nature portfolio

Peer Review File

Evidence of an amorphous intermediate phase during non-classical calcium hydroxide crystallization from cementitious pore solutions

Corresponding Author: Professor Torben Gaedt

This manuscript has been previously reviewed at another journal. This document only contains information relating to versions considered at Communications Materials.

This file contains all reviewer reports in order by version, followed by all author rebuttals in order by version.

Version 0:

Reviewer comments:

Reviewer #1

(Remarks to the Author)
This study investigates the existing forms of early-stage calcium hydroxide (CH) in cementitious pore solutions by employing a variety of characterization techniques, providing valuable insights into the formation of CH during the early hydration of cement. The experimental work and discussion are well-structured. Several concerns are listed below:
1.In the introduction section, the review of early studies on CH only lists the literatures without clearly comparing the differences in the results in different studies.
2.The use of TEM for characterizing the particle size distribution of the particles in the study is not sufficiently convincing.
3.Although the sample preparation parameters of cryo-HRTEM are described in detail in the experimental method section, the influence mechanism of different sample preparation parameters on the morphological feature of the sample is not presented, nor is the sample preparation repeatability verification data provided.
4.In the results and discussion section, the mechanism of sulfate ion inhibiting CH nucleation is only speculated, and the correlation analysis between the sulfate concentration in the pore solution and the CH nucleation induction time is not conducted. It is recommended to supplement this quantitative correlation study to verify the inhibition mechanism of sulfate ions.
5.The scale bars in the TEM images are not consistent.

Reviewer #2

(Remarks to the Author)
Review
Overall assessment
The manuscript contains very valuable information, and the experimental work is systematic and contributes meaningfully to a broader ongoing scientific discussion. I thank the authors for their significant effort and the high quality of much of the analytical work.
However, several issues affect the readability, clarity, and scientific rigor of the paper in its current form. My major comments and suggestions are summarized below.

Major Comments
1. Scope of cryo TEM investigations
The central criticism concerns the fact that only the aqueous phase of the cement suspension after 15 minutes was imaged by cryo TEM. This raises an important question:
Do the authors believe that at later stages of the induction period calcium hydroxide (CH) may in fact be present as prenucleation clusters (PNCs), but is simply not captured at the chosen time point?
A discussion of the temporal limitation of the sampling strategy is needed.
In relation to reference 40 (https://doi.org/10.1016/j.cemconres.2023.107258): can you explain why their cryo TEM results show ACH, while your study did not detect any? A discussion of this discrepancy is suggested.

---

2. Readability and dependence on supplementary data

The readability of the manuscript is currently reduced because several key aspects can only be understood by consulting the excessive supplementary material.

This applies in particular to:

• the TEM sample preparation procedure,

• parts of the ICP OES, XRD, TGA, and FTIR data.

Since these elements are critical for following the main argument, they should be moved from the supplementary section into the main manuscript.

On the other hand there are methods description in the main manuscript and the respective results are not shown in the main manuscript. Please consider to re-arrange materials and methods descriptions as such to align with results presentation in the main document.

---

3. Abstract and Introduction

Both sections require minor clarifications.

The weakest part is the explanation of why no CH (and also no C S H) precipitates during the induction period of Portland cement and C_3S hydration, even though supersaturation appears to be reached.

The concept of silicate poisoning is mentioned but not sufficiently discussed.

A stronger and more nuanced interpretation of the current literature is necessary.

---

4. Structure of the Results section

Currently, each subsection begins with interpretative statements before the experimental results are properly presented.

This structure is scientifically problematic—results should be shown first; interpretation must follow.

Reorganizing the chapter will significantly improve the scientific quality of the presentation.

Additional stylistic and technical corrections are required; these are indicated in the annotated version of the results section.

---

5. TEM EELS and EDX elemental analysis

The TEM EELS results presented are excellent.

However, I strongly encourage the authors to expand the analysis to additional relevant elements (K, S, Si, Al, …).

If this is not possible using EELS, the authors should at least evaluate the EDX data for these elements and provide the results, ideally in the supplementary section. I have added suggestions as comments alongside the manuscript and supplementary data files.

---

6. Blotting procedure during cryo sample preparation

A major open question concerns the blotting step applied before freezing.

Blotting is normally associated with partial drying of the sample, which contradicts one of the key advantages of cryo preparation (i.e., avoiding drying artefacts).

The authors should explain why blotting was used, how long it was applied, and whether it may influence state of the aqueous phase.

Minor Comments

7. ICP OES data

The ICP OES results, shown only in the supplementary section, demonstrate an unusual decrease in Ca^{2+} concentration from 1 to 15 minutes. Which probably indicates a precipitation event.

Since this deviates from typical literature trends (which usually show rising Ca^{2+} concentration during the induction period), these results must be:

• either discussed directly in the main manuscript,

• or, if not relevant to the core argument, removed entirely.

Possibly the ICP-OES results and saturation indices calculated could be used to discuss the major question I have raised above: Can you asses how relevant the investigation are for the aqueous phase of hydrating cement paste at the very laste stage of the induction period (should we expect ACH to occur at this stage?)

---

8. Figure captions

Figure captions should be shortened to essential information.

Descriptive or interpretative text should be moved into the Results and Discussion section.

Summary:

The main challenge of the manuscript is the large number of results and important information that is documented in the supplementary data only. I suggest recondisering to move essential informations and results to the main document. I have made suggestions along the pdf of the main document and the supplementary part. This I hope will improve the readability of the manuscript.

Several additional comments and corrections are provided throughout the manuscript and the supplementary data file. I hope they help strengthen the presentation and improve the overall flow of the manuscript.

Reviewer #3

(Remarks to the Author)
This paper investigates whether calcium hydroxide is present and in what form it exists during the early hydration of Portland cement. By employing a variety of advanced analytical techniques, it has further advanced our understanding of the hydration mechanism of Portland cement.
1 The abbreviation ACH is used without definition on its first occurrence.
2 Should the section “Materials and Methods” be placed before “Results and Discussion” in accordance with standard academic practice? If this is a requirement of the journal, please disregard this comment.
3 It is understandable that some unanticipated factors during testing may have caused sample artifacts, such as sample carbonation. It would be preferable if some of these tests could be repeated.
4 This work successfully demonstrates that spherical ACH particles observed by conventional TEM are drying artifacts. However, the central question—“the true native state of CH in cement pore solution”—is not fully answered, because the conclusion of “completely dissolved CH” relies on “non-detection” rather than direct evidence, and cannot be reliably extended to the in-situ environment of hydrating cement paste.
5 The phrase “clarifying a century-long question” is not recommended; scientific papers should maintain objectivity.
6 Regarding the transformation of ACH to crystalline CH driven by drying, does the author believe that the same mechanism applies in real cement systems?
7 This study was conducted at a water-to-cement ratio of 1.0. In the author’s view, how would CH formation in real cement systems differ under lower water-to-cement ratios?

Reviewer #4

(Remarks to the Author)
The manuscript entitled “Non-classical crystallization of calcium hydroxide from cementitious pore solutions: Evidence of an amorphous intermediate phase” presents a careful and methodologically rich investigation into the early-stage behavior of calcium hydroxide in cementitious systems. The combination of cryo-TEM, SAXS, and PDF analysis provides valuable insights into the role of drying-induced artifacts and supports the interpretation of non-classical crystallization pathways.

Overall, the manuscript is well written and scientifically sound. I recommend minor revision before acceptance. The following comments are intended to improve clarity, conciseness, and presentation.

1. Clarification of “undetectable” CH in early hydration
In the abstract and introduction, CH is described as “undetectable” during early hydration. For clarity, please specify that this refers to conventional techniques (e.g., XRD, SEM), rather than implying absolute absence. This distinction is important given the central conclusion that CH is present in dissolved form.

2. Abstract flow and logical transitions
The abstract moves rapidly from the observation of amorphous spheres to the conclusion that they are drying artifacts and finally to the dissolved state of CH. A brief transitional sentence clarifying this logical progression would improve readability.

3. Length of historical literature review in Introduction
The discussion of early studies (1970s–1980s) is thorough but somewhat lengthy. Consider condensing this section to better emphasize the unresolved question and the motivation for the present study.

4. Clear statement of research objectives
The final paragraph of the Introduction would benefit from a more structured summary of the study aims (e.g., objective, methods, and key findings in one concise statement).

5. Interpretation of core–shell structure (Figure 1)
The assignment of the particle core as “primarily composed of water” appears somewhat interpretative. Please consider softening the wording (e.g., “suggesting” or “consistent with”) unless further direct evidence is available.

6. Early indication of drying artifacts
The conclusion that large ACH particles are drying-induced artifacts is central to the manuscript but is only fully clarified later. Consider signaling this interpretation earlier when these particles are first introduced.

7. Consistency of terminology
The manuscript alternates between “ACH,” “amorphous CH,” and “amorphous calcium hydroxide.” Please standardize terminology after first definition to improve clarity.

8. Conclusion structure and conciseness
The conclusion section is comprehensive but somewhat dense. Consider organizing it into distinct points (e.g., key findings, methodological implications, mechanistic insights) and reducing minor repetitions for better readability.

Version 1:

Reviewer comments:

Reviewer #1

(Remarks to the Author)
The authors have provided comprehensive revisions in response to my previous comments, which greatly improves the integrity and logical rigor of this manuscript. However, several key scientific ambiguities, and descriptive flaws still remain unresolved.

1.Although the authors sorted and compared early research chronologically, the logical hierarchy of contradictions between different literature is still weak. The current text only lists each scholar's phenomenon observation but fails to systematically summarize viewpoints in existing research.
2.The authors completely deleted the particle size statistical content due to TEM drying artifacts, but there is a lack of alternative quantitative characterization of the size of particles.
3.The authors corrected individual inconsistent scale bars, but it is suggested to unify the standard of scale bar layout for all images in the full text: uniformly place the scale bar at the lower right corner of images, and mark the length unit font size uniformly, to avoid scattered and inconsistent visual presentation of figures, which affects the readability of the manuscript.

Reviewer #2

(Remarks to the Author)
Thank you for your careful and thorough responses to all of my questions and comments. As I noted previously, this is a highly important, well-executed, and internally consistent study. I greatly appreciate the effort you invested in addressing the review points and improving the manuscript.
It has been a pleasure to review this work, and I wish you the best with its publication.

Best regards
Christiane Rößler

Reviewer #3

(Remarks to the Author)
The authors have well answered my questions, and I recommend the acceptance of this paper.

Resubmission of COMMSMAT-26-0064-T: Non-classical crystallization of calcium hydroxide from cementitious pore solutions: Evidence of an amorphous intermediate phase – Response to Reviewers

Dear Dr. John Plummer,

Thank you, the editorial team of *Communications Materials* and the reviewers for the detailed feedback on our manuscript "*Non-classical crystallization of calcium hydroxide from cementitious pore solutions: Evidence of an amorphous intermediate phase*". We appreciate the time and effort you and the reviewers have dedicated to providing valuable feedback. We are grateful to the reviewers for their insightful comments, which have helped us improve our manuscript.

We have carefully addressed all reviewer concerns, highlighted the changes made in the document and believe the revised manuscript is substantially improved. The major changes include a restructuring and consolidation of the manuscript and the supplementary information to fundamentally improve its scientific readability, a more in-depth discussion of our key conclusions and core findings, and an experimental expansion of the analytical dataset through additional EDX/EELS analysis and a quantitative correlation between sulfate concentration and CH precipitation induction time. Below, we provide a detailed, point-by-point response to the reviewers' comments and concerns.

We believe these revisions have significantly strengthened the manuscript and that it now meets the standards for publication in *Communications Materials*. Thank you for giving us the opportunity to revise our work and to submit a revised draft of our manuscript. We look forward to your response regarding our submission and are happy to address any further questions or comments you may have.

Sincerely,

Torben Gädt

Reviewer 1

We thank Reviewer 1 for the thorough and technically rigorous evaluation of our manuscript. The specific concerns raised have prompted us to revisit and improve several methodological aspects of our work. We are confident that the revisions adequately address each point.

Comment 1.1 — *In the introduction section, the review of early studies on CH only lists the literatures without clearly comparing the differences in the results in different studies.*

Response: We thank Reviewer 1 for this constructive comment. We agree that the original presentation of the early literature was primarily descriptive and could have been more precise in describing similarities and differences among the studies. We have therefore restructured this paragraph to group the findings thematically. We now explicitly compare the results and highlight their interpretations, particularly regarding the nature of these particles. We believe this revised structure now more clearly conveys the relevant previous findings and better motivates the present study.

Revised text [Line 50-82]: A few reports from the late 1970s and early 1980s ~~have postulated the presence of the amorphous phase of CH~~ postulated the existence of an ACH (amorphous calcium hydroxide) phase during C_3S hydration, ~~although they have~~ though they received limited attention. ~~In 1977~~, Slegers *et al.* ~~observed early portlandite formation before the end of the induction period of C_3S hydration [28]. They~~ detected portlandite reflexes by ~~PXRD~~ powder X-ray diffraction (PXRD) during the induction period before supersaturation was reached in ~~the solution. However, the~~ solution [28], with an unusually low intensity of the 001 reflex of CH ~~was unusually low, which may indicate —~~ — an observation consistent with either silicate poisoning or the presence of an amorphous ~~CH~~ phase [29]. ~~Two years later, Ménétrier et al. prepared sintered C_3S pellets that were immersed in water for different time intervals. After 60 s, tiny, nearly spherical particles with diameters less than 100 nm became visible on the surface under the SEM. After 15 min, the first distinct C-S-H morphologies were detected, obscuring the smaller spherical structures [35]. In the same year, Midgley also reported both stacked CH and tiny spherical CH particles (below 100 nm) in an article about the differences in the quantification methods of CH in set cement paste [38]. Additionally,~~ Odler and Dörr found ~~in 1979, while investigating the early hydration of C_3S using XRD and thermogravimetry,~~ that adding crystalline CH as a seeding material did not reduce the dormant period. ~~They concluded from their findings that crystalline~~ , leading them to conclude that CH does not form through classical homogeneous crystallization from a

supersaturated solution. ~~Instead, its formation occurs in~~ but instead via a two-step process in which ~~amorphous CH is formed first, followed by its transformation into a~~ an amorphous precursor forms first, before transforming into the crystalline state [31, 34]. ~~The most convincing evidence supporting the existence of spherical, amorphous CH nanoparticles~~ Morphological evidence for this amorphous intermediate came from scanning electron microscopy studies: MÉNÉTRIER *et al.* and INGS and coworkers independently observed nearly spherical, sub–100 nm particles on the surface of ~~C_3S before the formation of C-S-H structures can be found in a publication~~ hydrating C_3S [35, 36], while MIDGLEY simultaneously reported both stacked CH and similarly sized spherical particles in set cement paste [38]. Notably, in the study by INGS and coworkers ~~from 1983. They studied the hydration of single-crystalline C_3S and observed in SEM micrographs that within 30 min, the surfaces were covered with micrometer-sized spheres of poorly crystallized CH. After 60 min,~~ these spherical particles disappeared after 60 min when typical C-S-H structures formed ~~on the surfaces, and the spherical material was no longer observable. From the data resented, it is~~ , leaving it unclear whether the CH spheres were covered, dissolved, or otherwise "converted" into C-S-H [36]. More recently, ~~in 2012,~~ REINHEIMER and CASANOVA ~~produced thin C_3S films using electron beam evaporation, achieving thicknesses of only a few tens of nanometers. The authors then employed scanning electron microscopy~~ confirmed the formation of spherical nanoparticles on hydrating C_3S thin films using SEM and atomic force microscopy ~~to observe the formation of spherical nanoparticles on the surface of the thin C_3S films during their hydration [40, 41]~~ (AFM) [40, 41]. Taken together, these studies consistently describe the appearance of spherical ACH particles during early hydration, yet it remains unresolved whether these particles represent a genuine amorphous precursor phase or a transient surface phenomenon.

Comment 1.2 — *The use of TEM for characterizing the particle size distribution of the particles in the study is not sufficiently convincing.*

Response: We thank Reviewer 1 for critically highlighting this issue. Although TEM is an excellent method for directly measuring particle size and distribution at the nanoscale, it has limitations, particularly when artifacts arise during sample preparation, such as particle aggregation during the drying process. In our study, we observed particles of vastly different sizes, ranging from less than 1 nm to over 1 µm. Given this variability, we believe that the automated particle size analysis we conducted does not add value to our understanding of the data or our conclusions. As a result, we have decided to remove this statement entirely from the manuscript, along with the corresponding section in the supplementary information. Therefore, particle size determination of individual particles will remain purely qualitative and will rely on individual TEM images.

Revised text [Line 146-147]: ~~Automated image analysis of 7,500 particles enabled the determination of the particle size distribution (see SI, Fig. S40) and the average diameter of the particles (105 nm ± 40 nm).~~

Comment 1.3 — *Although the sample preparation parameters of cryo-HRTEM are described in detail in the experimental method section, the influence mechanism of different sample preparation parameters on the morphological feature of the sample is not presented, nor is the sample preparation repeatability verification data provided.*

Response: We would like to thank Reviewer 1 for raising these two important points.

1. Regarding the influence of different sample preparation parameters, there are two differences in cryo-HRTEM preparation compared with cryo-TEM preparation: a smaller droplet volume and a significantly reduced blotting intensity. These adjustments were intentionally made to minimize the solution's contact time with the filter paper and to prevent partial drying of the sample before vitrification. This is crucial because partial drying can lead to the formation of large ACH spheres, as observed under conventional TEM. More aggressive blotting increases the drying rate of the thin liquid film, providing more time for ACH particle growth before vitrification halts the process. For this reason, ACH particles are visible in the cryo-TEM images, albeit much smaller than in conventional TEM images. By minimizing blotting before the cryo-HRTEM measurements, we aimed to preserve the native state of the pore solution to the greatest extent possible. However, most importantly, the key difference between cryo-TEM and cryo-HRTEM is that all cryo-HRTEM imaging was performed exclusively in areas of vitreous ice within the holes of the lacey carbon film — regions that were never in contact with the filter paper during blotting. These areas, therefore, remained submerged in an aqueous layer throughout sample preparation and never experienced direct drying. In the revised manuscript, we have expanded the experimental section on cryo-TEM preparation to clarify the rationale behind these preparation parameters.

2. Regarding reproducibility, we acknowledge that cryo-HRTEM measurements were conducted on only one sample and that additional independent replicates should ideally be provided. Unfortunately, further cryo-HRTEM experiments are not feasible within the timeframe of this revision due to limited access to the Titan Krios instrument required for these measurements. However, we want to emphasize that the central conclusion drawn from the cryo-HRTEM data — the absence of large ACH particles in the vitrified pore solution — is fully supported by two independent and artifact-free bulk techniques: SAXS and PDF analysis. Both techniques were performed directly on the native liquid pore solution without any sample preparation that could introduce drying artifacts. The cryo-HRTEM observations and the SAXS and PDF

analyses consistently indicated the presence of only sub-nanometer calcium sulfate species in the pore solution, providing strong independent validation of the cryo-HRTEM findings and significantly alleviating concerns about reproducibility. We have made this point clearer in the revised manuscript.

Revised text [Line 624-629]: Compared with the cryo-TEM preparation, the reduced blotting intensity was intentionally chosen to minimize the contact time between the pore solution and the filter paper, thereby limiting partial drying of the thin liquid film before vitrification and reducing the driving force for ACH particle growth during sample preparation. All cryo-HRTEM imaging was performed exclusively in areas of vitreous ice within the holes of the lacey carbon film — regions that were not in contact with the filter paper during blotting and therefore remained continuously submerged in an aqueous layer throughout sample preparation.

Revised text [Line 315-318]: We subsequently examined the samples prepared in this manner using a high-resolution ~~Titan Krios G2 microscope.~~ cryo-TEM. This time, imaging was performed exclusively in areas of vitreous ice within the holes of the lacey carbon film — regions that were not in contact with the filter paper during blotting and therefore remained continuously submerged in an aqueous layer throughout sample preparation.

Revised text [Line 345-347]: Furthermore, the absence of large ACH particles in the vitrified pore solution is fully consistent with the SAXS and PDF analyses performed directly on the native liquid pore solution (see below), both of which confirm the presence of only sub-nanometer calcium sulfate species and thus validate the cryo-HRTEM findings.

Comment 1.4 — *In the results and discussion section, the mechanism of sulfate ion inhibiting CH nucleation is only speculated, and the correlation analysis between the sulfate concentration in the pore solution and the CH nucleation induction time is not conducted. It is recommended to supplement this quantitative correlation study to verify the inhibition mechanism of sulfate ions.*

Response: We thank Reviewer 1 for this constructive suggestion. We agree that the inhibitory effect of sulfate ions on CH nucleation warranted quantitative experimental support beyond the speculative discussion in the original manuscript. We therefore conducted an additional series of precipitation experiments at 45 °C, adding different concentrations of soluble alkali sulfates or barium chloride to precipitate barium sulfate to 100 mL of separated pore solution (w/c = 1.0, separated after 15 min). The sodium-to-potassium ratio of the added sulfate salts was matched to that of the native pore solution to avoid confounding effects of the alkali cations. The induction

time for CH precipitation was determined from conductivity measurements, as described previously. The results reveal a clear exponential dependence of the induction time on the sulfate concentration in the pore solution, providing quantitative experimental confirmation of the proposed inhibition effect. The new conductivity curves are presented in Fig. 8, and the corresponding induction times, together with the ICP-OES data for the doped solutions, are compiled in Tab. S9 and Tab. S5. The results are discussed in the relevant section of the revised manuscript, and the experimental details have been added to the Methods section (see below).

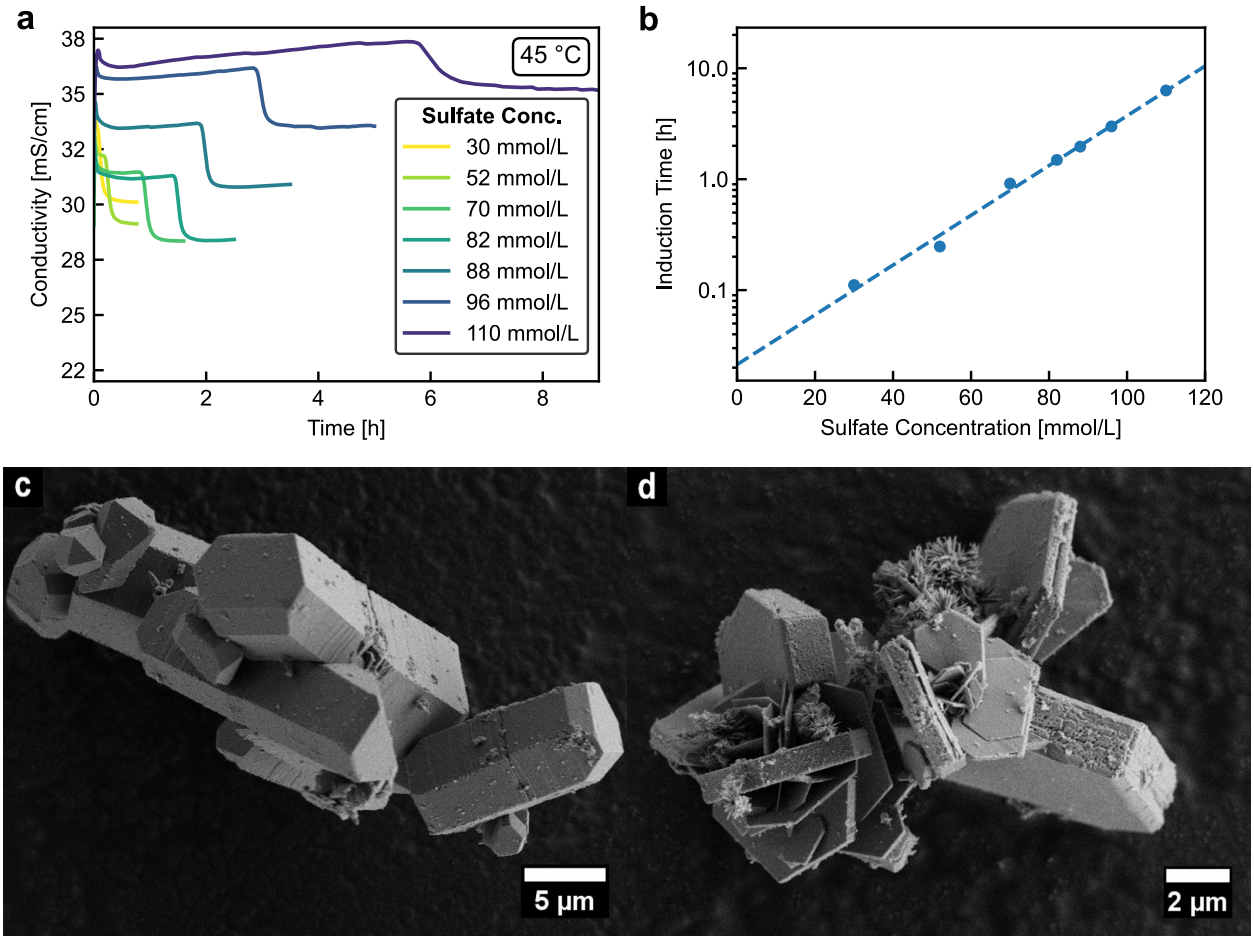

Figure 8: **Dependence of the induction time for CH precipitation from cementitious pore solution on the sulfate concentration of the solution.** **a** Conductivity measured over time at 45 °C of pore solutions separated 15 min after the start of hydration, with varying concentrations of sulfate ions in the solution. **b** Exponential relationship between the induction times for CH precipitation from the pore solution and the sulfate concentration. **c-d** SEM images of the isolated precipitates at the lowest sulfate concentration of 30 mmol L^{-1} (**c**), and at the highest sulfate concentration of 110 mmol L^{-1} (**d**). Scale bars represent 5 µm and 2 µm, respectively.

Revised text [Line 443-466]: Interestingly, the induction time for CH precipitation from a pure C_3S pore solution, which was separated and tested under the same conditions, is found to be several times shorter than that from a cementitious pore solution: 8 h vs. 37 h at 25 °C (see SI, Tab. S8 and Fig. S50). However, if a small amount of gypsum is mixed with C_3S before hydration, the induction time increases to levels similar to those observed in cementitious pore solutions (see SI, Tab. S8 and Fig. S50). This indicates that sulfate ions play a significant role in inhibiting CH precipitation. To further investigate the suspected inhibitory effect of sulfate ions, we conducted an additional series of precipitation experiments at 45 °C, a temperature at which gypsum is more soluble than at room temperature, thereby preventing gypsum precipitation. In this experiment series, we manipulated the sulfate concentration in the separated pore solutions by adding alkali sulfates (Na_2SO_4 and K_2SO_4 in a 1:7 molar ratio) to increase sulfate levels, and by precipitating $BaSO_4$ with $BaCl_2 \cdot 2\,H_2O$ to decrease sulfate levels. This method is almost perfectly selective for the removal of SO_4^{2-} and allowed us to adjust the sulfate concentration of the separated pore solution from 1000 to 3500 mg/L (see SI, Tab. S5 and Fig. S47). It was not possible to increase the sulfate concentration indefinitely, as doing so would cause gypsum to precipitate instead of portlandite. Even with a moderate increase in sulfate concentration (+ 30 mmol/L), gypsum began to co-precipitate (see Table 1 and SI, Fig. S42, Fig. S57, Fig. S65, and Fig. S73), whereas at lower sulfate concentrations, only portlandite precipitated (see Table 1 and SI, Fig. S43, Fig. S58, Fig. S66, and Fig. S74). The conductivity measurements and induction times for CH precipitation are presented in Figure 8 (and SI, Tab. S9). Due to the presence of additional alkali or chloride ions in solution, the measured conductivity in all experiments was higher than in the reference measurement (82 mmol/L). The induction time for CH precipitation from a cementitious pore solution shows an almost perfectly exponential relationship with sulfate concentration, clearly indicating that present sulfate ions inhibit CH nucleation in these solutions. However, since an induction period of 8 h for CH precipitation was also observed in a pure C_3S pore solution (see SI, Tab. S8 and Fig. S50) — where no sulfate ions are present — sulfate inhibition alone cannot fully account for the kinetic barrier to CH nucleation, suggesting that additional ionic species contribute to the observed metastability.

Revised text [Line 484-489]: This transformation of the crystal habit from prismatic to tabular, induced by additives such as sulfates, is clearly illustrated by comparing SEM images of the precipitates at the highest and lowest sulfate concentrations (see Figure 8 and SI, Fig. S42 and Fig. S43). Additionally, SEM images of precipitates from the C_3S pore solutions further demonstrate this change. When gypsum is mixed with C_3S before hydration, portlandite precipitates as flat hexagonal plates (see SI, Fig. S45) rather than elongated prismatic columns or very thin plate-like crystals (see SI, Fig. S44) from the separated pore solution.

Revised text [Line 680-699]: To determine how the induction time depends on the sulfate concentration of the pore solution, the sulfate concentration of the solution was adjusted immediately after dead-end filtration, but before starting the conductivity measurement. To increase the sulfate level, alkali sulfates were added after separation. The Na_2SO_4-to-K_2SO_4 ratio (1:7 molar ratio) was selected to maintain the sodium-to-potassium ratio in the pore solution largely unchanged. To decrease the sulfate level, part of the sulfate was precipitated as $BaSO_4$ by adding $BaCl_2 \cdot 2\,H_2O$. This process required an immediate secondary filtration of the pore solution to fully separate the $BaSO_4$ precipitate. The conductivity measurements at 45 °C, along with the isolation and characterization of the precipitates, were then performed as described above. Additional precipitation experiments were conducted at 25 °C using a pure C_3S pore solution and a pore solution derived from a C_3S–gypsum mixture at a 95:5 ratio.

Comment 1.5 — *The scale bars in the TEM images are not consistent.*

Response: We want to thank Reviewer 1 for bringing this to our attention. We had indeed overlooked an inaccuracy in Figure 1f, which has now been corrected. Additionally, to enhance the consistency of the electron micrographs' presentation, we have also revised the other figures to ensure that all scale bars are uniform.

Reviewer 2

We thank Reviewer 2 for the exceptionally thorough review and the detailed annotations provided alongside the manuscript. We appreciate the acknowledgment of our experimental work and the depth of the critical assessment, which have significantly contributed to enhancing the structure, clarity, and scientific rigor of the manuscript. We hope that the extensive revisions we have made in response to each point will meet the reviewer's expectations.

Major Comments

Comment 2.1 — *Scope of cryo TEM investigations*

The central criticism concerns the fact that only the aqueous phase of the cement suspension after 15 minutes was imaged by cryo TEM. This raises an important question: Do the authors believe that at later stages of the induction period calcium hydroxide (CH) may in fact be present as prenucleation clusters (PNCs), but is simply not captured at the chosen time point? A discussion of the temporal limitation of the sampling strategy is needed. In relation to reference 40 (https://doi.org/10.1016/j.cemconres.2023.107258): can you explain why their cryo TEM results show ACH, while your study did not detect any? A discussion of this discrepancy is suggested.

Response: We would like to thank Reviewer 2 for highlighting these two important points.

1. Regarding the temporal limitation of our sampling strategy, we acknowledge that the cryo-HRTEM analysis was conducted solely on the pore solution separated after 15 min of hydration. Therefore, the presence of ACH or CH prenucleation clusters at later stages of the induction period cannot be confirmed or ruled out based on our current data. We have added a discussion of this limitation to the revised manuscript. Although cryo-HRTEM measurements at later time points would be highly valuable, they fall outside the scope of this study and represent an important area for future research. That said, we believe that ACH can form in the cement paste as soon as portlandite begins to precipitate.

2. Regarding the discrepancy with Madeja *et al.* [1], we propose that the apparent contradiction can be explained by three key differences between the two studies. First, Madeja *et al.* employed a standard cryo-preparation method involving normal blotting, in contrast to our cryo-HRTEM preparation, where we aimed to minimize blotting intensity. Second, their experiments were conducted in model systems, whereas our cementitious pore solution contains

significant concentrations of other ions and species—especially sulfates and silicates—that kinetically inhibit CH nucleation. Third, the degree of supersaturation with respect to CH in their model systems at the time of sampling (SI = 1.20-1.90) was greater than that of our cementitious pore solution at 15 min (SI = 0.55). We have included a discussion of these points in the revised manuscript, which we believe enhances its quality and directly addresses the concerns raised.

Revised text [Line 386-390]: It should also be noted that the structural characterization of the pore solution was performed exclusively on the cementitious pore solution separated after 15 min of hydration, which represents the early dormant period of cement hydration. Whether CH prenucleation clusters or ACH may form at later stages of the induction period cannot be excluded or confirmed based on the present data and represents an important direction for future investigations.

Revised text [Line 337-345]: The absence of ACH in the cryo-HRTEM measurements contrasts with the findings of Madeja *et al.* [44], who detected ACH in cryo-TEM images. This discrepancy can be rationalized by several key differences between the two studies. First, Madeja *et al.* employed standard cryo-preparation involving normal blotting, in contrast to our cryo-HRTEM preparation method, where we aimed to minimize blotting intensity. Second, their samples were drawn from pure model systems ($CaCl_2$ + NaOH), whereas the cementitious pore solution contains significant concentrations of other ions (see SI, Tab. S4), which can kinetically inhibit CH nucleation. Third, the degree of supersaturation with respect to CH in their model systems at the time of sampling (SI = 1.20-1.90) exceeded that of the cementitious pore solution after 15 min (SI = 0.55).

Comment 2.2 — *Readability and dependence on supplementary data*

The readability of the manuscript is currently reduced because several key aspects can only be understood by consulting the excessive supplementary material. This applies in particular to:
- *the TEM sample preparation procedure,*
- *parts of the ICP OES, XRD, TGA, and FTIR data.*

Since these elements are critical for following the main argument, they should be moved from the supplementary section into the main manuscript. On the other hand there are methods description in the main manuscript and the respective results are not shown in the main manuscript. Please consider to re-arrange materials and methods descriptions as such to align with results presentation in the main document.

Response: We thank Reviewer 2 for the comment and regret that the manuscript's readability was compromised by excessive reliance on the supplementary information file. We have revised it ac-

cordingly to improve structure and readability. Specifically, we have moved the schematic overview (Fig. 9) of the four TEM grid preparation methods (drop casting, blotting, ethanol quenching, and cryo preparation) from the supplementary information into the main manuscript and added a table that directly supports the identification and the amount of the precipitated phases in the precipitation experiments (Tab. 1), while the PXRD, TGA, and FTIR data stayed in the supporting information.

We have also carefully revised the Methods section of the main manuscript and identified method descriptions whose corresponding results are presented exclusively in the supplementary information. The descriptions of ICP-OES, FTIR, PXRD, TGA-MS, and isothermal heat flow calorimetry have been relocated to the supplementary information to ensure that the Methods section of the main manuscript aligns directly with the results presented therein.

We believe these revisions significantly improve the readability of our manuscript. To ensure clarity, the changes are not explicitly listed here to maintain the readability of the rebuttal letter. However, all changes can be reviewed in detail in the "manuscript with markup".

Comment 2.3 — *Abstract and Introduction*

Both sections require minor clarifications. The weakest part is the explanation of why no CH (and also no C S H) precipitates during the induction period of Portland cement and C_3S hydration, even though supersaturation appears to be reached. The concept of silicate poisoning is mentioned but not sufficiently discussed. A stronger and more nuanced interpretation of the current literature is necessary.

Response: We agree with Reviewer 2 that the original introduction did not sufficiently discuss the concept of silicate poisoning and the broader question of why no CH precipitate during the induction period despite the solution being nominally supersaturated with respect to portlandite. We have therefore expanded the relevant passage in the introduction to include a more detailed discussion of the silicate poisoning theory, which proposes that the adsorption of silicate ions onto nascent crystallization nuclei kinetically inhibits their growth.

Revised text [Line 39-44]: The ~~CH~~ "silicate poisoning" theory suggests that the dormant period of cement hydration is primarily influenced by delayed CH nucleation, caused by dissolved silicate species poisoning CH nuclei [18, 19]. These mobile silicate species adsorb onto the active growth surfaces of embryonic CH nuclei, inhibiting nucleation and growth of portlandite [20]. During initial hydration, dissolved Ca^{2+} and OH^- ions thus accumulate until the poisoning effect is overcome, leading to rapid CH precipitation at the beginning of the acceleration period [7].

Comment 2.4 — *Structure of the Results section*

Currently, each subsection begins with interpretative statements before the experimental results are properly presented. This structure is scientifically problematic—results should be shown first; interpretation must follow. Reorganizing the chapter will significantly improve the scientific quality of the presentation. Additional stylistic and technical corrections are required; these are indicated in the annotated version of the results section.

Response: We thank Reviewer 2 for this important stylistic observation. We agree that interpretive statements should follow, rather than precede, the presentation of experimental results, and we have carefully revised the entire Results and Discussion section with this principle in mind. We identified the passages where this sequence was inverted and reorganized them in the revised manuscript so that experimental observations are presented first, followed by their interpretation. In addition, we have implemented the stylistic and technical corrections requested in the annotated manuscript. To ensure clarity and maintain readability, the revisions are not reproduced here, but all revisions are available in detail in the "manuscript with markup".

Comment 2.5 — *TEM EELS and EDX elemental analysis*

The TEM EELS results presented are excellent. However, I strongly encourage the authors to expand the analysis to additional relevant elements (K, S, Si, Al, ...). If this is not possible using EELS, the authors should at least evaluate the EDX data for these elements and provide the results, ideally in the supplementary section. I have added suggestions as comments alongside the manuscript and supplementary data files.

Response: We are pleased that Reviewer 2 particularly appreciated this section of our work. We remeasured the ACH particles using EELS to demonstrate the reproducibility of our results and to analyze all elements present in the pore solution. The results are available in the SI (see section S2.6).

Given the preparation method and the analysis, it was not possible to reliably detect the other relevant elements in the pore solution, aside from Ca, O, and C. Their signals were too weak to distinguish them from the noise. However, EDX measurements of the particle aggregates observed under the SEM indicate the presence of all other relevant elements in the pore solution. Most of these elements, including Al, Si, Fe, Mg, Na, and Cl, are present only in trace amounts. However, we clearly identified potassium sulfate residues in some areas adjacent to the ACH particles. The remaining elements are finely distributed throughout the entire sample.

We have revised the EDX spectra and elemental maps to include additional elements and have added tables detailing the elemental composition of the samples in the SI (see section S3.2). We

would also like to express our gratitude to Reviewer 2 for the accurate observation in identifying the incorrect assignment of the S peak to Mo. We had overlooked this error, and it has now been corrected in the revised SI.

Comment 2.6 — *Blotting procedure during cryo sample preparation*

A major open question concerns the blotting step applied before freezing. Blotting is normally associated with partial drying of the sample, which contradicts one of the key advantages of cryo preparation (i.e., avoiding drying artefacts). The authors should explain why blotting was used, how long it was applied, and whether it may influence state of the aqueous phase.

Response: We thank Reviewer 2 for raising this important methodological point. Blotting is a standard and necessary step in cryo-TEM sample preparation [2]. It reduces the sample thickness to below 100 nm, which is required for the electron beam to traverse the specimen, and thereby enables vitrification of an electronically transparent liquid film upon plunge freezing.

We fully acknowledge that blotting results in partial drying before vitrification. However, several aspects of our protocol mitigated this effect. First, blotting was performed at 95% relative humidity to limit evaporative water loss from the sample during this step. Second, the TEM grids were glow-discharged before sample application to render the carbon film hydrophilic, ensuring that the pore solution spreads uniformly and that the filter paper does not completely remove the aqueous film. Third, we intentionally minimized blotting intensity in our cryo-HRTEM preparation compared with that in our cryo-TEM preparation. Fourth, and most importantly, all cryo-HRTEM imaging was performed exclusively in areas of vitreous ice within the holes of the lacey carbon film — regions that were never in contact with the filter paper during blotting. These areas, therefore, remained submerged in an aqueous layer throughout sample preparation and never experienced direct drying. That is also exactly why we used these different TEM grids in cryo-TEM, since they provide unsupported areas for background-free imaging. We have now explicitly stated these aspects in the revised Methods section.

The concern that blotting-induced partial drying may nonetheless have affected the observed state of the aqueous phase is further addressed by the consistency of our cryo-HRTEM results with two independent bulk techniques — SAXS and PDF analysis — which require no sample preparation and were conducted directly on the native pore solution. Both methods confirm the absence of large ACH particles and identify only subnanometer calcium sulfate species, in full agreement with our cryo-HRTEM analysis. We therefore conclude that the blotting step did not introduce significant artifacts and that the absence of ACH particles accurately reflects the native state of the cementitious pore solution.

Revised text [Line 624-629]: Compared with the cryo-TEM preparation, the reduced blotting intensity was intentionally chosen to minimize the contact time between the pore solution and the filter paper, thereby limiting partial drying of the thin liquid film before vitrification and reducing the driving force for ACH particle growth during sample preparation. All cryo-HRTEM imaging was performed exclusively in areas of vitreous ice within the holes of the lacey carbon film — regions that were not in contact with the filter paper during blotting and therefore remained continuously submerged in an aqueous layer throughout sample preparation.

Revised text [Line 315-318]: We subsequently examined the samples prepared in this manner using a high-resolution ~~Titan Krios G2 microscope.~~ cryo-TEM. This time, imaging was performed exclusively in areas of vitreous ice within the holes of the lacey carbon film — regions that were not in contact with the filter paper during blotting and therefore remained continuously submerged in an aqueous layer throughout sample preparation.

Revised text [Line 345-347]: Furthermore, the absence of large ACH particles in the vitrified pore solution is fully consistent with the SAXS and PDF analyses performed directly on the native liquid pore solution (see below), both of which confirm the presence of only sub-nanometer calcium sulfate species and thus validate the cryo-HRTEM findings.

Minor Comments

Comment 2.7 — *ICP OES data*

The ICP OES results, shown only in the supplementary section, demonstrate an unusual decrease in Ca^{2+} concentration from 1 to 15 minutes. Which probably indicates a precipitation event. Since this deviates from typical literature trends (which usually show rising Ca^{2+} concentration during the induction period), these results must be:

- *either discussed directly in the main manuscript,*
- *or, if not relevant to the core argument, removed entirely.*

Possibly the ICP-OES results and saturation indices calculated could be used to discuss the major question I have raised above: Can you asses how relevant the investigation are for the aqueous phase of hydrating cement paste at the very laste stage of the induction period (should we expect ACH to occur at this stage?)

Response: We fully agree with Reviewer 2 that the significant decrease in Ca^{2+} concentration during the first 15 min of cement hydration reflects a precipitation event. However, this behavior is typical of very early cement hydration and aligns with findings in the literature [3]. In the

initial minutes of hydration, large amounts of ettringite precipitate, leading to sharp declines in both Ca^{2+} and sulfate concentrations in the pore solution (see Tab. S4 and Fig. S46). Because ettringite precipitation occurs only within the first few minutes, the Ca^{2+} concentration stabilizes at a relatively high level after about 15 min and increases only slightly during the dormant period. We have added a clarifying sentence to the relevant section of the main manuscript. Portlandite begins to precipitate in significant quantities only after sufficient sulfate has been consumed, marking the start of the acceleration period, which further reduces the Ca^{2+} concentration (see Tab. S4 and Fig. S46). In the system we studied, this transition occurs approximately 2.5 h after the start of hydration (see Fig. S75).

Regarding the broader question of whether ACH is expected in later stages of the induction period, the ICP-OES data and calculated saturation indices provide no relevant insight. Cryo-HRTEM measurements at later stages of the induction period, ideally combined with in situ scattering techniques, would be required to directly assess whether ACH forms, which is an important direction for future investigations.

Revised text [Line 435-437]: In particular, the initial rapid decrease in both sulfate and Ca^{2+} concentrations during the first 15 min is primarily attributable to ettringite formation [53].

Comment 2.8 — *Figure captions*

Figure captions should be shortened to essential information. Descriptive or interpretative text should be moved into the Results and Discussion section.

Response: We want to thank Reviewer 2 for this suggestion. We have carefully revised and condensed the captions for all figures. The captions now focus solely on the sample, sample preparation, experimental conditions, and image acquisition. Interpretations and discussions of the findings have been relocated to the main text. We hope this adjustment allows the figures to stand on their own and enhances overall readability.

Comment 2.9 — *Several additional comments and corrections are provided throughout the manuscript and the supplementary data file. I hope they help strengthen the presentation and improve the overall flow of the manuscript.*

Response: We would like to express our gratitude to Reviewer 2 for their thorough proofreading of both the manuscript and the supplementary information file. We have done our best to improve the manuscript based on the suggestions, and the changes are highlighted in the "manuscript with markup". We hope that these revisions will enhance the readability of our manuscript.

Reviewer 3

We thank Reviewer 3 for their thoughtful evaluation and for raising several conceptual questions that extend beyond the immediate scope of our manuscript. Engaging with these questions has prompted us to more carefully consider the broader implications and limitations of our findings. We hope the revised manuscript now addresses these points in a scientifically sound and satisfying manner.

Comment 3.1 — *The abbreviation ACH is used without definition on its first occurrence.*

Response: Thank you very much for pointing out that we forgot to define this important abbreviation. We have now introduced the abbreviation correctly at its first appearance.

Revised text [Line 50-52]: A few reports from the late 1970s and early 1980s ~~have postulated the presence of the amorphous phase of CH~~postulated the existence of an ACH (amorphous calcium hydroxide) phase during C_3S hydration, ~~although they have~~though they received limited attention.

Comment 3.2 — *Should the section "Materials and Methods" be placed before "Results and Discussion" in accordance with standard academic practice? If this is a requirement of the journal, please disregard this comment.*

Response: We agree with the reviewer's comment that the experimental section typically follows the introduction in scientific literature. However, some journals, including *Communications Materials*, have specific guidelines that require a different order. To comply with these guidelines, we cannot change the chapter arrangement.

Comment 3.3 — *It is understandable that some unanticipated factors during testing may have caused sample artifacts, such as sample carbonation. It would be preferable if some of these tests could be repeated.*

Response: In our experiments, we have consistently observed the formation of ACH during the drying of supersaturated CH solutions under various conditions, using TEM. We are thus confident in the reproducibility of our findings. In response to Comment 2.5 from Reviewer 2,

we conducted additional TEM experiments for the revision of our manuscript and again observed agglomerates of ACH from the pore solution of cement (see Fig. S28). However, it is important to note that carbonation of this amorphous phase is unavoidable, even with meticulous exclusion of CO_2 during sample preparation. This is because we intentionally used technical Portland cement for the preparation of our samples. During cement grinding, limestone is added, resulting in the cement containing significant amounts of soluble carbonates (see Tab. 2). These carbonates dissolve rapidly upon contact with water, ensuring that the aqueous phase is never completely free of carbonates. Even when using fully degassed water and preparing the samples completely under protective gas, carbonation of the detected ACH is thus inevitable.

Comment 3.4 — *This work successfully demonstrates that spherical ACH particles observed by conventional TEM are drying artifacts. However, the central question—"the true native state of CH in cement pore solution"—is not fully answered, because the conclusion of "completely dissolved CH" relies on "non-detection" rather than direct evidence, and cannot be reliably extended to the in-situ environment of hydrating cement paste.*

Response: We thank Reviewer 3 for this epistemological remark. A fundamental challenge in empirical science is "demonstrating the non-existence of something". This also concerns one of the most debated problems in the philosophy of science, as Carl Sagan famously stated: "Absence of evidence is not evidence of absence" [4]. We fully accept this epistemological constraint and agree that our conclusion cannot be presented as definitive proof of the absence of CH nanoparticles in the cementitious pore solution.

However, philosopher Elliott Sober has argued that absence of evidence can constitute meaningful evidence of absence when two conditions are satisfied: (i) the detection method is sensitive enough that the entity would have been detected if present, and (ii) multiple independent methods converge on the same result [5]. We believe both conditions are met in our study. First, cryo-HRTEM provides a detection limit well below the size range of ACH nanoparticles reported in any previous study. Second, these cryo-HRTEM results are independently corroborated by SAXS, which detected only small prenucleation clusters, and by PDF analysis, which revealed no signatures attributable to CH precursor species. Together, these three complementary and independent methods provide a meaningful experimental statement about the native state of CH in the cementitious pore solution.

We nonetheless agree with Reviewer 3 that the phrasing "completely dissolved CH" overstates the certainty warranted by our data and fails to convey important limitations of our work. We have revised the manuscript to more accurately reflect the evidential status of our conclusion.

Revised text [Line 9-13]: ~~Using~~ cryo-high-resolution transmission electron microscopy, combined with small-angle X-ray scattering and pair distribution function analysis, ~~we found that calcium hydroxide is completely dissolved in the pore solution, with only~~ shows their absence in the native pore solution after 15 min of hydration. Instead, calcium hydroxide exists as fully solvated ions or ion pairs, alongside tiny (1 nm) metastable gypsum prenucleation clusters ~~present~~.

Revised text [Line 328-337]: This finding leads to the following conclusions: both CH and calcium sulfate form from cementitious pore solutions via "non-classical" crystallization pathways. ~~While calcium sulfate forms small prenucleation clusters in solution, CH appears to be entirely dissolved, existing as fully solvated ions or ion pairs, below the detection limit of cryo-HRTEM (~ 1 nm).~~ Although both phases are nominally supersaturated in the pore solution during the first hour of cement hydration (see SI, Tab. ~~S1~~ S4), only prenucleation clusters of calcium sulfate were found, suggesting that the "non-classical" crystallization pathways for these two minerals are fundamentally different [65]. While calcium sulfate forms small prenucleation clusters in solution, no CH precursor species were detected above the detection limit of cryo-HRTEM (~ 1 nm). These results are most consistent with CH being present exclusively as fully solvated ions or ion pairs. However, it is important to note that this conclusion is based solely on the non-detection of CH-containing species and therefore represents a strong inference rather than definitive proof of their absence.

Comment 3.5 — *The phrase "clarifying a century-long question" is not recommended; scientific papers should maintain objectivity.*

Response: We fully agree with Reviewer 3 that scientific papers should always maintain objectivity. However, we believe that the hydration mechanisms of a 200+-year-old building material, which, despite centuries of research, are not fully understood, remain a topic of significant interest in the scientific community, and that the original phrase is thus both objective and scientific. Nonetheless, to align with the reviewer's recommendations, we have decided to remove the phrase from our text.

Revised text [Line 113-115]: This indicates that portlandite ~~must be~~ is completely dissolved in the pore solution ~~,clarifying the true nature of calcium hydroxide~~ during the early stages of cement hydration ~~— a question that has remained unresolved despite extensive research over the past century~~.

Comment 3.6 — *Regarding the transformation of ACH to crystalline CH driven by drying, does the author believe that the same mechanism applies in real cement systems?*

Response: We thank Reviewer 3 for this important question. We believe that the proposed non-classical crystallization mechanism of CH, or one very similar to it, truly applies to real cement systems for four reasons. First, ACH formation occurs similarly from cementitious pore solutions as from pure supersaturated CH solutions that contain no significant amounts of foreign ions [1, 6]. Second, multiple SEM studies [7, 8, 9, 10, 11] have observed spherical ACH particles on hydrating C_3S and OPC surfaces, consistent with the drying-induced formation of ACH during TEM sample preparation, as we demonstrated in our manuscript. Third, portlandite is known to form mainly within capillary pores and cavities in hardening cement paste rather than on cement particle surfaces [12, 13, 14, 15]. We suggest that crystalline portlandite formation in these areas may involve a transient ACH stage triggered by local concentration increases at these interfaces. We acknowledge that direct experimental evidence of ACH formation in hydrating cement paste is currently lacking and would require advanced in-situ techniques beyond the scope of this study. We have revised the manuscript to include these supporting arguments as well as this important clarification.

Revised text [Line 247-262]: ~~Although~~ While we cannot provide direct ~~evidence that portlandite~~ in situ evidence for ACH formation within the constrained, water-saturated pores of ~~a~~ hydrating cement paste ~~proceeds by the same mechanism as in isolated cementitious pore solutions, previous research indicates that portlandite, unlike other hydrate phases, does not form uniformly on cementsurfaces but instead forms in larger clusters within air pores, cavities, or aggregates [20, 52, 53, 54], which strongly supports this conclusion~~, some findings suggest that the "non-classical" crystallization pathway discussed here is also relevant to real cement systems. First, it is important to note that although the pore solution contains many foreign ions at high concentrations, the CH nucleation process appears to proceed similarly to that observed in pure model systems without additional ions [39,40]. Moreover, the spherical particles observed on the surfaces of hydrating C_3S and OPC in various SEM studies [24,25,28,29,30] are most plausibly reinterpreted as ACH formed during sample preparation, rather than as native surface species. Furthermore, portlandite is known to form preferentially within capillary pores and cavities in hardening cement paste [20, 52, 53, 54], rather than uniformly on the surfaces of cement particles, as other hydrate phases do [61]. This preferential location and the resulting non-uniform, clustered distribution of crystalline portlandite in hardened cement paste suggest that a transient ACH stage forming at these interfaces may facilitate portlandite crystallization in these regions. However, we emphasize that confirming this mechanism in cement paste will require future investigations using advanced in situ scattering and microscopy techniques, which are beyond the scope of this study.

Comment 3.7 — *This study was conducted at a water-to-cement ratio of 1.0. In the author's view, how would CH formation in real cement systems differ under lower water-to-cement ratios?*

Response: We appreciate Reviewer 3 highlighting this important point. First, we want to clarify that experiments at lower w/c ratios of 0.5 and 0.75 were indeed performed, and the corresponding electron micrographs are shown in the SI (Fig. S8 and Fig. S9). Across all three w/c ratios studied, the appearance, morphology, and formation process of ACH nanoparticles were consistent, suggesting that the fundamental mechanism of ACH formation in the pore solution is unaffected by the w/c ratio within this range. Choosing a w/c ratio of 1.0 as the main experimental condition was practical, as it provided sufficient pore solution volume (about 100 mL of filtrate per experiment) for the macroscopic precipitation experiments in which the induction time for CH precipitation was measured. Regarding the broader question — how CH formation might vary at lower w/c ratios in real cement systems — our experimental data indicate that the non-classical crystallization pathway involving an amorphous intermediate phase does not depend on the w/c. Although lower w/c ratios increase ionic strength and reduce water content in the pore solution, which influences supersaturation levels and nucleation kinetics, there is no reason to expect a fundamental change in the crystallization mechanism itself.

Revised text [Line 185-188]: Experiments conducted at w/c = 0.5 and w/c = 0.75 (see Figure 3c) yielded ACH particles that were morphologically identical to those observed at w/c = 1.0 (see SI, Fig. S8 and Fig. S9), confirming that the appearance, morphology, and formation mechanism of ACH are insensitive to the w/c ratio within this range.

Reviewer 4

We thank Reviewer 4 for the positive assessment and the carefully considered suggestions on clarity and presentation. The detailed comments have helped us improve the language and the overall readability of the manuscript. We believe the revisions we have made address the remaining concerns and that the manuscript is now considered ready for publication.

Comment 4.1 — *Clarification of "undetectable" CH in early hydration*

In the abstract and introduction, CH is described as "undetectable" during early hydration. For clarity, please specify that this refers to conventional techniques (e.g., XRD, SEM), rather than implying absolute absence. This distinction is important given the central conclusion that CH is present in dissolved form.

Response: We thank Reviewer 4 for this comment. However, we respectfully note that both the abstract and the introduction already specify the techniques to which "undetectable" refers. In the abstract, we wrote: "*undetectable by conventional scattering methods or thermal analysis*", and in the introduction: "*undetectable by X-ray diffraction (XRD) or scanning electron microscopy (SEM)*". We therefore believe that the requested clarification is already present in the manuscript.

Comment 4.2 — *Abstract flow and logical transitions*

The abstract moves rapidly from the observation of amorphous spheres to the conclusion that they are drying artifacts and finally to the dissolved state of CH. A brief transitional sentence clarifying this logical progression would improve readability.

Response: We would like to thank Reviewer 4 for this insightful comment. The original flow of the abstract was disjointed and difficult to follow, which made it hard to understand. The important intermediate step between mere observation of the ACH spheres and the conclusion that they are artifacts was missing. We have revised the abstract to better illustrate the logical sequence of thought, clarifying why the spheres are identified as artifacts and smoothly transitioning to the subsequent conclusion: that CH is completely dissolved.

Revised text [Line 1-19]: Calcium hydroxide, a primary hydration product of Portland cement, is undetectable by conventional scattering methods or thermal analysis during the ~~early~~

~~stages~~ dormant period of cement hydration. ~~The reasons for its undetectability and its specific formation pathways are not fully understood.~~ Its absence suggests it ~~may either be~~ is either dissolved in the ~~cementitious~~ pore solution or ~~exist~~ present in a non-crystalline state. ~~To address this long-standing question, we investigated the native state of calcium hydroxide,~~ prompting us to investigate its native state in cementitious pore solutions. While conventional transmission electron microscopy reveals large (100 nm) amorphous calcium hydroxide spheres, ~~we demonstrate that these are intermediate phases formed during the drying-induced crystallization process of portlandite. Using~~ cryo-high-resolution transmission electron microscopy, combined with small-angle X-ray scattering and pair distribution function analysis, ~~we found that calcium hydroxide is completely dissolved in the pore solution, with only~~ shows their absence in the native pore solution after 15 min of hydration. Instead, calcium hydroxide exists as fully solvated ions or ion pairs, alongside tiny (1 nm) metastable gypsum prenucleation clusters ~~present. Furthermore, an isolated pore solution remains metastable at temperatures below room temperature.~~ In addition to silicates, sulfate ions inhibit calcium hydroxide nucleation, keeping isolated pore solutions metastable for days at sub-ambient temperatures under inert gas ~~for several days. An increase in temperature or solvent evaporation, however,~~ whereas heating or evaporation triggers the multistage "non-classical" crystallization ~~process~~ of calcium hydroxide ~~and gypsum~~. Our findings confirm ~~the validity of~~ "non-classical" ~~nucleation pathways in Portland cement~~ crystallization pathways during early Portland cement hydration, the binder ~~within~~ of concrete, the most widely used man-made material.

Comment 4.3 — *Length of historical literature review in Introduction*

The discussion of early studies (1970s–1980s) is thorough but somewhat lengthy. Consider condensing this section to better emphasize the unresolved question and the motivation for the present study.

Response: We thank Reviewer 4 for this suggestion. We have condensed the historical literature section by removing redundant descriptive detail and restructuring the discussion around the key scientific question rather than presenting each study in chronological order. The revised paragraph retains all core findings of the cited literature while being more concise. We believe this revision improves the overall flow of the introduction and more directly leads the reader to the research question addressed here.

Revised text [Line 50-82]: A few reports from the late 1970s and early 1980s ~~have postulated the presence of the amorphous phase of CH~~ postulated the existence of an ACH (amorphous calcium hydroxide) phase during C_3S hydration, ~~although they have~~ though they received limited attention. ~~In 1977~~, Slegers *et al.* ~~observed early portlandite formation before the end of the induction period of C_3S hydration [28]. They~~ detected portlandite reflexes by ~~PXRD~~ powder X-ray diffraction

(PXRD) during the induction period before supersaturation was reached in ~~the solution. However, the~~ solution [28], with an unusually low intensity of the 001 reflex of CH ~~was unusually low, which may indicate —~~ — an observation consistent with either silicate poisoning or the presence of an amorphous ~~CH~~ phase [29]. ~~Two years later, Ménétrier et al. prepared sintered C_3S pellets that were immersed in water for different time intervals. After 60 s, tiny, nearly spherical particles with diameters less than 100 nm became visible on the surface under the SEM. After 15 min, the first distinct C-S-H morphologies were detected, obscuring the smaller spherical structures [35]. In the same year, Midgley also reported both stacked CH and tiny spherical CH particles (below 100 nm) in an article about the differences in the quantification methods of CH in set cement paste [38]. Additionally,~~ Odler and Dörr found ~~in 1979, while investigating the early hydration of C_3S using XRD and thermogravimetry,~~ that adding crystalline CH as a seeding material did not reduce the dormant period. ~~They concluded from their findings that crystalline~~ , leading them to conclude that CH does not form through classical homogeneous crystallization from a supersaturated solution. ~~Instead, its formation occurs in~~ but instead via a two-step process in which ~~amorphous CH is formed first, followed by its transformation into a~~ an amorphous precursor forms first, before transforming into the crystalline state [31, 34]. ~~The most convincing evidence supporting the existence of spherical, amorphous CH nanoparticles~~ Morphological evidence for this amorphous intermediate came from scanning electron microscopy studies: Ménétrier *et al.* and Ings and coworkers independently observed nearly spherical, sub–100 nm particles on the surface of ~~C_3S before the formation of C-S-H structures can be found in a publication~~ hydrating C_3S [35, 36], while Midgley simultaneously reported both stacked CH and similarly sized spherical particles in set cement paste [38]. Notably, in the study by Ings and coworkers ~~from 1983. They studied the hydration of single-crystalline C_3S and observed in SEM micrographs that within 30 min, the surfaces were covered with micrometer-sized spheres of poorly crystallized CH. After 60 min,~~ these spherical particles disappeared after 60 min when typical C-S-H structures formed ~~on the surfaces, and the spherical material was no longer observable. From the data resented, it is~~ , leaving it unclear whether the CH spheres were covered, dissolved, or otherwise "converted" into C-S-H [36]. More recently, ~~in 2012,~~ Reinheimer and Casanova ~~produced thin C_3S films using electron beam evaporation, achieving thicknesses of only a few tens of nanometers. The authors then employed scanning electron microscopy~~ confirmed the formation of spherical nanoparticles on hydrating C_3S thin films using SEM and atomic force microscopy ~~to observe the formation of spherical nanoparticles on the surface of the thin C_3S films during their hydration [40, 41]~~ (AFM) [40, 41]. Taken together, these studies consistently describe the appearance of spherical ACH particles during early hydration, yet it remains unresolved whether these particles represent a genuine amorphous precursor phase or a transient surface phenomenon.

Comment 4.4 — *Clear statement of research objectives*

The final paragraph of the Introduction would benefit from a more structured summary of the study aims (e.g., objective, methods, and key findings in one concise statement).

Response: We would like to thank Reviewer 4 for this helpful suggestion. We agree that the original concluding paragraph of the introduction lacked clear internal structure, as the objectives, methods, and key results were not clearly presented. To address this, we have restructured the paragraph to follow a more logical sequence. We start with a clear statement of the study's aim, followed by a concise summary of the methods used, and conclude with the most important results in the order they appear in the "Results and Discussion" section. We are confident that this new structure significantly enhances the readability of the introduction and provides readers with a clearer overview of the study before they move on to the "Results and Discussion" section.

Revised text [Line 100-122]: ~~For the first time, we describe~~ To clarify the native state of CH during the early stages of cement hydration, we studied the formation of this amorphous ~~intermediate phase of CH from the separated~~ precursor phase from the pore solution of a technical Portland cement.~~Notably, the~~ , aiming to clarify the native state of CH during the early stages of cement hydration. We investigated isolated cementitious pore solutions using conventional transmission and cryo-high-resolution transmission electron microscopy (cryo-HRTEM) combined with small-angle X-ray scattering (SAXS), pair distribution function (PDF) analysis, and macroscopic precipitation experiments. Our results demonstrate that rapid drying of the ~~cementitious~~ pore solution during conventional TEM ~~grid~~ sample preparation results in the formation of large (up to 1 µm) spherical ACH particles, which subsequently aggregate into hexagonal CH crystals with a morphology typical of Portland cement. ~~Our findings provide additional evidence that mineral phase nucleation is driven by distinct "non-classical" pathways, not only in controlled model systems and natural environments, but also in large-scale, multiphase materials such as Portland cement. Furthermore, we confirm that cementitious pore solutions do not contain these large ACH particles or any other nanoparticles, except for~~ In contrast, cryo-HRTEM combined with SAXS and PDF analysis of the native pore solution reveals the absence of these particles, showing instead only metastable gypsum prenucleation clusters~~, which exhibit diameters~~ of approximately 1 nm in diameter. This indicates that portlandite ~~must be~~ is completely dissolved in the pore solution~~, clarifying the true nature of calcium hydroxide~~ during the early stages of cement hydration ~~— a question that has remained unresolved despite extensive research over the past century. Additionally, nucleation~~ . Furthermore, we demonstrated that isolated pore solutions are highly metastable at room temperature under an inert atmosphere, a phenomenon attributable to the presence of different ions, particularly sulfates and silicates, which inhibit portlandite precipitation. Precipitation experiments conducted at elevated temperatures ~~revealed~~ further confirm that, after

prolonged induction times, only portlandite and gypsum precipitate from the separated ~~cementitious~~ pore solution, with no other hydrate phases, such as C-S-H or ettringite, forming. Our findings provide additional evidence that mineral phase nucleation is driven by distinct "non-classical" pathways, not only in controlled model systems and natural environments, but also in large-scale, multiphase materials such as Portland cement.

Comment 4.5 — *Interpretation of core–shell structure (Figure 1)*

The assignment of the particle core as "primarily composed of water" appears somewhat interpretative. Please consider softening the wording (e.g., "suggesting" or "consistent with") unless further direct evidence is available.

Response: We have softened the statement slightly, in line with the request.

Revised text [Line 149-150]: Given that the core exhibits low calcium but high oxygen signals, ~~we assume that it is~~this is consistent with a core primarily composed of water.

Comment 4.6 — *Early indication of drying artifacts*

The conclusion that large ACH particles are drying-induced artifacts is central to the manuscript but is only fully clarified later. Consider signaling this interpretation earlier when these particles are first introduced.

Response: We added a sentence before the paragraph that describes the nature of the particles, which helps anticipate their interpretation and provides the reader with some context.

Revised text [Line 140-144]: However, contrary to our expectations, we observed ACH nanoparticles under the TEM ~~when~~ after we applied the separated pore solution to a TEM grid at room temperature and let it dry (see Figure 1a-c and SI, Fig. ~~S2).~~ S1-3). As will be demonstrated below, these particles do not represent the native state of CH in the pore solution but are instead formed as an intermediate phase during drying of the pore solution on the TEM grid.

Comment 4.7 — *Consistency of terminology*

The manuscript alternates between "ACH," "amorphous CH," and "amorphous calcium hydroxide." Please standardize terminology after first definition to improve clarity.

Response: To improve clarity and conciseness, we have standardized terminology and consistently used the abbreviation ACH instead of "amorphous CH" or "amorphous calcium hydroxide".

Comment 4.8 — *Conclusion structure and conciseness*

The conclusion section is comprehensive but somewhat dense. Consider organizing it into distinct points (e.g., key findings, methodological implications, mechanistic insights) and reducing minor repetitions for better readability.

Response: We appreciate the suggestion made by Reviewer 4. We acknowledge that the original concluding section was somewhat dense and lacked a clear thematic structure, with several points presented in a disorganized manner and some statements implicitly repeated. We have therefore restructured the conclusion into the three distinct paragraphs suggested and removed redundant statements. We believe the revised conclusion is now more concise and clearer, while retaining all the essential results and conclusions of the original version.

Revised text [Line 501-543]: Conclusions

In summary, we ~~report the experimental detection of an amorphous intermediate phase of CH that forms during drying of a cementitious pore solution on a TEM grid, providing compelling evidence that portlandite crystallizes via a "non-classical" pathway. The amorphous nature and chemical composition of the ACH nanoparticles were confirmed by SAED and EELS, revealing a core-shell structure with a water- and hydroxide-ion-rich core, encased by a calcium-rich shell. Importantly, the sample preparation method significantly affected the observed morphology in conventional TEM imaging. We detected~~ provide insights into the native state of CH and its crystallization pathways in cementitious pore solutions.

We detected and analyzed large spherical ACH ~~nano~~ particles (up to 1 µm) ~~after blotting~~ using conventional TEM and showed that they form during drying of the pore solution ~~, whereas drop casting resulted in smaller (10 nm) liquid-like particles. In contrast, cryo-HRTEM revealed the presence of tiny (1-2 nm) amorphous clusters, consistent with SAXS and PDF measurements of the separated cementitious solution in its native liquid form, which indicated that the primary species in the pore solution are approximately 1 nm~~ prenucleation clusters. Both HRTEM and PDF analysis revealed that these clusters were, in fact, calcium sulfate species rather than ACH. This suggests that CH is fully dissolved in the pore solution and that ACH forms only as an intermediate phase during the drying-induced crystallization of portlandite. The observations of on a TEM grid. The sample preparation method critically governs the size, shape, and agglomeration state of the observed particles: blotting produces spherical particles approximately 100 nm in size, drop casting yields smaller agglomerated species below 20 nm, and ethanol quenching introduces additional solvent-induced structures. The spherical ACH particles ~~on the surfaces of hydrating C_3S, as~~ reported in earlier publications ~~,~~ on hydrating C_3S surfaces [30, 31, 32] can thus likely be attributed to ~~their formation during the sample preparation process.~~ similar preparation artifacts.

Cryo-HRTEM, SAXS, and PDF analysis confirmed that CH is completely dissolved in cementitious pore solution separated after 15 min, existing below the cryo-HRTEM detection limit as fully solvated ions or ion pairs. The only particulate species detected in the native pore solution are metastable gypsum prenucleation clusters of approximately 1 nm in diameter. Furthermore, the isolated cementitious pore solution remains metastable for several days under inert, low-temperature conditions ~~. Just as ACH crystallizes under the TEM only at higher electron-beam dose rates, as confirmed by SAED, portlandite precipitates rapidly from the pore solution only when the solution is heated, and calcium carbonate forms when the pore solution is exposed to atmospheric CO_2. The induction time for CH nucleation from the cementitious pore solution depends on~~ , and portlandite precipitates only upon heating or evaporation, with the induction time depending on both the temperature and the timing of separation (~~*i.e.*~~ i.e., the chemical composition) of the pore solution. ~~Notably, CH crystallizes earlier from the cementitious pore solution if the solution is separated from the cement paste at a later time~~ This metastability is primarily caused by the inhibitory effects of several ions in the pore solution, particularly sulfates and silicates, on CH precipitation.. Moreover, only portlandite (along with gypsum in the very early stage) crystallizes from a separated cementitious pore solution, whereas no C-S-H, ettringite, or any other hydrate phase does. ~~This discovery significantly enhances~~

Our observations confirm that both CH and calcium sulfate crystallize from cementitious pore solutions via "non-classical" pathways, though their crystallization routes appear fundamentally different. While calcium sulfate forms prenucleation clusters in solution, CH remains fully dissolved until nucleation is triggered. Once initiated, CH crystallization proceeds through a multi-stage process: dissolved ions associate into clusters, which coalesce into amorphous spherical nanoparticles, aggregate into networks, and ultimately transform into hexagonal portlandite crystals with the morphology characteristic of cementitious systems. These findings confirm the validity of "non-classical" nucleation pathways in Portland cement hydration and significantly advance our understanding of portlandite and gypsum formation during the early stages of cement hydration.

References

[1] Madeja, B. *et al.* New insights into the nucleation of portlandite and the effects of polymeric additives. *Cem. Concr. Res.* **173**, 107258 (2023).

[2] Grassucci, R. A., Taylor, D. J. & Frank, J. Preparation of macromolecular complexes for cryo-electron microscopy. *Nat. Protoc.* **2**, 3239–3246 (2007).

[3] Nickl, S. *et al.* Investigating the evolution of the cementitious pore solution during the first 15 minutes of hydration via dynamic crossflow filtration. *CEMENT* 100181 (2026).

[4] Sagan, C. *The Demon-Haunted World: Science As a Candle in the Dark* (Random House Publishing Group, Westminster, 2011).

[5] Sober, E. *Evidence and evolution: The logic behind the science* (Cambridge University Press, Cambridge, 2008).

[6] Rodriguez-Navarro, C., Burgos-Cara, A., Di Lorenzo, F., Ruiz-Agudo, E. & Elert, K. Nonclassical crystallization of calcium hydroxide via amorphous precursors and the role of additives. *Cryst. Growth Des.* **20**, 4418–4432 (2020).

[7] Ménétrier, D., Jawed, I., Sun, T. S. & Skalny, J. Esca and sem studies on early c3s hydration. *Cem. Concr. Res.* **9**, 473–482 (1979).

[8] Midgley, H. G. The determination of calcium hydroxide in set portland cements. *Cem. Concr. Res.* **9**, 77–82 (1979).

[9] Ings, J. B., Brown, P. W. & Frohnsdorff, G. Early hydration of large single crystals of tricalcium silicate. *Cem. Concr. Res.* **13**, 843–848 (1983).

[10] Rheinheimer, V. *A nanoscale study of dissolution and growth processes in cement hydrates.* Dissertation, Universitat Politècnica de Catalunya, Barcelona (2012).

[11] Rheinheimer, V. & Casanova, I. Hydration of c3s thin films. *Cem. Concr. Res.* **42**, 593–597 (2012).

[12] Bache, H. H., Idorn, G. M., Nepper-Christensen, P. & Nielsen, J. Morphology of calcium hydroxide in cement paste. In *Highway Research Board Special Report*, vol. 90, 154–174 (Highway Research Board, Washington, DC, 1966).

[13] Gallucci, E. & Scrivener, K. Crystallisation of calcium hydroxide in early age model and ordinary cementitious systems. *Cem. Concr. Res.* **37**, 492–501 (2007).

[14] Diamond, S. Calcium hydroxide in cement paste and concrete - a microstructural appraisal. In Skalny, J. P., Gebauer, J. & Odler, I. (eds.) *Materials Science of Concrete, Special Volume*, 37–58 (John Wiley & Sons, 2001).

[15] Diamond, S. The microstructure of cement paste and concrete—-a visual primer. *Cem. Concr. Compos.* **26**, 919–933 (2004).

Resubmission of COMMSMAT-26-0064-T: Evidence of an amorphous intermediate phase during non-classical calcium hydroxide crystallization from cementitious pore solutions – Response to Reviewers

Dear Dr. John Plummer,

Thank you, the editorial team of *Communications Materials*, and the reviewers for carefully evaluating our manuscript "Evidence of an amorphous intermediate phase during non-classical calcium hydroxide crystallization from cementitious pore solutions" and for the opportunity to submit a revised version.

We are pleased that Reviewer 2 and Reviewer 3 found that our previous revisions fully addressed their comments and that they recommend the manuscript for publication. The remaining concerns raised by Reviewer 1 have been carefully addressed, as detailed in the point-by-point response below, with all changes highlighted in the manuscript.

All editorial points have also been addressed: the transition from background to present findings in the Abstract has been clarified, the TEM sample preparation schematic has been moved to the Supplementary Information, the previously reserved Zenodo data repository has been published, and a Funding statement has been added as requested.

We believe the manuscript is now suitable for publication in *Communications Materials* and look forward to your decision.

Sincerely,

Torben Gädt

Reviewer 1

Comment 1.1 — *The authors have provided comprehensive revisions in response to my previous comments, which greatly improves the integrity and logical rigor of this manuscript. However, several key scientific ambiguities, and descriptive flaws still remain unresolved.*

Response: We thank Reviewer 1 for the positive assessment of our revisions and for the constructive comments that have helped improve our manuscript. We address the three remaining points below.

Comment 1.2 — *Although the authors sorted and compared early research chronologically, the logical hierarchy of contradictions between different literature is still weak. The current text only lists each scholar's phenomenon observation but fails to systematically summarize viewpoints in existing research.*

Response: We thank the Reviewer 1 for highlighting this important shortcoming. We have carefully re-examined the cited primary sources and thoroughly revised this paragraph in the introduction to move beyond a purely chronological listing of individual observations. Instead, we have organized the historical literature by type of evidence and explicitly highlighted disagreements among the studies. The revised paragraph now distinguishes between two independent lines of evidence: (i) indirect inferences regarding an ACH phase based on discrepancies between analytical methods [1, 2, 3] and (ii) direct microscopic observations of amorphous nanoparticles on hydrating C_3S surfaces, whose phase identity was inconsistently assigned across studies – as CH [3, 4] and as C-S-H [5, 6, 7]. We believe the revised paragraph now provides the systematic, hierarchically structured comparison of viewpoints requested by Reviewer 1. To ensure comparability, we have included the original text in red and the revised section in blue below.

Revised text [Line 43-64]: ~~A few reports from the late 1970s and early 1980s postulated the existence of an ACH (amorphous calcium hydroxide) phase during C_3S hydration, though they received limited attention. Slegers *et al.* detected portlandite reflexes by powder X-ray diffraction (PXRD) during the induction period before supersaturation was reached in solution [27]], with an unusually low intensity of the 001 reflex — an observation consistent with either silicate poisoning or the presence of an amorphous phase [28]. Odler and Dörr found that adding crystalline CH as a seeding material did not reduce the dormant period, leading them to conclude that CH~~

~~does not form through classical homogeneous crystallization from a supersaturated solution but instead via a two-step process in which an amorphous precursor forms first, before transforming into the crystalline state [29,30]. Morphological evidence for this amorphous intermediate came from scanning electron microscopy studies: MÉNÉTRIER *et al.* and INGS and coworkers independently observed nearly spherical, sub-100 nm particles on the surface of hydrating C_3S [31,32], while MIDGLEY simultaneously reported both stacked CH and similarly sized spherical particles in set cement paste [33]. Notably, in the study by INGS and coworkers, these spherical particles disappeared after 60 min when typical C-S-H structures formed, leaving it unclear whether the CH spheres were covered, dissolved, or otherwise "converted" into C-S-H [32]. More recently, REINHEIMER and CASANOVA confirmed the formation of spherical nanoparticles on hydrating C_3S thin films using SEM and atomic force microscopy (AFM) [34,35]. Taken together, these studies consistently describe the appearance of spherical ACH particles during early hydration, yet it remains unresolved whether these particles represent a genuine amorphous precursor phase or a transient surface phenomenon.~~

A few reports from the late 1970s and early 1980s addressed the possible existence of an ACH (amorphous calcium hydroxide) phase during C_3S hydration. One line of evidence for such a phase is indirect, arising from discrepancies among analytical methods rather than from direct observation. ODLER and DÖRR found that the CH content of hydrating C_3S pastes measured by PXRD was systematically lower than that determined by thermogravimetry or solvent extraction, and concluded that part of the CH must therefore be present in an amorphous form [27]. In a companion study, seeding with crystalline CH failed to shorten the induction period of C_3S hydration, which the authors took as evidence against classical crystallization of CH from a supersaturated solution and led them to propose a two-step formation pathway involving an amorphous intermediate phase [28]. A similar discrepancy between PXRD and thermogravimetric or extraction methods was also reported by MIDGLEY for set cement paste, alongside spherical ACH particles of approximately 100 nm observed by SEM amid the predominant crystalline CH platelets [29].

This direct morphological evidence for spherical nanoparticles on hydrating C_3S surfaces has also been reported by other authors, although their phase identity was assigned inconsistently across studies. INGS and coworkers observed spheres approximately 1 µm in size on C_3S single crystals after 30 min of hydration, which they attributed to amorphous or poorly crystallized CH and which were subsequently converted into acicular C-S-H after 60 min [30]. MÉNÉTRIER *et al.* observed morphologically similar but smaller particles on C_3S surfaces within a comparable time frame, but interpreted them as an early, poorly ordered form of C-S-H rather than CH [31]. More recently, RHEINHEIMER and CASANOVA used SEM and atomic force microscopy (AFM) to observe growing aggregated spherical nanoparticles on hydrating C_3S thin films, which they, however, attributed to C-S-H based on concurrent X-ray photoelectron spectroscopy (XPS) evidence

of silicate polymerization [32,33]. Taken together, these studies consistently report that CH is undetectable as a crystalline phase during the earliest stages of C_3S hydration, coinciding with the appearance of spherical amorphous nanoparticles. Yet they disagree on whether these nanoparticles are CH or C-S-H and whether they represent a genuine amorphous precursor phase or a transient surface phenomenon.

Comment 1.3 — *The authors completely deleted the particle size statistical content due to TEM drying artifacts, but there is a lack of alternative quantitative characterization of the size of particles.*

Response: We thank Reviewer 1 for raising this point. We intentionally removed the TEM-based particle size statistics, not primarily because of drying artifacts but because we demonstrate in this study that the particle sizes are governed by the TEM sample preparation method rather than reflecting the native state of the particles in the solution (see Fig. 4 and accompanying text), making such statistics scientifically misleading if reported as a material property. As a preparation-artifact-free alternative, our SAXS analysis already provides a quantitative size distribution of the native primary species in solution (see Fig. 6d and SI, Fig. S77–S78), which, however, are calcium sulfate and not calcium hydroxide prenucleation clusters. We have clarified and refined this reasoning explicitly in the manuscript.

Revised text [Line 326-328]: This SAXS-derived size provides a preparation-artifact-free quantitative measure of the native particle size, in direct contrast to the size distributions obtained from dried TEM samples (see SI, Fig. S2-S4).

Comment 1.4 — *The authors corrected individual inconsistent scale bars, but it is suggested to unify the standard of scale bar layout for all images in the full text: uniformly place the scale bar at the lower right corner of images, and mark the length unit font size uniformly, to avoid scattered and inconsistent visual presentation of figures, which affects the readability of the manuscript.*

Response: We appreciate Reviewer 1 for this suggestion, and have revised all figure panels to enhance their visual presentation. The scale bars are now consistently placed in the lower-right corner, with a uniform appearance, font size, and similar length throughout the manuscript. In Figures 1 and 6, we had to position the scale bars in the lower-left corner to avoid overlap with other elements of the figures. However, we believe this adjustment does not compromise the readability of the manuscript.

Reviewer 2

Comment 2.1 — *Thank you for your careful and thorough responses to all of my questions and comments. As I noted previously, this is a highly important, well-executed, and internally consistent study. I greatly appreciate the effort you invested in addressing the review points and improving the manuscript. It has been a pleasure to review this work, and I wish you the best with its publication.*

Response: We sincerely thank Reviewer 2 for the positive assessment of our revised manuscript and for the constructive engagement throughout the review process. We are glad that our responses have addressed all outstanding concerns.

Reviewer 3

Comment 3.1 — *The authors have well answered my questions, and I recommend the acceptance of this paper.*

Response: We thank Reviewer 3 for the positive evaluation and recommendation of our manuscript for publication.

References

[1] Odler, I. & Dörr, H. Early hydration of tricalcium silicate i. kinetics of the hydration process and the stoichiometry of the hydration products. *Cem. Concr. Res.* **9**, 239–248 (1979).

[2] Odler, I. & Dörr, H. Early hydration of tricalcium silicate ii. the induction period. *Cem. Concr. Res.* **9**, 277–284 (1979).

[3] Midgley, H. G. The determination of calcium hydroxide in set portland cements. *Cem. Concr. Res.* **9**, 77–82 (1979).

[4] Ings, J. B., Brown, P. W. & Frohnsdorff, G. Early hydration of large single crystals of tricalcium silicate. *Cem. Concr. Res.* **13**, 843–848 (1983).

[5] Ménétrier, D., Jawed, I., Sun, T. S. & Skalny, J. Esca and sem studies on early c3s hydration. *Cem. Concr. Res.* **9**, 473–482 (1979).

[6] Rheinheimer, V. *A nanoscale study of dissolution and growth processes in cement hydrates.* Dissertation, Universitat Politècnica de Catalunya, Barcelona (2012).

[7] Rheinheimer, V. & Casanova, I. Hydration of c3s thin films. *Cem. Concr. Res.* **42**, 593–597 (2012).