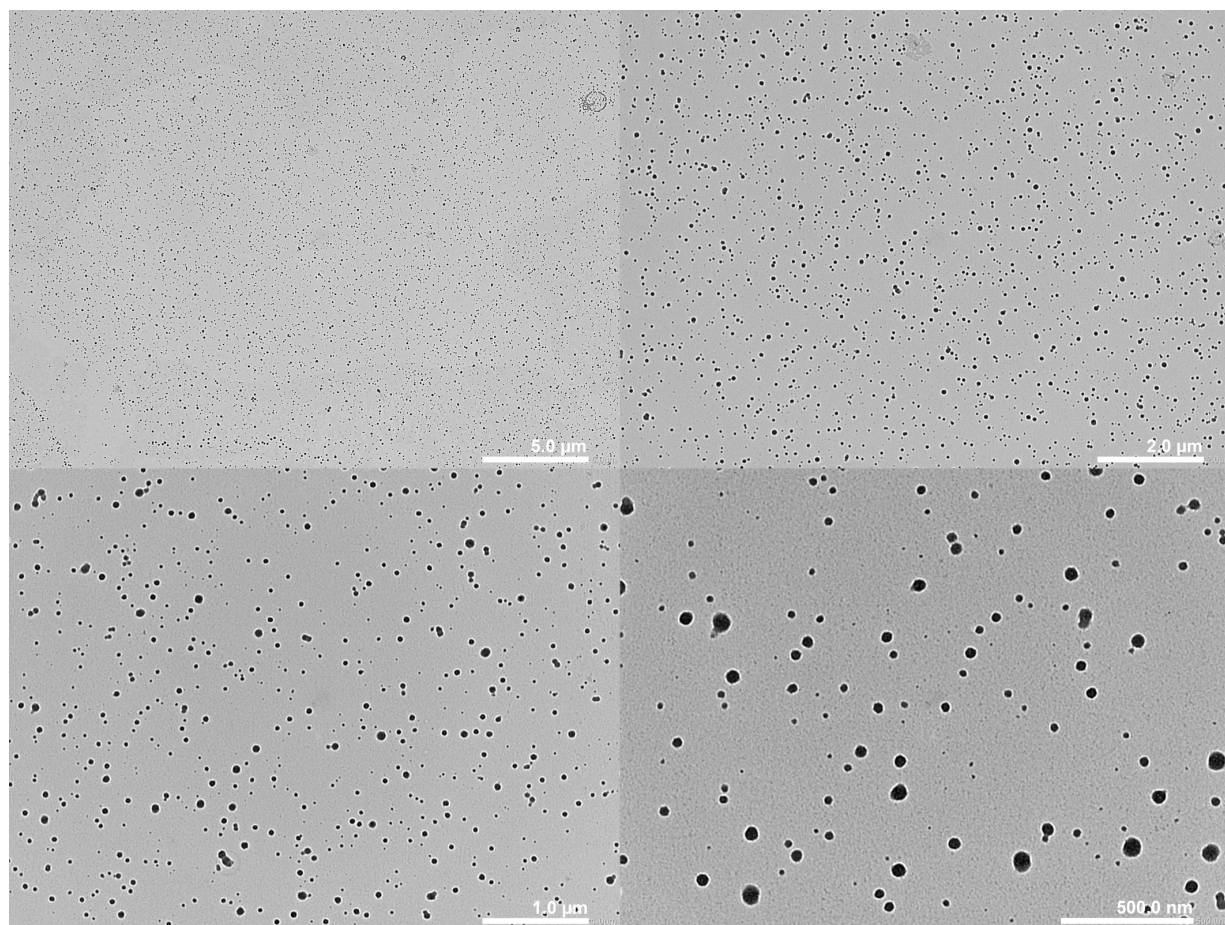


**Figure S13:** Electron micrographs taken on a *JEOL JEM-1400plus* of a supersaturated CH solution prepared by combining 50 mL of a 0.05 M calcium chloride ( $\text{CaCl}_2$ ) solution with 50 mL of a 0.1 M sodium hydroxide ( $\text{NaOH}$ ) solution. The TEM grid was prepared by the blotting method. The entire grid was covered with a vast number of ACH particles.



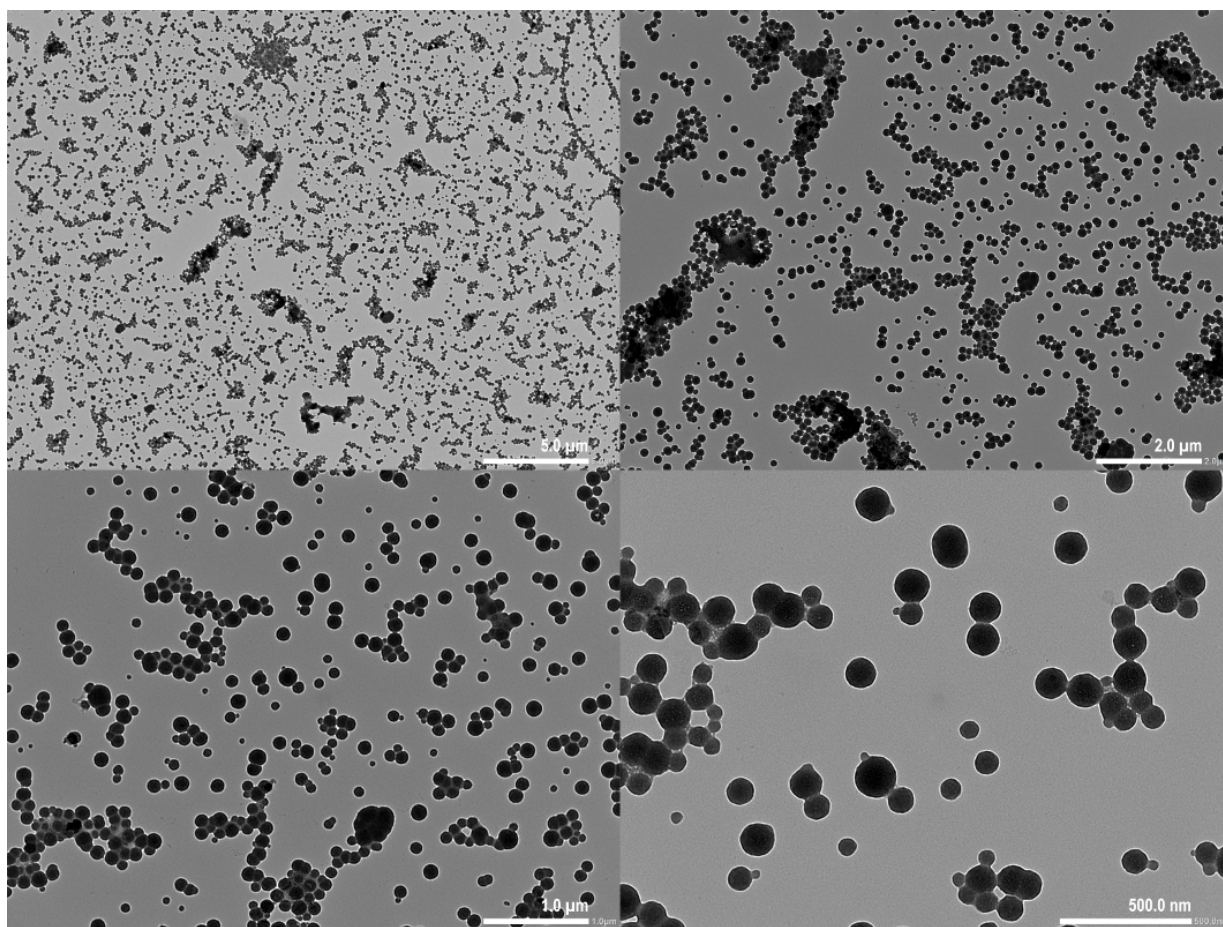
**Figure S14:** Electron micrographs taken on a *JEOL JEM-1400plus* of **C<sub>3</sub>S pore solution**, separated by centrifugation 15 min after the hydration started. The TEM grid was prepared by the blotting method. Various sizes of scattered ACH particles were observed.





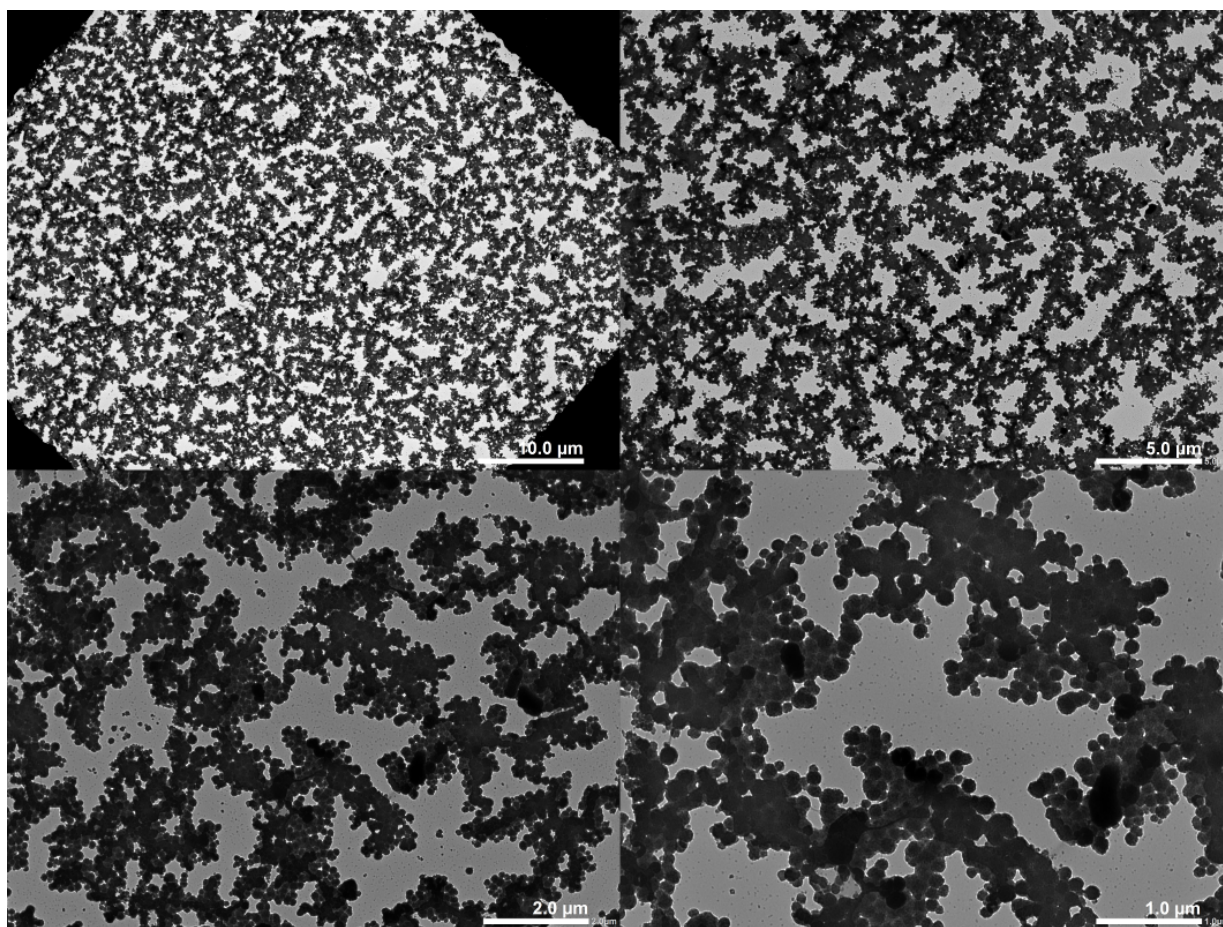
**Figure S15:** Electron micrographs taken on a *JEOL JEM-1400plus* of an **undersaturated CH solution (0.01 M) prepared by dissolving 40 mg (1 mmol) calcium metal (Ca) in 100 mL water**. The TEM grid was prepared by the blotting method. Small spherical ACH particles could be observed on the grid even though the prepared solution was undersaturated.

## S2.5 TEM sample preparation methods



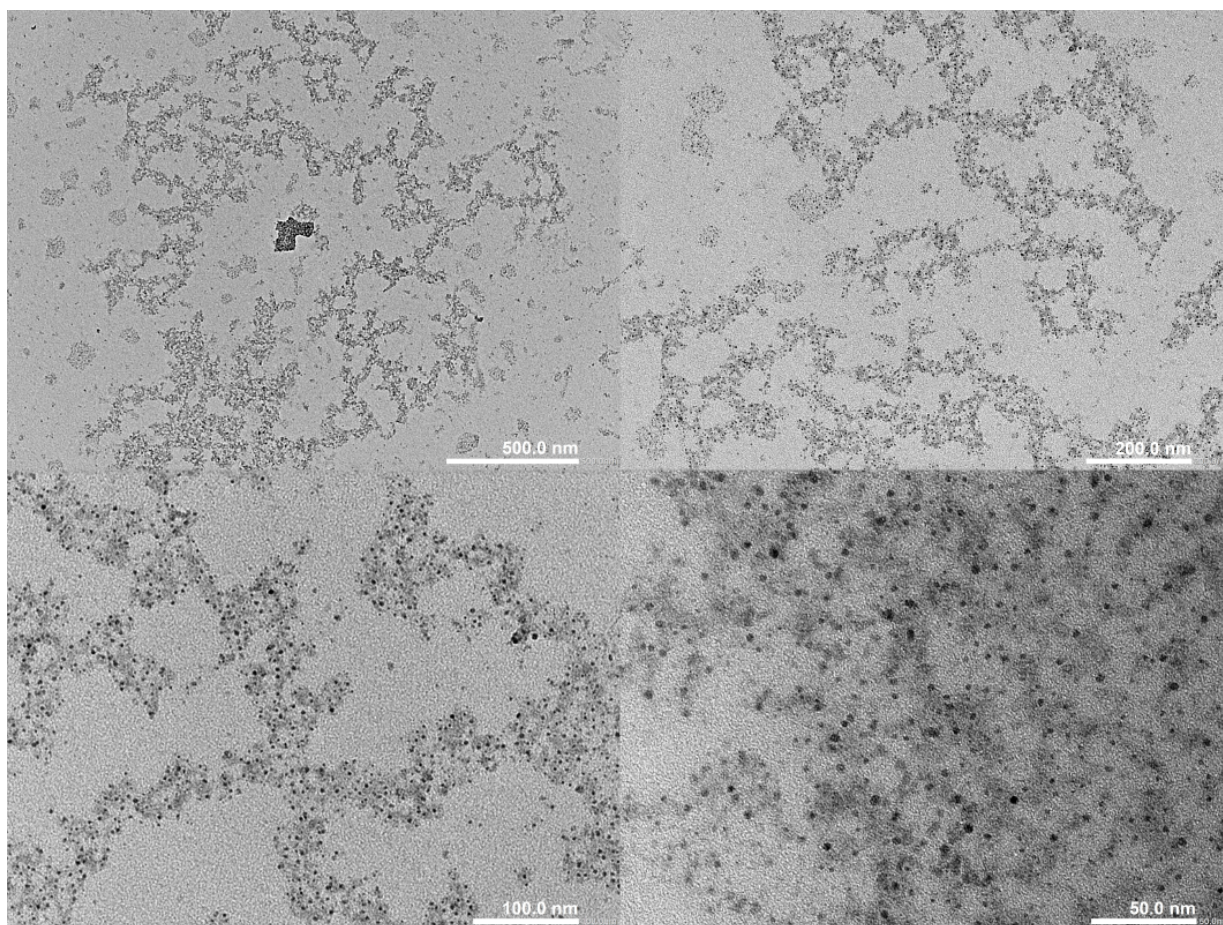
**Figure S16:** Electron micrographs taken on a *JEOL JEM-1400plus* of cementitious pore solution, separated by dead-end filtration 15 min after the hydration started. The TEM grid was prepared by the **blotting method**. The spherical ACH particles were approximately 100 nm in size and scattered over the entire grid.



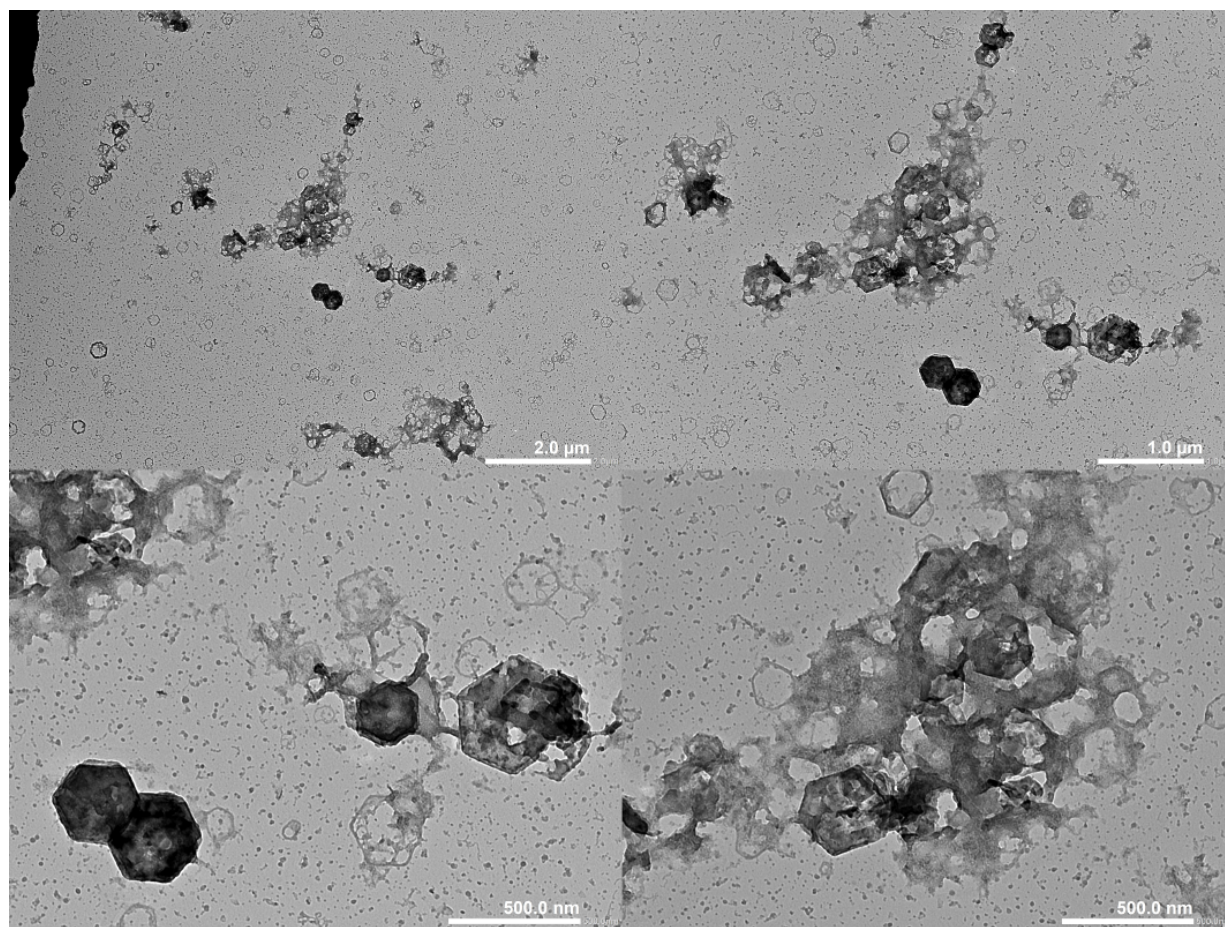


**Figure S17:** Electron micrographs taken on a *JEOL JEM-1400plus* of cementitious pore solution, separated by dead-end filtration 15 min after the hydration started. The TEM grid was prepared by the **blotting method**. Sometimes the ACH particles were so strongly aggregated that they formed a continuous layer covering the entire TEM grid.



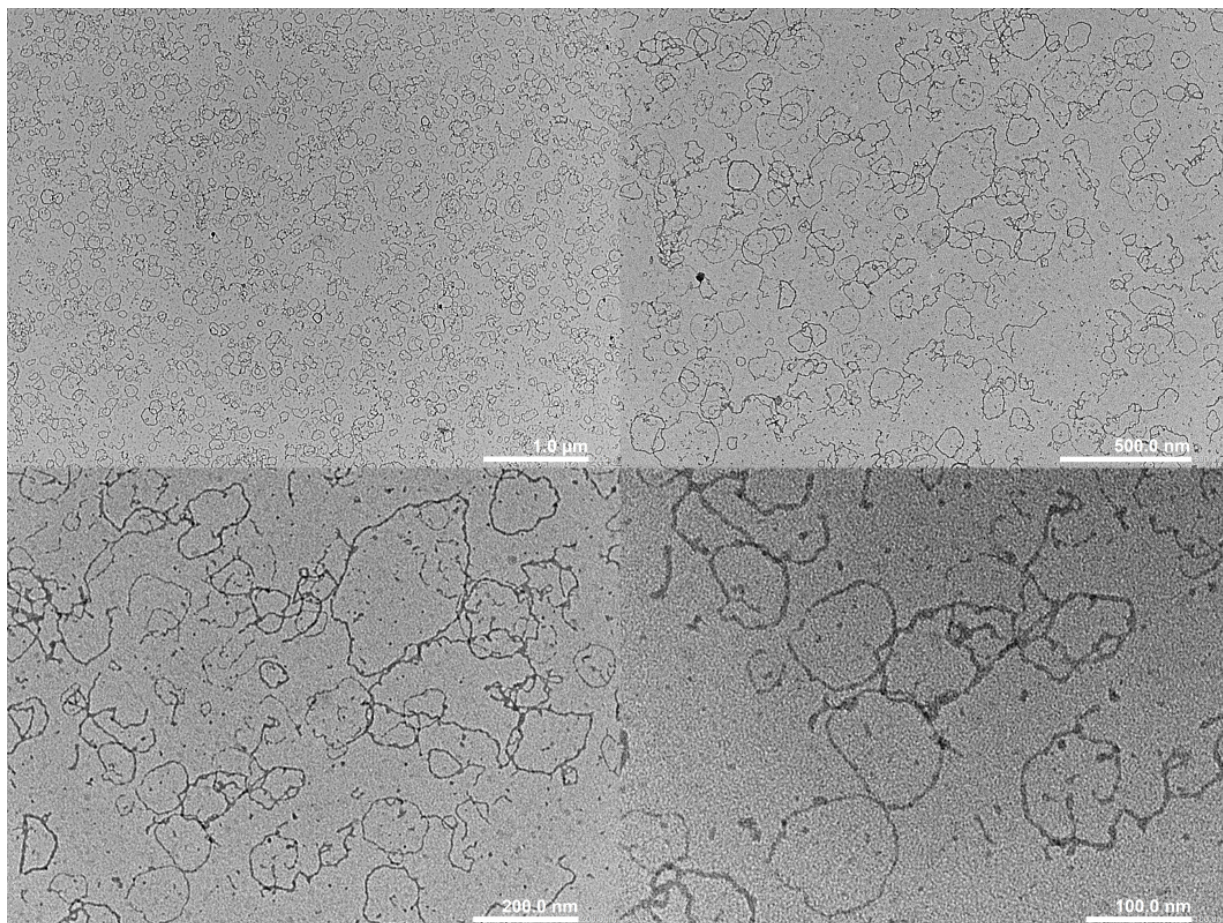


**Figure S18:** Electron micrographs taken on a *JEOL JEM-1400plus* of cementitious pore solution, separated by dead-end filtration 15 min after the hydration started. The TEM grid was prepared by the **Drop-Casting method**. The ACH particles were smaller than 20 nm but already highly agglomerated.



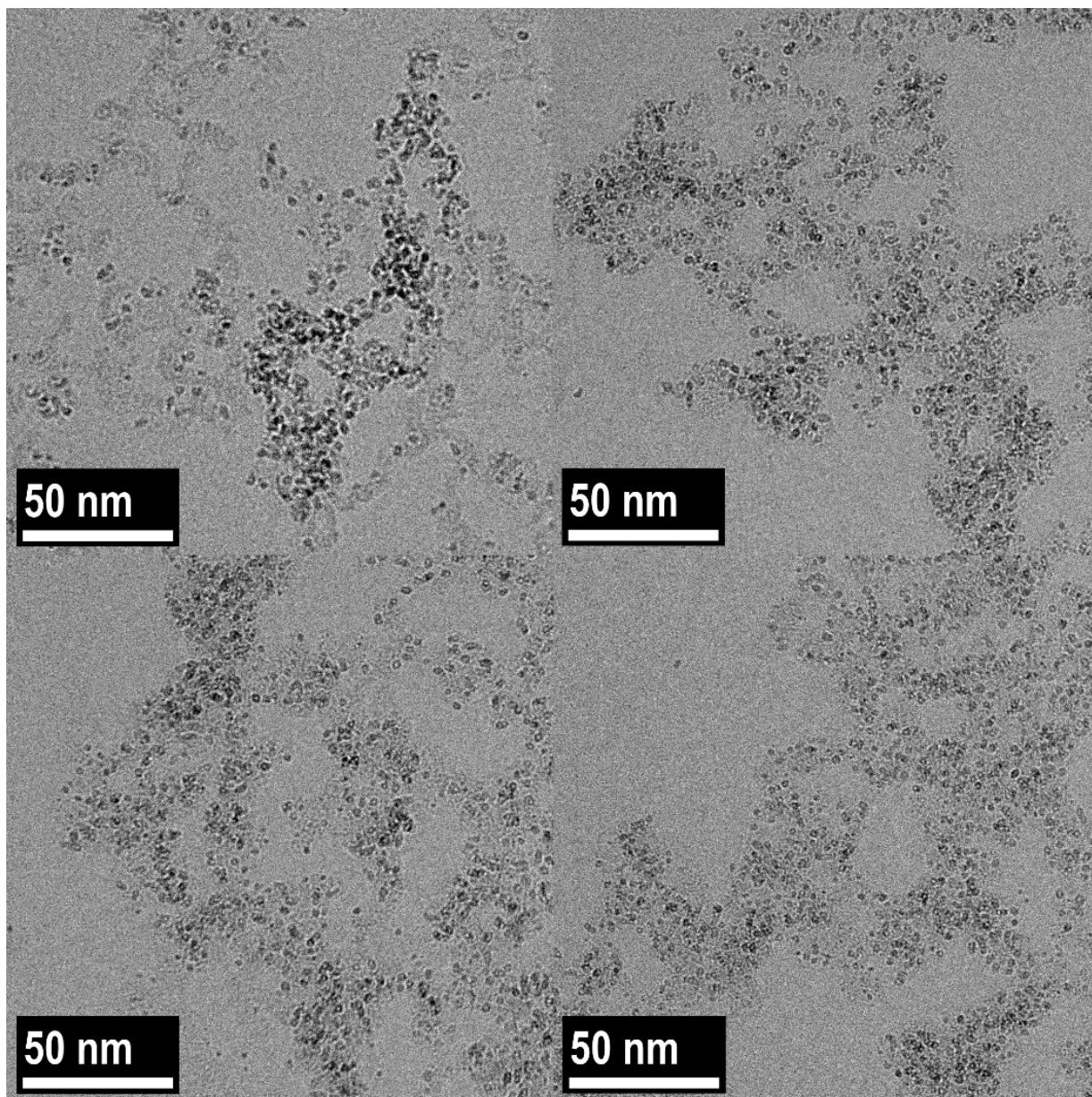
**Figure S19:** Electron micrographs taken on a *JEOL JEM-1400plus* of  $C_3S$  pore solution, separated by dead-end filtration 15 min after the hydration started. The  **$C_3S$  pore solution was quenched with ethanol (1:10) before blotting** the suspension on the TEM grid. In addition to scattered spherical ACH nanoparticles, ring-shaped hexagonal structures were also observed.





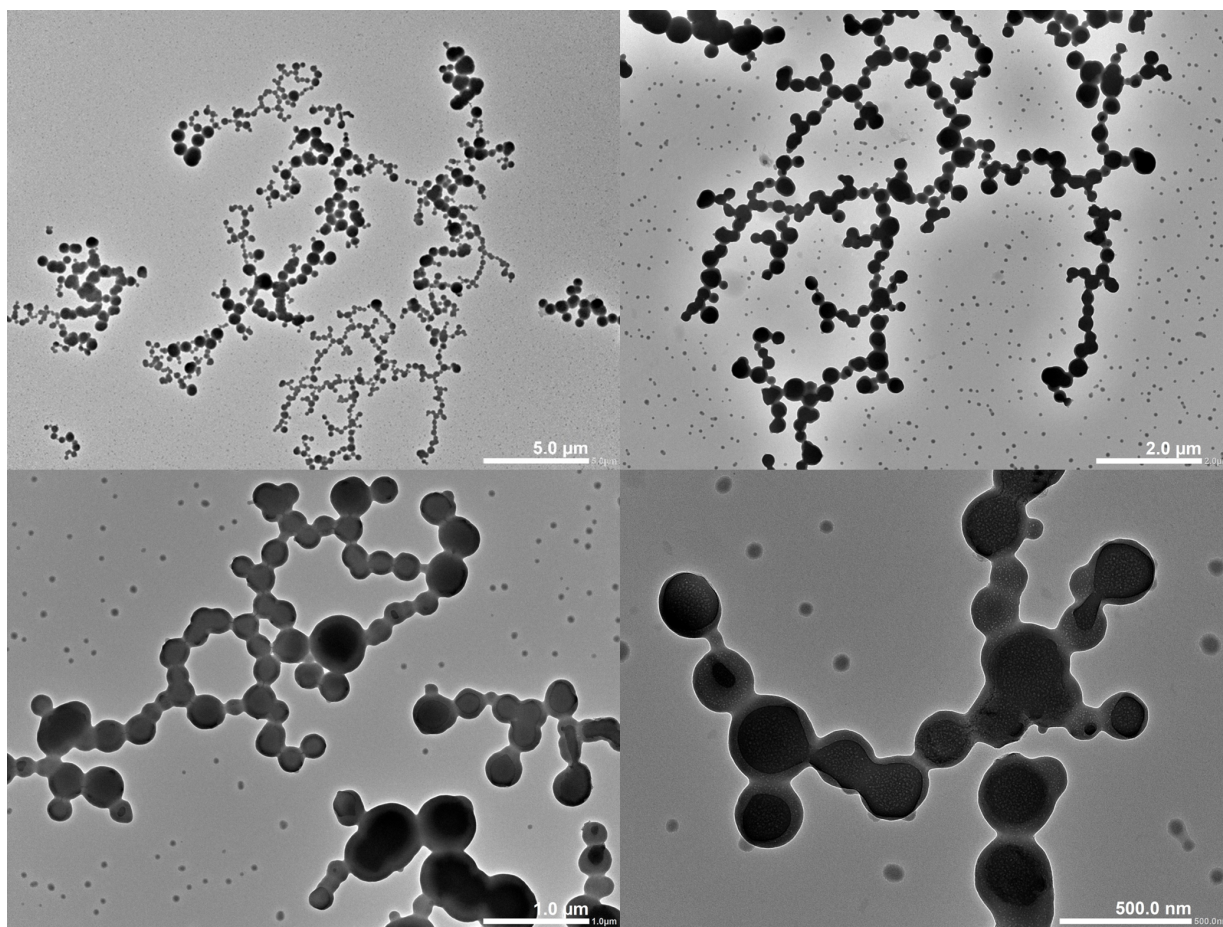
**Figure S20:** Electron micrographs taken on a *JEOL JEM-1400plus* of an **undersaturated CH solution (0.1 M)**, **that was quenched with ethanol (1:10) before blotting** on the TEM grid. In this case, smaller open ring-shaped hexagonal structures were found.



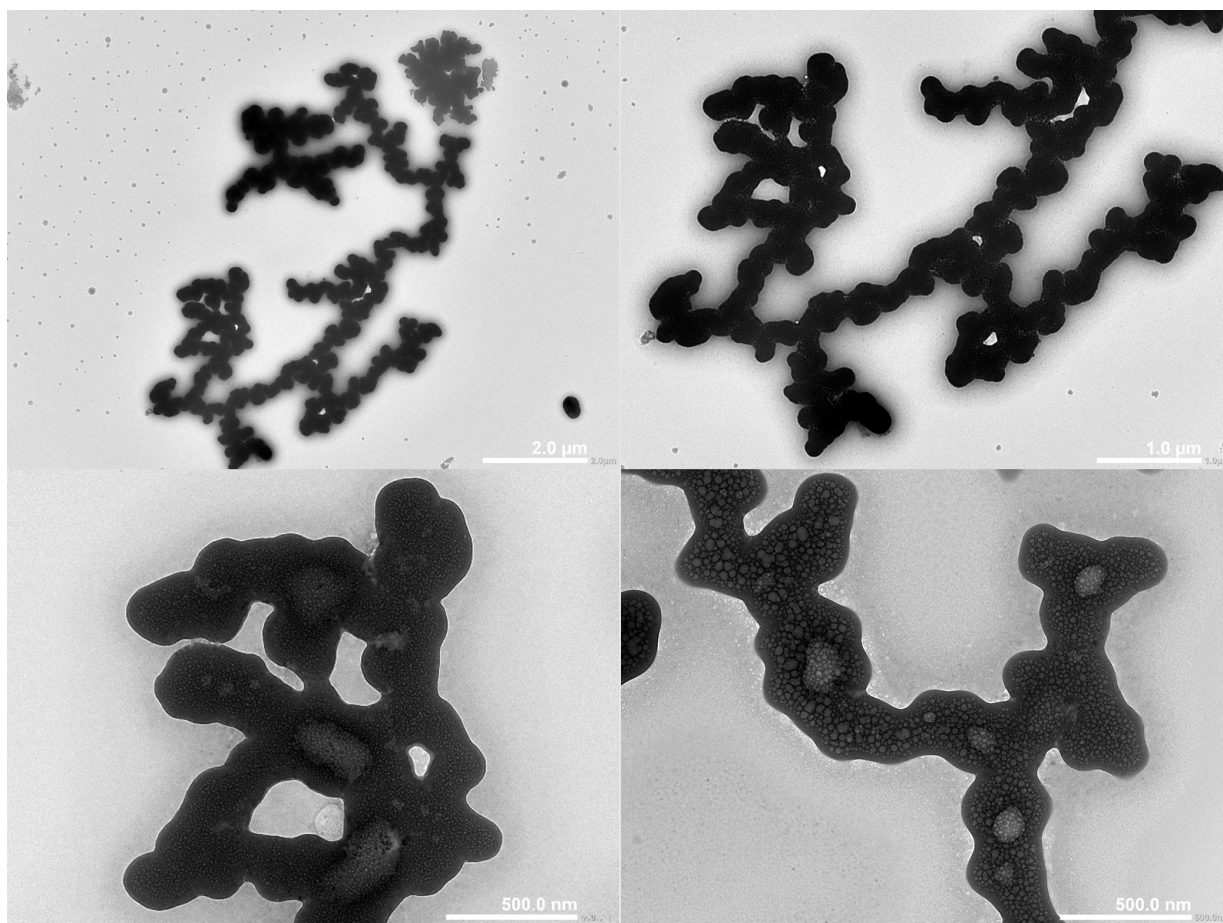


**Figure S21: Cryo-TEM images** of separated cementitious pore solution measured with a Glacios microscope. The particles observed in the frozen solution are significantly smaller (5-10 nm) compared to those seen under the conventional TEM after drying (100-200 nm). However, even in this stage, the particles tend to aggregate, forming large agglomerates.

## S2.6 Non-classical crystallization of ACH into CH and CC

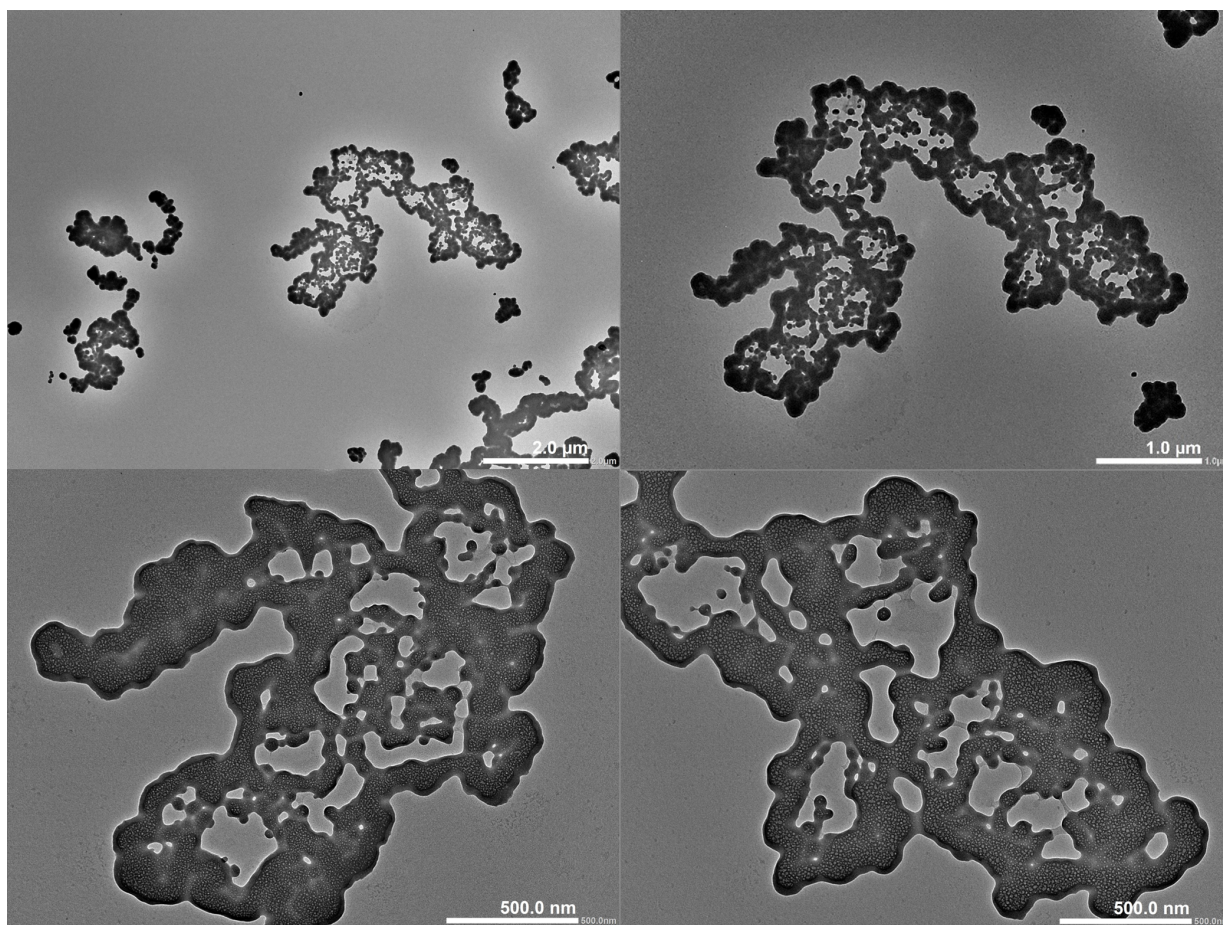


**Figure S22:** Electron micrographs taken on a *JEOL JEM-1400plus* of cementitious pore solution, separated by dead-end filtration. The TEM grid was prepared by the blotting method. The spherical amorphous particles form complex agglomerate structures composed of particles of different sizes. Additionally, smaller primary particles can be observed adjacent to these structures.

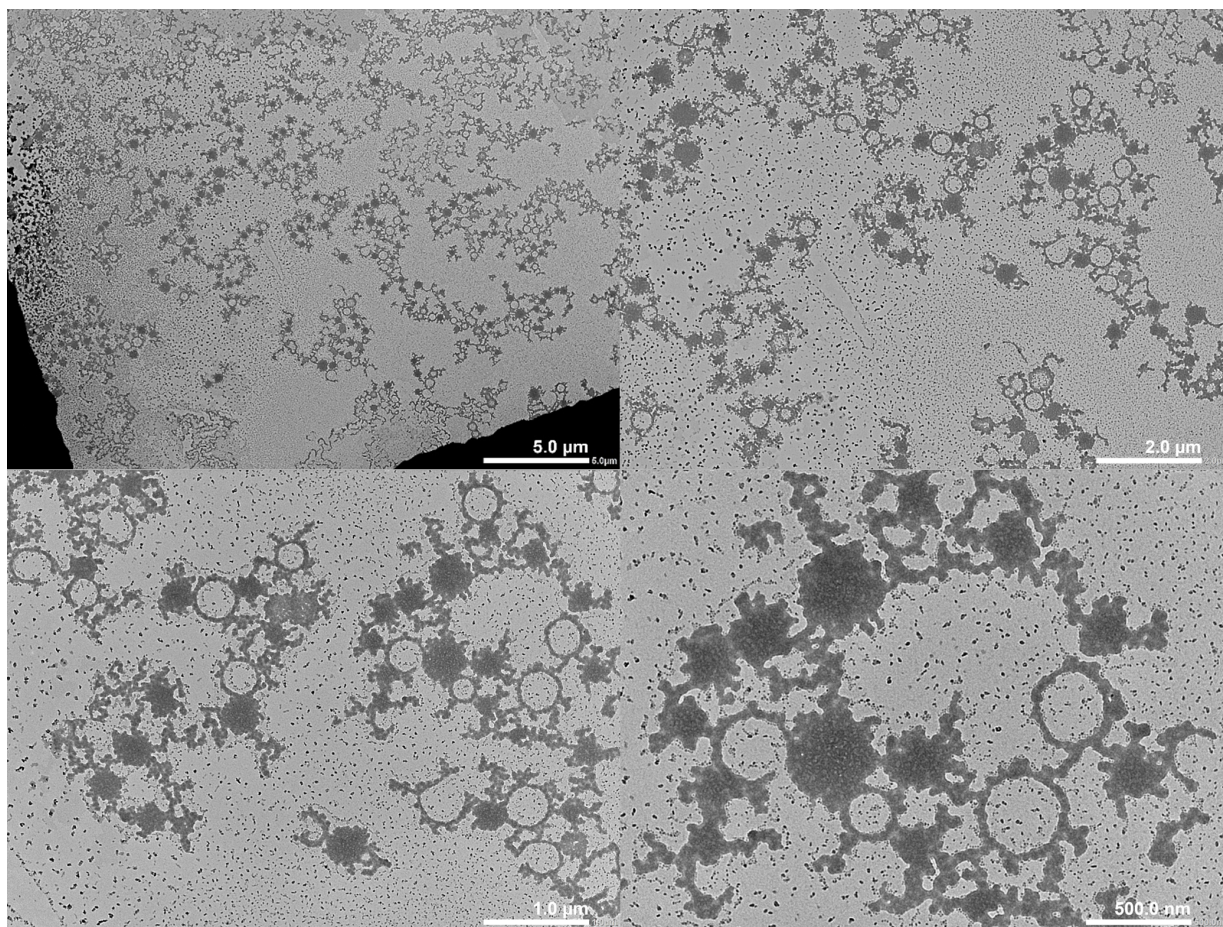


**Figure S23:** Electron micrographs taken on a *JEOL JEM-1400plus* of cementitious pore solution, separated by dead-end filtration. The TEM grid was prepared by the blotting method. The agglomerates have become denser, and the spherical amorphous particles are less round than before.



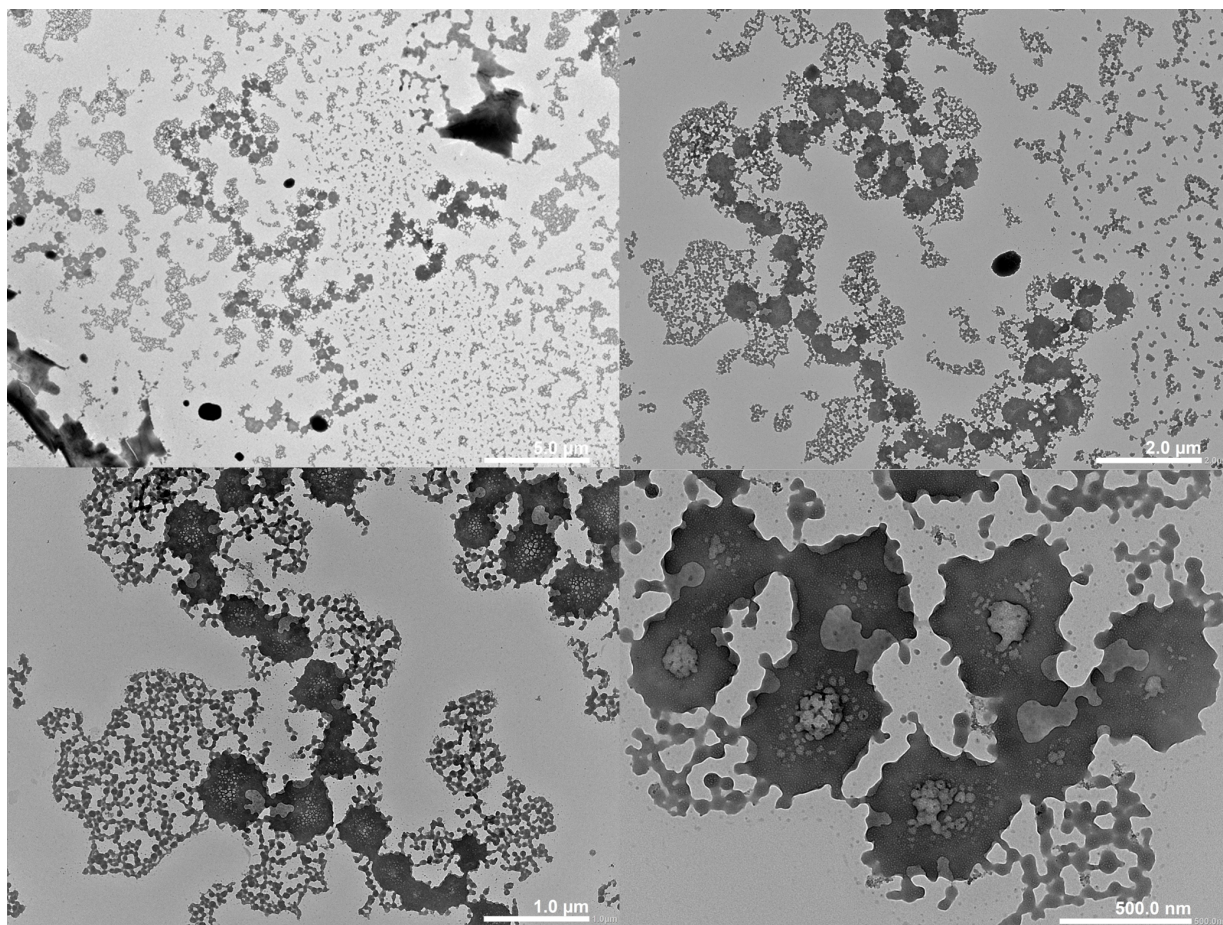


**Figure S24:** Electron micrographs taken on a *JEOL JEM-1400plus* of cementitious pore solution, separated by dead-end filtration. The TEM grid was prepared by the blotting method. The structures continue to condense and grow together, resulting in the loss of the original spherical shape.



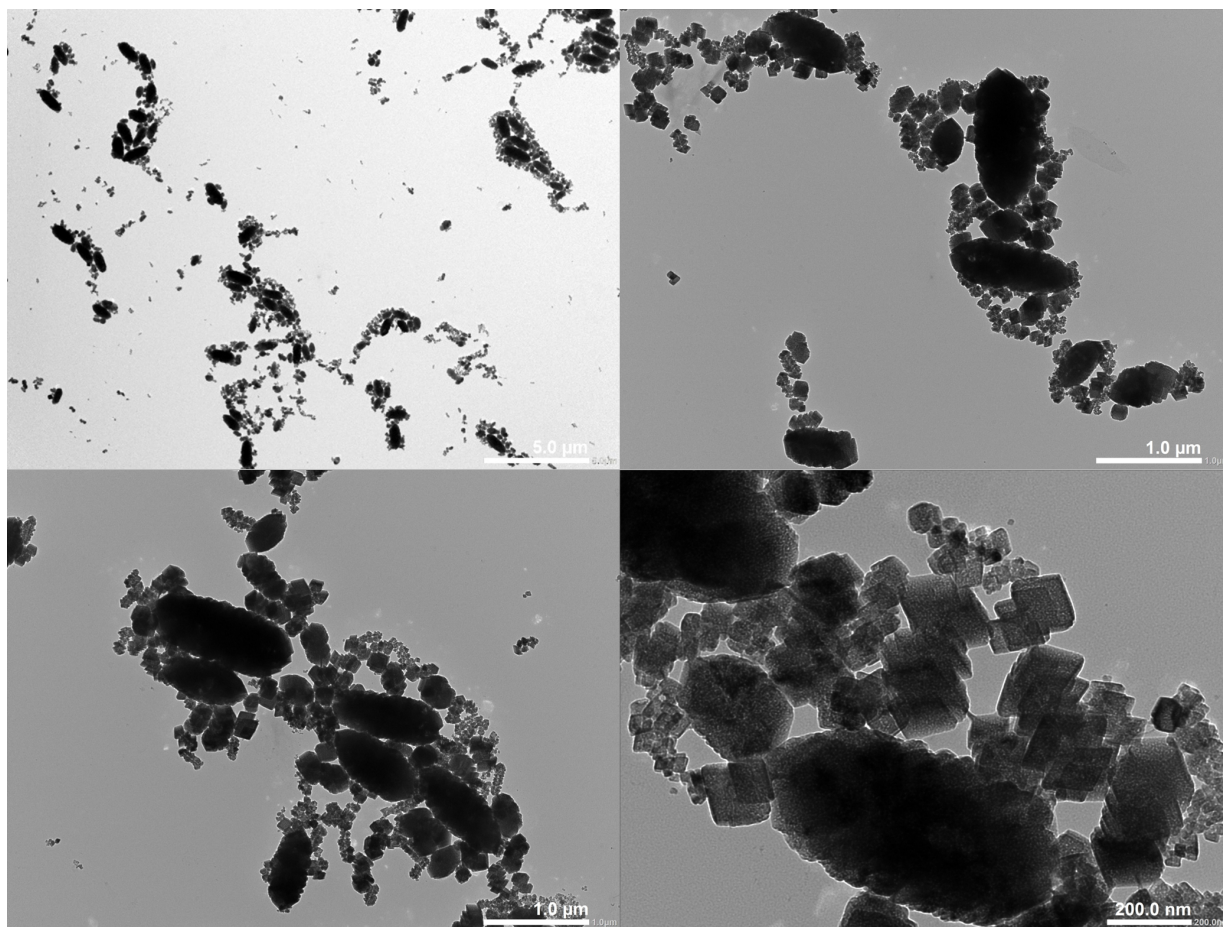
**Figure S25:** Electron micrographs taken on a *JEOL JEM-1400plus* of cementitious pore solution, separated by dead-end filtration. The TEM grid was prepared by the blotting method. The spherical amorphous particles first form larger circular structures, which subsequently condense and begin to adopt the characteristic hexagonal shape of what will eventually become calcium hydroxide crystals.





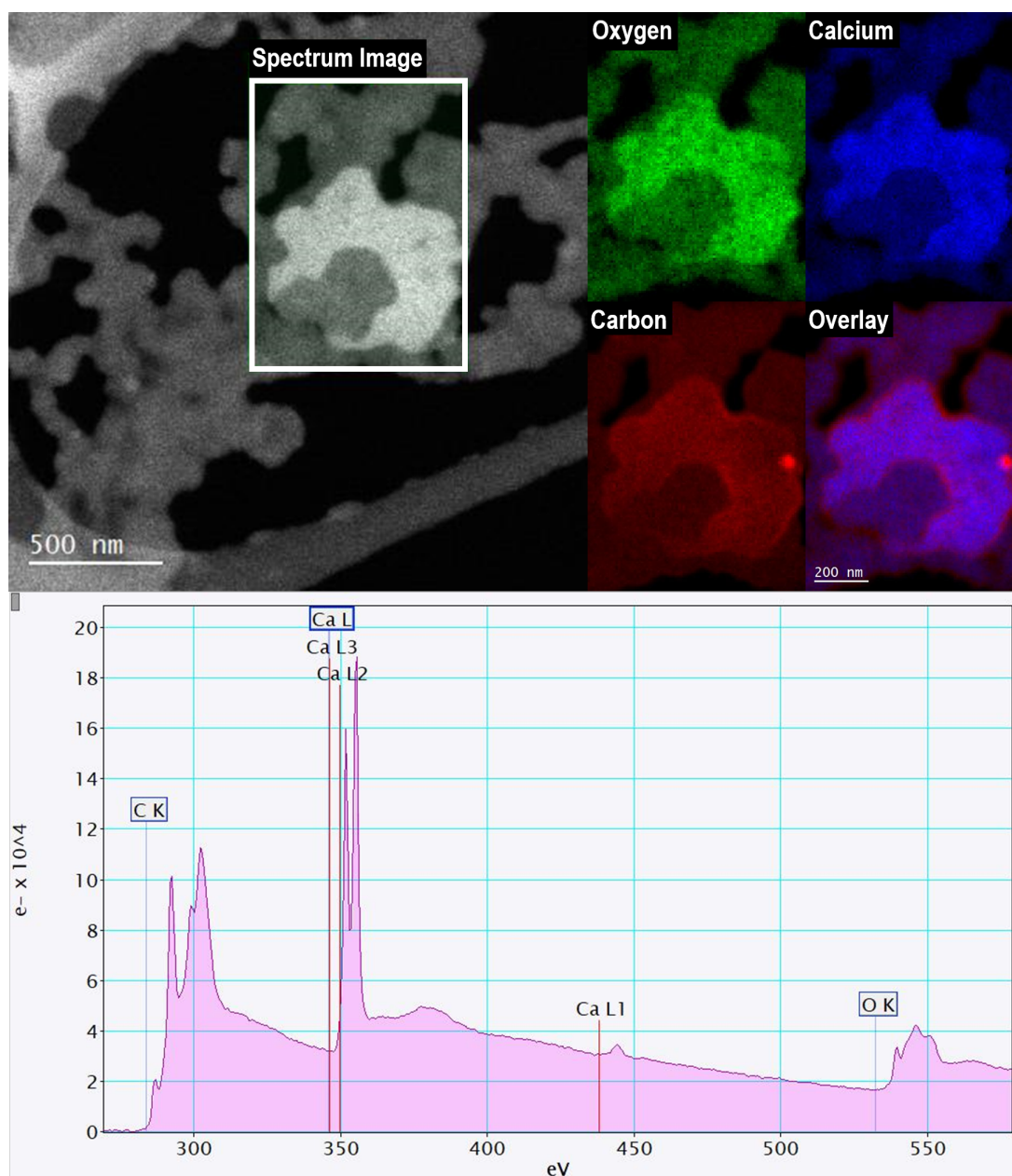
**Figure S26:** Electron micrographs taken on a *JEOL JEM-1400plus* of cementitious pore solution, separated by dead-end filtration. The TEM grid was prepared by the blotting method. The spherical amorphous particles have coalesced into contiguous structures, which begin to adopt the characteristic hexagonal shape of what will eventually become calcium hydroxide crystals.



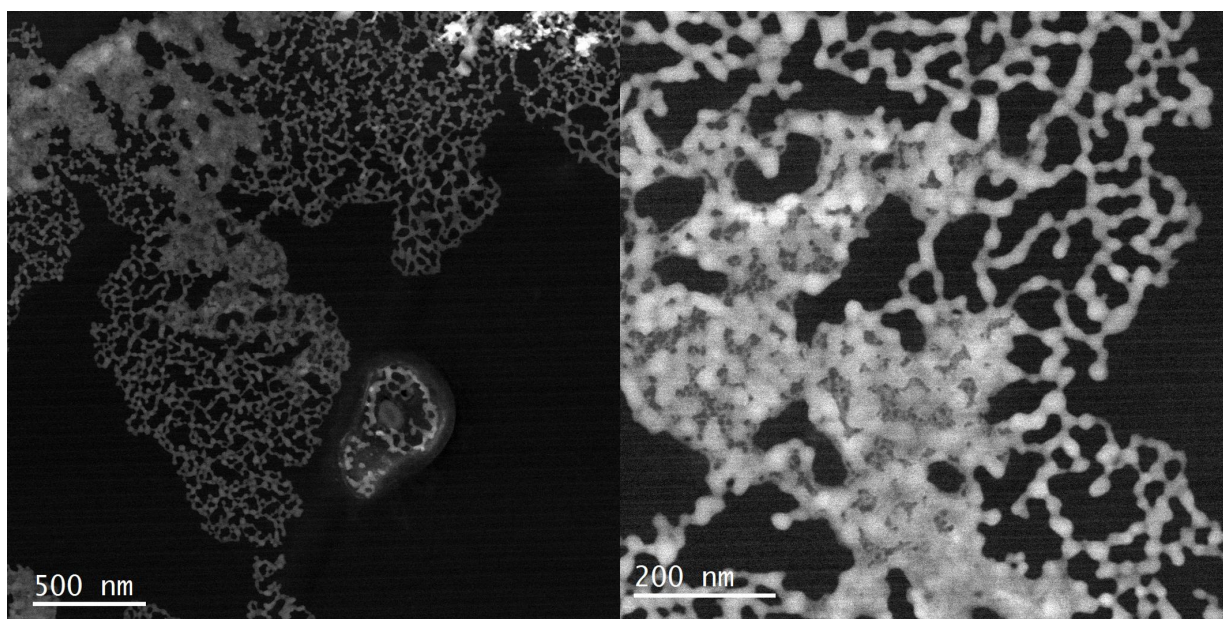


**Figure S27:** Electron micrographs taken on a *JEOL JEM-1400plus* of **cementitious pore solution** after being **exposed to air for one day**. The pore solution was separated by dead-end filtration 15 min after the hydration started. The initially amorphous spherical particles have transformed into stacks of crystalline particles exhibiting the characteristic calcite shape.

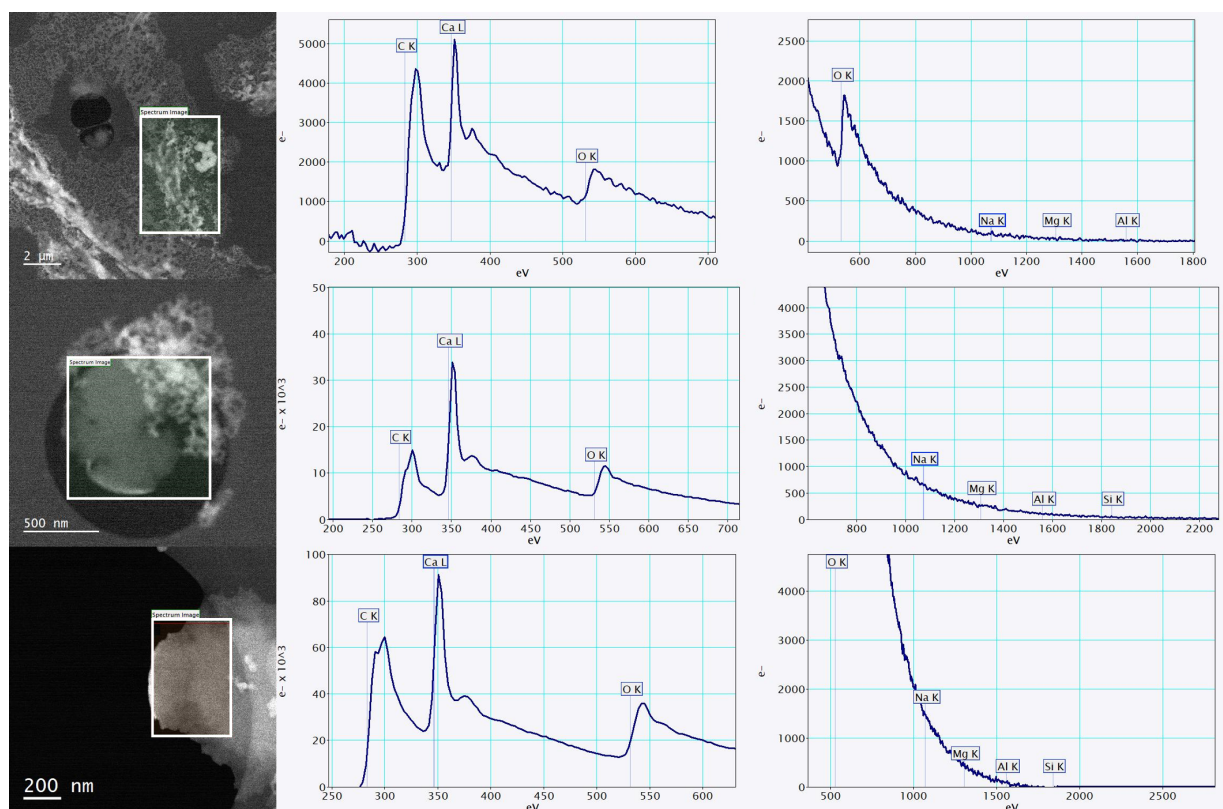
## S2.7 EELS spectra



**Figure S28:** EELS measurement in the highlighted area. An element map of this region and the EELS spectrum are shown. The amorphous particles primarily consist of oxygen and calcium and exhibit a core-shell microstructure. The carbon signal is concentrated at the particle surface. The ACH particles are coated with a carbonate layer due to exposure to air during sample handling.



**Figure S29:** ADF-TEM images showing ACH nanoparticle agglomerates, on which EELS measurements were performed in selected areas (see Figure S30).

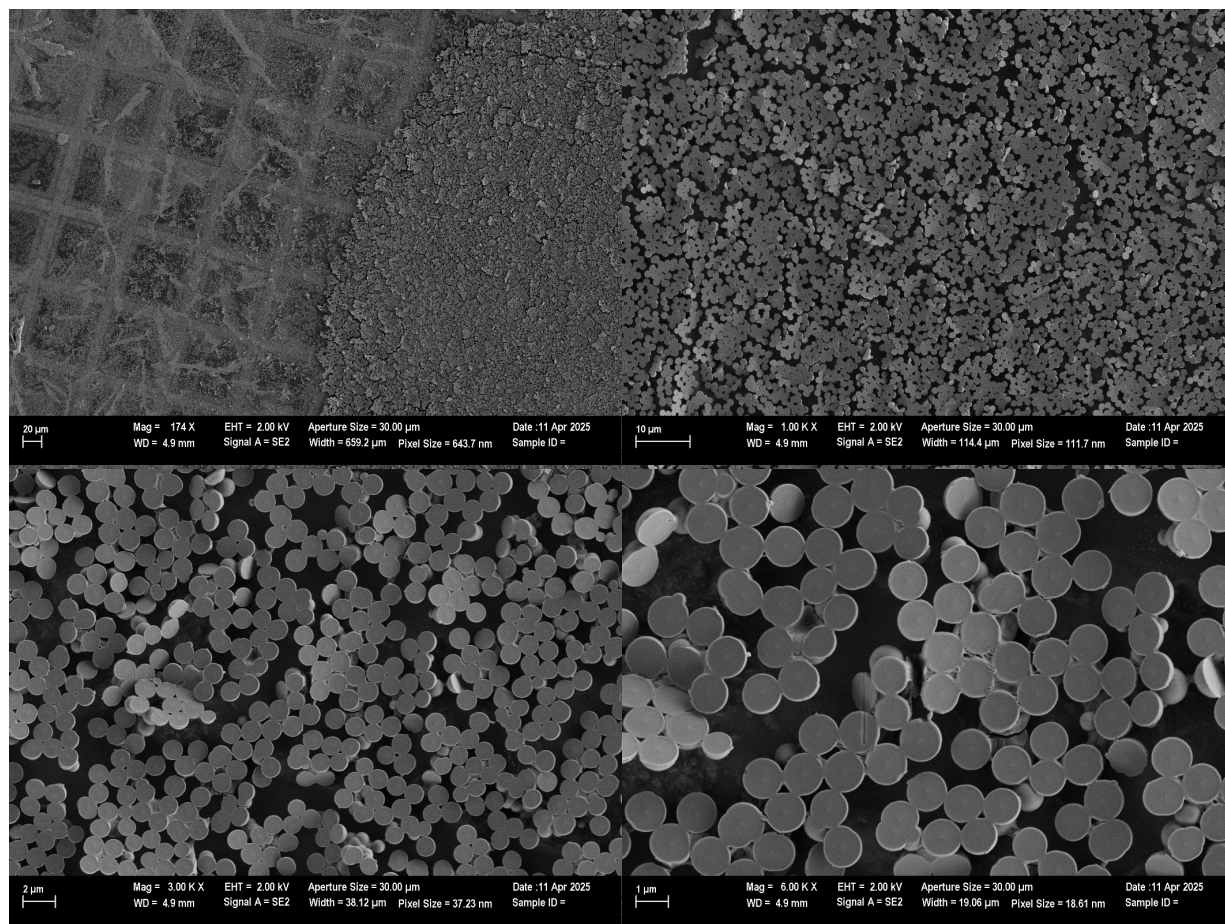


**Figure S30:** EELS measurements in the three highlighted morphologically distinct areas. The respective EELS spectra for these regions are shown for two energy ranges: 200 to 600 eV and 600 to 2000 eV. Only oxygen, calcium, and carbon signals were detectable, whereas the other important ions in the pore solution (K, Na, S, Al, Si, Mg, Fe, etc.) could not be observed because their signal intensity was too weak.

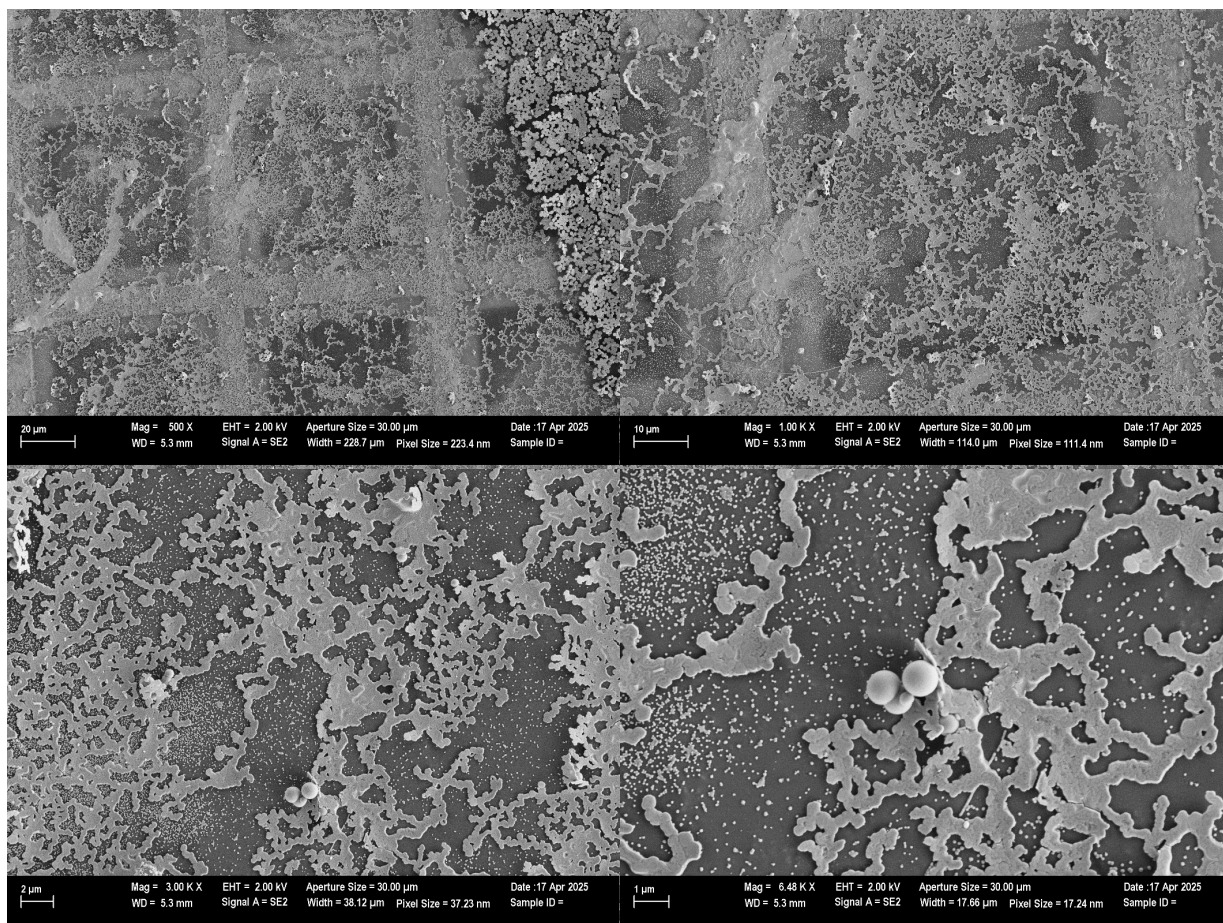


## S3 SEM data

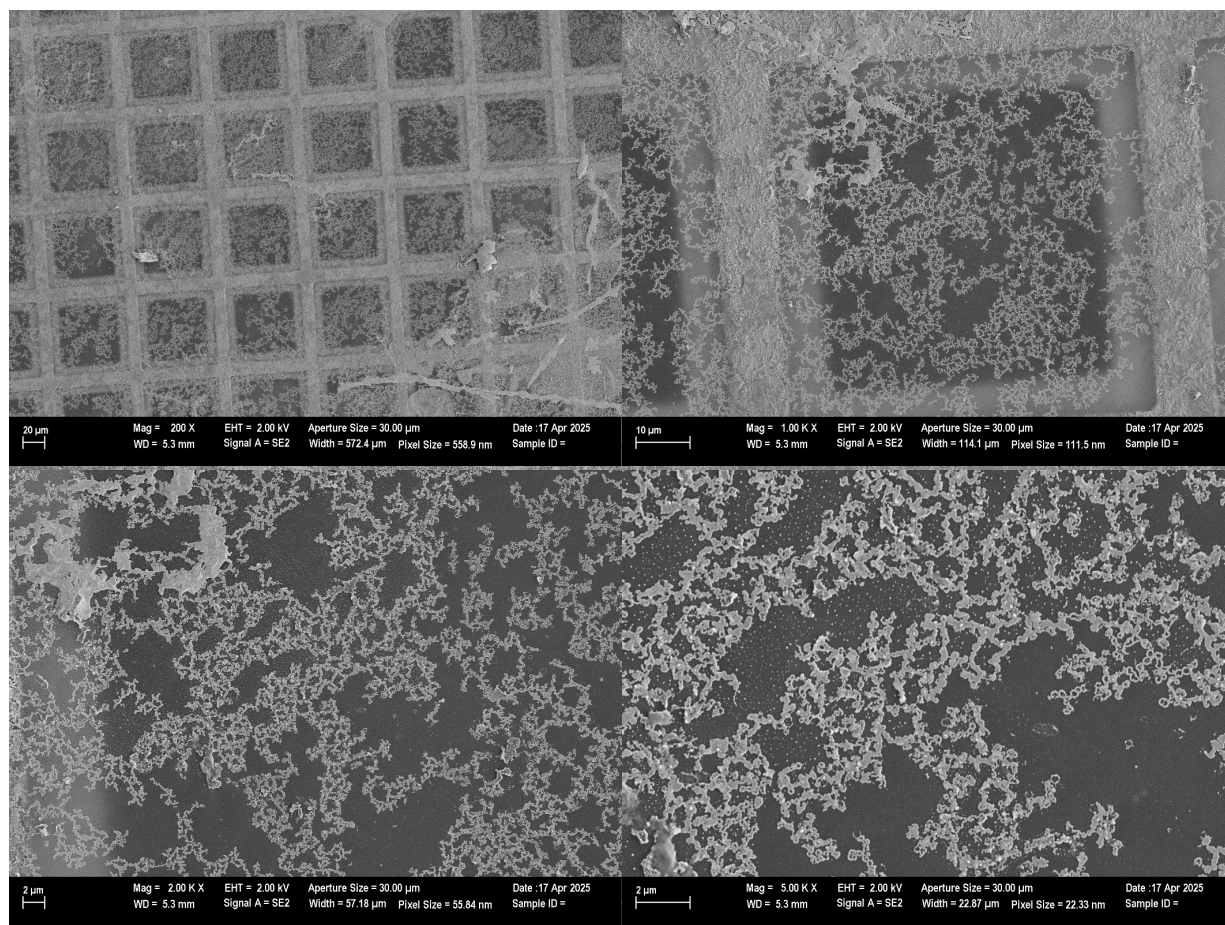
### S3.1 SEM images of ACH



**Figure S31:** SEM images of cementitious pore solution, separated by dead-end filtration 15 min after the hydration started. The cementitious pore solution was blotted onto a TEM grid and air-dried overnight before measurement. Additional imaged areas of the same sample are shown in Figure S32 and S33. A continuous network of approximately 1  $\mu$ m hemispheres located on the TEM grid was observed. The elemental composition of the detected particles, determined using EDX analysis, is displayed in Figure S35. The respective EDX spectrum can be found in Figure S36.

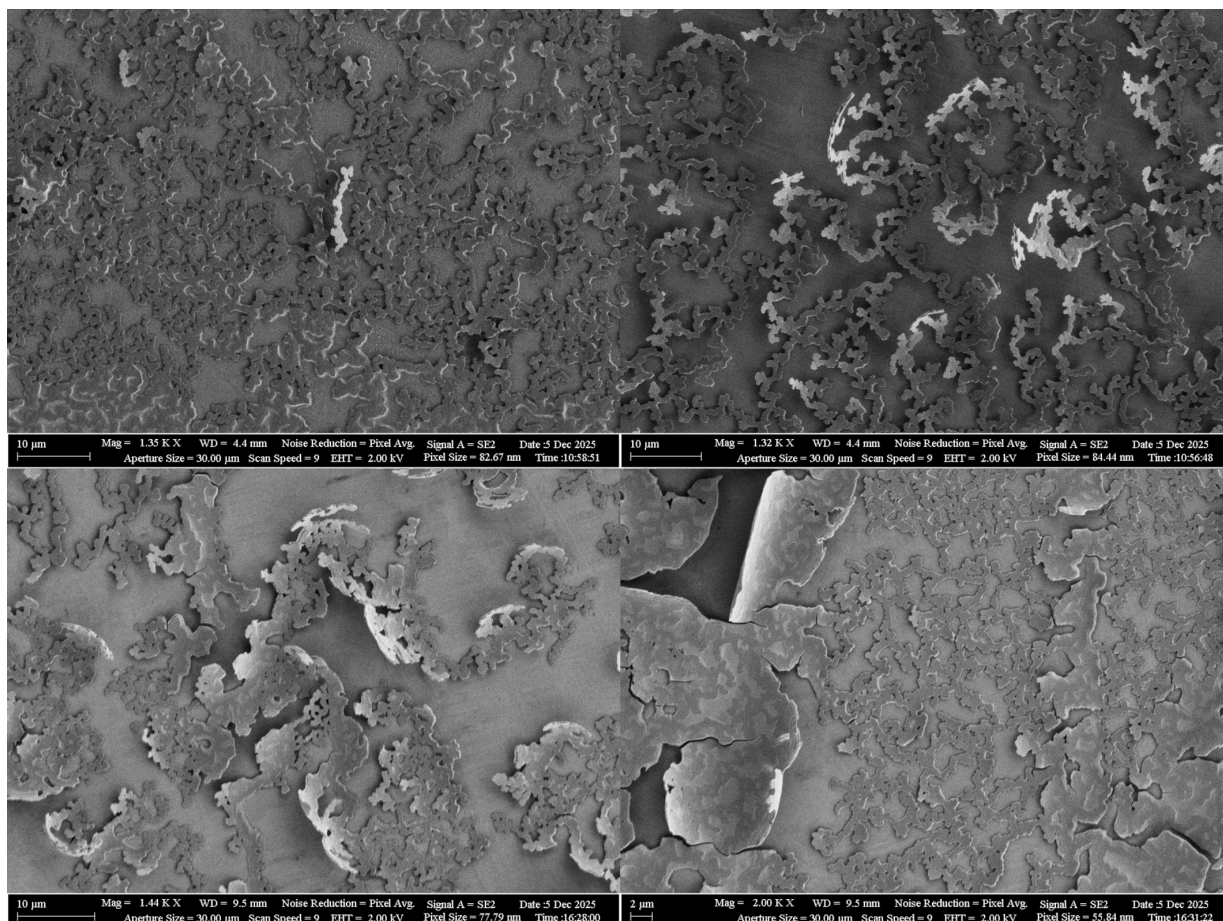


**Figure S32:** SEM images of cementitious pore solution, separated by dead-end filtration 15 min after the hydration started. The cementitious pore solution was blotted onto a TEM grid and air-dried overnight before measurement. Additional imaged areas of the same sample are shown in Figure S31 and S33. Alongside the large aggregates previously observed under the TEM we also monitored small scattered ACH particles.



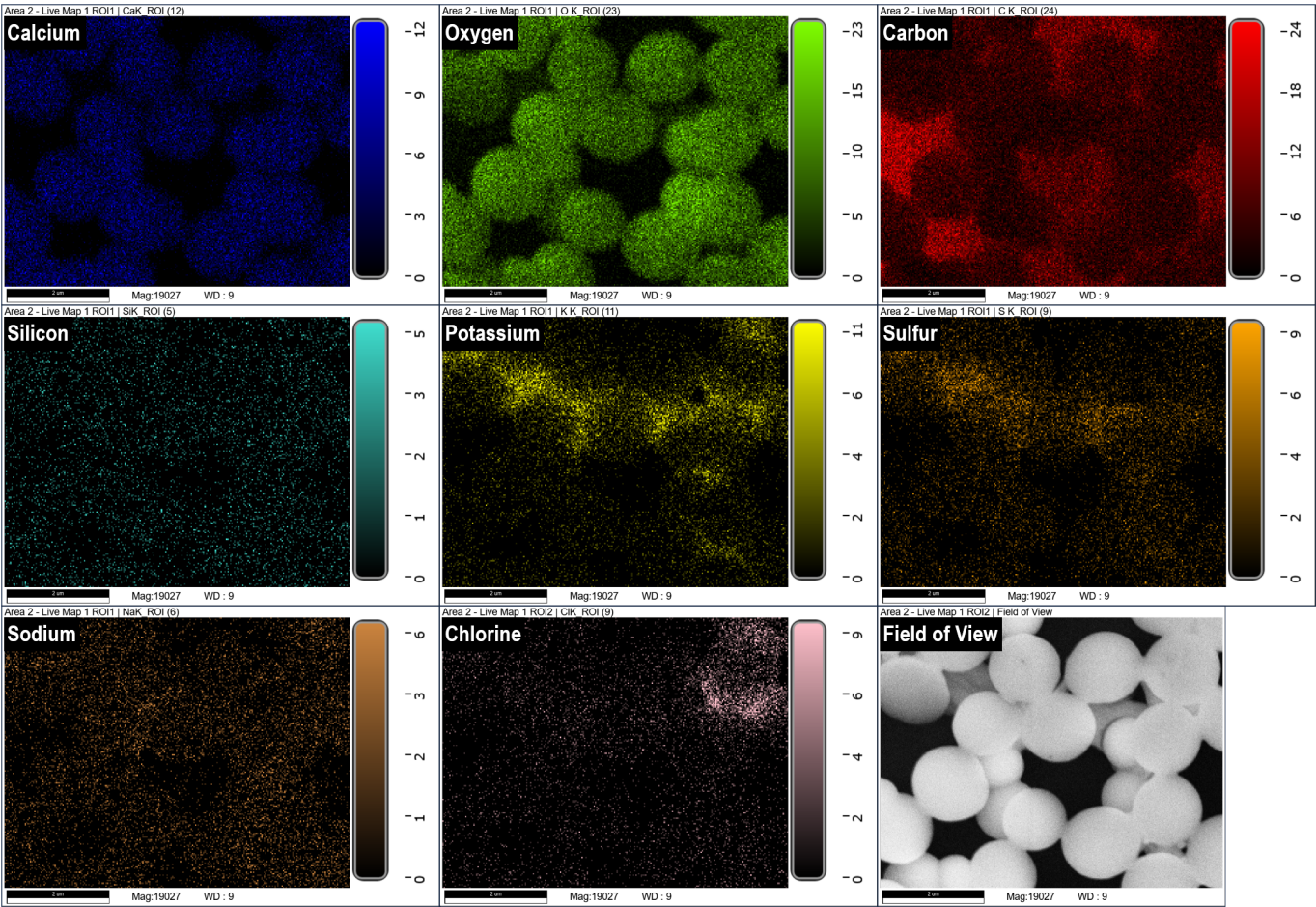
**Figure S33:** SEM images of cementitious pore solution, separated by dead-end filtration 15 min after the hydration started. The cementitious pore solution was blotted onto a TEM grid and air-dried overnight before measurement. Additional imaged areas of the same sample are shown in Figure S31 and S32. A continuous network formed by aggregates of ACH particles covered the TEM grid.



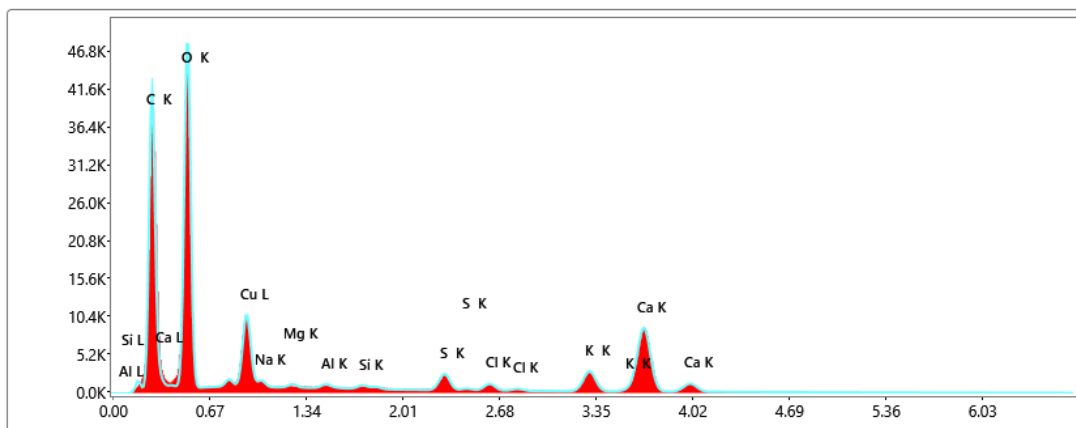


**Figure S34:** SEM images of cementitious pore solution, separated by dead-end filtration 15 min after the hydration started. The cementitious pore solution was blotted onto a silicon wafer and air-dried overnight before measurement. A coherent network of aggregated ACH spheres is visible, partially embedded within a layer of dried potassium sulfate. The elemental composition of the aggregates, determined using EDX analysis, is displayed in Figure S37. The respective EDX spectrum can be found in Figure S38.

S3.2 EDX analysis



**Figure S35:** Element maps showing the elements with the highest concentrations detected by EDX within the region of interest. The corresponding EDX spectrum is shown in Figure S36, and the elemental composition is presented in Table S2. The amorphous spheres (see Figure S31) primarily consist of oxygen and calcium. The copper and carbon signals originate from the TEM grid on which the sample was placed. The other elements in the pore solution (Mg, Al, Fe), which are not depicted, are detectable only at trace levels.

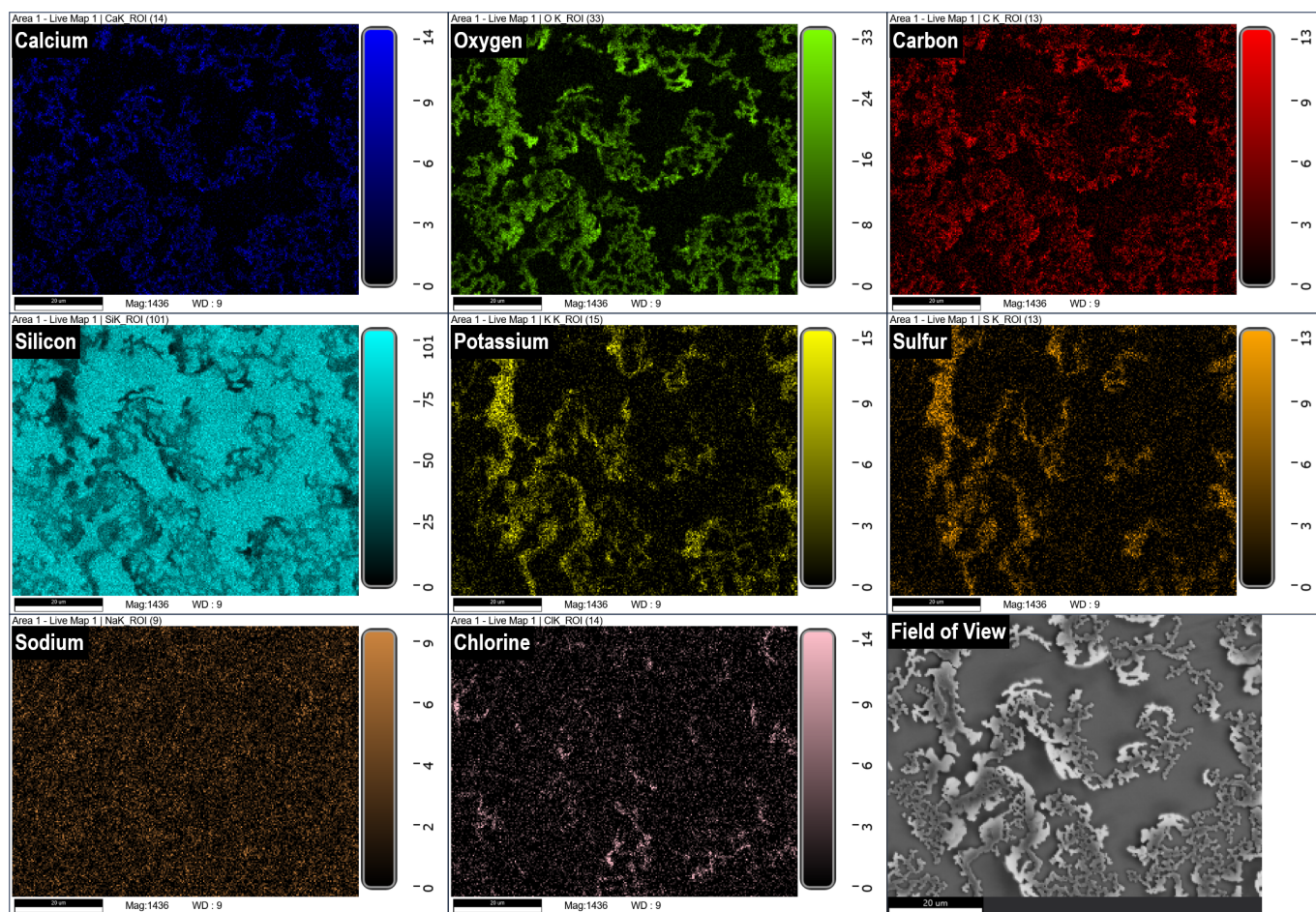


**Figure S36:** Spectrum of the EDX measurement in the highlighted area in Figure S35. The elemental composition is presented in Table S2. Individual element maps for each identified element can be found in Figure S35.

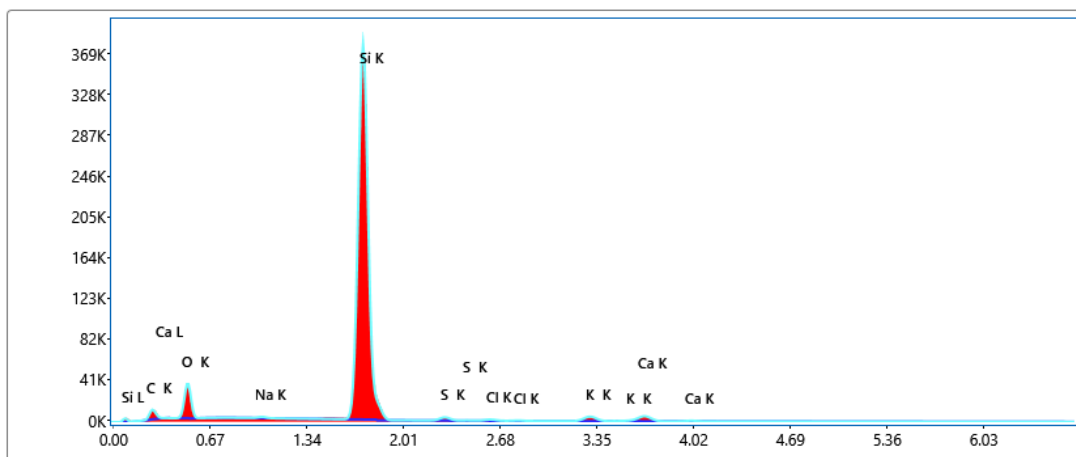
**Table S2:** Elemental composition of the EDX analysis shown in Figure S35. Listed are weight percent (wt.%), minimum detection limit (MDL), atomic percent (at.%), percentage error (Error%), net intensity (Net Int.), and the detection parameters R, A, and F for every element detected in Figure S36.

| Element | wt.%  | MDL  | at.%  | Error % | Net Int. | R      | A      | F      |
|---------|-------|------|-------|---------|----------|--------|--------|--------|
| C       | 26.07 | 0.05 | 39.92 | 8.67    | 768.78   | 0.9027 | 0.3349 | 1.0000 |
| O       | 38.78 | 0.07 | 44.57 | 9.17    | 1118.04  | 0.9156 | 0.2825 | 1.0000 |
| Na      | 0.31  | 0.04 | 0.25  | 9.93    | 19.13    | 0.9304 | 0.5539 | 1.0023 |
| Mg      | 0.21  | 0.04 | 0.16  | 11.01   | 13.66    | 0.9350 | 0.6825 | 1.0039 |
| Al      | 0.30  | 0.04 | 0.20  | 8.94    | 17.29    | 0.9393 | 0.7815 | 1.0066 |
| Si      | 0.26  | 0.04 | 0.17  | 6.73    | 15.74    | 0.9435 | 0.8511 | 1.0107 |
| S       | 2.07  | 0.06 | 1.19  | 4.16    | 85.66    | 0.9513 | 0.9311 | 1.0244 |
| Cl      | 1.03  | 0.06 | 0.53  | 5.40    | 36.91    | 0.9550 | 0.9479 | 1.0365 |
| K       | 4.41  | 0.08 | 2.08  | 4.35    | 124.07   | 0.9625 | 0.9729 | 1.0672 |
| Ca      | 19.16 | 0.10 | 8.79  | 3.55    | 411.08   | 0.9661 | 0.9753 | 1.0142 |
| Cu      | 7.41  | 0.15 | 2.14  | 7.26    | 209.00   | 0.9276 | 0.5106 | 1.0000 |





**Figure S37:** Element maps showing the elements with the highest concentrations detected by EDX within the region of interest. The corresponding EDX spectrum is shown in Figure S38, and the elemental composition is presented in Table S3. The aggregates of the amorphous particles (see Figure S34) mainly consist of oxygen, calcium, and carbon, and are partially embedded in a layer of dried potassium sulfate. The strong silicon signal detected originates from the silicon wafer on which the sample was placed.

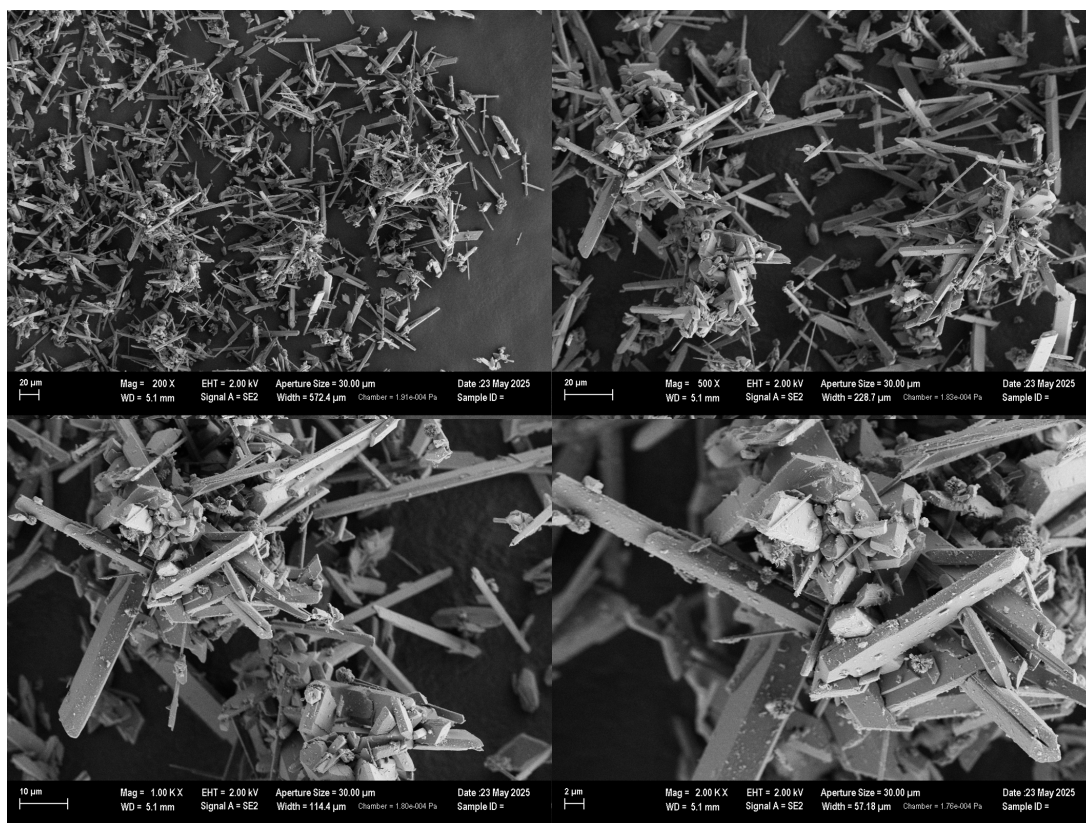


**Figure S38:** Spectrum of the EDX measurement in the highlighted area in Figure S37. The elemental composition is presented in Table S3. Individual element maps for each identified element can be found in Figure S37.

**Table S3:** Elemental composition of the EDX analysis shown in Figure S37. Listed are weight percent (wt.%), minimum detection limit (MDL), atomic percent (at.%), percentage error (Error %), net intensity (Net Int.), and the detection parameters R, A, and F for every element detected in Figure S38.

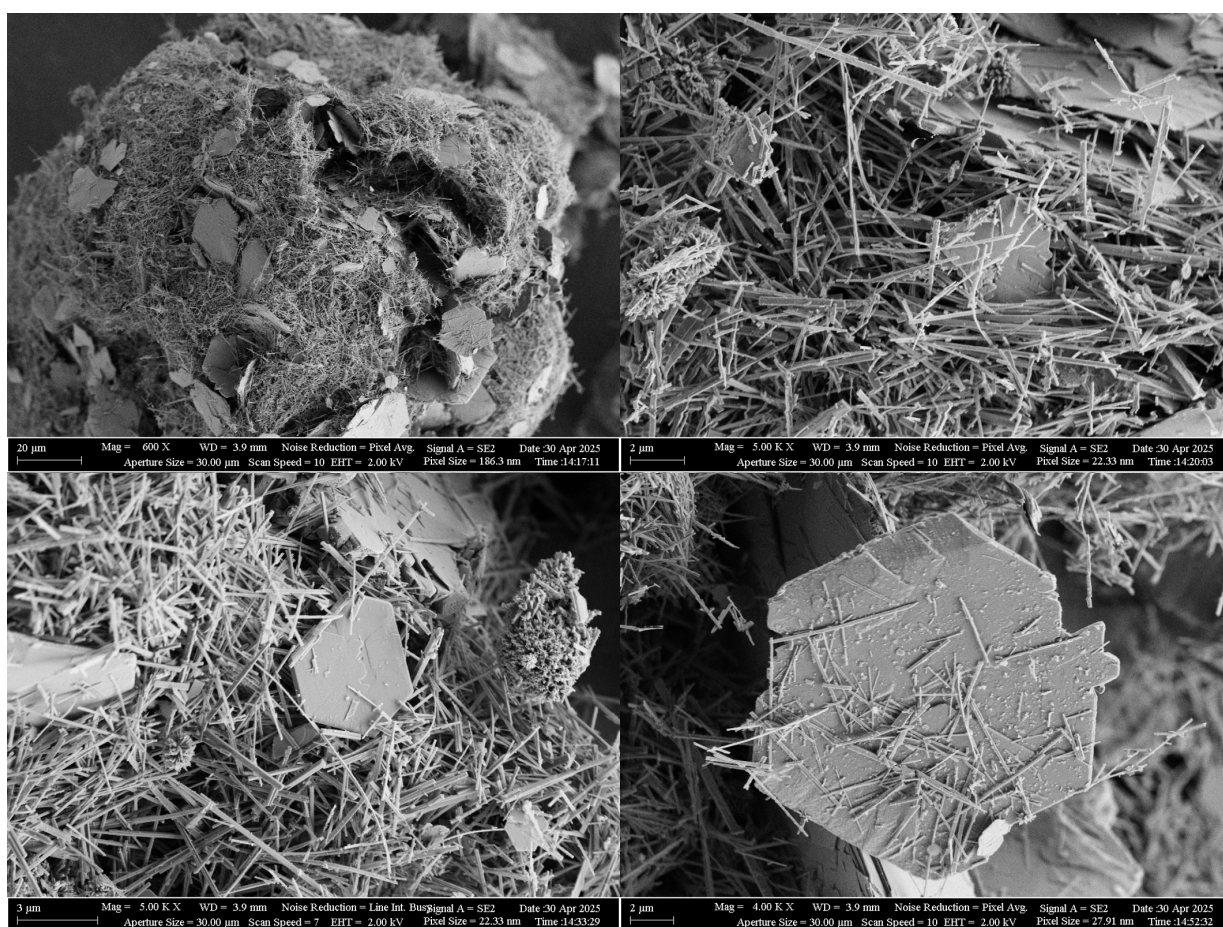
| Element | wt.%  | MDL  | at.%  | Error % | Net Int. | R      | A      | F      |
|---------|-------|------|-------|---------|----------|--------|--------|--------|
| C       | 7.87  | 0.21 | 16.00 | 11.72   | 59.63    | 0.8890 | 0.0893 | 1.0000 |
| O       | 9.08  | 0.07 | 13.85 | 8.84    | 287.75   | 0.9030 | 0.3222 | 1.0000 |
| Na      | 0.16  | 0.03 | 0.17  | 7.46    | 13.02    | 0.9192 | 0.7406 | 1.0158 |
| Si      | 73.88 | 0.03 | 64.21 | 2.90    | 4584.14  | 0.9337 | 0.9281 | 1.0029 |
| S       | 1.27  | 0.04 | 0.97  | 5.52    | 43.22    | 0.9425 | 0.8034 | 1.0065 |
| Cl      | 0.59  | 0.05 | 0.40  | 6.88    | 17.92    | 0.9467 | 0.8569 | 1.0095 |
| K       | 2.93  | 0.05 | 1.83  | 4.55    | 72.02    | 0.9551 | 0.9244 | 1.0157 |
| Ca      | 4.21  | 0.06 | 2.57  | 4.33    | 84.09    | 0.9594 | 0.9415 | 1.0128 |

### S3.3 Precipitates from the precipitation experiments

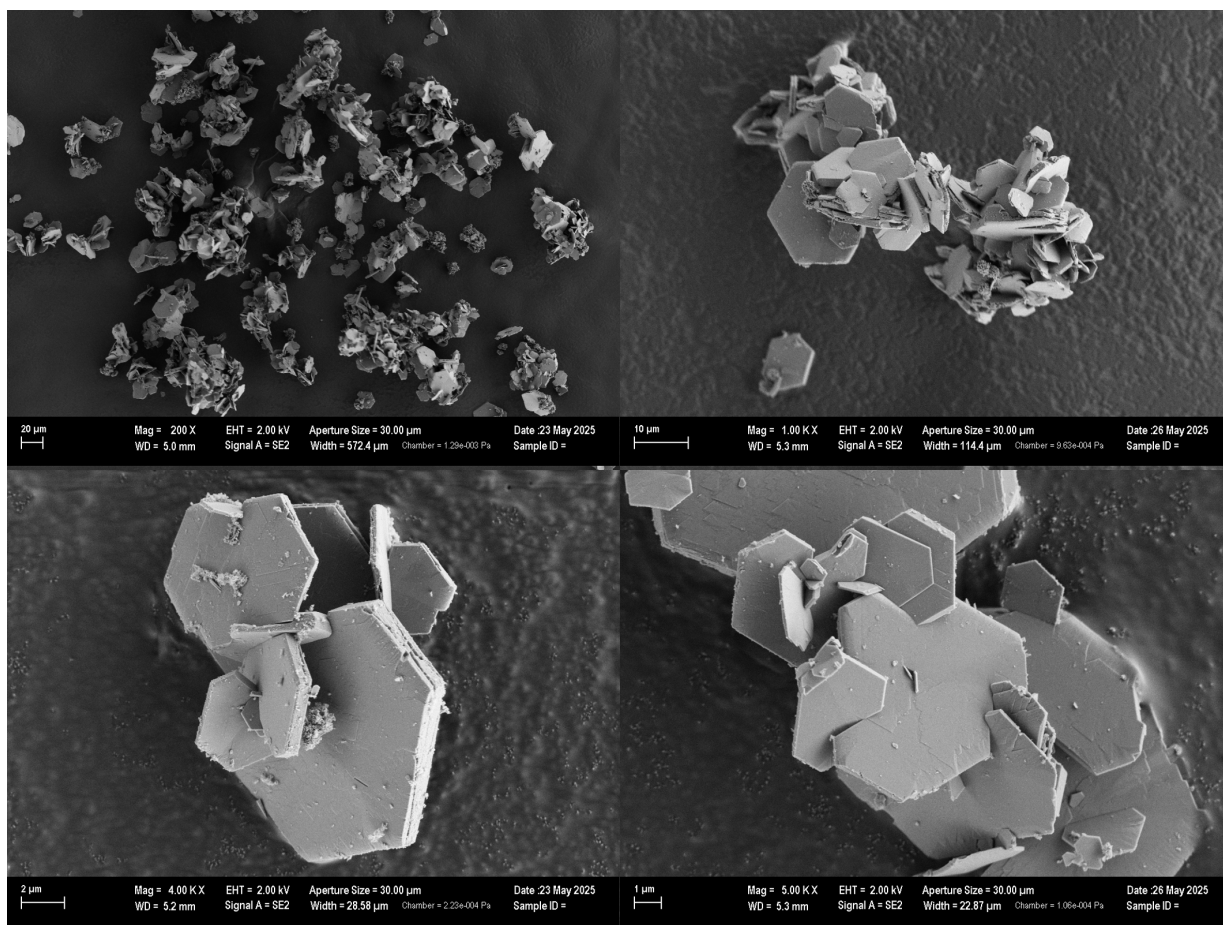


**Figure S39:** SEM images of the isolated precipitate from the precipitation experiment at 25 °C, in which the cementitious pore solution was separated by dead-end filtration after 1 min. Only gypsum precipitated as acicular to prismatic crystals, elongated along the crystallographic c-axis [001].

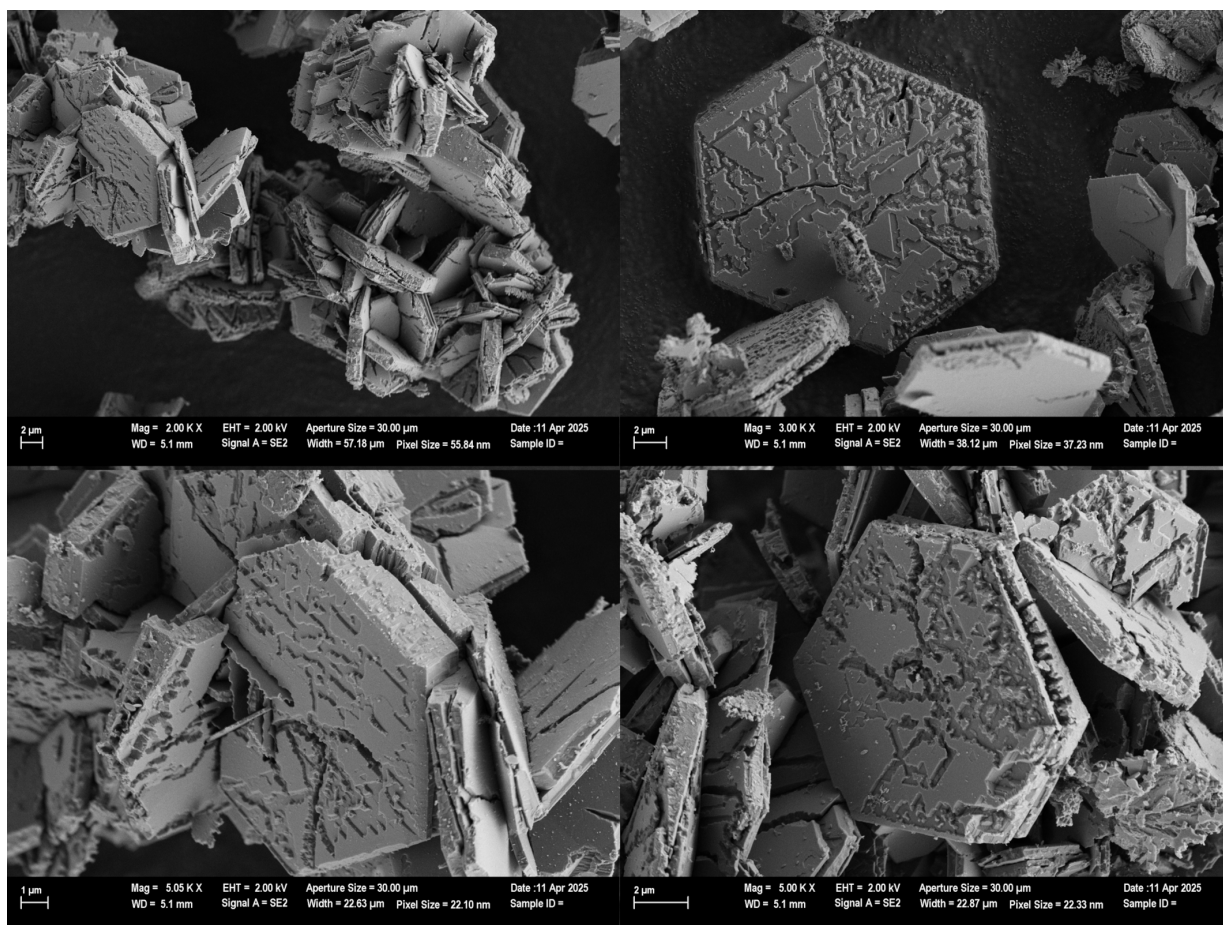




**Figure S40:** SEM images of the isolated precipitate from the precipitation experiment at 25 °C, in which the cementitious pore solution was separated by dead-end filtration after 15 min. CH and gypsum co-crystallized.

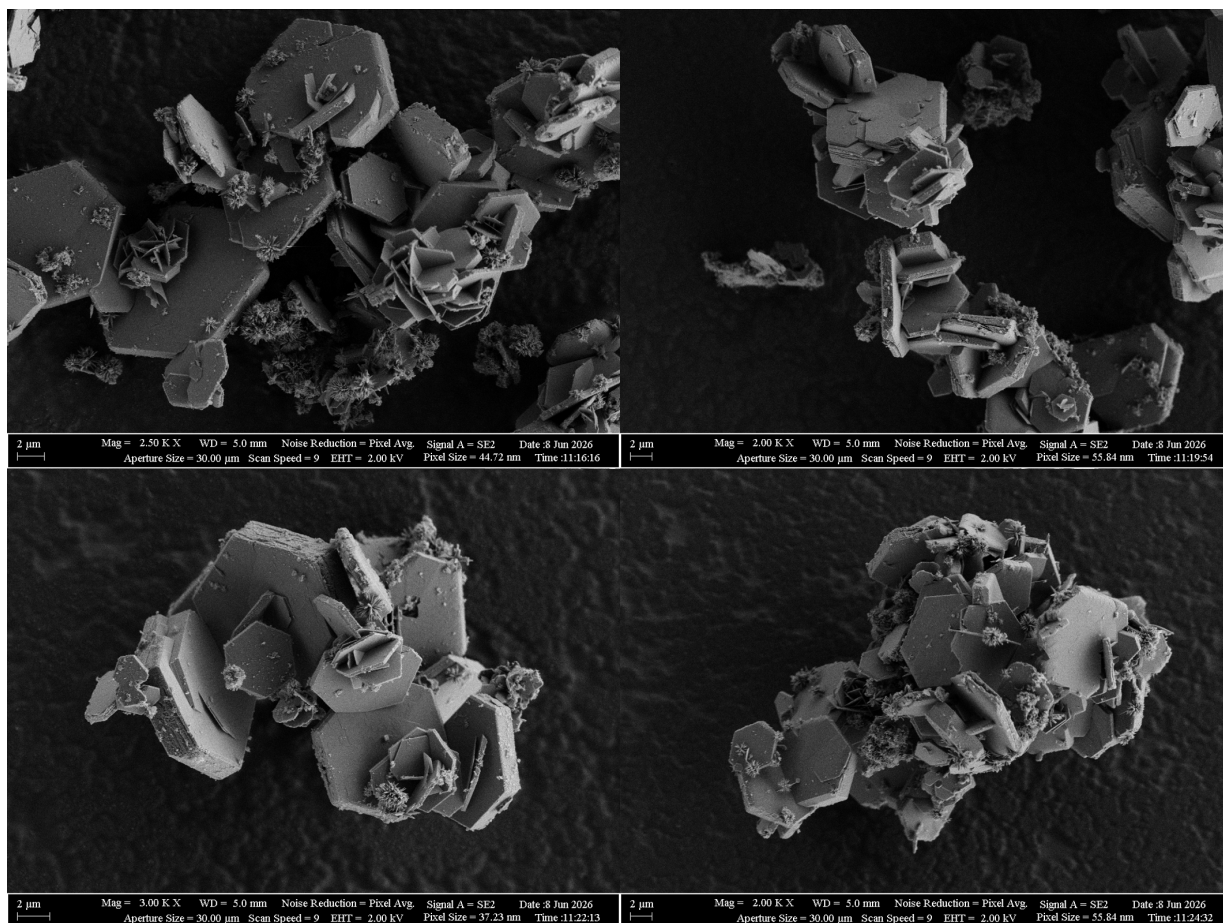


**Figure S41:** SEM images of the isolated precipitate from the precipitation experiment at 25 °C, in which the cementitious pore solution was separated by dead-end filtration after 60 min. The CH precipitated as hexagonal crystals with prism-shaped morphology.

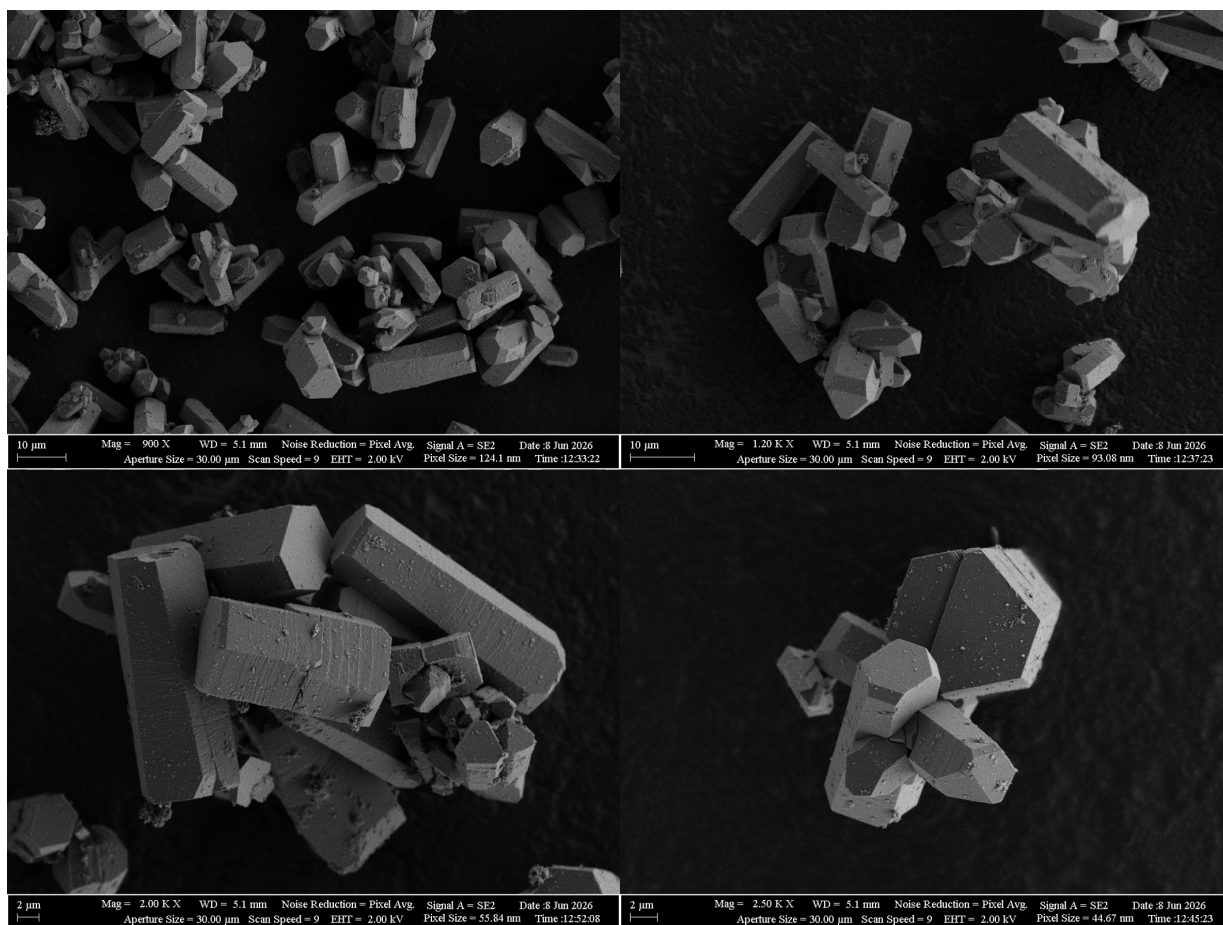


**Figure S42:** SEM images of the isolated precipitate from the precipitation experiment at 50 °C, in which the cementitious pore solution was separated by dead-end filtration after 15 min. The hexagonal portlandite crystals are superficially eroded because the precipitate was washed with water instead of a saturated CH solution.

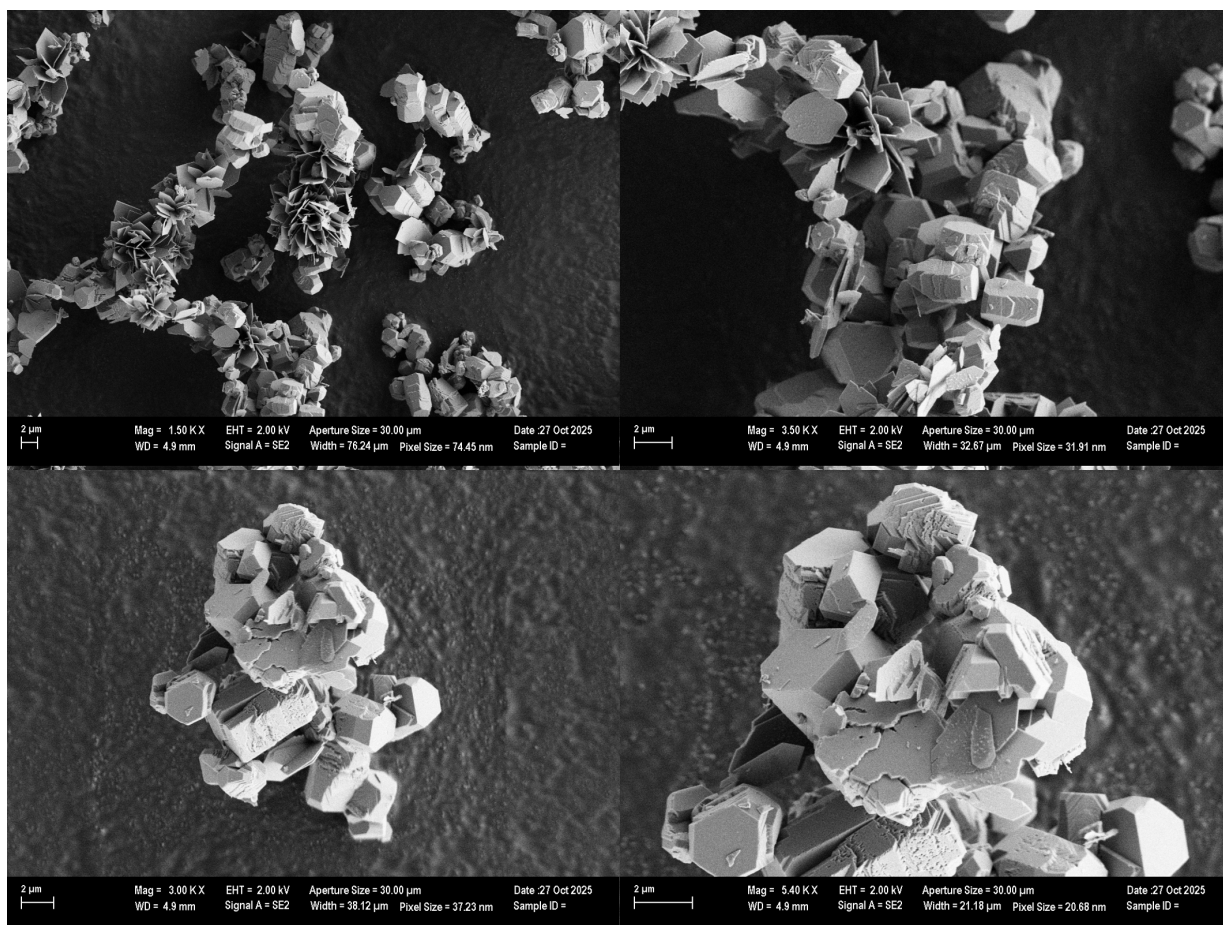




**Figure S43:** SEM images of the precipitate formed during precipitation experiments conducted at 45 °C in a nitrogen atmosphere. The cementitious pore solution was separated by dead-end filtration 15 min after hydration started. After separation, 30 mmol/L of soluble alkali sulfates ( $\text{Na}_2\text{SO}_4$  and  $\text{K}_2\text{SO}_4$ ) was added to the pore solution to increase its sulfate concentration. Portlandite precipitated as flat hexagonal platelets, together with small amounts of gypsum.

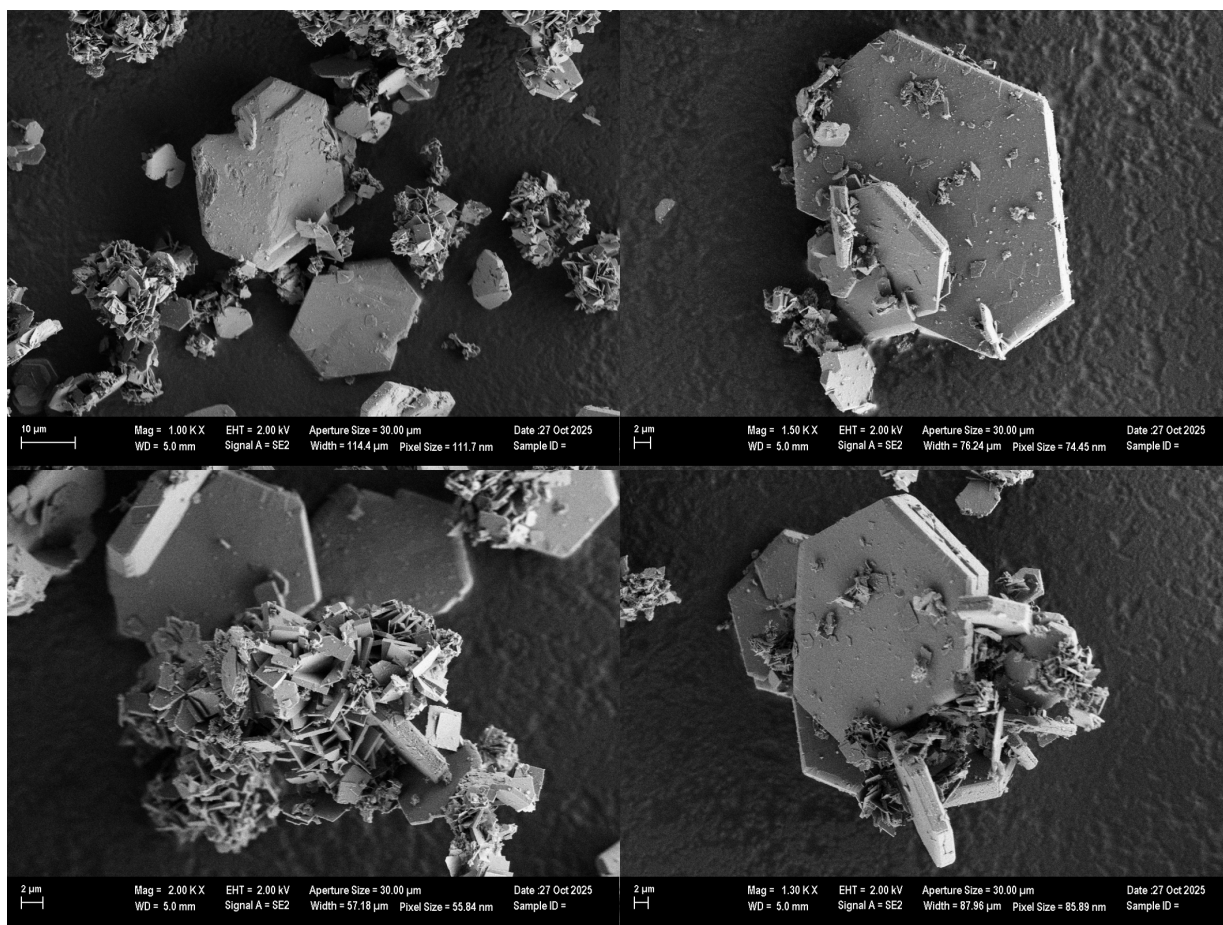


**Figure S44:** SEM images of the precipitate formed during precipitation experiments conducted at 45 °C in a nitrogen atmosphere. The cementitious pore solution was separated by dead-end filtration 15 min after hydration started. After separation, 40 mmol/L of BaSO<sub>4</sub> was precipitated by adding BaCl<sub>2</sub>·2 H<sub>2</sub>O to the pore solution to reduce its sulfate concentration. Portlandite precipitated as elongated prismatic columns.



**Figure S45:** SEM images of the isolated precipitate from the precipitation experiment at 25 °C, in which the pore solution of pure  $C_3S$  was separated by dead-end filtration after 15 min. The portlandite crystals exhibit a prismatic habit, elongated along the crystallographic c-axis [001], with a hexagonal base.





**Figure S46:** SEM images of the isolated precipitate from the precipitation experiment at 25 °C, in which the pore solution of a mixture of  $\text{C}_3\text{S}$  (95 wt.%) and gypsum (5 wt.%) was separated by dead-end filtration after 15 min. The hexagonal portlandite crystals display a plate-like habit.

## S4 Composition of the cementitious pore solution

The composition of the pore solutions, separated by dead-end filtration at various times after the start of hydration, was analyzed by measuring the ion concentration in solution using ICP-OES. ICP-OES measurements were performed using a 5800 Series ICP-OES instrument (*Agilent Technologies*, Santa Clara, CA, USA). Before each measurement, the tubes were rinsed with approximately 3% HNO<sub>3</sub> for 25 s, and the respective sample was then loaded using an autosampler. Each sample was stabilized for 15 s before being measured three times for 10 s each in radial mode (observation height: 8 mm; coil power: 1.2 kW). Aluminum, iron, and silicon were measured in axial mode (coil power: 1.2 kW). All samples were diluted to max. 50 mg/L with 6 M HNO<sub>3</sub> and DI-H<sub>2</sub>O. After dilution, the samples were immediately filtered through a syringe filter with a poly(ether sulfone) (PES) membrane (pore size 0.22 µm). The samples were stored at 4 °C until measurement.

Before sample measurement, the instrument was calibrated using a multipoint calibration procedure: calibration standards with concentrations of 50, 10, 1, and 0.1 mg/L were prepared by diluting a 1000 mg/L multi-element standard (ARISTAR Multi-element calibration standard IV for ICP, *VWR Chemicals*) and single-element standards for aluminum (Aluminum ICP Standard, *VWR Chemicals*), calcium (Calcium, plasma standard solution, Specpure, *Thermo Fisher Scientific*), silicon (Silicon Standard for ICP, *Sigma-Aldrich*) and sulfur (Sulfur Standard for ICP, *Sigma-Aldrich*) in DI-H<sub>2</sub>O and 6 M HNO<sub>3</sub>. The evaluated wavelengths for the ICP-OES measurements (Al: 396.152, Ca: 317.933, Fe: 259.940, K: 766.491, Mg: 279.553, Na: 588.995, S: 181.972, Si: 288.158) were chosen according to the optimal conditions for cement pore solutions reported by Caruso *et al.* [21].

The pH value of the pore solution was measured with a pH electrode InLab Micro Pro-ISM connected to an EasyFive instrument (both by *Mettler Toledo*, Greifensee, Switzerland). The pH electrode was calibrated before the measurement with three NIST/DIN pH buffer solutions according to DIN 19266 (pH = 6.865, 9.180 and 12.454). Based on this data, the supersaturation index of different hydrate phases was calculated using the Reaktoro framework [22] and the CEMDATA18 database [23]. The results are presented in Table S4 and Table S5.

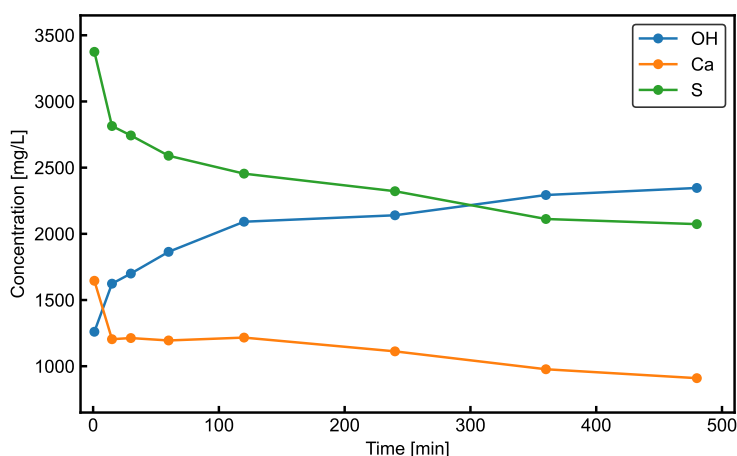
**Table S4:** pH-values, the concentrations of specific ions (Al, Ca, Fe, K, Mg, Na, S, Si) in the pore solutions, separated by dead-end filtration at various times ( $t_{sep}$ ) after the start of hydration, and the calculated supersaturation indices for ettringite (AFt), monosulfate (AFm), portlandite (CH), and gypsum (Gp).

| $t_{sep}$<br>[min] | pH    | Al<br>[mg/L] | Ca<br>[mg/L] | Fe<br>[mg/L] | K<br>[mg/L] | Mg<br>[mg/L] | Na<br>[mg/L] | S<br>[mg/L] | Si<br>[mg/L] | AFt  | AFm  | CH   | Gp    |
|--------------------|-------|--------------|--------------|--------------|-------------|--------------|--------------|-------------|--------------|------|------|------|-------|
| 1                  | 12.87 | 0.28         | 1645.40      | 0.33         | 6026.17     | 0.07         | 503.92       | 3374.74     | 1.55         | 8.08 | 2.25 | 0.45 | 0.27  |
| 15                 | 12.98 | 0.18         | 1204.03      | 0.17         | 6185.30     | 0.05         | 520.87       | 2814.43     | 2.33         | 7.39 | 1.80 | 0.55 | 0.09  |
| 30                 | 13.00 | 0.05         | 1212.72      | 0.16         | 6179.25     | 0.04         | 527.47       | 2743.16     | 2.28         | 6.32 | 0.75 | 0.60 | 0.08  |
| 60                 | 13.04 | 0.12         | 1194.50      | 0.20         | 6221.30     | 0.06         | 532.06       | 2589.97     | 2.36         | 7.17 | 1.66 | 0.67 | 0.05  |
| 120                | 13.09 | 0.19         | 1216.21      | 0.14         | 6251.21     | 0.06         | 537.20       | 2454.70     | 2.27         | 7.65 | 2.21 | 0.77 | 0.02  |
| 240                | 13.10 | 0.26         | 1112.27      | 0.17         | 6273.58     | 0.06         | 536.99       | 2321.99     | 2.31         | 7.77 | 2.39 | 0.76 | −0.03 |
| 360                | 13.13 | 0.18         | 977.08       | 0.16         | 6302.63     | 0.05         | 555.35       | 2112.08     | 2.29         | 7.20 | 1.97 | 0.76 | −0.12 |
| 480                | 13.14 | 0.18         | 909.75       | 0.14         | 6397.24     | 0.05         | 578.41       | 2073.34     | 2.31         | 7.00 | 1.85 | 0.75 | −0.16 |

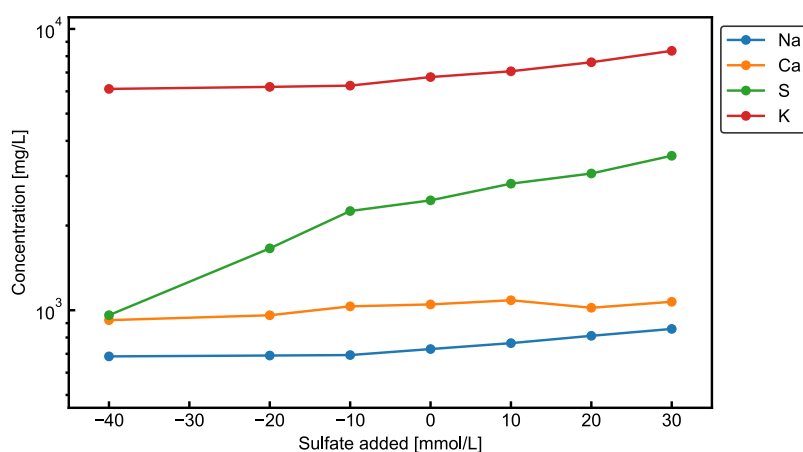
**Table S5:** pH-values, the concentrations of specific ions (Ca, K, Na, S) in the pore solutions, separated by dead-end filtration 15 min after the start of hydration, whose sulfate concentration was artificially modified by adding alkali sulfates ( $\text{Na}_2\text{SO}_4$  and  $\text{K}_2\text{SO}_4$ ) or by precipitating  $\text{BaSO}_4$  through the addition of  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ , as well as the calculated supersaturation indices for portlandite (CH) and gypsum (Gp).

| $\Delta \text{SO}_4^{2-}$<br>[mmol/L] | $\text{Na}_2\text{SO}_4$<br>[mmol/L] | $\text{K}_2\text{SO}_4$<br>[mmol/L] | $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$<br>[mmol/L] | pH    | Ca<br>[mg/L] | K<br>[mg/L] | Na<br>[mg/L] | S<br>[mg/L] | CH   | Gp    |
|---------------------------------------|--------------------------------------|-------------------------------------|-------------------------------------------------------|-------|--------------|-------------|--------------|-------------|------|-------|
| 30                                    | 3.75                                 | 26.25                               | 0                                                     | 12.80 | 1071.78      | 8358.24     | 858.22       | 3540.68     | 0.09 | −0.05 |
| 20                                    | 2.50                                 | 17.50                               | 0                                                     | 12.90 | 1020.60      | 7613.67     | 811.20       | 3062.94     | 0.27 | −0.12 |
| 10                                    | 1.25                                 | 8.75                                | 0                                                     | 13.00 | 1085.19      | 7071.39     | 763.94       | 2817.85     | 0.57 | −0.17 |
| 0                                     | 0                                    | 0                                   | 0                                                     | 12.99 | 1067.75      | 6280.63     | 688.20       | 2643.94     | 0.47 | −0.15 |
| −10                                   | 0                                    | 0                                   | 10                                                    | 12.98 | 1032.49      | 6287.42     | 692.94       | 2252.54     | 0.45 | −0.21 |
| −20                                   | 0                                    | 0                                   | 20                                                    | 13.01 | 959.80       | 6222.92     | 690.34       | 1659.70     | 0.50 | −0.35 |
| −40                                   | 0                                    | 0                                   | 40                                                    | 12.97 | 922.18       | 6120.29     | 685.49       | 960.28      | 0.44 | −0.56 |





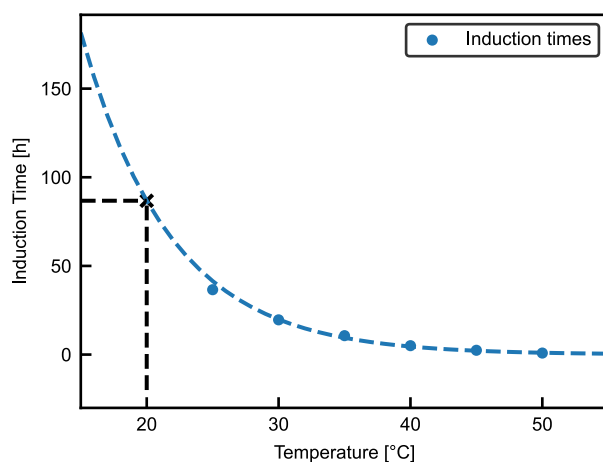
**Figure S47:** The concentrations of OH, Ca, and S ions in the pore solution change with the separation time. The experimentally determined values are listed in Table S4.



**Figure S48:** The concentrations of Na, Ca, S, and K ions in the pore solutions, separated by dead-end filtration 15 min after the start of hydration, whose sulfate concentrations were artificially modified by adding alkali sulfates ( $\text{Na}_2\text{SO}_4$  and  $\text{K}_2\text{SO}_4$ ) or by precipitating  $\text{BaSO}_4$  through the addition of  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ . While the concentration of S increases linearly, the concentrations of K and Na increase only when alkali sulfates are added, whereas the concentration of Ca remains nearly unchanged. The experimentally determined values are listed in Table S5.

## S5 Induction times for calcium hydroxide precipitation

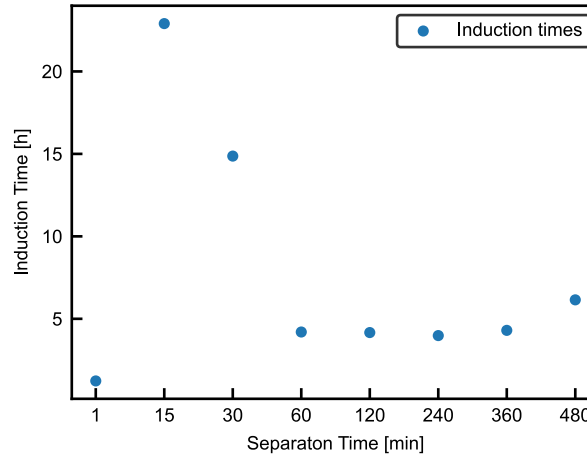
The induction times for the precipitation of CH from cementitious pore solutions were determined by measuring the conductivity of the solutions, which were separated at different times after cement hydration started, at 30 °C over time. Before these measurements, the temperature dependence of the induction time was established (see Figure S49 and Table S6), and based on these results, the temperature of 30 °C was chosen for further experiments (see Figure S50 and Table S7). Table S8 presents the induction times for CH precipitation from  $C_3S$  pore solutions measured at 25 °C (see Figure S51), and Table S9 displays the induction times for CH precipitation at different sulfate concentrations in cementitious pore solutions, measured at 45 °C. The induction time is defined as the point at which conductivity has decreased by half of its total drop relative to the stable conductivity recorded during the induction period. Conductivity was continuously monitored until a precipitate formed and the conductivity stabilized. The resulting solid was subsequently separated, washed, dried, and characterized by SEM, TGA-MS, PXRD, and FTIR (see section S3.3 and S6-S8).



**Figure S49:** Induction times for CH precipitation from the cementitious pore solution as a function of the temperature. The induction time decreases exponentially with increasing temperature. In all experiments, the cementitious pore solution was separated by dead-end filtration 15 min after hydration started. The determined induction times are listed in Table S6. The extrapolated induction time at 20 °C is 86.76 h.

**Table S6:** Induction times ( $t_{\text{ind}}$ ) for CH precipitation from cementitious pore solutions at different temperatures ( $T$ ). The induction time measured at 30 °C differs from the induction time listed for 15 min in Table S7 because induction time measurements are subject to significant fluctuations caused by the inherently statistical nature of nucleation processes.

| $T$ [°C] | $t_{\text{ind}}$ [h] |
|----------|----------------------|
| 25       | 36.55                |
| 30       | 19.60                |
| 35       | 10.67                |
| 40       | 5.02                 |
| 45       | 2.42                 |
| 50       | 0.85                 |

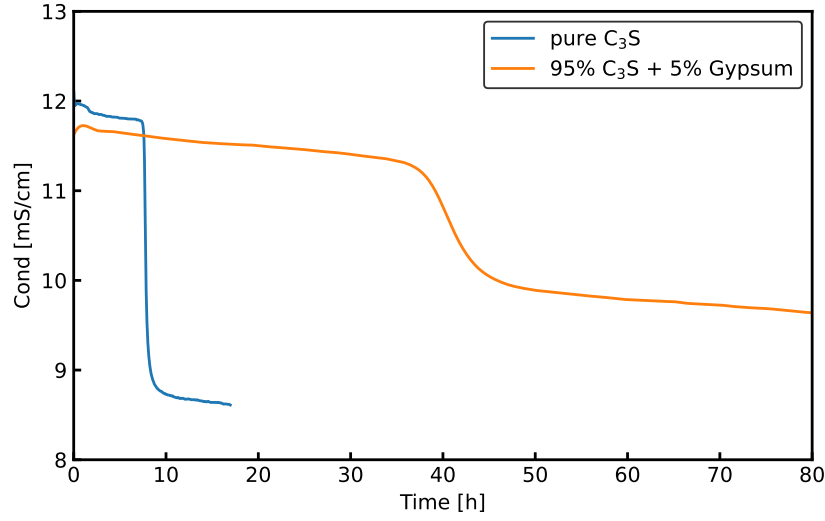


**Figure S50:** Induction times for CH precipitation from the cementitious pore solution as a function of the separation time. CH tends to precipitate earlier when the pore solution is separated later. The temperature was maintained at 30 °C in all experiments. The determined induction times are listed in Table S7.

**Table S7:** Induction times ( $t_{\text{ind}}$ ) for CH precipitation at 30 °C from cementitious pore solutions separated by dead-end filtration at different times ( $t_{\text{sep}}$ ) after the hydration started. The induction time measured at 15 min differs from the induction time listed for 30 °C in Table S6 because induction time measurements are subject to significant fluctuations caused by the inherently statistical nature of nucleation processes.

| $t_{\text{sep}}$ [min] | $t_{\text{ind}}$ [h] |
|------------------------|----------------------|
| 1                      | 1.23                 |
| 15                     | 22.90                |
| 30                     | 14.87                |
| 60                     | 4.20                 |
| 120                    | 4.17                 |
| 240                    | 3.98                 |
| 360                    | 4.30                 |
| 480                    | 6.15                 |





**Figure S51:** Induction times for CH precipitation from C<sub>3</sub>S pore solution separated 15 min after the start of hydration. In the first experiment (blue), pure C<sub>3</sub>S was hydrated at w/s = 1.0. In the second experiment (orange), 5 wt.% gypsum was mixed with C<sub>3</sub>S, before the resulting mixture was hydrated at w/s = 1.0. The temperature was maintained at 25 °C in both experiments. The determined induction times are listed in Table S8.

**Table S8:** Induction times ( $t_{\text{ind}}$ ) for CH precipitation at 25 °C from C<sub>3</sub>S pore solutions separated 15 min after the start of hydration. In the first experiment, pure C<sub>3</sub>S was hydrated at w/s = 1.0. In the second experiment, 5 wt.% gypsum was mixed with C<sub>3</sub>S, before the resulting mixture was hydrated at w/s = 1.0.

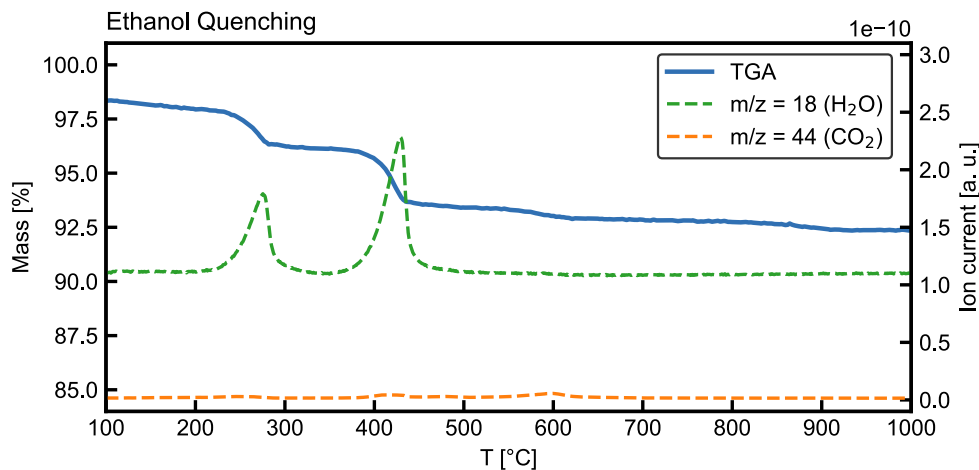
| Binder                           | $t_{\text{ind}}$ [h] |
|----------------------------------|----------------------|
| C <sub>3</sub> S                 | 7.82                 |
| C <sub>3</sub> S + 5 wt.% Gypsum | 41.07                |

**Table S9:** Induction times ( $t_{\text{ind}}$ ) for CH precipitation at 45 °C from cementitious pore solutions separated 15 min after the start of hydration and adjusted to different sulfate concentrations ( $c(\text{SO}_4^{2-})$ ).

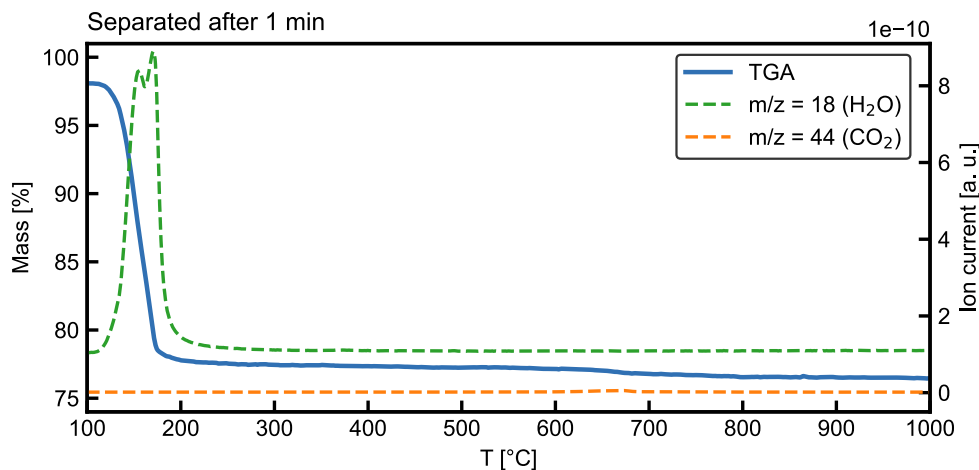
| $c(\text{SO}_4^{2-})$ [mmol/L] | $t_{\text{ind}}$ [h] |
|--------------------------------|----------------------|
| 30                             | 0.11                 |
| 52                             | 0.25                 |
| 70                             | 0.91                 |
| 82                             | 1.49                 |
| 88                             | 1.97                 |
| 96                             | 2.99                 |
| 110                            | 6.31                 |

## S6 TGA-MS

Thermogravimetric analysis was conducted on an STA 409 PC Luxx simultaneous thermal analyzer coupled to a QMS 403 C Aëolos quadro quadrupole mass spectrometer (both from *NETZSCH*, Selb, Germany) with a heated capillary inlet system ( $T_{\text{max}} = 300\text{ }^{\circ}\text{C}$ ). Samples of 10 mg were placed in an  $\text{Al}_2\text{O}_3$  crucible and heated at a rate of 10 K/min from 30  $^{\circ}\text{C}$  to 1000  $^{\circ}\text{C}$ . The measurements were performed under a constant flow of inert argon gas at a rate of 20 mL/min. The sample weight was continuously monitored as a function of temperature. Volatile gases produced during thermal degradation were directed to the mass spectrometer through a heated transfer line maintained at 240  $^{\circ}\text{C}$ . The mass spectrometer recorded the intensities of  $\text{H}_2\text{O}$  and  $\text{CO}_2$  ( $m/z = 18$  and 44).

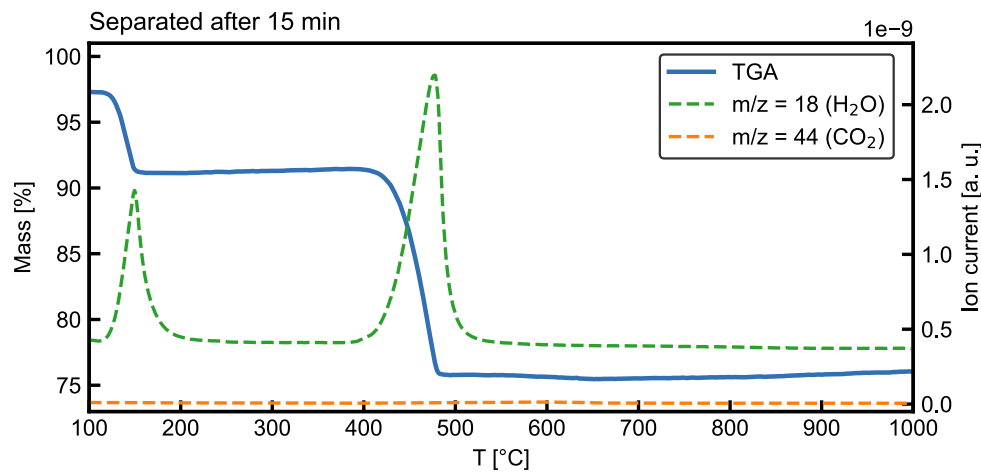


**Figure S52:** TGA curve for the precipitate formed after quenching the separated cementitious pore solution with ethanol (1:10). Between 240 and 290 °C, approximately 1.5% of the initial sample weight was lost due to the calcination of syngenite ( $\text{K}_2\text{Ca}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$ ) and approximately 2.2% of the initial sample weight was lost due to the calcination of ACH between 390 and 440 °C [24].

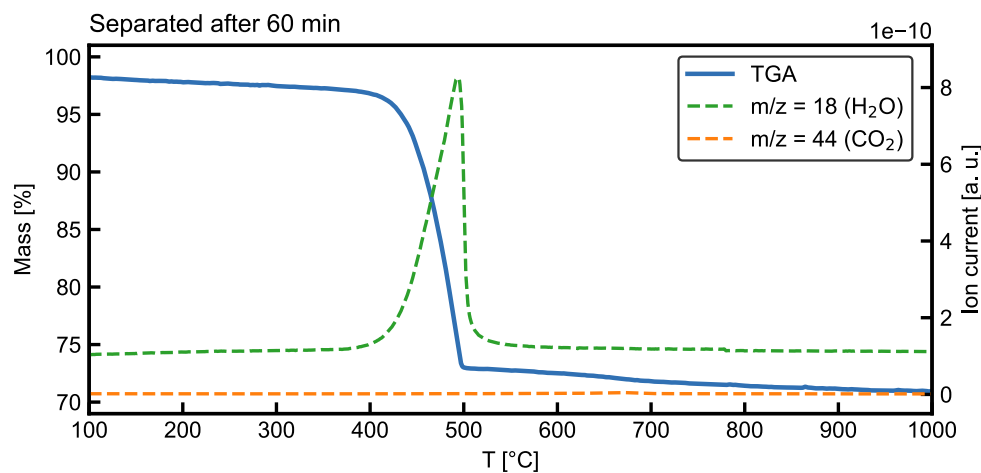


**Figure S53:** TGA curve for the precipitate formed during precipitation experiments conducted at 25 °C in a nitrogen atmosphere, when the cementitious pore solution was separated by dead-end filtration 1 min after hydration started. Between 100 and 200 °C, approximately 20% of the initial sample weight was lost due to the calcination of gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) [24].

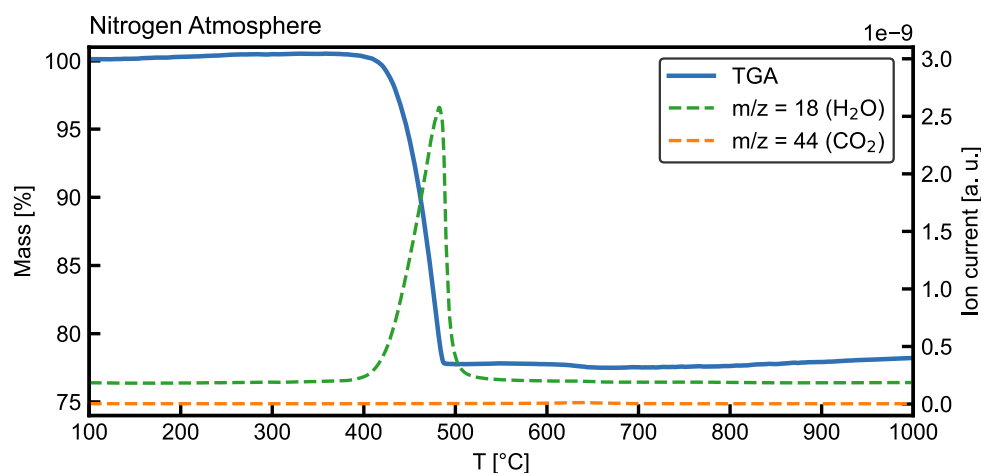




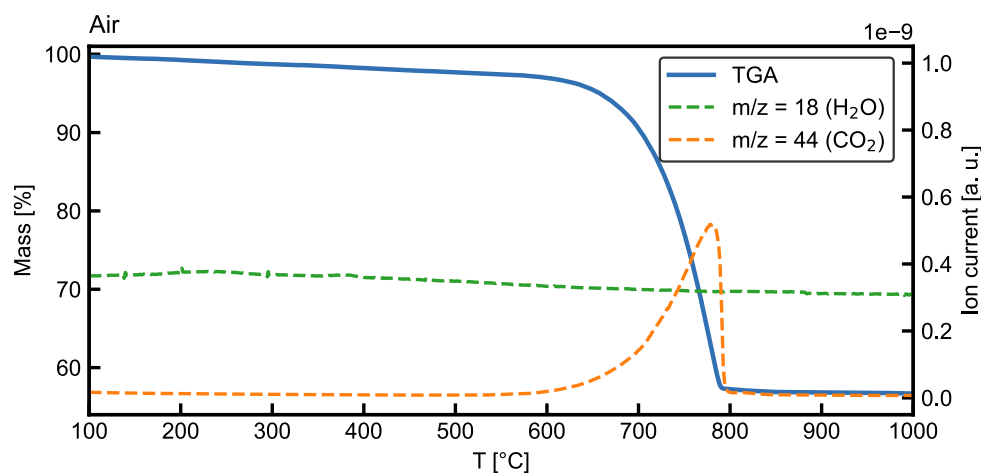
**Figure S54:** TGA curve for the precipitate formed during precipitation experiments conducted at 25 °C in a nitrogen atmosphere. The cementitious pore solution was separated by dead-end filtration 15 min after hydration started. Between 100 and 200 °C, approximately 8% of the initial sample weight was lost due to the calcination of gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ). Between 400 and 500 °C, approximately 16% of the initial sample weight was lost due to the calcination of portlandite ( $\text{Ca}(\text{OH})_2$ ) [24].



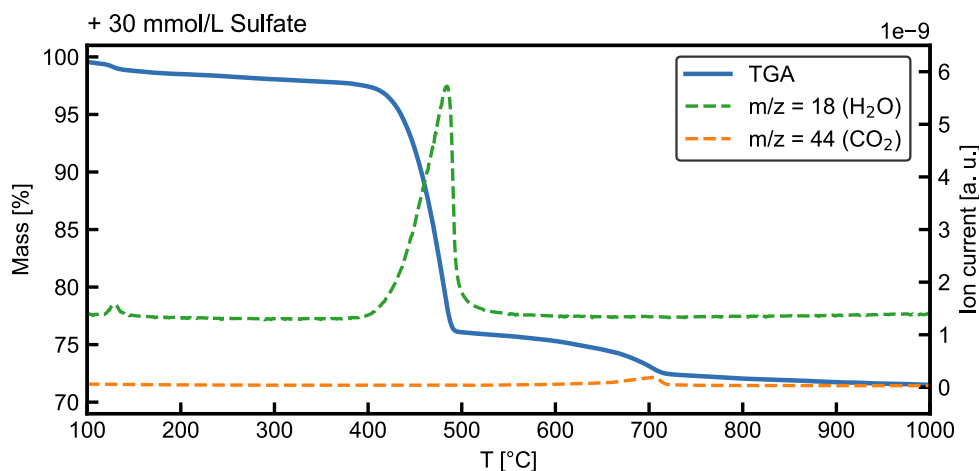
**Figure S55:** TGA curve for the precipitate formed during precipitation experiments conducted at 25 °C in a nitrogen atmosphere. The cementitious pore solution was separated by dead-end filtration 60 min after hydration started. Between 400 and 500 °C, approximately 26% of the initial sample weight was lost due to the calcination of portlandite ( $\text{Ca}(\text{OH})_2$ ) [24].



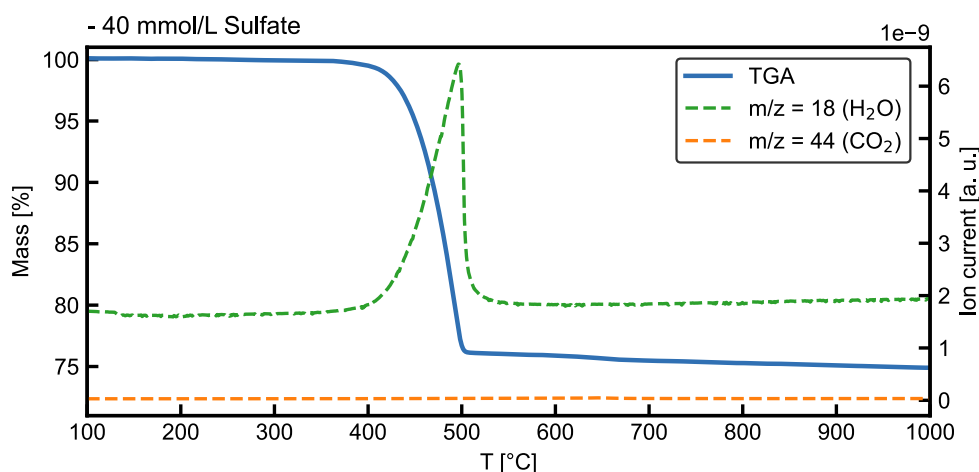
**Figure S56:** TGA curve for the precipitate formed during precipitation experiments conducted at 50 °C in a nitrogen atmosphere. The cementitious pore solution was separated by dead-end filtration 15 min after hydration started. Between 400 and 500 °C, approximately 22% of the initial sample weight was lost due to the calcination of portlandite ( $\text{Ca}(\text{OH})_2$ ) [24].



**Figure S57:** TGA curve for the precipitate formed during precipitation experiments conducted at 25 °C in air. The cementitious pore solution was separated by dead-end filtration 15 min after hydration started. Between 600 and 800 °C, approximately 42% of the initial sample weight was lost due to the calcination of calcite ( $\text{CaCO}_3$ ) [24].



**Figure S58:** TGA curve for the precipitate formed during precipitation experiments conducted at 45 °C in a nitrogen atmosphere. The cementitious pore solution was separated by dead-end filtration 15 min after hydration started. After separation, 30 mmol/L of soluble alkali sulfates ( $\text{Na}_2\text{SO}_4$  and  $\text{K}_2\text{SO}_4$ ) was added to the pore solution to increase its sulfate concentration. Between 100 and 200 °C, approximately 1% of the initial sample weight was lost due to the calcination of gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ). Between 400 and 500 °C, approximately 21% of the initial sample weight was lost due to the calcination of portlandite ( $\text{Ca}(\text{OH})_2$ ). Between 600 and 700 °C, approximately 2% of the initial sample weight was lost due to the calcination of calcite ( $\text{CaCO}_3$ ) [24].

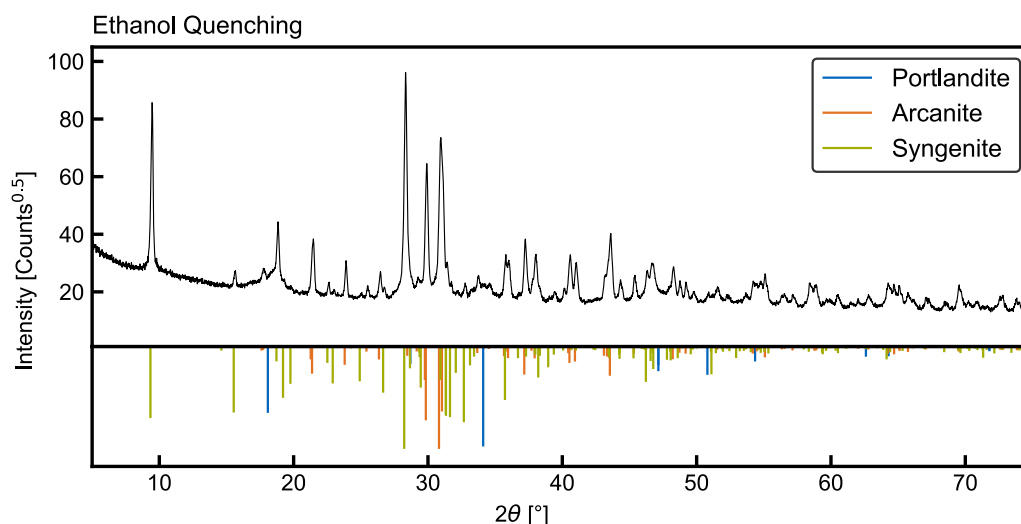


**Figure S59:** TGA curve for the precipitate formed during precipitation experiments conducted at 45 °C in a nitrogen atmosphere. The cementitious pore solution was separated by dead-end filtration 15 min after hydration started. After separation, 40 mmol/L of  $\text{BaSO}_4$  was precipitated by adding  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$  to the pore solution to reduce its sulfate concentration. Between 400 and 500 °C, approximately 23% of the initial sample weight was lost due to the calcination of portlandite ( $\text{Ca}(\text{OH})_2$ ) [24].

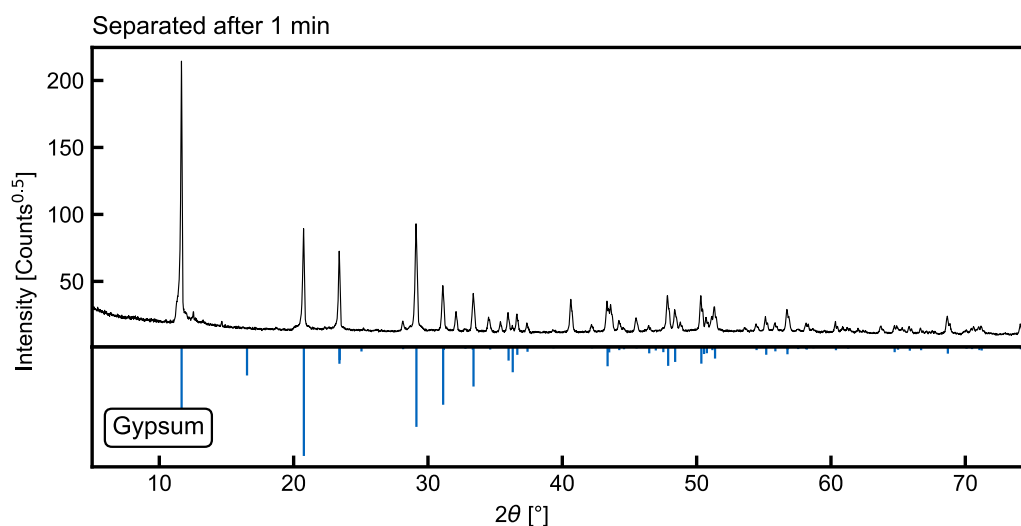


## S7 PXRD

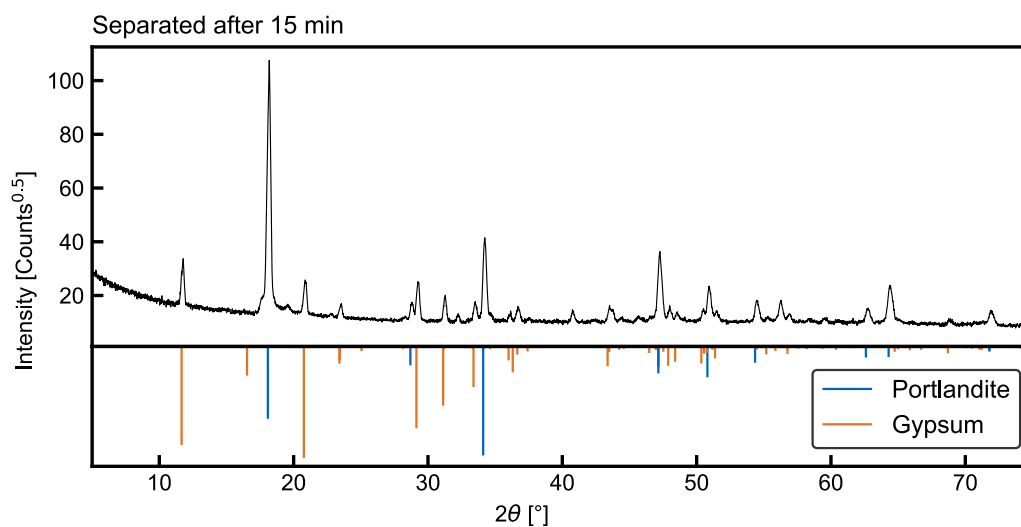
The PXRD measurements were conducted on a MiniFlex 600-C diffractometer (*Rigaku*, Tokyo, Japan) using Cu-K $\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ) and 5° Soller slits. The X-ray tube operated at 30 kV and 15 mA. The diffraction pattern was recorded in the  $2\theta$  range from 5° to 75° with a step width of 0.01° and a scan rate of 5°/min. The diffractogram was processed using the software Profex [25].



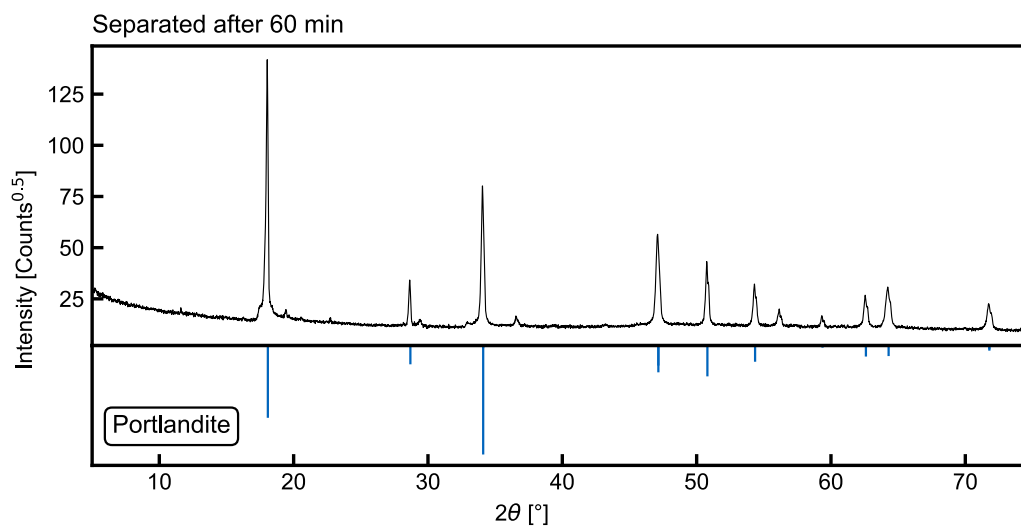
**Figure S60:** PXRD pattern of the precipitate formed after quenching the separated cementitious pore solution with ethanol (1:10). The observed distinct reflexes can be assigned to crystalline arcanite ( $\text{K}_2\text{SO}_4$ ) or syngenite ( $\text{K}_2\text{Ca}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$ ) [26, 27]. Additionally, very broad reflexes can be seen at the positions where the reflexes of portlandite ( $\text{Ca}(\text{OH})_2$ ) are expected [28].



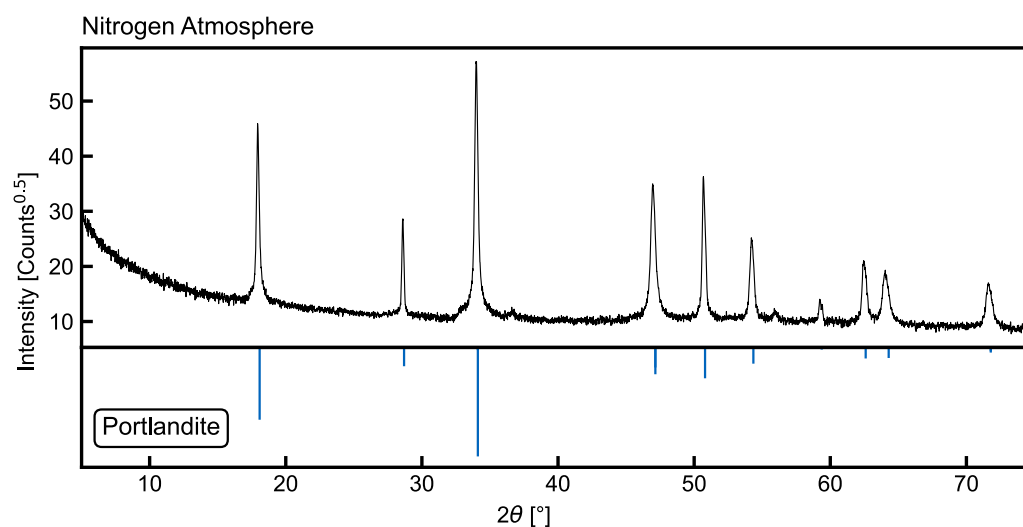
**Figure S61:** PXRD pattern of the precipitate formed during precipitation experiments conducted at 25 °C in a nitrogen atmosphere, when the cementitious pore solution was separated by dead-end filtration 1 min after hydration started. All observed reflexes can be assigned to crystalline gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) [29].



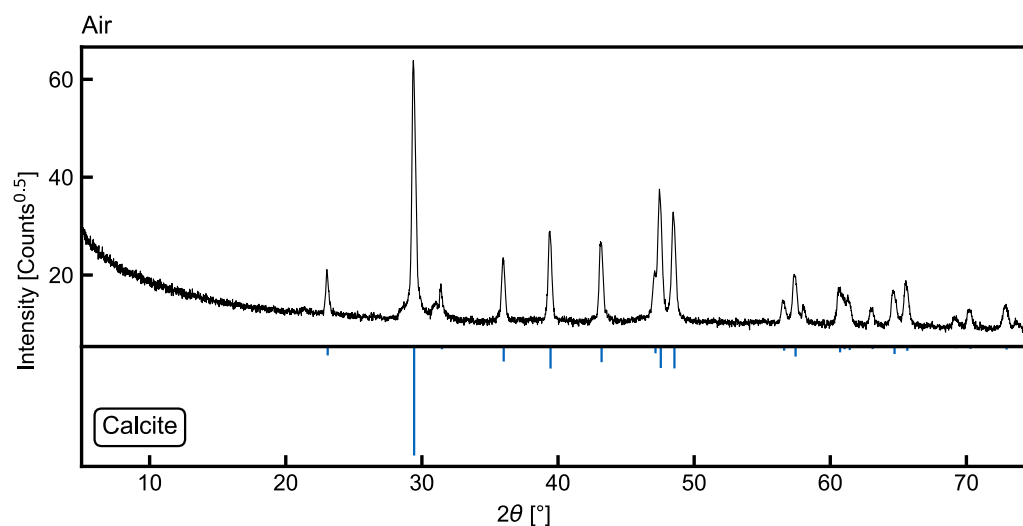
**Figure S62:** PXRD pattern of the precipitate formed during precipitation experiments conducted at 25 °C in a nitrogen atmosphere. The cementitious pore solution was separated by dead-end filtration 15 min after hydration started. All observed reflexes can be assigned to crystalline portlandite ( $\text{Ca}(\text{OH})_2$ ) and crystalline gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) [28, 29].



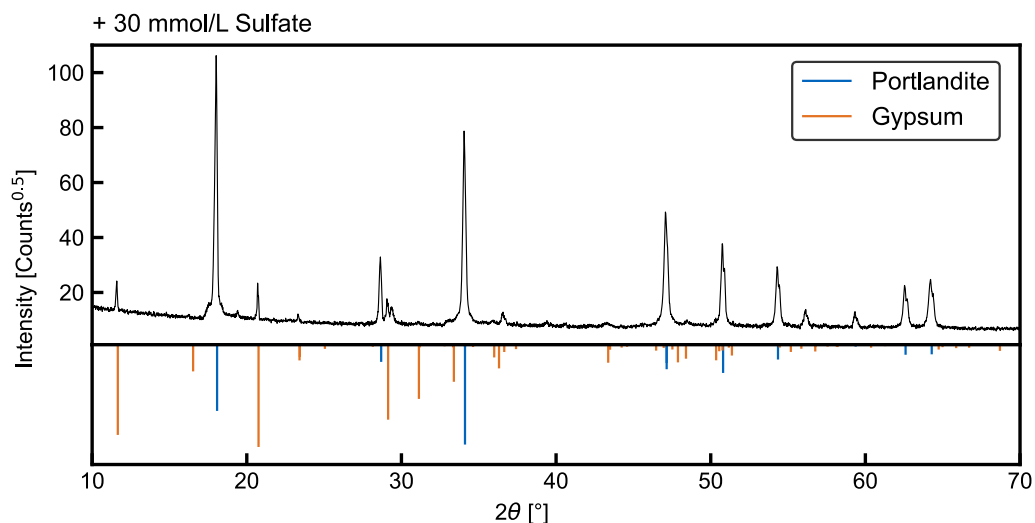
**Figure S63:** PXRD pattern of the precipitate formed during precipitation experiments conducted at 25 °C in a nitrogen atmosphere. The cementitious pore solution was separated by dead-end filtration 60 min after hydration started. All observed reflexes can be assigned to crystalline portlandite ( $\text{Ca}(\text{OH})_2$ ) [28].



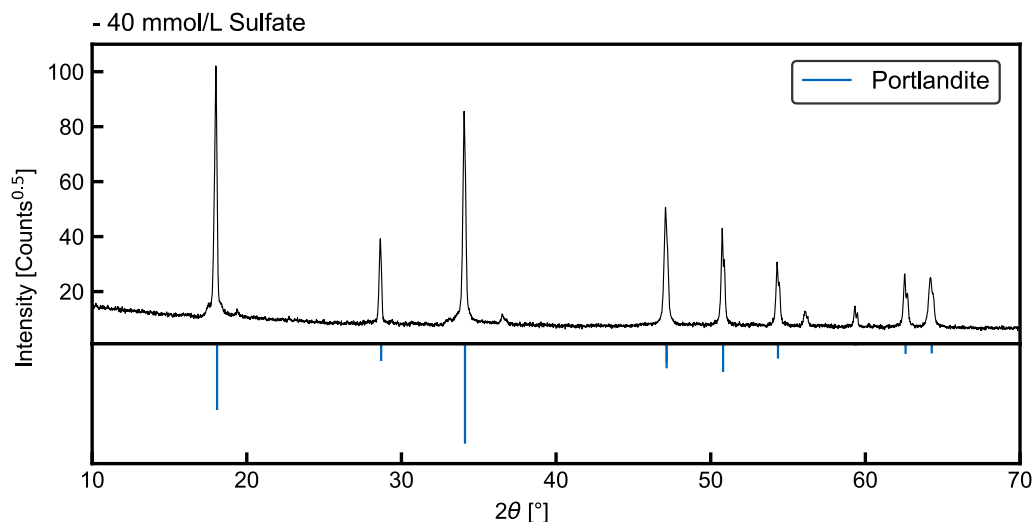
**Figure S64:** PXRD pattern of the precipitate formed during precipitation experiments conducted at 50 °C in a nitrogen atmosphere. The cementitious pore solution was separated by dead-end filtration 15 min after hydration started. All observed reflexes can be assigned to crystalline portlandite ( $\text{Ca}(\text{OH})_2$ ) [28].



**Figure S65:** PXRD pattern of the precipitate formed during precipitation experiments conducted at 25 °C in air. The cementitious pore solution was separated by dead-end filtration 15 min after hydration started. All observed reflexes can be assigned to crystalline calcite ( $\text{CaCO}_3$ ) [30].



**Figure S66:** PXRD pattern of the precipitate formed during precipitation experiments conducted at 45 °C in a nitrogen atmosphere. The cementitious pore solution was separated by dead-end filtration 15 min after hydration started. After separation, 30 mmol/L of soluble alkali sulfates ( $\text{Na}_2\text{SO}_4$  and  $\text{K}_2\text{SO}_4$ ) was added to the pore solution to increase its sulfate concentration. All observed reflexes can be assigned to crystalline portlandite ( $\text{Ca}(\text{OH})_2$ ) and crystalline gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) [28, 29].

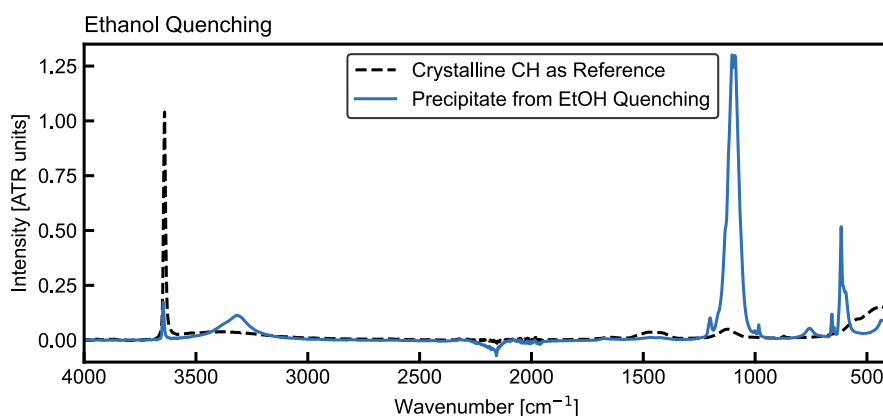


**Figure S67:** PXRD pattern of the precipitate formed during precipitation experiments conducted at 45 °C in a nitrogen atmosphere. The cementitious pore solution was separated by dead-end filtration 15 min after hydration started. After separation, 40 mmol/L of  $\text{BaSO}_4$  was precipitated by adding  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$  to the pore solution to reduce its sulfate concentration. All observed reflexes can be assigned to crystalline portlandite ( $\text{Ca}(\text{OH})_2$ ) [28].

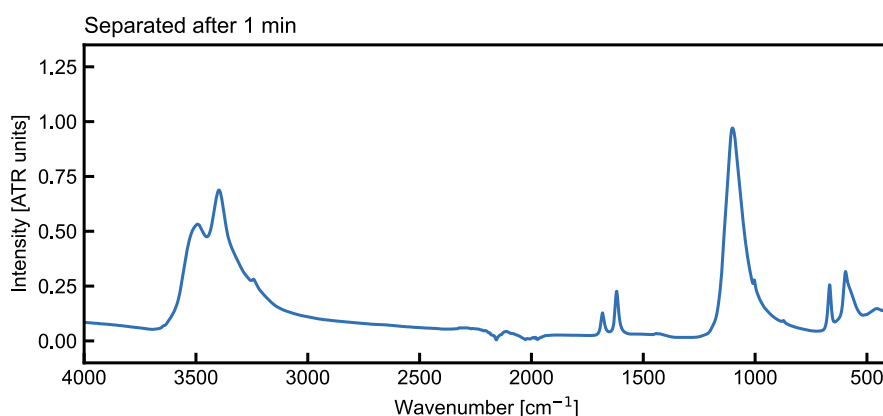


## S8 FTIR

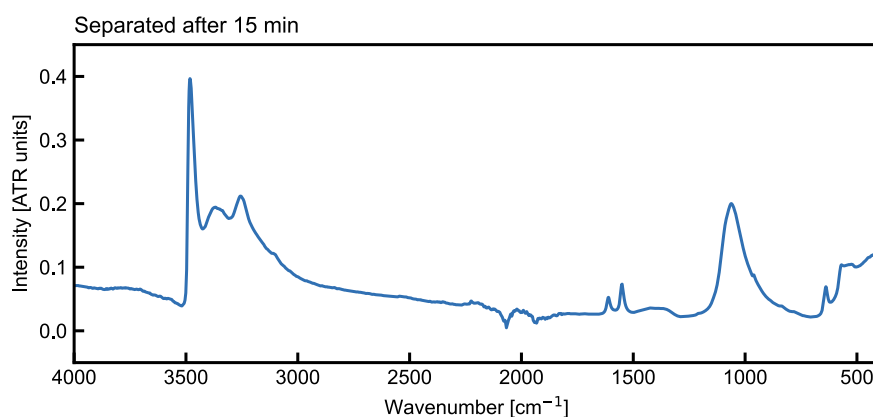
FTIR spectra were recorded in the range of 4000–450  $\text{cm}^{-1}$  on an FTIR spectrometer equipped with an attenuated total reflection (ATR) unit (Vertex 70, *Bruker*, Billerica, MA, USA) using the OPUS Software Version 7.5. The recorded spectra are the average of 32 scans and were obtained at a spectral resolution of 4  $\text{cm}^{-1}$ .



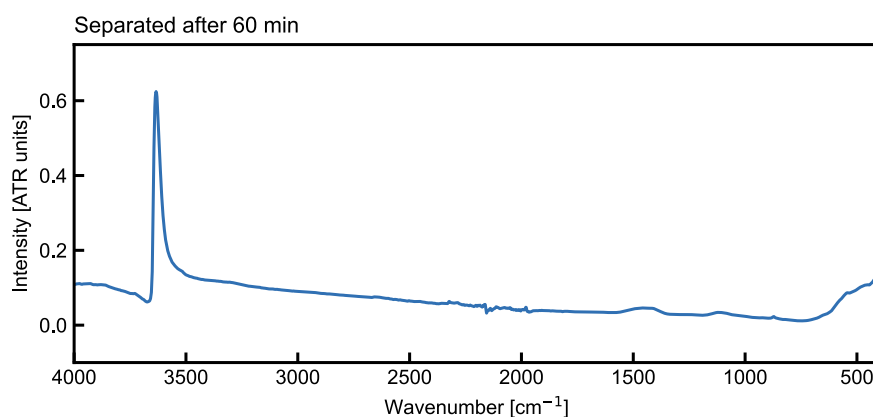
**Figure S68:** FTIR spectrum of the precipitate formed after quenching the separated cementitious pore solution with ethanol (1:10). The characteristic peaks at 650  $\text{cm}^{-1}$  and at 1185  $\text{cm}^{-1}$  correspond to the sulfate modes of crystalline arcanite ( $\text{K}_2\text{SO}_4$ ) and syngenite ( $\text{K}_2\text{Ca}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$ ) [31, 32]. The broad peak between 3200 and 3500  $\text{cm}^{-1}$  in the high-frequency region belongs to the OH-stretching vibration of the crystal water in the syngenite [32]. The additional peak at 3640  $\text{cm}^{-1}$  corresponds to the OH-stretching vibration of ACH. The stretching vibration occurs at similar values to the vibration found in crystalline CH.



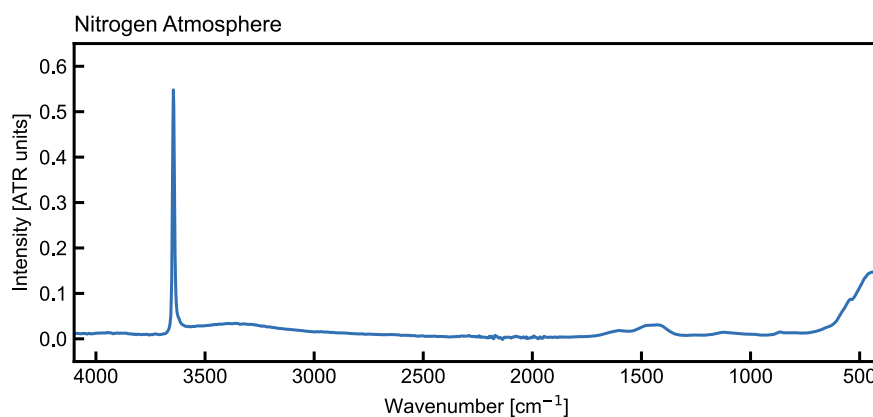
**Figure S69:** FTIR spectrum of the precipitate formed during precipitation experiments conducted at 25  $^{\circ}\text{C}$  in a nitrogen atmosphere, when the cementitious pore solution was separated by dead-end filtration 1 min after hydration started. The characteristic peak between 1100  $\text{cm}^{-1}$  corresponds to the strong sulfate stretching vibration of crystalline gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ). The two broad peaks between 3300 and 3600  $\text{cm}^{-1}$  in the high-frequency region belong to the OH-stretching vibrations of the crystal water in the gypsum [33].



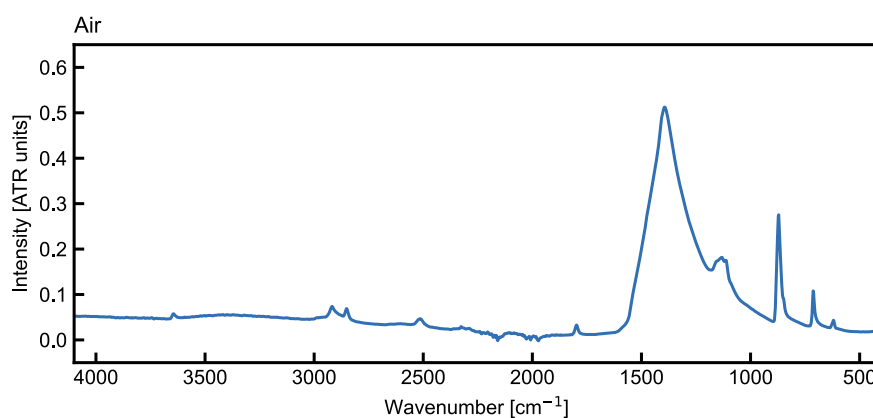
**Figure S70:** FTIR spectrum of the precipitate formed during precipitation experiments conducted at 25 °C in a nitrogen atmosphere, when the cementitious pore solution was separated by dead-end filtration 15 min after hydration started. The characteristic peak between 1100 cm<sup>-1</sup> corresponds to the strong sulfate stretching vibration of crystalline gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ). The two broad peaks between 3300 and 3600 cm<sup>-1</sup> in the high-frequency region belong to the OH-stretching vibrations of the crystal water in the gypsum [33]. The characteristic peak at 3640 cm<sup>-1</sup> corresponds to the OH-stretching vibration of crystalline portlandite ( $\text{Ca}(\text{OH})_2$ ) [34].



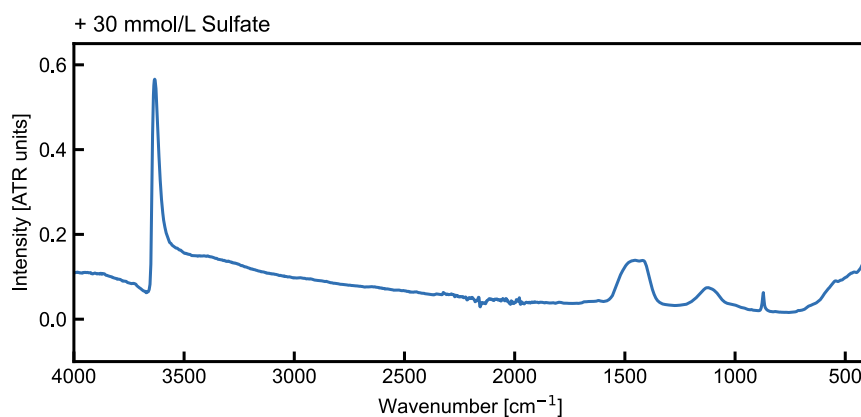
**Figure S71:** FTIR spectrum of the precipitate formed during precipitation experiments conducted at 25 °C in a nitrogen atmosphere, when the cementitious pore solution was separated by dead-end filtration 60 min after hydration started. The characteristic peak at 3640 cm<sup>-1</sup> corresponds to the OH-stretching vibration of crystalline portlandite ( $\text{Ca}(\text{OH})_2$ ) [34].



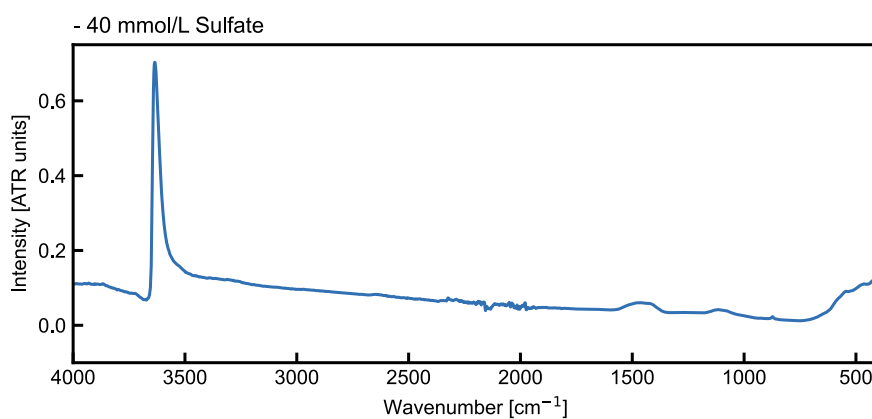
**Figure S72:** FTIR spectrum of the precipitate formed during precipitation experiments conducted at 50 °C in a nitrogen atmosphere. The cementitious pore solution was separated by dead-end filtration 15 min after hydration started. The characteristic peak at 3640 cm<sup>-1</sup> corresponds to the OH-stretching vibration of crystalline portlandite (Ca(OH)<sub>2</sub>) [34].



**Figure S73:** FTIR spectrum of the precipitate formed during precipitation experiments conducted at 25 °C in air. The cementitious pore solution was separated by dead-end filtration 15 min after hydration started. The characteristic peak at 1420 cm<sup>-1</sup> corresponds to the CO-stretching vibration of crystalline calcite (CaCO<sub>3</sub>) [35].



**Figure S74:** FTIR spectrum of the precipitate formed during precipitation experiments conducted at 45 °C in a nitrogen atmosphere. The cementitious pore solution was separated by dead-end filtration 15 min after hydration started. After separation, 30 mmol/L of soluble alkali sulfates ( $\text{Na}_2\text{SO}_4$  and  $\text{K}_2\text{SO}_4$ ) was added to the pore solution to increase its sulfate concentration. The characteristic peak at  $3640\text{ cm}^{-1}$  corresponds to the OH-stretching vibration of crystalline portlandite ( $\text{Ca}(\text{OH})_2$ ) [34].



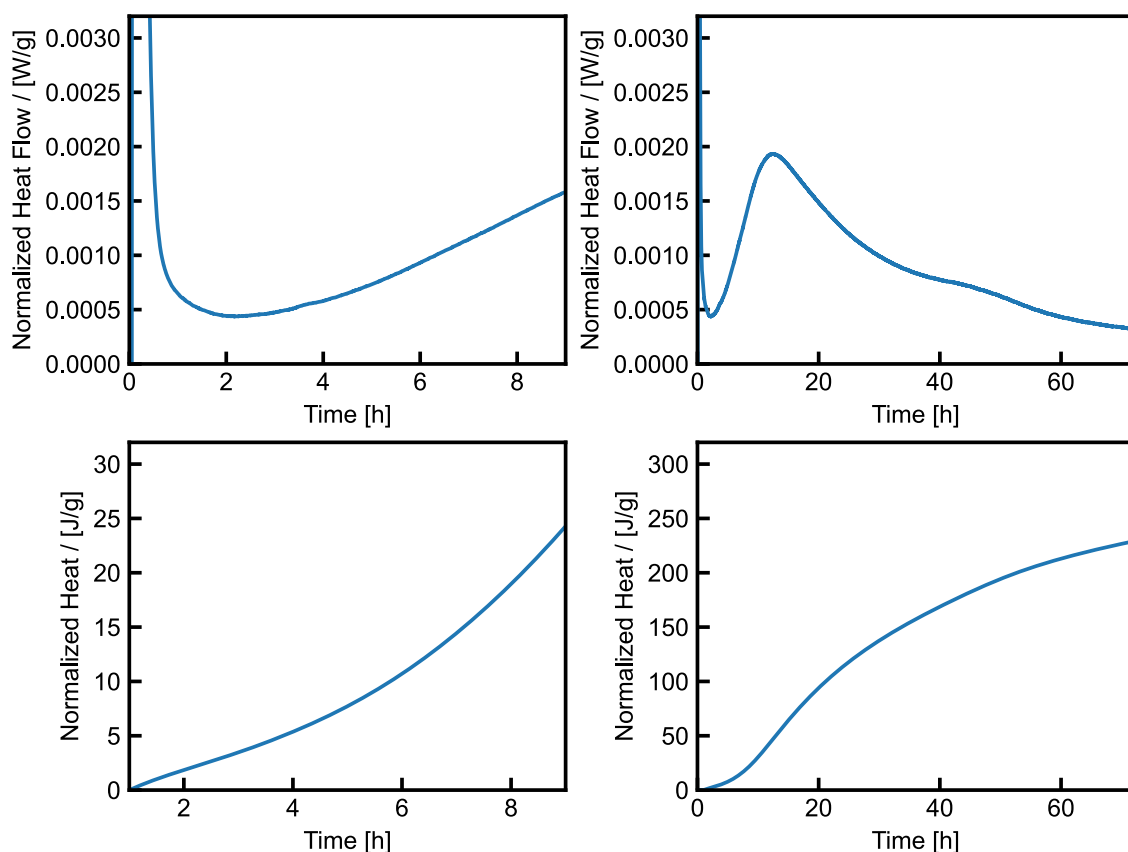
**Figure S75:** FTIR spectrum of the precipitate formed during precipitation experiments conducted at 45 °C in a nitrogen atmosphere. The cementitious pore solution was separated by dead-end filtration 15 min after hydration started. After separation, 40 mmol/L of  $\text{BaSO}_4$  was precipitated by adding  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$  to the pore solution to reduce its sulfate concentration. The characteristic peak at  $3640\text{ cm}^{-1}$  corresponds to the OH-stretching vibration of crystalline portlandite ( $\text{Ca}(\text{OH})_2$ ) [34].



## S9 Isothermal heat flow calorimetry

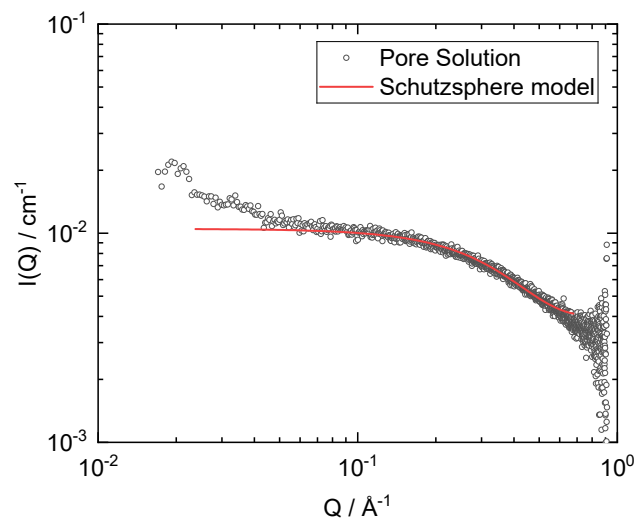
The heat generated during the hydration of OPC was measured using an eight-channel isothermal calorimeter (TAM Air, *TA Instruments*, Milford, MA, USA). The temperature inside the isothermal calorimeter was maintained at 20 °C under atmospheric pressure. Quartz sand with the same heat capacity as the samples was used as a reference material. The amount of quartz sand required was calculated according to WADSÖ [36].

40 g of OPC was added to 40 g DI-H<sub>2</sub>O to obtain a w/c ratio of 1. The mixture was stirred for 1 min using an overhead stirrer (*IKA Nanostar 20 digital*, Staufen, Germany) equipped with a four-bladed propeller at 500 rpm. After mixing, 6.0 g of the cement paste was transferred into a polypropene ampoule and sealed. The plastic ampoule (polypropene vials with a volume of 20 mL, a diameter of 27 mm, and a height of 60 mm) was then inserted into the calorimeter within ten minutes after the start of hydration. The heat of hydration was recorded for 72 h, and the heat flow data were normalized to the OPC content of the mixture.

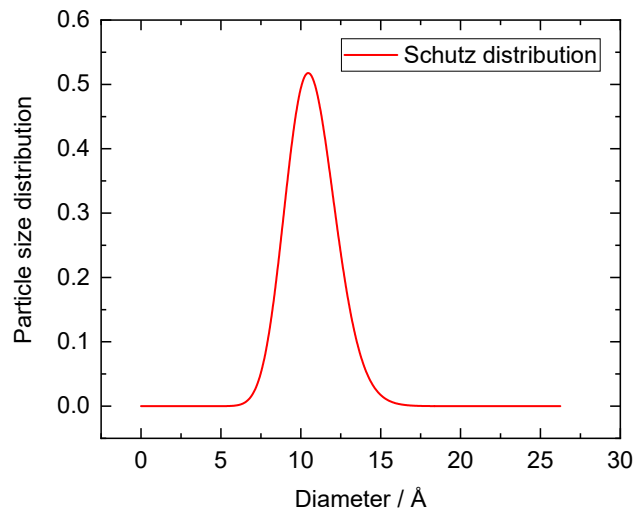


**Figure S76:** Calorimetric measurements of OPC with a w/c-ratio of 1.0 without additives. The normalized heat flow is displayed at the top for the first 9 h and over 72 h. Below, the corresponding normalized cumulative heat for the same timeframes is presented.

## S10 SAXS data

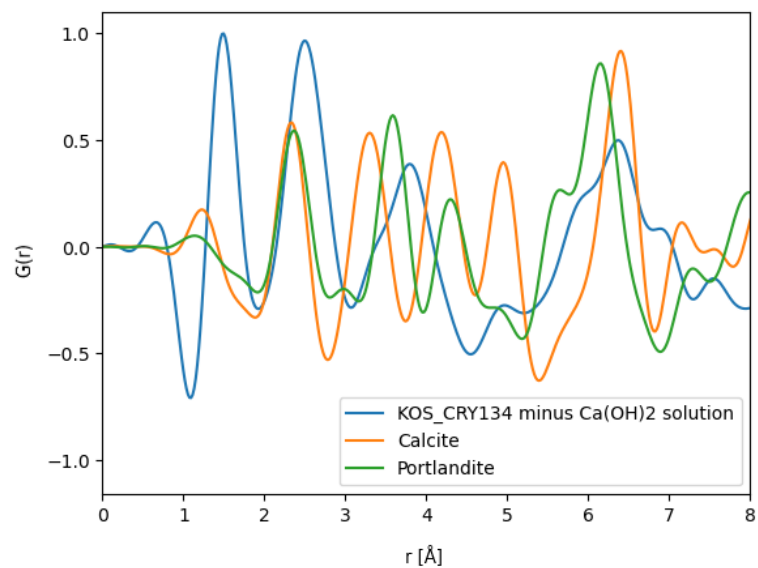


**Figure S77:** SAXS profile of the cementitious pore solution with Schutzsphere model [37]. The Schutzsphere model for spherical particles produces a narrow diameter distribution (see Figure S78) and a good fit for the scattering of the primary particles with an average diameter of 1.06 nm.



**Figure S78:** The Schutz distribution of the primary particle diameters.

## S11 PDF data



**Figure S79:** Comparison of the PDF analysis from cementitious pore solution (KOS\_CRY134) minus an undersaturated (0.01 M) CH solution with the PDF analysis from calcite and portlandite. There is no similarity between the PDF analyses.

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