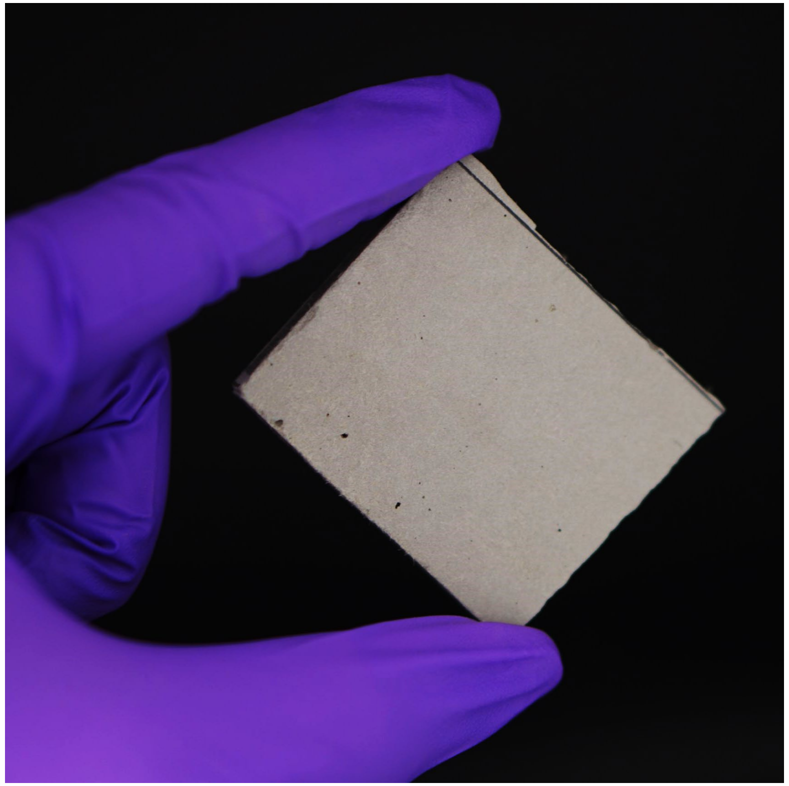
Understanding the role of cellulose nanocrystals on the hydration of Portland cement: Investigation with tricalcium silicate as a model component



Sreenath Raghunath
Ph.D. Student

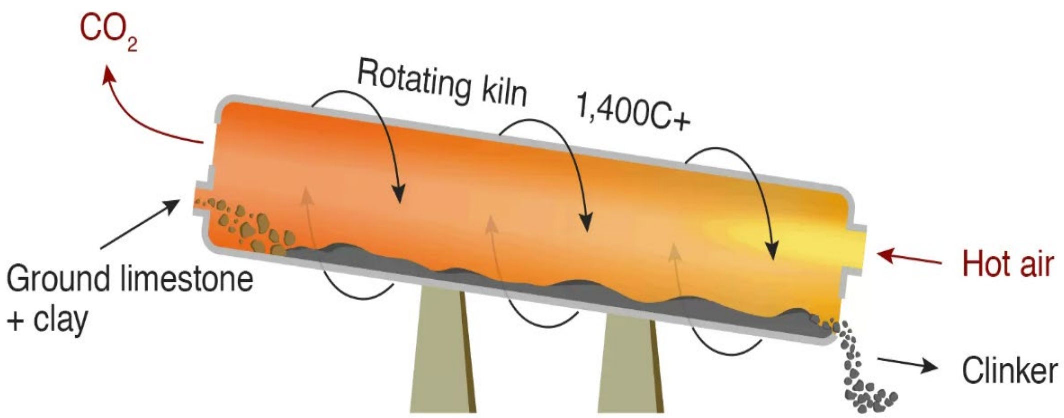
Dr. Mahfuzul Hoque
Postdoctoral fellow

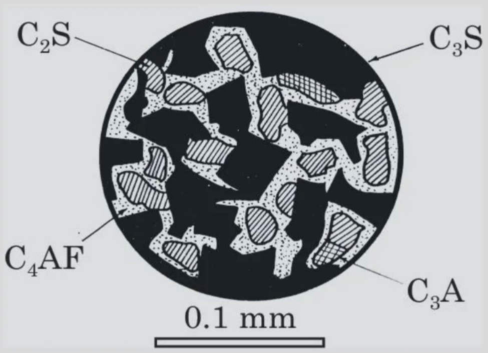
Principle Investigator : Dr. E. Johan Foster

Foster's Advanced Materials Group (AMG)
Department of Chemical & Biological Engineering (CHBE)
University of British Columbia (UBC)

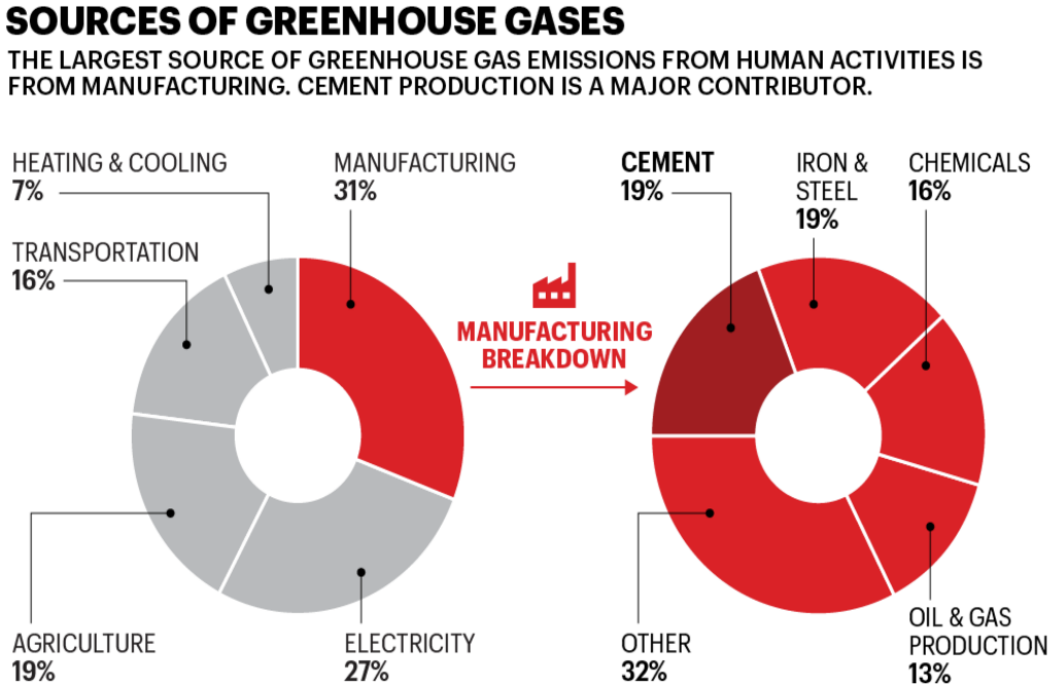
CO_2 Emission Related to Cement Production

Current Scenario





Schematic representation of the composition of portland cement

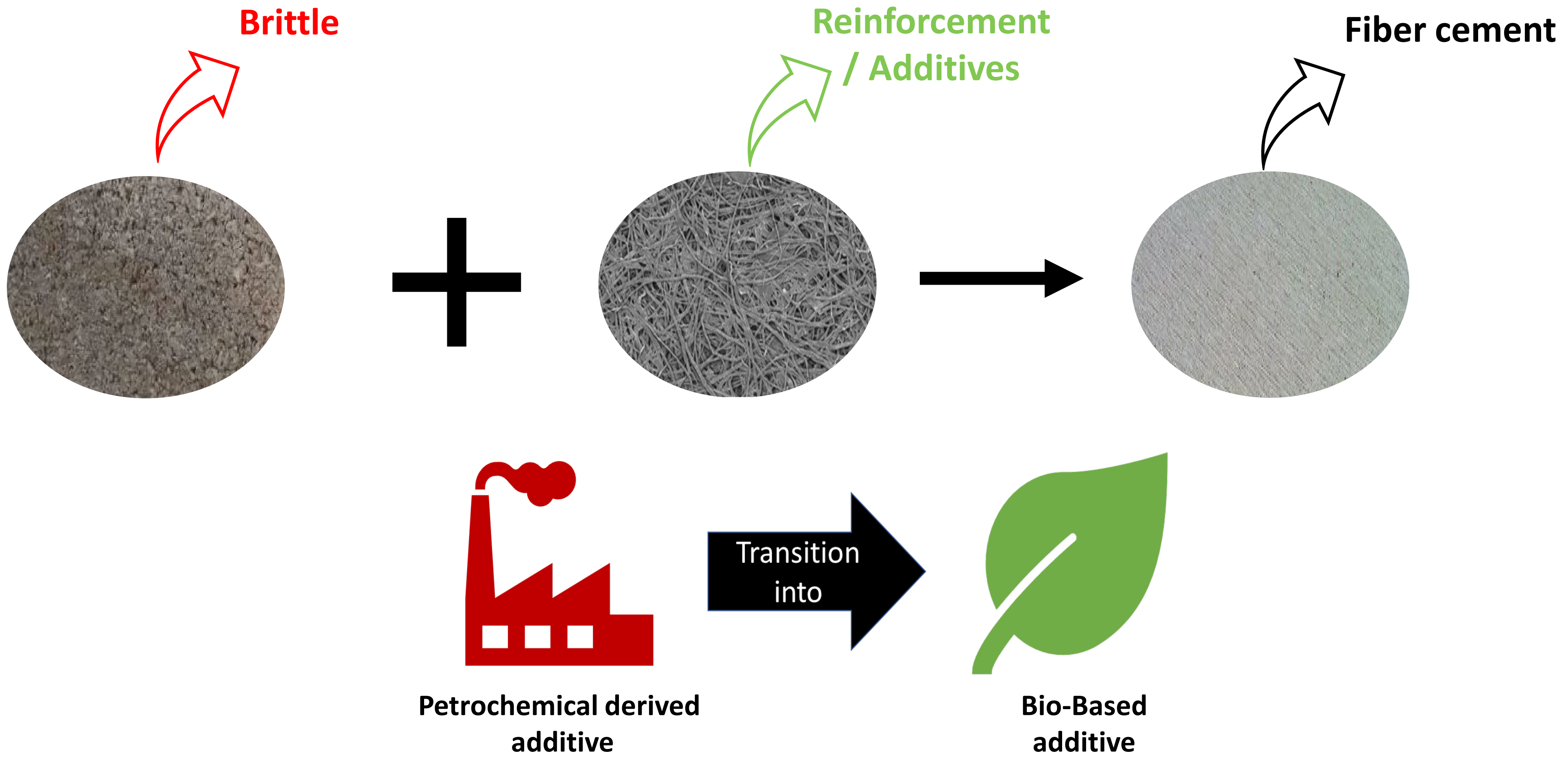


Current environmental concerns demand us to look for more bio-based and sustainable building materials

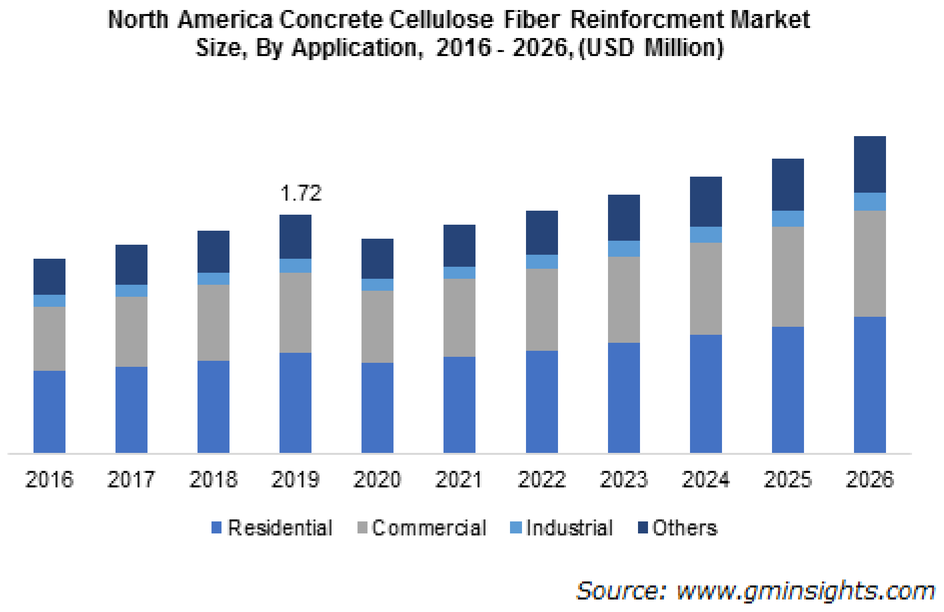
https://www.bbc.com/news/science-environment-46455844

https://fortune.com/2021/02/16/concrete-steel-construction-design-climate/

Introduction : Fibre Cement

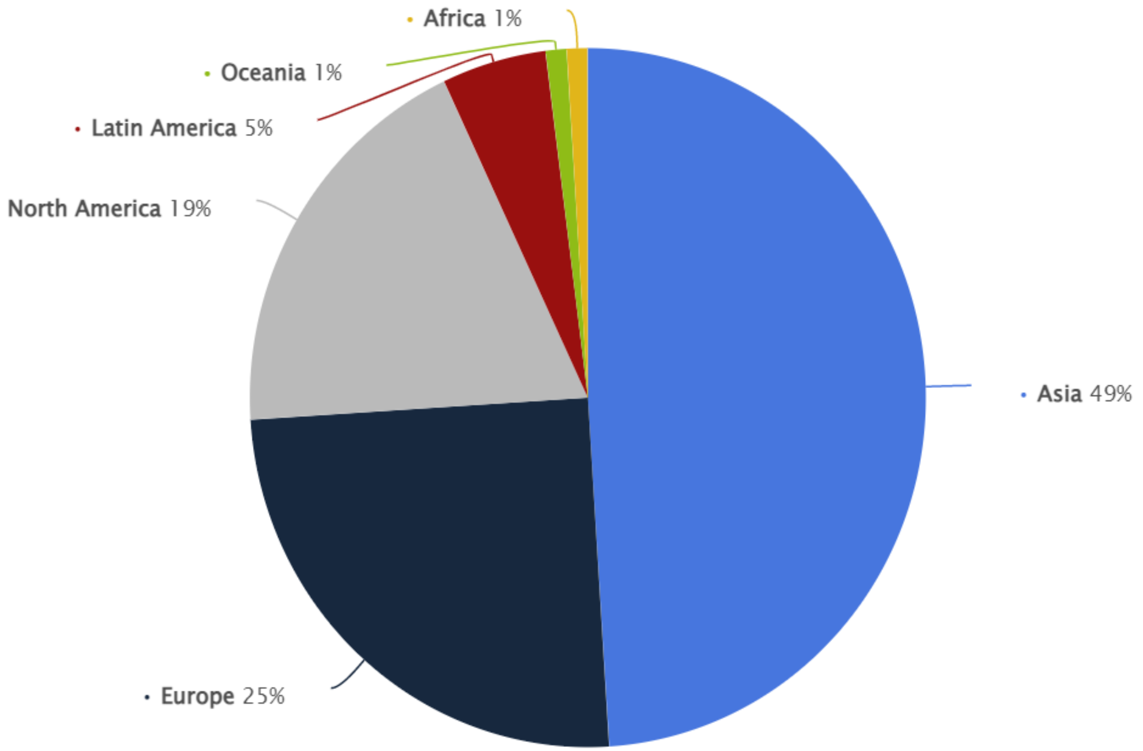


Market Forecast: Cellulose in Fibre Cement



If we want to push in more fibers we would need to make use of additives/superplasticizers such that the fluidity of the cement paste is not affected

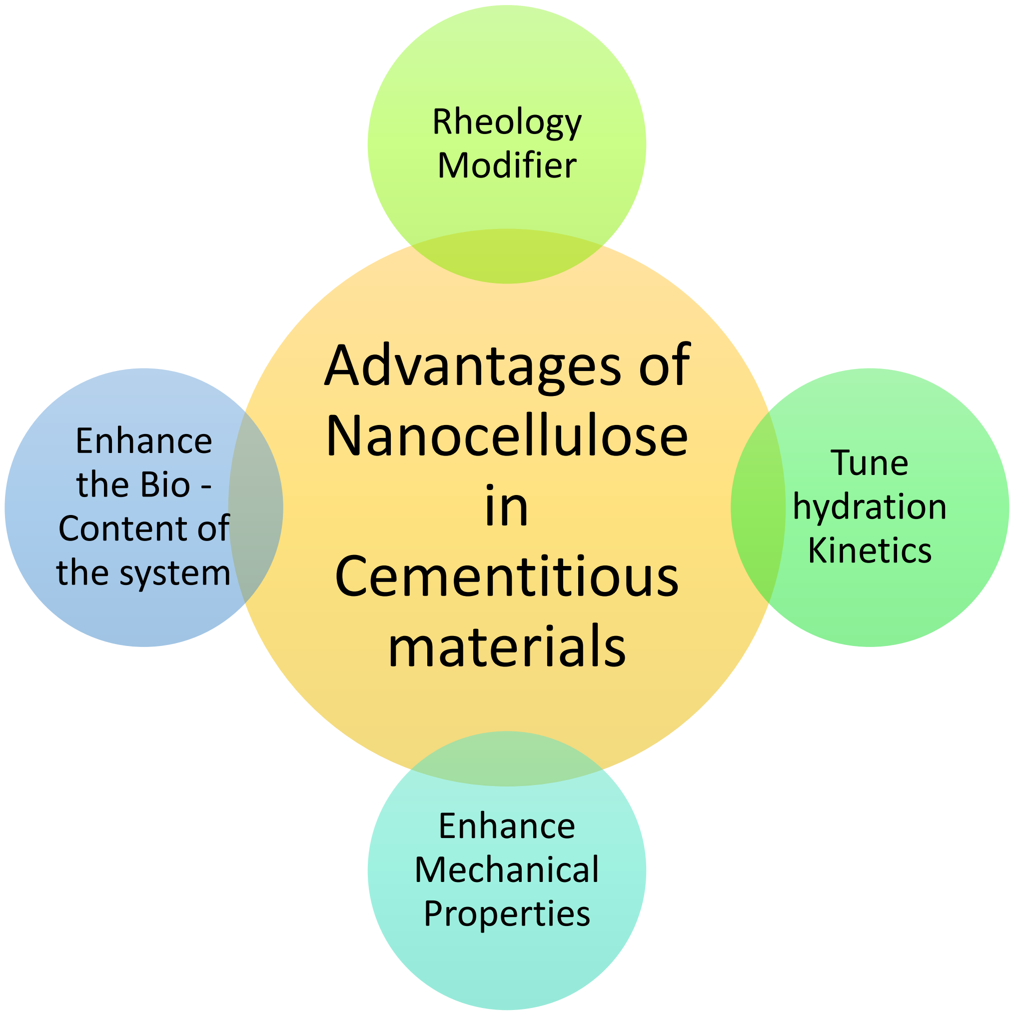
Pulp Production (Region-wise): Year 2022

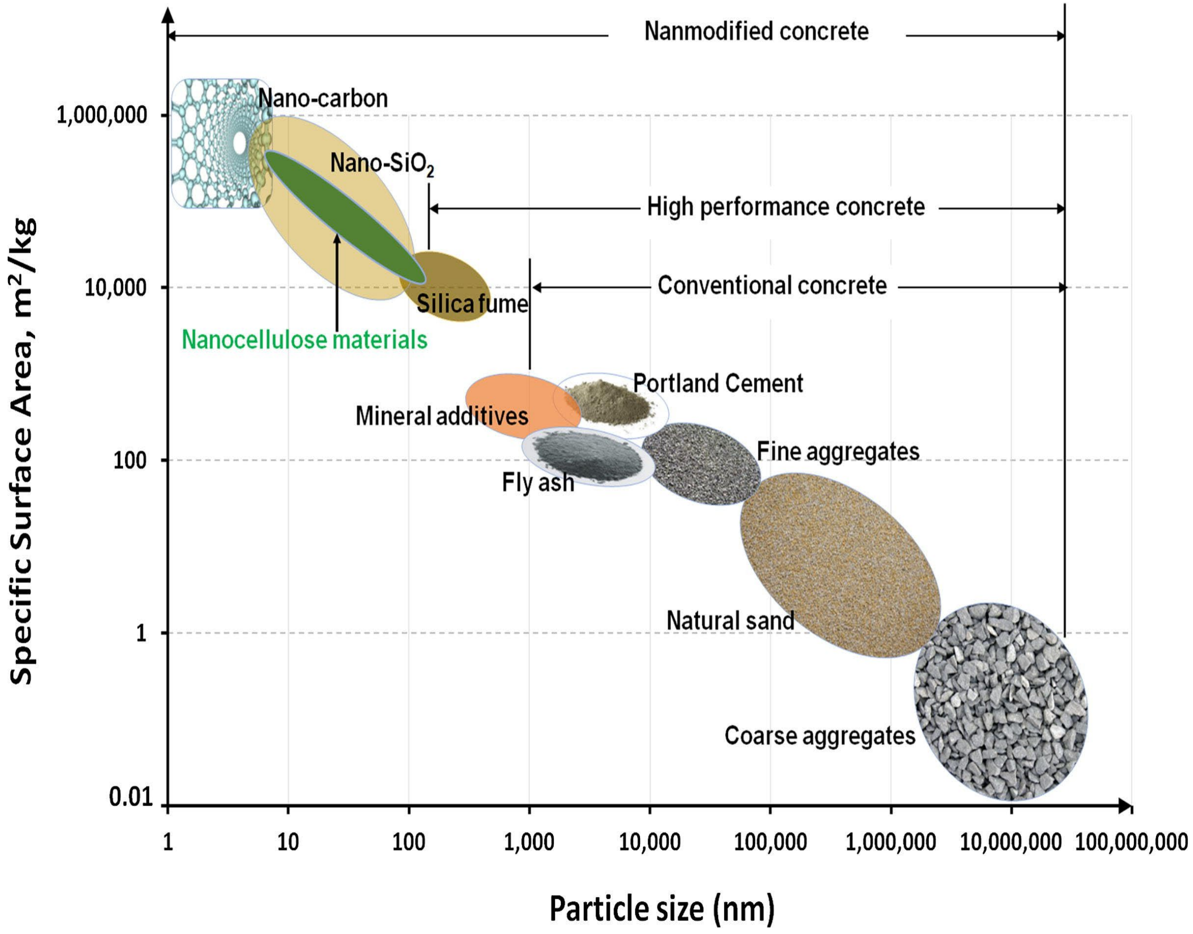


https://www.gminsights.com/industry-analysis/north-america-concrete-cellulose-fiber-reinforcement-market

https://www.statista.com/statistics/595787/paper-production-worldwide-distribution-by-region/

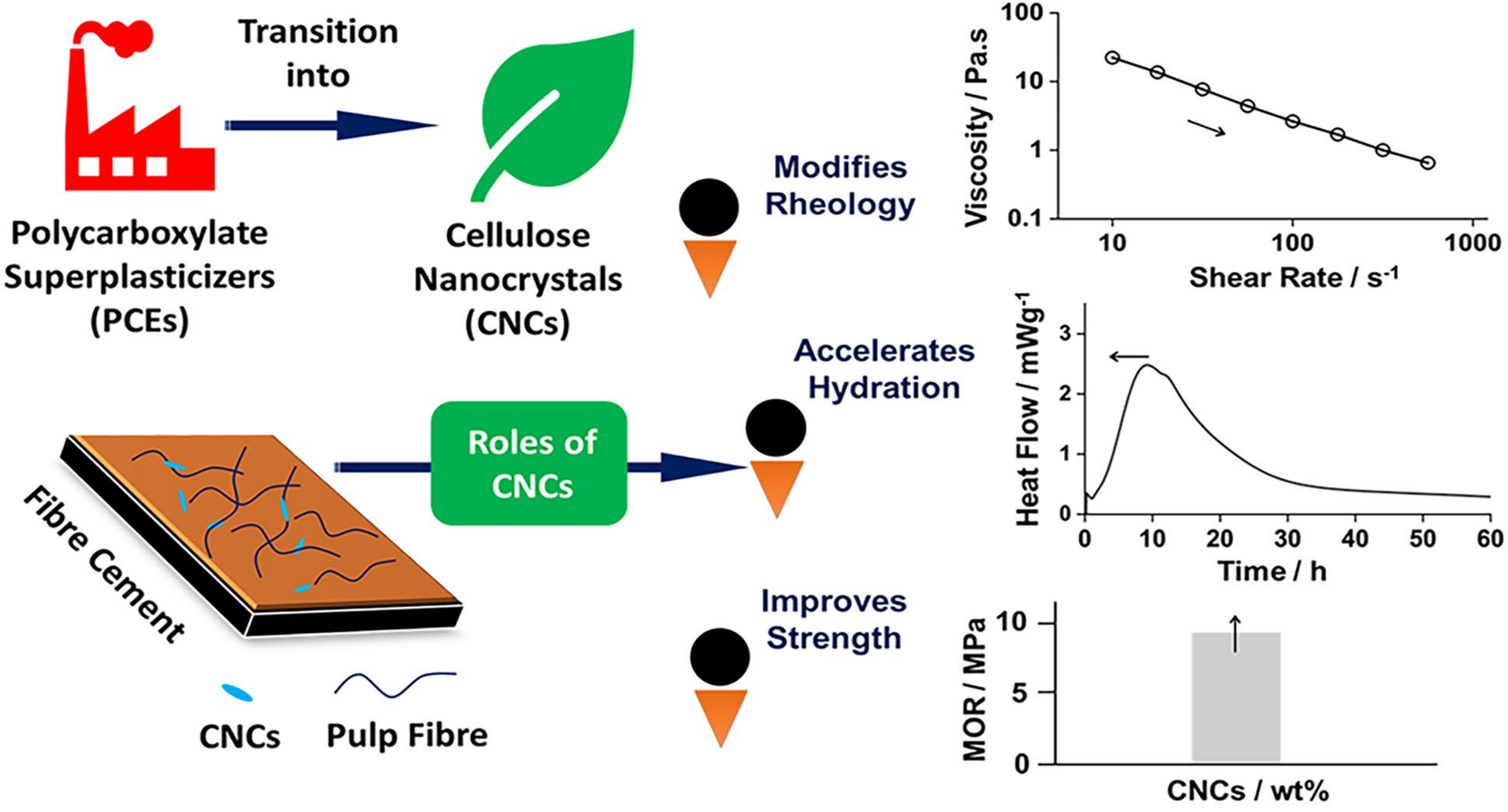
Application of Nanocellulose in Cementitious Materials



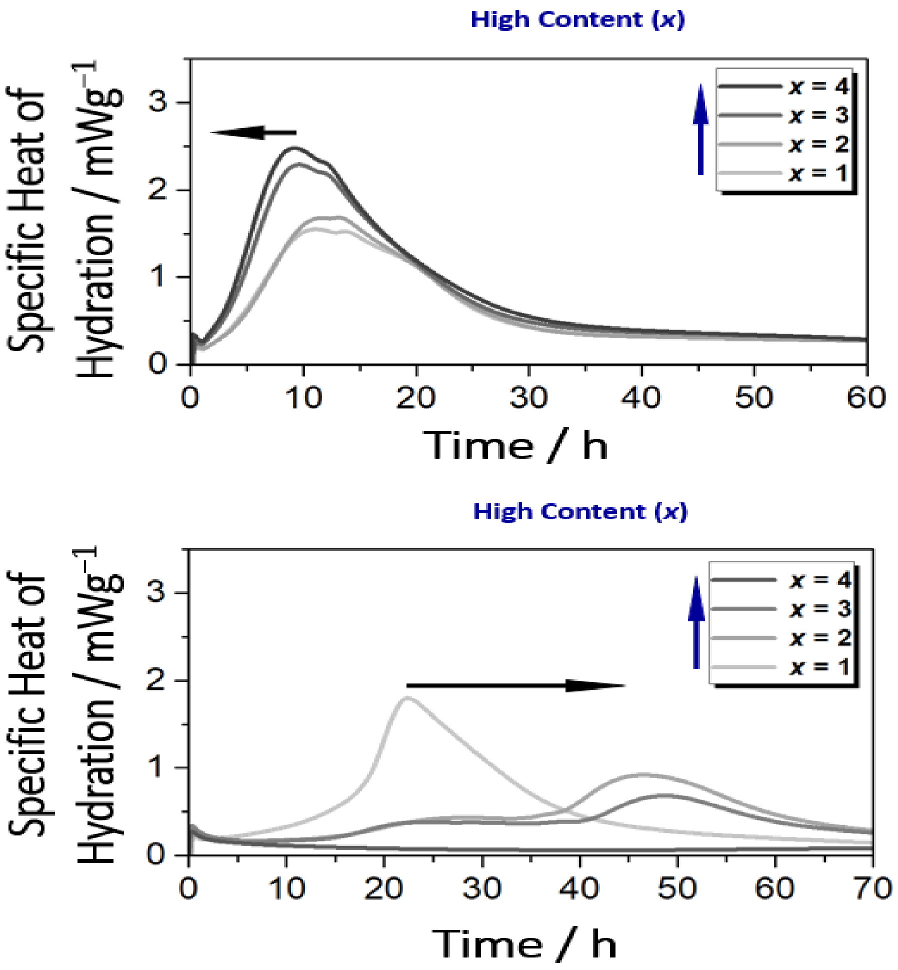


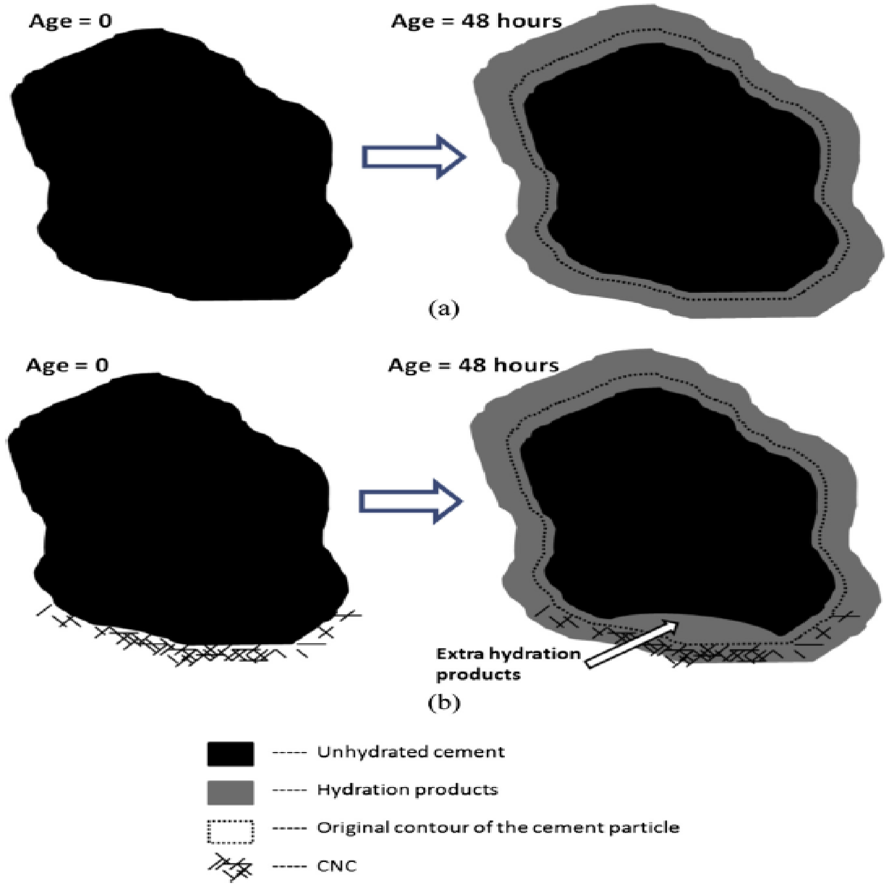
F. Sanchez, K. Sobolev,Nanotechnology in concrete – a review, Constr. Build. Mater., 24 (11) (2010), pp. 2060-2071

Multifunctional Roles of CNCs in Fiber Cement



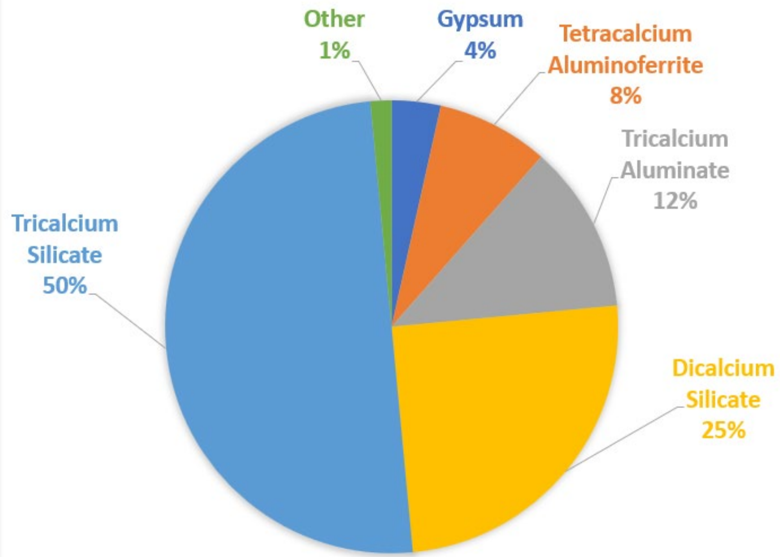
Hydration Kinetics: Isothermal Calorimetry



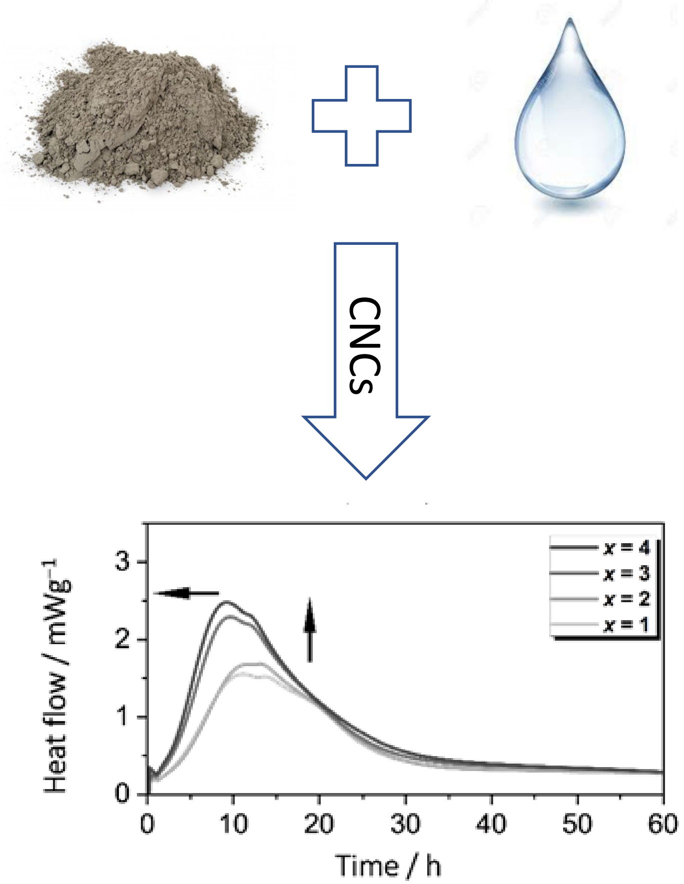


The Objective for this Study

Cement composition

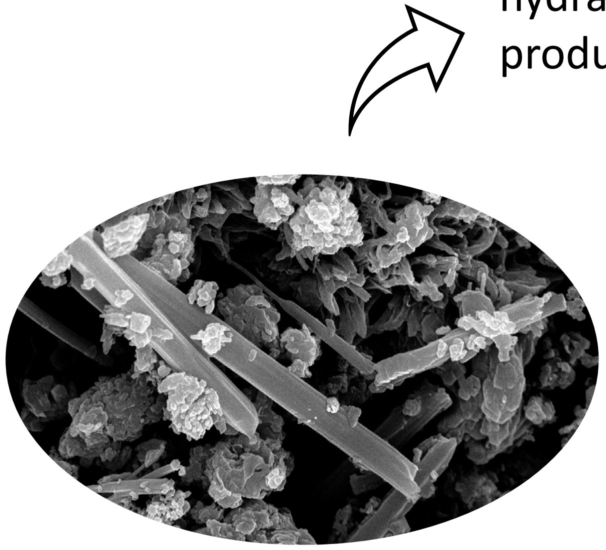


Cement hydration



Hydration product quantification

Increased hydration product



Cement Hydration: Reactions & Products

$$C_3S + H_2O \rightarrow C\text{-}S\text{-}H^* + Ca(OH)_2$$

$$C_2S + H_2O \rightarrow C\text{-}S\text{-}H + Ca(OH)_2$$

H* - H20

S – SO3

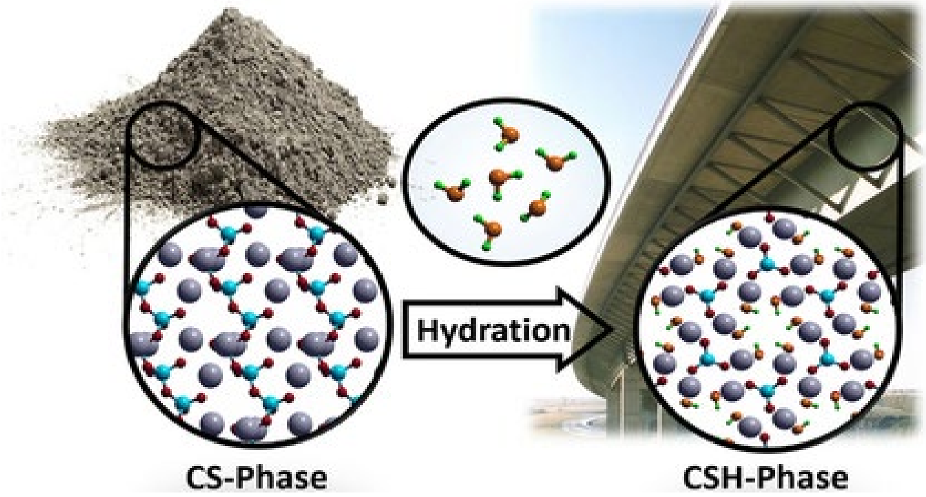
Silicate Reaction

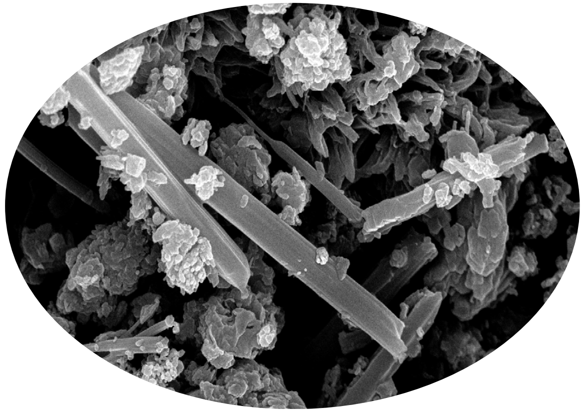
Aluminate Reaction

$$C_3A + H_2O \text{-}\rightarrow C_3AH_6$$

$$C_3A + H_2O + CaSO_4 \rightarrow CAC\bar{S}H_{12}$$

$$C_4AF + H_2O \text{-}\rightarrow C_3AH_6 + CFH$$

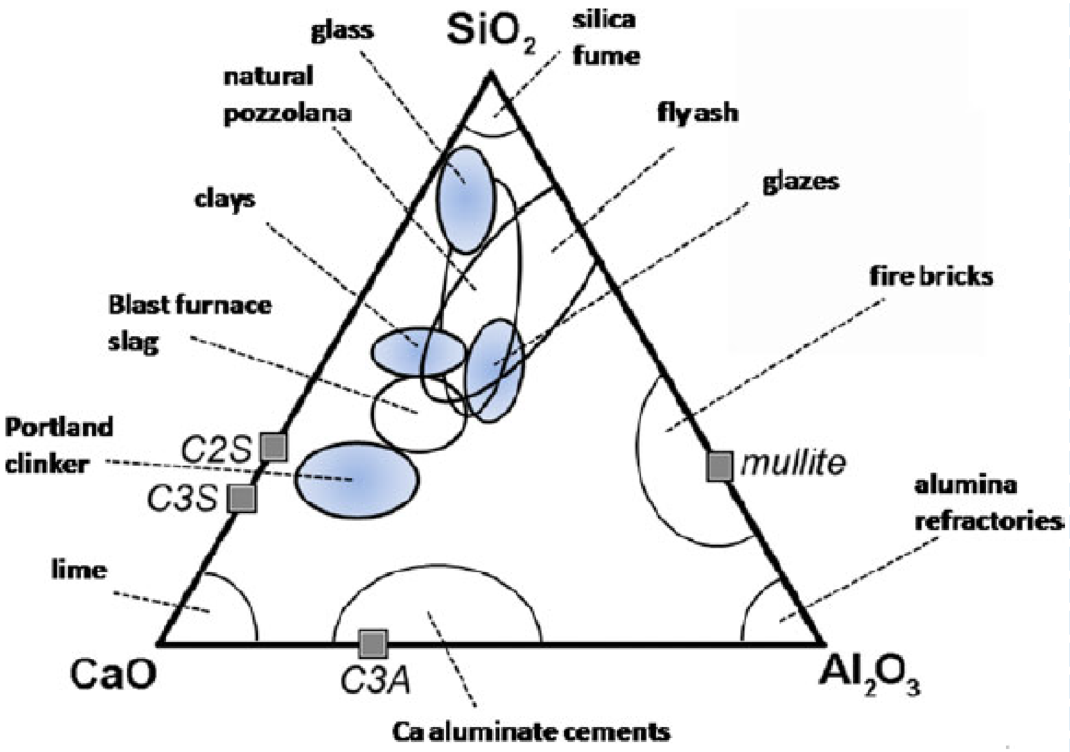




Morphologically distinct hydration products

Hydration. https://www.engr.psu.edu/ce/courses/ce584/concrete/library/construction/curing/Hydration.htm (accessed 2023-03-05).

Using Tricalcium Silicate (C_3S) :as a model component

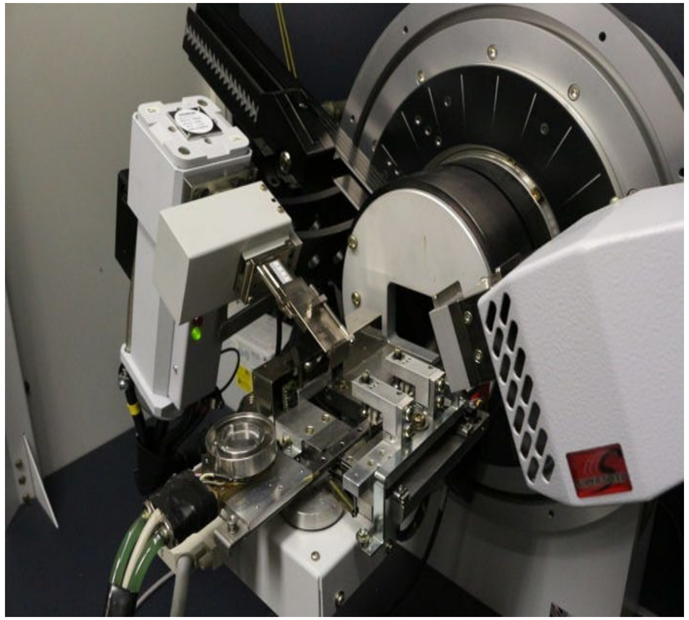


Phase	Composition	Wt% range
Alite	C_3S (Tricalcium Silicate)	50-70
Belite	C_2S (Dicalcium Silicate)	15-30
Aluminate	C_3A (Tricalcium Aluminate)	5-10
Ferrite	C_4AF (Tetracalcium aluminoferrite)	5-15

Artioli, G. and Bullard, J.W. (2013) ‘Cement hydration: The role of adsorption and Crystal Growth’, *Crystal Research and Technology*, 48(10), pp. 903–918.

Quantification of Cement Hydration Products

Bulk Phase Analysis



Powder X-Ray Diffractometry

Surface Probing Technique

Raman Surface Mapping

Surface Probing Technique: Advantages & Limitations

Non-destructive technique

Quick and easy

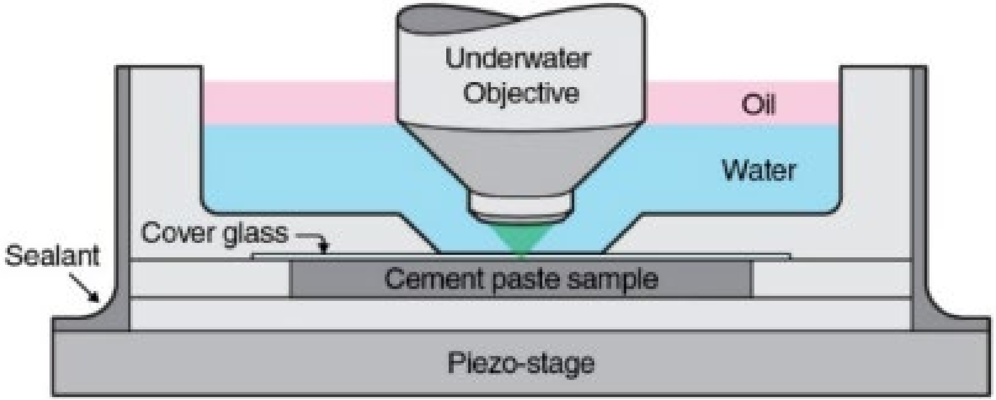
No additional sample preparation required

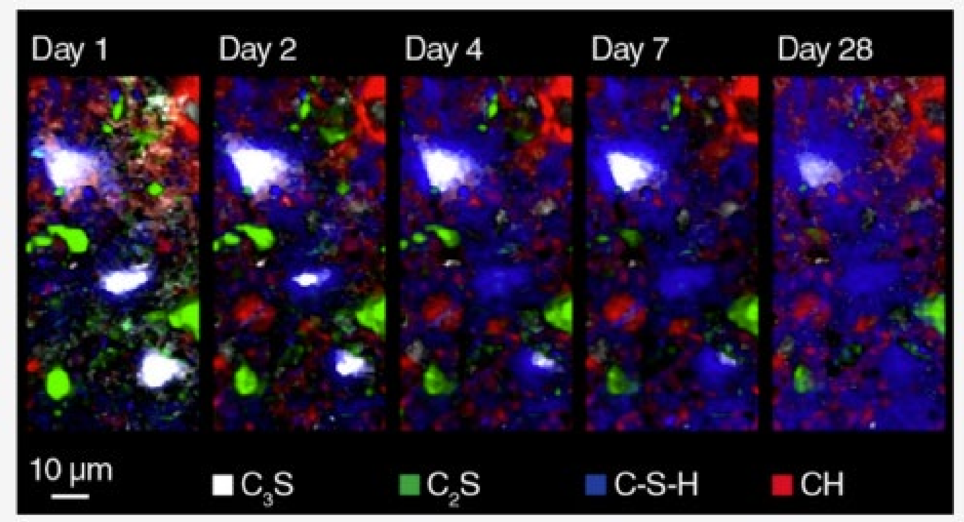
Surface Technique

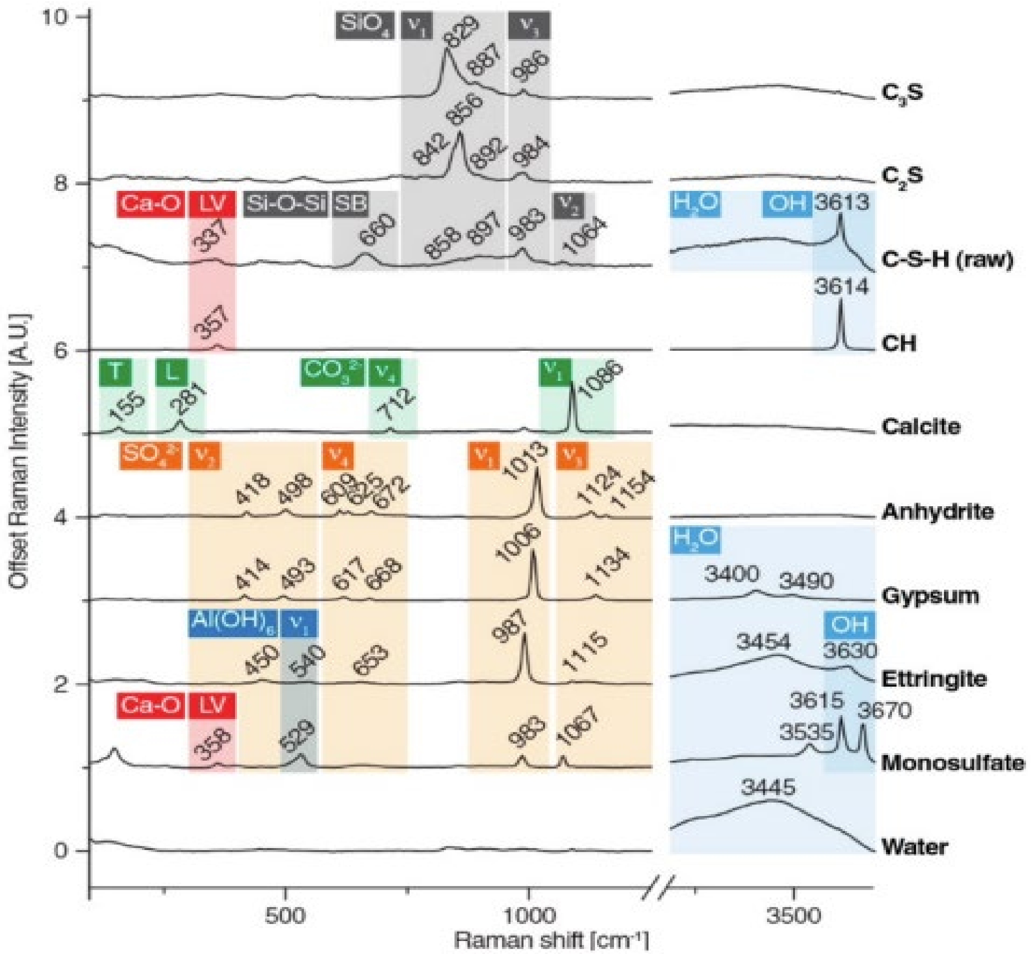
Weak signals can lead to long accusation time

Auto fluorescence

Inspiration: In situ quantification of OPC hydration Products – Study by Chae Loh et al.,







Loh, H.-C. et al. (2021) 'Time-space-resolved chemical deconvolution of cementitious colloidal systems using Raman spectroscopy', Langmuir, 37(23), pp. 7019–7031.

Sample Preparation and Experimental Technique

C_3S and CNCs are hand-mixed prior to mixing. A w/C_3S ratio of 0.8 was used to mix the samples. 8wt% of Sio_2 is also added for the purpose of calibrating the XRD data.

inVia™ InSpect confocal Raman microscope

Spectrum measurement rage
246 cm^{-1} to 1486 cm^{-1}
Grating – 2400 l/mm (Vis)
Exposure time – 10 S
Laser power % - 50

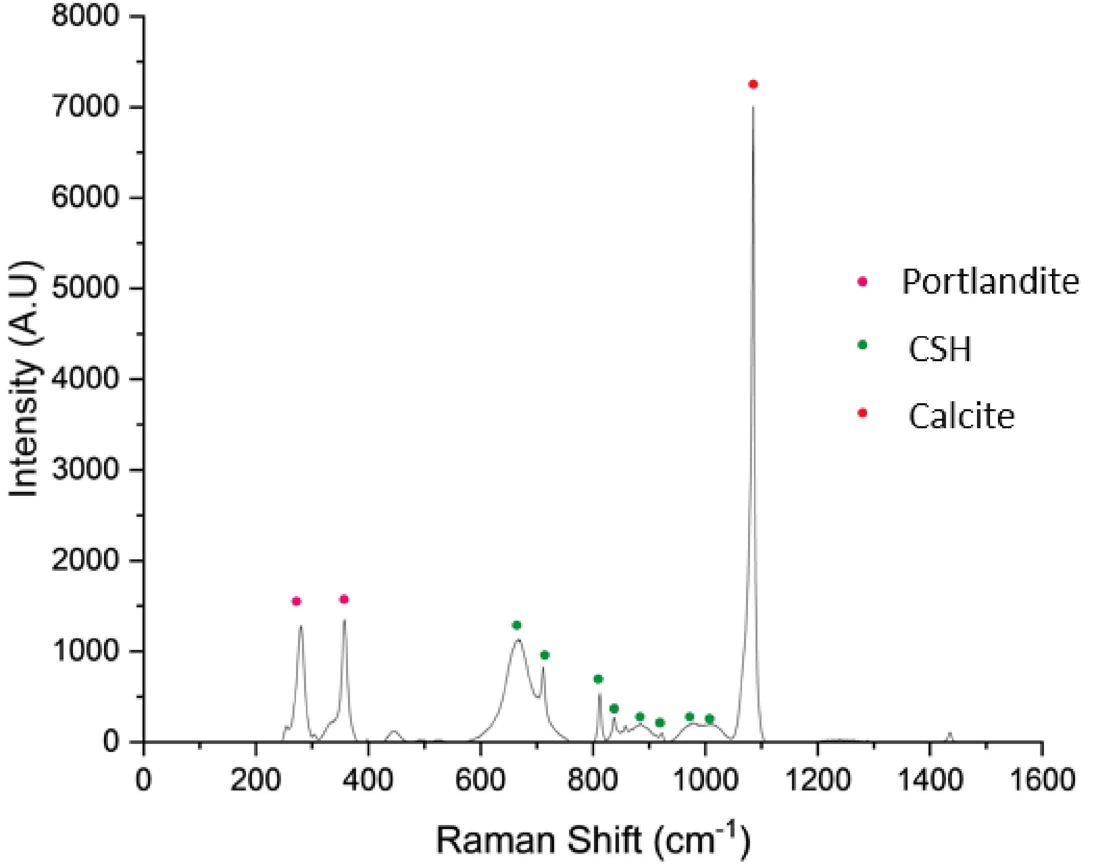
Raman spectra were obtained using a laser excitation wavelength of 532nm.

For 20× objective
The lateral resolution = 0.65 µm
Depth resolution = ~ ± 1490 nm

$$\Delta_{\text{lat}} = \frac{0.61\lambda}{(N.A.)}$$

$$\Delta_{\text{depth}} = \pm \frac{4.4\lambda n}{2\pi (N.A.)^2}$$

The Peak of Interest and its Assignments – C_3S Hydration



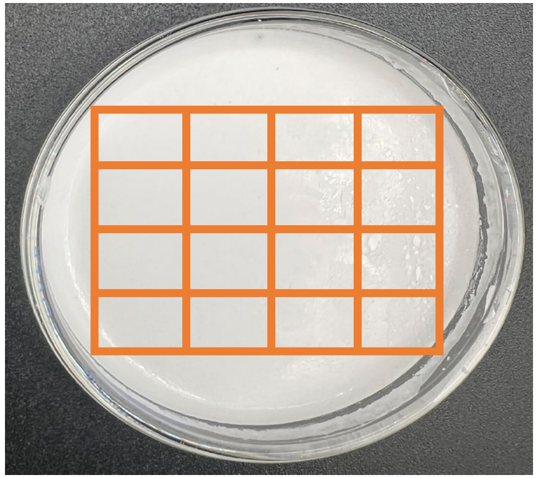
Frequency ranges and assignments for peaks observed in Raman spectra of CSH and related crystalline hydrous Ca - silicates

Frequency or Frequency Range (cm^{-1})	Assignment
1077	Symmetrical C–O stretching in carbonate groups.
800–1080	Symmetrical stretching (SS) of Si–O tetrahedra.
1080	SS of Q^3 tetrahedra.
950–1010	SS of Q^2 tetrahedra.
870–900	SS of Q^1 of tetrahedra.
740	Symmetrical in-plane C–O–C bending in carbonate groups.
600–700	Symmetrical bending (SB) of Si–O–Si linkages (deformation of Ca–O polyhedra may contribute, e.g., E_g mode of portlandite).
650–680	SB involving Q^2 Si tetrahedra.
600–630	SB involving Q^3 Si tetrahedra.
430–540	Internal deformations of Si–O tetrahedra (O–Si–O bending).
300–350	Vibrations involving Ca–O polyhedra, e.g., A_{1g} mode of portlandite.
<280	Complex vibrations, presently not understood. May involve Ca–O polyhedra.

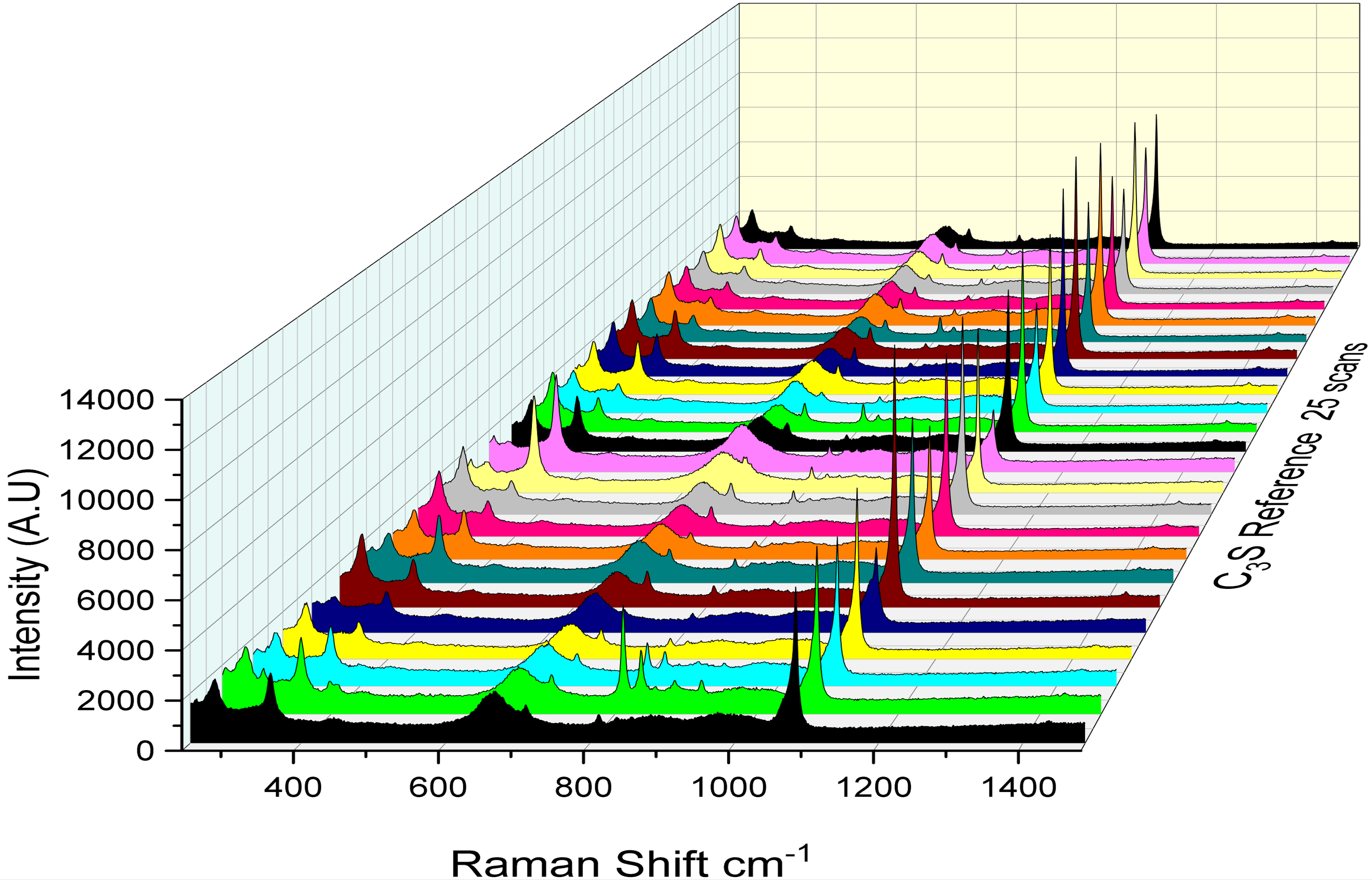
Kirkpartick, R. J., Yarger, J. L., McMillan, P. F., Yu, P., & Cong, X. (1997). Raman spectroscopy of C-S-H, tobermorite, and jennite. Advanced Cement Based Materials, 5(3-4), 93-99.

Raman Surface Mapping

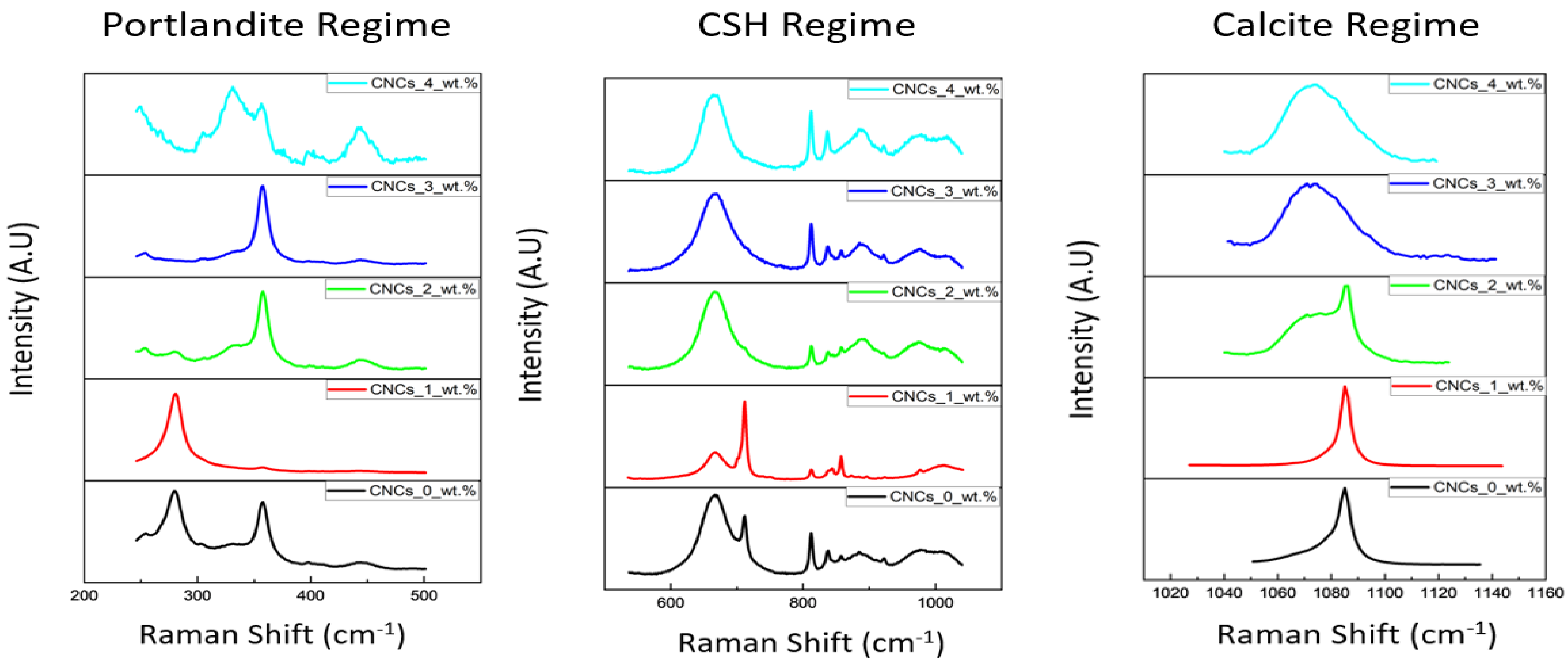
Mapping Area



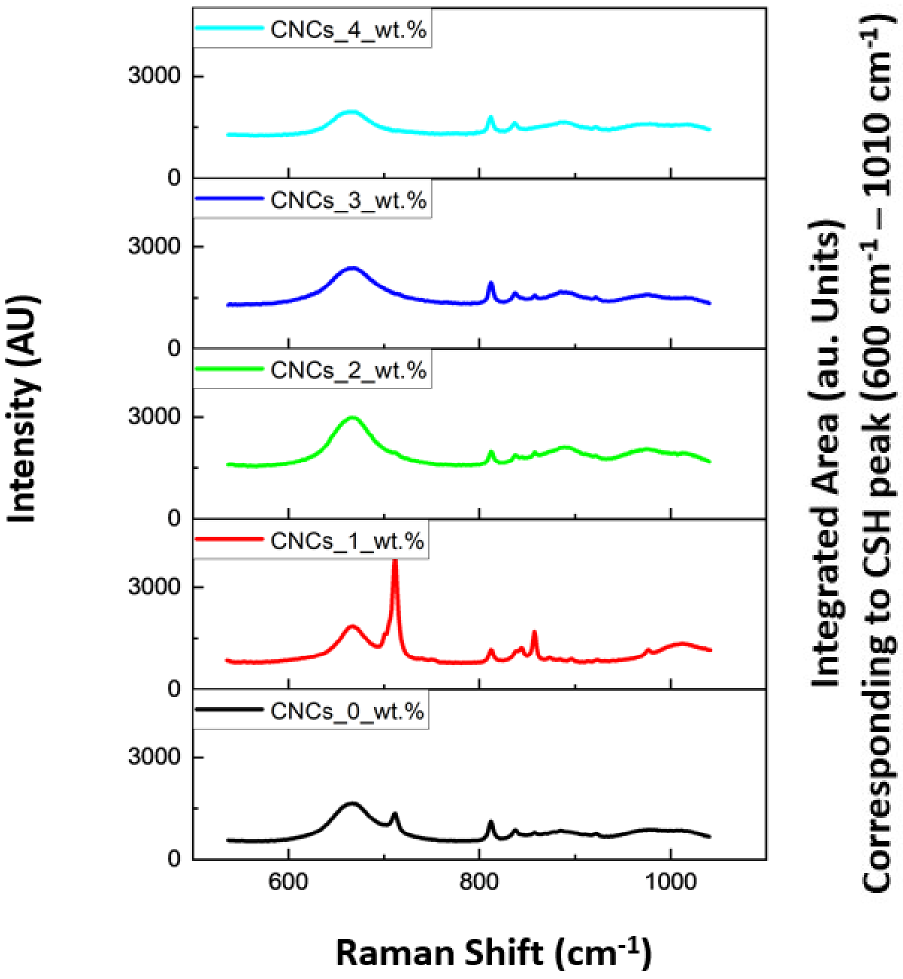
Points
X = 5
Y= 5
The step size of 10 microns.
Total of 25 Scans per specimen

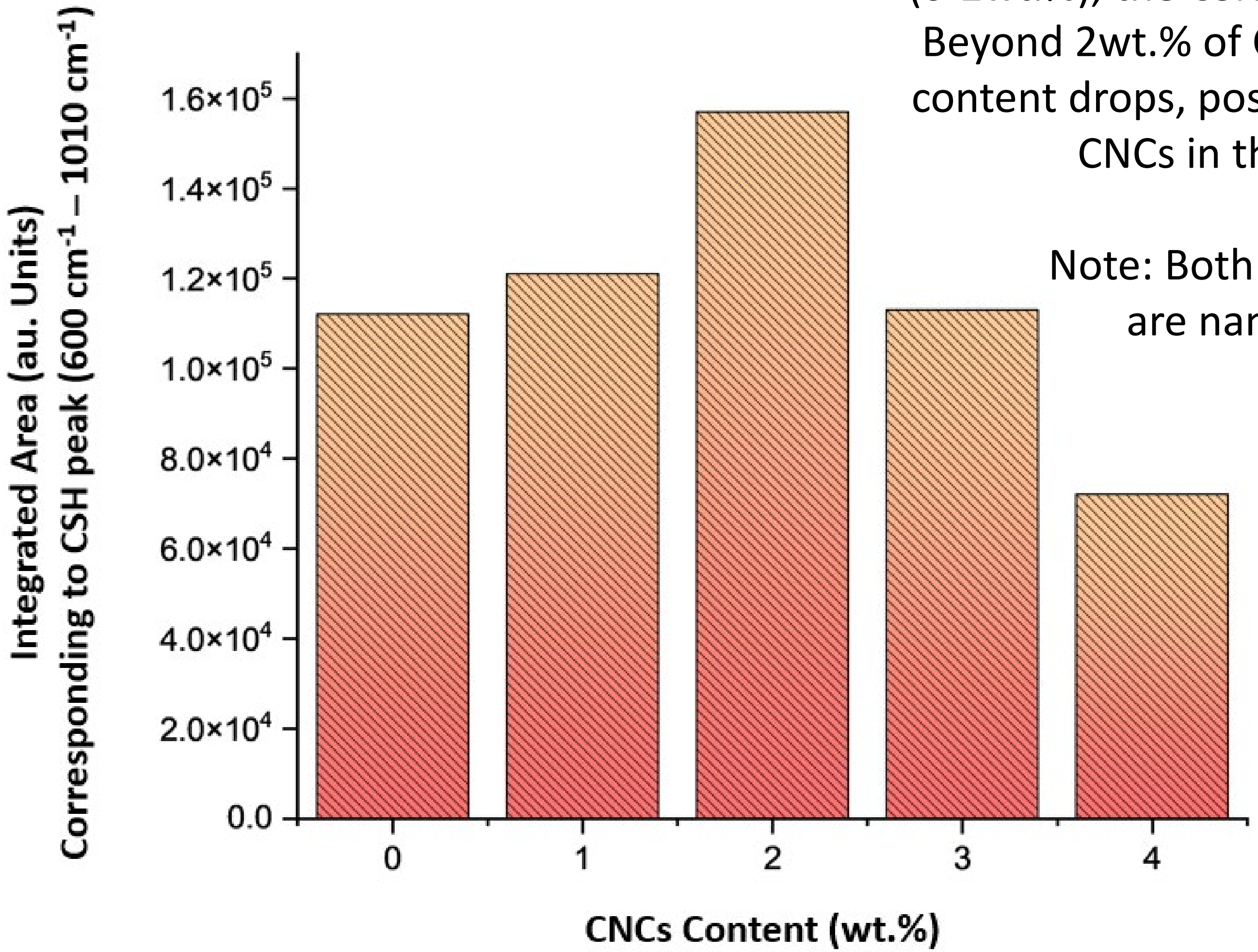


Average Raman peaks corresponding to Portlandite, CSH & Calcite Regimes



Quantification of CSH (600 cm^{-1} - 1010 cm^{-1})

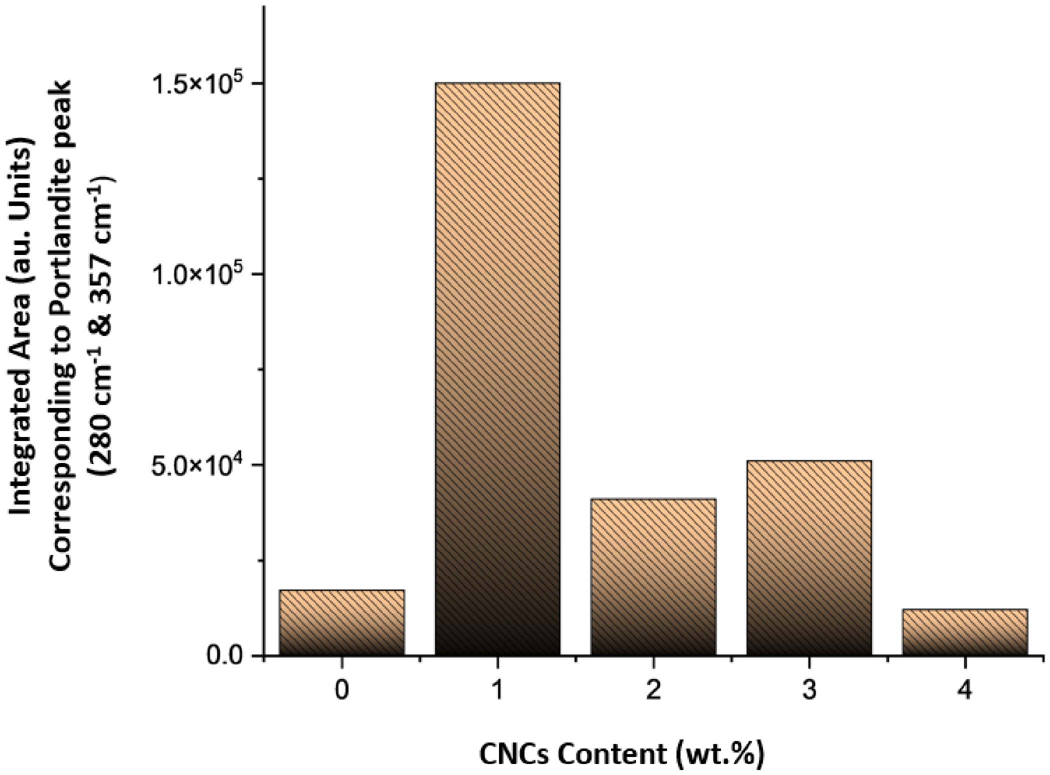


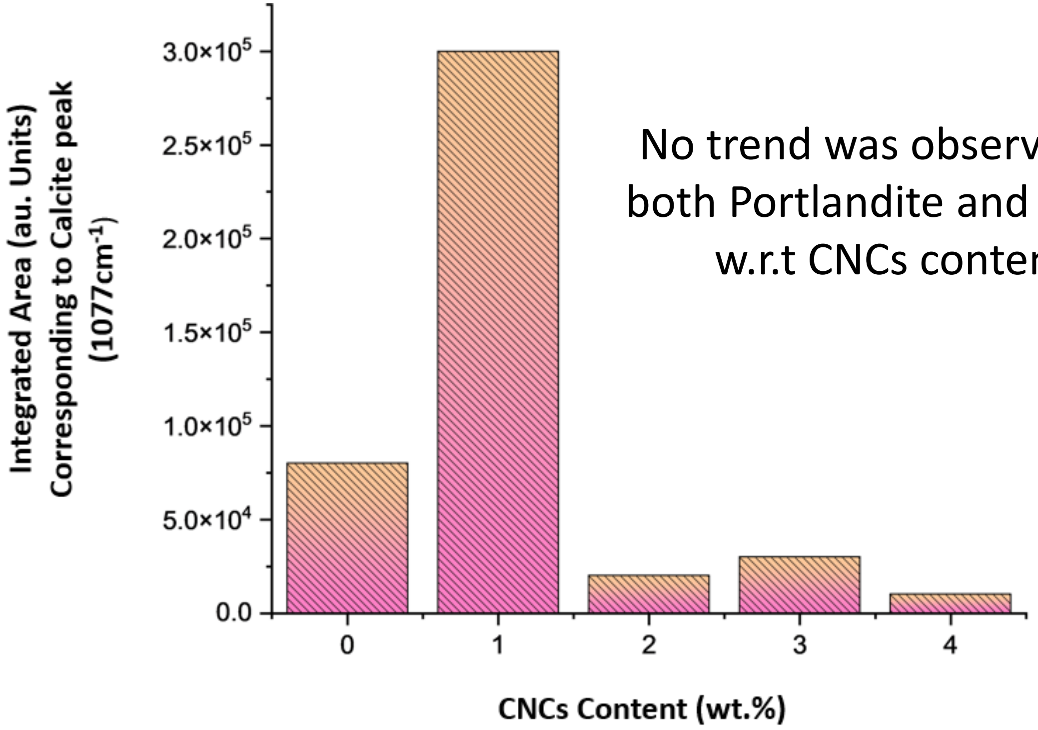


As the CNCs content increases from (0-2wt.%), the CSH content increases. Beyond 2wt.% of CNCs content, CSH content drops, possibly due to excess CNCs in the system.

Note: Both C_3S & CNCs are nanoscale.

Quantification of Portlandite and Calcite





No trend was observed for both Portlandite and Calcite w.r.t CNCs content.

Portlandite almost instantaneously reacts with Co_2 in the air to form Calcite.
Hence there is always a trade-off between portlandite and calcite formation.
Therefore, quantification of Portlandite and Calcite using surface mapping may not yield accurate results.

Conclusion

The presence of CNCs does aid the formation of CSH gel crystal, thereby contributing to the strength of the CNCs-cement composite.

Raman Mapping can effectively act as a quick and non-destructive tool to probe and quantify nanoscale CSH gel content.

A combination of surface Raman mapping and XRD Rietveld refinement can effectively be used to probe cement hydration products.

For the nanoscale characterization of cement hydration products (<100nm), peak broadening tends to occur in XRD measurements and quantification of semicrystalline structures such as CSH gel can be tricky:- Hence Raman surface mapping.

For quantification of crystalline products such as Portlandite and Calcite, XRD could be used as a valuable tool to probe the products.

Next steps

Further deconvolute CSH peaks to understand the speciation of CSH structure under the influence of CNCs.

Perform XRD Rietveld analysis to validate the results obtained from quantification of hydration products via Raman surface mapping.

Acknowledgment

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BioProducts Institute