Supplementary Information

Phosphate Additive Modification of C-S-H and C-A-S-H Crystallization Pathways

*Yannick H. Emminger[a], Annika Bastian[a], Luca Ladner[a], Tobias Steiner[a], Cristina Ruiz-Agudo[a]**

[a]*Physical Chemistry, University of Konstanz, Universitätsstrasse 10, 78457 Konstanz, Germany*

**Corresponding Author: Dr. Cristina Ruiz-Agudo (Email: cristina.ruiz-agudo@uni-konstanz.de)*

Keywords: Cement hydrates, C-S-H, C-A-S-H, Non-classical crystallization, Additives

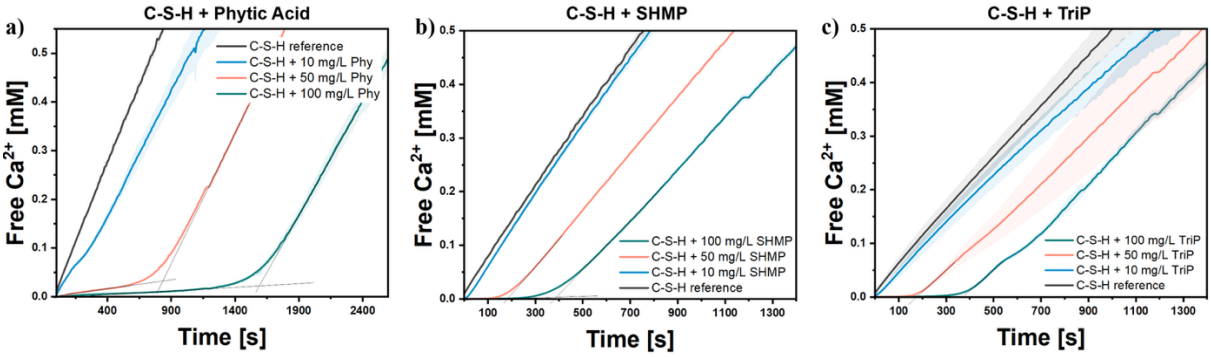


Figure SI-1: Close-up of the Ca^{2+} binding region shown by the delay in the increase of free-Ca^{2+} concentration during the precipitation titration of C-S-H in presence of a) phytic acid, b) SHMP and c) TriP in concentrations of 10, 50 and 100 mg/L.

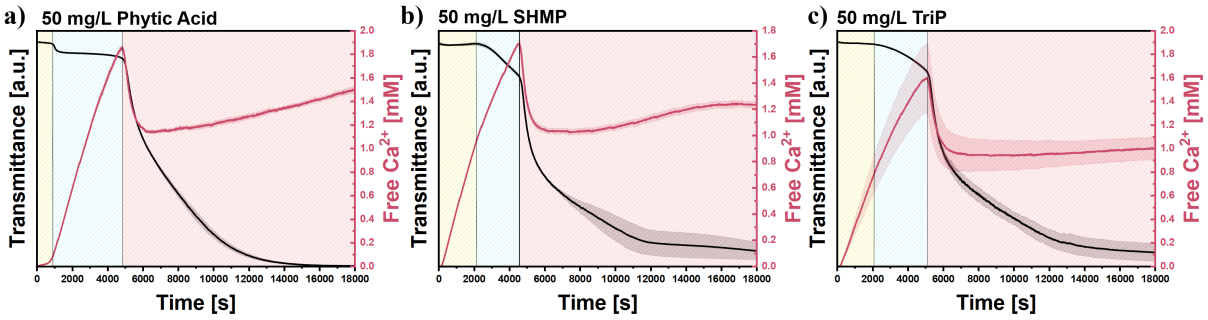


Figure SI-2: The highlighted separate regimes of the C-S-H crystallisation in presence of a) phytic acid, b) SHMP and c) TriP for the concentration of 50 mg/L, shown by the transmittance and free-Ca^{2+} concentration curves.

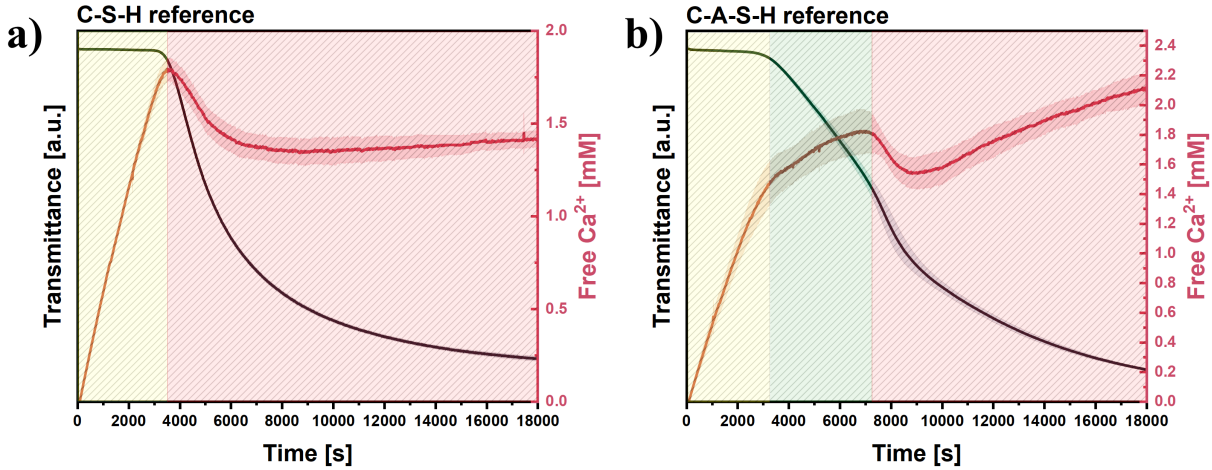


Figure SI-3: Reference plots for the pure C-S-H and C-A-S-H system with the highlighted regimes of the crystallisation.

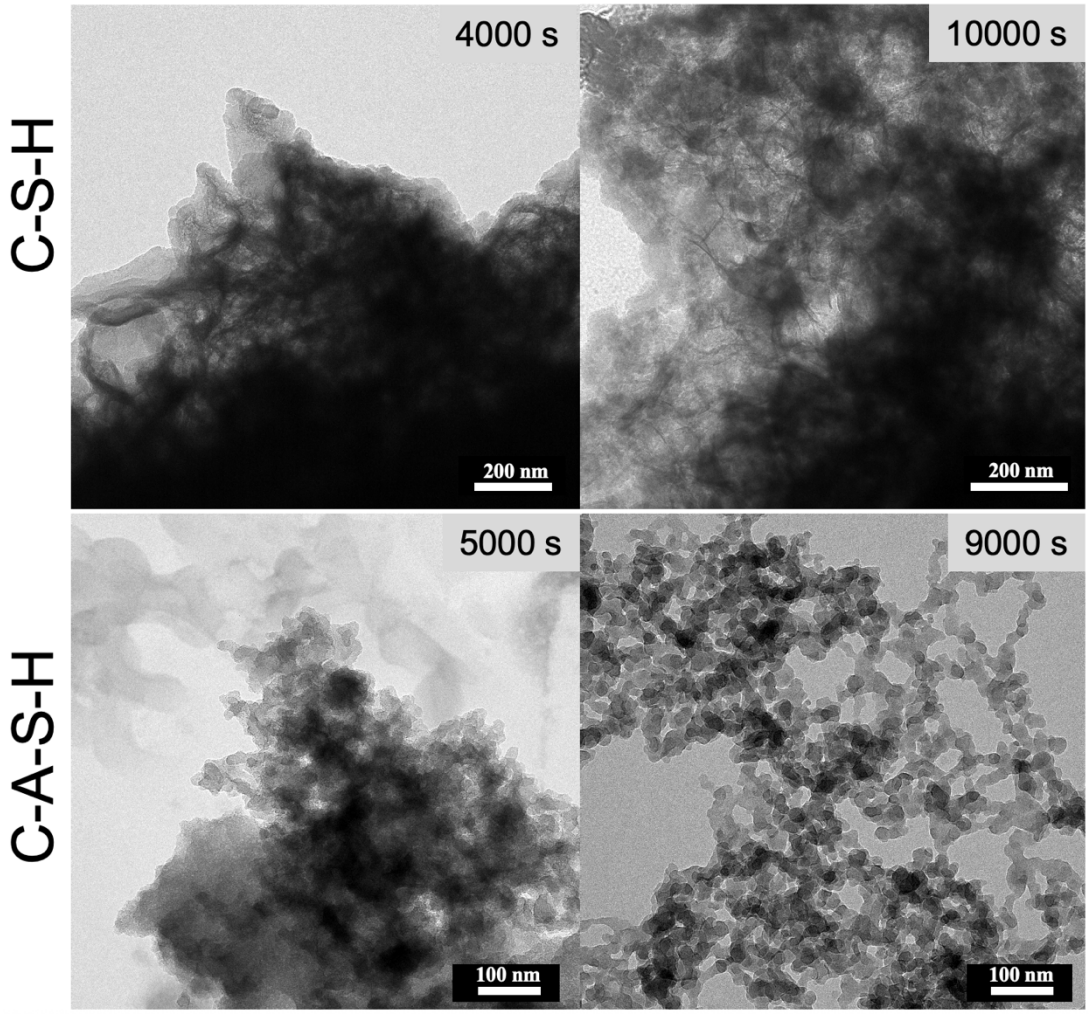


Figure SI-4: Reference TEM images of pure C-S-H and C-A-S-H aliquots at respective times shown in the images.

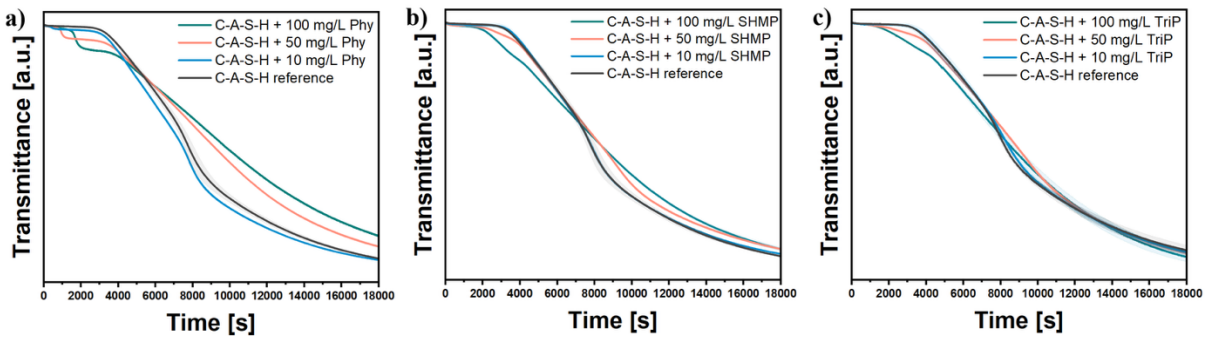


Figure SI-5: In-situ transmittance data from the precipitation titration of C-A-S-H in presence of a) phytic acid, b) SHMP and c) TriP in concentrations of 10, 50 and 100 mg/L.

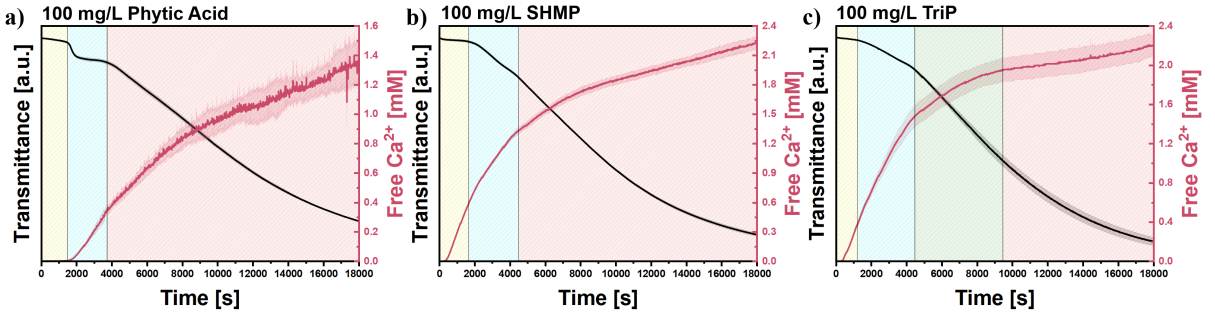


Figure SI-6: The highlighted separate regimes of the C-A-S-H crystallisation in presence of a) phytic acid, b) SHMP and c) TriP for the concentration of 100 mg/L, shown by the transmittance and free-Ca^{2+} concentration curves.

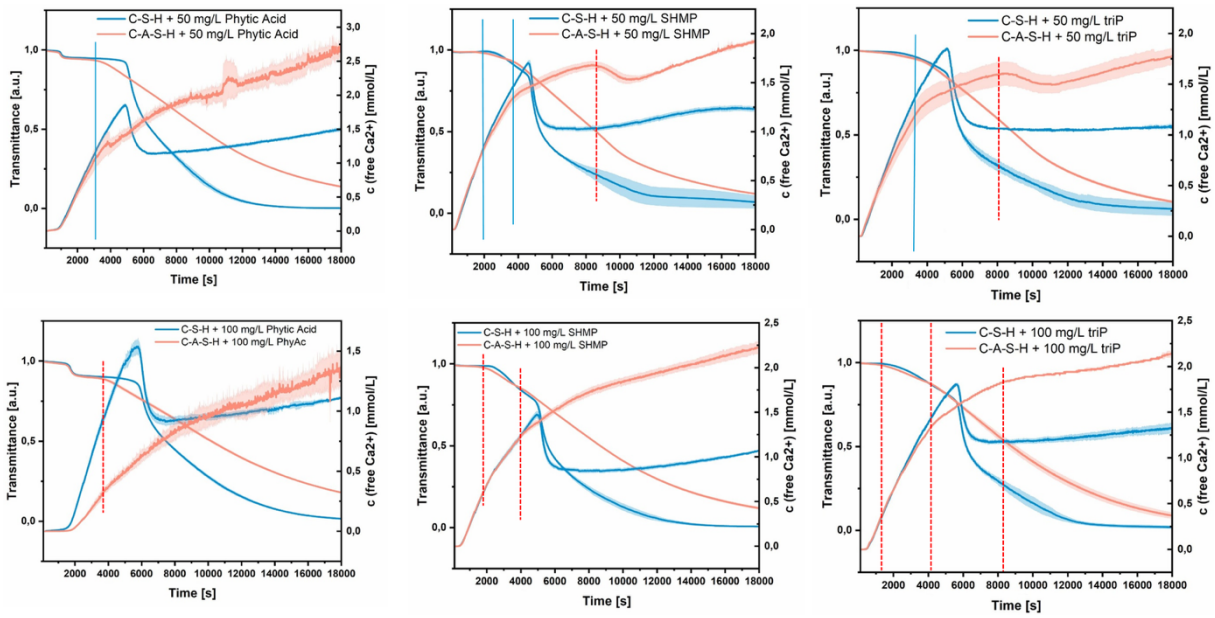


Figure SI-7: Overlapping transmittance and free-Ca^{2+} concentration curves from the C-S-H (blue) and C-A-S-H (orange) precipitation titration in the presence of phytic acid, SHMP and TriP in concentrations of 50 and 100 mg/L. Highlighted are important time spots where the PoNs, specific drops in transmittance or kinks in the curves occur, each in the respective colour.

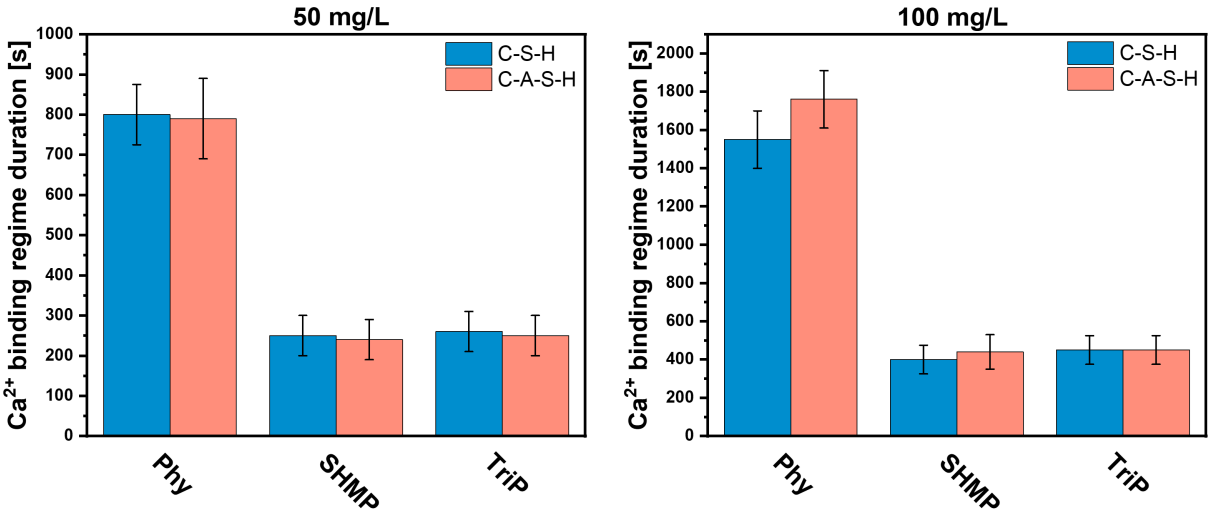


Figure SI-8: Durations of the Ca^{2+} binding regime for each additive (phytic acid, SHMP, TriP) in concentrations of 50 and 100 mg/L.

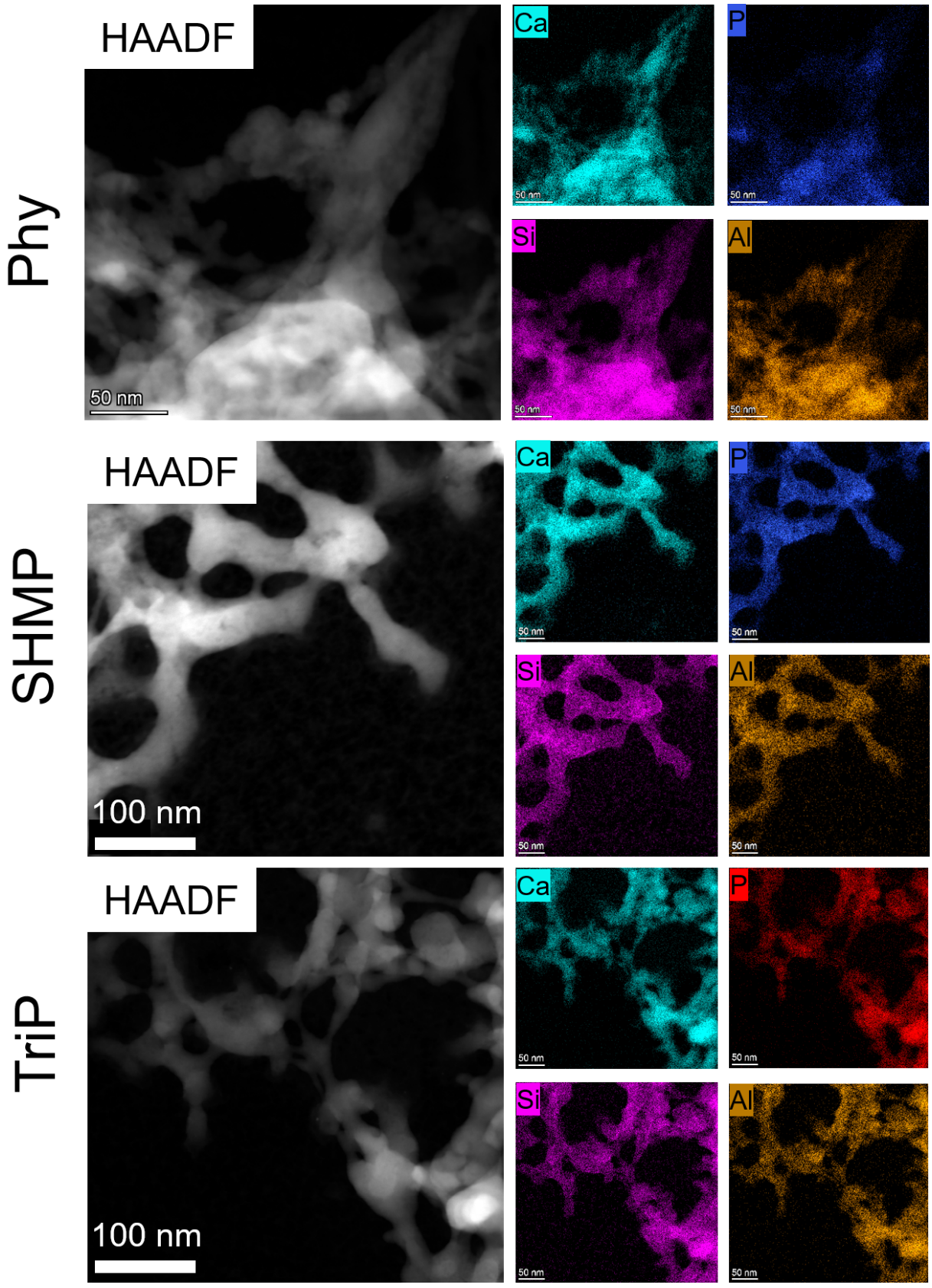


Figure SI-9: TEM images and corresponding EDX mappings for Ca, P, Si and Al of the obtained solids from the C-A-S-H aliquots after 4000 s in presence of phytic acid, SHMP and TriP at a concentration of 100 mg/L. Scale of the EDX mappings: 50 nm.

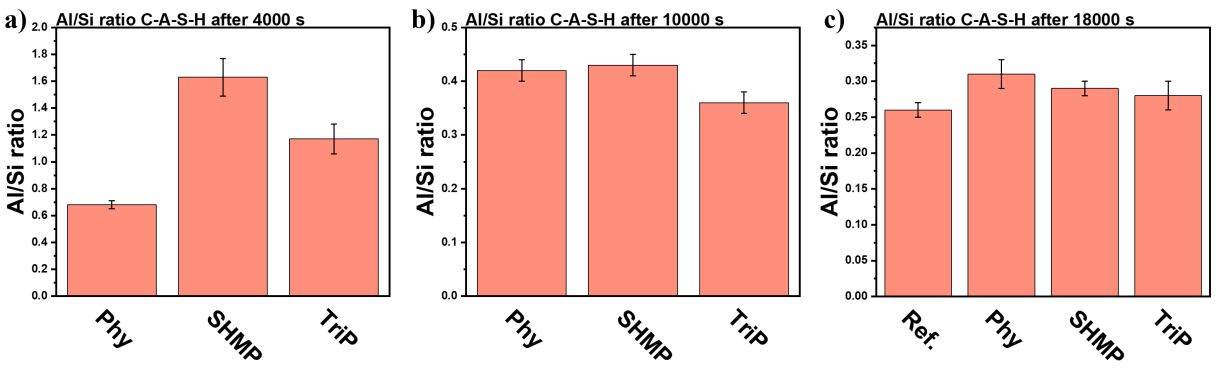


Figure SI-10: Measured Al/Si ratios by quantitative EDX analysis of the different C-A-S-H aliquots in presence of 100 mg/L phytic acid, SHMP and TriP after a) 4000 s, b) 10000 s and c) 18000 s.

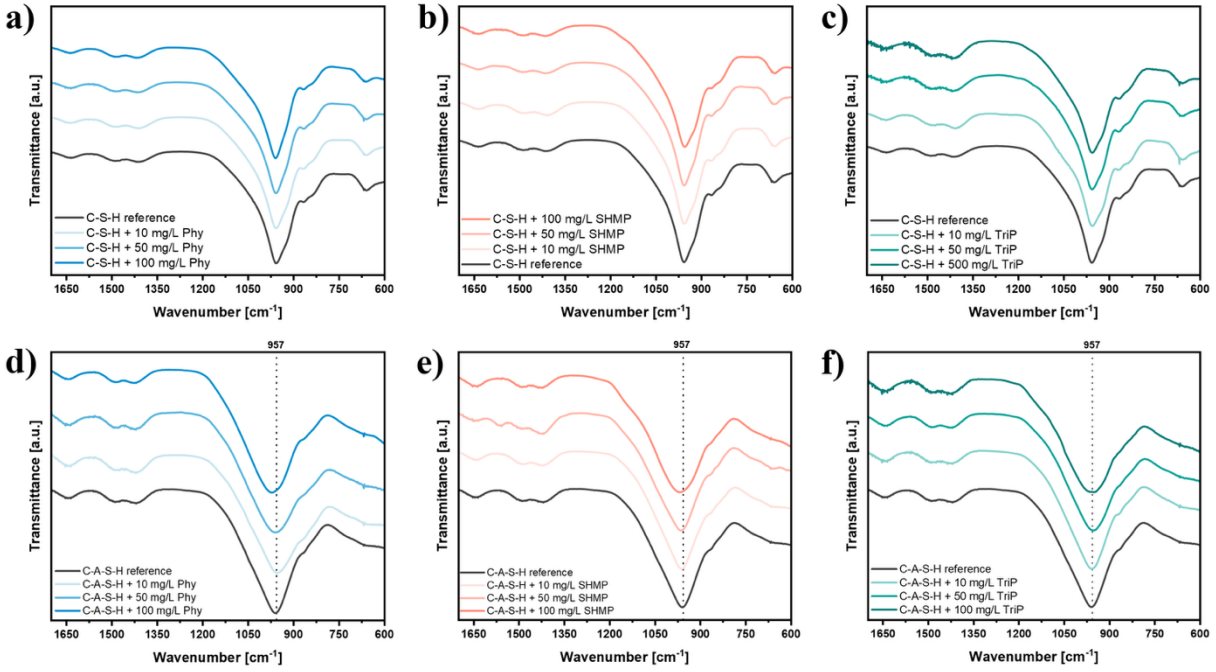


Figure SI-11: Zoomed-in FTIR spectra of the 1700 -600 cm^{-1} region of the obtained C-S-H (a-c) and C-A-S-H (d-f) solids from the precipitation titration experiments in presence of phytic acid (a,d), SHMP (b,e) and TriP (c,f)

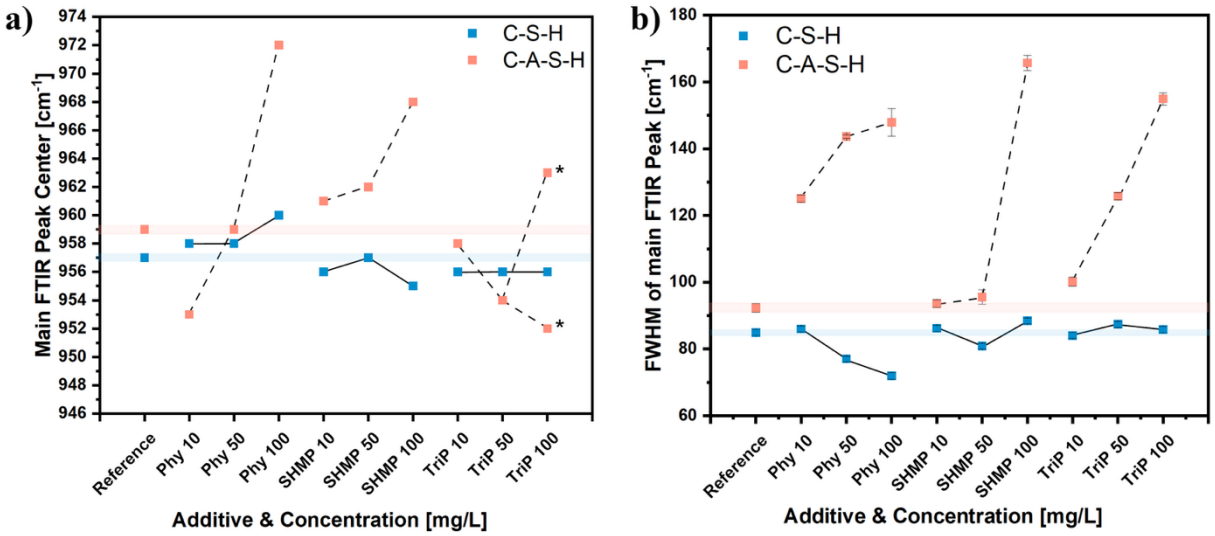


Figure SI-12: a) Location of the main FTIR peak of each experiment of all additives and concentrations (*: Main peak is split in two) for C-S-H (blue) and C-A-S-H (orange). b) Corresponding fitted FWHM of the main peak in respective FTIR spectrum of each experiment.

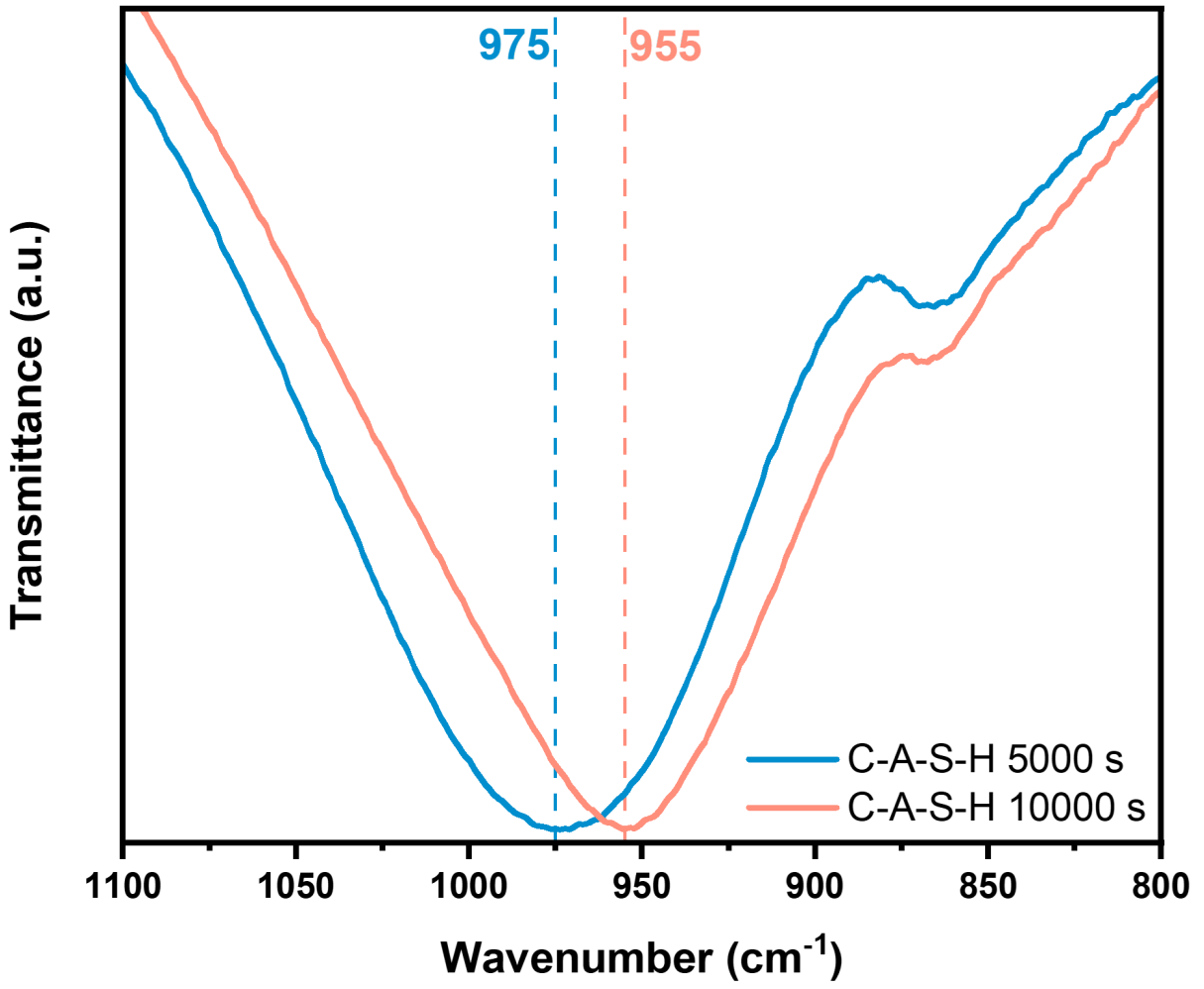


Figure SI-13: Main peak shifting in the FTIR spectrum after time for the C-A-S-H aliquots samples highlighting the higher degrees of polymerisation of early C-A-S-H species.

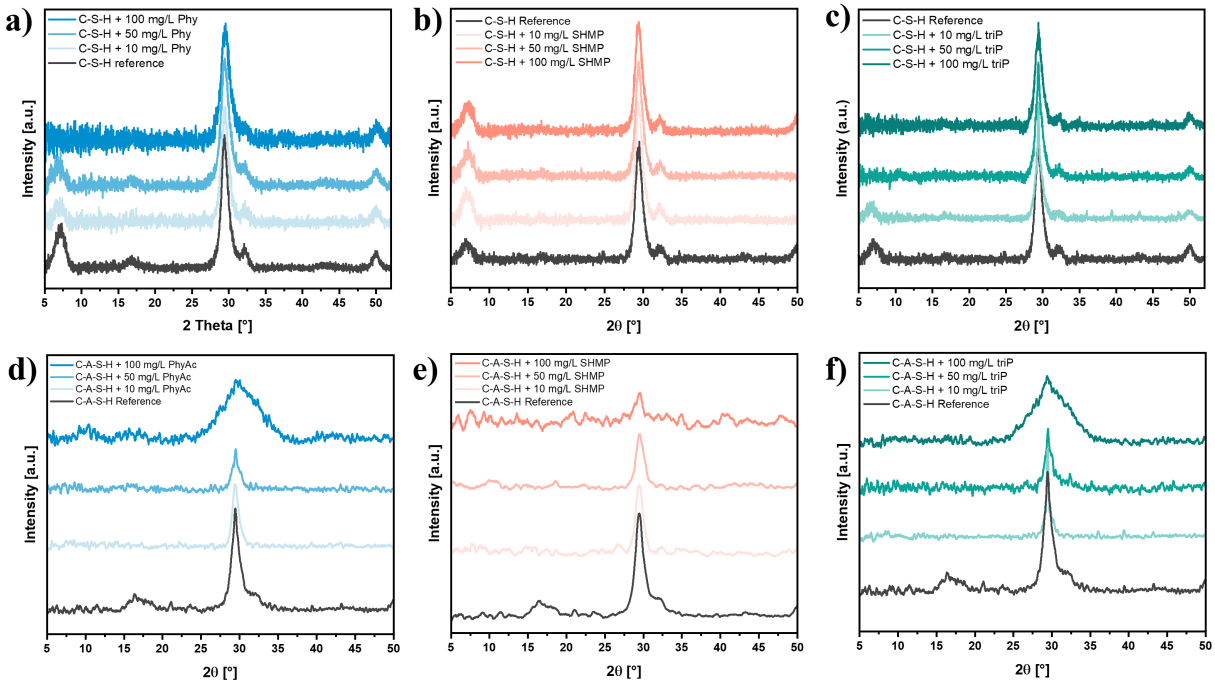


Figure SI-14: PXRD measurements of the obtained solids from the precipitation titration synthesis of C-S-H and C-A-S-H in the presence of phytic acid, SHMP and TriP in concentrations of 0, 10, 50 and 100 mg/L.

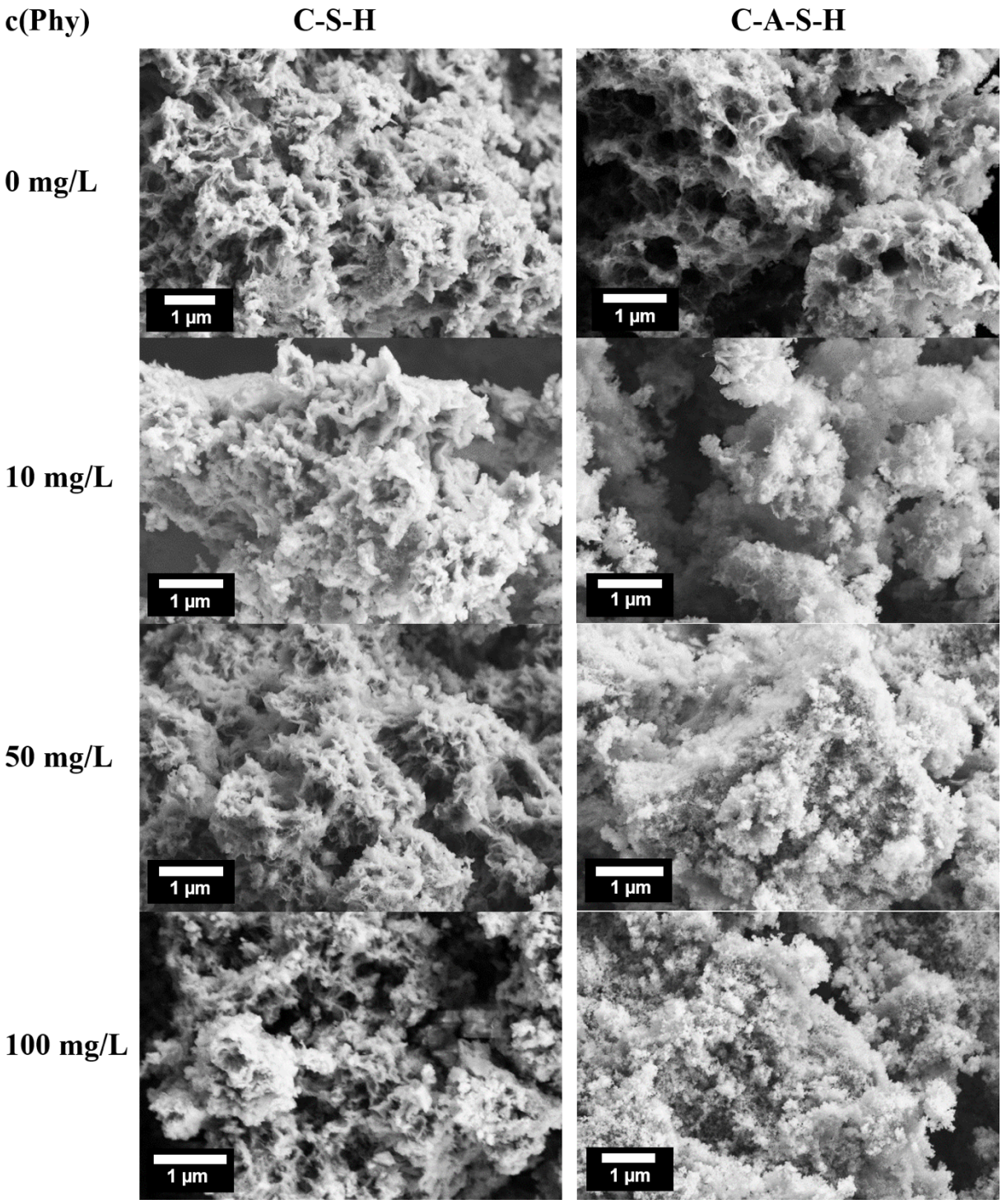


Figure SI-15: SEM images of the obtained precipitates from the C-S-H and C-A-S-H synthesis in presence of phytic acid in concentrations of 0, 10, 50 and 100 mg/L.

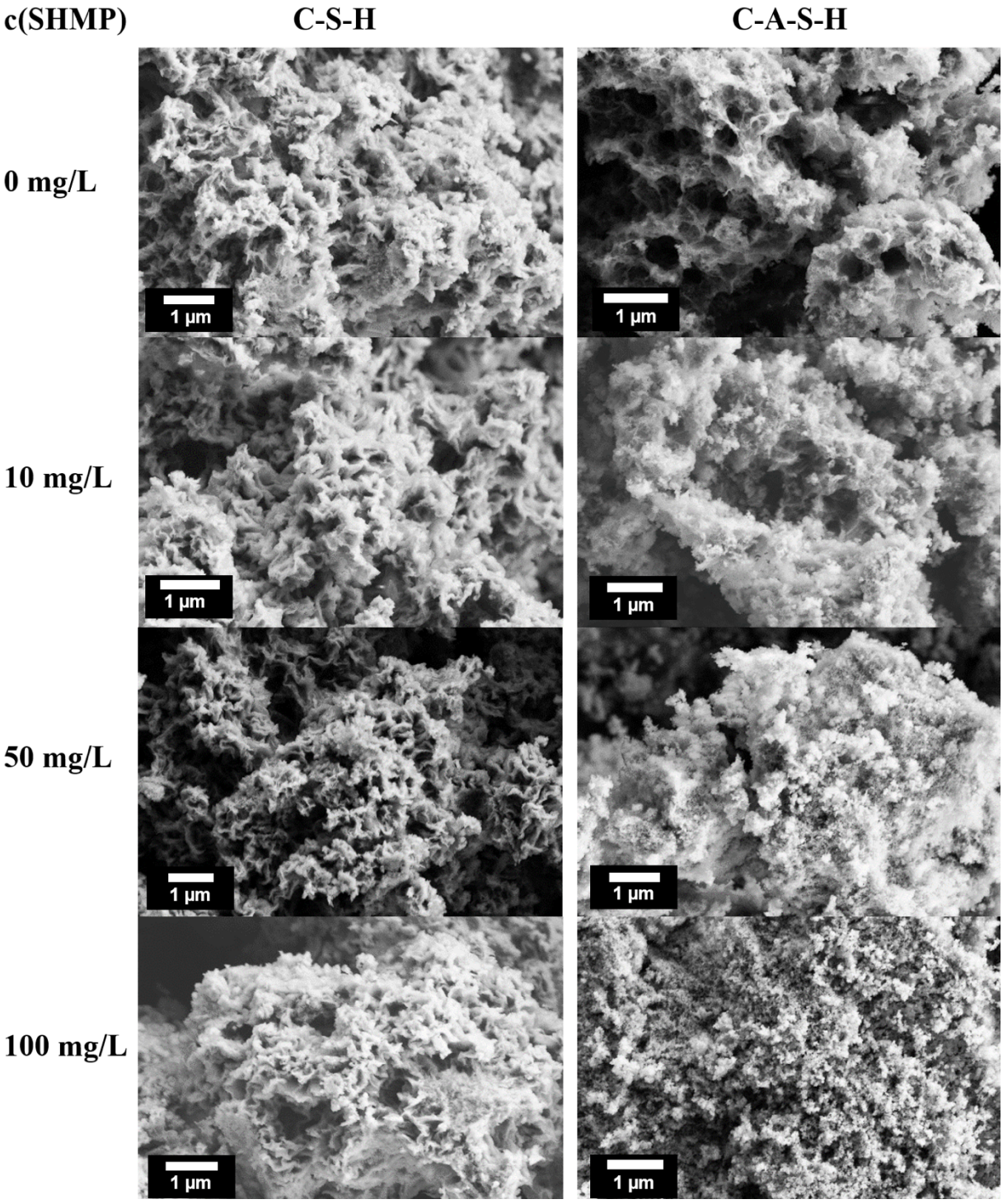
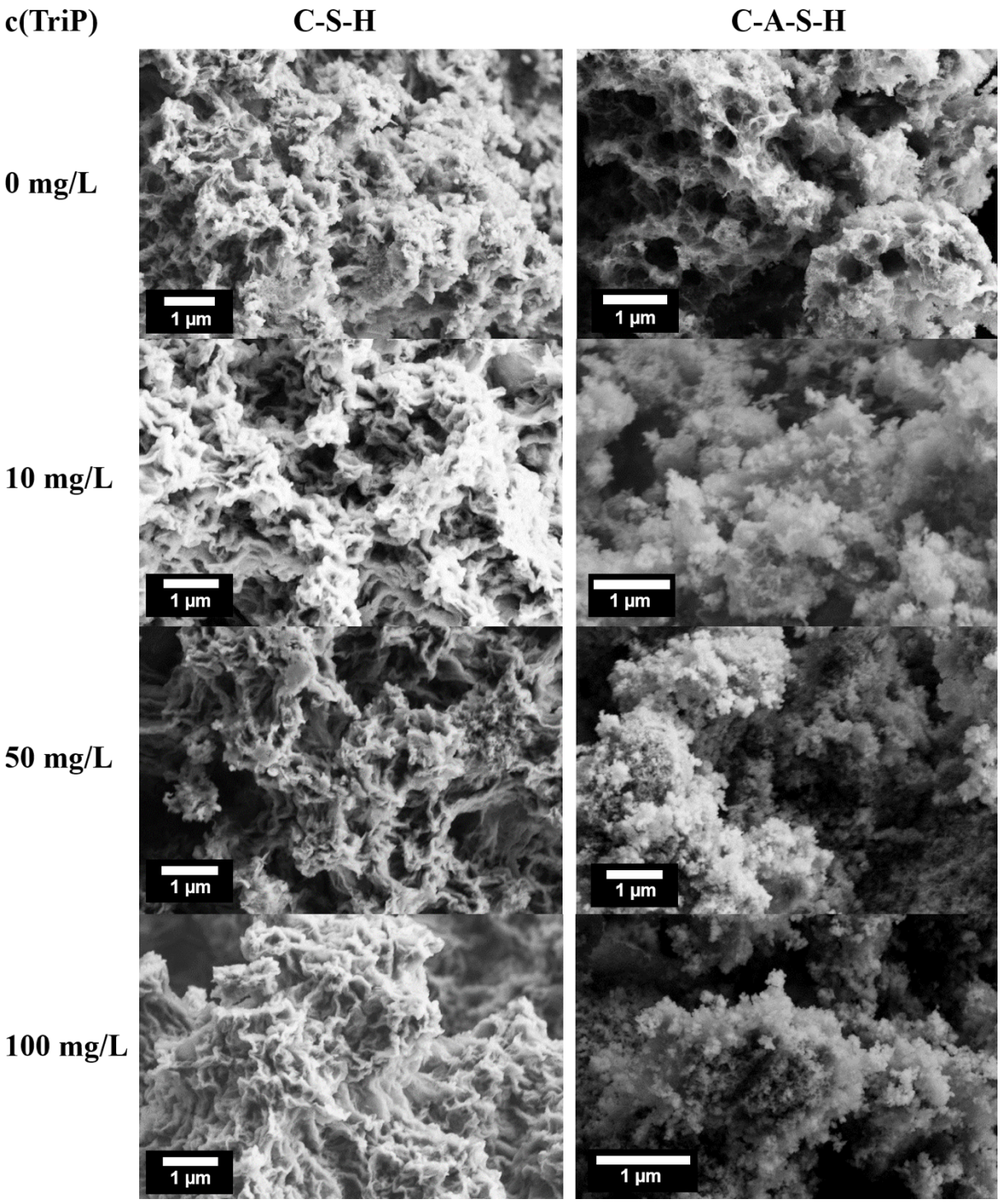


Figure SI-16: SEM images of the obtained precipitates from the C-S-H and C-A-S-H synthesis in presence of SHMP in concentrations of 0, 10, 50 and 100 mg/L.



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107 **Figure SI-17: SEM images of the obtained precipitates from the C-S-H and C-A-S-H synthesis in**
108 **presence of TriP in concentrations of 0, 10, 50 and 100 mg/L.**

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